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PROJECT SQUID

TECHNICAL REPORT BRN-11-P

THE VISCOSITY OF THE ISOTOPES OF HYDROGEN AND THEIR INTERMOLECULAR FORCE POTENTIALS

By

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AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

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Summary

The paper presents carefully measured values of the viscosity of the three isotopes of hydrogen: H_2 , HD, and D_2 at $20^\circ C$ and at $30^\circ C$, all under atmospheric pressure. The ratios of the viscosity of any one pair of the above gases is obtained very accurately, the major source of error being connected with the uncertainties in our knowledge of the impurities present in the gases.

On the basis of the Chapman-Enskog theory for the viscosity of gases composed of spherically-symmetrical molecules whose potentials can be represented by the product $V(r) = \epsilon f(\sigma/r)$, it is concluded that all three isotopes have different intermolecular constants. However, the differences which characterize the intermolecular potentials of H_2 and D_2 are not likely to be large

Calculations which attempt to take into account the differences in the potentials of H_2 and D_2 by differences in polarizability are not confirmed by the present measurements.

1. Introductory remarks

The work described in this paper arose from a suggestion made to the authors by Professor I. Amdur of the Massachusetts Institute of Technology. Noting that our oscillating-disk viscometer¹⁾²⁾³⁾ is capable of producing highly precise values of the viscosity of gases at room temperature, it has been suggested that an attempt might be made to measure the ratios of the viscosity of hydrogen, H_2 , to that of deuterium, D_2 , and hydrogen deuteride, HD , in order to see if conclusions could be drawn regarding their respective intermolecular force potentials. The measurements are absolute and usually yield an accuracy of better than 0.2%; however, the ratios of the three viscosities can be obtained much more accurately if all experiments are performed in the same instrument and with the same setting, because errors in the determination of the instrument constant cancel. It is considered that these ratios can be determined with an accuracy of 0.06%.

2. Instrument

The instrument used in this work has been adequately described elsewhere¹⁾²⁾³⁾, and its theory, due to G. F. Newell was also given³⁾⁴⁾. The characteristics of the suspension system used in this work are shown in Table 1. It is noteworthy that the value of the instrument constant $C_N = 1.094_0$ computed from the knowledge of the physical dimensions of the suspension system is very close to the experimentally obtained check-value $C_N^1 = 1.094_4$. The latter was obtained with the aid of measurements on nitrogen at 20°C in the range from 1 to 2 atm and was based on the value of viscosity

$$\frac{\mu}{\text{micropoise}} = 175.52 + 0.1234 \frac{p}{\text{atm}} + 1.20 \times 10^{-3} \left(\frac{p}{\text{atm}} \right)^2 \quad (1)$$

quoted by J. Kestin and W. Leidenfrost¹⁾.

3 Purity of gases

The gases used were supplied commercially their purities, as indicated by the respective manufacturers, are given in Table 2. In the case of hydrogen deuteride, two lots were available together with a complete analysis of impurities.

4 Reproducibility and accuracy

The reproducibility attained in this work can be judged from Fig. 1 which compares the experimentally determined values of the instrument constant C_N with the theoretical value C_N . The latter does not include the drag of the mirror, and $C_N' > C_N$ as expected. The measurements of C_N were performed periodically over a long interval of time during which it was ascertained that the maximum deviation from the average value $C_N' = 1.094$ did not exceed $\pm 0.03\%$.

Taking into account the uncertainties in the various quantities which enter into the working equation it is found that the relative accuracy of the determinations was

$$\frac{\Delta\mu}{\mu} = \pm 0.1\%$$

However, since the uncertainty in the values (1) for the viscosity of nitrogen was $\pm 0.1\%$, the overall uncertainty in the indications of the absolute viscosity is estimated to be of the order of $\pm 0.2\%$.

When taking ratios of the viscosity of one gas to that of another, it is found that the uncertainty is reduced to

$$\frac{\Delta \left(\frac{\mu_1}{\mu_2} \right)}{\mu_1/\mu_2} = 0.06\%$$

owing to a cancellation of terms.

