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SELF-DIFFUSION OF BENZENE AND DIFFUSIONS OF SULFUR AND IODINE IN BENZENE UNDER PRESSURE

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Introduction

There now exist rather extensive works on both self-diffusion and mutual diffusion in liquids, but most of them were made at atmospheric pressure. At the atmospheric pressure, however, both temperature and density vary simultaneously, and so it is impossible to separate the effects of these two factors on diffusion. There has been no attempt to separate the two effects on self-diffusion of organic liquids except carbon tetrachloride1) and carbon disulfide2).

In the present report studies on the self-diffusion of benzene and on the diffusions of iodine and sulfur in benzene under pressure are presented. Benzene is likely amenable to treatment by Eyring's rate process theory of diffusion and viscosity3) because it is unassociated and because its geometry should lead to diffusion preferentially in the benzene ring plane. The thermodynamic properties of sulfur solution in benzene, in which sulfur is in the well-defined S_8 ring form, were studied by Hildebrand and are amenable to treatment by the Hildebrand's regular solution theory4), whereas the iodine in benzene forms a charge transfer complex with benzene5). In this paper the models of diffusion in liquids will be discussed.

Experimentals

Materials Benzene used as the solvent or for the exchange was the purest commercially available and was dried over metallic sodium to be distilled off. The radioactive benzene was purchased from the Radiochemical Centre, Amersham, Buckinghamshire, England. Iodine was purified by repeated sublimation and sulfur by repeated recrystalization from its benzene solution.

Apparatus and procedures Diffusion was measured by the capillary cell method described by Anderson and Saddington6) and adapted by Haycock, Alder and Hildebrand7) for high pressure. The diffusion cells were accurately calibrated capillaries, about 4 cm in length and 0.02 ml in volume in the study on the self-diffusion of benzene, and from 3 to 5 cm in length and from 0.05 to 0.1 ml in volume in the studies on diffusions of iodine and sulfur in benzene.

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1) H. Watts, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **23**, 659 (1955)

2) R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.*, **21**, 267 (1953)

3) S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Company, 1941

4) J. H. Hildebrand and R. L. Scott, *Solubility of Non-electrolytes*, Reinhold Publishing Corp., 1952

5) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949)

6) S. Anderson and K. Saddington, *J. Chem. Soc.*, **1949**, 5381

7) E. W. Haycock, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **21**, 1601 (1953)

In the former study the cells were filled with C_6H_6 containing C^{14} sufficient to give 1900 counts per minute in the counting system used. In the latter studies the cells were filled with benzene containing 2.77×10^{-3} mole fraction of iodine or sulfur. The cells were immersed in a stainless steel reservoir of pure inactive benzene in a thermostat constant to ±0.02°C. The quantity of benzene per one cell is from 100 to 200 ml according to the size of the reservoir, which is enough to be assumed to be infinite in the calculation of diffusion coefficient. Diffusion was allowed to proceed for 3 to 5 days according to the diffusion rate under the experimental conditions. The cells were then removed and their residual radioactivity of benzene or the residual concentration of sulfur or iodine in benzene in the cells was determined as described below.

The apparatus for the study of diffusion under pressure was schematically shown in Fig. 1.

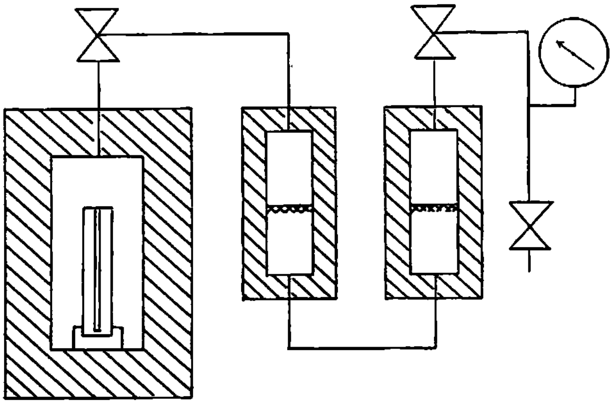

Fig. 1 Diagram of apparatus for the study of diffusion coefficient under pressure

Pressures were measured on a Bourdon type gauge calibrated so that it could be read to ±5 kg/cm². The benzene was completely separated from the pressure transmitting fluid by a mercury U-tube. The loading and unloading operations took approximately 15 minutes.

