393. *Isotope Effects in Diffusion Cross-sections for Flexible Hydrocarbons.*

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Mass diffusion coefficients have been measured for straight- and branched-chain C_7- and C_8-alkanes. Comparisons between hydrogen, deuterium, and helium as carrier gases have permitted estimates of the relative importance of low mass and of high internal energy quanta in leading to anomalously large collision " diameters " (the " hydrogen effect ") for flexible hydrocarbons. Nitrogen and argon have also been used as carrier gases for reference. Results show anomalies which are in the sequence $H_2 > D_2 > He$.

Previous researches in momentum and mass transport in gaseous hydrocarbons [1,2] have indicated that in the gas phase flexible hydrocarbon molecules adopt an average configuration which is substantially crumpled. Relative efficiencies for transference of vibrational energy in ultrasonic waves to ethylene by collision with different hydrocarbons roughly parallel the molecular flexibilities.[3] Another method of studying inelastic collisions involving transfers of translational to internal energy is to measure relative collision " diameters " in mass transport. Different carrier gases used with the same flexible hydrocarbons lead to different apparent collision diameters. These can be attributed to variations in molecular " roughness." An enlargement of flexible hydrocarbons observed in diffusion with hydrogen has been termed the " hydrogen effect." [2,4] It is still uncertain how far such effects are due to the low mass of the hydrogen, or to its large quanta of rotational internal energy. Researches described below give, for the hydrocarbons studied previously, comparative results with hydrogen and with deuterium, which exert effectively similar force fields but differ in mass and rotational quanta. Comparisons are also made between deuterium and helium, where the mass is the same but the internal energies and force fields differ. Nitrogen has been used as reference carrier gas. Argon was also used in a few experiments though the relatively large atomic mass of argon makes it less satisfactory experimentally.

Experimental

Materials.—n-*Octane*. This was part of the pure sample used previously [2] and had $n_D^{20\cdot3}$ 1·3975.

2 : 2 : 4-*Trimethylpentane*, n-*heptane*, *and* 2 : 4-*dimethylpentane*. These were gifts from the British Petroleum Co. to whom thanks are offered for their continual help in supplying compounds of high purity. Samples of the first two were stored over sodium wire, refluxed, and finally distilled. The dimethylpentane was used as received.

Refractive indices were, respectively, $n_D^{19\cdot8^\circ}$ 1·3918, $n_D^{20\cdot0^\circ}$ 1·3879, and $n_D^{20\cdot4^\circ}$ 1·3816.

Helium. This was provided by the British Oxygen Company. Limits of impurities were stated to be carbon dioxide ~2 v.p.m.; oxygen less than 10 v.p.m.; other carbonaceous compounds as CO_2 ~2 v.p.m. To remove carbon dioxide and other condensable impurities, the gas was passed through a liquid-air trap packed with glass wool [5] attached to the apparatus (Fig. 1).

Deuterium. This was from two sources, (*a*) a kind gift from Dr. K. E. Weale of this Department which had been prepared by electrolysis of deuterium oxide,[6] and (*b*) as a check, a sample of deuterium was prepared *in situ* by treating 99·75% deuterium oxide with powdered magnesium

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[1] McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961.
[2] Cummings and Ubbelohde, *J.*, 1953, 3751.
[3] McGrath and Ubbelohde, *Proc. Roy. Soc.*, 1954, *A*, **227**, 1.
[4] Cummings, McLaughlin, and Ubbelohde, *J.*, 1955, 1141.
[5] Ubbelohde, *J.*, 1933, 972.
[6] Lachowicz, Newitt, and Weale, *Trans. Faraday Soc.*, 1955, **51**, 1198.

at 490°. The method was based on that described by Knowlton and Rossini [7] for a reduced scale (Fig. 1).

