

Calculations on several three-dimensional models with symmetrical spatial arrangement of the possible sites have been completed, and the results are qualitatively similar to those for a single-axis rotator. A distribution of dielectric relaxation times and a low polarizability appear when one site is more stable than the others, but only a single relaxation time with a polarizability of $\mu_0^2/3kT$ is found when the sites are equivalent. Work has also been completed on a single-axis rotator with four rate constants.

¹ J. D. Hoffman and H. G. Pfeiffer, *J. Chem. Phys.* **22**, 132 (1954).

² It should be noted that Table II is for the C_{ij} for $k' \gg k$ and not $k' = k$.

Rare Gas Permeation through Polymers

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IN a study of gas permeation through solids, an unexpected result was obtained. It was found that the heavier rare gases may have a faster steady-state rate of permeation through some polymers than does helium.

The procedure for measuring rates of permeation was similar to that employed in the determination of helium diffusion through a variety of glasses.¹ The mass spectrometer was used to positively identify the gas and to measure its permeation rate through a 50-mil polymer sheet.

The permeation rate is given in units employed by Dushman² and Barrer,³ that is, in cubic centimeters of gas at normal temperature and pressure (760 mm Hg, 0°C) per second per cm² area per millimeter thickness per cm Hg gas differential, partial pressure.

At 25°C, the following rates of permeation were found.

	Xenon	Helium
Perbunan	8×10^{-10}	38×10^{-10}
Butyl rubber	11×10^{-10}	40×10^{-10}
Neoprene	100×10^{-10}	45×10^{-10}
Natural rubber	430×10^{-10}	230×10^{-10}

The explanation probably lies in the balance between the two factors for permeation: solubility and internal diffusion. One would expect the diffusion to be faster for the smaller atom. However, in some cases, as for water, xenon solubility is higher than helium solubility.⁴ High solubility is also often accompanied by high permeability. So here, the high permeability for natural rubber would probably be accompanied by high solubility for xenon. This is related to the fact that long times, often several days, were required to establish steady-state flow rates for xenon at 25°C, and long periods were subsequently needed to degas the 50-mil membrane free of xenon. Where the permeation rate is low, as xenon through perbunan, the diffusion factor predominates over the solubility factor.

¹ F. J. Norton, *J. Am. Ceramic Soc.* **36**, 90-96 (1953).

² S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949).

³ R. M. Barrer, *Diffusion In and Through Solids* (Macmillan Company, New York, 1941).

⁴ E. Lange and R. Watzel, *Z. physik. Chem. (A)* **181**, 1 (1938).

Erratum: Flame Zone Studies by the Particle Track Technique. I. Apparatus and Technique

[*J. Chem. Phys.* **22**, 106 (1954)]

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THE last term in Eq. (2), page 107, was inverted. The equation should read

$$T_1 = T_0 [v_i/v_0] [r_i/r_0] [M_i/M_0]. \quad (2)$$

The authors are indebted to Mr. E. E. Frost for bringing this error to our attention.

The Anomalous Magnetic Behavior of UI_3 from 1-4.2°K

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MEASUREMENTS¹ by J. K. Dawson have shown that the magnetic susceptibility of UI_3 follows a Curie-Weiss law in the temperature region 200°K-394°K with a Weiss constant of 5°K. The small value of the Weiss constant suggested the possibility of a magnetic transition in the liquid helium temperature region. We have measured the differential magnetic susceptibility at 500 cycles on two 10-gram powder UI_3 samples using a cryostat and mutual inductance bridge described elsewhere.² Figures 1 and 2 give plots of the reactive component χ'

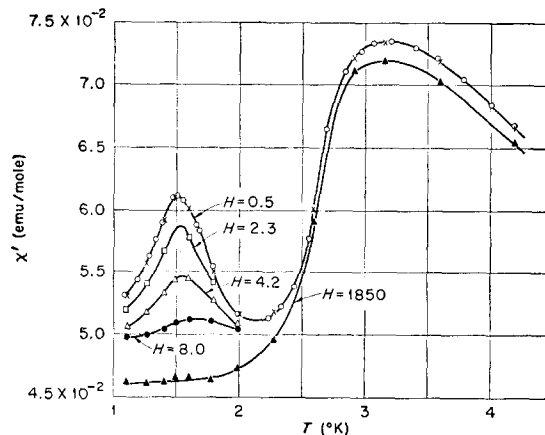


FIG. 1. Reactive component of the magnetic susceptibility of UI_3 as a function of temperature and magnetic field— H is in gauss.