5. Experimental results

The measurements were performed at the two nominal temperatures of 20°C and 30°C; the viscosity of hydrogen, H₂, and deuterium, D₂, was determined in a range of pressures from 1 to 6 atm, whereas the viscosity of deuterium was determined at a pressure of 1 atm only. In the case of hydrogen and deuterium the effect of pressure on the viscosity in the range covered turned out to be negligible, as expected.

The experimental results, corrected to the nominal temperatures, are given in Table 3. The largest difference between the actual and nominal temperature was 0.15°C so that uniform corrections could be applied. These were: 0.20 micropoise/°C for hydrogen, 0.25 micropoise/°C for hydrogen deuteride, and 0.28 micropoise/°C for deuterium.

The purity of the hydrogen used was very high, and no correction for it was required; the impurities in deuterium were unknown, and could not be corrected for. In the case of hydrogen deuteride, the effect of impurities could be partially eliminated by corrections. The effect of adding impurities to hydrogen deuteride was estimated on the basis of the prior measurements performed by A. O. Rietveld, A. van Isterbeek and C. A. Velds⁵⁾, and the following mean values were assumed

$$\frac{\partial \eta}{\partial x_{H_2}} = 0.186 \text{ micropoise}/\% H_2$$

$$\frac{\partial \eta}{\partial x_{D_2}} = -0.117 \text{ micropoise}/\% D_2$$

In this manner, the estimated viscosity of pure HD turned out to be

at 20°C	from HD 1	111.67 micropoise
	from HD 2	112.09 micropoise
at 30°C	from HD 1	114.70 micropoise
	from HD 2	114.85 micropoise

giving the average values indicated in Table 3.

It is seen from these calculations that the uncertainties in the determination of the nature of the impurities contributed a relatively large error to the values of viscosity; this is estimated at

0.5%	for	D_2
0.4%	for	HD
0.0%	for	H_2

These uncertainties by far exceed those estimated earlier for the ratios of viscosity; consequently, the errors in the ratios of viscosity can be assumed to be due primarily to the uncertainties in composition. A summary of the uncertainties is given in Table 4, and the most probable values at 1 atm are given in Table 5 together with their tolerances.

6. Comparison with previous measurements

The viscosity of hydrogen and deuterium was determined previously by J. Kestin and W. Leidenfrost¹⁾ in the same instrument but with a different suspension system. In the previous determination, the purity of deuterium was the same as at present (99.5%), whereas that of hydrogen was slightly inferior (99.974%). The results are seen compared in Figs. 2 and 3. It is seen that the present value of the viscosity of hydrogen at 20°C has turned out to be about 0.5% lower; this discrepancy cannot be accounted for by the difference in the amount of impurities present, but must be accepted as a measure of long-range reproducibility of the instrument. On the other hand, the difference for deuterium is remarkably small, and does not exceed 0.08%.

A similar comparison with the results in ref. 5 shows very good agreement in the case of hydrogen, Fig. 2, and a discrepancy of + 1% in the case of deuterium, Fig. 3, allowing for the somewhat inferior reproducibility of the other data. A comparison for HD shows that the present value is about 5% higher than the two values of 107.5 micropoise and 106.9 micropoise quoted in ref. 5. It must, however, be remembered that the gas used in ref. 5 had a purity of only $93.0 \pm 2.0\%$ and that no correction for impurities was applied. If this were done, an estimated discrepancy of 3% would still remain.

7. Discussion

According to the Chapman-Cowling theory, the low-density viscosity of a gas with a spherically-symmetric force field (essentially a monatomic gas) is given by the equation⁶⁾

$$\mu = 266.93 \frac{\sqrt{MT}}{\sigma^2 \tilde{\Omega}(T^*)} \quad (2)$$

on condition that the potential of the intermolecular forces is of the form

$$V(r) = \epsilon f\left(\frac{r}{r_0}\right)^{\#} \quad (3)$$

Here M denotes the molecular mass, T is the absolute temperature, σ the collision diameter in $\text{\AA}$, and

$$\tilde{\Omega}(T^*) = \left[\frac{\zeta_{\eta}^{(k)}(T^*)}{\Omega^{(2,2)*}(T^*)} \right]^{-1} \quad (3)$$

is a collision integral which depends on the form of the potential function $f(\sigma/r)$ of molecular interaction and which is expressed in terms of the reduced temperature

$$T^* = \frac{kT}{\epsilon} \quad (4)$$

Here, finally, k denotes the Boltzmann constant, and ϵ/k in $^{\circ}\text{K}$ is a parameter which characterizes a scale of the potential function of interaction.

