

Concentration Dependence of the Diffusion Coefficient in Polymer Solution and Molecular Weight Distribution Determined by the Diffusion Method

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Synopsis

The effects of the concentration dependence of the diffusion coefficient of a polymer solution (polystyrene in benzene and cyclohexane) in determining molecular weight distribution by the diffusion method are briefly discussed. The value of the ratio D_{m_0}/D_{A_0} in a good solvent was found to be close to 1.0 for a polydisperse polymer and less than 1.0 for monodisperse polymers. Molecular weight distribution curves of the polydisperse sample were obtained by the diffusion method in cyclohexane and benzene, respectively. The molecular weight distribution curve obtained for the polymer used in benzene solution looked as if the polymer had a narrow molecular weight distribution. The phenomena cited above were interpreted in the light of the concentration dependence of the diffusion coefficient of polymer solutions.

INTRODUCTION

Diffusion measurement of polymer solutions has proved to be a useful method for obtaining the molecular weight distribution of a polymer.^{1,2} This method is based upon the fact that the observed diffusion constants are the moments of various orders of a weight distribution function of diffusion constants. For example, when an appropriate distribution function of a diffusion constant is assumed, a weight distribution curve of the diffusion constant can be drawn using the observed diffusion constants D_{A_0} of the area method and D_{m_0} of the moment method. The apparent average D_{A_0} and D_{m_0} for a polydisperse polymer are shown in good approximation by the following equations¹:

$$D_{A_0} = \left[\frac{\sum_i w_i / \sum_i (w_i / D_i^{1/2})}{\sum_i w_i} \right]^2, D_{m_0} = \frac{\sum_i w_i D_i}{\sum_i w_i} \quad (1)$$

$$D_{A_0} < D_{m_0} \quad (2)$$

where w_i is the weight fraction of the polymer having a diffusion constant D_i . For a monodisperse polymer sample, the value of D_{m_0} is reasonably set equal to that of D_{A_0} . On the other hand, there are several observations of

abnormal values in the ratio of D_{m_0}/D_{A_0} , i.e., the value of D_{A_0} is equal to that of D_{m_0} in a good solvent and in some cases the former is larger than the latter even in the case of a polydisperse polymer sample.³ In such a case it is impossible to obtain the molecular weight distribution of a polymer by means of measuring diffusion constants. No explanation has been presented with regard to these phenomena. In the present paper, we discuss this problem by taking account of the concentration dependence of diffusion coefficients of polymer solutions. Molecular weight distribution curves of polystyrene in benzene and cyclohexane were obtained by the diffusion method, and these curves were compared with a molecular weight distribution curve obtained by column fractionation.⁴ A discrepancy appearing in the molecular weight distribution curve obtained from benzene solution is discussed. In addition, observation of decreasing diffusion coefficient at the θ point with increasing concentration of the polymer solution will be reported.

EXPERIMENTAL

Samples used in the present study were a commercial unfractionated polystyrene (ASAHI DOW Styron 683-7) as polydisperse sample and N.B.S polystyrenes 705 and 419 as monodisperse samples. Molecular weight distribution curves were obtained only for the polydisperse sample. The pellets of these samples were dissolved in purified methyl ethyl ketone and precipitated with methanol. After washing with methanol, the samples were dried under reduced pressure at 60°C until a constant weight was obtained. The number-average and the weight-average molecular weights of the samples observed and the ratios of two average molecular weights are shown in Table I.

TABLE I
Molecular Weights of Samples^{4,5}

| Sample | $M_w \times 10^{-4}$ | $M_n \times 10^{-4}$ | M_w/M_n |
|--------------|----------------------|----------------------|------------------|
| Styron 683-7 | 27.7 | 12.5 | 2.2 ₂ |
| N.B.S. 705 | 17.9 | 17.1 | 1.0 ₆ |
| N.B.S. 419 | 41.1 | — | — |

