TRANSIENT EFFECTS IN THE DISTRIBUTION OF CARBON-14 IN NATURE

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A prerequisite for accurate dating by means of carbon-14 is the existence of a steady state in the specific activity of the carbon in the atmosphere. The studies[1] which have been made of carbon activity supported the view that there was a state of dynamic equilibrium in the carbon exchange between natural reservoirs. A disturbance in this state is known to arise from the discharge of the combustion products from fossil fuels into the atmosphere. The resulting dilution of the specific carbon activity of the atmosphere by the addition of this inert carbon dioxide (the Suess effect) has been discussed recently elsewhere,[2,3] and will not be considered here. Of present interest is how a disturbance in the absolute amount of carbon-14 in a natural reservoir such as the atmosphere disappears through exchange with other reservoirs. There has been such a disturbance in the world equilibrium of carbon-14 by the explosion of nuclear bombs. The redistribution of the excess radiocarbon produced by nuclear explosions may be calculated as a function of time from the fundamental transient solutions which are presented here. These fundamental solutions are those obtained for an instantaneous increment of carbon-14 introduced into the stratosphere or the troposphere. The net result of all nuclear explosions to date may then be determined by summation of such solutions when the intensity and date of the explosions are given. This summation has been carried out by the authors and is presented elsewhere.

The steady state conditions for ordinary carbon and radiocarbon determine exchange rate constants for radiocarbon. Arnold and Anderson[4] have evaluated these constants from the steady state relations for a two and for a three reservoir model of the natural carbon reservoirs. Their "upper reservoir" includes the atmosphere, land-life, and humus; a second reservoir is the oceans. Their three reservoir model is formed by a separation of the oceans reservoir into two portions. The steady state behavior of a more elaborate model, consisting of five reservoirs, has been examined by Craig.[5] The reservoirs in this model are: the atmosphere, the land biosphere, the land humus, the ocean mixed layer, and the deep oceans.

The transient solution which is developed here uses Craig's reservoir model with a slight extension. This extension consists in a division of the atmosphere into two reservoirs: the stratosphere and the troposphere. The justification for the development of this six reservoir model comes from the possibility that experimental observations of the carbon-14 transients which have been produced may give further information on the effective exchange rates between troposphere and stratosphere.

Steady State Relations for the Six Reservoir Model.—The reservoir model is shown schematically in Figure 1. The conditions for a steady state in the distribution of carbon-12 are expressed directly in terms of the rates of efflux J_{ik} of carbon-12 from reservoir i to reservoir k. Steady state in the stratosphere gives, for example,
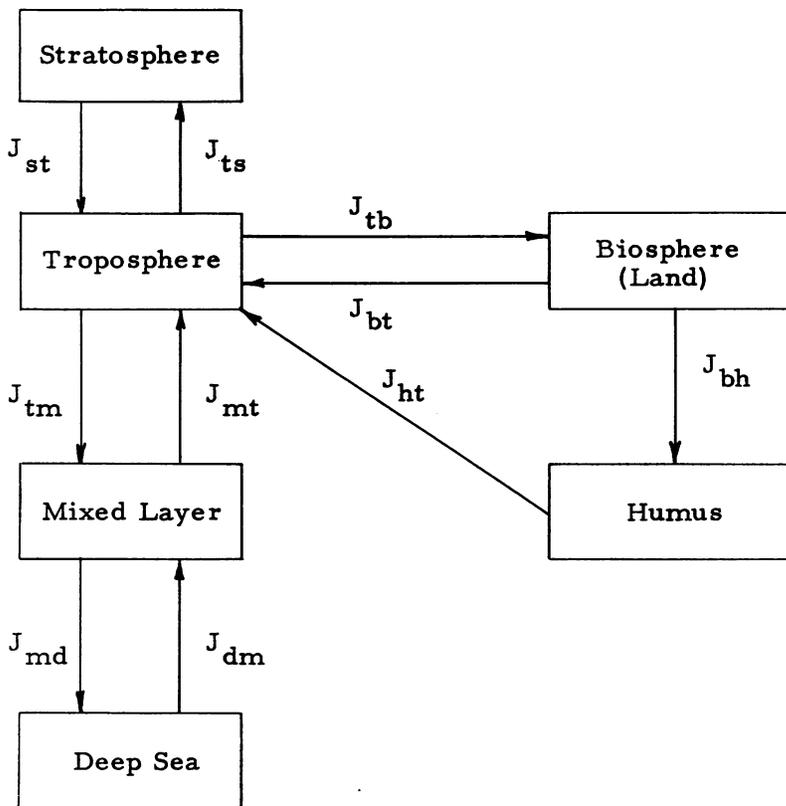
$$-J_{st} + J_{ts} = 0, \tag{1}$$

