A MODEL FOR A SIMPLE DIFFUSION PROCESS

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The problem of deterniming the amount of a given substance that has diffused into one life form given that a known amount has diffused into a second similar life form under the same conditions is studied under the assumption that: free molecular diffusion is the only process involved, the mass diffusion coefficients are known constants and the external concentration of the diffusing substance remains constant. The solution of this *comparative diffusion problem* is obtained in terms of the external concentration value and the physical properties of each life form for the special case of a cylinder-cylinder configuration of the pair. The properties of this solution are then determined for all reasonably small and sufficiently large values of the external concentration value. This study represents a first attempt to resolve what appears to be a new class of diffusion problems.

Introduction

The biologist is often confronted with the task of maintaining an important plant free from intruding parasites and epiphytes. He may find manual separation awkward, time consuming, or even damaging to his object of study. In this case, the possibility of having the host-intruder system immersed for a brief time in a solution containing chemicals so as to reach lethal concentration in intruder while inflicting as little damage as possible to the host is certain to be worth his consideration, especially if the damage done is insignificant. However, to be able to use such a method efficiently certain questions, arising quite naturally in this context, have to be answered. Assuming that the lethal concentration τ necessary to neutralize the intruder is known, one has to know the duration of exposure of the host-intruder system to the chemical in use when the concentration $c > \tau$ is given. More importantly, since only the smallest possible concentration of the same substance should be permitted to enter the host, one has to know whether long exposures with smaller concentrations or short exposures with correspondingly larger concentrations are preferable. In the present paper we discuss these questions in the case of a cylinder-cylinder configuation of the host-irtruder system in which the following hypotheses hold:

1. The process by which the toxic chemical is taken in by both life forms is free molecular diffusion.
2. The diffusion coefficient is a constant for each life form (and is known *a priori* or can be determined experimentally).
3. The concentration c of the toxic chemical remains unchanged during the exposure of host-intruder to it.

Similar analyses, under less stringent assumptions, *eg* when diffusion and reaction occur simultaneously or the process is membrane dependent *etc*, are certainly possible. However, for this initial simplified model assumptions 1 - 3 are maintained throughout.

The cylinder-cylinder configuration

In this configuration the valuable and unwanted life forms are represented by two cylinders A and B of radius r_A and r_B respectively. The cylinders are considered to be infinite in length or, if of finite extent, have ends which do not permit diffusion.

For a given cylinder of base radius r_0, let $C(r,t)$ denote the molar concentration (g - moles/cm^3) of diffused chemical at time t (sec) at each point a distance r (cm) from the center of the cylinder after it has been immersed in a solution containing a molar concentration c of the toxic chemical. Then according to assumptions 1 and 3, $C(r,t)$ is a solution of the initial-boundary value problem for the diffusion equation*
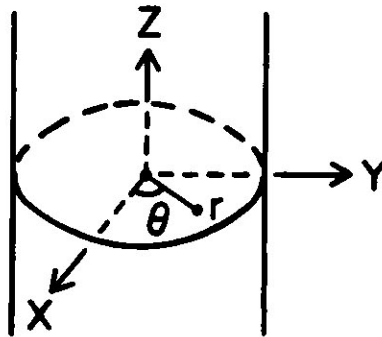
(1)
$$\begin{cases} C_t = k\,(C_{rr} + C_r/r) & 0 < r < r_0\,, t > 0 \\ C(r_0,t) = c\,, & t > 0 \\ C(r,0) = 0\,, & 0 < r < r_0 \end{cases}$$

where k is the mass diffusion coefficient (cm^2/sec) for the given cylinder and $C_r \equiv \frac{\partial C}{\partial r}, C_t \equiv \frac{\partial C}{\partial t}$. If one also wanted to take into account a reaction process which produced or eliminated the diffusing chemical, then the diffusion equation would be

$$C_t = k(C_{rr} + C_r/r) + R$$

where $R(r)$ would be the molar rate (g - moles cm^{-3} sec^{-1}) of production or elimination of c at r. Problem (1) can be solved by the technique of separation of variables.

