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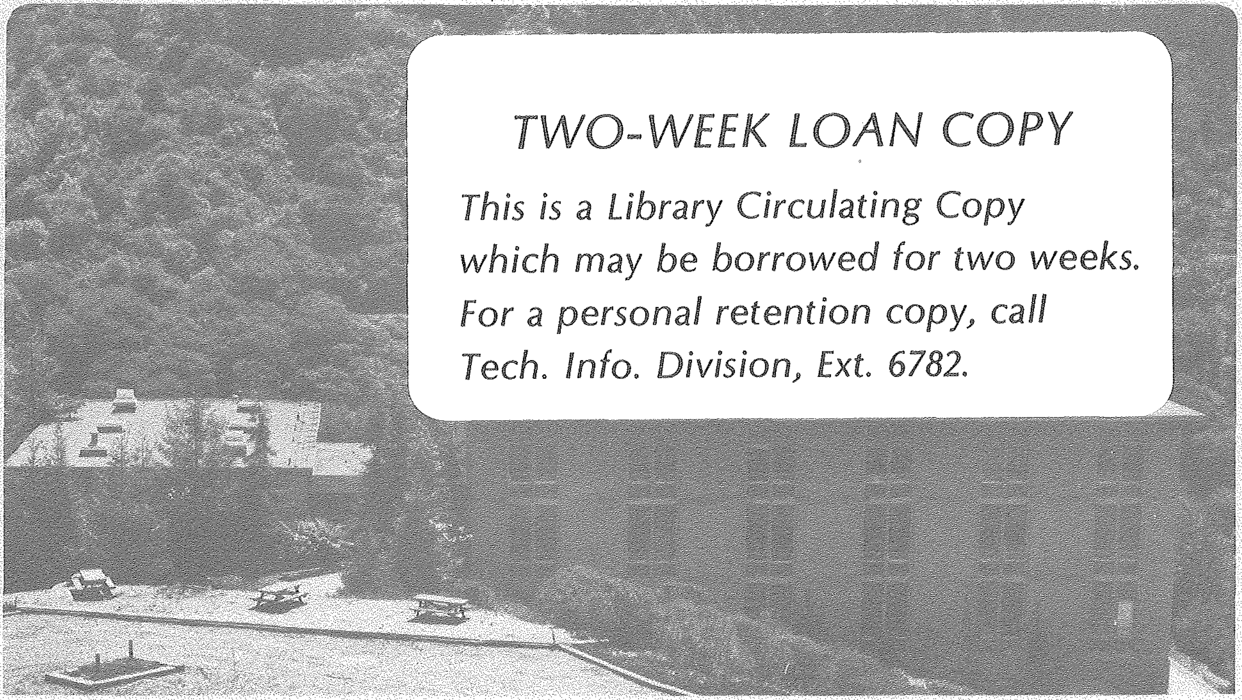

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Vibrational Relaxation of D_2O (ν_2)

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The method of laser-excited vibrational fluorescence has been used to measure vibrational relaxation rates for the bending mode of D_2O in collisions with D_2O, D_2, HD, H_2, He and Ar. The rate constants at 295 K are found to be $(3.2 \pm 0.2)\cdot 10^{-11}$, $(3.6 \pm 0.2)\cdot 10^{-13}$, $(1.2 \pm 0.1)\cdot 10^{-12}$, $(3.3 \pm 0.2)\cdot 10^{-12}$, $(7.1 \pm 0.9)\cdot 10^{-14}$ and $(3.0 \pm 1.2)\cdot 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1}, respectively. Relaxation times have been measured for two D_2O-HDO-H_2O mixtures and relaxation probabilities, $P_{D_2O\text{-}HDO}$ and $P_{D_2O\text{-}H_2O}$, were estimated to be not very different from $P_{D_2O\text{-}D_2O}$. The temperature dependence of the relaxation was measured for pure D_2O. The rates are $(1.80 \pm 0.08)\cdot 10^{-11}$ at 400, $(2.1 \pm 0.1)\cdot 10^{-11}$ at 350 and $(4.0 \pm 0.3)\cdot 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} at 260 K.
The corresponding probabilities are fit by
$P(T) = C \exp(\varepsilon/kT)$ with $\varepsilon = (778 \pm 34)$ K and $C = 1.1 \times 10^{-2}$.

I. INTRODUCTION

The rate of vibration to translation and rotation (V→T,R) energy transfer for the lowest fundamental of D_2O (ν_2) is expected to be fast since it is known that the V→T,R relaxation of H_2O[1] and other hydrogen bonding systems such as NH_3[2] and HF[3] is also very fast. The strong hydrogen bonding interaction and the small moments of inertia are believed to be responsible for such very rapid relaxation in those systems. Data for D_2O should be especially valuable for developing models of vibrational relaxation in such systems. Recently IR-IR double resonance experiments have given a relaxation probability of 0.16 for self deactivation of D_2O and much lower rates for V-T,R relaxation of D_2O by buffer gases.[4] A model calculation[5] showed strong negative temperature dependence for the relaxation of $H_2O(\nu_2)$ in the 200-400 K range. Such behavior has been observed experimentally for several hydrogen bonding systems and may be expected for D_2O.[6,7]

The rates reported here were measured by the method of laser-excited vibrational fluorescence. The experimental data and rate constants obtained from them are presented in Section III. They include measurements of the relaxation of D_2O in collisions with different buffer gases at room temperature and temperature dependence data for pure D_2O. The results serve as an independent check on earlier D_2O data, as a test of theoretical treatments, and as a calibration for semiempirical estimates of rates for hydrogen-bonded systems.

