applicable to spores dropping from 95% of the sporophores. The kind and size of fruit or similar plant part, while affecting the size of the sporophores, did not exert a similar influence upon the spores. The size of the spores remained very constant when a strain of *Coprinus lagopus* from *Agropyron smithii* was successively cultured on glumes of *A. cristatum*, seedballs of beets, and fruits of New Zealand spinach.

The size of the sporophores, the constancy of spore measurements, the ease of transfer of the fungus from fruits of one plant species to those of others, and the failure of the large edible species to grow upon fruits indicate that the harefoot mushroom is the species of *Coprinus* that has been observed at Geneva, New York, and at State College, New Mexico.

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The Validity of the Use of Tracers to Follow Chemical Reactions

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In the use of tracers, either stable or radioactive, it is important to know how much difference in chemical properties there is between the isotopic molecules. The thermodynamic properties of systems containing isotopic molecules in chemical equilibrium can be calculated by simple formulae (*1*).

Recently Urey (*4*) tabulated the equilibrium constants of various exchange reactions for isotopic compounds of elements in the first row of the periodic table, as well as the halogens. In many cases the isotopic molecules are not in equilibrium with respect to various exchange reactions. In such cases it is important to know whether or not the specific activity of the product of some chemical transformation of the substrate isotopic molecules is the same as the initial specific activity. If the initial specific activity is known, then the specific activity of the product can be calculated by integration of the rate equations for the respective reactions. In this paper we shall neglect changes in the specific activity by radioactive decay or other nuclear processes. These corrections can be made by the use of the equations of radioactive transformation (*3*).

We shall consider the general case where the isotopic molecules A_1 and A_2 react either with each other or with other molecular species B, C, etc. to give the isotopic molecules X_1 and X_2 amongst the products. Frequently the isotopic molecule A_2 may be a mixed molecule and contain two different isotopes of one element in chemically equivalent positions, e.g., CH_3D. A mixed molecule may react in one of two ways. It may give the products X_2, Y, etc. or X_3, Y_2, etc. In most cases X_3 will be the same as X_1 but we shall retain the symbol X_3 to avoid confusion. If the isotopic molecule A_2 is present only in tracer amounts, then the reaction will always be first order in A_2. If a_1^0 and a_2^0 are the initial concentrations of A_1 and A_2 respectively, then the amounts of X_1, X_2 and X_3, dx_1, dx_2 and dx_3 respectively, formed in a time interval dt at the time t by reaction according to the following equations

$$A_1 + B + C + \ldots \xrightarrow{k_1} X_1 + Y_1 + \ \ldots \tag{1}$$

$$A_2 + B + C + \ldots \xrightarrow{k_2} X_2 + Y_1 + \ \ldots \tag{2}$$

$$A_2 + B + C + \ldots \xrightarrow{k_3} X_3 + Y_2 + \ \ldots \tag{3}$$

are

$$dX_1 = k_1(a_1^0 - lX_1)^n(B)^b(C)^c \ldots dt \tag{4}$$

$$dX_2 = k_2(a_2)(a_1^0 - lX_1)^{n-1}(B)^b(C)^c \ldots dt \tag{5}$$

$$dX_3 = k_3(a_2)(a_1^0 - lX_1)^{n-1}(B)^b(C)^c \ldots dt \tag{6}$$

where $a_2 = a_2^0 - mX_2 - nX_3$.

The coefficients l, m, and n are small numbers which are derived from the stoichiometry of the reaction.

From equations (5) and (6) it follows that

$$dX_3 = (k_3/k_2)\,dX_2 \tag{7}$$

and

$$X_3 = (k_3/k_2)X_2 \tag{8}$$

Thus

$$a_2 = a_2^0 - (m + nk_3/k_2)X_2 \tag{9}$$

From equations (4), (5), and (9) we get

$$\frac{k_2}{k_1}\int_0^{x_1}\frac{dX_1}{(a_1^0 - lX_1)} = \int_0^{x_2}\frac{dX_2}{a_2^0 - (m + nk_3/k_2)X_2} \tag{10}$$

Integration of equation (10) gives

$$\frac{X_2}{a_2^0} = \frac{1 - (1 - lX_1/a_1^0)^{k_2(m+nk_3/k_2)/k_1l}}{m + nk_3/k_2} \tag{11}$$