FIG. 1.—Diagram of the model of the carbon reservoirs in the exchangeable system.

or in the troposphere

$$-J_{ts}-J_{tb}-J_{tm}+\ J_{st}+\ J_{bt}+\ J_{mt}+\ J_{ht}=0. \tag{2}$$

The remaining four steady state relations are of similar homogeneous form. If now j_{ik} is the steady state flow of carbon-14 from reservoir i to reservoir k, then one has

$$\frac{j_{ik}}{J_{ik}}\ =\ \alpha_i\,\frac{n_i}{N_i}, \tag{3}$$

where n_i is the amount of carbon-14 in reservoir i, N_i is the amount of carbon-12 in reservoir i, and α_i is the isotopic fractionation factor which takes account of the effect of isotopic mass difference in the transport process. Equation (3) is a relation of general validity between the flow rates of two isotopic species and their reservoir contents. The factor α_i is of course unity if the exchange process between i and k is not affected by the isotopic mass difference, and is close to unity otherwise. The α_i's are found[6] from the experimental observations on the isotopic fractionation factors α_i' for carbon-13 so that, if

$$\alpha_i'=1+\delta_i',$$

then one has

$$\alpha_i = \alpha_i'^2 \cong 1 + 2\delta_i'.$$

The exchange rate constant, k_{tr}, for the transport of carbon-14 from reservoir i to reservoir r is defined by the relation

$$j_{tr} = n_i k_{tr}, \tag{4}$$

and it follows from Equation (3) that

$$k_{tr} = \alpha_i \frac{J_{tr}}{N_i}. \tag{5}$$

It is apparent from Equation (5) that the radiocarbon exchange rate constants are constants only if the amounts and transport mechanisms of ordinary carbon are fixed.

The determination of the radiocarbon exchange rate constants is completed if, in addition to the information given in the equations of the type (1) and (5), one uses the conditions for a steady state of carbon-14 in all the reservoirs. These steady state relations differ from those for carbon-12 since there is a loss of carbon-14 in each reservoir i at the radioactive decay rate λn_i. These decay losses in all the reservoirs must be exactly compensated by the production of carbon-14 from cosmic ray neutrons absorbed in atmospheric nitrogen. This source will be taken here as appearing entirely in the stratosphere reservoir. The steady state relations analogous to Equations (1) and (2) for the stratosphere and the troposphere are

$$\lambda Q - \lambda n_s - j_{st} + j_{ts} = 0, \tag{1'}$$

$$-\lambda n_t - j_{ts} - j_{tb} - j_{tm} + j_{st} + j_{bt} + j_{mt} + j_{ht} = 0, \tag{2'}$$

where Q is the total amount of carbon-14 in all the reservoirs in the steady state

$$Q = n_s + n_t + n_b + n_h + n_m + n_d. \tag{6}$$

The exchange rate constants are readily found to be the following:

$$k_{st} = \frac{\lambda(Q - n_s)/N_s}{n_s/N_s - n_t/N_t}; \qquad k_{ts} = \frac{\lambda(Q - n_s)/N_t}{n_s/N_s - n_t/N_t};$$

$$k_{tb} = \frac{\lambda}{n_t/n_b - \alpha_t N_t/\alpha_b N_b};$$

$$k_{bt} = \frac{\lambda \alpha_t N_t/\alpha_b N_b}{n_t/n_b - \alpha_t N_t/\alpha_b N_b} - \frac{\lambda}{n_b/n_h - \alpha_b N_b/\alpha_h N_h};$$

$$k_{md} = \frac{\lambda \alpha_d/\alpha_m}{\alpha_d n_m/\alpha_m n_d - N_m/N_d}; \qquad k_{dm} = \frac{\lambda N_m/N_d}{\alpha_d n_m/\alpha_m n_d - N_m/N_d};$$

$$k_{ht} = \frac{\lambda N_b/N_h}{\alpha_h n_b/\alpha_b n_h - N_b/N_h}; \qquad k_{bh} = \frac{\lambda}{n_b/n_h - \alpha_b N_b/\alpha_h N_h};$$

$$k_{mt} = \frac{\lambda(n_m/n_t + n_d/n_t)}{\alpha_m N_m/\alpha_t N_t - n_m/n_t};$$

$$k_{tm} = \frac{\lambda(n_m/n_t + n_d/n_t)(\alpha_m N_m)/(\alpha_t N_t)}{\alpha_m N_m/\alpha_t N_t - n_m/n_t}.$$