and the resistive component χ'' of the susceptibility as a function of temperature and magnetic field. The maximum in χ' at 3.20°K is interpreted to be an antiferromagnetic transition. In this temperature region χ'' remains very small, and both components of the susceptibility are found to be insensitive to the magnetic field up to 500 gauss. The peak at 1.50°K in χ' is quite different from that at the Néel temperature. In this region the loss component χ'' rises sharply to a maximum at 1.38°K and both components are remarkably sensitive to a static magnetic field which is applied with a solenoid magnet mounted coaxially with the susceptibility measuring coils.² Both χ' and χ'' are found to decrease almost linearly with increasing field up to about 5 oersted and this decrease appears to saturate at 300 to 500 gauss. These phenomena were observed to be virtually independent of frequency and amplitude of the oscillating field up to 1000 cycles and 3 oersted.

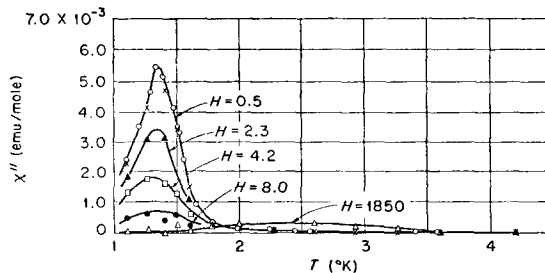


FIG. 2. Resistive component of the magnetic susceptibility of UI_3 as a function of temperature and magnetic field— H is in gauss.

The foregoing behavior was duplicated in two samples of UI₃ prepared by different chemical procedures: one by direct combination of the elements and the other by the action of methyl iodide on UH₃.³ This fact suggests that these are intrinsic properties of this compound. To prevent chemical decomposition of the sample by oxygen or water, the samples were handled only in a dry box and were sealed under a helium atmosphere in a glass vial. It is noted that the anomalous behavior of χ' and χ'' in the lower temperature region is in some respects similar to the ferromagnetic effects found by Kurti and Simon in manganous ammonium sulfate near 0.1°K and more recently investigated by Hudson and McLane⁴ and by Steenland⁵ for chromium methylamine sulfate at even lower temperatures. Further susceptibility measurements and a specific heat measurement are in progress.

¹ J. K. Dawson, AERE C/R 578, September, 1950.

² Erickson, Roberts, and Dabbs, Rev. Sci. Instr. (in press).

³ National Nuclear Energy Series VIII-5, "The Chemistry of Uranium," pp. 533-536.

⁴ R. P. Hudson and C. K. McLane, International Conference on Low Temperature Physics, Houston (1953).

⁵ M. J. Steenland, International Conference on Low Temperature Physics, Houston (1953).

Altered Proportions of Isotopes of Molecular Nitrogen as Evidence for a Monomolecular Reaction

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WHEN nitrogen gas is prepared by adding hypobromite to an amine or ammonium salt, the gas satisfies the following equilibrium



Similarly, in compounds of the form $\text{H}_2\text{N}-\text{X}-\text{NH}_2$ the proportions of the forms $\text{H}_2\text{N}^{14}-\text{X}-\text{N}^{14}\text{H}_2$, $\text{H}_2\text{N}^{15}-\text{X}-\text{N}^{15}\text{H}_2$, and $\text{H}_2\text{N}^{14}-\text{X}-\text{N}^{15}\text{H}_2$ are described by the same equilibrium constant

$$K = \frac{[\text{N}^{14}\text{N}^{15}]^2}{[\text{N}^{14}\text{N}^{14}][\text{N}^{15}\text{N}^{15}]} = \frac{[\text{H}_2\text{N}^{14}-\text{X}-\text{N}^{15}\text{H}_2]^2}{[\text{H}_2\text{N}^{14}-\text{X}-\text{N}^{14}\text{H}_2][\text{H}_2\text{N}^{15}-\text{X}-\text{N}^{15}\text{H}_2]} = 4.$$

However, when N^{15} -enriched nitrogen gas is mixed with normal nitrogen the equilibrium is not attained under ordinary conditions, and a calculated $K \neq 4$. Similarly, when a portion of a compound containing two nitrogen atoms synthesized from N^{15} -enriched nitrogen is combined with an unenriched portion of the same compound, $K_{\text{calc}} \neq 4$.

It occurred to us that nitrogen evolved from such a mixture should produce gas in which $K_{\text{calc}} \neq 4$, provided that the reaction is monomolecular. In other words, provided that both of the nitrogen atoms in each nitrogen molecule are derived from the same $\text{H}_2\text{N}-\text{X}-\text{NH}_2$ molecule, the distribution of the three isotopes of molecular nitrogen will be identical to the distribution of the three isotopic forms of the compound. If the three isotopic forms are not present in proportions which fulfill the statistical equilibrium shown above, the evolved nitrogen gas will not exhibit statistical equilibrium either.

