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Citation: *The Journal of Chemical Physics* **28**, 430 (1958); doi: 10.1063/1.1744152

View online: <http://dx.doi.org/10.1063/1.1744152>

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Reaction Rates by Nuclear Magnetic Resonance*

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(Received October 30, 1957)

The Bloch equations for nuclear magnetic resonance are modified to describe the magnetic resonance of a single nuclear species X which is transferred back and forth between two (or more) magnetic environments (A, B) by kinetic molecular processes. The modified Bloch equations involve the usual assumptions of the Bloch theory and, in addition, require (a) that the X nuclear relaxation times be independent of the molecular exchange rates, and (b) that the X nuclear magnetization in A relax independently of the X magnetization in B , and vice versa. The modified Bloch equations are easily solved in the slow passage case, with arbitrary rf saturation. Earlier relations between reaction rates, and resonance line shapes, which were developed by Gutowsky, McCall, and Slichter, and extended by a number of other investigators, are easily derived using the modified Bloch equations. In the present work the modified equations are used to show how rapid exchange rates can sometimes be measured in solutions where the X relaxation times are relatively long in one system, A , and short in the second, B .

INTRODUCTION

GUTOWSKY, McCall, and Slichter¹ (GMS) have shown how the classical Bloch equations² may be solved to obtain quantitative relations between nuclear resonance line shapes and the rates of certain fast reversible chemical exchange reactions. These line-shape reaction-rate relations apply to the case of slow passage and no rf saturation. The method developed by GMS to solve the Bloch equations with chemical exchange has been extended by Gutowsky and Saika,³ McConnell and Berger,⁴ and Grunwald, Loewenstein, and Meiboom⁵ to a number of reaction-rate line-shape problems. The purpose of the present work is to show how the Bloch equations² can be directly generalized to include the effects of chemical exchange. This reduces the previous rather involved derivations of (line-shape reaction-rate) formulas^{1,3-5} to almost trivial algebraic operations, and also permits the treatment of the effects of rf saturation in the presence of chemical exchange. The present approach also brings out certain important approximations implicit in the earlier work of GMS.¹

BLOCH EQUATIONS WITH CHEMICAL EXCHANGE

Consider, for brevity, a simple chemical exchange system such that rapid reversible molecular processes transfer a nucleus X back and forth between two molecular environments, A and B . The first-order life times of X in A and B are τ_A and τ_B . Using the notation of Bloch,² we let u , v , and M_z denote the components of the X nuclear magnetization which are in phase with the effective rotating component of the rf field, out of phase with this rotating rf field, and in the direction of

the large stationary field, respectively. These magnetizations can be written as the sum of the contributions of the A and B systems:

$$u = u_A + u_B \quad (1)$$

$$v = v_A + v_B \quad (2)$$

$$M_z = M_z^A + M_z^B. \quad (3)$$

The modified Bloch equations are

$$\dot{u}_A + \Delta\omega_A v_A = -u_A/\tau_{2A} + u_B/\tau_B \quad (4)$$

$$\dot{u}_B + \Delta\omega_B v_B = -u_B/\tau_{2B} + u_A/\tau_A \quad (5)$$

$$\dot{v}_A - \Delta\omega_A u_A = -v_A/\tau_{2A} + v_B/\tau_B - \omega_1 M_z^A \quad (6)$$

$$\dot{v}_B - \Delta\omega_B u_B = -v_B/\tau_{2B} + v_A/\tau_A - \omega_1 M_z^B \quad (7)$$

$$\dot{M}_z^A - \omega_1 v_A = M_0^A/T_{1A} - M_z^A/\tau_{1A} + M_z^B/\tau_B \quad (8)$$

$$\dot{M}_z^B - \omega_1 v_B = M_0^B/T_{1B} - M_z^B/\tau_{1B} + M_z^A/\tau_A, \quad (9)$$

where M_0^A and M_0^B are the equilibrium z magnetizations of the X nuclei in A and B , $\omega_1 = \gamma H_1$, and

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A}, \quad (10)$$

$$\frac{1}{\tau_{2A}} = \frac{1}{T_{2A}} + \frac{1}{\tau_A}. \quad (11)$$

In (10) and (11) T_{1A} and T_{2A} are the longitudinal and transverse relaxation times of X in A . Similar definitions apply for τ_{1B} and τ_{2B} .

