

201. Some Measurements of the Self-diffusion Coefficients of Liquids.

By K. GRAUPNER and E. R. S. WINTER.

By use of deuterium as tracer element, the self-diffusion coefficients of water, benzene, bromoethane, and ethanol have been measured over the temperature range 15—45°. For water, some measurements have also been made by using ^{18}O .

SELF-DIFFUSION measurements have been reported upon only two liquids, namely, lead (Groh and Hevesy, *Ann. Physik*, 1920, **63**, 85) and water (Temkin, *Nature*, 1935, **136**, 552; Orr and Butler, *J.*, 1935, 1273; Lamm, *Nova Acta Regiae Soc., Upsala*, 1937, **10**, No. 6; Rögner, *Z. Electrochem.*, 1941, **47**, 164; Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 510, 4181). This lack of experimental work is somewhat surprising since there is a large and growing body of work upon self-diffusion coefficients in solids, and recently those of a number of gases have been measured (Hutchinson, *Phys. Rev.*, 1947, **72**, 1256; Winn, *ibid.*, 1948, **73**, 698; 1950, **80**, 1024; Winter, *Trans. Faraday Soc.*, 1951, **47**, 342). With the present ready availability of tracer isotopes, both stable and radioactive, many more experimental measurements upon self-diffusion may be expected: this paper presents data for the self-diffusion coefficients of water, benzene, bromoethane, and ethanol, over the temperature range 15—45°. Deuterium has been used as the tracer element, and in the case of water some observations have also been made by using the oxygen isotope ^{18}O .

EXPERIMENTAL

Materials.—Monodeuterobenzene: Deuterium oxide (29% D_2O ; 0.48 g.-mol.) was slowly added to a stirred ethereal solution of phenylmagnesium bromide (0.48 g.-mol.) cooled in ice-water. The ether and deuterobenzene were distilled off, finally *in vacuo*, and carefully fractionated; the yield was 24 g. (57%) of benzene containing 1.7% of ether. The ether was removed by treatment with 60% perchloric acid (Best and Wilson, *J.*, 1946, 239). Final purification was effected by successive distillations *in vacuo* from phosphoric oxide; the benzene obtained contained 25% of $\text{C}_6\text{H}_5\text{D}$. The normal benzene used was Baker's C.P. thiophen-free, distilled *in vacuo* from phosphoric oxide.

2-Deuterobromoethane, $\text{CH}_2\text{D}\cdot\text{CH}_2\text{Br}$, was prepared by addition of deuterium bromide to ethylene on a bismuth bromide-asbestos catalyst (Wibaut, Dickmann, and Rutgers, *Rec. Trav. chim.*, 1928, **47**, 477). Yields of about 24% were found, in contrast to the 80—90% reported by Wibaut *et al.* The resulting ethyl bromide and the normal material (May and Baker) were purified by distillation from phosphoric oxide, the fraction, b. p. 38—40°, being collected.

Ethyl deuterioxide was prepared by adding 1.6 ml. of 3% D_2O to 29 ml. of dry "AnalaR" ethyl alcohol, followed by drying with barium oxide and twice with anhydrous copper sulphate. The barium oxide treatment reduces the water content to 0.6% (Smith, *Ind. Eng. Chem. Anal.*, 1929, **1**, 72): the first batch of copper sulphate became slightly blue, but the second did not, so the alcohol contained certainly less than 0.6% water. The light alcohol used (Burnett's) had been kept for some months over anhydrous copper sulphate; it boiled at 78°: the ethyl deuterioxide was distilled *in vacuo* from the copper sulphate immediately before use.

Combustions.—Samples of benzene were burnt by vapourising the liquid slowly in a stream of dry oxygen which was passed over copper oxide at 800° with a contact time of about 20 seconds. The combustion water was collected in traps cooled in solid carbon dioxide and further purified by distillation *in vacuo* over granular copper oxide at 700°. Bromoethane and ethanol were similarly burnt in a rapid stream of oxygen over asbestos at 800°. In spite of the known exchange reaction of hydrogen from asbestos (Wilson and Wylie, *loc. cit.*), we found no trouble from this cause under our experimental conditions: our asbestos was outgassed at 800° before use, and this treatment may remove the reactive hydrogen. Excess of bromine was removed from the combustion water from ethyl bromide by treatment with carefully dried silver oxide: similar treatment was found necessary for the combustion water from ethanol before consistent density measurements could be obtained.

