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Measurements of He^3-He^4 and H_2-D_2 Gas Diffusion Coefficients*

PHILIP J. BENDT
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

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The gas diffusion coefficient for He^3-He^4 has been measured between 1.74 and 296°K, and for H_2-D_2 between 13.9 and 296°K. The diffusion bridge used to make the measurements is described. The experimental results are compared with viscosity measurements, and with classical and quantum-mechanical calculations based on the Lennard-Jones 12-6 and on the modified Buckingham exp-6 intermolecular potential fields.

I. INTRODUCTION

INTEREST in the transport properties of gases results from the information they supply regarding intermolecular potential fields. A number of authors[1] has used measurements of viscosity and second virial coefficients of hydrogen and helium to determine constants in empirical potential functions. Measurements of the diffusion coefficient and thermal conductivity provide additional tests of the accuracy of these functions.

There are no previous gas diffusion measurements on helium reported in the literature. With the exception of a single measurement at 20.4°K on hydrogen,[2] no gas diffusion measurements have been reported at temperatures lower than 78°K. To make measurements in the low-temperature region, an apparatus called a "diffusion bridge" has been built.

II. ANALYSIS OF THE DIFFUSION BRIDGE

The diffusion bridge is shown schematically in Fig. 1. A measurement is made while there is steady-state flow of gas through the four capillaries, A, B, C, and E, and through the "diffusion tube," which joins the capillaries in the temperature bath. The pressures in the two reservoirs are adjusted according to the viscosities of the isotope mixtures flowing in the capillaries, so that the pressure gradient in the diffusion tube is made as small as possible. Capillaries C and E are alternately connected to the mass spectrometer for analysis of the effluent gas. The mole fractions, χ_3, of He^3 with which the capillaries are labeled are illustrative of a typical measurement.

The diffusion coefficient, D, is defined for a gas mixture of two isotopes, i and j, at uniform temperature and atomic density, n, in a frame of reference in which the gas as a whole is at rest, and in which a concentration gradient exists in the z direction for each isotope, by the expression

$$\chi_i c_i = -D d\chi_i/dz, \tag{1}$$

where c_i is the average diffusion velocity of isotope i. There are two equations which express continuity of flow through the diffusion tube:

$$q_i = na\chi_i(c_i+v), \tag{2}$$

$$q_i + q_j = nav, \tag{3}$$

where q_i is the flow in atoms/second, a is the cross-sectional area, and v is the net flow velocity (due to pressure gradient) in the diffusion tube. Eliminating $\chi_i c_i$ between Eqs. (1) and (2), and integrating from the junction A, C to the junction B, E gives

$$\frac{lv}{D} = \ln\left[1 + \frac{\chi_i(E) - \chi_i(C)}{\chi_i(C) - q_i/(q_i+q_j)}\right], \tag{4}$$

where l is the length of the diffusion tube. The quantity $\chi_i(C)$ stands for the concentration of isotope i in the effluent gas from capillary C, which is also the concentration at the A, C end of the diffusion tube. If isotope i enters the diffusion tube only through capillary B, we may write $q_i = -q(C)\chi_i(C)$, where $q(C)$ is the total flow rate through capillary C. If one writes $\Delta\chi_i$ for $[\chi_i(E) - \chi_i(C)]$, the second term in the brackets is nearly equal to $[\Delta\chi_i/\bar{\chi}_i][v/\bar{c}_i]$, where $\bar{\chi}_i$ and $\bar{c}_i$ are average values over the length of the diffusion tube.

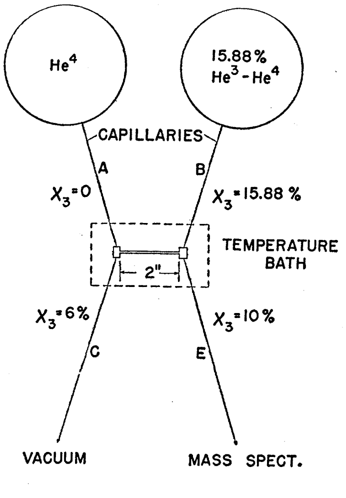

FIG. 1. Schematic diagram of the diffusion bridge.

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[1] J. de Boer and A. Michels, Physica **5**, 945 (1938); H. S. W. Massey and R. A. Buckingham, Proc. Roy. Soc. (London) **A168**, 378 (1938); **169**, 205 (1939); E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 522 (1954); Kilpatrick, Keller, and Hammel, Phys. Rev. **97**, 9 (1955).