The substance of our modification of these equations can be seen by a comparison of Eqs. (4) and (11), for example. Equation (4) differs from the usual Bloch equation by the addition of two terms to the right-hand side, $-u_A/\tau_A$ and u_B/τ_B . The first of these, $-u_A/\tau_A$, measures the rate at which u_A decreases due to the chemical transfer of u magnetization out of the A system; u_B/τ_B measures the rate at which u_A increases due to chemical transfer of u magnetization into the A system, from the B system. Similar considerations apply to Eqs. (5)–(9) for u_B , v_A , v_B , M_z^A , M_z^B .

Equations (4)–(9) require approximations in addi-

* Sponsored by the National Science Foundation.

† Contribution No. 2270.

¹ Gutowsky, McCall, and Slichter, *J. Chem. Phys.* **21**, 279 (1953).

² F. Bloch, *Phys. Rev.* **70**, 460 (1946).

³ H. S. Gutowsky and A. Saika, *J. Chem. Phys.* **21**, 1688 (1953). See also H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 1228 (1956).

⁴ H. M. McConnell and S. B. Berger, *J. Chem. Phys.* **27**, 230 (1957).

⁵ Grunwald, Loewenstein, and Meiboom, *J. Chem. Phys.* **27**, 630 (1957).

tion to those intrinsic to the ordinary Bloch equations. It is of course presumed that any magnetic environment of X other than A or B (e.g., a transition state, or "activated complex"), is so short lived as to produce no change in the components of magnetization as the X nuclei move from A to B , and vice versa. Furthermore, most foreseeable applications of (4)–(9) to reaction rate determinations will require that the relaxation times T_{1A} , T_{2A} , T_{1B} , T_{2B} be independent of τ_A and τ_B . This condition can be most easily realized when the X nuclear relaxations are due to time dependent perturbations which are of high frequency relative to τ_A^{-1} , τ_B^{-1} . Equations (4)–(9) also require that the X nuclear magnetizations of the A and B systems relax independently of one another, except for the chemical exchange effects. This situation can certainly be realized in practice when the X nuclear relaxations are dominated by magnetic couplings with some other nuclear species (Y), or when these relaxation times are due to nuclear electric quadrupole interactions. Strong magnetic coupling between the X nuclei in A , and the X nuclei in B —especially coherent couplings as electron coupled spin-spin interactions in the same molecule—cannot be accounted for in terms of (4)–(9), and require the inclusion of additional terms.

Equations (4)–(9) can be applied to reactions of any order, but under these circumstances the lifetimes τ_A and/or τ_B are to be related to pseudo first-order rate constants. Thus, if two molecules of A react to give one of B , $2A \rightleftharpoons B$, and the bimolecular rate constant for the disappearance of A is k (liters mole⁻¹ sec⁻¹), then $\tau_A = 1/k(A)$ where (A) is the molar concentration of species A .

EXAMPLES

Equations (4)–(9), together with their obvious extensions to systems involving more than two magnetic nuclear environments, and to experiments with more than one oscillatory rf field, clearly encompass a great variety of phenomena relating reaction rates to line shapes. Thus, rapid passage transient phenomena which are dependent on the effects of chemical exchange⁶ can be treated by Eqs. (4)–(9). The simplest problems to treat are, however, those obtaining for the slow passage case, where

$$\dot{u}_A = \dot{u}_B = \dot{v}_A = \dot{v}_B = \dot{M}_z^A = \dot{M}_z^B = 0. \quad (12)$$

Under these circumstances the set of coupled differential equations, (4)–(9), becomes a complete set of ordinary simultaneous linear equations in six unknowns, which is easily solved in closed form in many special cases of interest, and which can always be solved numerically in the most general case. For example, the problem treated by GMS¹ involves two magnetic environments A , B so that $T_{2A} = T_{2B} = T_2$; $\tau_A = \tau_B = \tau$; $1/\tau_2 = 1/T_2 + 1/\tau$; $M_0^A = M_0^B = M_0/2$. It is further assumed by GMS that there is no rf saturation. In this case M_z^A and M_z^B can be replaced by $M_0/2$. Equations (4) and