Deuterium Analyses.—The deuterium contents of the relatively highly enriched compounds obtained by the synthetic methods outlined above, and that of the water used, were determined by pycnometer: both the Parker and Parker pycnometer (*J. Physical Chem.*, 1925, **29**, 130)

and the Fontana and Calvin semi-micropycnometer (*Ind. Eng. Chem. Anal.*, 1942, **14**, 185) were used. The results so obtained were confirmed by accurately diluting a small quantity of the heavy material with sufficient of the normal compound to give <1 atom % of D, and then determining the deuterium content of the water obtained from the diluted material by combustion. The deuterium content of the original heavy compound was calculated by use of Weldon and Wilson's equation (*J.*, 1946, 235). Proper corrections were made throughout to allow for variations in ^{18}O and D content of the reference compounds and reagents (for a detailed account see Graupner, Thesis, London, 1950). The deuterium contents of samples of water containing <1% of D_2O were measured by the semi-micro-silica float method of Briscoe *et al.* (*J.*, 1934, 1207; 1937, 1492; Spoor, Thesis, London, 1938). All water samples were first purified by distillation *in vacuo* from a trace of potassium permanganate and sodium peroxide and then from a trace of phosphoric oxide as described by Spoor. H_2^{18}O contents were determined in the same manner.

Diffusion Measurements.—Two Northrop-McBain cells (McBain and Dawson, *Proc. Roy. Soc.*, 1935, **148**, 32; cell type I), made from Pyrex glass, were used: they had capacities of approx. 4 and 11 ml. and porosities G3 and G4, respectively. All diffusion runs lasted some 18 hours: for each compound one run at each temperature was carried out in both cells, and the mean of the two results recorded (except for water at 25° and the two experiments with H_2^{18}O , all of which were performed in cell I only). The duplicate measurements were in reasonable agreement, except in the case of bromoethane where the differences were much larger, owing we believe, to the difficulty of handling and of burning this relatively volatile liquid: the results are summarised in Table 1. The diffusion runs were followed by determining the density

TABLE 1. *Self-diffusion measurements.*

Temp.	Liquid	$D \times 10^5; \text{cm.}^2 \text{sec.}^{-1}$		Mean
		Cell I	Cell II	
15°	$\text{D}_2\text{O}-\text{H}_2\text{O}$	1.60	1.65	1.62 ± 0.03
25	$\text{D}_2\text{O}-\text{H}_2\text{O}$	2.04	—	2.04
35	$\text{D}_2\text{O}-\text{H}_2\text{O}$	2.69	2.77	2.73 ± 0.04
45	$\text{D}_2\text{O}-\text{H}_2\text{O}$	3.42	3.25	3.34 ± 0.08
25	$\text{H}_2^{18}\text{O}-\text{H}_2\text{O}$	2.09	—	2.09
45	$\text{H}_2^{18}\text{O}-\text{H}_2\text{O}$	3.20	—	3.20
15	$\text{C}_6\text{H}_5\text{D}-\text{C}_6\text{H}_6$	1.88	1.89	1.88 ± 0.01
25	$\text{C}_6\text{H}_5\text{D}-\text{C}_6\text{H}_6$	2.21	2.10	2.15 ± 0.05
35	$\text{C}_6\text{H}_5\text{D}-\text{C}_6\text{H}_6$	2.43	2.37	2.40 ± 0.03
45	$\text{C}_6\text{H}_5\text{D}-\text{C}_6\text{H}_6$	2.61	2.74	2.67 ± 0.06
15	$\text{C}_2\text{H}_5\text{DBr}-\text{C}_2\text{H}_5\text{Br}$	3.23	3.97	3.60 ± 0.37
22.5	$\text{C}_2\text{H}_5\text{DBr}-\text{C}_2\text{H}_5\text{Br}$	4.06	3.55	3.80 ± 0.76
30	$\text{C}_2\text{H}_5\text{DBr}-\text{C}_2\text{H}_5\text{Br}$	4.15	3.77	3.96 ± 0.19
15	$\text{C}_2\text{H}_5\text{OD}-\text{C}_2\text{H}_5\text{OH}$	0.79	0.81	0.80 ± 0.01
25	$\text{C}_2\text{H}_5\text{OD}-\text{C}_2\text{H}_5\text{OH}$	1.03	1.08	1.05 ± 0.03
35	$\text{C}_2\text{H}_5\text{OD}-\text{C}_2\text{H}_5\text{OH}$	1.25	1.38	1.31 ± 0.07
45	$\text{C}_2\text{H}_5\text{OD}-\text{C}_2\text{H}_5\text{OH}$	1.73	1.67	1.70 ± 0.03