The accurate values of the viscosity ratios quoted in Table 5 permit us to examine a question of long-standing, namely to investigate whether the intermolecular force potentials are identical for the three isotopes H_2 , HD and D_2 .

[#] This assumption naturally restricts the generality of the conclusions drawn subsequently. However, such a restriction is unavoidable, because the influence of molecular mass cannot be made explicit for a more general form of the potential.

If the intermolecular force potentials as well as the collision diameters are identical for two gases 1 and 2, then it follows as a necessary condition that at a common temperature T

$$\frac{\sigma_1^2 \bar{\Omega}_1}{\sigma_2^2 \bar{\Omega}_2} = \sqrt{\frac{M_1}{M_2}} \cdot \frac{\mu_2}{\mu_1}, \quad (5)$$

that is that the dimensionless group

$$A_m = \sqrt{\frac{M_1}{M_2}} \cdot \frac{\mu_2}{\mu_1} = 1. \quad (5a)$$

The condition is necessary, but not sufficient, because when $A_m = 1$, σ_1 may differ from σ_2 and ϵ_1 may differ from ϵ_2 in a manner to render

$$\sigma_1^2 \bar{\Omega}_1 = \sigma_2^2 \bar{\Omega}_2. \quad (6)$$

We first examine the experimental values of A_m on the basis of Table 5 for the three pairs of ratios of viscosity listed in it. The values of the molecular masses $M_{H_2} = 2.01565$, $M_{HD} = 3.02193$ and $M_{D_2} = 4.08204$ on the carbon -12 scale have been taken from the American Institute of Physics Handbook,⁷⁾ and the result of the computation is given in Table 6.

The numerical values given in Table 6 together with their bands of uncertainty show that the value $A_m = 1$ is not included in the range of possible values for any one of the three pairs of gases. Hence it must be concluded that all isotopes of hydrogen have different intermolecular force potentials. This result is not surprising when hydrogen deuteride is compared with hydrogen or deuterium. The comparison between hydrogen and deuterium requires further comment.

It has been thought for a long time that the intermolecular force constants for hydrogen and deuterium are identical. The present measurements show that they are not, but the differences between them cannot be very large, except for the unlikely circumstance that the differences, though large, still produce values of $\sigma^2 \tilde{\Omega}$ which are very nearly equal for the two gases.

Although great care has been taken to evaluate the uncertainties quoted in Table 6, it is necessary to bear in mind that the upper limit for the ratio $A_m(H_2/D_2)$ has the value of 0.998 which is very close to unity.

Similar conclusions have been reached by H.F.P. Knaap and J.J.M. Beenakker⁸⁾. Although A. Michels, W. de Graaf and C. A. ten Seldam⁹⁾ have shown that the behavior of the virial coefficients of either hydrogen or deuterium forces the conclusion that neither gas obeys a Lennard-Jones six-twelve potential, it is, nevertheless, useful to discuss the values ϵ and σ of a pseudo-Lennard-Jones potential by way of approximation. According to Knaap and Beenakker⁸⁾

$$\frac{\epsilon_{H_2} - \epsilon_{D_2}}{\epsilon_{H_2}} = 0.043 \pm 0.009 \quad (7)$$

and

$$\frac{\sigma_{H_2} - \sigma_{D_2}}{\sigma_{H_2}} = 0.002 \pm 0.009 . \quad (7a)$$

Since there exists no general agreement as to the values of the intermolecular force potentials for hydrogen, we have selected several values⁶⁾⁹⁾¹⁰⁾¹¹⁾ and computed from them the viscosity of hydrogen and deuterium from eqn. (2). The results of these computations are shown in Table 7.

