

NUCLEAR MAGNETIC RESONANCE STUDIES IN MULTIPLE PHASE SYSTEMS: LIFETIME OF A WATER MOLECULE IN AN ADSORBING PHASE ON SILICA GEL

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Further evaluation studies of nuclear resonance relaxation phenomena of the hydrogen nuclei of H_2O adsorbed on silica gel observed by means of radio frequency pulse techniques are described. A stochastic theory for multiphase systems sometimes encountered in relaxation phenomena is presented. Special emphasis is directed toward a theoretical understanding of two phase systems observed in the study of water vapor adsorbed on silica gel. Adsorption experiments are discussed which directly demonstrate, for a specific x/m value, the simultaneous existence of (a) two phase behavior for transverse (T_2) relaxation measurements and (b) single phase behavior for longitudinal relaxation (T_1) data. Finally, a close estimate is obtained of the life-time of a water molecule in an adsorbing phase at low coverage on silica gel.

Introduction

Previous investigations¹ of adsorbed water on silica gel by nuclear resonance spin-echo² techniques have demonstrated two-phase behavior for transverse (T_2) relaxation data. This phenomenon was interpreted as proof for the co-existence of two adsorbing phases for the water molecules on the surface of the silica gel. In this initial study not only were relaxation values available from the experimental data but also, under suitable conditions, estimates of the relative amounts of water molecules in the two adsorbing phases were possible.

The purpose of this paper is to describe further investigations, both theoretical and experimental, of adsorption phenomena by nuclear resonance pulse techniques. Special emphasis is placed on (a) the development of a stochastic theory of relaxation for multiphase behavior which describes the essential features of the relaxation processes encountered so far in adsorption phenomena, including asymptotic conditions of very fast and very slow exchange of molecules between adsorbing phases, (b) the formulation of this theory to practical measurements of spin-echo and free nuclear decay signals for determining transverse and longitudinal relaxation times, (c) the extension of n - m - r measurements to longitudinal (T_1) relaxation data for the adsorption of water vapor on silica gel, and (d) an estimate of the lifetime of a water molecule in an adsorbing phase on silica gel. The experimental details of the adsorption apparatus used in this study are the same as those described previously.¹

Theory

Stochastic Theory of Relaxation Times for Multiple Phase Spin Systems.—The spin system is assumed to be composed of a finite number of phases; each phase is characterized by a single relaxation time. If T_i is the relaxation time for the i th phase, then the problem to be solved is one of determining how an initial magnetic moment will decay with time.³ It is assumed that if a spin is

present in the i th phase, its transition to the j th phase occurs with a probability independent of its previous history. In other words, it is assumed that the exchange of spins among the various phases can be described by means of a stationary Markoff process.

Let P_i be the time independent probability that a spin chosen at random be found in the i th phase. Experimentally, P_i is the fraction of the total spin population present at any time in the i th phase. The stationary nature of the process finds expression in the time independence of P_i . The condition that each spin must be in some phase is expressed by the relation

$$\sum_i P_i = 1 \quad (1)$$

Let $P_{ij}(t)$ be the probability that a spin, initially in the i th phase, be found in the j th phase at a time, t , later. The probabilities, $P_{ij}(t)$, satisfy the Chapman-Kolmogoroff equations⁴

$$\frac{dP_{ik}(t)}{dt} = -C_k P_{ik}(t) + \sum_l P_{il}(t) C_l p_{lk} \quad (2)$$

where C_k is the probability per second that a spin in the k th phase leaves the k th phase, and where p_{lk} is the conditional probability that if a spin leaves the l th phase it will transfer to the k th phase. Clearly

$$p_{kk} = 0, \text{ and } \sum_k p_{lk} = 1 \quad (3)$$

From an introduction of the matrices

$$P(t) = [P_{ij}(t)] \text{ and } D = [\delta_{ij}C_j - p_{ij}C_i] \quad (4)$$

equations 2 may be written as a single matrix differential equation

$$\frac{dP}{dt} = -PD \quad (5)$$

which is to be solved with the initial condition

$$P(0) = 1 \quad (6)$$

i.e., $P_{ij}(0) = \delta_{ij}$. The solution of (5) with the initial condition (6) is

$$P(t) = e^{-Dt} \quad (7)$$

polarizing magnetic field. This theory makes no distinction between T_1 and T_2 , but it should apply equally well to either T_1 or T_2 relaxation phenomena. T_1 will represent either T_{11} or T_{21} , whichever relaxation process is desired.

(4) W. Feller, "Probability Theory and Its Application," Chapt. 17, John Wiley and Sons, New York, N. Y., 1950.

(1) J. Zimmerman, B. Holmes and J. Lesater, *THIS JOURNAL*, **60**, 1157 (1956).

(2) E. Hahn, *Phys. Rev.*, **80**, 580 (1950).