If we define the specific activity of the product as $N_x = X_2/X_1$ and the initial specific activity as $N_{A^0} = a_2^0/a_1^0$, then

$$\frac{N_X}{N_{A^0}} = \frac{1 - (1 - lX_1/a_1^0)^{k_2(m+nk_3/k_2)/k_1l}}{(m + nk_3/k_2)X_1/a_1^0} \tag{12}$$

For small amounts of conversion, $lX_1/a_1 << 1$,

$$\frac{N_X}{N_{A^0}} = k_2/k_1 \tag{13}$$

At complete conversion, $X_1 = a_1/l$,

$$\frac{N_X}{N_{A^0}} = \frac{l}{m + nk_3/k_2} \tag{14}$$

In a forthcoming publication from this laboratory (*2*) a general equation is derived for the ratio of the rate constants for reactions involving isotopic molecules. For reactions which occur at room temperature and above, the ratio of the rate constants can be expressed approximately by the equation

$$\frac{k_1 s_1{\ddagger} s_2}{k_2 s_2{\ddagger} s_1} = \left(\frac{m_2^*}{m_1^*}\right)^{1/2}\left(1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n^1-6} G(u_i{\ddagger})\Delta u_i{\ddagger}\right) \tag{15}$$

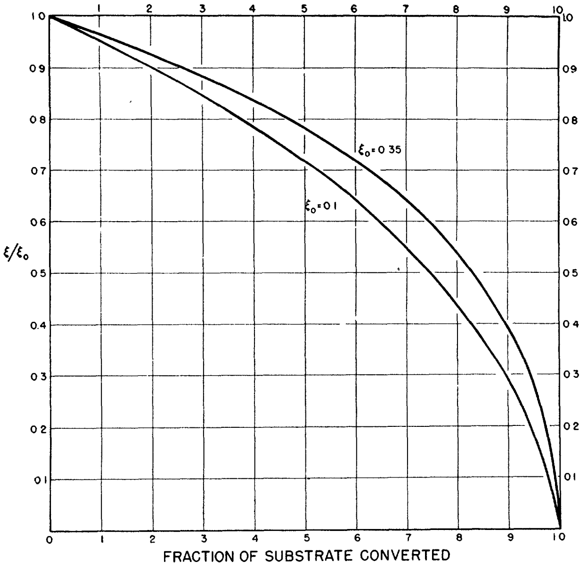

FIG. 1. Isotope effect in a chemical reaction involving isotopic molecules reacting with nonidentical rate constants vs. amount of reaction.

where the subscripts 1 and 2 refer to the light and heavy isotopic molecules respectively. A similar equation holds for the ratio k_3/k_2. The righthand side of equation (15) gives the amount that a simple statistical consideration must be corrected by. The symbol ‡ refers to a property of the activated complex in the reaction. The quantity s is the symmetry number; m^* is the effective mass of the activated complex along the reaction coordinate; $G\ (u)$ is a function of the normal vibrations of the molecule (*1*); $\Delta u_i = \frac{hc}{kT}\ (\omega_{i_1} - \omega_{i_2})$ where ω_i is a normal frequency of the molecule.

It is important to see how the specific activity of the product, N_X, compares with the initial specific activity, N_{A_0}, as a function of the amount of reaction. We shall consider the special case, which is one of wide generality, where $k_3 = 0$, and l, m, and the ratio $s_1 ‡ s_2/s_2 ‡ s_1$, are each unity. We shall now define ε and ε_0 by the relations

$$\frac{N_X}{N_{A_0}} = 1 - \varepsilon \qquad (16)$$

$$\frac{k_2}{k_1} = 1 - \varepsilon_0 \qquad (17)$$

In Fig. 1 curves are drawn for $\varepsilon/\varepsilon_0$ as a function of the amount of reaction for two values of ε_0. It is clear that for complete conversion of the substrate, $X_1/a_1 = 1$, $\varepsilon = 0$. This holds independently of the value of ε_0. For $\varepsilon_0 = 0.35$ the specific activity of the product is 4% different from the initial specific activity, even at 99% conversion.

