Self-diffusion of Benzene under Pressure

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Most of the works on diffusion in liquids have been made at atmospheric pressure. At atmospheric pressure, however, both the temperature and the density are varying 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 tetrachloride[1] and carbon disulfide[2]. In advance of the present work, diffusion of iodine and sulfur in benzene under pressure was studied[3]. In this communication a study on the self-diffusion of benzene under pressure is presented.

Diffusion was measured by the capillary-cell method. The diffusion cells were accurately calibrated capillaries about 4 cm. in length and 0.02 ml. in volume and were filled with benzene containing carbon-14 sufficient to give 1900 counts per minute in a counting system used. The cells were immersed in a reservoir of pure inactive benzene in a thermostat constant to ±0.01 °C. Diffusion was allowed to proceed for about 3 days, after which benzen in the cell was transferred into a combustion apparatus by a gas-phase sampling technique and was converted into barium carbonate by wet combustion method. The activity was measured by an α-β-γ proportional counter. Three to six determinations were carried out at each experimental conditions and the maximum deviation occurred was as large as 3.5 per cent from the mean. The results were presented in Table I with Graupner's data[4] at atmospheric pressure.

According to Eyring's theory[5], if the mechanism of activation in diffusion can be assumed identical with that of viscous flow, the relation between self-diffusion coefficient and viscosity in liquids is given by

$$D\eta/\boldsymbol{k}T=\lambda_1/(\lambda_2\lambda_3) \tag{1}$$

where the common notation is used. The constancy of the values of $D\eta/\boldsymbol{k}T$ is shown in Table I, where at 35°C the values of λ_1 and $(\lambda_2\lambda_3)^{1/2}$, obtained on the assumption that $\lambda_1\lambda_2\lambda_3$ is equal to the mean molecular volume, are also given. The distance between two adjacent layers of graphite is 3.40 Å and the molecular diameter of benzene is 4.96 Å, and thus the values of λ_1 and $(\lambda_2\lambda_3)^{1/2}$ agree fairly well with the known dimensions of the molecule. From the self-diffusion coefficient of carbontetrachloloride determined by Hildebrand et al., $\lambda_1=2.24$ Å and $(\lambda_2\lambda_3)^{1/2}=8.48$ Å at 25°C is obtained with the same assumption as used above. Although benzene is particularly amenable to Eyring's theory, because its geometry should lead to diffusion preferentially in the direction of benzene ring plane, it is strange that in the case

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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, ibid., **21**, 267 (1953).

[3] H. Hiraoka, to be published in *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62** (1959).

[4] K. Graupner and E. R. S. Winter, *J. Chem. Soc.*, **1952**, 1145.

[5] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Co., New York, (1941), p. 477.

Table I
SELF-DIFFIUSION COEFFICIENTS OF BENZENE

	Temp. (°C)									
	15		25		35				45	
Pressure	$D\times10^5$	$D\eta/kT \times10^6$	$D\times10^5$	$D\eta/kT \times10^6$	$D\times10^5$	$D\eta/kT \times10^6$	λ_1	$(\lambda_2\lambda_3)^{1/2}$	$D\times10^5$	$D\eta/kT \times10^6$
(kg/cm²)	$\left(\frac{cm^2}{sec.}\right)$	$\left(\frac{1}{cm^2}\right)$	$\left(\frac{cm^2}{sec.}\right)$	$\left(\frac{1}{cm.}\right)$	$\left(\frac{cm^2}{sec.}\right)$	$\left(\frac{1}{cm.}\right)$	(Å)	(Å)	$\left(\frac{cm^2}{sec.}\right)$	$\left(\frac{1}{cm.}\right)$
1.03	1.83	3.23	2.13	3.12	2.42	2.99	2.12	8.42	2.86	3.00
	1.88[a]		2.15[a]		2.40[a]				2.67[a]	
250	1.47	3.19	1.69	3.02	1.97	2.96	2.09	8.39	2.29	2.93
500			1.39	3.04	1.59	2.92	2.06	8.38	—	—
660									1.64	2.88

a) ref. 4)

of carbontetrachloride λ_1 is much smaller than $(\lambda_2\lambda_3)^{1/2}$. It can not be concluded that the valuse of λ_1 and $(\lambda_2\lambda_3)^{1/2}$ thus calculated are true dimensions in liquid state, as Partington et al.[6] and other investigators did.

The relation between the experimental activation energy of diffusion at a constant volume, E_v, and the experimental activation energy at a constant pressure, E_p, is given by

$$E_v = E_p + (RT^2)(\alpha/\beta)(\partial \ln D/\partial P)_T \qquad (2)$$

where α is the isobaric expansion coefficient and β the isothermal compressibility. From the values in Table I the following results are obtained: E_p=2,780 cal./mole, $(RT^2)(\alpha/\beta)(\partial P \ln D/\partial)_T$=2,000 cal./mole, E_r=780 cal./mole. According to Eyring, the increase of internal energy for the activation process, $\Delta E^{\neq}$, is given by

$$\Delta E^{\neq} = E_v - RT \qquad (3)$$

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

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[6] J. R. Partington, R. F. Hudson and K. W. Bagnall, *J. Chem. Phys.*, 55, 77 (1958).