The radioactivity of benzene was counted with a proportional counter model PC-3 serial No. 35, Nuclear Measurements Corp., Indianapolis, after it was converted into barium carbonate by the wet combustion method with Van Slyke-Floch's oxidizing agent. The concentration of sulfur in benzene was determined according to the method recommended by Bartlett and Skoog[8]. The benzene solution in the cell was dissolved in the acetone solvent, into which the sodium cyanide solution and the ferric chloride solution were added. The absorbance was then determined by means of Beckmann model D. U. spectrophotometer at the wave length 465 mμ. The concentration of iodine in benzene was determined from the direct measurement of its absorption of light with a standard photoelectric colorimeter using a blue filter.

Calculation of Diffusion Coefficients

Different from usual measurements at atmospheric pressure, it is necessary in this experiment

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[8] J. K. Bartlett and D. A. Skoog, *Anal. Chem.*, 26, 1008 (1954)

to take account for the contraction of liquid in the capillary due to pressurizing at the beginning of the experiment and for the expansion of the liquid due to the pressure releasing at the end. The general solution of the differential equation for the one dimentional diffusion under the boundary conditions: zero flux at time $t=0$, zero solute concentration for $x=l$, where x is coordinate and l is the length of the capillary and initial concentration $f(x)$ is[9]

$$C=\frac{2}{l}\sum_{n=0}^{\infty}\left\{\exp\left[\frac{-(2n+1)^2\pi^2Dt}{4l^2}\right]\right\}\cos\frac{(2n+1)\pi x}{2l}\int_0^l f(x')\cos\frac{(2n+1)\pi x'}{2l}dx', \tag{1}$$

where c is the concentration of the solute at time t and coordinate x, and D is the diffusion coefficient.

For the case $f(x)=C_0$ at $t=0$ and $0<x<l\,(1-\beta P)$, where β is the isothermal compressibility, P the pressure and βlP the contraction of the liquid in the capillary, and $f(x)=0$ for $l(1-\beta P)\leqq x$, Eq. (1) reduces to

$$\frac{C_{av.}}{C_0}=\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2Dt}{4l^2}\right]\sin^2\left[\frac{(2n+1)\pi(1-\beta P)}{2}\right], \tag{2}$$

where $C_{av.}$ is the average concentration of the solute for $0<x<l\,(1-\beta P)$. For $Dt/l^2>0.2$, Eq. (2) reduces to

$$\frac{Dt}{l^2}=\frac{4}{\pi^2}\ln\left[\frac{8}{\pi^2}\frac{C_0}{C_{av.}}\sin^2\frac{\pi}{2}(1-\beta P)\right] \tag{3}$$

Eq. (3) was used in computing the data of the present investigation.

Experimental Results

The self-diffusion coefficient of benzene was studied over the temperature range of 15 to 45°C and over the pressure range of 1 atm to 660 kg/cm². The experimental results are given in Table 1 with Graupner and Winter's data at atmospheric pressure[10] and are shown graphically in Fig. 2. The integral diffusion coefficient of sulfur from a 2.77×10^{-3} mole fraction of sulfur solution in benzene into pure benzene was studied over the temperature range of 25 to 45°C and over the pressure range of 1 atm to 800 kg/cm². Its experimental results are given in Table 2

Table 1 Values of the self-diffusion coefficients of benzene ($D\times10^5$, cm²/sec)

Pressure kg/cm²	Temperature, °C			
	15	25	35	45
1.03	1.83±0.06	2.13±0.06	2.44±0.02	2.86±0.03
	1.88[a]	2.15[a]	2.40[a]	2.67[a]
250	1.47±0.06	1.69±0.01	1.97±0.06	2.29±0.01
500		1.39±0.05	1.59±0.06	....
660				1.64±0.04

a) *ref.* 10)