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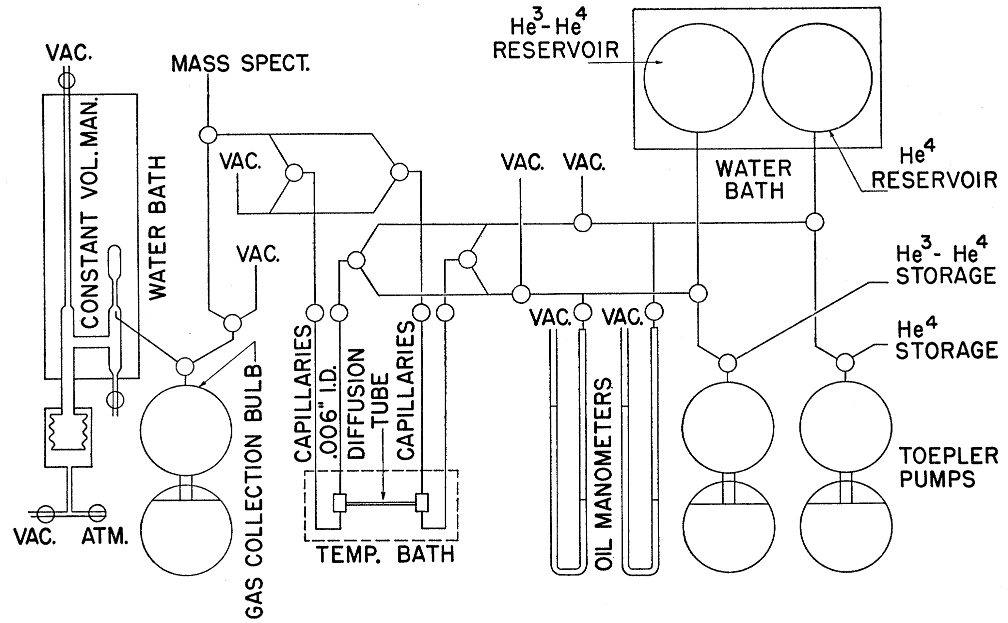

FIG. 2. Schematic diagram of the apparatus.

This expression was never larger than 0.02 during the measurements. Replacing the right-hand side of Eq. (4) with the first two terms of the expansion for $\ln(1+u)$ introduces an error less than 0.02%. This leads to the equation used to determine nD:

$$nD=\left(\frac{l}{a}\right)\left(\frac{\chi_i(C)}{\Delta\chi_i}\right)[q(C)+(q_i+q_j)]$$
$$\times\left[1-\frac{1}{2}\left(\frac{\Delta\chi_i}{\chi_i(C)}\right)\left(\frac{q_i+q_j}{q(C)+(q_i+q_j)}\right)\right]^{-1}. \quad (5)$$

If all of isotope j enters through capillary A, and all of isotope i through capillary B, then (q_i+q_j) is equal to $[q(E)\chi_j(E)-q(C)\chi_i(C)]$. During the helium measurements, He^4 entered through both A and B, and it was necessary to measure (q_i+q_j) by closing valves at the ends of capillaries B and E, and noting the change in $q(C)$. Owing to readjustment of the pressure at the diffusion tube, this change is $\frac{1}{2}(q_i+q_j)$, provided the viscosity of the gas in capillary C does not change.

III. APPARATUS AND ERRORS

A schematic diagram of the apparatus is shown in Fig. 2. The four stainless steel capillaries were 0.006-in. i.d. and 20-in. long. The capillaries were vacuum jacketed, so that the gas flow rate, which varies with temperature through the temperature dependence of the viscosity, would not change with refrigerant level. Measurements were made with a stainless steel diffusion tube 0.0266-in. i.d. and 2.0075-in. long at 20°C. An end correction[3] of 0.82 times the i.d. was added to the length to give $l/a=1448.3$ cm^{-1} at 20°C. The change in l/a due to thermal contraction at low temperatures was calculated. Two brass cylinders $\frac{1}{10}$-in. i.d. by $\frac{1}{8}$-in. long were soldered to the ends of the diffusion tube, with their axes in line with the tube. Two capillaries entered each cylinder, through opposite sides.