In Fig. 1, *C* is a Pyrex capsule containing deuterium oxide which had been degassed by repeated freezing and melting under a vacuum. The Pyrex reaction tube *E* containing magnesium powder of graded fineness was heated electrically. A tight packing of purified glass wool at the top of the magnesium packing and in the liquid-air trap L_3 prevented the passage of oxide particles into the main section of the apparatus. The magnesium column was baked under a vacuum at 480—500° for a day before the reaction was carried out. The capsule *C* was then fractured by placing liquid oxygen around the outer wall, and the deuterium evolved initially was taken off in the pumps before the diffusion apparatus was filled.

Results with stored deuterium agreed within $\frac{1}{2}$% with those for the specially prepared deuterium in the case of 2 : 2 : 4-trimethylpentane–deuterium. Stored deuterium was therefore used for the remaining measurements.

FIG. 1.

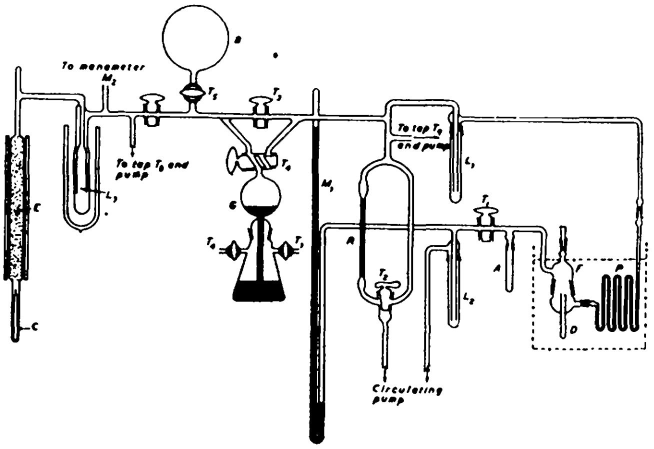
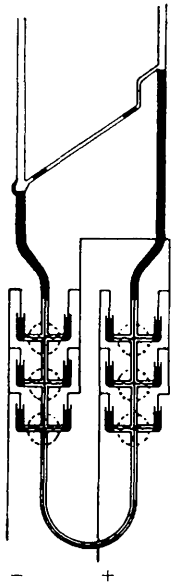


FIG. 2.



Hydrogen, nitrogen, and argon were used as supplied by the British Oxygen Company.

Apparatus and Technique.—The Stefan method of measuring gaseous interdiffusion was employed. (A recent review of diffusion techniques is given by Wilke and Lee.[8])

(*a*) For measurements with hydrocarbons and permanent gases the technique described previously [2] was used. The thermostat temperature was measured by means of a N.P.L. certified mercury-in-glass thermometer reading to 0·02° c.

The diffusion tubes used were of internal bore 2·5—3 mm. The measured diffusion coefficient was found by the conventional technique to be independent of flow rate of the carrier gas down to 50 c.c./min. The lowest flow rate previously investigated [2] was 100 c.c./min. Low flow rates are particularly convenient when circulation of rare gases is necessary, as below.

(*b*) For measurements with deuterium and helium it was necessary to recycle the gas through a closed system capable of being evacuated to $<10^{-4}$ mm. Hg. Initially a wholly enclosed centrifugal blower was employed, using a magnetic induction drive. This was not adequate owing to trouble with bearings. A more satisfactory form of apparatus employed an electromagnetically operated Sprengel-type pump having no mechanically moving parts.[9] This consisted of six electromagnetic units (Fig. 2). Current was supplied through the platinum seals from a bridge rectifier and step-down transformer (11·5 v) fed from the a.c. mains through a Variac transformer. With permanent magnets of field strengths 5000—6000 gauss,

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[7] Knowlton and Rossini, *J. Res. Nat. Bur. Stand.*, 1937, **19**, 605.

[8] Wilke and Lee, *Ind. Eng. Chem.*, 1955, **47**, 1253.