Cyclohexane and benzene were used as solvents in this study, since the former is a θ solvent at 35°C and the latter is a good solvent for polystyrene. The solvents were purified by the ordinary methods. Measurements of diffusion constants were carried out in a Hitachi HTB-type electrophoresis apparatus using a modified Neurath-type cell at 35°C which is the θ point of polystyrene in cyclohexane. Temperature of the cell was controlled within $\pm 0.05^\circ\text{C}$ by circulating thermostated water in the chamber of the apparatus. The concentration of the solution was about 1g/100 ml. Patterns of diffusion boundary were photographed by means of a Schlieren optical system once every 4 hr. From the photographs of diffusion pat-

terns, the diffusion coefficients D_A and D_m were calculated respectively by the area method and the moment method as follows:

$$D_A = \frac{1}{4\pi t} \left(\frac{m_0}{H_{x=0}} \right)^2, \quad D_m = \frac{1}{2t} \frac{m_2}{m_0} \quad (3)$$

where

$$m_0 = \int_{-\infty}^{\infty} y dx, \quad m_2 = \int_{-\infty}^{\infty} |x|^2 y dx \quad (4)$$

where y is the height of the diffusion pattern at distance x from the initial boundary x_0 , $H_{x=0}$ is the height of the diffusion pattern at x_0 , and t is the diffusion time. The diffusion constants at infinite dilution, D_{A_0} and D_{m_0} , were calculated by Gralen's method as follows:

$$D_c = D_0 \left[1 + \frac{k_D C_0}{2} \right] \quad (5)$$

$$\frac{k_D C_0}{2} = \frac{m_0}{2\sigma^2} \cdot \frac{x_0}{H_{\max}} \quad (6)$$

$$\sigma_2 = m_2/m_0 \quad (7)$$

where D_0 is the diffusion constant at infinite dilution, D_c is the diffusion coefficient at concentration C_0 , k_D is the concentration coefficient of diffusion coefficient, and H_{\max} is the maximum height of the diffusion pattern.

Molecular weight distribution curves of the unfractionated polystyrene were obtained according to the method proposed by Gralen,¹ assuming the logarithmic normal distribution function for molecular weight distribution. The following equations are obtained for the weight distribution function of diffusion constant D :

$$dw = (k/\gamma_0 \pi^{1/2}) \exp \{-Z^2\} dD \quad (8)$$

$$Z = (1/\gamma_0) \ln (D/D_0) \quad (9)$$

where D_0 is the most probable diffusion constant, γ_0 is the parameter of distribution function, and k is the normalization factor. Combining eqs. (8), (9), and (1), the equations obtained are as follows:

$$D_{A_0} = D_0 \exp \{3\gamma_0^2/8\} \quad (10)$$

$$D_{m_0} = D_0 \exp \{3\gamma_0^2/4\} \quad (11)$$

Substituting the experimental values for D_{A_0} and D_{m_0} in eqs. (10) and (11), we can estimate the values of D_0 and γ_0 in the distribution function of the diffusion constant. The weight distribution curve of the diffusion constant can be obtained according to eqs. (8) and (9). Then, we can calculate a

molecular weight distribution curve from the weight distribution curve of the diffusion constant obtained by the following equation:

$$D = K_D M^{-\gamma} \quad (12)$$

where D and M are diffusion constant and molecular weight of polymer, respectively, and K_D and γ are constants.

RESULTS AND DISCUSSION

Examples of diffusion patterns for a polydisperse sample are shown in Figure 1. Skewing of the diffusion patterns toward the solvent side is marked in benzene solution. The diffusion patterns are apparently symmetrical in cyclohexane at the θ point. Results of precise calculation of the latter diffusion coefficient, however, show that the concentration coefficient of the diffusion coefficient k_D has a small negative value, which corresponds to the fact that the diffusion pattern skews very slightly toward the solution side at the θ point. According to Fujita's calculation,⁶ the diffusion pattern skews toward the solvent side or toward the solution side when the concentration dependence of the diffusion coefficient is represented as $k_D > 0$ or $k_D < 0$, respectively, as shown in Figure 2.

The diffusion patterns in Figure 1 show that k_D is positive in benzene and negative in cyclohexane at 35°C. The dependence of the second moment and of the height of the diffusion pattern on time are shown in Figure 3, where a linear relationship was obtained between m_2/m_0 , or $(m_0/H_{x=0})^2$, and the diffusion time t .