We have confirmed this hypothesis by examination of the proportions of nitrogen gas isotopes evolved in the reaction of hypobromite with urea. N^{15} -enriched urea containing 61.8 atoms percent N^{15} was synthesized by the ammonolysis of diphenyl carbonate. 1 mg was combined with 99 mg of ordinary urea (0.3676 atoms percent N^{15}) and dissolved in water. Portions of this mixture and of the two urea samples individually were allowed to react with hypobromite, and the intensities of the peaks at apparent mass (M/e) 28, 29, and 30 were measured in the mass spectrometer (C.E.C. Model 21-201). The results are shown in Table I. Calculated values were obtained by computing the weights of the three molecular species, $\text{H}_2\text{N}^{14}\text{CON}^{14}\text{H}_2$, $\text{H}_2\text{N}^{15}\text{CON}^{15}\text{H}_2$,

TABLE I. Proportions of isotopes of molecular nitrogen evolved from normal urea, enriched urea, and a mixture of the two.

Sample	$\text{N}_2^{28}/\text{N}_2^{28}$	$\times$	$\text{N}_2^{29}/\text{N}_2^{29}$	$=$	K_{calc}
Ordinary urea	0.007381	— ^a	—		3.992 ^b
Enriched urea	3.23		1.20		3.88
99:1 } obs	0.01232		3.20		0.0394
Mixture } calc	0.01216		3.13		0.0381

^a The peak at M/e 30 in normal nitrogen is too small to be measured accurately.

^b Theoretical value, see H. C. Urey, J. Chem. Soc. 1947; 562.

and $\text{H}_2\text{N}^{14}\text{CON}^{15}\text{H}_2$ in the individual samples and in the mixture. Assuming that the reaction is monomolecular, the proportions of the three species should give the relative intensities of the three peaks. The close agreement between observed and calculated values confirms that the reaction is monomolecular.

It is interesting to note that calculation of the atoms percent N^{15} in the mixture from the ratio of M/e 29 to M/e 28 in the usual fashion yields a value of 0.6122 atoms percent, whereas the true value is 0.9819 atoms percent. This latter value was obtained when the urea mixture was converted to ammonium sulfate before addition of hypobromite.

It appears that this principle might be useful in distinguishing whether other gas-evolving reactions are monomolecular. Any N_2 -evolving reaction in which both nitrogen atoms are released from the same molecule might be employed.

W. J. McCarville kindly synthesized the urea from N^{15} which was generously provided by Dr. J. Sendroy. Dr. S. L. Friess gave much helpful criticism.

Electrically and Elastically Active Relaxation Modes

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IN a recent paper¹ Hoffman and Pfeiffer discuss the dielectric relaxation of a single-axis rotator in a crystalline field. Closely related to their problem is the behavior of an ion that can occupy a number of potential wells, separated from one another by energy barriers.

Examples: (A) cations in inorganic glasses,² and (B) cation vacancies in alkali halides each captured either by a divalent impurity cation (e.g., in NaCl containing a small amount of Cd^{2+}) or by an anion vacancy.^{3,4}

The number of electrically active polarization modes may be found by group-theoretical methods: the representation induced by the wells of the wells-and-barriers systems is written as a sum of irreducible representations of the corresponding symmetry group and the number of electrically active modes is equal to the number of those irreducible representations in the sum, to which polar vectors (e.g., the coordinates x, y, z) belong.

Consider as an example an octahedral system of equivalent wells and barriers with wells 1, 2 at $(x, y, z) = (\pm l, 0, 0)$; 3, 4 at $(0, \pm l, 0)$; and 5, 6 at $(0, 0, \pm l)$. The system induces the representations $A_{1g} + E_g + T_{1u}$ of symmetry group O_h .⁵ The identity representation A_{1g} corresponds to the equilibrium distribution. T_{1u} is a triply degenerate electrically active representation. It corresponds to particle jumps from well 1 either directly or via wells 3, 4, 5, 6, to well 2 and vice versa, to particle transfer from 3 to 4 and from 5 to 6.

The doubly degenerate representation E_g corresponds to particle jumps from wells 1 and 2 to wells 3, 4, 5, 6, and vice versa, and to transfer from wells 3 and 4 to wells 5 and 6 and vice versa. Such a transfer does not correspond to a change of polarization and is therefore electrically inactive. It may, however, be caused by suitable elastic stresses and will therefore be called elastically