following new data lead us to believe that the "extra" molecule is bound merely by weak lattice forces and that the scandium compound is a lattice compound, capable of existence only in the solid state, and similar to Cs_3CoCl_5 and $(NH_4)_3ZrF_7$ discussed by Emeléus and Anderson.[3]

Experimental

The toluene employed as solvent was reagent grade, purified by distillation through a 12 to 15 theoretical plate column. The oxine was purified by double sublimation and contained less than 0.1% total impurities when so prepared. The scandium oxinate was prepared as described previously.[1]

Results and Discussion

Solutions of pure oxine in toluene from $1.41_4 \times 10^{-3}$ to 4.39×10^{-5} mole per liter of toluene at 25° were studied in a Beckman DU spectrophotometer equipped with a thermostated cell compartment. Appreciable absorption was found only in the region 280–400 mμ, with a band maximum at 317 mμ and molar extinction coefficient of 2490 at the band maximum.[4] In this concentration range, Beer's law is obeyed.

Similar studies of the absorption of pure $Sc(On)_3{\cdot}HOn$ in toluene[5] indicated absorption maxima at 375 and 317 mμ. In solutions ranging from 2.36 to 0.589×10^{-4} molar in $Sc(On)_3{\cdot}HOn$, Beer's law is not obeyed; the apparent molar extinction coefficient varied regularly from 5200 to 3820 at 375 mμ and from 7775 to 8340 at 317 mμ.

Additional studies were then made of the absorption of systems containing both HOn and $Sc(On)_3{\cdot}HOn$. In one series of studies, seven solutions with constant $ScOn_3{\cdot}HOn$ concentration and varying concentrations of added free HOn were examined. A second series of studies consisted of six systems with a fixed concentration of total oxine and oxinate; and varying scandium concentrations. Analysis of the resulting data[6] clearly indicated that there was no dissociation equilibrium in the system of the type: $Sc(On)_3{\cdot}HOn \rightleftarrows ScOn_3 + HOn$. On the basis of the spectrophotometric data, $Sc(On)_3{\cdot}HOn$ is either completely undissociated, or else completely dissociated in toluene; however, it is not possible to determine from this evidence which is the case.

The apparent molecular weight of the $Sc(On)_3{\cdot}HOn$ in benzene was then determined, by freezing point depression, to be 330 ± 60. Since the calculated molecular weight of the compound is 622 the solutions must contain two particles per molecule and it is apparent that the substance must be completely dissociated into $Sc(On)_3$ and free HOn in benzene and toluene.

It seems reasonable that the energy of solvation of the scandium oxinate in toluene and benzene is quite small, probably less than 1 kcal. per mole. The binding cannot be either covalent or ionic because the compound is completely dissociated in these solvents and because such bond energies would have to be of the order of 30 to 50 kcal. per mole. It is difficult to see how solvation could account for the large energies required to dissociate either an ionic or covalent bond, or any bond of intermediate character. It follows that the binding can only be by weak lattice forces in the molecular crystal.

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[3] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1944, pp. 80–81.

[4] The absorption of the solvent becomes too large below 280 mμ to permit measurements at shorter wave lengths.

[5] It should be noted that these solutions, like solutions of gallium and thallium(III) oxinates recently reported by Moeller and Cohen, *Anal. Chem.*, **22**, 686 (1950), are subject to slow photochemical decomposition. In diffuse light this phenomenon does not interfere seriously with the validity of the measurements if they are carried out within a few hours after preparation of the solutions.

[6] L. Pokras, "The Chemistry of Scandium," Ph.D. dissertation, Illinois Institute of Technology, 1952, pp. 68–80.

Diffusion of Hydrocarbon Vapors into Polyisobutylene. II[1]

By S. Prager, E. Bagley and F. A. Long

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Previous studies[2] of the rates of diffusion of the vapors of several hydrocarbons into polyisobutylene have been extended to higher and lower temperatures in order to determine the temperature coefficients for the diffusion and especially to determine variations in the energy of activation with size and shape of the diffusing molecule. The studies at 35° showed that the diffusion obeyed Fick's law (with the usual assumption of equilibrium concentration of vapor at the polymer surface) but with a concentration dependent diffusion coefficient. Furthermore, the magnitude of the diffusion coefficient at a given concentration depended on the size and particularly on the shape of the diffusing species.

Similar studies have now been made at 25 and 46.5° with the five hydrocarbons: *n*-butane, *n*-pentane, isobutane, isopentane and neopentane. The experimental procedures and materials were the same as used previously,[2] as was the method of evaluation of the diffusion coefficients from sorption and desorption data at various pressures. As at 35°, the diffusion coefficients at the other temperatures increased exponentially with concentration, following the equation

$$\bar{D} = \bar{D}_0 e^{AC} \qquad (1)$$

where $\bar{D}$ is the integral diffusion coefficient, C is concentration expressed as grams of hydrocarbon per gram of dry polymer and $\bar{D}_0$ and A are constants characteristic of a given hydrocarbon. All of these studies were made in the concentration range of from $C = 0$ to $C = 0.1$ g. of hydrocarbon per gram of polymer.

Table I gives values of the parameters $\bar{D}_0$ and A for the five hydrocarbons at the three temperatures, 25, 35 and 46.5°. Also included are values of V_m, the molar volume of the hydrocarbons at 25°.[3]

It is seen that at each temperature the values of $\bar{D}_0$, the diffusion coefficient at zero concentration,

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[1] Research supported by Army Ordnance.

[2] S. Prager and F. A. Long, This Journal, **73**, 4072 (1951).

[3] U. S. Nat. Bureau of Standards, API Res. Project 44, Properties of Hydrocarbons.

