

Self-Diffusion in Solid Krypton

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An isotropic exchange apparatus has been developed and used to measure tracer diffusion in solid krypton in the temperature region $90 < T < 115^\circ\text{K}$. The crystals of krypton were grown from the melt in a cell with a conical bottom and annealed carefully before use. While the crystals could not be examined *in situ* for physical perfection, the reproducibility of the diffusion results from specimen to specimen indicates that the crystals contained few gross imperfections. For some of the crystals, the diffusion could be described within the experimental uncertainty by the simple Arrhenius expression $D = D_0 e^{-Q/RT}$, but for others Q showed a temperature dependence. The addition of O_2 appeared to depress D over the entire temperature range studied. The magnitude of these results in relation to those for pure krypton suggests that the temperature dependence of Q may be caused by impurities. If the observed Q at the highest temperature (4800 ± 200 cal mole $^{-1}$) is interpreted in terms of intrinsic diffusion via single vacancies and decomposed into an energy of formation (1780 ± 200 cal mole $^{-1}$) and an energy for mobility, the ratio of the energies E_v/E_m turns out to be appreciably smaller than has been estimated theoretically.

I. INTRODUCTION

TESTS of models of the rare-gas solids are currently being made with a variety of experimental data: thermodynamic properties such as the heat capacity, $^{1-5}$ thermal expansion $^{6-10}$ or compressibility, $^{9-11}$ and transport properties. $^{12-16}$ The models represent various levels of sophistication from simple two-body central forces and a Lennard-Jones type of interatomic potential to many-body forces and more elaborate potentials. The general situation is well described in recent reviews. $^{17-19}$ Although many of the experimental observations can

now be rationalized in terms of the models, there is still a need for more refined experimental data.

Self-diffusion data contain information about the formation and migration of imperfections, both of which depend sensitively on the interatomic forces. The measurement of diffusion in krypton is particularly interesting at this time because the vacancy concentration as a function of temperature has been determined from thermal expansion 6 and calorimetric 2 data. In this paper, we describe in detail diffusion measurements that we have made by means of an isotopic exchange technique. [Krypton has a radioisotope (^{85}Kr) that is an ideal tracer for diffusion experiments (radiation: 0.67-MeV β ; half-life: 10.6 years).] The results are later correlated with similar ones for other rare-gas solids. A preliminary account of the work has been published. 20

II. EXPERIMENTAL

A. Isotopic Exchange Technique

The crystal, containing a uniform concentration of the tracer, is exchanged with inactive vapor. Provided that the exchange of atoms at the surface of the crystal is rapid compared with diffusion within, the boundary conditions for the experiment lead to the following expression 21 for the time dependence of the exchange between crystal and vapor:

$$dn^2/dt = 4A^2 C_0^2 D^* / \pi. \quad (1)$$

Here, n is the number of tracer atoms in the gas phase at time t (usually the observed counting rate), A is the actual surface area of the crystal involved in the exchange, C_0 is the initial concentration of tracer in the crystal, and D^* is the tracer diffusion coefficient. In practice, exchange experiments are done at a series of

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successively higher temperatures and n^2 is given by²¹

$$(n^2)_{t_1+t_2+\dots} = (4A^2C_0^2/\pi)(D_1^*t_1 + D_2^*t_2 + \dots). \quad (2)$$

At each temperature, a value of D^* (i.e., D_1^* , D_2^* , etc.) is obtained from the slope of a plot of n^2 against t . In the example of krypton, the exchange technique could be used as long as the vapor pressure exceeded 15 to 20 Torr ($T \geq 90^\circ\text{K}$).

B. Specimen Chamber

The essential internal parts of the system mounted inside an evacuated container are illustrated in Fig. 1. The mass of the specimen chamber was fairly large (~ 300 g) so that thermal inertia would be considerable. Sensitive temperature control ($\pm 0.005^\circ$) was attained by balancing a cold leak along the copper wire (#28 AWG) against heat supplied to the specimen chamber and to the brass insert in the copper wire. A carbon resistor attached to the specimen chamber was used as the sensing element of a Wheatstone bridge, the amplified off-balance signal of which controlled the amount of power dissipated in the heaters. The stability of the control was comparable to the sensitivity for periods of days and even weeks.