II. EXPERIMENTAL

D_2O was excited by the R(22) line of a TEA CO_2 laser at 9.26 μm. The pulses at 1 Hz were about 0.05-1 J in 100 nsec without a tail. The beam diameter at the cell was 10-15 mm. The D_2O absorption of R(22) is 10^{-3}/cm at a pressure of 1 Torr.[8] The laser pumped the 5_{33}-4_{22} transition of the (000)-(010) band. The cell had Brewster angle ZnSe laser-quality input and output windows and NaCl fluorescence windows perpendicular to the laser beam. The infrared emission from the excited sample was focused by a NaCl lens onto a liquid helium cooled Cu:Ge detector ($\tau < 100$ nsec). The signals were averaged for enough laser pulses to get a signal-to-noise ratio of about 30, typically 150-400 shots. The experimental set up has been described in detail previously.[2]

Temperature dependence measurements were made in a cell with BaF_2 windows.[7] For high temperature measurements an oil bath was heated by a 750 W heating coil and stirred by a vibration-isolated stirrer. A Fenwol Thermoswitch with regulation accuracy of ± 1.5 K was used for temperature control. For the 260 K measurement a Lauda K-4/R recirculating isopropanol bath with ± 0.5 K accuracy was used. Temperatures were measured accurately with mercury thermometers. For all the measurements with this cell dry N_2 was flowed through a Cu coil immersed in the bath and over the cell windows to protect them from fogging.

Two identical OCLI narrow band interference filters with half power points at about 7.7 and 8.3 μm were placed between the NaCl lens and the detector to attenuate scattered light

from the laser. Their transmission at 8 μm was more than 80 per cent.

All measurements were done on mixtures of D_2O with a buffer gas because the absorption and the fluorescence are increased by pressure broadening. The heat capacity is increased by an even greater factor than absorption and thus unwanted heating effects are prevented.

Pressures of D_2O were measured by a Celesco pressure transducer. Since adsorption of water on surfaces is strong the whole vacuum line was first saturated with D_2O and allowed to equilibrate for two to three hours (until the pressure was constant for at least 15 minutes). Then a buffer gas was added and allowed to mix until two consecutive fluorescence curves appeared identical. Typical mixing times at lower pressures were 0.5-1 hr and more than one hr for higher pressures. Heavy water pressures varied from 0.3-0.6 Torr for room temperature and 260 K measurements and were double at higher temperatures.

Buffer gas pressures, except HDO and H_2O, were measured by a mercury manometer or by another Celesco transducer. The vacuum system leak rate was less than 10^{-4} Torr/h.

The D_2O used was 99.8 % from Bio-Rad Laboratories. The H_2O was double distilled and ion-free. Argon was Linde 99.996 % and HD was Merck 99.0 % pure. All other gases used were from Matheson: D_2, 99.5 atom % of D minimum; H_2, 99.95 %; and He, 99.9999 %. In addition, each of the buffer gases was held over a dry ice bath or liquid N_2 to remove H_2O.

III. RESULTS AND ANALYSIS

The relaxation time τ of the (010) level, where there are several collisional partners, is given by:

$$(p\tau)^{-1} = k_{D_2O}X_{D_2O} + k_M X_M + k_N X_N + \ldots \qquad (1)$$

where p is the total pressure, k_{D_2O} the rate constant for $D_2O(\nu_2)$ deactivation by collisions with other D_2O molecules, k_M and k_N the rate constants for deactivation of D_2O by collisions with M and N and X are mole fractions. For a given sample, τ can be derived from the decay of fluorescence. All the fluorescence curves show rise times which depend on pressure, Fig. 1. The slow rotational relaxation found in Ref 4 is believed to be responsible for this rise. The fluorescence decays are good single exponentials and yield well-defined rate constants.

A. Relaxation of D_2O by other buffer gases and by itself

Equation (1) can be rewritten as:

$$(p\tau)^{-1} = (k_{D_2O} - k_M)\ X_{D_2O} + k_M \qquad (2)$$

when there is only one buffer gas. A plot of $1/p\tau$ vs mole fraction of D_2O should be a straight line with intercept k_M, and slope $k_{D_2O} - k_M$. Values of k_M are also given by the slope of the line $\tau^{-1} - k_{D_2O}\, p_{D_2O} = k_M p_M$.

Pressures of D_2O in mixtures with H_2 varied from 0.406-0.417 Torr, and with HD from 0.379-0.410 Torr. D_2 measurements were done with 0.494 Torr of D_2O. The results of these measurements are displayed in Figures 2 and 3. The rates of relaxation

decrease going from lighter to heavier isotopic forms of hydrogen. The value of $k_{D_2} = (1.0 \pm 0.4) \times 10^4$ sec^{-1} Torr^{-1} from Ref. 4 is in agreement with our value of $(1.18 \pm 0.08) \cdot 10^4$ sec^{-1} Torr^{-1}.

The D_2O-He measurements, Figure 3, were used to obtain k_{D_2O} and k_{He}. The value $k_{D_2O} = (1.03 \pm 0.05) \times 10^6$ sec^{-1} Torr^{-1} is in very good agreement with the k_{D_2O} derived from measurements with all other buffer gases. This value is reported here because it has the lowest uncertainty. It is also in good agreement with the value of $(1.0 \pm 0.2) \cdot 10^6$ sec^{-1} Torr^{-1} which was found by IR-IR double resonance in Ref. 4. The constant k_{He} is $(2.3 \pm 0.3) \cdot 10^3$ sec^{-1} Torr^{-1}. The dependence of k_{D_2O} on temperature, Fig. 5, was measured using He as a buffer gas.

