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THE RATE OF WATER EXCHANGE FROM HYDRATED MAGNESIUM ION

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THE RATE OF WATER EXCHANGE FROM
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A direct measurement of the water exchange rate from Mg^{2+} at room temperature has been made possible by observation of the oxygen-17 NMR signal of the waters in the first coordination sphere of Mg^{2+} ion. Interference from the bulk water resonance was avoided by addition of sufficient Mn^{2+} to broaden the bulk water resonance to at least ten times that of the bound water signal. Under these conditions the general two site exchange equation⁽¹⁾ can be shown to reduce to

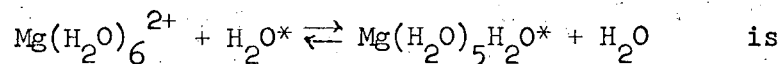
$$\delta\omega = \frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \quad (1)$$

where $\delta\omega$ is $\sqrt{3}/2$ times the peak to peak width of the derivative curve measured in radians/sec., T_2 is the transverse relaxation time, $1/T_{2M}$ is the first order relaxation rate constant of the ^{17}O in the first coordination sphere of Mg^{2+} ion and $1/\tau_M$ is the first order rate constant for exchange of a particular water molecule from the first coordination sphere of Mg^{2+} into the bulk solvent. The $1/T_{2M}$ term has been shown by Connick and Wüthrich⁽²⁾ to be nearly the same as that of ^{17}O in pure water, which is many orders of magnitude smaller than the observed line widths. Therefore the observed relaxation rate of the bound waters can be associated directly with the rate of water exchange.

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- (1) T. J. Swift and G. P. Weinberger, J. Am. Chem. Soc., 90, 2023, (1968) (equation 2). (In term C a plus sign has been omitted between T_{2A}^{-1} and the remainder of the expression).
- (2) R. E. Connick and K. Wüthrich, University of California, Berkeley, California, UCRL - 19018 (To be published in J. Chem. Phys.)
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The results of a temperature study from -22°C . to $+23^{\circ}\text{C}$. are shown in Fig. 1. A representative spectrum is shown in Fig. 2. The rate of the reaction



$$k = 5.3 \times 10^5 \text{ sec}^{-1} \text{ at } 25^{\circ}\text{C}.$$

with an enthalpy and entropy of activation of 10.2 kcal/mole and 2 eu. respectively.

Approximate value of the rate of exchange of water molecules from the first coordination sphere of Mg^{2+} ion have been determined previously by various methods. Sonic relaxation and temperature-jump techniques³⁻⁶ are incapable of measuring reactions where no net chemical change takes place, such as water exchange. However, an estimate of the water exchange

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- (3) M. Eigen and K. Tamm, Z. Elektrochem., 66, 107 (1962).
 - (4) M. Eigen and G. G. Hammes, J. Am. Chem. Soc., 82, 5951 (1960).
 - (5) H. Diebler, M. Eigen and G. G. Hammes, Z. Naturforsch., 156, 554 (1960).
 - (6) Gordon Atkinson and Sergio Petrucci, J. Phys. Chem., 70, 3122, (1966).
-

rate can be obtained by measuring the rate at which a water molecule is replaced by some other ligand in the first coordination sphere, if it is assumed that the rate is primarily controlled by the difficulty of removing the water. The rate at which various divalent anions enter the first coordination sphere of Mg^{2+} at room temperature has been measured to be $1 \times 10^5 \text{ sec}^{-1}$. (3)

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Proton magnetic resonance techniques^{7,8} are capable of measuring the rate of exchange directly but the resonance of the bound protons is resolved from that of the bulk protons only at temperature below -60°C . Rate data have been obtained only for mixed water-acetone solvents which given an extrapolated room temperature value of ca. $4-6 \times 10^6 \text{ sec.}^{-1}$ (7). Possible solvent effects and the large interval of extrapolation to room

(7) R. G. Wawro and T. J. Swift, J. Am. Chem. Soc., 90, 2792 (1968).

(8) N. A. Matwiyoff and H. Taube, J. Am. Chem. Soc., 90, 2796 (1968).

temperature make a direct comparison with the present results dubious.

The magnitude of the difference between the present result and the sound absorption and temperature jump data is not surprising. Differences of the same relative size have been noted previously for transition metal ions⁽⁹⁾. The rate of water exchange would be expected to be $4/3$ that

(9) T. J. Swift and R. E. Connick, J. Chem. Phys., 37, 307 (1962).

of the rate of a ligand entering the first coordination sphere if it is assumed that only molecules on the faces of a first sphere octahedron of waters can enter a vacated site. The fact that the observed water rate is much greater than $4/3$ the ligand rate may be an indication of the extent to which water is electrostatically and/or sterically favored over the other ligands studied in competing for a vacated coordination site.