An examination of Table 7 reveals that at the present state of knowledge it is impossible uniquely to determine an optimum set of values of the pseudo-Lennard-Jones potential for either hydrogen or deuterium. On the present evidence, and on the present evidence alone, it would appear that the parameters

$$\left. \begin{aligned} \sigma &= 2.968 \text{ \AA}; \quad \epsilon/k = 33.3^\circ\text{K} & \text{for } \text{H}_2 \\ \text{and} \\ \sigma &= 2.952 \text{ \AA}; \quad \epsilon/k = 35.2^\circ\text{K} & \text{for } \text{D}_2 \end{aligned} \right\} \quad (8)$$

are to be recommended, because they reproduce our data with the least deviation, and within the band of uncertainty; they are not, however, the only pairs which achieve the same result.

From these values we can compute that

$$\frac{\epsilon_{\text{H}_2} - \epsilon_{\text{D}_2}}{\epsilon_{\text{H}_2}} = -0.057 \quad \text{and that} \quad \frac{\sigma_{\text{H}_2} - \sigma_{\text{D}_2}}{\sigma_{\text{H}_2}} = +0.005 \quad (9)$$

and note that the difference in the parameter ϵ is opposite to that quoted in eqn. (7) from ref. 8 on the basis of experimental P,V,T data; the order of magnitude of the difference in σ is the same and of the same sign as the experimental value (7a) from ref. 9, but opposite in sign to that calculated in ref. 9 on the supposition that the difference can be accounted for by a difference in polarizability.

Thus no unequivocal conclusion can be drawn.

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[#] May be obtained by request.

Table 1. Characteristics of suspension system.

Suspension wire	0.002" 92 Pt 8 W
Stress relieved	
Wire damping	$\Delta_0 = 0.00004 \pm 0.000004$
Total separation between plates	$D = 0.28448 \pm 0.00005$ cm
Upper and lower separations	$b_1 = b_2 = 0.09012 \pm 0.00005$ cm
Radius of disk	$R = 3.4902 \pm 0.0001$ cm
Thickness of disk	$d = 0.10424 \pm 0.00005$ cm
Moment of inertia of suspension system	$I = 53.5837 \pm 0.0047$ gcm ²
Natural period of oscillation at 20°C	$T_{20} = 29.587 \pm 0.002$ sec
at 30°C	$T_{30} = 29.530 \pm 0.002$ sec
Instrument constant	
theoretical	$C_N = 1.0940 \pm 0.0002$
experimental	$C'_N = 1.0944 \pm 0.0003$

Table 2. Purity of gases.

Gas	Supplier	Purity	Impurities	
H ₂	The Matheson Company	99.999	Unknown	
D ₂	The Matheson Company	99.5	Unknown	
N ₂	Air Products, Inc.	99.998	Unknown	
HD1	Nichem Company	98.32	H ₂ - 1.12%	D ₂ - 0.56%
HD2	Nichem Company	99.3	H ₂ - 0.13%	D ₂ - 0.57%

Table 3. Experimental results.

Pressure P atm	Density ρ g/cm ³	Viscosity μ micropoise
a. Hydrogen at 20°C		
6.076	0.0005975	86.48
5.069	0.0005235	86.28
4.061	0.0003361	86.25
3.041	0.0002543	86.25
2.014	0.0001685	86.29
1.490	0.0001247	86.27
1.020	0.00008539	86.29
c. Deuterium at 20°C		
5.495	0.0009190	127.80
4.082	0.0006593	127.83
2.361	0.0003817	127.75
1.048	0.0001696	127.76
e. Hydrogen deuteride at 20°C (HD1)		
1.039	0.0001305	111.52
1.000	0.0001257	111.49
0.964	0.0001211	111.53
1.033	0.0001297	111.53
g. Hydrogen deuteride at 20°C (HD2)		
1.003	0.0003860	112.14
i. Hydrogen deuteride at 20°C (corrected)		
1. 1.000	0.0001257	111.67
2. 1.000	0.0001257	112.09