The results of D_2O-Ar measurements are displayed in Fig. 4. The value of $(1.0 \pm 0.4) \cdot 10^3$ sec^{-1} Torr^{-1} for k_{Ar} is about 70 times greater than the value reported in Ref. 4. Such a value, five orders of magnitude smaller than k_{D_2O}, should be almost impossible to measure. In fact great care was required to obtain data of the quality shown in Fig. 4 as the intercepts of graphs such as Fig. 3 approach zero.

Straight lines were drawn through the data by least squares. Statistical uncertainties were calculated for the slopes and intercepts. These uncertainties were only a few percent. Possible systematic errors and uncertainties in pressure and temperature determinations increase uncertainties by 5-10%.

B. Relaxation of D_2O by HDO and H_2O

Two different liquid mixtures of D_2O and H_2O were prepared, one which contained 51.9 and another 76.5 mole % of D_2O. Partial vapor pressures and mole fractions of each isotopic form in gas phase were calculated employing Raoult's law for ideal solutions. Two sources of data were used;[9,10] the pressures in Table I are averages. Relaxation times of both mixtures were measured at several values of total pressure and the results are summarized in Table I. The rate constants for deactivation with HDO and H_2O cannot be determined accurately because of the uncertainty regarding V→V transfer to HDO. It is quite clear that $k_{H_2O} > k_{D_2O}$. Neither k_{H_2O} nor k_{HDO} are much different from k_{D_2O}. The value of $k_{H_2O} = 0.8 \pm 0.3$ μsec^{-1} $torr^{-1}$ reported in Ref. 4 is consistent with the results here. Since the experiments in Ref. 4 on static samples of H_2O/D_2O were carried out on a timescale long compared to the ~1 sec required for equilibration with HDO,[11] some combination of k_{H_2O} and k_{HDO} was in fact measured.

IV. DISCUSSION

The rate constants for $D_2O(\nu_2)$ relaxation are summarized in Table II. The data for pure D_2O and D_2O-D_2 agree well with those of Ref. 4. Data in Table I and from Ref. 4 indicate that k_{HDO} and k_{H_2O} are the same as k_{D_2O} within a factor of two.

The V→T,R relaxation probability for pure D_2O is very large, 0.28, but only about half that for H_2O, 0.47.[1] The probability increases as temperature decreases. Other systems with strong hydrogen bonding such as ammonia[2] and hydrogen

halides[3,12,13] also have very fast relaxation times and negative temperature dependences near room temperature. The importance of hydrogen bonding in D_2O is further demonstrated by the large decrease in probabilities from D_2O-D_2O to D_2O-He and D_2O-Ar. The ratio is about 600, while the analogous ratio for CH_4, a system without hydrogen bonding, is 1.2.[14]

That D_2O relaxes about a factor of two less rapidly than H_2O inspite of its lower frequency indicates the importance of rotational velocities for vibrational relaxation. The average thermal velocity ratios are the inverse square roots of the moment of inertia ratios. The latter are 1.8, 2.0 and 1.9 for I_A, I_B and I_C respectively. Relaxation probability ratios for other hydride/deuteride combinations are $P_{HF}/P_{DF} = 2.5$,[6] $P_{HCl}/P_{DCl} = 4$,[15] $P_{NH_3}/P_{ND_3} = 7$,[2,7] and $P_{CH_4}/P_{CD_4} = 2$.[16] For DCl deactivated by HCl the probability is 2.3 times greater than for DCl deactivated by DCl.[17] For D_2O, relaxation by HDO or H_2O does not seem to be so much faster. The much stronger hydrogen bonding (compared to HCl) of the D of the vibrationally excited molecule to the O of the collision partner may leave the H (or D) of the collision partner out of the region of strongest intermolecular forces.

The decreasing probabilities for D_2O relaxed by H_2, HD, and D_2 reflects the decreasing velocities of both translation and rotation. The 4.7-fold decrease in probability comparing D_2 to He indicates the D_2 rotation, and presumably HD or H_2 rotation, significantly enhances D_2O relaxation. The two rare gases He and Ar exhibit probabilities of the same order of

magnitude. Comparable values are found for $P_{O_2} = 3.6 \cdot 10^{-4}$ and $P_{N_2} = 3.4 \cdot 10^{-4}$ in Ref. 4.

Quantitative theoretical treatments of vibrational relaxation for hydrogen bonding polyatomics with energy transfer cross sections approaching gas kinetic are not likely to be available soon. Useful information comes from detailed treatment of HF,[18] from simple closed-form models,[5] and from empirical correlations.[19-21] These works provide some qualitative understanding of the collision dynamics in the presence of strong attractive forces which result in negative temperature dependences. For D_2O the data of Table III exhibit a negative temperature dependence, Fig. 5, which fits the empirical equation[19-21]

$$P(T) = C \exp(\varepsilon/kT)$$

where $\varepsilon = (778 \pm 34)$ K and $C = 1.1 \cdot 10^{-2}$, Fig. 6. This value of ε fits well with those correlated by Gordon.[19]

A following paper will present relaxation probabilities for D_2S and H_2Se along with a more complete consideration of the role of hydrogen bonding in vibrational relaxation.