Since evaporation or condensation of krypton in the specimen chamber could drastically affect the observed counting rate in the vapor, it was important to have efficient heat exchange for the circulating vapor. This was accomplished through the exchangers e and f (Fig. 1), the design and dimensions for which were developed by trial and error.

C. Specimen Growth and Handling

The crystal specimens (1.3–9.7 g) were grown from Matheson Research Grade krypton (total impurity content ~ 25 ppm), to which ^{85}Kr had been added. After the diffusion experiments, samples of most of the specimens were analyzed by gas chromatography, and the impurities found were in the range ≤ 150 ppm.

To grow a specimen, we condensed the krypton into the brass chamber at about 2° above the triple point (115.8°K) and allowed the chamber to cool at the rate of $0.005^\circ/\text{min}$. Under these conditions, a gradient of approximately 0.2° existed over the length of the specimen chamber. After complete solidification of the krypton, the chamber was maintained at 113°K for 48 h and subsequently cooled to the starting temperature of a diffusion experiment at a rate between 0.005° and $0.01^\circ/\text{min}$. Normally, the specimens were annealed at this temperature for 12 h or more. In some experiments, a small amount of krypton was removed by gentle pumping to ensure that the crystal specimen was not stuck to the walls of the brass chamber.

In effect, crystal growth was achieved by the Bridgman technique. Because heat was withdrawn from the

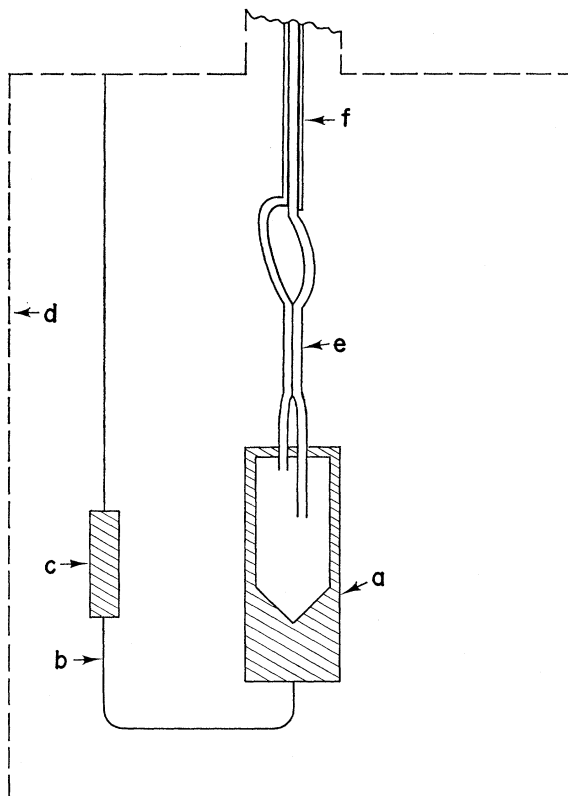


Figure 1. Schematic representation of the interior of the cryostat. (a) Brass specimen chamber; (b) copper wire; (c) brass insert; (d) container at $T = 78^\circ\text{K}$; (e) heat exchanger consisting of two flattened German silver tubes soldered together; (f) concentric-tube heat exchanger (outer tube 4 mm diam, inner tube 2 mm diam, length 60 cm).

base of the specimen chamber, the conical bottom should have acted as a nucleation tip for crystallization, and crystal growth should have occurred from the bottom up. Visual inspection of the crystal specimens could not be made. However, the reproducibility of the measured diffusion coefficients (see Sec. III) suggests that the specimens were not grossly imperfect. Daniels *et al.*²² have succeeded in growing and cooling (down to 79°K) single crystals of krypton in a cell not unlike that used here, except that their crystals were grown under higher pressures (up to 2.31 kbar).

D. Vapor Circulation and Counting System

The main technical problem in the experiment, apart from temperature control, was developing a method for exchanging a relatively large volume of vapor and for mixing it quickly and thoroughly. Figure 2 is a schematic representation of the apparatus that was designed to do this.