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* The differential equation in (1) is called Fick's second law of diffusion or the diffusion equation (Bird *et al* 1960,) and is the equation (in polar coordinates) often used for the analysis of diffusion in solids or stationary liquids; k is a measure of the molar diffusion flux, which is the number of moles of the chemical that pass through a unit area of the material in unit time and depends on temperature, pressure, and composition of the material.

Substitution of $C(r,t) = c + R(r)T(t)$ into the differential equation and boundary condition in (1) gives

(2) $$\frac{T'}{kT} = \frac{1}{R}(R'' + \frac{R'}{r}) = -\lambda^2 , \quad 0 < r < r_0 , \quad t > 0$$

$$R(r_0)T(t) = 0 , \quad t > 0$$

where λ is the separation constant and $R' = \frac{dR}{dr}$. $T' = \frac{dT}{dt}$.
It follows that for each $j = 1,2,...$

$$R_j(r)T_j(t) = J_0(\lambda_j r) \exp(-\lambda_j^2 kt)$$

satisfies (2) with $\lambda = \lambda_j$ where the eigenfunctions

$$J_0(\lambda_j r) = \sum_{n=0}^{\infty} \left[(-1)^n (\lambda_j r/2)^{2n} \ (n!)^{-2}\right] \text{are the Bessel functions of order zero}$$

and the corresponding eigenvalues λ_j satisfy $J_0(\lambda_j r_0) = 0$. The unique solution of (1) is then expressed in terms of that linear combination of the $R_j(r)T_j(t)$'s for which $C(r,0) = 0 , 0 < r < r_0$ .Thus

$$C(r,t) = c + \sum_{j=1}^{\infty} a_j J_0(\lambda_j r) \exp(-\lambda_j^2 kt)$$

where for each $j = 1,2,...$,

$$a_j = (2/(r_0 J_1(\lambda_j r_0))^2) \cdot \int_0^{r_0} r J_0(\lambda_j r) \cdot (-c)dr$$

$$= -2c/(\lambda_j r_0 J_1(\lambda_j r_0)) ,$$

the integration following from the special property of Bessel functions:
$\frac{d}{dx}(x^\nu J_\nu(x)) = x^\nu J_{\nu-1}(x)$, ν real. The above series and its derivatives converge absolutely and uniformly with respect to r and t ($t \geq t_0, t_0 > 0$), and its sum $C(r,t)$ is a continuous function of r and t for $0 \leq r \leq r_0, t > 0$. One consequence of this is that the series can be integrated termwise without affecting its convergence. Integration of $C(r,t)$ over a representative segment of unit length of the given cylinder and subsequnet division by the volume of that segment (πr_0^2) gives the mean concentration M of the toxic chemical in the sement at time t

(3) $M(t,r_0,c) = (2\pi \int_0^{r_0} rC(r,t) \, dr) / \pi \, r_0^2$

$$= c (1 - \sum_{j=1}^{\infty} \frac{4}{r_0^2 \lambda_j^2} \exp(-\lambda_j^2 kt)).$$

and $M(t,r_0,c)$ satisfies: $0 < M(t,r_0,c) < c$ for every c and $t > 0$, $M(0,r_0,c) = 0$ and $M(t,r_0,c)$ is a continuous, strictly increasing function of $t > 0$ for fixed c with $\lim_{t \to \infty} M(t, r_0, c) = c$.

Applied to cylinders A and B , (3) gives

$$M(t,r_B,c) = c(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \alpha_j^2} \bullet \exp(-\alpha_j^2 k_B t))$$

and

(4) $M(t,r_A,c) = c(1 - \sum_{j=1}^{\infty} \frac{4}{r_A^2 (\frac{r_B}{r_A} \alpha_j)^2} \cdot \exp(-(\frac{r_B}{r_A} \alpha_j)^2 k_A t))$

$$= c(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \alpha_j^2} \exp(-\alpha_j^2 k_B \rho t))$$

where $\rho = \dfrac{r_B^2 k_A}{r_A^2 k_B}$ and $M(t, r_A, c)$ and $M(t,r_B,c)$ are the mean concentrations of the toxic chemical in the representative segments of A and B after their immersion in the solution at time $t = 0$, k_A , and k_B are the diffusion constants for A and B , and α_j are the eigenvalues, $J_0(\alpha_j r_B) = 0$, $j = 1,2,..., $. Let $t = T(c)$ denote the time required for $M(t,r_B,c)$ to attain the value τ for a given value of $c > \tau$ (clearly c must be chosen such that $c > \tau$ since $M(t,r_B,c) < c$ for all t). Then