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Table I. Relaxation Times for D_2O-HDO-H_2O Mixtures.

% D_2O in Liquid Mixtures	Gas Phase X_{D_2O}	Gas Phase X_{HDO}	Gas Phase X_{H_2O}	$(p\tau)^{-1}$ μsec^{-1} $Torr^{-1}$	P(Torr)
100	1.000	0.000	0.000	1.03 ± 0.09	-
76.5	0.565	0.373	0.063	1.01 ± 0.09	0.970 - 1.536
51.9	0.251	0.498	0.251	1.12 ± 0.08	0.766 - 1.315

Table II. Measured Rate Constants for Vibrational Relaxation of $D_2O(\nu_2)$ by M at 295 K.

M	$k(sec^{-1}\ Torr^{-1})$	$k(cm^3\ molecule^{-1}\ sec^{-1})$	$d^a(nm)$	P^b
D_2O	$(1.03 \pm 0.05)\cdot10^6$	$3.2\cdot10^{-11}$	0.280	0.162
D_2	$(1.18 \pm 0.08)\cdot10^4$	$3.6\cdot10^{-13}$	0.247	$1.20\cdot10^{-3}$
HD	$(3.9 \pm 0.4)\cdot10^4$	$1.2\cdot10^{-12}$	0.247	$3.5\cdot10^{-3}$
H_2	$(1.08 \pm 0.05)\cdot10^5$	$3.3\cdot10^{-12}$	0.247	$8.2\cdot10^{-3}$
He	$(2.3 \pm 0.3)\cdot10^3$	$7.1\cdot10^{-14}$	0.224	$2.6\cdot10^{-4}$
Ar	$(1.0 \pm 0.4)\cdot10^3$	$3.0\cdot10^{-14}$	0.286	$1.8\cdot10^{-4}$

[a] Average values obtained from gas viscosities and Van der Waals b.

[b] $P = k/k_{gk}$ where k_{gk} is calculated from:

$$k_{gk} = d_{AB}^2\left(\frac{8\Pi RT}{\mu}\right)^{1/2},\ \mu = \text{reduced mass.}$$

Table III. Temperature Dependence of $D_2O(\nu_2)$ Deactivation Probabilities.

T(K)	k(sec^{-1} $Torr^{-1}$)	k(cm^3 $molecule^{-1}$ sec^{-1})	P
260	$(1.5 \pm 0.1) \cdot 10^6$	$4.0 \cdot 10^{-11}$	0.22
295	$(1.03 \pm 0.05) \cdot 10^6$	$3.2 \cdot 10^{-11}$	0.162
350	$(5.8 \pm 0.3) \cdot 10^5$	$2.1 \cdot 10^{-11}$	0.100
400	$(4.3 \pm 0.2) \cdot 10^5$	$1.80 \cdot 10^{-11}$	0.079

FIGURE CAPTIONS

Figure 1. Semilog plot of fluorescence intensity vs time for a D_2O-D_2 mixture. $P_{D_2O} = 0.494$ Torr; $X_{D_2O} = 0.0618$; rise time = 0.23 μsec; fall time = 1.63 μsec.

Figure 2. Plot of $1/p\tau$ vs X_{D_2O} for D_2O-H_2. Slope = $0.92 \cdot 10^6$ sec^{-1} $Torr^{-1}$; intercept = $1.08 \cdot 10^5$ sec^{-1} $Torr^{-1}$.

Figure 3. Plot of $1/p\tau$ vs X_{D_2O} for D_2O-HD, D_2O-D_2 and D_2O-He. ○-HD, slope = $0.99 \cdot 10^6$ sec^{-1} $Torr^{-1}$, intercept = $3.89 \cdot 10^4$ sec^{-1} $Torr^{-1}$; ●-D_2, slope = $1.01 \cdot 10^6$ sec^{-1} $Torr^{-1}$, intercept = $1.18 \cdot 10^4$ sec^{-1} $Torr^{-1}$; □-He, slope = $1.03 \cdot 10^6$ sec^{-1} $Torr^{-1}$, intercept = $2.3 \cdot 10^3$ sec^{-1} $Torr^{-1}$.

Figure 4. Results of D_2O-Ar measurements P_{D_2O} varied between 0.33 and 0.42 Torr. Slope = $1.0 \cdot 10^3$ sec^{-1} $Torr^{-1}$.

Figure 5. Temperature dependence of $D_2O(\nu_2)$ relaxation:

○-260 K, $k_{D_2O} = 1.49 \cdot 10^6$ sec^{-1} $Torr^{-1}$;

■-295 K, $k_{D_2O} = 1.03 \cdot 10^6$ sec^{-1} $Torr^{-1}$;

●-350 K, $K_{D_2O} = 5.84 \cdot 10^5$ sec^{-1} $Torr^{-1}$;

□-400 K, $K_{D_2O} = 4.33 \cdot 10^5$ sec^{-1} $Torr^{-1}$.

Figure 6. Plot of lnP vs 1/T for D_2O. Slope = (778 ± 34) K.