Gas used in the experiment was purified by passing it through a liquid hydrogen or liquid helium trap. The gas pressure in the one liter reservoirs was varied between 15 and 30 mm Hg. Output from the capillaries was directed to a Consolidated Engineering Corporation model 21-201 mass spectrometer. The flow rates, q, from the capillaries were measured by calibrating the sensitivity of the mass spectrometer at some time during each measurement. This calibration was made by comparing the mass spectrometer signal voltage with the quantity of gas collected in an evacuated bulb during a measured time of 5 to 10 minutes.

Systematic errors dependent on physical measurements of the apparatus, calibration of thermometers, etc., are believed to be an order of magnitude smaller than errors associated with measurements of isotope concentration and gas flow. Small fluctuations in sensitivity of the mass spectrometer, and in steady-state flow through the diffusion bridge, especially at low temperatures, limited the accuracy of the measurements. Every measurement was repeated three to six times, and the errors quoted in Tables I and III are the standard deviation of repeated measurements.

The value of l/a of the diffusion tube was not large enough for precise measurements when $nD\mu$ (μ is the reduced mass) is larger than about 70×10^{-6} g/cm-sec. The limitation is that $\Delta\chi_i$ in Eq. (5) becomes a small difference between two nearly equal numbers.

It was necessary that the flow rate through the

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[3] J. W. Strutt (Lord Rayleigh), *Theory of Sound* (Dover Publications, New York, 1945), Vol. II, p. 183.

capillaries be sufficiently fast that a concentration gradient was not set up in the capillaries due to the thermal gradient between the low temperature bath and room temperature. The criteria used to establish that measurements were not affected by thermal concentration gradients was that the measurements should not be dependent on the lapsed time from the start of gas flow. To support an adequate flow required the pressure in the diffusion tube to be about 9 mm Hg at liquid helium temperatures. Condensation of the helium gas at this pressure prevented making diffusion measurements at lower temperatures than 1.74°K.

IV. RESULTS FOR He^3-He^4

The quantity nD has been measured at various temperatures between 1.74 and 296°K. One reservoir bulb contained pure He^4, and the other 15.88% He^3 in He^4, so the average concentration $\bar{x}_3$ equaled 7.94%. Experimental values are tabulated in Table I, and $nD\mu$ is plotted in Fig. 3. The quantity μ is the reduced mass for a collision of a He^3 atom with a He^4 atom, equal to 2.8454×10^{-24} g.

TABLE I. Measurements of the He^3-He^4 gas diffusion coefficient.

Temp. °K	$nD\mu$ 10^{-6} g/cm-sec	D(760 mm) cm²/sec	Error %
1.74	3.99		6
2.00	4.49		4
2.31	5.21		3
2.66	5.75		2
3.08	6.32		3
3.96	7.66		2
14.4	18.1	0.0124	3
19.6	21.2	0.0199	2
64.8	47.5	0.147	3
76.1	51.4	0.187	2
192	91.7	0.843	4
296	118	1.68	4

It is of interest to compare the agreement between theory and experiment for viscosity as well as for the diffusion coefficient. This is because the collision integrals used to calculate the two phenomena are different. The third transport property, thermal conductivity, is calculated from the same collision integrals as the viscosity.

Measurements[4] of the viscosity $\eta(He^4)$ are also plotted in Fig. 3. Above 14°K, both $\eta(He^4)$ and $nD\mu$ can be represented quite well by straight lines on a log-log plot against temperature. The temperature dependence of the two quantities is the same within the experimental error of the measurements, and equals $T^{0.64}$. Measurements[5] of the thermal conductivity of He^4 show that it also has the same temperature dependence over this range.

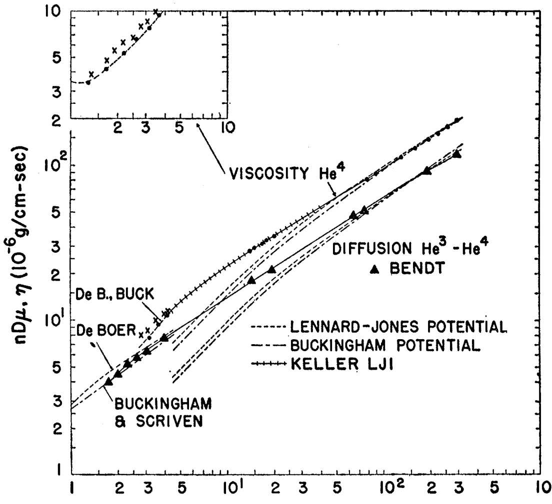

FIG. 3. Viscosity $\eta(He^4)$ and $nD(He^3\text{-}He^4)\mu$. Viscosity measurements[4] above 80°K by Johnston and Grilly; 14 to 20°K by Becker and Misenta; below 4°K, dots by Becker, Misenta, and Schmeissner, and crosses by Van Itterbeek *et al.*