(5) $M_B(c) \equiv M(T(c), r_B,c)$

$$= c(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \alpha_j^2} \exp(-\alpha_j^2 k_B T(c))) = \tau , c > \tau$$

and $M_A(c) \equiv M(T(c), r_A, c)$ is the mean concentration of toxic chemical in the valuable component at time $t = T(c)$. This function $T(c)$ is a continuous, strictly decreasing function of $c > \tau$. Indeed, if we set $G(T,c) = M_B(T,r_B,c) - \tau$, $c > \tau$, then

$$G(T,c) = 0, \frac{\partial G}{\partial c} = 1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \alpha_j^2} \exp(-\alpha_j^2 k_B T) > 0$$

$$, \frac{\partial G}{\partial T} = c \sum_{j=1}^{\infty} \frac{4 k_B}{r_B^2} \exp(-\alpha_j^2 k_B T) > 0$$

and by the Implicit Function Theorem (Courant 1947), $T'(c)$ exists and

$$T'(c) = -\left(\frac{\partial G}{\partial c} / \frac{\partial G}{\partial T}\right) < 0, c > \tau.$$

From (5) it also follows that $\lim_{c \to \infty} T(c) = 0$ and $\lim_{c \to \tau^+} T(c) = \infty$. The really important question, of course, is how does $M_A(c)$ vary as a function of that c (and corresponding $T(c)$) for which $M_B(c) = \tau$, since this will determine the procedure to be used in the operation of the process. A partial answer to this question is given by the following theorem and is illustrated in Figure 1. Unfortunately, the strictly decreasing ($\varrho < 1$) and strictly increasing ($\varrho > 1$) behavior of $M_A(c)$ could not be established for all values of $c > \tau$, but only for all reasonably small and sufficiently large values of the external concentration c. However, all the numerical and theoretical evidence to date suggests that this is actually the case.
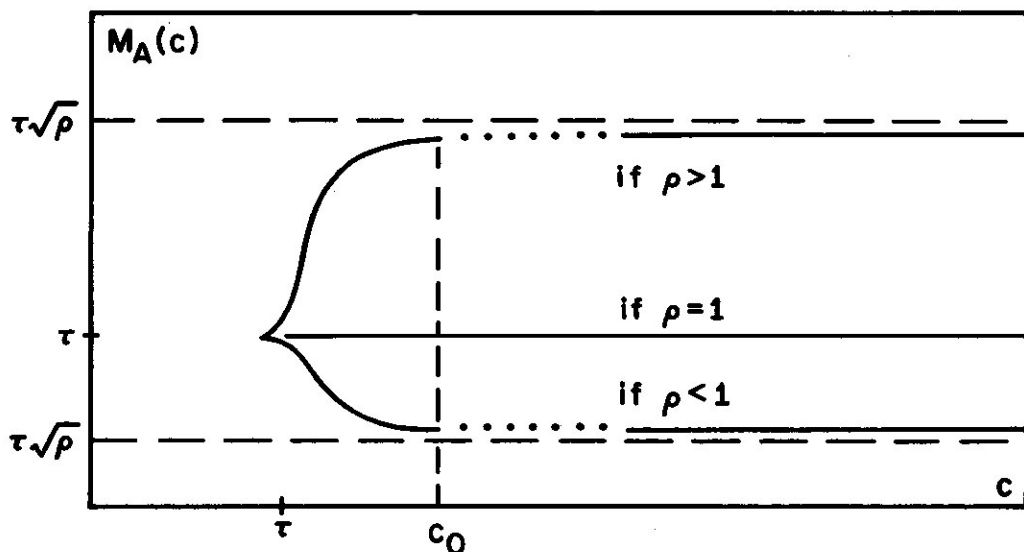
Theorem 1 $M_A(c)$ is a differentiable function of $c > \tau$ which is strictly decreasing for $\varrho < 1, \tau < c < c_0$ and strictly increasing for $\varrho > 1, \tau < c < c_0$ where c_0 is given by $T(c_0) = 1/(\alpha_1^2 k_B)$ with $T(c)$ given implicitly by (5). In addition, $M_A(c)$ satisfies

(i) $\lim_{c \to \tau^+} M_A(c) = \tau$

(ii) $\lim_{c \to \infty} M_A(c) = \tau \sqrt{\varrho}$

where $\varrho = r_B^2 k_A / r_A^2 k_B$.