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9) H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford Univ. Press., London, 1947

10) K. Graupner and E. R. S. Winter, *J. Chem. Soc.*, **1952**, 1145

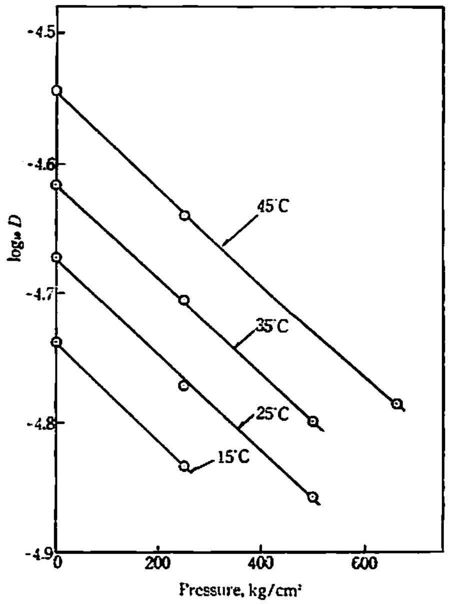

Fig. 2 Pressure dependence of the self-diffusion coefficient of benzene as a function of temperature

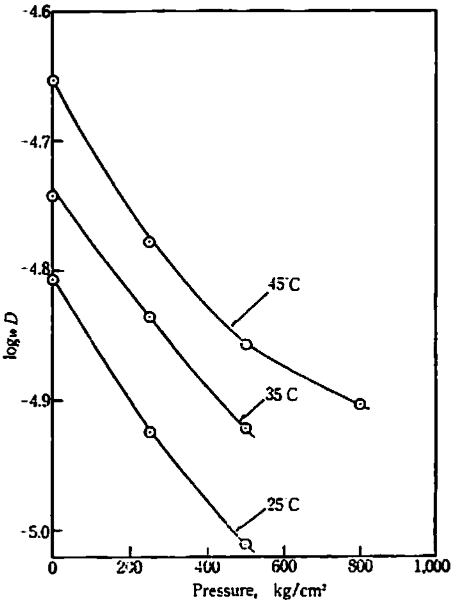

Fig. 3 Pressure dependence of the diffusion coefficient of sulfur in benzene as a function of temperature

Table 2 Values of the diffusion coefficients of sulfur in benzene ($D\times10^6$, cm²/sec)

Pressure kg/cm²	Temperature, °C		
	25	35	45
1.03	1.56±0.04	1.81±0.02	2.22±0.05
250	1.19±0.01	1.46±0.01	1.67±0.05
500	0.98±0.02	1.20±0.03	1.39±0.05
800			1.25±0.06

Table 3 Values of the diffusion coefficient of iodine in benzene ($D\times10^6$, cm²/sec)

Pressure kg/cm²	Temperature, °C		
	25	35	51
1.03	2.15±0.08 2.14[b]	2.76±0.04	3.12±0.08
250	1.83±0.12	2.31±0.05	2.64±0.01
900		1.63±0.04	1.89±0.07

b) *ref.* 11)

and shown graphically in Fig. 3. The integral diffusion coefficient of iodine from a 2.77×10^{-3} mole fraction of iodine solution in benzene into pure benzene was studied over the temperature range of 25 to 51°C and over the pressure range of 1 atm to 900 kg/cm². The experimental results are given in Table 3 with Stokes, Dunlop and Hall's data[11] at 25°C and at atmospheric pressure

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11) R. H. Stokes, P. J. Dunlop and J. R. Hall, *Trans. Faraday Soc.*, 49, 886 (1953)

and shown graphically in Fig. 4.

Graupner and Winter's values for the self-diffusion of benzene with C_6H_5D as a tracer and with diaphragm cell method and Stokes, Dunlop and Hall's values for iodine in benzene with the diaphragm cell method agree fairly well with the results of the present work. The logarithms of the diffusion coefficients are plotted against the reciprocal of the absolute temperature in Fig. 5.