The vapor was circulated with a small glass pump b based on a design by Bennett.²³ Constant flow rates up

²² W. B. Daniels, G. Shirane, B. C. Frazer, H. Umebayashi, and J. A. Leake, *Phys. Rev. Letters* **18**, 548 (1967).

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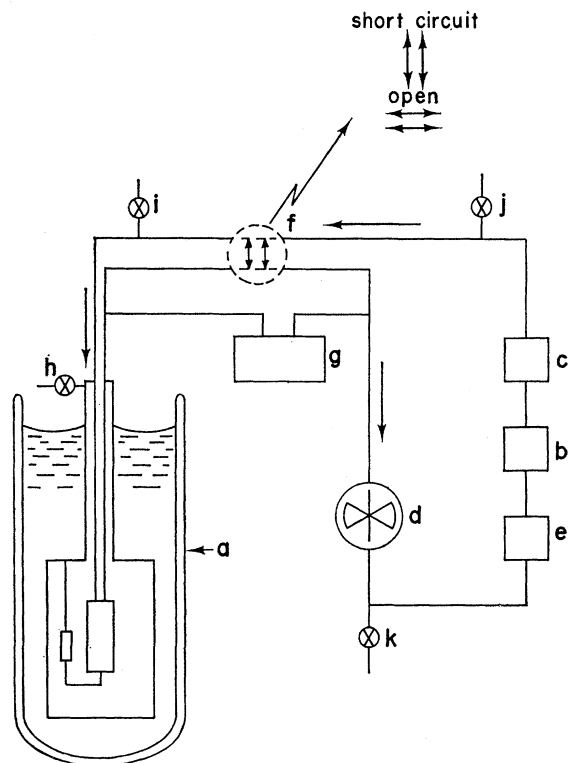


FIG. 2. Exchange apparatus. (a) Dewar flask filled with liquid nitrogen; (b) circulating pump; (c) flow meter; (d) 5-liter reservoir; (e) solid-state detector; (f) special stopcock; (g) sensitive spiral gauge; (h)-(k) connections to vacuum system. Direction of vapor flow is indicated by arrows.

to $40 \text{ cm}^3 \text{ min}^{-1}$ could be attained with pressure fluctuations of less than $\pm 0.03 \text{ Torr}$. Mixing of the vapor was achieved with the paddle-wheel stirrer that revolved at a rate of $\sim 100 \text{ rpm}$ in the 5-liter reservoir d.

The counting rate in the vapor was determined with a dE/dx solid-state detector (Simtec Ltd.) and recorded by means of a standard counting rate meter and a scaler. High counting efficiency was achieved by placing the detector in a brass chamber through which the vapor circulated.

E. Procedure for a Diffusion Experiment

After a crystal was grown, annealed, and cooled, with stopcock f (Fig. 2) in the short-circuit position, the circulating system was filled with nonradioactive krypton to a pressure equal to the vapor pressure of the crystal. The balancing of the pressure was accomplished with the null spiral gauge g to a sensitivity of $\pm 0.03 \text{ Torr}$. Stopcock f was opened, circulation was commenced, and diffusion was allowed to proceed until the slope of a plot of n^2 against t was determined to better than $\pm 5\%$. At the lowest temperatures, the time required was 24 h or more, but near the triple point, 1 or 2 h was a sufficient period.

TABLE I. Summary of data for krypton specimens.

Specimen	Weight (g)	Total surface area (cm^2)	Cooling rate (deg min^{-1})	Annealing time (h)	$10^9 \times D^*$ at $10^3/T=9$ ($\text{cm}^2 \text{ sec}^{-1}$)
1	6.06	9.5	0.005	48	3.2
2	9.70	12.2	0.01	48	2.6
3 ^b	1.28	5.5	0.005	36	1.3
4 ^a	2.50	6.9	0.005	48	0.5
5	3.18	7.4	0.005	48	2.3
6	7.27	10.4	0.005	48	2.2
7 ^b	6.59	9.9	0.005	48	2.2
8	6.26	9.7	0.005	48	(1.3) ^c

^a Krypton +0.4% O₂.
^b Portion of crystal sublimed before start of diffusion experiment (see Sec. IIC).
^c Estimated (actual measurements terminated at $10^3/T=9.15$).