Proof. It follows from the differentiability of $T(c)$ that $M_A(c)$ is a differentiable and continuous function of $c > \tau$. By (4),

$$(6) \quad M_A(c) = c \left(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \, \alpha_j^2} \exp\left(-\alpha_j^2 k_B \varrho \, T(c)\right)\right), \, c > \tau$$

where the explicit dependence on c can be removed using (5), that is, by replacing c by

$$c = \tau / \left(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \, \alpha_j^2} \exp\left(-\alpha_j^2 k_B \, T(c)\right)\right).$$

Then (6) becomes

$$(7) \quad M_A(c) = F(T(c)) = \tau \; \frac{\left(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \, \alpha_j^2} \exp\left(-\alpha_j^2 k_B \varrho \, T(c)\right)\right)}{\left(1 - \sum_{j=1}^{\infty} \frac{4}{r_B^2 \, \alpha_j^2} \exp\left(-\alpha_j^2 k_B \, T(c)\right)\right)}$$

The remaining properties of $M_A(c)$ are determined from $F(T)$. $F(T)$ can be written in the form

$$F(T) = \tau \; \frac{\sum\limits_{j=1}^{\infty} \frac{1}{\alpha_j^2} \left(1 - \exp\left(-\alpha_j^2 k_B \varrho \, T\right)\right)}{\sum\limits_{j=1}^{\infty} \frac{1}{\alpha_j^2} \left(1 - \exp\left(-\alpha_j^2 k_B T\right)\right)}$$

If we differentiate $F(T)$ w.r.t. $T > 0$, then $F'(T) \gtrless 0$ leads to the corresponding inequality

$$\frac{\varrho T \sum\limits_{j=1}^{\infty} \exp(-\alpha_j^2 k_B \varrho T)}{\sum\limits_{j=1}^{\infty} (1-\exp(-\alpha_j^2 k_B \varrho T))/\alpha_j^2} \gtrless \frac{T \sum\limits_{j=1}^{\infty} \exp(-\alpha_j^2 k_B T)}{\sum\limits_{j=1}^{\infty} (1-\exp(-\alpha_j^2 k_B T))/\alpha_j^2}$$

or, denoting the R.H.S. by $\phi(T)$ to

$$\phi(\varrho T) \gtrless \phi(T).$$

Now computing

$$\phi'(T) = \frac{\sum\limits_{j=1}^{\infty} (1-\alpha_j^2 k_B T) \exp(-\alpha_j^2 k_B T)}{\sum\limits_{j=1}^{\infty} (1-\exp(-\alpha_j^2 T))/\alpha_j^2}$$

$$-\frac{T \sum\limits_{j=1}^{\infty} \exp(-\alpha_j^2 T)}{(\sum\limits_{j=1}^{\infty} (1-\exp(-\alpha_j^2 T))/j^2)^2}$$

it follows easily that

$$T \geq 1/(\alpha_1^2 k_B)$$

$$\Rightarrow \phi'(T) < 0$$

$$\Rightarrow \phi(\varrho T) \gtrless \phi(T) \text{ for } \varrho \lessgtr 1$$

$$\Rightarrow F'(T) \gtrless 0 \quad \text{for } \varrho \lessgtr 1$$

$$\Rightarrow \frac{d}{dc} M_A(c) = F'(T) \, T'(c) \lessgtr 0 \text{ for } \varrho \lessgtr 1$$

(recall, $T'(c) < 0$ for all $c > \tau$).

Therefore

$$(8) \quad \text{sgn} \left[\frac{d}{dc} M_A(c)\right] = \begin{cases} -1 \text{ for } \varrho < 1, \tau < c < c_0 \\ +1 \text{ for } \varrho > 1, \tau < c < c_0 \end{cases}$$

since $T(c) \geq T(c_0)$ for all $\tau < c \leq c_0$ (see Fig. 1, $\tau < c < c_0$), where c_0 is given by $T(c_0) = 1/(\alpha_1^2 k_B)$ and $T(c_0)$ is given implicitly by (5).