For the numerical evaluation of these exchange rate constants, the amounts of exchangeable carbon, N_i, in the various reservoirs were taken to have the values given by Craig[5] except that the amount in the atmospheric reservoir was divided so as to put 22 per cent in the stratospheric reservoir and 78 per cent in the tropospheric reservoir. These values, which are given in Table 1, are somewhat lower than those presented by other authors.[1, 4] In the calculation of the k_{ir}'s, however, only ratios of amounts enter so that such differences need not be serious. Table 1 also sum-

TABLE 1

Reservoir	Carbon Content N_i, gm/cm²	Carbon-14 Isotopic Fractionation Factor, α_i	Specific Activity, R_i	Carbon-14 Content, n_i, (gm/cm²) × 10¹²
Stratosphere	0.0277	1.037	$1.037\,R_w$	0.0356
Troposphere	0.983	1.037	$1.037\,R_w$	0.126
Land biosphere	0.060	1.000	$1.000\,R_w$	0.0744
Land Humus	0.215	1.000	$0.940\,R_w$	0.251
Mixed layer	0.151	1.047	$1.000\,R_w$	0.187
Deep Seas	7.32	1.047	$0.902\,R_w$	8.187

Carbon contents are expressed per unit area of the earth's surface (5.1×10^{18} cm²). R_w has been taken to be 1.24×10^{-12}.

marizes the isotopic fractionation factors α_i and the specific activities $R_i = n_i/N_i$. Craig's data determine all the values tabulated except those for R_h and R_d. These have been calculated, following a suggestion made by Craig, by taking an average age of 500 years for the carbon-14 in land humus and an average age of 1200 years for the carbon-14 in the deep seas. It follows that

$$R_h = 1.000e^{-500/8030}R_w = 0.940R_w;$$
$$R_d = 1.047e^{-1200/8030}R_w = 0.902R_w;$$

where the mean lifetime, $1/\lambda$, of carbon-14 has been taken to be 8030 years, and R_w is the specific activity of modern wood.[7]

The exchange rate constants are found to have the following values in (years)$^{-1}$:

$$k_{dm} = 1.15 \times 10^{-3}; \qquad k_{bh} = 6.99 \times 10^{-1};$$
$$k_{md} = 5.55 \times 10^{-2}; \qquad k_{mt} = 1.18 \times 10^{-1};$$
$$k_{ht} = 1.95 \times 10^{-3}; \qquad k_{tm} = 1.84 \times 10^{-1}.$$

With the data given in Table 1, the remaining four exchange rate constants are infinite. While, for example, k_{tb} and k_{bt} have infinite values, their ratio has a definite value

$$\frac{k_{bt}}{k_{tb}} = \frac{\alpha_t N_t}{\alpha_b N_b}. \tag{7}$$

This behavior means, of course, that any increment in exchangeable radio carbon in either the troposphere or the biosphere is instantly distributed through the two reservoirs in such a way as to preserve the ratio $\alpha_t N_t/\alpha_b N_b$. In this sense, this combination is not separable into two reservoirs. The separation does have significance in that the exchange processes with adjacent reservoirs are not the same as for the nonseparated model. In the treatment of the transient problem which follows, the troposphere and biosphere will be kept distinct, and k_{bt} with k_{tb} will be made infinite in the final results with the fixed ratio (7).

A similar situation obtains for k_{st} and k_{ts}.   The data of Table 1 give $n_s/N_s = n_t/N_t$ so that the remarks just made for the troposphere-biosphere combination apply also to the stratosphere-troposphere combination.   This latter combination will, however, be treated differently.   There is evidence from analysis of fallout data[8] that the exchange between the stratosphere and the troposphere is not instantaneous. There is, however, considerable uncertainty about this exchange rate and there are, in addition, indications that this exchange has a latitude dependence.   For these reasons, the results of the solution of the transient problem will be given for three different values of k_{st}: 0.1, 0.2, ∞ (years)$^{-1}$.   For all of these values, the ratio k_{ts}/k_{st} has the fixed value 0.282.