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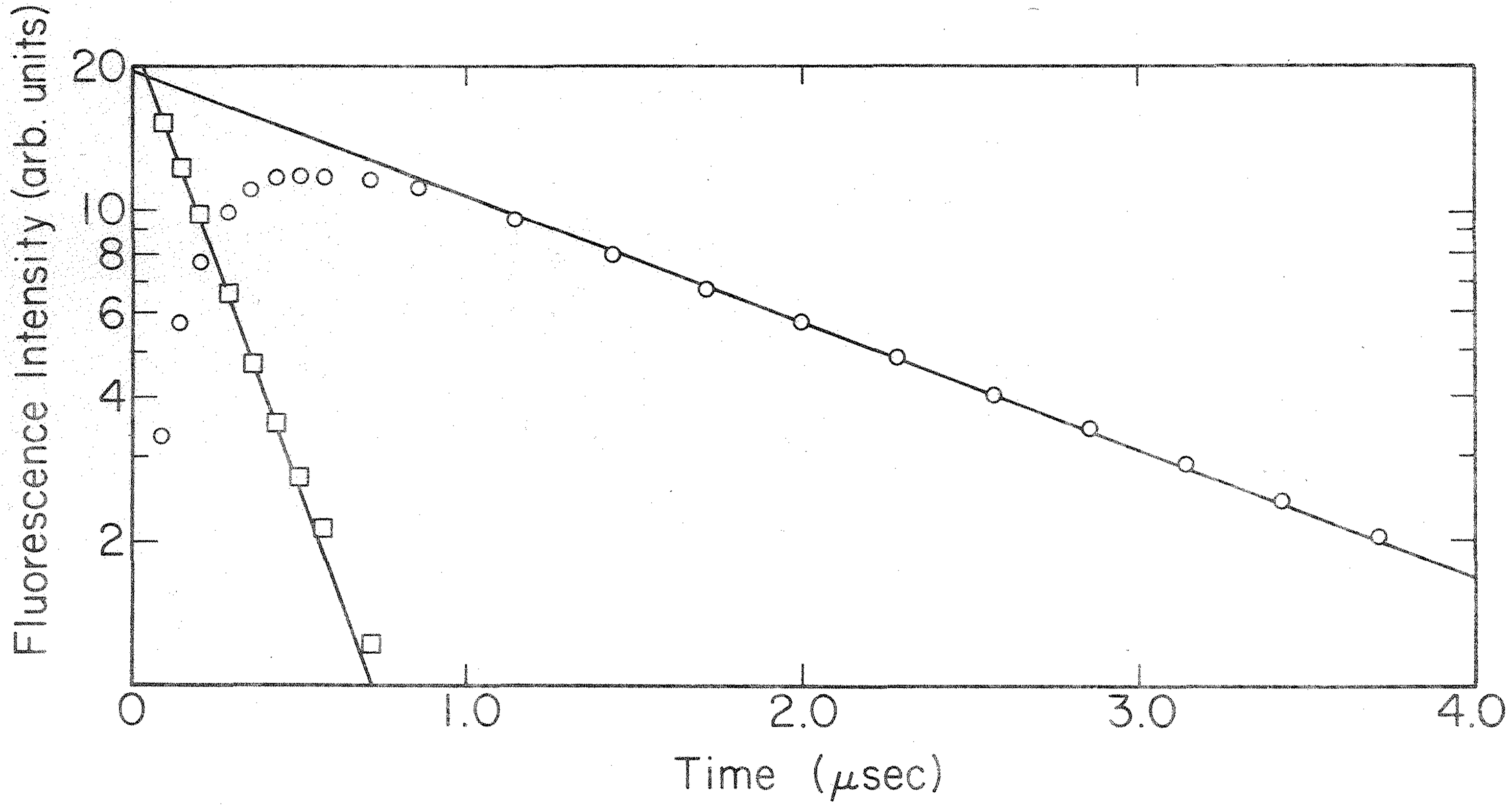
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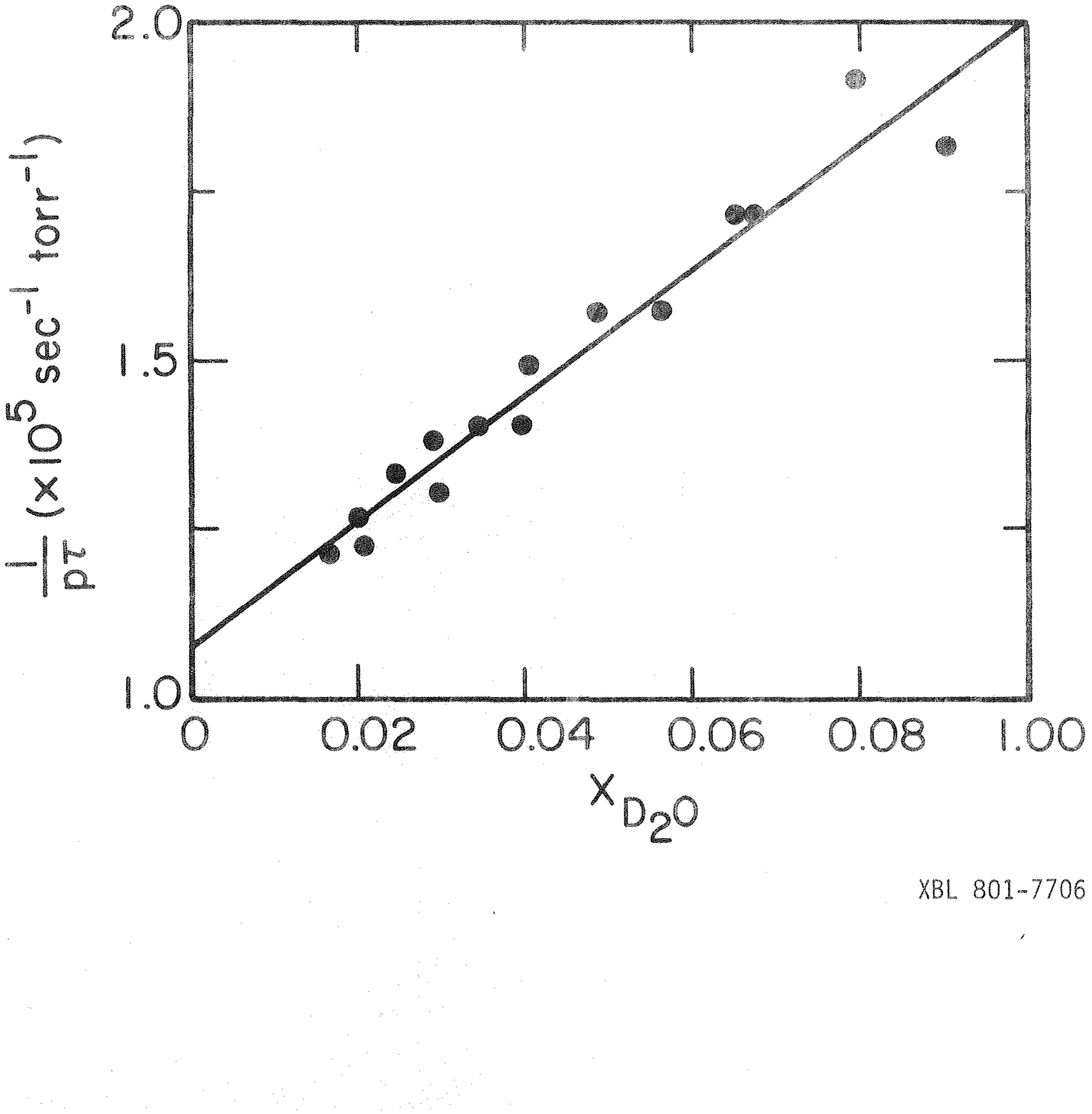