Pressure P atm	Density ρ g/cm ³	Viscosity μ micropoise
b. Hydrogen at 30°C		
6.022	0.0004863	90.40
4.076	0.0003295	90.36
3.028	0.0002449	90.40
2.014	0.0001630	90.38
1.504	0.0001218	90.41
1.014	0.00008211	90.43
d. Deuterium at 30°C		
5.096	0.0008515	124.78
3.735	0.0006246	124.76
2.375	0.0003974	124.76
f. Hydrogen deuteride at 30°C (HD1)		
1.054	0.0001280	114.54
0.992	0.0001205	114.55
h. Hydrogen deuteride at 30°C (HD2)		
1.057	0.0001282	114.85
1.003	0.0001204	114.85
j. Hydrogen deuteride at 30°C (corrected)		
1.000	0.0001205	114.70
1.000	0.0001205	114.85

Table 4. Summary of uncertainties.

<u>Viscosity</u>		<u>Viscosity ratios</u>	
H_2	$\pm 0.1\%$	$\frac{\mu_{H_2}}{\mu_{HD}}$	$\pm 0.5\%$
HD	$\pm 0.5\%$	$\frac{\mu_{HD}}{\mu_{D_2}}$	$\pm 1.0\%$
D_2	$\pm 0.6\%$	$\frac{\mu_{H_2}}{\mu_{D_2}}$	$\pm 0.6\%$

Table 5. Most probable values at 1 atm
with their tolerances.

Gas	Viscosity μ micropoise	
	at 20°C	at 30°C
Hydrogen, H_2	88.28 ± 0.08	90.42 ± 0.09
Hydrogen deuteride, HD	111.88 ± 0.56	114.75 ± 0.57
Deuterium, D_2	124.76 ± 0.75	127.76 ± 0.77
Symbol	Viscosity ratio	
	at 20°C	at 30°C
$\frac{\mu_{H_2}}{\mu_{HD}}$	0.789 ± 0.004	0.788 ± 0.004
$\frac{\mu_{HD}}{\mu_{D_2}}$	0.897 ± 0.009	0.898 ± 0.009
$\frac{\mu_{H_2}}{\mu_{D_2}}$	0.708 ± 0.004	0.708 ± 0.004

Table 6. Experimental values of the criterion

 A_m from eqn. (5a).

(A value $A_m = 1$ admits the possibility that the intermolecular force potentials are identical; if $A_m \neq 1$, the possibility is excluded.)

Gas 1	Gas 2	Value of $A_m = (\sqrt{M_1/M_2}) (\mu_2/\mu_1)$	
		at 20°C	at 30°C
H ₂	D ₂	0.992 ± 0.005	0.992 ± 0.006
H ₂	HD	1.035 ± 0.005	1.036 ± 0.005
HD	D ₂	0.959 ± 0.010	0.958 ± 0.010

Table 7. Values of the viscosity of hydrogen and deuterium computed with the aid of eqn. (2) and different values of the force-constants.

σ Å	ϵ/k °K	Source	Viscosity at 20°C in micropoise		Viscosity at 30°C in micropoise	
			calc	meas	calc	meas
<u>Hydrogen</u>						
2.968	33.3	Ref. 6; viscosity	86.25		90.21	
2.915	38.0	Ref. 6; viscosity	89.55		91.56	
2.87	29.2	Ref. 6; virial coeff.	96.34	88.28	98.45	90.42
2.958	36.7	Ref. 9;	87.46	± 0.08	89.43	± 0.09
2.892	46.2	Ref. 10;	88.00	(88.35 max	90.02	(90.50 max
2.928	37.0	Ref. 11;	89.15	88.21 min)	91.15	90.34 min)
<u>Deuterium</u>						
2.948	39.3	Ref. 6; viscosity	123.08	124.76	125.86	127.76
2.87	31.1	Ref. 6; virial coeff.	134.85	± 0.75	137.85	± 0.77
2.952	35.2	Ref. 9;	124.98	(125.70 max	127.79	(128.74 max.
2.928	37.0	Ref. 11;	126.01	123.82 min)	128.85	126.78 min)