(3) For longitudinal relaxation, the quantity $(M_z - M||)$ decays with a rate determined by T_1 , where M_z is the equilibrium moment, and where $M||$ is the moment parallel to the constant polarizing magnetic field. For transverse relaxation the quantity, M_{\perp} decays with a rate determined by T_2 , where M_{\perp} is the moment normal to the

Since D is a finite, say $n \times n$, matrix, e^{-Dt} can be expressed as a polynomial in D . Hence

$$e^{-Dt} = \sum_{m=0}^{n-1} f_m D^m \tag{8}$$

where f_m are functions of t . If D has distinct eigenvalues $\lambda_1, \dots, \lambda_n$, then representations of D and e^{-Dt} with respect to the basis of eigenvectors of D are given by

$$\begin{bmatrix} \lambda_1 & & \\ & \ddots & \\ & & \lambda_n \end{bmatrix}$$

and

$$\begin{bmatrix} e^{-\lambda_1 t} & & \\ & \ddots & \\ & & e^{-\lambda_n t} \end{bmatrix} = \begin{bmatrix} \sum_m f_m \lambda_1^m & & \\ & \ddots & \\ & & \sum_m f_m \lambda_n^m \end{bmatrix}$$

respectively. Hence

$$e^{-\lambda_n t} = \sum_{m=0}^{n-1} f_m \lambda_n^m \tag{9a}$$

If one sets

$$e(t) = \begin{bmatrix} e^{-\lambda_1 t} \\ e^{-\lambda_2 t} \\ \vdots \\ e^{-\lambda_n t} \end{bmatrix}, f = \begin{bmatrix} f_0 \\ f_1 \\ \vdots \\ f_{n-1} \end{bmatrix}$$

and $\Omega = [\Omega_{ik}] = [(\lambda_i)^{-1}]^{k-1}$, $i, k = 1, \dots, n$, then (9a) may be expressed as the matrix equation

$$e(t) = \Omega f \tag{9b}$$

which has the solution

$$f = \Omega^{-1} e(t) \tag{10}$$

Theory of Relaxation.—If a spin is in the i th phase, certain quantities, Q_i , associated with the relaxation process decay at a rate

$$\frac{dQ}{dt} = -Q/T_i \tag{11}$$

where $Q = Q_0$ at $t = 0$. Hence, the problem is to find the average value, $\overline{Q(t)}$, of

$$Q(t) = Q_0 e^{-\int_0^t dt/T(t)} \tag{12}$$

where $T(t)$ is a random variable taking on the values, T_i , as the system⁶ jumps from phase to phase. The relaxation process is completely described by the average value of the integral

$$I(t) = e^{-\int_0^t dt/T(t)} \tag{13}$$

The method of Kubo⁷ is very convenient for finding the average value, $\overline{I(t)}$, of $I(t)$.

Let $I_{ij}(t)$ be the average value of $I(t)$ on the condition that the system is initially in the i th phase and at time, t , is in the j th phase. Since P_i is the probability that the system be found initially in the i th

phase, and since all final phases are possible, it follows that

$$\overline{I(t)} = \sum_{i,j} I_{ij}(t) P_i \tag{14}$$

The quantities $I_{ij}(t)$ satisfy equations which are similar to the Chapman-Kolmogoroff equations; *i.e.*

$$\frac{dI_{ij}(t)}{dt} = -\sum_l I_{il}(t) F_{lj} \tag{15}$$

where

$$\begin{aligned} F_{lj} &= \delta_{lj} (C_l + 1/T_l) - C_l P_{lj} \\ &= D_{lj} + \delta_{lj}/T_l = D_{lj} + E_{lj} \end{aligned} \tag{16}$$

In matrix notation $F = D + E$, where $D = [D_{ij}]$, $E = [E_{ij}]$, and $F = [F_{ij}]$. If one sets the matrix $I = [I_{ij}(t)]$, equations 15 can be written in the form

$$dI/dt = -IF \tag{17}$$

If one sets

$$\phi_0 = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} \text{ and } \tilde{\phi}_0 = [P_1, P_2, \dots, P_n] \tag{18}$$

then the average value, $\overline{I(t)}$, may be simply expressed as

$$\overline{I(t)} = \tilde{\phi}_0 I \phi_0 = \tilde{\phi}_0 e^{-(D+E)t} \phi_0 \tag{19}$$

Hence

$$\overline{Q(t)} = Q_0 \overline{I(t)} \tag{20}$$

The notation $(\phi_0, \tilde{\phi}_0)$ is used to signify that $(\phi_0, \tilde{\phi}_0)$ form a conjugate pair of eigenvectors of D . In fact, it is easily verified that⁸

$$D\phi_0 = 0 \text{ and } \tilde{\phi}_0 D = 0 \tag{21}$$

Asymptotic Expressions for Very Slow and Very Rapid Exchange. (a) **Very Slow Exchange.**—For the case of a very slow exchange, the relaxation is relatively rapid; and C_l , which is the reciprocal lifetime for the l th phase, is considered to be very small compared to $1/T_l$. For $C_l \ll 1/T_l$, $F_{kl} \sim E_{kl} = \delta_{kl}/T_l$, and

$$\overline{I(t)} \sim \tilde{\phi}_0 \left[\begin{array}{ccc} e^{-t/T_1} & & \\ & e^{-t/T_2} & \\ & & \ddots \\ & & & e^{-t/T_n} \end{array} \right] \phi_0 \tag{22}$$

Hence

$$\overline{I(t)} \sim \sum_{i=1}^n P_i e^{-t/T_i}$$

Equation 22 shows that, for very slow exchange the relaxation is the weighted average of effects taking place separately in each phase.