Whenever the temperature of the specimen chamber was increased for a new determination of D^* , stopcock f was first placed in the short-circuit position. Non-radioactive krypton was added to the circulating system to balance the new vapor pressure, and exchange was then allowed to occur as before, yielding a new n^2 -versus- t relation. The amounts of vapor and crystal were always such that, under all conditions, the amount of exchange was less than 20% of the total possible.

The quantity C_0 [see Eq. (1)] was obtained by adding the observed counting rate at the end of a diffusion experiment to the counting rate found when the crystal specimen was evaporated into the circulation system. The mass of the specimen was obtained easily by transferring the evaporation krypton to a calibrated volume and measuring its pressure.

III. EXPERIMENTAL RESULTS

The weights and thermal histories of all the specimens used in the diffusion experiments are recorded in Table I. It was not thought practicable to use cooling rates lower than $0.005 \text{ deg min}^{-1}$.

The plots of n^2 against t were linear within experimental error for all of the specimens. The gradients of the plots were obtained (to $\pm 5\%$ or better) from a weighted least-squares fit to the data, the statistical counting error being used to weight each point. A typical plot is shown in Fig. 3.

TABLE II. Arrhenius parameters.

Specimen	D_0 ($\text{cm}^2 \text{ sec}^{-1}$)	Q (cal mole^{-1})
1	$2.3^{+4.2}_{-1.5}$	4500 ± 200
2	$4.1^{+1.9}_{-1.3}$	4700 ± 80
3	$7.0^{+10.8}_{-4.3}$	5000 ± 200
4 ^a	$4.0^{+13.9}_{-3.1}$	5000 ± 300
7	$9.6^{+8.2}_{-4.1}$	4900 ± 140
Mean values for pure specimens	5^{+5}_{-3}	4800 ± 200

^a Krypton +0.4% O₂.

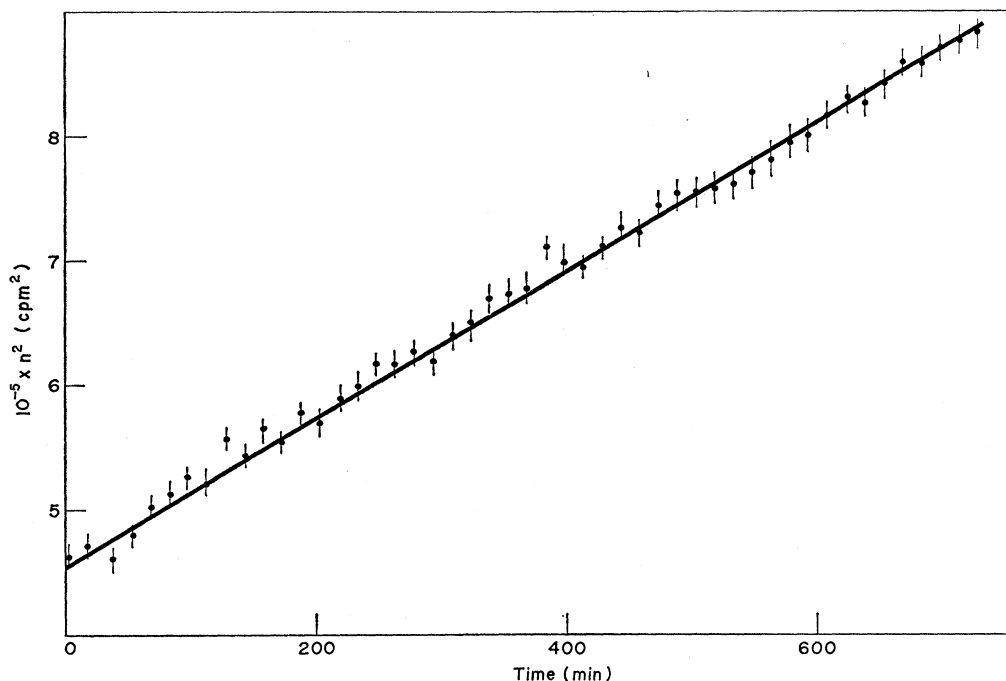


Fig. 3. Typical plot of n^2 against time (specimen 2 at $T=102.6^\circ\text{K}$). Vertical bars indicate magnitude of statistical counting error.