Extension of the Model to Nonequilibrium Conditions.—In a nonequilibrium situation the amount of carbon-14 in the i'th reservoir will be denoted by $n_i^*(t)$ where the argument t denotes the time.   The symbols n_i will continue to denote the constant equilibrium values as used in the preceding section.   Then in place of equations such as (1') and (2') for the stratosphere and troposphere, one has

$$\frac{dn_s^*}{dt} = \lambda Q - \lambda n_s^* - n_s^* k_{st} + n_t^* k_{ts}, \tag{8}$$

$$\frac{dn_t^*}{dt} = -\lambda n_t^* - n_t^* k_{ts} - n_t^* k_{tb} - n_t^* k_{tm} + n_s^* k_{st} + n_b^* k_{bt} + n_m^* k_{mt} + n_h^* k_{ht}, \tag{9}$$

where as before Q is given by Equation (6).   It is somewhat more convenient to use the variables

$$\begin{aligned} x &= n_s^* - n_s; & y &= n_t^* - n_t; & z &= n_b^* - n_b; \\ u &= n_m^* - n_m; & v &= n_d^* - n_d; & w &= n_h^* - n_h; \end{aligned} \tag{10}$$

in place of the n_i^*'s.   Each of the variables $x, y, \ldots$ represents the excess of carbon-14 in a reservoir over the equilibrium amount.   The differential equations satisfied by these new variables are the same as those satisfied by the n_i^*'s except that the term λQ in the stratosphere equation for dx/dt no longer appears.

The problem of present concern is an initial value problem following a state of equilibrium:

$$x = y = z = u = v = w = 0, \qquad \text{for } t < 0, \tag{11}$$

and such problems are conveniently treated by means of Laplace transforms.   The transforms of $x, y, \ldots$ are functions of a transform variable so that

$$\tilde{x}(s) = \mathcal{L}[x(t)]; \qquad \tilde{y}(s) = \mathcal{L}[y(t)]; \text{ etc.} \tag{12}$$

The transformed functions satisfy equations of the form

$$\sum_j a_{ij}\tilde{x}_j = \gamma_i \tag{13}$$

where the coefficients a_{ij} are either independent of s or are linear functions of s, and $\tilde{x}_1$ is $\tilde{x}$, $\tilde{x}_2$ is $\tilde{y}$, etc.

If the determinant of the system of Equations (13) is

$$\Delta(s) = |a_{ij}|, \tag{14}$$

than the roots of this determinant, s_i, determine the characteristic time constants of the system as $\tau_i = -1/s_i$.   The determinant Δ is a polynomial of sixth degree in s

with coefficients which depend on λ and the k_{tr}'s. If one goes to the limit, k_{tb}, k_{bt} $\rightarrow \infty$, this polynomial reduces to the fifth degree. One of these roots, say s_1, has the value

$$s_1 = -\lambda = -1.250 \times 10^{-4} (\text{years})^{-1}.$$

The remaining roots are all real and negative as would be expected, and they are evaluated numerically without difficulty. These roots have been determined for three different values of the exchange rate constant between stratosphere and troposphere and are collected in Table 2.

TABLE 2

ROOTS OF THE DETERMINANT $D(s)$, IN $(\text{YEARS})^{-1}$
(The characteristic decay periods are given by $\tau_i = -1/s_i$.)

	$k_{st} = 1/10$	$k_{st} = 1/5$	$k_{st} = \infty$
$-s_1$	1.250×10^{-4}	1.250×10^{-4}	1.250×10^{-4}
$-s_2$	1.99×10^{-3}	1.99×10^{-3}	1.99×10^{-3}
$-s_3$	2.37×10^{-2}	2.41×10^{-2}	2.44×10^{-2}
$-s_4$	1.10×10^{-1}	1.91×10^{-1}	2.51×10^{-1}
$-s_5$	2.78×10^{-1}	3.14×10^{-1}	....