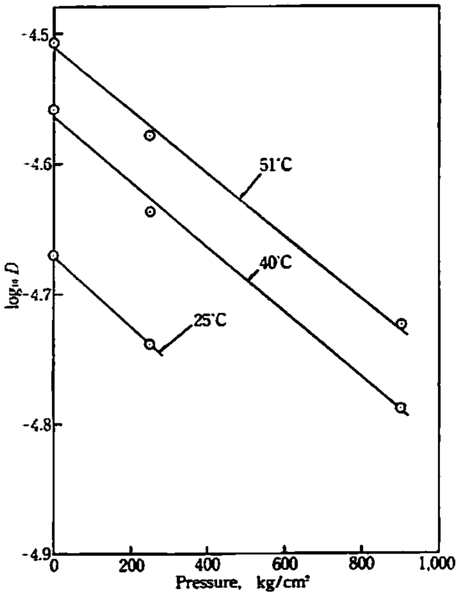

Fig. 4 Pressure dependence of the diffusion coefficient of iodine in benzene as a function of temperature

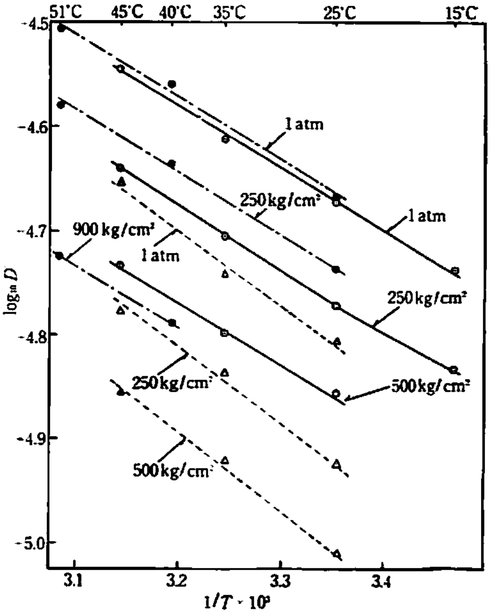

Fig. 5 Temperature dependence of the diffusion coefficients as a function of pressure

—⊙—: self-diffusion of benzene

—●—: diffusion of iodine in benzene

—△—: diffusion of sulfur in benzene

Discussions

Relation between viscosity and diffusion coefficient With reference to the general theories of transport processes in liquids, it is interesting to study, as a function of temperature and pressure, the constancy of the quantity, $D\eta/kT$. This quantity should be a constant for an incompressible pure liquid. The values $D\eta/kT$ calculated from the diffusion coefficients obtained in this work and the viscosity interpolated from the published values in *American Institute of Physics Handbook*[12] and from the Bridgman's data[13] are shown in Table 4 for the self-diffusion of benzene, in Table 5 for sulfur in benzene and in Table 6 for iodine in benzene. The nearly constant values are found in Table 4 where the mean is $3.02 \times 10^6\,\text{cm}^{-1}$ with the average deviation

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[12] D. E. Gray, *American Institute of Physics Handbook*, McGraw-Hill Book Company, 1957

[13] P. W. Bridgman, *Physics of High Pressure*, Bell & Sons, London, 1949

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Table 4 $D\eta/kT\times10^{-6}$ (cm^{-1}) for the self-diffusion of benzene

Pressure kg/cm²	Temperature, °C 15	25	35	45
1.03	3.23	3.12	2.99	3.00
250	3.19	3.02	2.96	2.93
500		3.03	2.92	……
660				2.88

Table 5 $D\eta/kT\times10^{-6}$ (cm^{-1}) for the diffusion of sulfur in benzene

Pressure kg/cm²	Temperature, °C 25	35	45
1.03	2.28	2.23	2.34
250	2.13	2.20	2.13
500	2.13	2.20	2.16
800			2.44

Table 6 $D\eta/kT\times10^{-6}$ (cm^{-1}) for the diffusion of iodine in benzene

Pressure kg/cm²	Temperature, °C 25	40	51
1.03	3.15	3.14	2.98
250	3.28	3.20	3.04
900		3.75	3.58

$\pm0.08\times10^6$ cm^{-1} and in Table 5 where the mean is 2.22×10^6 cm^{-1} with the average deviation $\pm0.08\times10^6$ cm^{-1}. But there found some large fluctuation in $D\eta/kT$ for iodine in benzene, which is excusible because in this system iodine forms a charge transfer complex with benzene.