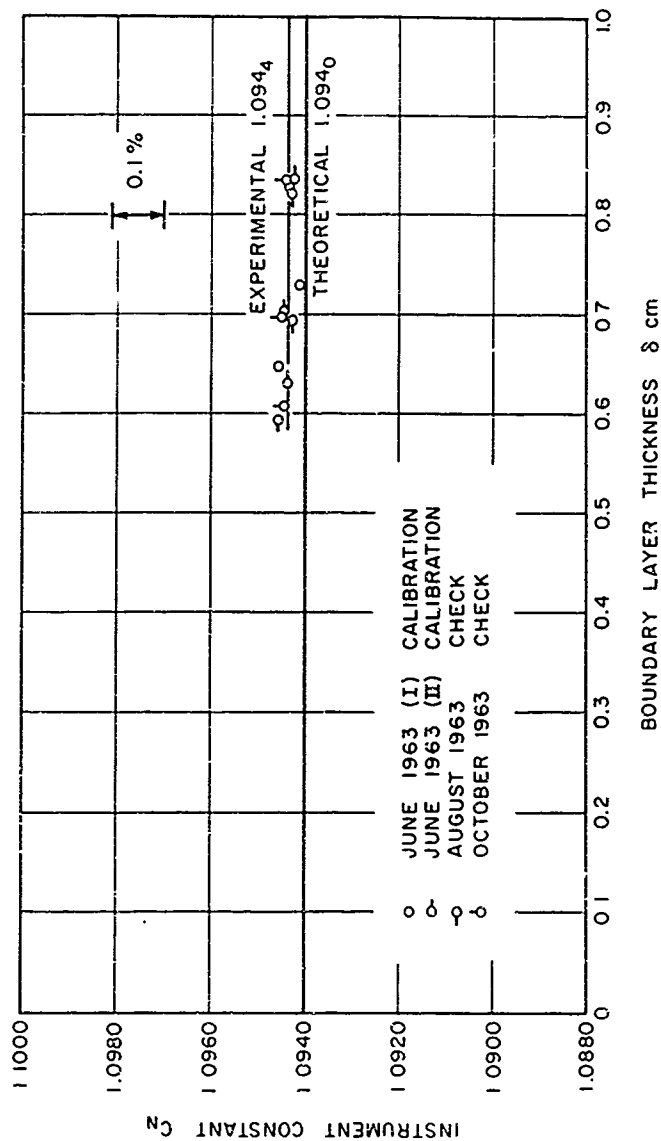


FIG.1 EXPERIMENTAL DETERMINATION OF INSTRUMENT CONSTANT C_N WITH REFERENCE TO NITROGEN

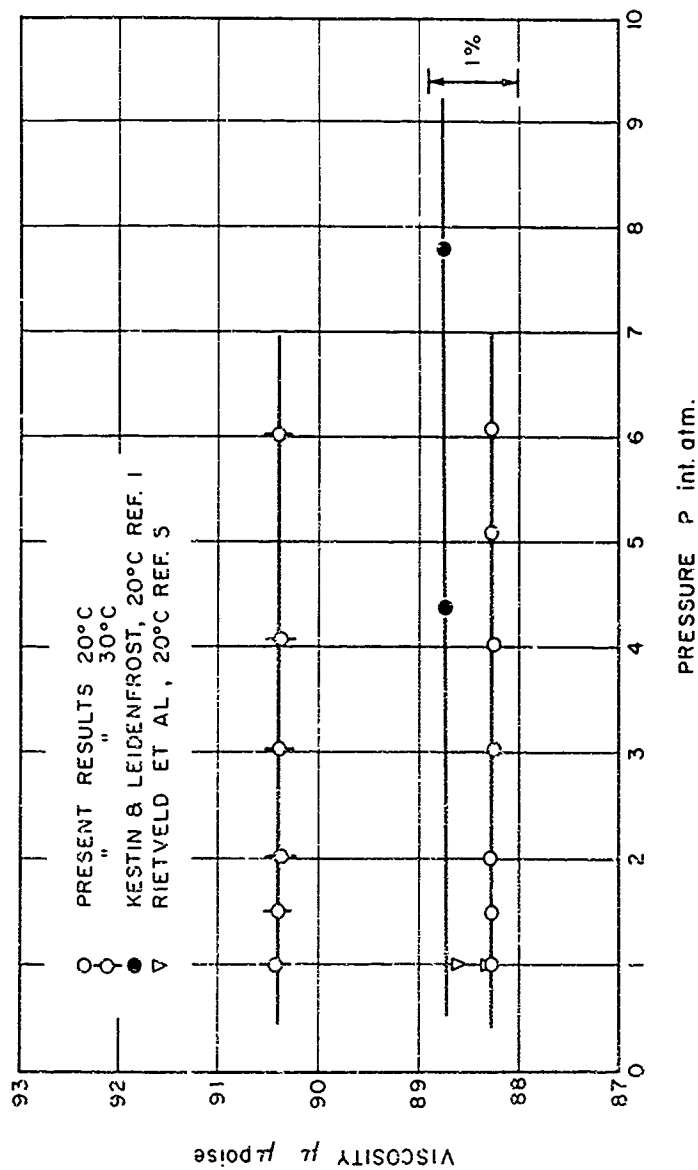