At least two assumptions can be made for the value of A to be used to determine absolute values of D^* from Eq. (2). The area involved in the exchange might be the total surface area of the specimen, or, if the specimen were stuck to the walls of the brass chamber, just the top surface area. An attempt was made to distinguish between these possibilities by varying the size of the specimens and by subliming portions of some of the specimens before the beginning of an exchange experiment. The result was not completely clear-cut, as may be deduced from the data given in Table I. However, the minimum variation in D^* was found if A were assumed to be the total surface area (the basis for the last column in Table I).

Gross imperfections such as dislocations and grain boundaries could, in principle, affect the magnitude of D^* . That they did not do so is indicated by the small variation in D^* from specimen to specimen; the density of gross imperfections would be expected to vary by much more than a factor of two.

The results for specimens 1, 2, 4, and 7 are plotted in Fig. 4 in the form of $\log_{10} D^*$ against $1/T$. Within their precision, they can be represented by the Arrhenius relation

$$D^* = D_0 e^{-Q/RT}, \quad (3)$$

as is indicated by the dashed lines. Specimen 4 was "doped" with 0.4% of O_2 and D^* for it has been depressed by a factor of about 5 over the entire experimental temperature range. Arrhenius parameters for five specimens obtained by a least-squares treatment of

the data are given in Table II. They are somewhat misleading in that the striking difference displayed by the data for specimen 4 is no longer apparent. Because more data have been included, the mean value of D_0 listed in Table II is slightly different from that given in the preliminary report.²⁰

Another effect is displayed by the data for specimens 5 and 8 that are plotted in Fig. 5. Here the relation of $\log_{10} D^*$ versus $1/T$ shows definite curvature, and the actual values of D^* lie between those obtained for the pure and doped specimens (dashed lines from Fig. 4). A power failure forced the premature termination of the experiment with specimen 8. It would have been interesting to see if, at temperatures near the triple point, D^* for this specimen continued to approach a limit of D^* for specimens 1, 2, and 7.

IV. DISCUSSION

For the pure specimens, the value of D^* at the triple point is about $10^{-8} \text{ cm}^2 \text{ sec}^{-1}$. This is similar to tracer self-diffusion coefficients found for metals²⁴ and plastic molecular solids²⁵ at their melting points. Moreover, D_0 lies within the range 0.1 to $10 \text{ cm}^2 \text{ sec}^{-1}$ that seems generally acceptable for diffusion via point defects.²⁴ The apparent activation energy ($4800 \pm 200 \text{ cal mole}^{-1}$) is consistent with that for a single-vacancy mechanism.

²⁴ See D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 71.

²⁵ J. N. Sherwood, *Proc. Brit. Ceram. Soc.* 9, 233 (1967).