Diffusion coefficients D_A and D_m were calculated from the slopes of the curves in Figure 3 according to eq. (3). The diffusion constants at infinite

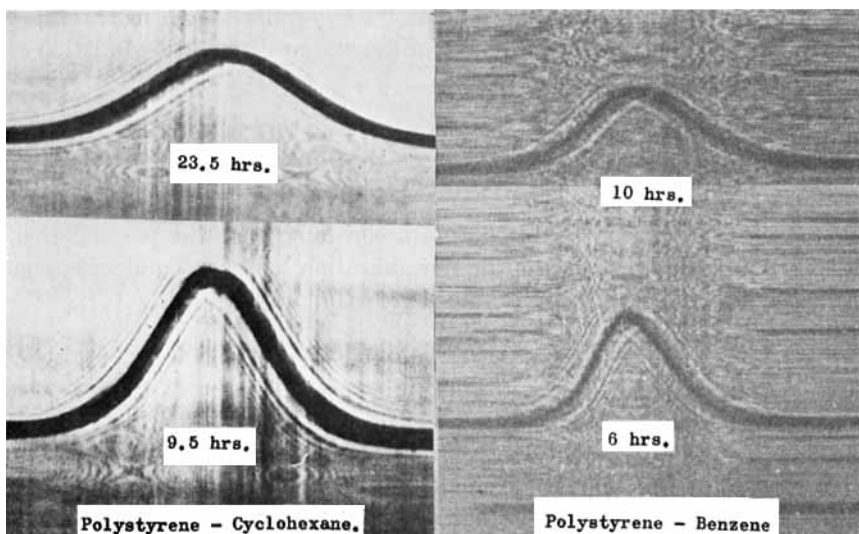


Fig. 1. Diffusion patterns of a polydisperse sample.

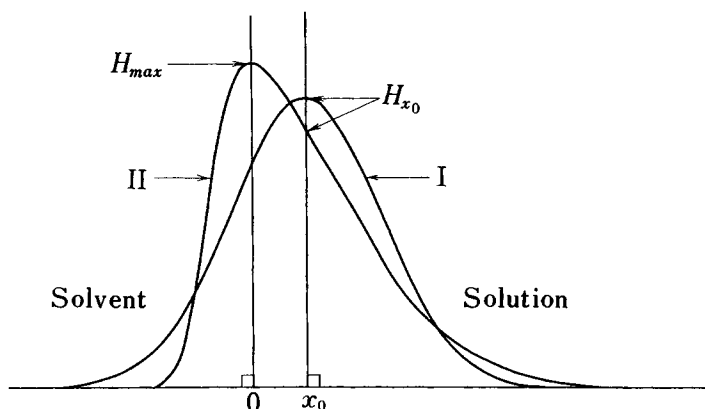


Fig. 2. Comparison of diffusion curves: (I) constant diffusion coefficient; (II) diffusion coefficient varying with concentration, $k_D > 0$.

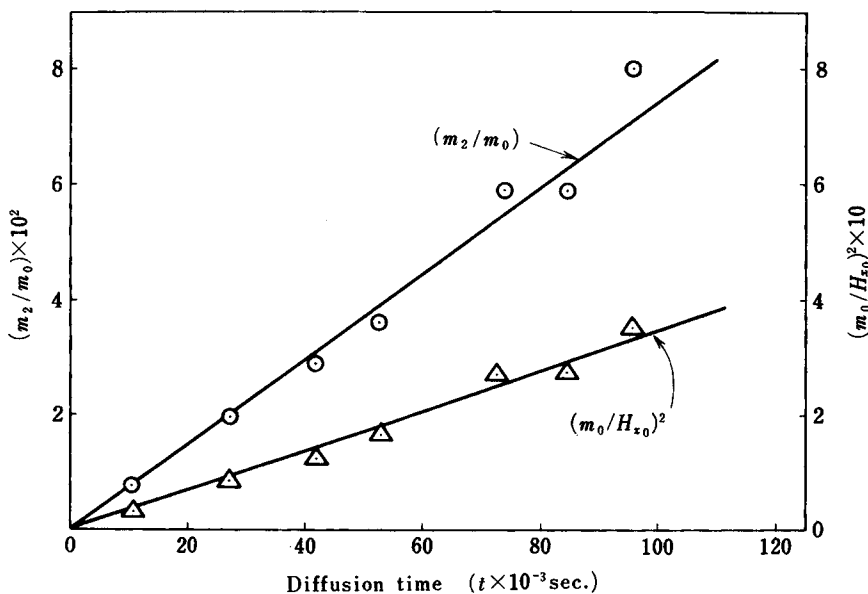


Fig. 3. Plots of m_2/m_0 and $(m_0/H_{x_0})^2$ vs. t for Styron 683-7 in cyclohexane at 35°C.

dilution, D_{A_0} and D_{m_0} , were calculated by putting the values thus obtained into eqs. (5), (6), and (7). The values of the two diffusion constants D_{m_0} and D_{A_0} , their ratios D_{m_0}/D_{A_0} , and k_D are tabulated in Table II.