[9] Cf. Puddington, *Canad. J. Technol.*, 1951, **29**, 311.

a d.c. current of about 17 amp. through each unit gave a total pumping speed of about 100 c.c./min. No serious loss of performance was found with a moderate flow resistance in the apparatus; this permitted the inclusion of a specially calibrated rotameter *R* (Fig. 1) to provide a check on flow rates.

The hydrocarbon to be studied was degassed under a vacuum in *A* and was distilled into the diffusion tube *D*. After preliminary "washing" of the walls with the gas to be used and pumping out, the apparatus was filled with gas to about one atmosphere, the Töpler pump *G* being used if necessary, and the hydrocarbon was cautiously melted. Taps T_3 and T_4 were closed, liquid oxygen was placed around the traps L_1 and L_2, and circulation of the gas at 90—100 c.c./min. commenced. The copper preheater *P* (path 250 cm.) and the diffusion cell *F* were then placed in a thermostat ($\pm 0{\cdot}02°$); measurements of the rate of fall in the liquid level as in (*a*), and readings of pressure on M_1 and of thermostat temperature were made every half-hour. At least two hours were allowed for attainment of a steady-state condition before readings were recorded. From measurements of the rate of drop in level of hydrocarbon, calculations of the diffusion coefficient D_{12} were made for hydrocarbon 2 in carrier gas 1, by conventional procedures.

Results are in Table 1.

TABLE 1. *Diffusion coefficients of paraffins in various carrier gases.*

Carrier gas	Temp. (° K)	D_{12} (cm.^{2} sec.$^{-1}$)	No. of obsns.	Precision of *D* (±)	Carrier gas	Temp. (° K)	D_{12} (cm.^{2} sec.$^{-1}$)	No. of obsns.	Precision of *D* (±)
		n-Octane					*n*-Heptane		
N_2	303·1	0·0726	9	0·0012	N_2	303·3	0·0740	19	0·001
H_2	303·2	0·277	6	0·003	H_2	303·1	0·283	6	0·0023
D_2	303·2	0·208	8	0·0005	D_2	303·2	0·218	18	0·0005
He	303·2	0·248	18	0·0023	He	303·2	0·265	16	0·0008
A	303·2	0·0587	7	0·0018	A	303·2	0·0658	12	0·0010
		2 : 2 : 4-Trimethylpentane					2 : 4-Dimethylpentane		
N_2	303·1	0·0713	8	0·0014	N_2	303·1	0·0744	23	0·0007
H_2	303·1	0·292	20	0·0025	H_2	303·3	0·297	14	0·0034
D_2	303·2	0·212	26	0·0004	D_2	303·2	0·224	16	0·0003
He	303·2	0·253	27	0·0007	He	303·2	0·263	16	0·0006
A	303·2	0·0599	10	0·0003	A	303·2	0·0655	8	0·0003

DISCUSSION

Fairly satisfactory treatments are available for the description of transport phenomena in monatomic and simple polyatomic gases.[10, 11] Larger molecules, in general, possess features which make less justifiable, in varying degrees, the assumptions used with atoms and simpler molecules. Consequently, it becomes more difficult to relate force constants, deduced by kinetic theory from transport properties, with detailed molecular geometry. Calculation of the parameters is usually quite straightforward but the problem lies in interpreting them in terms of molecular behaviour. Two main methods of approach may be used in which inadequacies in the application of simple theory do not vitiate the conclusions reached:

(1) Where a series of molecules of closely similar structure depart to much the same extent from the simplest idealised models of kinetic theory, observed trends in formal kinetic-theory parameters derived from experimental results give significant relative molecular sizes, or relative collision areas, in such series.

(2) Instead of the simplest idealised models, models including approximations of higher order may be applied in calculating experimental parameters. Relative deviations from predicted behaviour may again be examined through the series of closely related molecules. Effects of differences of structure on the significance of the higher approximations can become apparent in this way.

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[10] Chapman and Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, 2nd Ed., 1954.

[11] Hirschfelder, Curtiss, and Bird, "The Molecular Theory of Gases and Liquids," Wiley, New York, 1954.