There are two fundamental solutions which are required for the evaluation of the radiocarbon transient produced by nuclear explosions. The first of these is characterized by Equation (11) and in addition by the initial conditions

$$\text{x} = \gamma, \qquad \text{y} = \text{z} = \text{u} = \text{v} = \text{w} = 0, \qquad \text{for t} = 0. \tag{15}$$

These conditions correspond to equilibrium values in all the reservoirs until $t = 0$ at which time an amount γ in excess of the equilibrium amount is instantaneously introduced into the stratosphere. The calculation of the Laplace transforms from Equation (13) is a straightforward algebraic process, and the inversions of such Laplace transforms are also well known.[9] One obtains in this way

$$x(t) = \gamma \left[\frac{N(s_1)e^{s_1 t}}{(s_1 - s_2)(s_1 - s_3)(s_1 - s_4)(s_1 - s_5)} + \frac{N(s_2)e^{s_2 t}}{(s_2 - s_1)(s_2 - s_3)(s_2 - s_4)(s_2 - s_5)} + \cdots \right.$$
$$\left. \cdots + \frac{N(s_5)e^{s_5 t}}{(s_5 - s_1)(s_5 - s_2)(s_5 - s_3)(s_5 - s_4)} \right], \tag{16}$$

where $N(s)$ is a polynomial in s with coefficients which are functions of the k_{tr}'s. Expressions of similar form are obtained for $y(t)$, $z(t)$, etc.

The second fundamental solution corresponds to the conditions of Equation (11) and in addition to the initial conditions

$$y = \epsilon, \qquad x = z = u = v = w = 0, \qquad \text{for } t = 0. \tag{17}$$

As in the previous case, one finds

$$x(t) = \epsilon \left[\frac{M(s_1)e^{s_1 t}}{(s_1 - s_2)(s_1 - s_3)(s_1 - s_4)(s_1 - s_5)} + \cdots + \frac{M(s_5)e^{s_5 t}}{(s_5 - s_1)(s_5 - s_2)(s_2 - s_3)(s_2 - s_4)} \right], \tag{18}$$

with expressions of similar form for $y(t)$, $z(t)$, etc.

The behavior of the two sets of solutions is shown in Figures 2–6. Among the values of k_{st} used is infinity, corresponding to an instantaneous division of an excess of radiocarbon between the stratosphere and the troposphere. In this case, the determinant $\Delta(s)$ reduces to a polynomial of fourth degree, and there is no fifth root s_5. The solutions (16) and (18) are correspondingly modified to contain only four terms.

Discussion and Conclusion.—The mathematical description of even a moderately detailed reservoir model is involved with rather cumbersome algebra although the procedures required are in principle quite simple. As has been remarked, the transient behavior of the radiocarbon exchange system is essentially determined by
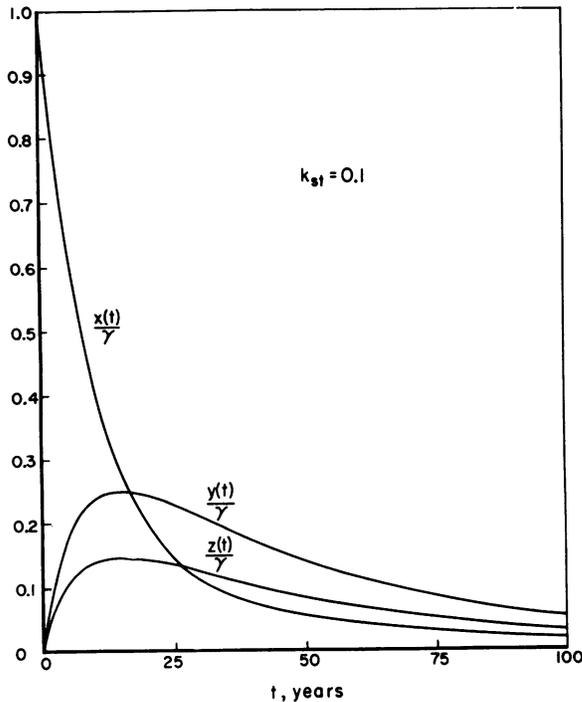
FIG. 2.—The quantities $x(t)$, $y(t)$, and $z(t)$ are the excesses of carbon-14 over the equilibrium amounts in the stratosphere, the troposphere, and the land biosphere respectively. Their variations with time are shown for $k_{st} = 0.10$ (year)$^{-1}$ when an excess of carbon-14 of amount γ is introduced into the stratosphere at $t = 0$.