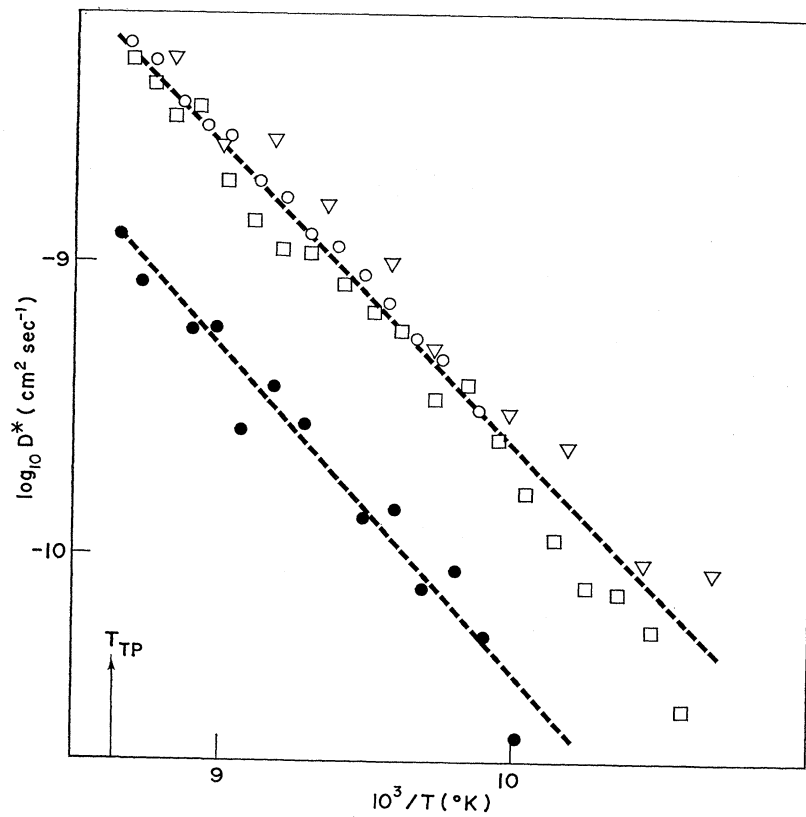


FIG. 4. ^{85}Kr diffusion as a function of temperature for specimens 1(∇), 2(\circ), 4(\bullet), and 7(\square). Dashed lines representing least-squares fitting of the data to the Arrhenius relation $D^* = D_0 e^{-Q/RT}$.

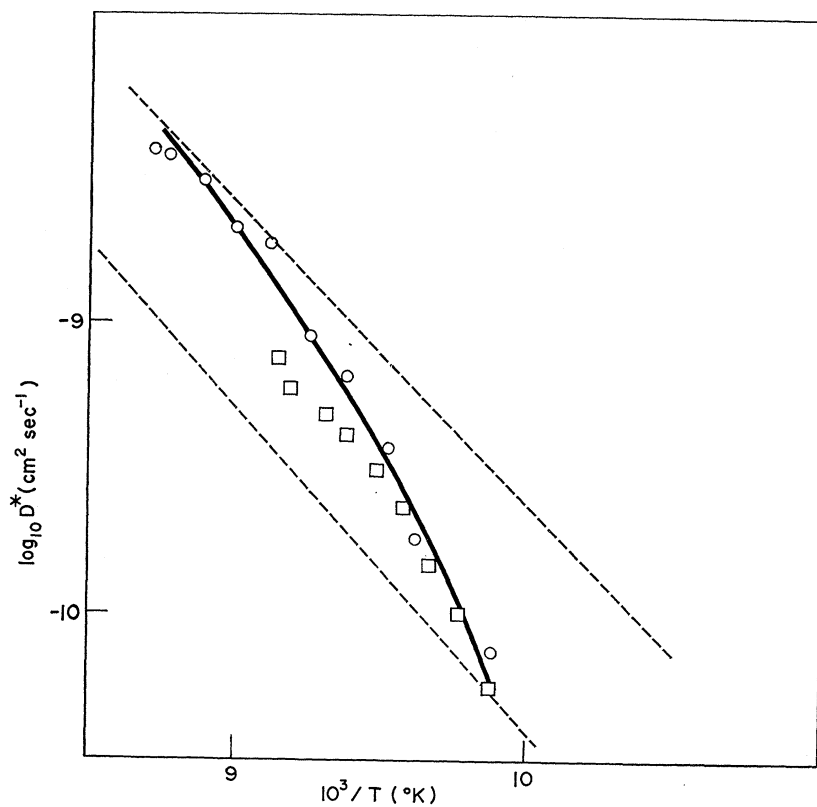


FIG. 5. ^{85}Kr diffusion as a function of temperature for specimens 5(\circ) and 8(\square). Dashed lines the same as in Fig. 4.