Each of these methods has been used in previous analyses of experimental results for hydrocarbons.[4, 12] In the present work a similar method of approach is used; collision "parameters" are defined on the basis of the formulæ of kinetic theory for idealised models, and values deduced are examined for hydrocarbons of similar structure.

The measured diffusion coefficients in Table 1 have been analysed on the basis of two molecular models, *viz.*, the rigid-sphere model and a model assuming the Lennard-Jones 6 : 12 potential. The rigid-sphere diameter σ_{12} is defined by the standard formula:[10]

$$\left[D_{12}\right]_1 = \frac{3}{8n\sigma_{12}^2}\left\{\frac{kT(m_1 + m_2)}{2\pi m_1 m_2}\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ_{12} is the heteromolecular collision diameter, while the corresponding diameter for the Lennard-Jones potential is given by:

$$\left[D_{12}\right]_1 = \frac{3}{8n\sigma_{12}^2}\left\{\frac{kT(m_1 + m_2)}{2\pi m_1 m_2}\right\}^{\frac{1}{2}}\cdot\frac{1}{W^1(1;\ kT/\varepsilon_{12})} \quad . \quad . \quad . \quad . \quad (2)$$

where $W^1(1;\ kT/\varepsilon_{12})$ is the collision integral for mass transport. Such integrals are tabulated by Hirschfelder and his co-workers.[11, 13]

Values of the collision diameter for the hydrocarbon are derived from σ_{12} by using values of σ_{11} for the carrier gas from viscosity data listed below (Table 2). Use is made of the empirical relations,

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \quad . \quad . \quad . \quad (3); \qquad \varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}} \quad . \quad . \quad . \quad (4)$$

In the case of the Lennard-Jones potential, values of ε_{22}/k for the hydrocarbons from viscosity data were used in the evaluation of σ_{22}. For the C_8-hydrocarbons values of viscosities previously measured in this programme were used.[14] For the C_7-hydrocarbons viscosity results of Lambert and co-workers[15] were fitted to a 6 : 12 potential. With the 6 : 12 potential the same diameter σ_{11} was used for deuterium as for hydrogen as measurements were not available for the viscosity above room temperature.

TABLE 2. *Gas-kinetic collision diameters of carrier gases.*

Gas	Rigid sphere model σ_{11} (Å)	6 : 12 Model σ_{11} (Å)	ε/k (°K)	Ref. for viscosity data
H_2	2·71	2·97	33·3	*a*
N_2	3·75	3·68	91·5	*a*
D_2	2·73	—	—	*b*
He	2·16	2·58	10·22	*c*
A	3·66	3·42	124	*c*

(*a*) Johnston and McCloskey, *J. Phys. Chem.*, 1940, **44**, 1038. (*b*) van Itterbeek and van Paemal, *Physica*, 1940, **7**, 265, 273. (*c*) Johnston and Grilly, *J. Phys. Chem.*, 1942, **46**, 938.

Consideration of the nature of the colliding molecules makes it clear that neither of these two physical models can be wholly adequate. Even if the simpler molecules of the carrier gases may be treated as rigid spheres, or as sources of centrosymmetric 6 : 12 forces, this is certainly not permissible for polyatomic hydrocarbons, especially for structures ("flexible molecules") where changes of potential energy required to effect changes of rotational configuration are small. Formally, however, the basis of definition of the parameters to be compared is quite specific.

The Hydrogen Effect with Flexible Molecules.—In accord with previous studies,[2, 4] the

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[12] Cummings, McCoubrey, and Ubbelohde, *J.*, 1952, 2725.

[13] Hirschfelder, Bird, and Spotz, *J. Chem. Phys.*, 1948, **16**, 968.

[14] Cummings and McCoubrey, *J.*, 1955, 2523.