(b) **Very Rapid Exchange.**—For this case, C_l , the reciprocal lifetime for the l th phase is very

(8) The result that $\tilde{\phi}_0 D = 0$ follows from the fact that, independent

of the value i , $\lim_{t \rightarrow \infty} P_{ij}(t) = P_j$. Therefore, $\lim_{t \rightarrow \infty} [P_{ij}(t)] = \begin{bmatrix} \phi_0 \\ \tilde{\phi}_0 \\ \vdots \\ \phi_0 \end{bmatrix}$

The result that $D\phi_0 = 0$ follows directly from $\sum D_{lj} = 0$.

(5) For T_2 phenomena, $Q = M_i$; for T_1 phenomena, $Q = M_s - M_{|i}$
 (6) Here "system" refers to a single spin, and the averaging technique gives results for the entire ensemble or multiphase system.
 (7) R. Kubo, *J. Phys. Soc. Japan*, **9**, 939 (1954).

large compared to T_1 , the relaxation time associated with the l th phase; *i.e.*, $C_1 \gg T_1$. At first, one might be tempted to argue that for this exchange rate limit, $D \gg E$, and hence that

$$\bar{I}(t) \sim \tilde{\phi}_0 e^{-Dt} \phi_0 = 1 \quad (23)$$

However, equation 23 neglects relaxation completely and is not the desired result. In order to obtain a correct limiting result, first-order perturbation theory is used to calculate an approximation for e^{-Ft} . The perturbation theory presented is merely a generalization of the customary perturbation theory employed in atomic physics.

Let $(\phi_k, \tilde{\phi}_k)$ be the normalized eigenvectors of D ; *i.e.*,⁹

$$D\phi_k = \lambda_k \phi_k, \quad \tilde{\phi}_k D = \lambda_k \tilde{\phi}_k \quad k = 0, \dots, n-1 \quad (24)$$

and $\tilde{\phi}_k \phi_l = \delta_{kl}$. Also let $(\psi_k, \tilde{\psi}_k)$ be the approximate eigenvectors of $F = D + E$, and let μ_k be the approximate eigenvalues of F , so that

$$F\psi_k = \mu_k \psi_k, \quad k = 0, \dots, n-1 \quad (25)$$

The first-order perturbation procedure yields

$$\psi_k = \phi_k + \sum_{i \neq k} \phi_i \tilde{\phi}_i E \phi_k / (\lambda_k - \lambda_i) \quad (26)$$

and

$$\mu_k = \lambda_k + \tilde{\phi}_k E \phi_k$$

The matrix, S , which diagonalizes F is, to first order, given by

$$S = [\psi_0, \psi_1, \dots, \psi_{n-1}] \quad (27)$$

To a first approximation, for the case of very rapid exchange, all corrections to (ϕ_k, λ_k) may be neglected except that one for $\lambda_0 = 0$. Therefore

$$\left. \begin{aligned} \psi_k &\sim \phi_k, \quad k = 0, 1, \dots, n-1 \\ \mu_0 &= \tilde{\phi}_0 E \phi_0 = \sum_{i=1}^n P_i/T_i \end{aligned} \right\} \quad (28)$$

and

$$\mu_k = \lambda_k, \quad k = 1, \dots, n-1$$

When equations 28 are substituted into the expression

$$\bar{I}(t) = \tilde{\phi}_0 S \begin{bmatrix} e^{-\mu_0 t} \\ e^{-\lambda_1 t} \\ \vdots \\ e^{-\lambda_{n-1} t} \end{bmatrix} S^{-1} \phi_0$$

the result becomes

$$\begin{aligned} I(t) &= \tilde{\phi}_0 [\phi_0, \phi_1, \dots, \phi_{n-1}] \begin{bmatrix} e^{-\mu_0 t} \\ e^{-\lambda_1 t} \\ \vdots \\ e^{-\lambda_{n-1} t} \end{bmatrix} \begin{bmatrix} \tilde{\phi}_0 \\ \tilde{\phi}_1 \\ \vdots \\ \tilde{\phi}_n \end{bmatrix} \phi_0 \\ &= [1, 0, 0, \dots, 0] \begin{bmatrix} e^{-\mu_0 t} \\ e^{-\lambda_1 t} \\ \vdots \\ e^{-\lambda_{n-1} t} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \\ I(t) &= e^{-\mu_0 t} = e^{-\left(\sum_{i=1}^n P_i/T_i\right)t} \quad (29) \end{aligned}$$

(9) The labelling $k = 0, 1, \dots, n-1$ is done because $\lambda_0 = 0$ in this notation.