In principle one could determine from the intensity of the bound water signal the number of waters coordinated to magnesium ion in the first

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coordination sphere. No such attempt was made because of experimental errors which were large enough to render meaningless any such results. Within experimental accuracy no chemical shift was observed between the first coordination sphere waters and pure water.

Figure 1. Rate of water exchange versus reciprocal of absolute temperature. Composition of solution was

1.30gm H₂O enriched to 20% in oxygen-17

1.00gm Mg(ClO₄)₂ anhydrous

0.30gm Mn(ClO₄)₂·6H₂O

- Figure 2. A. Oxygen-17 NMR spectrum of the waters in first coordination sphere of Mg^{2+} at $-22^{\circ}C$. Spectrum is the average of 25 scans.
- B. Pure water sample run at a later time on side band mode to calibrate the scale. Distance between side bands is 1591.2 HZ.

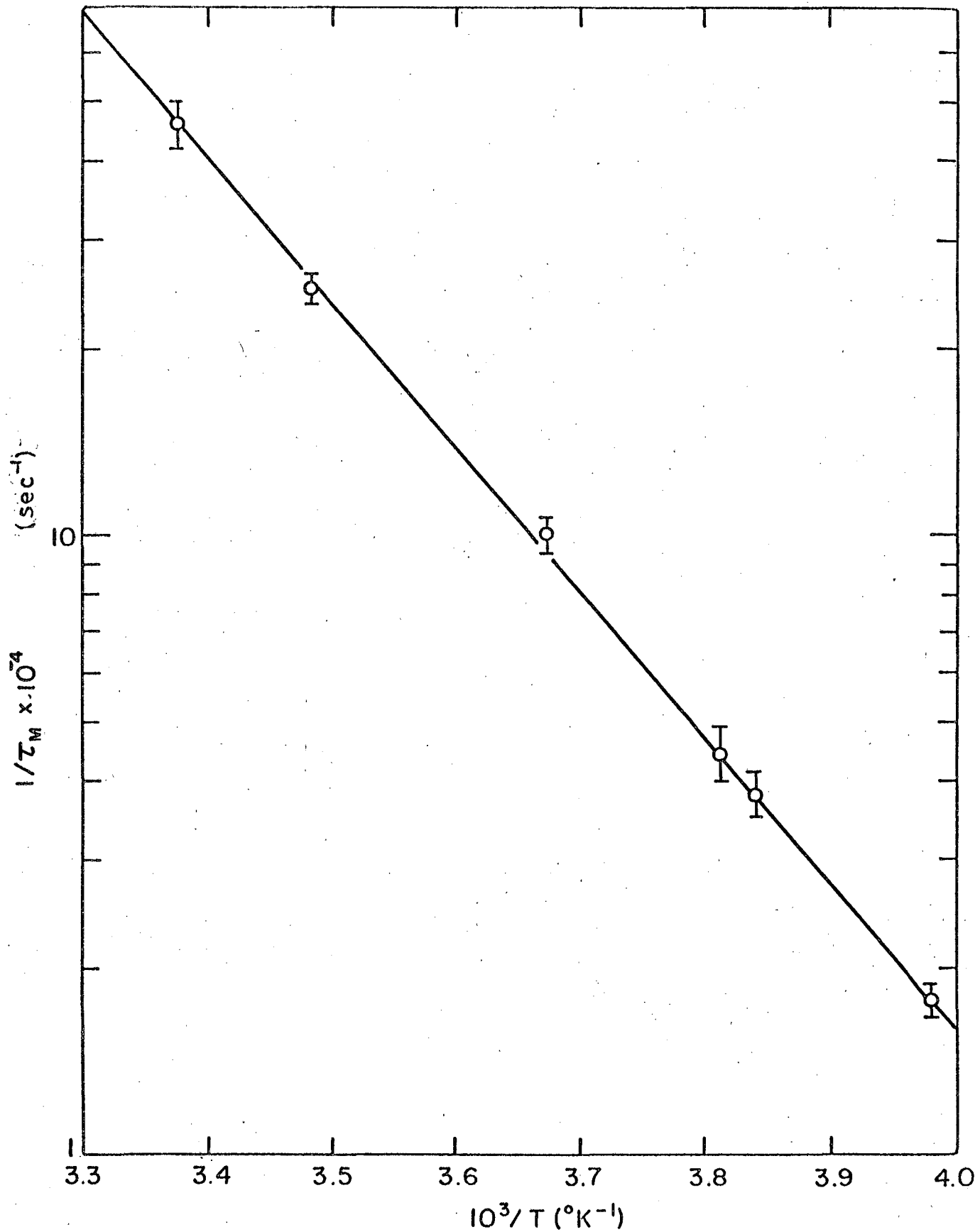


Fig. 1

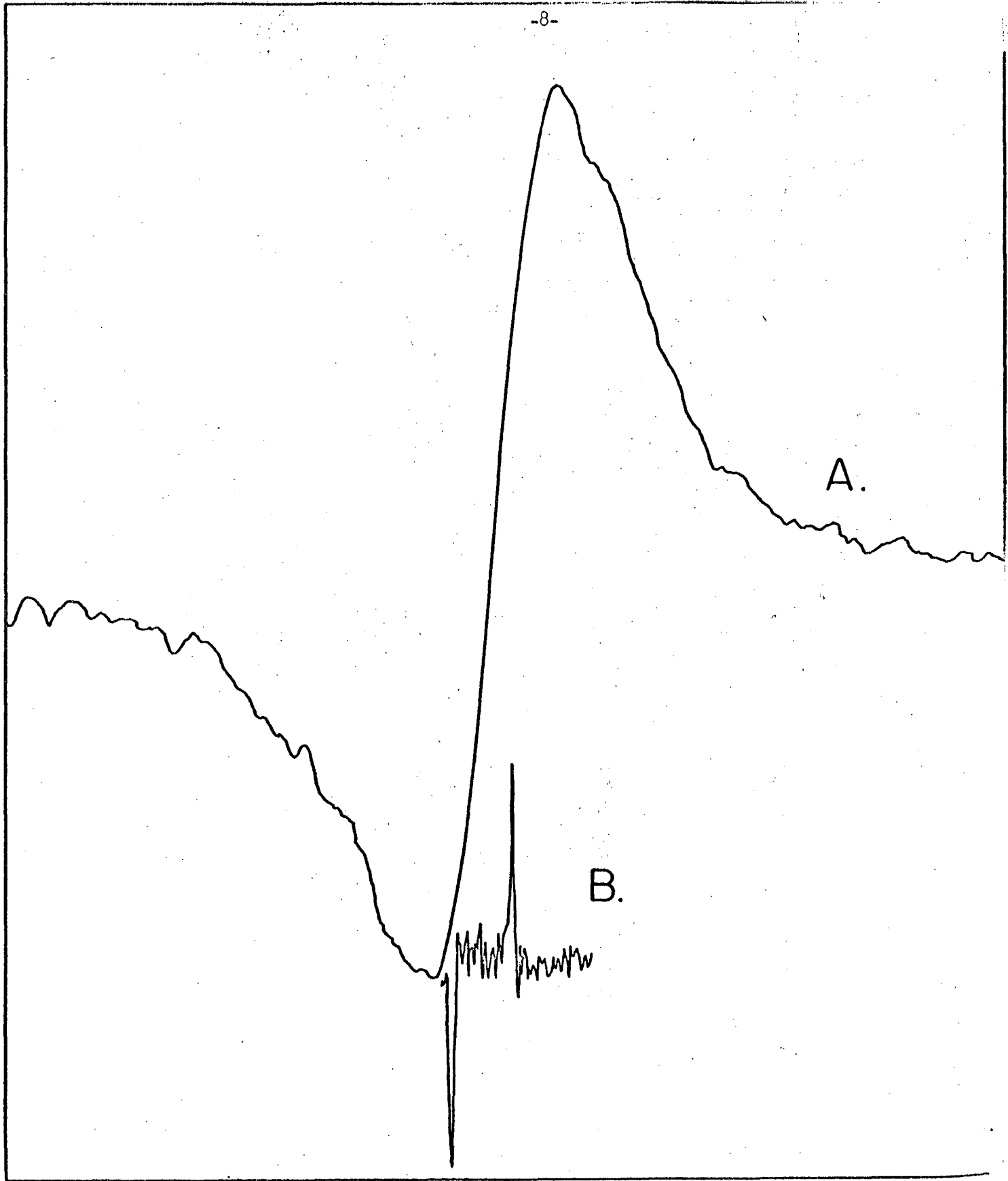


Fig. 2

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