[15] Lambert, Cotton, Pailthorpe, Robinson, Scrivens, Vale, and Young, *Proc. Roy. Soc.*, 1955, *A*, **231**, 280.

kinetic-theory cross-sections for collisions of hydrocarbons with hydrogen are seen to be greater than those for the corresponding collisions with nitrogen when the hydrocarbon is flexible. In column 7 of Table 3 the quantity Δ, defined as $\sigma_{22}(H_2) - \sigma_{22}(N_2)$, has a finite positive value for the flexible hydrocarbons but has a much lower value for the stiffer molecules of equal mass. Parameters based on the Lennard-Jones potential show the same general trends.

Inadequacy of the first approximation to the coefficient of diffusion [(1) and (2) above] cannot account for a deviation in the predicted collision diameters, of more than about 0·1% for the molecules studied at concentration ratios used in the measurements. Other assumptions and approximations made in developing a practicable theory of transport properties in gases have been examined as possible sources of the differences observed.[4] Further reasons for rejecting quantum effects as responsible for the finite differences Δ in Table 3 emerge from application of the principle of corresponding states.[23] Deviations in reduced diffusion coefficients Δ_{ij} of hydrocarbon–hydrogen systems from a corresponding-states curve in which Δ_{ij} is plotted against $T/T_{c,12}$ are in the opposite sense to any deviation shown for H_2–H_2 self-diffusion for which quantum effects should be greatest owing to the small molecular masses. This result is found whether T_c and V_c of hydrogen are taken to be the experimental values or the effective critical constants used by Guggenheim and McGlashan [17] which correct in a semi-empirical way for quantum effects.

The Pidduck rough-sphere model [10] indicates the effect of interchange of translational and internal energy on the transport properties. On this model such enery transfer increases the apparent collision diameter for mass diffusion. This is in the sense shown with the more flexible hydrocarbons when hydrogen is the carrier gas. Present results strengthen the conclusion that the observed " hydrogen effects " indicate a greater efficiency for transferring energy to internal modes with hydrogen than with nitrogen; this ability is more pronounced with flexible than with inflexible hydrocarbons.

TABLE 3. *Calculated kinetic theory parameters σ_{22} for the systems studied* (Å).

	(H_2)	(D_2)	(He)	(N_2)	(A)	$\Delta = \sigma_{22}(H_2) - \sigma_{22}(N_2)$
		Rigid-sphere model				
n-Octane	7·33	7·06	6·83	6·94	7·44	+0·39
2 : 2 : 4-Trimethylpentane	7·07	6·97	6·73	7·02	7·33	+0·05
n-Heptane	7·23	6·84	6·54	6·91	6·92	+0·32
2 : 4-Dimethylpentane	7·00	6·71	6·57	6·88	6·94	+0·12
		Lennard-Jones 6 : 12 model				
n-Octane	7·26	7·15	7·23	6·25	6·68	+1·01
2 : 2 : 4-Trimethylpentane	7·12	7·04	7·22	6·61	6·77	+0·51
n-Heptane	7·52	7·13	7·17	6·81	6·73	+0·71
2 : 4-Dimethylpentane	7·21	6·94	7·16	6·69	6·66	+0·52

Comparisons between Hydrogen and Deuterium: Influence of Mass on " Roughness ".— Comparisons involving these two molecules are particularly valuable since in collisions only mass, and not force-field, differences occur, to a first approximation. On either model, deuterium systematically yields smaller diameters than hydrogen (columns 2 and 3 of Table 3), indicating that it is less efficient in transferring energy to the internal degrees of freedom of the hydrocarbon, so that collisions are on average less rough. These differences are larger for the more flexible unbranched hydrocarbons, where " wrestling collisions " [16] might be expected to be more enveloping.

So far as results are available, ultrasonic methods of studying energy transfer yield the same general conclusions. In collisions leading to 0–1 vibrational quantum uptake

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[16] McCoubrey, Parke, and Ubbelohde, *Proc. Roy. Soc.*, 1954, *A*, **223**, 155.