The self-diffusion coefficient $D(He^4)$ for He^4 can be obtained from the experimental data by applying the mass correction factor,[6]

$$D(He^4)=[2m_3/(m_3+m_4)]^{\frac{1}{2}}D(He^3-He^4)$$
$$=0.927D(He^3-He^4), \quad (6)$$

TABLE II. Potential function constants used in calculating viscosity and diffusion coefficients.

	Helium	Hydrogen
	Lennard-Jones 12-6:	
Classical		
ϵ/k (°K)	10.22[a]	33.3[a]
σ (angstroms)	2.576[a]	2.968[a]
Quantum-mechanical		
ϵ/k (°K)	10.22[b]	37.0[e]
σ (angstroms)	2.556[b]	2.928[e]
	Buckingham exp-6:	
Classical		
ϵ/k (°K)	9.16[c]	37.3[c]
r_m (angstroms)	3.135[c]	3.337[c]
α	12.4[c]	14.0[c]
	Buckingham exp-6-8:	
Quantum-mechanical		
ϵ/k (°K)	10.17[d]	
r_m (angstroms)	2.943[d]	
α	13.6[d]	
β	0.2[d]	

[a] See reference 6, p. 1110.
[b] See Cohen, Offerhaus, and de Boer, reference 9.
[c] See Mason and Rice, reference 1.
[d] See Buckingham and Scriven, reference 9.
[e] See reference 12.

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[4] H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942); Van Itterbeek, Schapink, van den Berg, and van Beek, Physica **19**, 1158 (1953); Becker, Misenta, and Schmeissner, Phys. Rev. **93**, 244 (1954); Z. Physik **137**, 126 (1954); E. W. Becker and R. Misenta, Z. Physik **140**, 535 (1955).

[5] J. B. Ubbink and W. J. de Haas, Physica **10**, 465 (1943).

[6] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Chap. 8 and Appendix.

TABLE III. Measurements of the H_2-D_2 gas diffusion coefficient.

Temp. °K	$nD\mu$ 10^{-6} g/cm-sec	D(760 mm) cm²/sec	Error %	Author
13.9	4.27		2	
19.5	6.38		1	
20.4	6.26	0.00706[a]	2.5	Harteck and Schmidt[b]
65.1	22.0	0.0871	2	
76.6	24.9	0.116	2	
85	28.7	0.149[a]	4.7	Harteck and Schmidt[b]
192	49.8	0.583	2	
273	66.8	1.113[a]	0.3	Harteck and Schmidt[b]
288	70.5	1.24		Heath, Ibbs, and Wild[c]
293.2	67.7	1.21[a]		Waldmann[d]
296	70.2	1.27	3	

[a] Mass correction factor Eq. (7) applied to original measurements.
[b] See reference 2.
[c] See Heath *et al.*, reference 10.
[d] See Waldmann, reference 10.

where m_3 and m_4 are the atomic weights of the isotopes. The value of the Schmidt number $S(\mathrm{He}^4)=\eta(\mathrm{He}^4)/\rho D(\mathrm{He}^4)$, where ρ is the gas density, is 0.76 ±0.02 at 0°C. This may be compared with the following values obtained for other low-mass gases[7]: $S(\mathrm{Ne})=0.73$, $S(\mathrm{A})=0.75$, $S(\mathrm{N}_2)=0.74$, $S(\mathrm{CH}_4)=0.70$, $S(\mathrm{O}_2)=0.74$, $S(\mathrm{CO}_2)=0.71$, and $S(\mathrm{H}_2)=0.73$.

Using the collision integrals $\Omega^{(l,s)*}$ given in Hirschfelder, Curtiss, and Bird,[6] we have calculated classically the viscosity and diffusion coefficient using the Lennard-Jones 12-6 potential function,[6] and also using the modified Buckingham exp-6 potential function.[8] The constants used in the potential functions are given in Table II. The results, as shown in Fig. 3, are in poor agreement with the measurements below about 60°K.