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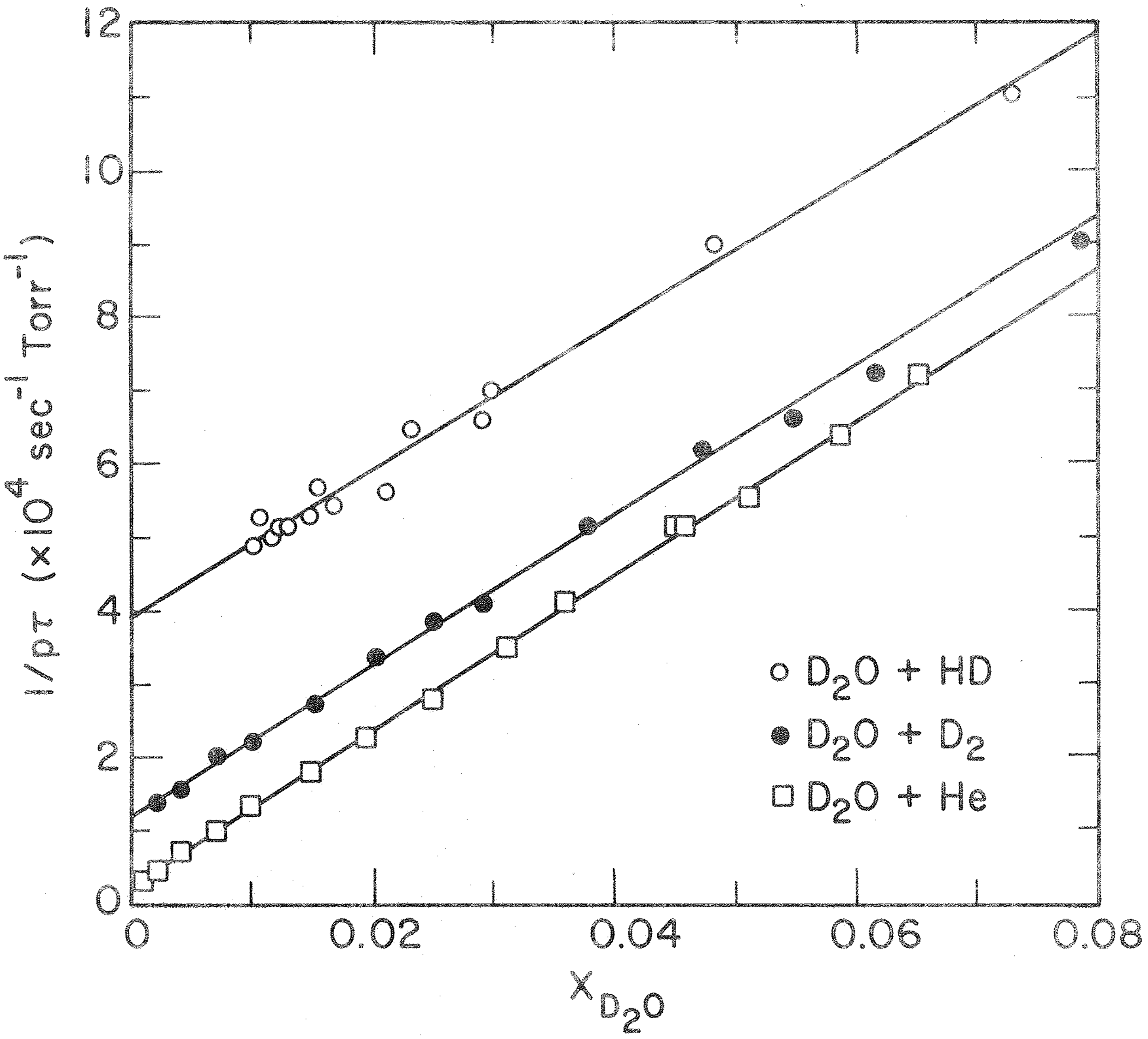