Equation 29 shows that for very rapid exchange the relaxation is described by a single relaxation time, whose reciprocal is a weighted average of the reciprocals of the various relaxation times; *i.e.*

$$(1/T)_{av} = \sum_{i=1}^n P_i/T_i \quad (30)$$

Stochastic Theory of Relaxation Times for Two-phase Systems.—The Chapman-Kolmogoroff equation $dP/dt = -PD$ are particularly simple for a two-phase system. Since $p_{12} = 1$

$$D = \begin{bmatrix} C_1 & -C_1 \\ -C_2 & C_2 \end{bmatrix} \quad (31)$$

$$D^2 = (C_1 + C_2)D$$

Hence

$$P(t) = e^{-Dt} = 1 + \frac{e^{-\lambda t} - 1}{\lambda} D \quad (32)$$

where $\lambda = C_1 + C_2$. The explicit results in (32) are expressed by

$$\left. \begin{aligned} P_{11}(t) &= P_1 + P_2 e^{-\lambda t} \\ P_{12}(t) &= P_2 - P_2 e^{-\lambda t} \\ P_{21}(t) &= P_1 - P_1 e^{-\lambda t} \\ P_{22}(t) &= P_2 + P_1 e^{-\lambda t} \end{aligned} \right\} \quad (33)$$

with $\lambda = C_1 + C_2$. The matrix F is given by

$$F = \begin{bmatrix} C_1 + 1/T_1 & -C_1 \\ -C_2 & C_2 + 1/T_2 \end{bmatrix} \quad (34)$$

The eigenvalues (μ_1, μ_2) of F are the solutions of $\det [F - \mu I] = 0$. These are given by

$$\left. \begin{aligned} 2\mu_1 &= (C_1 + C_2 + 1/T_1 + 1/T_2) - \\ &\quad \{(C_2 - C_1 + 1/T_2 - 1/T_1)^2 + 4C_1 C_2\}^{1/2} \\ \text{and} \\ 2\mu_2 &= (C_1 + C_2 + 1/T_1 + 1/T_2) + \\ &\quad \{(C_2 - C_1 + 1/T_2 - 1/T_1)^2 + 4C_1 C_2\}^{1/2} \end{aligned} \right\} \quad (35)$$

It can be shown readily that

$$e^{-Ft} = g_0(t)1 + g_1(t)F \quad (36)$$

where

$$\left. \begin{aligned} g_0(t) &= \frac{\mu_2 e^{-\mu_1 t} - \mu_1 e^{-\mu_2 t}}{\mu_2 - \mu_1} \\ g_1(t) &= \frac{e^{-\mu_2 t} - e^{-\mu_1 t}}{\mu_2 - \mu_1} \end{aligned} \right\} \quad (37)$$

Thus

$$\bar{I}(t) = \tilde{\phi}_0 e^{-Ft} \phi_0$$

or

$$\bar{I}(t) = a_1 e^{-\mu_1 t} - a_2 e^{-\mu_2 t} \quad (38)$$

where

$$\left. \begin{aligned} a_1 &= \frac{1}{\mu_2 - \mu_1} (\mu_2 - 1/T_{av}) \\ a_2 &= \frac{1}{\mu_2 - \mu_1} (\mu_1 - 1/T_{av}) \end{aligned} \right\} \quad (39)$$

and

$$(1/T)_{av} = P_1/T_1 + P_2/T_2$$

Therefore, the quantity $\bar{Q}(t)$ decays according to the expression

$$\bar{Q}(t) = Q_0 \{a_1 e^{-\mu_1 t} - a_2 e^{-\mu_2 t}\} \quad (40)$$

Asymptotic Expressions for Slow and Fast Exchange in Two-phase Systems.—It is of interest to observe explicitly how the results described by (38) for two phase systems reduce to the multiple

phase expressions already obtained for very slow and very rapid exchange.