According to Eyring's theory, if the mechanism of activation for diffusion can be assumed identical with that of viscous flow, the relation between viscosity and diffusion coefficient is given by

$$\frac{D\eta}{kT}=\frac{\lambda_1}{\lambda_2\lambda_3} \qquad (4)$$

where λ_1 is the distance between layers of liquid molecules parallel to the concentration gradient for diffusion or the shearing force in viscosity and $(\lambda_2\lambda_3)^{1/2}$ the area of the molecule whose normal is perpendicular to the concentration gradient or the shearing force. The constancy of $D\eta/kT$ is given by other theories such as Stokes-Einstein's theory, $D\eta/kT=1/3\pi\lambda$, where the frictional forces are those by the Stokes' expression for a relatively large particle falling through a continuous medium. λ_1 and $(\lambda_2\lambda_3)^{1/2}$ in Eq. (4) could be calculated with the assumption that $(\lambda_1\lambda_2\lambda_3)$ is equal to the mean molecular volume.

Table 7 λ_1 and $(\lambda_2\lambda_3)^{1/2}$ for the self-diffusion of benzene

Pressure	Temperature, °C 15		25		35		45	
	λ_1	$(\lambda_2\lambda_3)^{1/2}$	λ_1	$(\lambda_2\lambda_3)^{1/2}$	λ_1	$(\lambda_2\lambda_3)^{1/2}$	λ_1	$(\lambda_2\lambda_3)^{1/2}$
kg/cm²	Å	Å	Å	Å	Å	Å	Å	Å
1.03	2.18	8.21	2.15	8.31	2.12	8.42	2.14	8.45
250	2.15	8.20	2.10	8.35	2.09	8.39	2.09	8.42
500			2.09	8.28	2.06	8.38	……	……
660							2.04	8.45

The results of the calculation for the self-diffusion are shown in Table 7. It will be seen that λ_1 is more decreased with pressure than $(\lambda_2\lambda_3)^{1/2}$, which invariably increases with temperature. The distance between the two adjacent layers of graphite is 3.40 Å and the molecular diameter of benzene is 4.96 Å, thus the values of λ_1 and $(\lambda_2\lambda_3)^{1/2}$ agree fairly well with the known dimension of the molecule. From the self-diffusion coefficient of carbon tetrachloride determined by Hildebrand *et al.*, however, $\lambda_1=2.24$ Å and $(\lambda_2\lambda_3)^{1/2}=8.48$ Å at 25°C are obtained with the same assumption as used above, whereas the C-C distance from X-ray scattering is 6.4 Å14) and there found no anisotropical arrangement of CCl_4 molecule in the liquid. The cause of this inconsistency could be attributed whether Eyring's equation is too simple to evaluate λ_1 and $(\lambda_2\lambda_3)^{1/2}$, or the diffusion mechanism is different from those in viscous flow in carbon tetrachloride.

Because it could not be determined which cause is correct, it can not be concluded that the values of λ_1 and $(\lambda_2\lambda_3)^{1/2}$ calculated from Eq. (4) are true dimensions in liquid state as Partington *et al.*15), Fishman16) and other investigators did.