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● D_2O + D_2
□ D_2O + He

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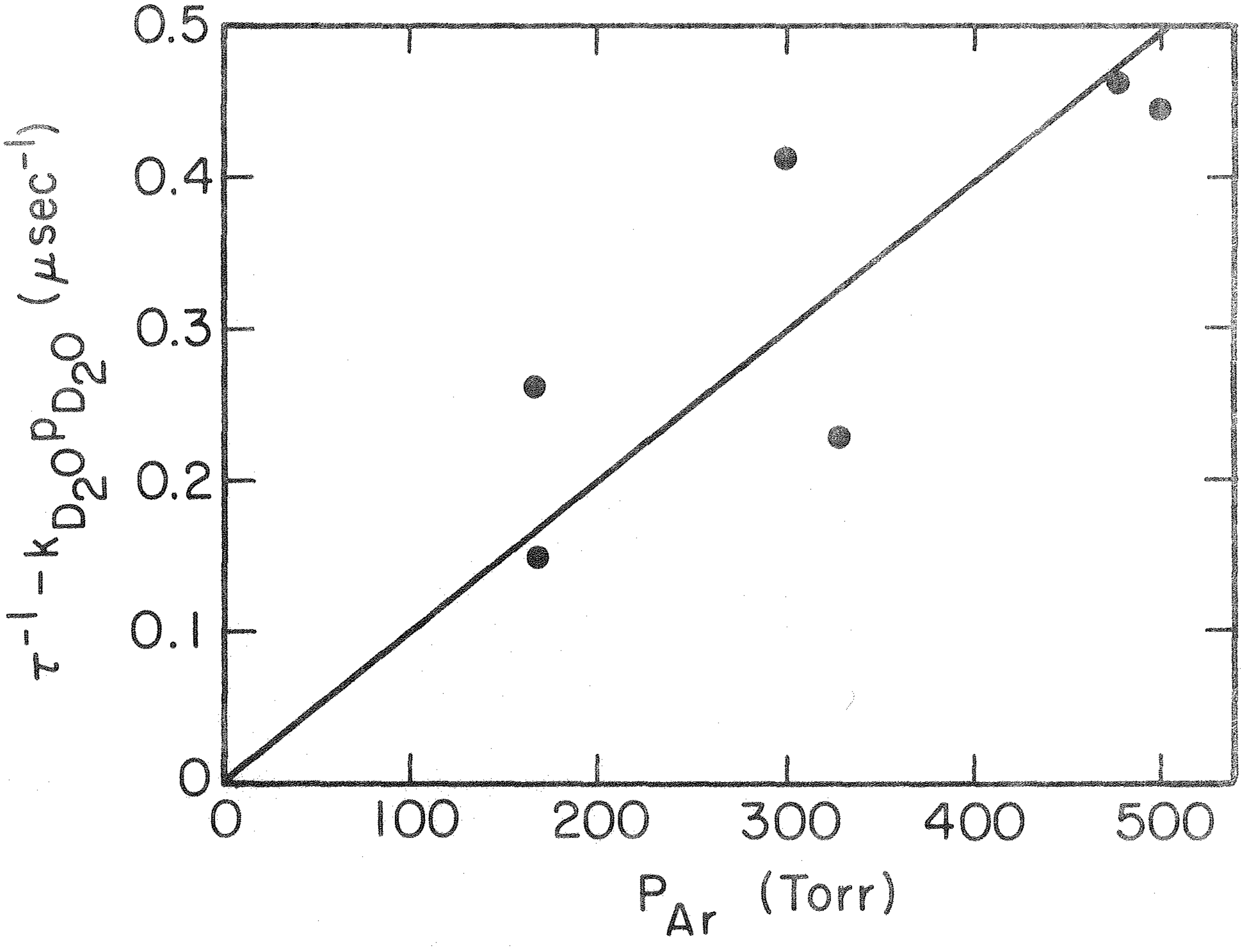
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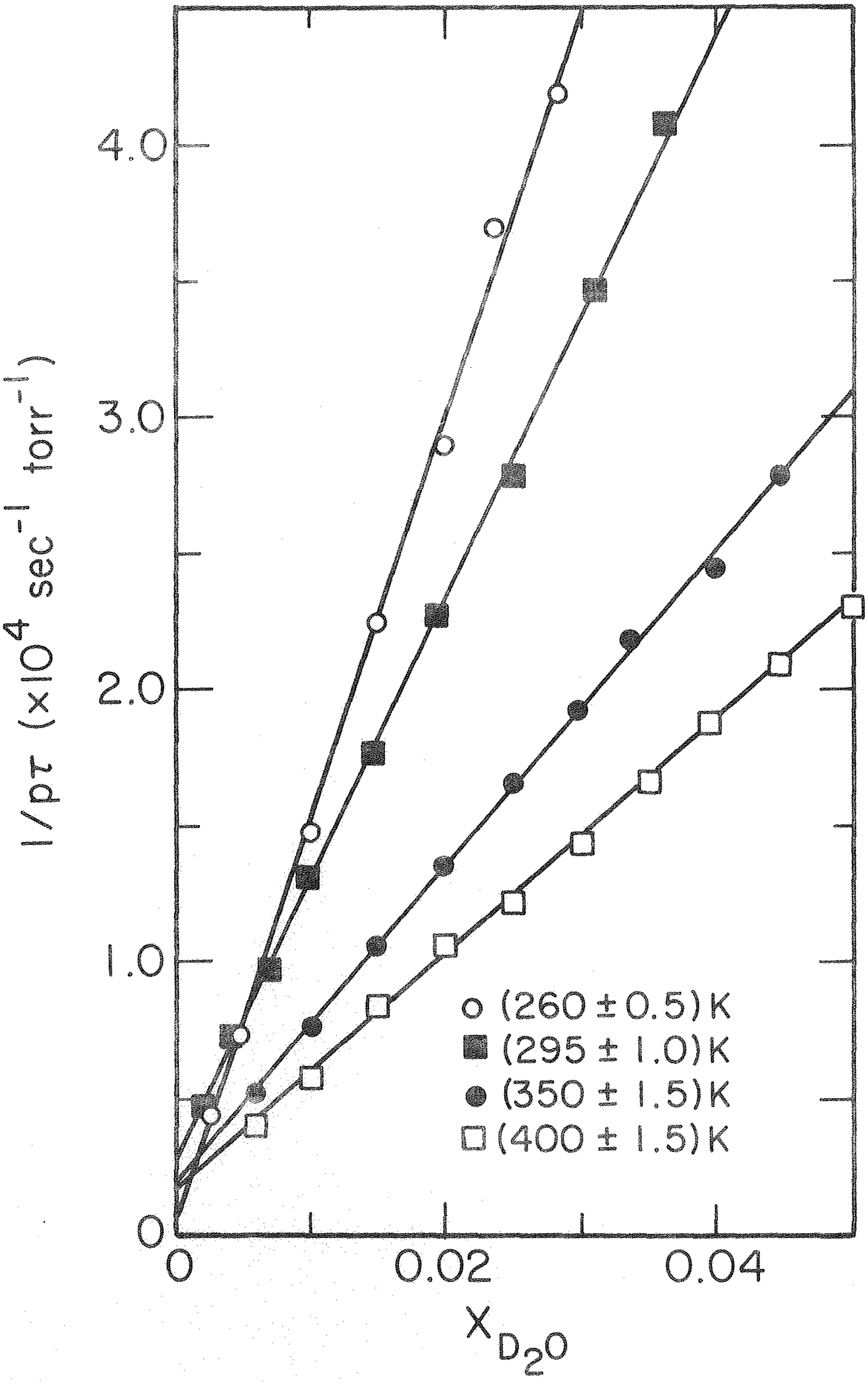