Quantum mechanical calculations of the viscosity and the diffusion coefficient have been made up to 4.1°K by Cohen, Offerhaus, and de Boer,[9] using the Lennard-Jones potential, and up to 5°K by Buckingham and Scriven,[9] using a modified Buckingham potential with an added 8-power attractive term. The low-temperature measurements of the diffusion coefficient lie nearly midway between the theoretical curves of de Boer and of Buckingham.

Keller[9] has extended the quantum mechanical viscosity calculations using the Lennard-Jones potential (LJ1), and an exp-6 potential, up to 40°K. Best agreement with measurements by Becker and Misenta[4] in the 14–20°K range was obtained with the calculations based on LJ1, which are shown in Fig. 3. Below 4°K, the calculations of de Boer, Buckingham, and Keller are all very similar, and agree with the viscosity measurements of Becker, Misenta, and Schmeissner.[4] The viscosity measurements of Van Itterbeek *et al.*[4] are about 10% higher.

V. RESULTS FOR H_2-D_2

Diffusion measurements were made using hydrogen gas which analyzed 99.53% H_2 and 0.47% HD, and deuterium gas which analyzed 98.31% D_2 and 1.69% HD. The ortho- and para-compositions of the hydrogen and of the deuterium were the equilibrium compositions at room temperature. The average concentration $\bar{\chi}_4$ at which measurements were made was 49.45%. During the diffusion measurements, the concentrations of HD molecules at the two ends of the diffusion tube were very nearly equal, and in this situation the correct procedure for calculating the product nD from Eq. (5) is to ignore the presence of the HD molecules.

Experimental values, as well as previous measurements[2,10] of the diffusion coefficient of ortho- and parahydrogen and of H_2-D_2, are tabulated in Table III, and $nD\mu$ is plotted in Fig. 4. Here n is the density of H_2 and D_2 molecules, and μ is the reduced mass, equal to 2.2312×10^{-24} g. The self-diffusion coefficient $D(H_2)$ is obtained by applying the mass correction factor,

$$D(H_2)=[2m_4/(m_2+m_4)]^{\frac{1}{2}}D(H_2-D_2)=1.155D(H_2-D_2). \quad (7)$$

Measurements[11] of $\eta(H_2)$ are also plotted in Fig. 4. Above 65°K both the viscosity and $nD\mu$ can be represented quite well by straight lines on a log-log plot against temperature. The temperature dependence of the two quantities is not the same, $nD\mu$ being proportional to $T^{0.77}$, while $\eta(H_2)$ is proportional to $T^{0.68}$. The value of the Schmidt number $S(H_2)=0.73\pm0.015$ at 0°C.

Using the collision integrals $\Omega^{(l,s)*}$ given in Hirschfelder, Curtiss, and Bird,[6] we have calculated classically

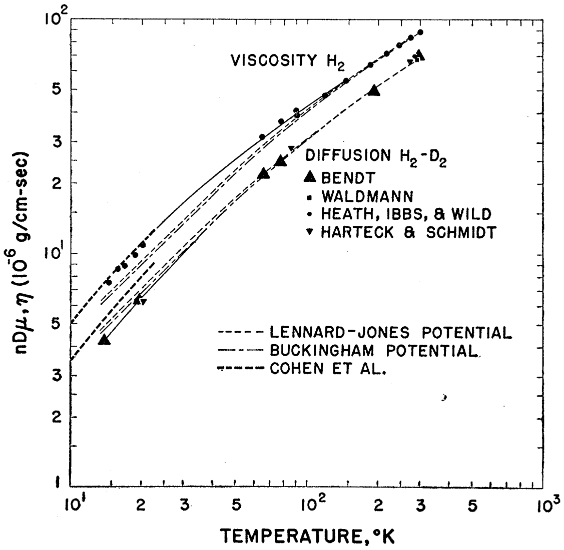

FIG. 4. Viscosity $\eta(H_2)$ and $nD(H_2$-$D_2)\mu$. Viscosity measurements[11] above 90°K by Johnston and McClosky; below 90°K by Becker and Misenta.

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[7] See reference 6, p. 16.

[8] See reference 6, p. 180.