Temperature dependence of diffusion The quantity usually described as the energy of activation for diffusion, denoted here by E_p in contradistinction to the energy E_v at constant volume, is calculated from the observed variation of diffusion with temperature using the equation,

$$E_p=RT^2\left(\frac{\partial \ln D}{\partial T}\right)_p, \tag{5}$$

whereas E_v is defined by the equation,

$$E_v=RT^2\left(\frac{\partial \ln D}{\partial T}\right)_v. \tag{6}$$

Since both density and diffusion rate change simultaneously with temperature at constant pressure, E_p has not any precise meaning. In general, in the calculation of E_p, it has been assumed that the simultaneous density changes on heating would be so small as to be negligible, but this is not the case as it has been pointed out by Hildebrand for the self-diffusion of carbon tetrachloride. In the following a different approach from that by Hildebrand is presented. The relation between E_v and E_p is given by

$$E_v=E_p+(RT^2)\frac{\alpha}{\beta}\left(\frac{\partial \ln D}{\partial P}\right)_T \tag{7}$$

where α is the isobaric expansion coefficient and β the isothermal compressibility. From the data in this work the following results are obtained, where for simplicity the second term on the right of Eq. (7) is denoted by E_r: for the self-diffusion of benzene $E_p=2{,}780$ cal/mole, $E_r=2{,}000$ cal/mole and $E_v=780$ cal/mole, and for the diffusion of sulfur in benzene when the isothermal line at 45°C is used $E_p=3{,}340$ cal/mole, $E_r=2{,}480$ cal/mole and $E_v=860$ cal/mole between 1 atm and 250 kg/cm², $E_r=1{,}700$ cal/mole and $E_v=1{,}640$ cal/mole between 300 and 500 kg/cm², $E_r=940$ cal/

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14) F. F. Gray and N. S. Gingrich, *J. Chem. Phys.*, **11**, 351 (1943)
15) J. R. Partington, R. F. Hudson and K. W. Bagnall, *J. Chim. Phys.*, **55**, 76 (1958)
16) E. Fishman, *J. Phys. Chem.*, **59**, 469 (1955)

mole and $E_v=2.400$ cal/mole between 600 and 800 kg/cm², and for the diffusion of iodine in benzene $E_p=2,780$ cal/mole, $E_r=1,550$ cal/mole and $E_v=1,230$ cal/mole.

The same results with the above could be obtained from the isochoric lines as Hildebrand did. Benzene has much the same volume, 89.3±0.1 ml, at 25°C and 1 atm and at 45°C and 250 kg/cm², so that from Eq. (6) $E_v=700$ cal/mole is obtained for the self-diffusion of benzene. It is remarkable that the approximate activation energy at constant volume is necessary for the self-diffusion of benzene and for the diffusion of sulfur in benzene, at low pressures but the activation energy for iodine in benzene is a bit higher than those for the other processes. The reason for this will be discussed later. E_v for sulfur in benzene increases with pressures and so with density. This is consistent with the general idea that the potential energy barrier between two neighboring equilibrium positions in liquids increases with increasing density and it is expected so for the self-diffusion of benzene at higher density than that in the case of the present work. According to Eyring, the increase of the internal energy for the activation processes, $\Delta E^{\ddagger}$, is given by

$$\Delta E^{\ddagger}=E_v-RT \tag{8}$$

This gives $\Delta E^{\ddagger}=170$ cal/mole for the self-diffusion of benzene, which is so small that it is difficult to consider any high potential energy barrier for diffusion in benzene.

Pressure dependence of diffusion The activation volume, $\Delta V^{\ddagger}$, gives some light upon the diffusion prosesses. It is calculated by

$$\Delta V^{\ddagger}=-RT\left(\frac{\partial \ln D}{\partial P}\right)_T \tag{9}$$

The results of calculations are as follows: for the self-diffusion of benzene $\Delta V^{\ddagger}=22$ ml, for the diffusion of sulfur in benzene when the isothermal lines at 45°C is used, $\Delta V^{\ddagger}=29$ ml at 1 atm, $\Delta V^{\ddagger}=26$ ml at 250 kg/cm², $\Delta V^{\ddagger}=15$ ml at 500 kg/cm² and $\Delta V^{\ddagger}=8$ ml at 800 kg/cm² and for the diffusion of iodine in benzene $\Delta V^{\ddagger}=15$ ml. It is to be noted that for diffusion of sulfur in benzene $\Delta V^{\ddagger}$ is decreased with increasing pressure. The heat of activation for diffusion, $\Delta H^{\ddagger}$, minus $\Delta E^{\ddagger}$ is given by