For very slow exchange, $C_k \ll 1/T_k$; hence

$$\left. \begin{aligned} \mu_1 &\sim 1/T_1 \\ \mu_2 &\sim 1/T_2 \end{aligned} \right\} \quad (41)$$

$$a_1 \sim \frac{1}{\mu_2 - \mu_1} \{ \mu_2 - \mu_1 P_1 - \mu_2 P_2 \} = P_1$$

and

$$a_2 = -P_2$$

Therefore

$$\overline{I(t)} = P_1 e^{-t/T_1} + P_2 e^{-t/T_2} \quad (42)$$

For very rapid exchange, $C_k \gg 1/T_k$, and

$$2\mu \sim (C_1 + C_2 + 1/T_1 + 1/T_2) \pm \{ (C_1 + C_2)^2 - 2(C_2 - C_1)(1/T_2 - 1/T_1) \}^{1/2}$$

If the preceding expression is expanded by the binomial theorem, then

$$\left. \begin{aligned} \mu_2 &\sim \lambda = C_1 + C_2 \\ \mu_1 &\sim (1/T)_{av} \end{aligned} \right\} \quad (43)$$

It follows from (39) that

$$\left. \begin{aligned} a_1 &\sim \frac{1}{\mu_2 - \mu_1} (\mu_2 - \mu_1) = 1 \\ a_2 &\sim \frac{1}{\mu_2 - \mu_1} (\mu_1 - \mu_1) = 0 \end{aligned} \right\} \quad (44)$$

Therefore

$$I(t) = e^{-t/T_{av}} \quad (45)$$

with

$$1/T_{av} = P_1/T_1 + P_2/T_2$$

The special two-phase results expressed by (42) and (45) are in complete agreement with the general results of equations 22 and 30.

Experimental

Transverse (T_2) Relaxation N-M-R Measurements.—In the preceding theory no distinction was made between T_1 and T_2 phenomena, but rather it was pointed out that the theory should apply equally well to both T_1 and T_2 measurements. For transverse relaxation the quantities $\overline{Q(t)}$ and Q_0 to be associated with nuclear resonance relaxation processes are given by

$$\left. \begin{aligned} \overline{Q(t)} &= M_{\perp} \\ \text{and} \\ Q_0 &= M_{\perp 0} \end{aligned} \right\} \quad (46)$$

where M_{\perp} is the moment normal to the polarizing magnetic field at time t and where $M_{\perp 0}$ is the moment at $t = 0$. It follows immediately from equation 40 that for two-phase systems the net transverse moment will decay according to the general expression

$$M_{\perp} = M_{\perp 0} (a_1 e^{-\mu_1 t} - a_2 e^{-\mu_2 t}) \quad (47)$$

where the a_i 's and μ_i 's are functions of the P_i 's, T_i 's, and C_i 's as defined in equations 39 and 35, respectively.

Only to a very limited extent does the general expression described by (47) lend itself to experimental attack; however, the asymptotic expressions for (a) very slow exchange ($C_i \ll 1/T_i$) and (b) very fast exchange ($C_i \gg 1/T_i$) are particularly significant to an interpretation of the experimental relaxation measurements described in this paper.

(a) **Very Slow Exchange.**—The transverse moment decay expression in this case is obtained directly from equation 42. Therefore

$$M_{\perp} = M_{\perp 0} (P_1 e^{-t/T_{21}} + P_2 e^{-t/T_{22}}) \quad (48)$$

The corresponding signal amplitudes observed in spin-echo² techniques are given by

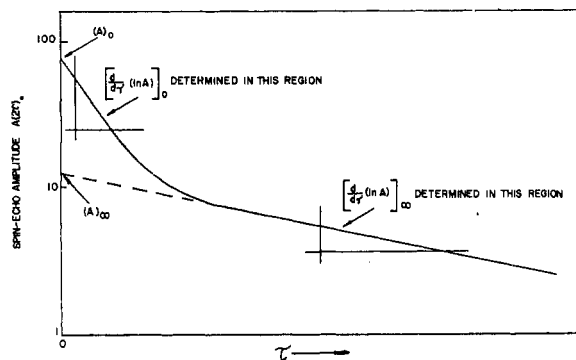


Fig. 1.—Theoretical transverse relaxation plot for two-phase systems.

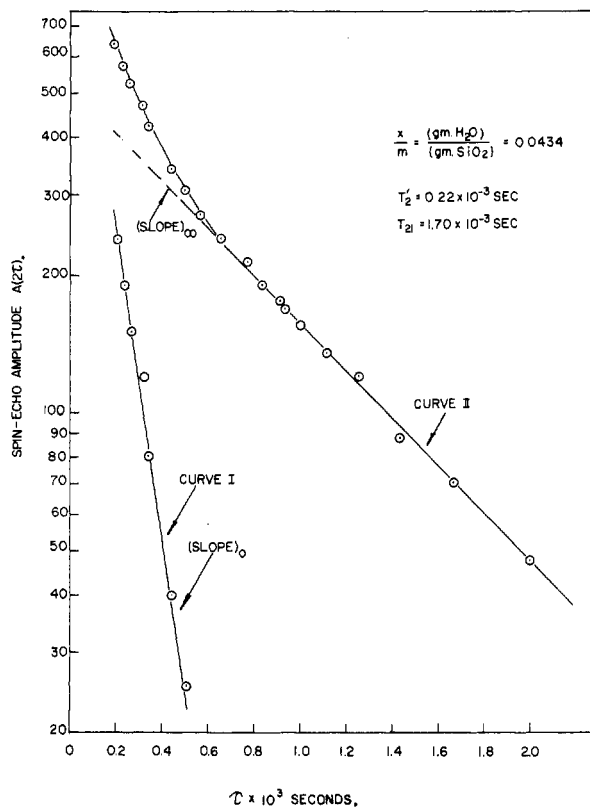


Fig. 2.—Transverse relaxation times for H₂O adsorbed on silica gel at a low coverage illustrating two-phase behavior.