We shall show presently that apart from the isotopes of hydrogen, the values of ε_0 are *usually* so small that there is little error made by assuming that it is zero. By comparison of equations (15) and (17) it is seen that ε_0 is equal to the deviation of the reciprocal of the righthand side of equation (15) from unity. The function $G\ (u_i)$ as well as Δu_i is always positive (*1*). $G\ (u_i) = \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1}$ and its value will fall between 0 and 1/2. Thus the maximum value of the ratio $k_1 s_1 ‡ s_2/k_2 s_2 ‡ s_1$ will occur when $\Sigma_1\ G\ (u_i ‡)\ \Delta u_i ‡$ is equal to zero. This corresponds to the physical situation where the isotopic atoms are essentially free, unbound chemically, in their respective activated complexes. The values of $\Sigma_i\ G\ (u_i)\ \Delta u_i$ for a considerable number of isotopic molecules of the light elements have been tabulated (*4*). It is not difficult to calculate additional values for other elements. Thus we can arrive at estimates for upper limits of the ratio of the rate constants for reactions involving many of the common tracers. These are tabulated in Table 1.

It is clear that the maximum isotope effects in the rates of reaction decrease rapidly as one goes to isotopic compounds of higher atomic number. Of the common tracers, H^2, H^3, C^{13}, and C^{14}, may require special consideration in their use in nonequilibrium systems. There are very few reactions of carbon compounds in which the activated complex contains even loosely bound carbon atoms. In fact, $\Sigma_i\ G\ (u_i ‡)\ \Delta u_i ‡$ will usually be approximately equal to $\Sigma_i\ G\ (u_i)\ \Delta u_i$. If we define ε_0^1 by the relation

$$k_1 s_1 ‡ s_2/k_2 s_2 ‡ s_1 = 1 + \varepsilon_0^1 \qquad (18)$$

we may anticipate that in any reaction involving C^{13} or C^{14} the values of ε_0^1 will not be greater than .12 and .25 respectively at room temperature. In any case the contribution of $\left(\frac{m_2}{m_1}\right)^{1/2}$ to ε_0^1 can usually be calculated and ε_0^1 can be approximated by setting $\Sigma_i\ G\ (u_i)\ \Delta u_i = \Sigma_i^1\ G\ (u_i ‡)\ \Delta u ‡$. This amounts to calculating the relative collision frequencies of gases. If an accuracy of this order of magnitude will suffice, then it is safe to assume that C^{13} and C^{14} are faithful tracers in both equilibrium

TABLE 1

ESTIMATED MAXIMUM RATIOS IN SPECIFIC RATE CONSTANTS AT 25° C

Stable isotope	Tracer isotope	$k_1 s_2 s_1 ‡/k_2 s_1 s_2 ‡$
H^1	H^2	18
H^1	H^3	60
Li^6	Li^7	1.1
Be^9	Be^7	1.15
Be^9	Be^{10}	1.08
B^{10}	B^{11}	1.3
C^{12}	C^{13}	1.25
C^{12}	C^{14}	1.5
N^{14}	N^{15}	1.14
N^{14}	N^{13}	1.14
N^{14}	N^{16}	1.25
O^{16}	O^{18}	1.19
F^{19}	F^{18}	1.25
N^{23}	Na^{22}	1.03
N^{23}	Na^{24}	1.03
Mg^{24}	Mg^{27}	1.08
P^{31}	P^{32}	1.02
S^{32}	S^{35}	1.05
Cl^{35} (natural abundance)	Cl^{36}	1.03
Cl^{37} (natural abundance)	Cl^{38}	1.14
Ca^{40}	Ca^{45}	1.08
I^{127}	I^{131}	1.02

and nonequilibrium systems. In quantitative work it will be necessary to determine $\varepsilon_0{}^1$ experimentally or to estimate it theoretically. In many experiments an appreciable fraction of the substrate is allowed to react. From equation (12) and Fig. 1 it is obvious that the isotope effect decreases with the amount of reaction and thus the isotope effects in the use of C^{13} and C^{14} will be even smaller than .12 and .25 respectively.