the values of the characteristic decay constants, s_i, which are presented in Table 2 for three values of k_{st}. The variation of these constants with k_{st} is of particular interest. The longest of the characteristic periods is the mean lifetime for carbon-14 decay:

$$\tau_1 = \frac{1}{\lambda} = -\frac{1}{s_1} = 8{,}030 \text{ years.}$$

This value which will always appear in a theory of the present form is, of course, unaffected by the value of k_{st}. The next longest characteristic decay period is essentially independent of k_{st}, and has the value

$$\tau_2 = -\frac{1}{s_2} = 500 \text{ years.}$$

The third characteristic period is very nearly independent of k_{st} and varies only from 42 to 41 years as $1/k_{st}$ goes from 10 years to zero.   A significant variation appears first in τ_4 which has the value 9.1 years for $1/k_{st} = 10$ years, 5.2 years for $1/k_{st} = 5$

Fig. 3.—The variations with time of the excesses of carbon-14 over the equilibrium amounts in the stratosphere, $x(t)$, in the troposphere, $y(t)$, and in the land biosphere, $z(t)$, are shown under the conditions of Fig. 2 except that k_{st} has the value 0.20 (year)$^{-1}$.
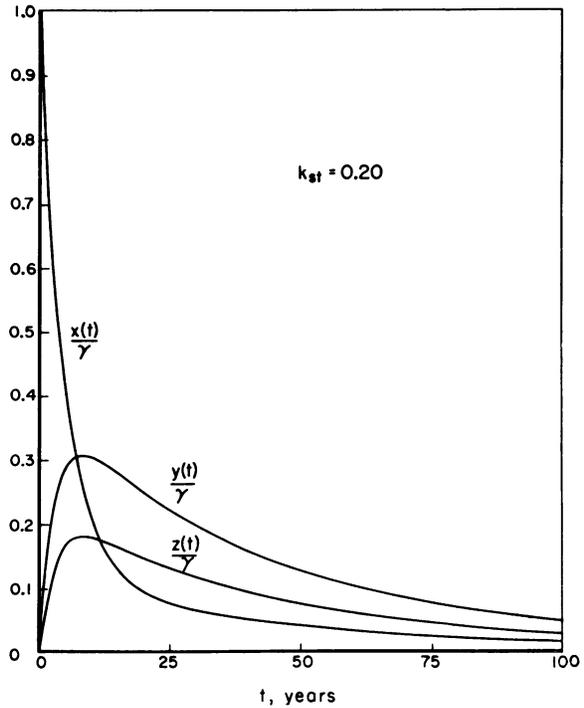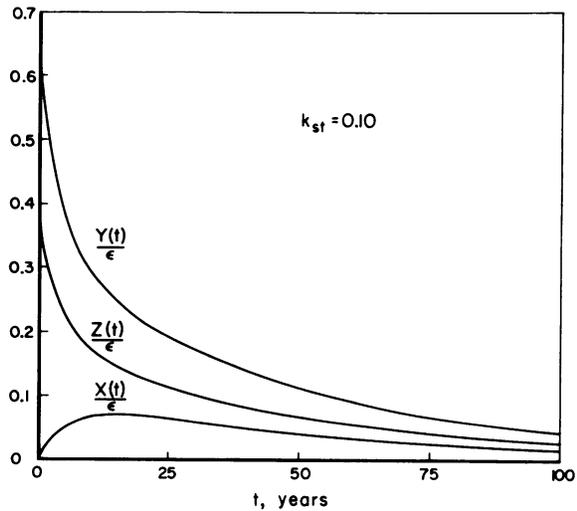

Fig. 4—The quantities $x(t)$, $y(t)$, and $z(t)$ are the excesses of carbon-14 in the stratosphere, the troposphere, and the land biosphere respectively when an excess of carbon-14 of amount ϵ is introduced into the troposphere at $t = 0$.   The stratosphere to troposphere exchange rate constant, k_{st}, has been given the value 0.10 (year)$^{-1}$.

years, and 4.0 years for $1/k_{st} = 0$.   Finally, the fifth period, τ_5, has the value 3.6 years for $1/k_{st} = 10$ years, 3.2 years for $1/k_{st} = 5$ years, and is of course absent for $1/k_{st} = 0$.   It follows from this behavior of $\tau_i = -1/s_i$ that only moderately long

times are needed for the decay of an excess introduced into the stratosphere or troposphere to be practically independent of the value of k_{st}.