TABLE I

VALUES OF $\overline{D}_0$ AND A IN EQUATION (1)

Hydrocarbon	V_m, ml./mole	Temp., °C.	$D_0 \times 10^9$ (cm.^{2} sec.$^{-1}$)	A
n-Butane	101.4	25	1.17	28.0
		35	3.29	25.8
		46.5	7.54	22.8
Isobutane	105.5	25	0.53	28.8
		35	1.46	23.6
		46.5	3.75	19.0
n-Pentane	116.1	25	1.08	25.8
		35	2.59	24.7
		46.5	6.55	22.0
Isopentane	117.4	25	0.47	26.6
		35	1.34	22.5
		46.5	3.60	18.8
Neopentane	122.1	25	0.20	17.2
		35	0.60	14.5
		46.5	1.26	16.7

decrease from the smaller to the larger hydrocarbons. However, it is also evident that $\overline{D}_0$ is actually more influenced by the amount of branching than by the molar volume. Somewhat similar results have recently been reported by Park[4] for diffusion of various small molecules into polystyrene.

The temperature coefficient data fit the Arrhenius equation, $\overline{D} = B \exp(\Delta E^*/RT)$, since plots of log $\overline{D}$, for diffusion coefficients at a given concentration, *versus* $1/T$ give straight lines. Values of the Arrhenius parameters for $\overline{D}_0$ are given in Table II. As might be expected in view of the comparatively small variation in $\overline{D}_0$ with hydrocarbon, the values of the energy of activation do not vary widely, in fact by not much more than the estimated experimental error of ±0.5 kcal. (±1 kcal. for neopentane). However, there does appear to be a consistent trend in that ΔE^* values are lowest for the straight chain hydrocarbons and larger for the branched ones. These results show clearly that the diffusion is an activated process and are consistent with the notion that the slow step is formation of a hole in the polymer network.[2] However it should be noted that the variation of ΔE^* is surprisingly small in view of the considerable differences in the molar volumes and particularly in the minimal cross sectional areas of the molecules.

TABLE II

ARRHENIUS PARAMETERS FOR D_0 VALUES (CM.^{2} SEC.$^{-1}$)

Hydrocarbon	$10^9 D_0$, 35°	log B	ΔE^*, kcal.
n-Butane	3.3	3.4	16.7
Isobutane	1.5	3.6	17.5
n-Pentane	2.6	2.8	16.0
Isopentane	1.3	4.0	18.1
Neopentane	0.6	3.5	18

Values of energies of activation to compare with the above are available for polystyrene and polyvinyl acetate. For polystyrene, data are given by Park[5] for diffusion of methyl iodide (V_m = 62), methylene chloride (V_m = 63) and chloroform (V_m = 80). The calculated energies of activation vary with small molecule type and concentration and range from 14 to 27 kcal./mole. For polyvinyl acetate, values are available for acetone[6] (V_m = 73), propyl alcohol[7] (V_m = 75) and benzene[7] (V_m = 89 ml./mole).[7] For these three species, the energies of activation at zero concentration are 39, 41 and 37 kcal. per mole, respectively. Thus for diffusion into the two non-polar polymers the energies of activation are much lower than for the polar polyvinylacetate. This is the expected result since it implies that hole formation is considerably more difficult in a polar polymer.

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[4] G. S. Park, *Trans. Faraday Soc.*, **47**, 1007 (1951).

[5] G. S. Park, *ibid.*, **46**, 684 (1950).

[6] R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

[7] R. J. Kokes, unpublished work.

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Irradiation of Liquid Ammonia[1]

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Considerable evidence has been presented which has led to the concept of the existence of free electrons in alkali metal ammonia solutions.[3] Mass spectral data[4] indicate that ionization of ammonia to $NH_3^+ + e^-$ occurs more readily than any of the other possible ionization processes. Ionization along the path of the high energy bombarding ray has been postulated as one of the initial processes in the radiation effects of gamma and cathode rays. The above evidence led to an attempt to ascertain whether or not stabilized free electrons are formed by the high energy irradiation of liquid ammonia.

The ammonia was purified by distillation from a potassium solution in a suitable vacuum line. The sample for irradiation was collected in a conductivity cell with bright platinum electrodes. This was maintained at −70 to −73° by using chilled acetone inside the cell holder and Dry Ice external to this. The holder was designed so that the thin wall of the cell could be directly irradiated with the cathode ray beam. The source of radiation was a 2-Mev. electrostatic generator constructed by the High Voltage Engineering Corporation, which can be operated to produce either 2-Mev. cathode rays or X-rays. The cell dimensions were such that the cathode ray beam did not penetrate to ammonia as far as the vicinity of the electrodes. In X-ray irradiations the entire cell was exposed. The cell constant was determined by comparison of the resistance of conductivity water in the cell with that observed in a cell with a known cell constant. A 1000 cycle a.c. bridge with earphones or cathode ray oscillograph was used to measure the resistance of the liquid ammonia. The experimental results are shown in Table I.

The data in Table I show no evidence for the formation of conducting species during the irradiation. Even though the ammonia used had a lower specific resistance than the literature value[3a] the impurity, in equivalents of alkali metal ion, was between 10^{-7} and 10^{-8} mole per liter. A change in conductivity equivalent to a concentra-

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[1] Research carried out under the auspices of the Atomic Energy Commission.

[2] Office of Naval Research, Washington 25, D. C.

[3] (a) C. A. Kraus, THIS JOURNAL, **36**, 864 (1914); (b) S. Freed and N. Sugarman, *J. Chem. Phys.*, **14**, 295 (1946); (c) C. A. Hutchison and R. C. Pastor, *Phys. Rev.*, **81**, 282 (1951).

[4] M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **58**, 346 (1940).