$$A(2\tau) = \sum_{i=1}^2 A_{oi} e^{-2\tau/T_{2i}} \quad (49)$$

where A_{oi} is an experimental amplitude which is directly proportional to the quantity $M_{\perp 0} P_i$. A theoretical plot of $\log A(2\tau)$ vs. τ is shown in Fig. 1. Such a curve is typical of two-phase behavior. From such a plot the T_{2i} 's and the relative population ratio, A_{o1}/A_{o2} , can be obtained.

Two phase behavior of transverse relaxation data at low coverage of adsorbed water vapor on silica gel has been observed in previous studies.¹ Of particular importance for the conclusions to be reached in this investigation is the relaxation data for a coverage of $x/m = 0.0434$ (g. H₂O/g. SiO₂). The results shown in Fig. 2 clearly demonstrate the existence of two distinct phases; i.e., two independent relaxation times T'_{2} and T_{21} are obtained.

(b) **Very Fast Exchange.**—From equations 45 the transverse moment decay becomes

$$\left. \begin{aligned} M_{\perp} &= M_{\perp 0} e^{-t/T_2} \\ \text{where} \\ 1/T_2 &= P_1/T_{21} + P_2/T_{22} \end{aligned} \right\} \quad (50)$$

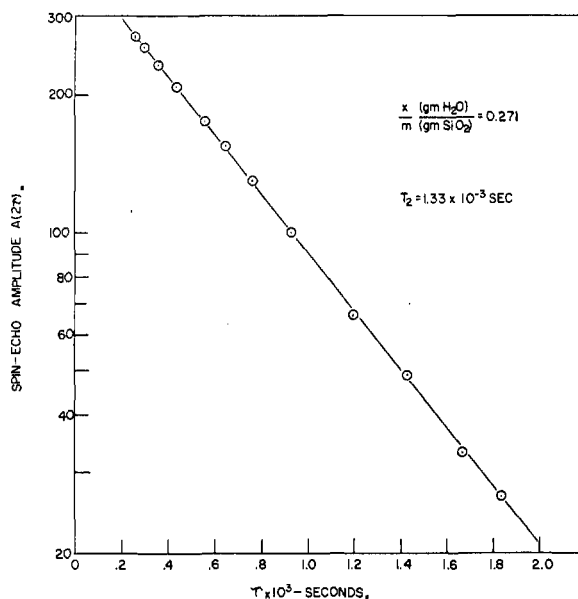


Fig. 3.—Typical transverse relaxation time plot for H_2O adsorbed on silica gel illustrating single-phase behavior.

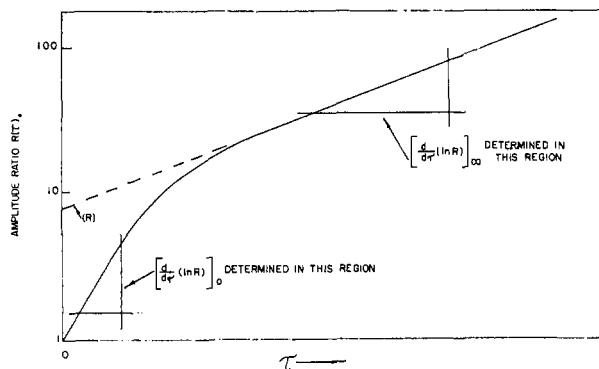


Fig. 4.—Theoretical longitudinal relaxation plots for two-phase systems.

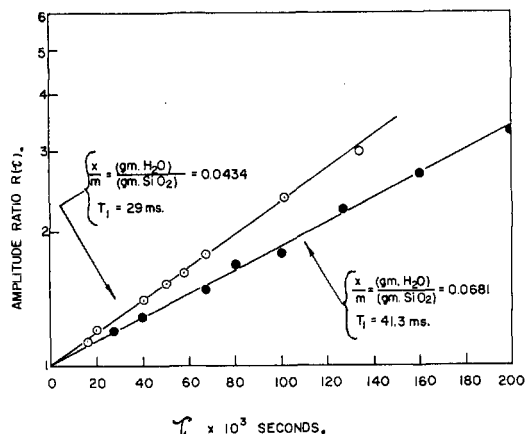


Fig. 5.—Typical longitudinal relaxation time plots for H_2O adsorbed on silica gel at low coverages illustrating single-phase behavior.