TABLE 2. *Diffusion cell data.*

	Cell I	Cell II		Cell I	Cell II
Porosity	G3	G4	Vol. of sintered diaphragm at		
A/L , cm.	0.59	2.31	20°, ml.	0.075	0.203
Vol. of cell at 20°, ml.*	3.91	10.94	Cell constant, K , cm.†	0.131	0.192

* Excluding volume of sintered disc.

† Obtained from Table 3, and equation (2).

of the combustion water, obtained as outlined above by burning samples of liquid, from the two cell compartments at the end of the diffusion. The deuterium concentrations were so chosen that the maximum deuterium content encountered was <1 atom %.

The diffusion cells were suspended from rubber tubing attached to a rigid external support inside air-thermostats surrounded by a water-thermostat. The temperature of the water-thermostat was held constant within $\pm 0.04^\circ$ over long periods, and Beckmann-thermometer readings in the air-thermostats were constant to better than $\pm 0.001^\circ$. Information relating to the two cells is given in Table 2: the volumes of each cell and of the sintered discs of each cell were determined by filling with water and weighing. In order to perform a diffusion run, the contents of cell I were allowed to diffuse into a volume of 3.91 ml. (delivered into the bottom part of the cell by a specially made pipette), and those of cell II were allowed to diffuse into a volume of 10 ml. The cells were frequently cleaned by immersion in a beaker of chromic-sulphuric acid and heating this solution until fuming occurred: after cooling, the cells were

washed through with water and dried. This procedure led to no change in the cell constant. Silicone vacuum stop-cock grease was used on the taps of the cells.

The diffusion cells were calibrated at 25° by allowing 0.1N-potassium chloride to diffuse into water, and employing Gordon's value for $D_i^{25} = 1.838 \times 10^{-5}$ cm.² sec.⁻¹ (*Ann. N.Y. Acad. Sci.*, 1945, **46**, 285). The sintered discs were outgassed in the manner described by McBain and Lui (*J. Amer. Chem. Soc.*, 1931, **53**, 59), and freshly outgassed potassium chloride solution was employed in the calibration: the time allowed for the preliminary diffusion was 30 minutes. Details of the calibration results are given in Table 3, together with some figures obtained at

TABLE 3. *Diffusion with potassium chloride.*

Cell	Temp.	Time (hr.)	$KD_i \times 10^6$, sec. ⁻¹	Cell	Temp.	Time (hr.)	$KD_i \times 10^6$, sec. ⁻¹
I	20°	22	2.14	II	20°	17	3.13
		19	2.11			18	3.17
		17	2.17			} mean 3.15	
I	25	18	2.39	II	25	22	3.54
		23	2.42			20	3.54
		17	2.38			17	3.57
		16	2.46			18	3.50
		17	2.40			20	3.51
		15	2.42			16	3.53
				15	3.58	} mean 3.53	

20°. The cell constants, K , were calculated from the relations:

$$\left. \begin{aligned} \text{for cell I,} & \quad KD_i = (1/t) \ln (c'_f + c''_f)/(c'_f - c''_f) \\ \text{for cell II,} & \quad KD_i = (1/t) \ln (c'_f + 10c''_f/10.94)/(c'_f - c''_f) \end{aligned} \right\} \dots \dots (1)$$

with the time, t , in seconds, c'_f , c''_f being the normalities of potassium chloride at the end of the diffusion in the upper and in the lower portion respectively of the cell.

Values of A/L in Table 2 were obtained by using:

$$K = A(V' + V'')/2.303LV'V'' \dots \dots \dots (2)$$

where V' , V'' , are the volumes of the upper and the lower portion of the cells.