The results in Table II show that the values of D_{m_0}/D_{A_0} are larger in cyclohexane than in benzene and that the absolute values of k_D are smaller in cyclohexane than in benzene. Moreover, it is significant that the values of k_D at the θ point are small and negative. In other words, a small negative concentration dependence of the diffusion coefficient can be observed at the θ point and k_D will increase as increasing solvent power passes through

TABLE II
Diffusion Constants and Concentration Coefficients of Diffusion Coefficients

| Samples | Styron 683-7 | | N.B.S 705 | | N.B.S. 419 | |
|--|------------------|--------------|------------------|--------------|------------------|--------------|
| | cyclo- hexane | ben- zene | cyclo- hexane | ben- zene | cyclo- hexane | ben- zene |
| $D_{m_0} \times 10^7, \text{ cm}^2/\text{sec}$ | 3.86 | 3.26 | 3.19 | 3.29 | 2.67 | 1.57 |
| $D_{A_0} \times 10^7, \text{ cm}^2/\text{sec}$ | 2.71 | 3.20 | 2.88 | 3.88 | 2.71 | 2.05 |
| D_{m_0}/D_{A_0} | 1.71 | 1.02 | 1.10 | 0.76 | 0.99 | 0.76 |
| $k_D, 100 \text{ ml/g}$ | -0.06 | 0.45 | -0.04 | 0.22 | -0.04 | 0.59 |

the point at $k_D = 0$. For monodisperse samples in benzene, the values of D_{m_0}/D_{A_0} are smaller than 1.0. As D_{m_0}/D_{A_0} is a parameter of polydispersity,¹ it is strange that the value of D_{m_0}/D_{A_0} is smaller than 1.0. However, this phenomenon can be interpreted from a consideration of the fact that concentration dependence of diffusion coefficient makes a significant contribution to the value of D_{m_0}/D_{A_0} . In the system which has concentration dependence of the diffusion coefficient, the moment of the n th order of diffusion pattern around the initial boundary is expressed by the following equation⁷:

$$\begin{aligned}
 m_n &= \int_{-\infty}^{\infty} (|x - x_0|)^n y dx \\
 &= \int_{-\infty}^{\infty} |x|^n y dx - nx_0 \int_{-\infty}^{\infty} |x|^{n-1} y dx + 0(x_0^2, x_0^3 \dots) \\
 &= m'_n - nx_0 m'_{n-1} + 0(x_0^2, x_0^3 \dots)
 \end{aligned} \tag{13}$$

where x_0 is the position of the initial boundary and m'_n and m'_{n-1} are moments of the n th and the $(n - 1)$ th order of diffusion pattern around the origin at which the height of diffusion pattern has its maximum value, H_{max} . Since $x_0 \ll 1$, the terms of the higher order power in the right-hand side of eq. (13) are negligible. Therefore, we have to use the following equation instead of eq. (4) to calculate the value of D_m .

$$m_2 = \int_{-\infty}^{\infty} (x - x_0)^2 y dx = m'_2 - 2x_0 m'_1. \tag{14}$$

The value of m_2 decreases with the increasing value of x_0 , so that the value of D_m becomes smaller. On the other hand, as the value of $H_{x=0}$ becomes smaller with the increasing value of x_0 , the value of D_{A_0} becomes larger. Thus the value of D_{m_0}/D_{A_0} comes close to 1.0 and in some cases it may be smaller than 1.0. Recently the following relationship between k_D and the second virial coefficient A_2 has been given⁸:

$$k_D = 2A_2 M - k_s \tag{15}$$

where M is the molecular weight of the polymer and k_s is the concentration coefficient of the sedimentation coefficient. Though k_s depends upon A_2 ,⁸