Unfortunately, no straightforward procedure has yet been found to prove that (8) is true for all $c > \tau$.

The first of the required limits is a consequence of (7) and the fact that $\lim_{c \to \tau^+} T(c) = \infty$. Thus

$$\lim_{c \to \tau^+} M_A(c) = \lim_{T \to \infty} F(T) = \tau.$$

For the second limit we use L'Hospital's rule. Thus,

$$\lim_{c \to \infty} M_A(c) = \lim_{T \to 0^+} F(T)$$

$$= \lim_{T \to 0^+} \tau \varrho \; \left(\frac{\sum\limits_{j=1}^{\infty} \exp(-\alpha_j^2 k_B \varrho T)}{\sum\limits_{j=1}^{\infty} \exp(-\alpha_j^2 k_B T)} \right)$$

and the required limit follows from the well known result (Watson 1952) that for large N

$$\alpha_j r_B \, \varepsilon \, (\pi (j - \tfrac{1}{4}), (\pi (j + \tfrac{1}{4}))) \quad \text{for all } j \geq N \text{ and from the result}$$

$$\int_0^{\infty} e^{-x^2} dx = \sqrt{\pi}/2$$

This proves the theorem.

The following example is intended to give a more precise picture of the behavior of $M_A(c)$ (cf Fig 1) for a particular set of values for k_A, k_B, r_A, r_B, and τ and suggests one area in which the results obtained here might be applied. Since little is known regarding the prediction of values for the mass diffusion coefficients for particular substances and the corresponding toxic chemicals, a more specific example would require some experimentation to determine values for these diffusion coefficients and τ. Here values for these constants have been assigned (International Critical Tables) on the basis of what one might reasonably expect from the types of substances involved. However, it should be pointed out that an approximation to the value k for a particular substance and corresponding toxic chemical can be obtained directly using formula (3). Thus, if the given substance (which is assumed to be cylindrical in shape with radius r_0) is immersed for a fixed time t_0 in a solution containing a known molar concentration c of the toxic chemical and if after time t_0, the total amount (number of moles) c_0 of the chemical which has diffused into a

representative segment of unit length can be determined, then (3) gives

$$c_0 = \pi r_0^2 M(t_0, r_0, c) = \pi r_0^2 c (1 - \sum_{j=1}^{\infty} \frac{4}{r_0^2 \lambda_j^2} \exp(-\lambda_j^2 k t_0))$$

which can be solved for k.

An example, some recent studies off the coast of Nova Scotia, have involved the cultivation of a commercially valuable seaweed (*Gracilaria* sp) which is densely intertwined by an epiphyte (*Enteromorpha intestinalis*). One process which might be used to eliminate the effect of the epiphyte without actual physical separation is the immersion of the entangled mass in a solution containing a chemical which is toxic to the epiphyte and possibly also toxic to the valuable component. A choice of the toxic chemical might by $CuSO_4$. Approximating the seaweed and epiphyte by cylinders A and B of radius $r_A = 0.4$ cm. and $r_B = 0.025$ cm. respectively and setting