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Shielding of Syringes Used for Injecting Radioactive Solutions[1]

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The delayed general effects of total body radiation, intermittant, subclinical, and of no apparent immediate significance, have had serious consequences for some radiologists and radium therapists (*3, 5*). The introduction of radioisotope therapy offers additional sources of exposure to these persons since they are, in general, best trained to handle the new tools. Similarly, lesions appearing on the hands of some radiologists later in life indicate the latent effects of localized ionizing radiations (*2, 4*).

During an investigation of the biological significance of radiogallium (Ga^{72}), it was found that for protection against the strong gamma spectrum (2.5 mev) of this isotope some type of remote central apparatus or some dense shield over a standard syringe was necessary. Because of the difficulty of using a remote control injection apparatus clinically, there have been designed and constructed two types of shields to be placed over syringes of standard stock sizes.

Fig. 1 presents details of construction of a two-piece Lucite shield adequate to protect the hands of persons injecting alpha emitters and beta emitters having energies less than 2 mev. This type of shield offers protection against the following isotopes: C^{11}, C^{14}, F^{18}, P^{32}, S^{35}, Cu^{64}, and Sr^{89}. It is emphasized that the isotopes listed here emit no gamma radiation. For those which do, the metal shield described in Fig. 2 must be used.

The design of the Lucite shield (Fig. 1) is similar to that described by Anthony and Norris (*1*), the essential difference being in arrangment for locking the needle in place by tightening the threaded top. This prevents loosening of the needle and subsequent leakage, which is a serious hazard when very active or long half-life isotopes are being injected.

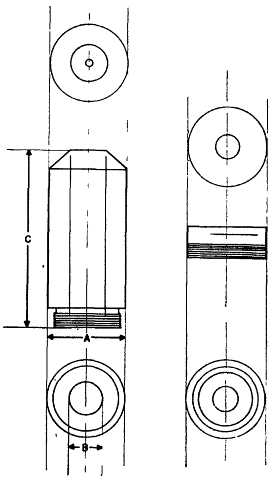

FIG. 1. Plastic syringe holder.

Dimensions:		A	B	C
Size	$\frac{1}{4}$ cc.	$1\frac{1}{2}$ in.	$\frac{5.5}{16}$ in.	$3\frac{11}{16}$ in.
"	1 "	1 "	$\frac{3}{8}$ "	$2\frac{15}{16}$ "
"	5 "	$1\frac{3}{16}$ "	$\frac{10.5}{16}$ "	4 "

Fig. 2 presents details of a metal syringe shield which has been constructed in sizes to fit all standard syringes from 1/4 cc to 30 cc. This piece of apparatus is made by filling an aluminum tube with a commercially available lead alloy (type metal—82 Pb, 12 Sb, 4 Sn), and machining to the dimensions shown in Fig. 2. The slot, which is milled in the metal case, permits observation of liquid levels, absence of air bubbles, etc. To facilitate these observations, a dark colored solution is preferable, and the inside surface of the shield is coated either with

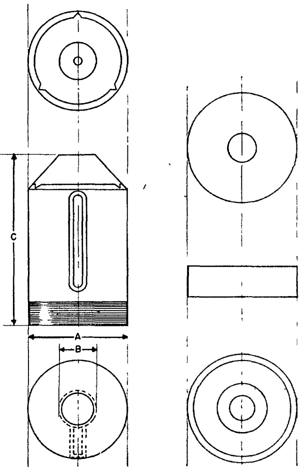

FIG. 2. Metal (Pb) syringe holder.

Dimensions:		A	B	C
Size	$\frac{1}{4}$ cc.	$1\frac{1}{2}$ in.	$\frac{5}{16}$ in.	$3\frac{1}{4}$ in.
"	1 "	$1\frac{1}{2}$ "	$\frac{3}{8}$ "	$4\frac{3}{16}$ "
"	5 "	2 "	$\frac{3}{4}$ "	$3\frac{3}{4}$ "
"	10 "	2 "	$\frac{7}{8}$ "	$4\frac{3}{4}$ "
"	20 "	$2\frac{1}{2}$ "	1 "	$5\frac{1}{2}$ "
"	30 "	3 "	$1\frac{1}{8}$ "	$6\frac{3}{4}$ "

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[1] The opinions or assertions contained herein are the private ones of the writers and are not to be construed as official or reflecting the views of the Navy Department or the naval service at large.