Diffusion via divacancies or interstitials would be expected to involve larger activation energies.^{26,27}

While the addition of O₂ appears to decrease D^* , the apparent activation energy is unchanged. A similar effect has been observed in dilute metal alloys, e.g., for Ag diffusion in Ag-Pd,²⁸ although the dependence upon Pd concentration was less marked. The observations in metals have been related to the lower mobility of the impurity compared with that of the solvent.²⁹ By analogy, it might be inferred that the diffusion of O₂ is lower than that of krypton. Unfortunately, it is not possible to draw any quantitative conclusions from this single experiment. O₂ is a volatile impurity, and so a full thermodynamic study of the system O₂+Kr would have to precede the determination of the dependence of Kr diffusion on O₂ concentration.

An impurity effect is the probable explanation for the somewhat different behavior of specimens 5 and 8 (Fig. 5). A slight amount of impurity in the surface region of a specimen could easily depress D^* at the lowest temperatures and have an insignificant effect at the highest temperatures. A rough computation shows that the amount needed is much less than would have been detected by chromatographic analysis of the entire specimen.

At some stage, effects of impurities, especially of O₂, will have to be studied more fully because of their possible consequence on comparisons of absolute values of diffusion coefficients obtained from tracer and NMR experiments. It is a common practice to enhance NMR signals by the addition of strategic impurities to a solid. For example, about 1% of O₂ was added to solid Xe for the determination of D by a magnetic resonance method.¹⁵

The magnitude of Q found from the present measurements (4800 ± 200 cal mole⁻¹) is in reasonable agreement with that which can be deduced from diffusion experiments on other rare-gas solids through application of the principle of corresponding states. If the interatomic interaction is described by a reducible pair potential, e.g., of the Lennard-Jones 6-12 type, it can be shown³⁰ that

$$Q \propto \epsilon \quad \text{and} \quad D_0 \propto \sigma(\epsilon/m)^{1/2}, \quad (4)$$

where ϵ is the depth of the potential well, m the mass, and σ a characteristic distance of separation. This method of correlation works well for the rare-gas liquids

Ar, Kr, and Xe.³¹ Its application to diffusion results for Ar^{14,16} and Xe¹⁶ yields for Q of Kr values between 5000 and 5300 cal mole⁻¹. Details are given in Table II of Ref. 20.

If diffusion in krypton occurs via single vacancies, the concentration of which is thermally controlled, Q may be decomposed into the sum of an energy of formation (E_v) and an energy of migration (E_m). Calculations of E_v for rare-gas solids based upon simple pair potentials^{12,26,32,33} usually lead to the conclusion that distortion and relaxation around a vacancy are small, and therefore to the general result that E_v is of the magnitude of the heat of sublimation. For vacancy diffusion in a close-packed solid, E_m would be expected to be approximately equal to E_v . These two results suggest that $Q \simeq 2\Delta H_s$, a relation that appears to hold for tracer diffusion in solids comprised of globular molecules.²⁶ The heat of sublimation of krypton² at the triple point is 2579 ± 3 cal mole⁻¹ so that the estimated Q would be 5160 cal mole⁻¹, which is only slightly higher than that observed. A detailed calculation of Q based upon absolute rate theory and a Mie-Lennard-Jones potential yields¹² the estimate $Q = 5250$ cal mole⁻¹.

While the foregoing indicates reasonable agreement between theory and experiment, a closer examination shows that the separate contributions to Q have not been well estimated. A direct determination of E_v for krypton has been made from the simultaneous measurement of lattice and bulk expansivities,⁶ with the result $E_v = 1780 \pm 200$ cal mole⁻¹, which is only two-thirds of the heat of sublimation. An almost identical value has been derived² from the analysis of premelting heat capacities. It follows that the ratio E_v/E_m becomes ~ 0.6 rather than unity as expected, a result that has also been found¹⁶ for self-diffusion in argon. The origin of the discrepancy possibly lies in the assumption that diffusion takes place through the motion of single vacancies. Recent calculations that take into account some many-body interactions suggest³⁴ that divacancies may contribute strongly to diffusion in rare-gas solids at high temperatures.

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³² J. J. Burton and G. Jura, *J. Phys. Chem. Solids* **27**, 961 (1966).

³³ H. R. Glyde, *J. Phys. Chem. Solids* **27**, 1659 (1966).

³⁴ J. J. Burton, *Phys. Rev.* **182**, 885 (1969).