TABLE III
Parameters in Equation (9) for Styron 683-7

| | Cyclohexane | Benzene |
|---|-------------------|-------------------|
| $D_0 \times 10^7, \text{cm}^2/\text{sec}$ | 1.91 ₇ | 3.14 ₁ |
| γ_0 | 0.96 ₆ | 0.22 ₄ |

k_D is larger in a good solvent, so that D_{m_0} becomes smaller and D_{A_0} becomes larger. Our experimental results are consistent with this treatment. At the θ point, eq. (15) is written as follows:

$$k_D = -k_s. \quad (16)$$

the negative k_D value at the θ point obtained in our experiment is explained successfully when eq. (16) is treated with a positive k_s value.⁸

Taking account of the above discussion, the results of the molecular weight distribution obtained experimentally by the diffusion method were examined. The values of the parameters in eq. (9) are given in Table III. Integral weight distribution curves of the diffusion constant are shown in Figure 4. The distribution is narrower in benzene than in cyclohexane. Molecular weight distribution curves were obtained by the following equations:

$$D = 1.21 \times 10^{-4} M^{-0.50} \text{ (in cyclohexane)}^9 \quad (17)$$

$$D = 3.05 \times 10^{-4} M^{-0.55} \text{ (in benzene)} \quad (18)$$

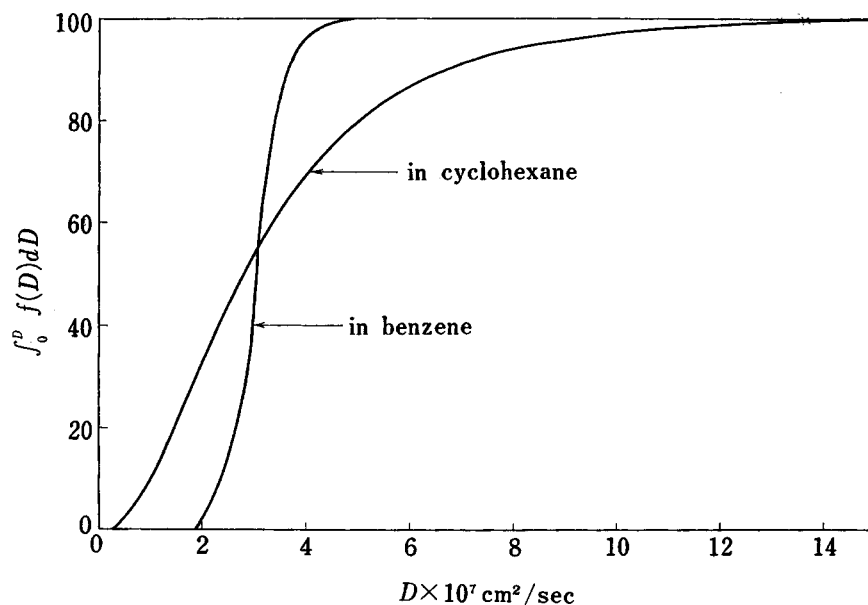


Fig. 4. Integral weight distribution curves of diffusion constant for Styron 683-7.

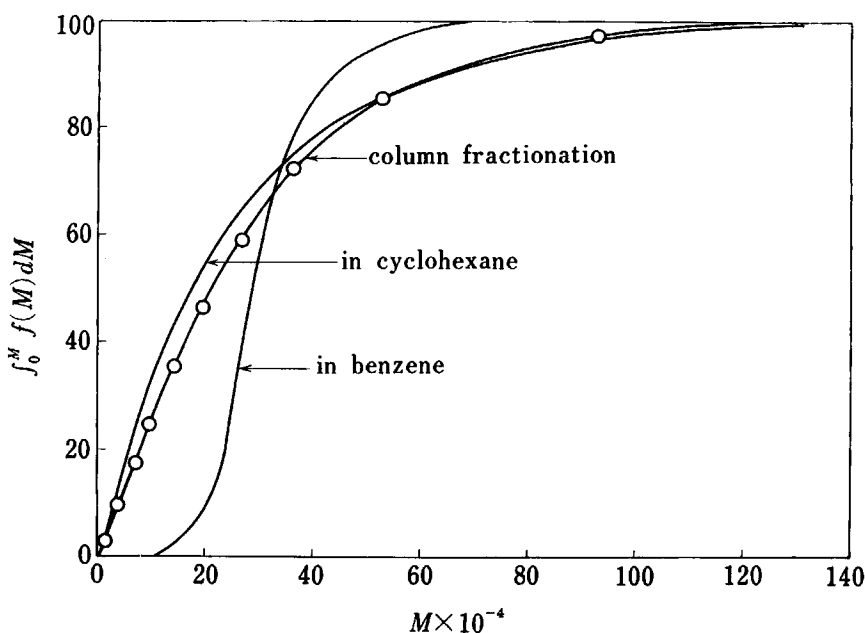


Fig. 5. Integral molecular weight distribution curves of Styron 683-7.