$$k_A = k_B = .35 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$

$$\tau = .00005 \text{ gm. moles./cm.}^3$$

gives from (5) and (6),
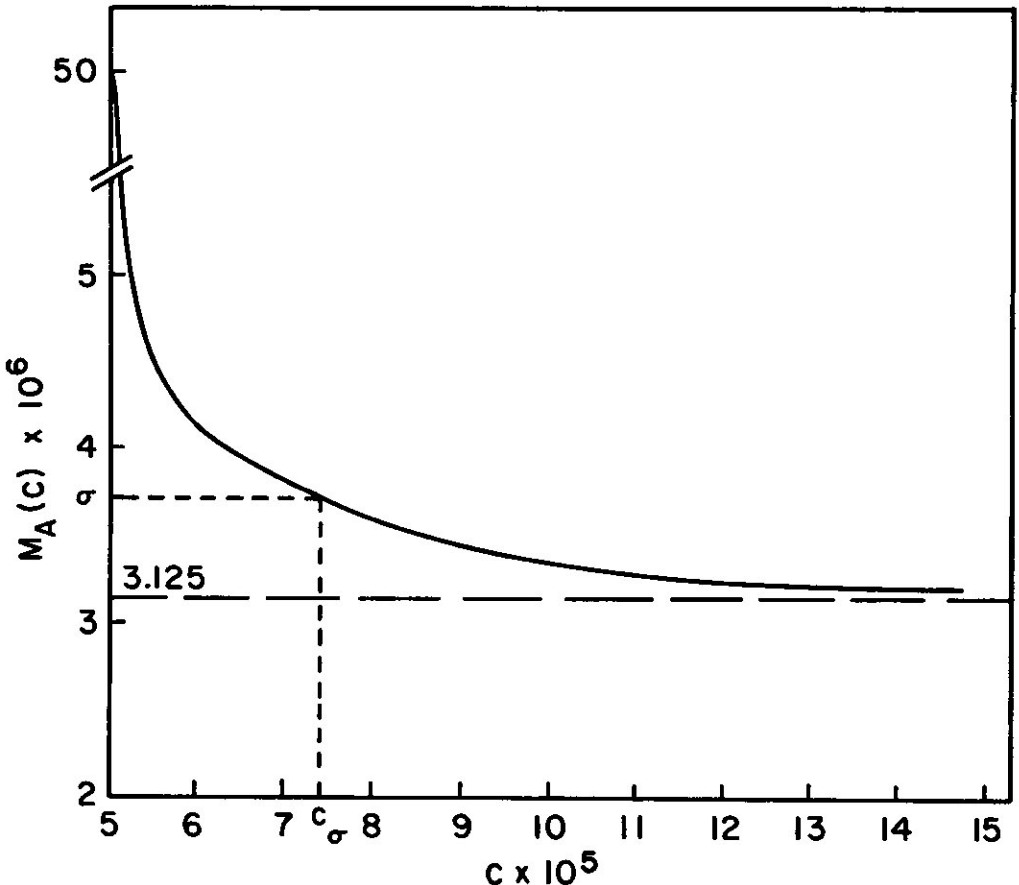
If the sensitivity of the valuable life form σ (the minimum mean molar concentration of the toxic chemical which produces permanent damage) is known and satisfies $\sigma \geq t$, then there is considerable freedom in the choice of c and one would choose it so as to attain a small concentration of the toxic material in the host. If, however, σ satisfies, $\sqrt{\varrho}\,\tau < \sigma < \tau$, then there is a $c = c_\sigma$ such that $M_A(c) < \sigma$ for all $c > c_\sigma$ and for such c the host will absorb a sublethal amount of toxicity.

Discussion

The main result of our analysis - the general description of $M_A(c)$ as a function of c - suggests that the best strategy in the application of toxicity to the removal of unwanted life forms depends on whether $\varrho < 1$ or $\varrho > 1$. In the first case a brief exposure to a high concentration is indicated. Of course an upper limit on that concentration will usually be imposed by technical and other considerations, the obvious one resulting from the difficulty of controlling extremely brief exposures. More importantly, since $M_A(c)$ represents an average concentration it is possible that parts of the host plant may temporarily receive a lethal dose of the chemical. Since upon removal from immersion the averaging of concentration occurs rather rapidly, it seems safe to assume that in most cases little damage will be inflicted on the host. When this is not so then an additional, empirically determinable, upper limit for c would have to be imposed.

In the second case, *ie* $\varrho > 1$, a concentration close to but not substantially greater than τ would be indicated. Here again it might be necessary to avoid inordinately long exposures as impractical.

Finally, it must be remembered that ours is an idealized model in which the hypothese of the geometric shape and the type of diffusion (absence of reaction between the chemical and the plants *etc*) are essential. This notwithstanding it may still be feasible to make use of it in situations where there is reason to believe that these hypotheses are not entirely invalid. In such cases it would be necessary to run a series of preliminary experiments in which the constants of the model would be approximately determined. These in turn could be used to fit a graph of $M_A(c)$ as a function of c so as to enable the experimenter to determine the procedure he would like to adopt.

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