The spin-echo amplitude signal is given by

$$A(2\tau) = A_0 e^{-2\tau/T_2} \quad (51)$$

where τ is the time between r-f pulses. A plot of $\log A(2\tau)$ vs. τ would, of course, be a simple straight line. It should be emphasized that, regardless of the number of phases in-

involved, under the conditions of fast exchange the experimental data indicate only a single phase system; *i.e.*, only an average relaxation time is observed. An example of T_2 data for a single-phase system observed in the study of adsorbed water vapor on silica gel is illustrated in Fig. 3.

Longitudinal (T_1) Relaxation N-M-R Measurements.—For longitudinal relaxation the quantities $Q(t)$ and Q_0 in equation 40 are expressed by

$$\left. \begin{aligned} Q(t) &= M_0 - M_{\parallel} \\ \text{and} \\ Q_0 &= M_0 \end{aligned} \right\} \quad (52)$$

where M_0 is the equilibrium moment, and where M_{\parallel} is the moment parallel to the constant polarizing magnetic field. Hence

$$M_{\parallel} = M_0(1 - a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t}) \quad (53)$$

where the a_i 's and μ_i 's are functions of the P_i 's, T_{1i} 's and C_i 's. The asymptotic expressions for (a) very slow exchange and (b) very fast exchange are again the ones of primary interest for the observed experimental data.

(a) **Very Slow Exchange.**—For $C_i \ll 1/T_{1i}$, it follows from (42) that

$$M_{\parallel} = M_0 \left(1 - \sum_{i=1}^2 P_i e^{-t/T_{1i}} \right) \quad (54)$$

If free decay signals which immediately follow each of two successive r-f pulses are used to determine T_1 values, then the experimental amplitude expression can be conveniently written as

$$R(\tau) = (\sum P_i e^{-\tau/T_{1i}})^{-1} \quad (55)$$

where

$$R(\tau) = M_0 / (M_0 - M_{\parallel})$$

and where τ is the time between r-f pulses. A theoretical plot of $\log R(\tau)$ vs. τ for a longitudinal relaxation two-phase system is shown in Fig. 4. In respects similar to two-phase T_2 data described earlier, both the T_1 's and the relative population ratio, P_1/P_2 , are available in principle from such a plot.

(b) **Very Fast Exchange.**—Again from equation 45, the longitudinal moment decay expression is of the form

$$M_{\parallel} = M_0(1 - e^{-t/T_1})$$

where

$$1/T_1 = P_1/T_{11} + P_2/T_{12} \quad (56)$$

The corresponding experimental expression for determining T_1 values by free decay signals is simply

$$R(\tau) = M_0 / (M_0 - M_{\parallel}) = e^{\tau/T_1} \quad (57)$$

A plot of $\log R(\tau)$ vs. τ would, of course, yield a straight line curve. Figure 5 illustrates such effective single phase behavior for two separate x/m values of water vapor adsorbed on silica gel.

Lifetime of a Molecule in an Adsorbing Phase on Silica Gel.—The average lifetime of a spin in a given phase characterized by a single relaxation time T_i is simply $\bar{t}_i = 1/C_i$. The problem to be answered is whether a limiting value might be placed on the lifetime of a water molecule in an adsorbing phase on silica gel. Two assumptions enter into any such lifetime estimate: (a) The lifetime of a water molecule in an adsorbing phase is to be identified with the lifetime of a hydrogen nuclear spin in a given relaxation phase. (b) If a two-phase system exists for transverse (T_2) relaxation phenomena, then a corresponding two-phase system exists for longitudinal (T_1) relaxation phenomena.

Assumption (b) might be more clearly stated as follows. If a two-phase system exists for transverse relaxation, then there are two distinct average nuclear correlation times, τ_{N1} and τ_{N2} , associated with the relaxation processes. These correlation times will then be expected to give rise to not only two transverse relaxation times but also two longitudinal relaxation times. The existence of such multiple phase systems is no guarantee that experimental measurements will resolve multiple T_{21} 's and T_{11} 's. In other words, if the average lifetime, $1/C_i$, of the molecule in the *i*th phase is very short compared with the time required to obtain an experimental measurement, averaging processes between

phases occur; and only an average relaxation time would be observed.

A comparison of T_1 and T_2 relaxation times for protons adsorbed on silica gel is shown in Fig. 6. A plot of both T_1 and T_2 values as a function of coverage is described for x/m values below a monolayer. Below a coverage of $\theta = 0.5$, a two-phase system is observed for T_2 measurements, whereas a single phase system in T_1 measurements is obtained. Of particular interest is the x/m value of 0.0434. Figures 2 and 5, which have already been discussed, illustrate the experimental behavior.