$$\Delta H^{\ddagger}-\Delta E^{\ddagger}=P\Delta V^{\ddagger} \tag{10}$$

When the external pressure is taken as P, the result from Eq. (10) is inconsistent with that from Eq. (7), but the internal pressure should be taken as P, because the activation processes for diffusion involves the volume increase against the intermolecular force between the molecules. Then for the self-diffusion of benzene $\Delta H^{\ddagger}-\Delta E^{\ddagger}=(\partial E/\partial V)_T\Delta V^{\ddagger}=1,860$ cal/mole, which agree well with the result 2,000 cal/mole from Eq. (7).

Relative magnitudes of diffusion coefficients The absolute magnitudes calculated³⁾ is very different from those measured, as Graupner pointed out. There is no practical diffusion theory except Eyring's application to a non-spherical molecule such as benzene. The relative magnitude of diffusion coefficient, however, may be given by

$$\frac{D_{\mathrm{I}}}{D_{\mathrm{II}}}=\left(\frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}\right)^{1/2}\cdot\left(\frac{V_{\mathrm{II}}}{V_{\mathrm{I}}}\right)^{2/3} exp\left(\frac{\Delta E_{\mathrm{II}}{}^{\ddagger}-\Delta E_{\mathrm{I}}{}^{\ddagger}}{RT}\right) \tag{11}$$

Table 8 Relative magnitude of diffusion coefficient

	$\left(\frac{m\mathbf{I}}{m\mathrm{I}}\right)^{1/2}$	$\left(\frac{V\mathbf{I}}{V\mathrm{I}}\right)^{2/3}$	$exp\left(\frac{\Delta E_{\mathbf{I}}{}^{\ddagger}-\Delta E_{\mathrm{I}}{}^{\ddagger}}{RT}\right)$	*Calc.*	*Obs.**
$D_{C_6H_6}/D_{CCl_4}$	1.40	1.06	1.80	2.66	1.55
$D_{C_6H_6}/D_{S_8 in C_6H_6}$	1.81	1.32	1.1	2.6	1.36
$D_{C_6H_6}/D_{I_2 in C_6H_6}$	1.80	0.76	2.1	2.9	1.01
$D_{C_6H_6}/D_{I_2-C_6H_6 in C_6H_6}$	2.06	1.40	2.1	6.1	1.01

* Diffusion coefficients at low pressures are used.

when the activity coefficients are assumed to be constant. The results of the calculation according to Eq. (11) are shown in Table 8. The agreement between the calculated and the observed is not so good, partly due to the ambiguity in the activation energy and in the cross section of the molecule, but it is noteworthy that if the charge transfer complex of iodine with benzene diffuses, its diffusion coefficient should be much smaller than those observed. The equilibrium constant between iodine and the charge transfer complex in benzene has not yet been reported, but in carbon tetrachloride the reported equilibrium constant is 1.72 at 25°C[4]. Therefore, it can be assumed that a single iodine molecule primarily determines the diffusion rate. This assumption may be supported by the small activation volume for the diffusion of iodine in benzene reported in the preceding section.

Conclusions

In conclusion, the self-diffusion coefficient of benzene and the diffusion coefficients of sulfur and iodine in benzene were determined over the temperature range from 15 to 51°C and over the pressure range from 1 atm to 900 kg/cm^2.

The quantity $D\eta/kT$ for each system is nearly constant over a wide range of temperature and pressure for the systems except iodine solution in benzene.

The activation energy at constant volume is so small that it is difficult to consider that there is any high potential energy barrier for diffusion in benzene except in the high density region which the hole theory claims.

The difference between $\Delta H^{\ddagger}$ and $\Delta E^{\ddagger}$ could be explained by using the internal pressure as the pressure.

It can be assumed that a single iodine molecule primarily determines the diffusion rate in benzene solution.

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