The values of K_D and γ in eq. (18) were 3.05×10^{-4} and 0.55, respectively, which were calculated by the following equation¹⁰:

$$\gamma = (1 + \alpha)/3, k_D = (P^{-1} \Phi^{1/2}) (kT/\eta_0)/K_V^{1/2} \quad (19)$$

where α and K_V are the constants in a viscosity-molecular weight relation; and $P^{-1}\Phi^{1/2}$, η_0 , k , and T are the universal constant, the viscosity of the solvent, Boltzmann's constant, and absolute temperature, respectively. The viscosity-molecular weight relation¹¹ used is $[\eta] = 2.91 \times 10^{-4} M^{0.68}$.

Integral molecular weight distribution curves are shown in Figure 5. The molecular weight distribution curve obtained by column fractionation⁴ is also shown in Figure 5. The curve obtained in cyclohexane agrees well with that obtained by the column method. The distribution curve obtained in benzene, however, looks as if the polymer had a narrow molecular weight distribution. Molecular weights calculated from these distribution

TABLE IV
Molecular Weights of Styron 683-7 Calculated from Molecular Weight Distribution Curves and Obtained from Light Scattering

| | $M_w \times 10^{-4}$ | $M_n \times 10^{-4}$ | M_w/M_n |
|-----------------------------------|----------------------|----------------------|------------------|
| Diffusion in cyclohexane | 28.4 | 12.8 | 2.2 ₂ |
| Diffusion in benzene | 32.2 | 30.5 | 1.0 ₆ |
| Column fractionation ⁴ | 27.7 | 12.5 | 2.2 ₂ |
| Light scattering ⁴ | 30.2 | — | — |

curves are given in Table IV as well as molecular weights obtained by light scattering measurement.

From these results of molecular weight distribution measurements, it is accepted that, in polymer-good solvent system such as polystyrene in benzene, the diffusion method leads to a large error in obtaining the molecular weight distribution. This is due to the large concentration dependence of the diffusion coefficient, that is, the value of D_{m_0}/D_A is close to 1.0 in a good solvent even for polydisperse polymers. At the θ point, the absolute value of k_D is very small though not equal to zero. Therefore, the molecular weight distribution curve is not affected by the concentration dependence of the diffusion coefficient, agreeing with the results of column fractionation. Thus the diffusion measurement for obtaining molecular weight distribution has to be carried out under an ideal system in which the value of k_D is zero. We have not yet obtained the condition where k_D becomes zero. Therefore, in order to obtain the molecular weight distribution, it is best to carry out diffusion measurements at the θ point.

References

1. N. Gralen, *Kolloid Z.*, **95**, 188 (1941).
2. W. Burchard and H.-J. Cantow, *Polymer Fractionation*, Academic Press, New York, 1967, p. 285.
3. H. Kobayashi, *J. Polym. Sci.*, **39**, 369 (1969).
4. A. Kotera, H. Matsuda, Y. Miyazawa, K. Okamoto, and S. Kuroiwa, Polymer Symposium, Kyoto, Japan, 1965.
5. National Bureau of Standards Certificate, (S.R.M. 705).
6. H. Fujita, *J. Colloid Sci.*, **9**, 269 (1954).
7. H. Matsuda and S. Kuroiwa, *Rept. Progr. Polym. Phys. Japan*, **10**, 35 (1967).
8. C. W. Phun and M. Fixman, *J. Chem. Phys.*, **41**, 937 (1964).
9. H.-J. Cantow, *Makromol. Chem.*, **30**, 169 (1959).
10. N. Yamada, H. Matsuda, and H. Nakamura, *Kobunshi Kagaku*, **18**, 452 (1961).
11. C. Banford and M. Dewar, *Proc. Roy. Soc., Ser. A*, **192**, 329 (1948).

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