The transverse relaxation times, T_2' and T_{21} , which are evaluated from the data shown in Fig. 2, are not necessarily the relaxation times corresponding to asymptotic conditions; *i.e.*, $C_i \ll 1/T_{21}$. This statement follows directly from the general decay expression 40. If T_{21}^* and $T_2'^*$ are defined as the actual relaxation times which would be measured under very slow exchange conditions, then it is easy to show that

$$T_2' \leq T_2'^* \leq T_{2(av)} \leq T_{21} \leq T_{21}^* \quad (58)$$

where $T_{2(av)}$ is the relaxation time which would be obtained under very fast exchange conditions. In the measurement of T_1 for an $x/m = 0.0434$, a single relaxation time exists (see Fig. 5). If T_{11} and T_{12} are the longitudinal relaxation times which would be observed under asymptotic conditions of slow exchange ($C_i \ll 1/T_{11}$), then

$$T_{12} \leq T_{1(av)} \leq T_{11} \quad (59)$$

From Fig. 2 a rough estimate of the relative population of the two adsorbing phases is possible—namely, $(P_{21}/P_2') \sim (3/7)$. Therefore, from equation 45, $T_{2(av)} \sim 3 \times 10^{-4}$ second. Also $T_{1(av)} = 29 \times 10^{-3}$ second from Fig. 5. An estimate of the average lifetime, t , of a water molecule in an adsorbing phase on silica gel is now possible. Hence, within an order of approximation, 3×10^{-4} sec. $\ll t \ll 29 \times 10^{-3}$ sec. or $t \sim 3 \times 10^{-3}$ sec. for the particular coverage of $x/m = 0.0434$.

Conclusion

A stochastic theory of relaxation times for multiple phase systems has been developed which accounts explicitly for the essential features of very slow ($C_i \ll 1/T_i$) and very fast ($C_i \gg 1/T_i$) exchange; *i.e.*, for very slow exchange the relaxation is the weighted average of effects taking place separately in each phase; and for very fast exchange, the relaxation is described by a single relaxation time, whose reciprocal is a weighted average of the reciprocals of the various relaxation times.

From the stochastic multiple phase theory, decay expressions are obtained for the special case of two-phase systems. This theory describes the essential features of the relaxation processes encountered in adsorption studies not only for the asymptotic conditions of slow and fast exchange but also for the overlapping region of exchange rates; *i.e.*, for $C_i \sim 1/T_i$. It is clear from the decay expressions for a two-phase system that the relaxation times, T_1 and T_2 , which are evaluated from the data, are not necessarily the relaxation times corresponding to the asymptotic conditions of exchange (see expression 40).

Adsorption studies of water vapor on silica gel by means of nuclear magnetic resonance tech-

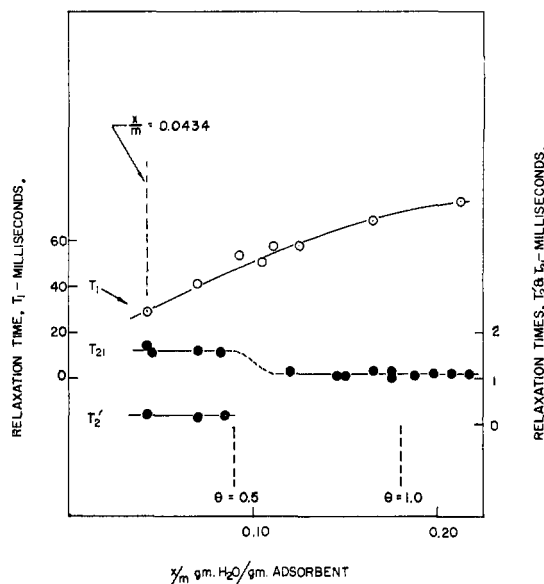


Fig. 6.—A comparison of relaxation times T_1 and T_2 for protons adsorbed on silica gel for x/m values below a monolayer.

niques have demonstrated the simultaneous existence, for a given coverage, of two-phase behavior for transverse (T_2) relaxation measurements and single phase behavior for longitudinal (T_1) relaxation measurements. From a combination of this experimental data and theory of stochastic processes in relaxation phenomena, the lifetime of a water molecule in an adsorbing phase on silica gel is estimated to be $t \sim 3 \times 10^{-3}$ second. One assumption in the evaluation of this lifetime should not be overlooked—namely, if the time required to obtain relaxation data could be made sufficiently short for both T_1 and T_2 measurements, such that the time of measurements would be much less than the lifetime of the molecules in the adsorbing phases, then both transverse and longitudinal relaxation data would describe two-phase systems. Investigations are underway which do verify this assumption for specific systems; these will be reported on at a later time.

DISCUSSION

J. J. BIKERMAN.—Is it possible to compare the relaxation times found for the hydrogen nuclei in the "adsorbed state" with their relaxation times in, say, water and in a molecule such as $\text{Si}(\text{OH})_4$?

J. R. ZIMMERMAN.—Certainly qualitative comparisons are possible. For example, the transverse relaxation time of water at room temperature is a few seconds; the relaxation times of adsorbed water in these experiments are of the order of milliseconds. For ice the transverse relaxation time of the hydrogen is of the order of microseconds. However, for quantitative comparisons, the simplified BPP model which relates a single nuclear correlation time to the relaxation processes is generally not an adequate model for adsorption phenomena.