It is by no means certain that the cell constant, obtained by calibration with aqueous potassium chloride solution as above, is the correct value when the cell is used for studies upon non-polar non-conducting liquids such as benzene, ethyl bromide, etc. Such a profound change in the nature of the fluid in the sintered-glass disc could greatly alter the electrokinetic potential between the pore walls and the liquid phase, which change in potential could produce significant alterations in the electro-viscous effect (cf. Elton, *Proc. Roy. Soc.*, 1948, *A*, **194**, 259, 275; 1949, *A*, **197**, 568; Hirschler, *ibid.*, 1949, *A*, **198**, 581), in the thickness of stagnant layers, and in the speed of diffusion (see, *e.g.*, Tolliday, Woods, and Hartung, *Trans. Faraday Soc.*, 1949, **45**, 148, for the effect of adsorbed ions in cupric ferrocyanide membranes upon the activation energy for diffusion of potassium chloride through the membrane). To test this possibility, two diffusions were performed at 20° with each cell, the upper portion being filled with redistilled and outgassed carbon tetrachloride, and diffusion was allowed to take place into pure benzene. The extent of diffusion was determined by measuring refractive indices on an Abbé refractometer, and reading off concentrations (correct to $\pm 0.2\%$) from a calibration curve constructed from the refractive indices of known mixtures of the two liquids. The values of Münter (*Ann. Physik*, 1931, **10**, 437) and of Gerlach (*ibid.*, 1931, **11**, 558) for the free diffusion of these liquids were used to calculate (by Gordon's method, *loc. cit.*, Section F), a value for D_i corresponding to our concentration ranges.

TABLE 4. *Diffusion coefficients for carbon tetrachloride-benzene at 20°.*

	$D^{20} \times 10^5$, cm. ² sec. ⁻¹		$D^{20} \times 10^5$, cm. ² sec. ⁻¹
Cell I	11.4	Cell II	1.77
„	11.2	„	1.74
		Calc. (Münter & Gerlach)...	1.63

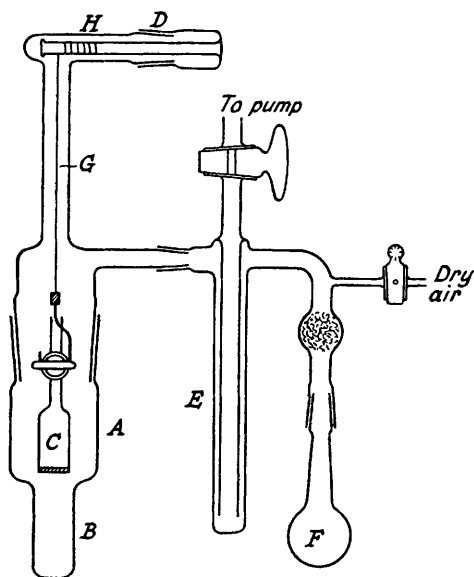
Our experimental figures and the value so calculated are given in Table 4. It is evident that, owing to the relatively great density difference (carbon tetrachloride is nearly twice as dense as benzene), extensive streaming has taken place through the coarser sinter of cell I, but the value for the second cell is in reasonable agreement with the figure obtained from the measurements by Gerlach and Münter upon diffusion in the absence of a sintered diaphragm.

Time did not permit a more extensive study of this interesting and important matter, but we may perhaps conclude from these few observations that in the absence of large density differences the cell constants as determined by potassium chloride calibration are satisfactory for use with organic liquids.

In order to outgas the sintered diaphragms and to fill the cells with the deuterated liquids, which were available in only small amount and required care and economy in handling, the whole operation was carried out *in vacuo*, the evacuated cells being lowered diaphragm down-

wards on to the outgassed liquid with which they were to be filled. The tap of the cell was in the off position, so that when dry air was later admitted to the apparatus the liquid was slowly driven into the cell through the sintered disc. The apparatus used is shown in Fig. 1: the cell *C* was suspended from the glass rod *H*, and was raised or lowered by rotation of the ground-glass socket *D*. *A* was a B55 socket, constricted to an appendix *B* into which was vacuum-distilled the liquid from *F*. The material in *F* was outgassed by alternately melting and freezing it with intermittent pumping, loss of material being prevented by the trap *E*.

FIG. 1.