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■ (295 ± 1.0) K
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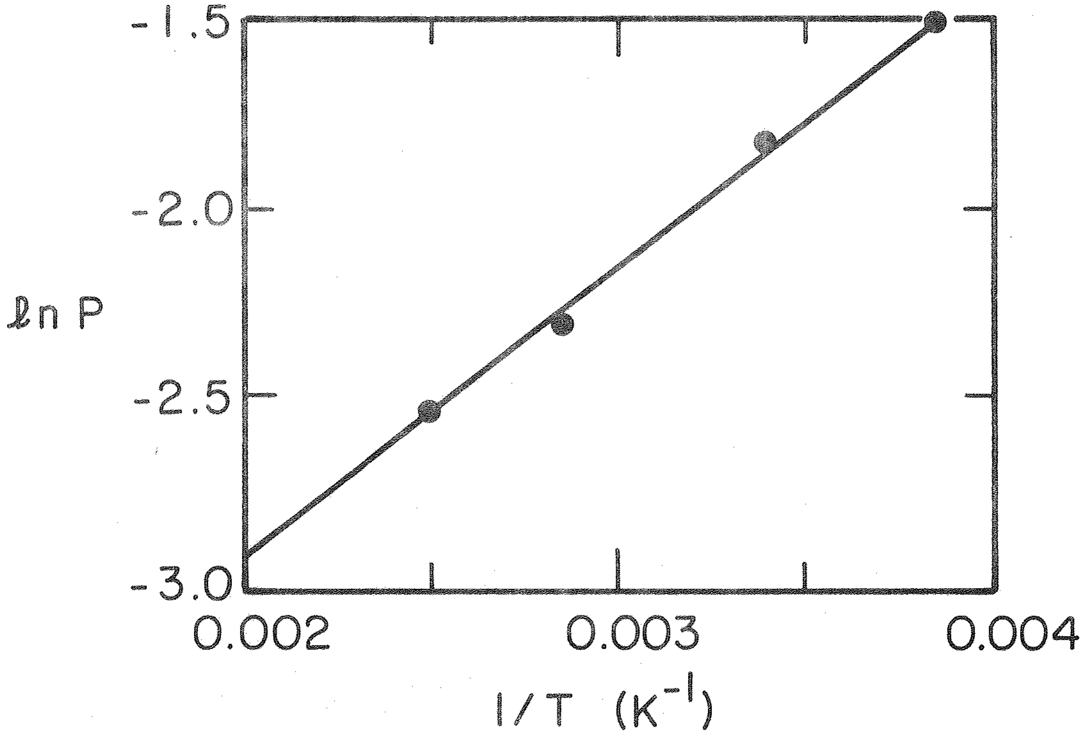

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