FIG.2 COMPARISON OF RESULTS FOR HYDROGEN

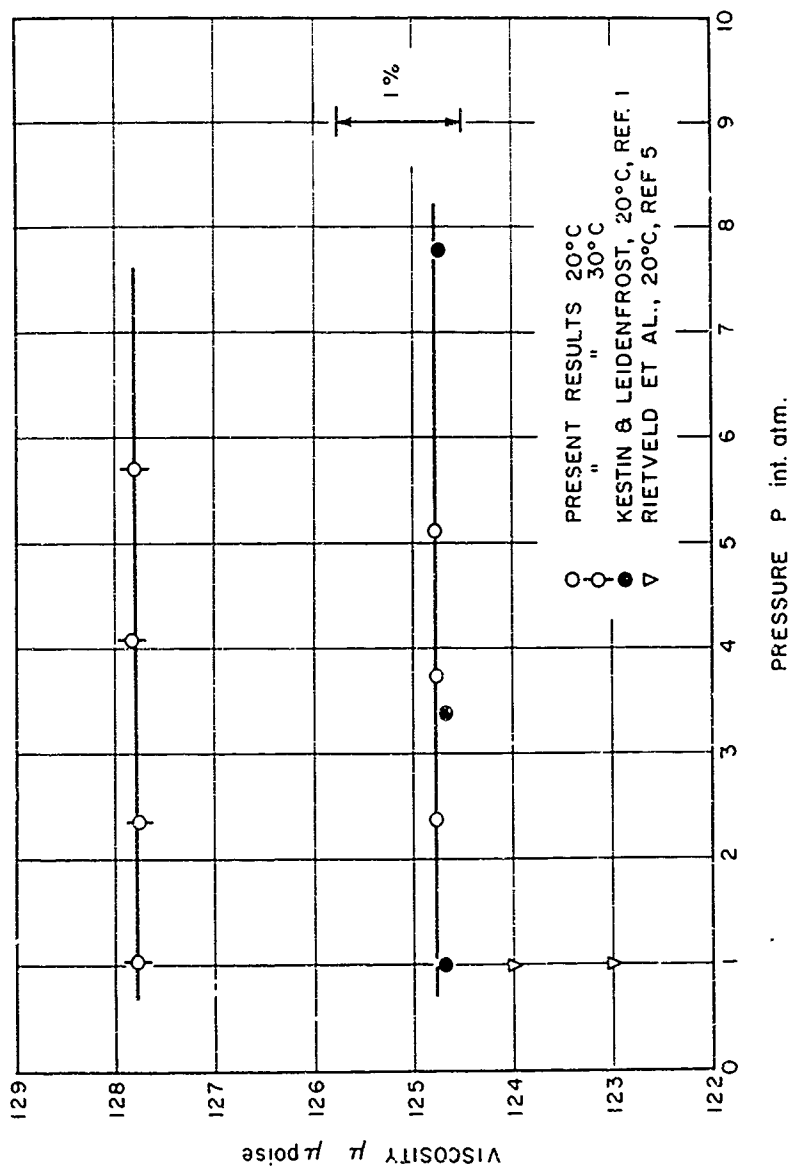


FIG. 3 COMPARISON OF RESULTS FOR DEUTERIUM

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