(6) can be combined to give,

$$(1/\tau_2 - i\Delta\omega_A)G_A = G_B/\tau_B - i\omega_1 M_0/2 \quad (13)$$

and (5) and (7) yield

$$(1/\tau_2 - i\Delta\omega_B)G_B = G_A/\tau_A - i\omega_1 M_0/2. \quad (14)$$

Here $G_A = u_A + iv_A$, $G_B = u_B + iv_B$. Equations (13) and (14) can be solved for $G = G_A + G_B = u + iv$:

$$G = \frac{-i\omega_1 M_0 \tau \{2 + [1/T_2 - i(\Delta\omega_A + \Delta\omega_B)/2]\tau\}}{\tau^2(1/\tau_2 - i\Delta\omega_A)(1/\tau_2 - i\Delta\omega_B) - 1}. \quad (15)$$

The result (15) is essentially identical with that obtained by GMS.¹ Similarly, the problems treated by McConnell and Berger,⁴ and by Grunwald, Loewenstein, and Meiboom⁵ can be solved using (4)–(6).

We may further illustrate applications of (4)–(9) by another reaction rate-line shape problem of considerable practical interest. Suppose that the exchange process which transfers X back and forth between A and B is first order in (A) and (B) , and that the nuclear relaxation times of X in B are extremely short,

$$T_{1B}, T_{2B} \ll T_{1A}, T_{2A}, \quad (16)$$

$$T_{1B}, T_{2B} \ll \tau_B, \quad (17)$$

$$\omega_1^2 T_{1B} T_{2B} \ll 1. \quad (18)$$

Such short relaxation times in the B system could be brought about by hyperfine interactions with unpaired electrons, or strong nuclear electric quadrupole relaxation. Provided the relative number of A and B systems are comparable—say, $\tau_A \gtrsim \tau_B$ —then under these conditions the only significant perpendicular magnetization (u, v) will be due to the X nuclei in A . That is $v \approx v_A$, $u \approx u_A$. Then we may set $v_B \approx u_B \approx 0$ in (4) and (6) and let $M_z^B = M_0^B$ in (8). Under these conditions one obtains for the absorption mode in slow passage

$$v = \frac{-\omega_1 M_0^A \tau_{2A}}{1 + \Delta\omega_A^2 \tau_{2A}^2 + \omega_1^2 \tau_{1A} \tau_{2A}}. \quad (19)$$

The lifetime τ_A can then be obtained from an observed line shape conforming to Eq. (19) provided $\tau_A \lesssim T_{2A}$. If $\tau_A \gg T_{2A}$, but $\tau_A \lesssim T_{1A}$, then a study of the effect of rf saturation on the absorption intensity will permit an evaluation of τ_A .

If one does not make the requirement that T_{1B} be very short, relative to τ_B , then the B system can be saturated through rf saturation of the A system. In this more general case, the absorption mode is given by the equation,

$$v = \frac{-\omega_1 M_0^A \tau_{2A} \left[\frac{1}{T_{1A}} + \frac{\tau_{1B}}{T_{1B} \tau_A} \right] \left/ \left[\frac{1}{\tau_{1A}} - \frac{\tau_{1B}}{\tau_A \tau_B} \right] \right.}{1 + \Delta\omega_A^2 \tau_{2A}^2 + [\tau_{2A} \omega_1^2] \left/ \left[\frac{1}{\tau_{1A}} - \frac{\tau_{1B}}{\tau_A \tau_B} \right] \right.}. \quad (20)$$

In conclusion it may be remarked that the modified Bloch equations represent only one of several possible theoretical treatments of the reaction-rate line-shape problem. Alternative approximations will be discussed in subsequent work.

⁶ H. M. McConnell and D. D. Thompson, J. Chem. Phys. 26, 958 (1957).