[9] R. A. Buckingham and R. A. Scriven, Proc. Phys. Soc. (London) **A65**, 376 (1952); Cohen, Offerhaus, and de Boer, Physica **20**, 501 (1954); W. E. Keller, Phys. Rev. **105**, 41 (1957).

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[11] H. L. Johnston and K. E. McCloskey, J. Phys. Chem. **44**, 1038 (1940); E. W. Becker and R. Misenta, Z. Physik **140**, 535 (1955).

the viscosity and diffusion coefficient using the Lennard-Jones 12-6 potential function, and also using the modified Buckingham exp-6 potential function. The constants used in the potential functions are given in Table II; the results are plotted in Fig. 4. It can be shown that no choice of parameters for either potential function can give better agreement between classical calculations and measurements for both viscosity and diffusion coefficient, in the 14 to 20°K temperature range.

Cohen, Offerhaus, van Leeuwen, Roos, and de Boer[12] have made quantum mechanical calculations up to 22°K of $\eta(H_2)$ and ρD(ortho-para-H_2), using the Lennard-Jones potential. Their viscosity calculation is shown in Fig. 4. Their diffusion coefficient results have been multiplied by $n\mu/\rho$ and by the mass correction factor, Eq. (7), before plotting in Fig. 4. According to the principle of corresponding states, the mass correction factor applies to the quantum mechanical calculation, since the diffraction effects depend in this manner on the masses of the colliding particles. Since H_2 and D_2 are different molecules, just as ortho-H_2 and para-H_2 are different molecules, the quantum mechanical symmetry effects should be the same, and the calculation of Cohen *et al.* should apply to the H_2-D_2 diffusion coefficient. The measurements at 13.9 and 19.5°K are about 20% below the quantum mechanical calculations.

Classical calculations in second approximation indicate the dependence of the diffusion coefficient on H_2-D_2 isotopic ratio increases with temperature. At 300°K, the change in diffusion coefficient between a 50%-50% mixture and a 95%-5% mixture is about 0.7%. The experiment is not sufficiently precise to look profitably for this effect.

ACKNOWLEDGMENTS

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[12] Cohen, Offerhaus, van Leeuwen, Roos, and de Boer, Physica **22**, 791 (1956).

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Nuclear Levels in P^{30}, S^{33}, and S^{35}†

P. M. Endt, *Fysisch Laboratorium der Rijksunversiteit, Utrecht, The Netherlands*

AND

C. H. Paris, *Physics Department and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts*

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Targets of natural antimony sulfide have been bombarded with deuterons accelerated by the MIT-ONR electrostatic generator to energies of 6.0 and 6.5 Mev. Charged reaction products, protons, alpha particles, and elastically scattered deuterons, were observed at angles of 50, 90, and 130 degrees to the deuteron beam with a high-resolution, broad-range magnetic spectrograph.

The ground-state Q value of the $S^{32}(d,\alpha)P^{30}$ reaction is measured as 4.887±0.010 Mev. The previously reported first level in P^{30} appears to be a doublet with components at 0.680 and 0.708 Mev. On intensity grounds, an isobaric spin $T=1$ is assigned to the lower level. Twenty-eight additional levels in P^{30} are observed in a region of excitation up to 5.8 Mev.

The ground-state Q value of the $S^{32}(d,p)S^{33}$ reaction is 6.413±0.006 Mev, and one hundred four levels are observed up to an excitation energy of 8.0 Mev. Some levels stand out as single-particle states because of the high intensities of the corresponding proton groups.

Six weak proton groups were assigned to the $S^{34}(d,p)S^{35}$ reaction. The ground-state Q value is 4.757±0.010 Mev.

I. INTRODUCTION

In the last few years, there has been a considerable interest in the level schemes of self-conjugated odd-odd nuclei. Of prime importance is the position of the lowest $J=0^+$, $T=1$, state. Strong evidence[1,2] has been collected from the $Si^{29}(p,\gamma)P^{30}$ reaction, showing that in P^{30} this state is to be found at an excitation energy of 0.69 Mev. Recently, however, the $T=1$ character of this state has been questioned, because an intense alpha-particle group proceeding to this level has been observed from the $S^{32}(d,\alpha)P^{30}$ reaction.[3] The isobaric spin-selection rule only allows transitions to $T=0$ levels in this reaction.

Ground-state Q-value measurements of reactions

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