DISCUSSION

It is interesting first to note that from our results on the diffusion of 0.1N-potassium chloride into water we may calculate $\bar{D}_i^{20}/\bar{D}_i^{25}$: taking the mean values given in Table 3, we obtain for this ratio 0.888 for cell I and 0.892 for cell II. These figures are in good agreement with that of McBain and Dawson (*loc. cit.*), *viz.*, 0.888.

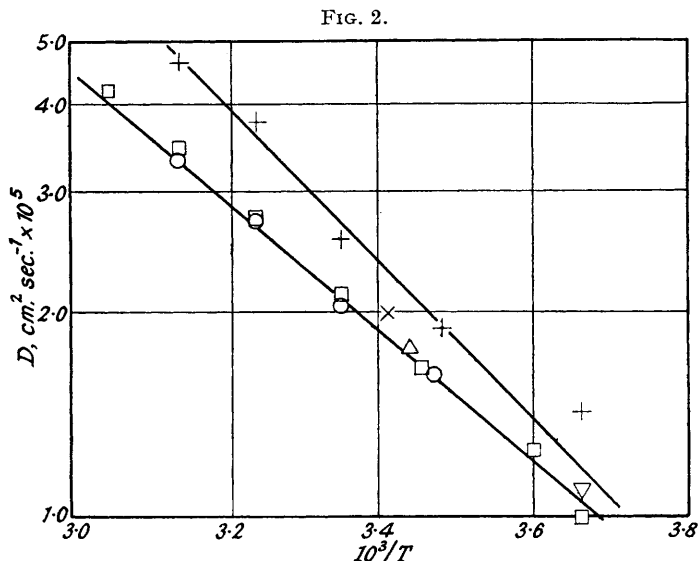
Turning now to the results for water, we have plotted all the available experimental figures and our own in Fig. 2. The values reported by Orr and Butler (*loc. cit.*) were based on \bar{D}_i^{20} for 0.1N-potassium chloride into water equal to 1.68×10^{-5} cm.² sec.⁻¹ (Cohen and Bruins, *Z. physikal. Chem.*, 1923, 103, 349, 404), a value which is now known to be incorrect. Taking $\bar{D}_i^{25} = 1.838 \times 10^{-5}$ cm.² sec.⁻¹ and $\bar{D}_i^{20}/\bar{D}_i^{25} = 0.888$, we find that Orr and Butler's results should be multiplied by 0.974 throughout: this has been done before plotting Fig. 2.

It is seen that Orr and Butler's corrected figures are still consistently greater than ours, although the experimental methods were essentially the same. Wang's results for D₂O agree quite well with ours; it should, however, be noted that the absolute values of his figures depend upon the accuracy of the method adopted to calibrate his cell. In fact, Wang assumed that Rögenger's result for D₂O at 14.7° to be correct; this is a rather doubtful procedure since Rögenger's diffusion technique leaves much to be desired.* However, as can be seen from the figure, Rögenger's result agrees closely with our own. Lamm and Temkin's results, obtained by different experimental techniques, are also in reasonable agreement with ours. Our observation that the self-diffusion coefficient, and its activation energy, are the same whether deuterium or ¹⁸O is used as the tracer element is of interest in demonstrating that the diffusion process in liquid water involves the water molecule as an entity. Wang's figures for diffusion of ¹⁸O in water also show that the activation energy is the same as for the diffusion of deuterium, but differ from ours in that substantially higher rates of diffusion (some 40% faster) were found for ¹⁸O. This discrepancy is difficult to account for and can only be resolved by further work. Orr and Butler have already shown that the rate of diffusion of deuterium in D₂O-H₂O mixtures

* This criticism does not apply to Wang's diffusions from capillary tubes, which yielded results in good agreement with the results obtained with the McBain cell.

is only slightly reduced in the presence of N-sulphuric acid or N-sodium sulphate, owing probably to the electrostrictive effect of the ions.