[17] Guggenheim and McGlashan, *ibid.*, 1951, *A*, **206**, 448.

in ethylene, deuterium is less efficient than hydrogen.[18] Deuterium is, however, more efficient than nitrogen.[18, 19]

Comparisons between deuterium and the nitrogen reference gas show somewhat different relative collision diameters in the present experiments according to which model is used (columns 3 and 5). This is because the less marked " hydrogen effect " with the isotopic deuterium is insufficient to outweigh other factors whose contribution in the two models differs. Such factors include molecular anisotropy and molecular attractive fields; but since the 6 : 12 model gives the more plausible sequence $H_2 > D_2 > N_2$ for the apparent collision diameters, contributions from the allowance for attractive force fields seem likely to account for the differences referred to.

These findings about the roughness of molecular collisions can be explained on the basis of the degree of approximation to adiabatic collisions in molecular encounters. Impact times will be shorter in collisions with hydrogen than with deuterium or nitrogen; short collisions tend to be less adiabatic and the probability of transfer of energy may be increased as a result.[20]

Influence of Rotational Quanta on Energy-transfer. Comparisons between Deuterium and Helium.—Alternatively to the above explanation, it has been suggested that the peculiar efficiency of the hydrogen molecule in effecting transfer of internal energy may be connected with the large magnitude of its rotational quanta;[21] the idea is that rotational degrees of freedom might absorb much of the excess of energy after vibrational deactivation. To illustrate this, Table 4 gives the magnitudes of the rotational quanta in terms of characteristic temperatures.[24]

TABLE 4. *Characteristic temperatures for rotation* (°K).

Molecule	H_2	D_2	N_2
$\theta_{\text{rot.}} = \dfrac{h^2}{8\pi^2 Ik}$	85·0	42·5	2·84

It is to be noted that both hydrogen and deuterium must change their rotational levels by several units of $k\theta_{\text{rot.}}$ at a time, unless spin isomerisation occurs during a collision. The vibrational quanta of hydrogen ($h\nu/k = 6140°$) and of deuterium ($h\nu/k = 4340°$) lie too high to contribute effectively in internal energy transfers.

In order to throw further light on the possible rôle of large rotational-energy quanta in permitting efficient transfer of internal energy, comparisons may be made between deuterium and helium (columns 3 and 4 of Table 3). The rigid-sphere model which makes no allowance for force fields or anisotropy factors gives $D_2 > \text{He}$ with no marked difference between branched and unbranched hydrocarbons. Allowance for force fields, but not for anisotropy, brings $\text{He} > D_2$ to an extent just outside probable error. It seems reasonable to conclude that the efficiencies of deuterium and of helium do not differ largely and that mass effects are considerably more important than any rotational-energy effects. On balance, ultrasonic measurements indicate that deuterium is more efficient than helium in converting translational into internal energy[19, 22] of its collision partners, but further experiments seem desirable to test whether deuterium is uniformly somewhat more efficient than helium, by virtue of its rotational energy.

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[18] Richards, *J. Chem. Phys.*, 1936, **4**, 561.

[19] Richards and Reid, *J. Chem. Phys.*, 1934, **2**, 206.

[20] Bethe and Teller, Aberdeen Proving Grounds, Ballistics Research Laboratory Report No. X-117, 1941; see also De Wette and Slawsky, *Physica*, 1954, **20**, 1169.

[21] Zener, *Phys. Rev.*, 1931, **37**, 556; cf. Oldenberg, *ibid.*, 1952, **87**, 786.

[22] Eucken and Jaacks, *Z. phys. Chem.*, 1935, **30**, *B*, 85; Petralia, *Nuovo cim.*, Suppl., 1952, **9**, 1; van Itterbeek and Mariens, *Physica*, 1940, **7**, 909.

[23] Rowlinson and Townley, *Trans. Faraday Soc.*, 1953, **49**, 20.

[24] Guggenheim, "Thermodynamics," North Holland Publ. Co., Amsterdam, 1949.