The diffusion figures for the four liquids we have studied can best be considered by using Eyring's approach to the theory of diffusion processes in liquids (Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw Hill, 1941), since Frenkel's equations ("Kinetic Theory of Liquids," Oxford Univ. Press, 1946) are too qualitative for our present needs, and the theories of Born and Green *et al.* (*Proc. Roy. Soc.*, 1946, **188**, A, 16; 1947, **190**, A, 455; **191**, A, 168; and later papers) and of Kirkwood (*J. Chem. Physics*, 1946, **14**, 180), although much more exact and detailed mathematically, are as yet



This work, ○; Orr and Butler, +; Lamm, ×; Rögener, △; Temkin, ▽; Wang, □.

applicable only to liquids composed of spherical monatomic molecules, and in any case lead to exceedingly complex expressions. All these theories lead to the general equation

$$D = A \exp - [E_D/RT] \quad \dots \quad (3)$$

where E_D is the activation energy for diffusion. We discuss our observations by reference to Eyring's calculation of the frequency term A and of E_D . Eyring (*op. cit.*, p. 525) has developed the equation

$$D = \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} \frac{\lambda^2}{v_f^{\frac{1}{3}}} \exp - \left[\frac{E_V}{nRT} \right] \quad \dots \quad (4)$$

where v_f is the mean free volume per molecule, given (Eyring and Hirschfelder, *J. Phys. Chem.*, 1937, **41**, 249) by

$$v_f = (RT/NP_V) \exp - \left[\frac{E_V + RT}{RT} \right] \quad \dots \quad (5)$$

In the above equations k is the Boltzmann constant, $\lambda^3 \approx V/N$, m the mass of one molecule, E_V the activation energy for vaporisation, P_V the vapour pressure, V the molar volume, N Avogadro's number, and n a small number, usually 3.0—3.5.

In his treatment, Eyring assumes that $n = E_V/E_D$, *i.e.*, that $E_D = E_D$; this, however, is not the case for any of the four liquids we have examined, as is shown in Table 5. We have therefore preferred in our calculations to use equation (4), but to use our experimental values of E_D instead of E_V/n . In this way, using equation (5) and values of P_V obtained from the International Critical Tables, we find the values of $A_{\text{calc.}}$ and $R = D_{\text{obs.}}/D_{\text{calc.}}$ shown in Table 6. From the values of the ratio R and from comparison of $A_{\text{calc.}}$ with $A_{\text{obs.}}$

given in Table 5, it is clear that Eyring's equations give only the order of magnitude of the diffusion coefficients; not enough liquids have been examined to decide whether there is any particular significance in the fact that for hydrogen-bonded liquids $R > 1$, whereas

TABLE 5.

	$A_{\text{obs.}}$ cm. ² sec. ⁻¹	E_D	E_η kcal./g.-mol.	E_V	E_V/E_D	E_V/E_η
Benzene	7.75×10^{-4}	2.1	2.4	7.7	3.5	3.0
Bromoethane	2.86×10^{-4}	1.2	1.75	6.0	5.0	3.5
Water	3.78×10^{-2}	4.6	3.28	9.4	2.0	2.9
Ethanol	2.37×10^{-2}	4.5	3.85	9.8	2.2	2.5

[The energies of activation of vaporisation and viscous flow (E_V and E_η) were taken from Grunberg and Nissan (*Trans. Faraday Soc.*, 1949, **45**, 125).

TABLE 6.

H ₂ O		C ₂ H ₅ -OH		C ₆ H ₆		H ₂ O		C ₂ H ₅ -OH		C ₆ H ₆			
Temp.	$10^3 A_{\text{calc.}}$	R	$10^3 A_{\text{calc.}}$	R	$10^3 A_{\text{calc.}}$	R	Temp.	$10^3 A_{\text{calc.}}$	R	$10^3 A_{\text{calc.}}$	R		
15°	4.87	9.76	6.10	3.24	2.75	0.261	35°	4.42	10.8	6.59	2.95	2.49	0.291
25	4.63	9.90	6.52	3.06	2.62	0.278	45	4.24	10.9	6.35	3.16	2.38	0.305

$R < 1$ for the "normal" liquid benzene. We have not included bromoethane in this discussion as we do not consider the accuracy of our diffusion measurements warrants detailed calculations.

In view of this lack of agreement between theory and experiment, there is no object in pushing any further the discussion of the rate-process approach to the theory of liquids. Further detailed discussion of this nature for the case of water is given by Wang (*loc. cit.*).

One of us (K. G.) thanks the Surrey County Council for the award of a County Major Scholarship.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[Received, November 9th, 1951.]