A question of some interest which may be asked is how long a time is required for a carbon-14 excess introduced into the stratosphere or troposphere to be distributed

$k_{st} = 0.20$

$\frac{Y(t)}{\epsilon}$

$\frac{Z(t)}{\epsilon}$
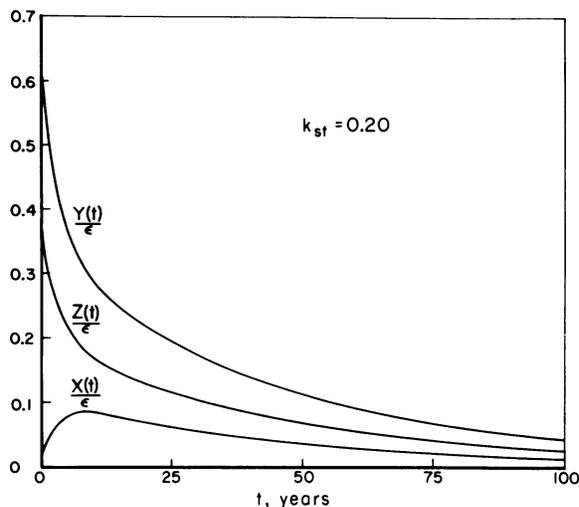
$\frac{X(t)}{\epsilon}$

t, years

Fig. 5.—The changes of $x(t)$, $y(t)$, and $z(t)$ with the time are shown for the same conditions as those of Fig. 4 except that $k_{st} = 0.20$ (year)$^{-1}$.

over all reservoirs. When such a redistribution has taken place, the excess in each reservoir will decay in time essentially like $e^{-\lambda t}$. In principle, the redistribution takes an infinitely long time, but an effective time may be found from the present solutions for this sharing of an excess introduced at some instant into the strato-

$k_{st} = \infty$

$\frac{y(t)}{\gamma}$

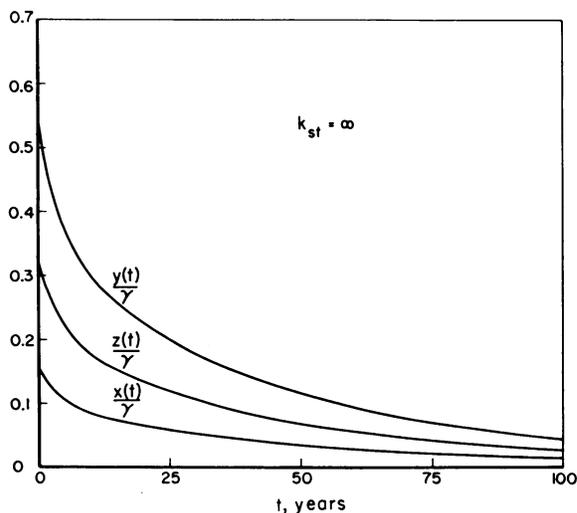$\frac{z(t)}{\gamma}$

$\frac{x(t)}{\gamma}$

t, years

Fig. 6.—The excesses of carbon-14 in the stratosphere, $x(t)$, in the troposphere, $y(t)$, and in the land biosphere, $z(t)$, are shown for $k_{st} = \infty$ for an excess γ introduced at $t = 0$. In this case, these excesses are always in a fixed ratio with each other.

sphere or troposphere. For example, in 250 years the excess which decays with period $\tau_1 = 1/\lambda$ amounts to 90 per cent of the total; the other contributions which decay with the shorter periods amount to 10 per cent. After 1,000 years, these percentages are 99 per cent and 1 per cent respectively. These times are insensitive to the value of k_{st}.

A modification of the usual theory has been used in this paper which consists in the partition of a reservoir into physically distinguishable parts, and maintaining this separation for the situation in which the numerical data give infinite exchange constants. An example of this partition is the troposphere-biosphere combination for which the data give $k_{tb} = k_{bt} = \infty$. These reservoirs have been kept distinct here and the results are evaluated in the limit k_{bt}, $k_{tb} \to \infty$. Such a procedure modifies the exchange rates since these exchange rates with adjacent reservoirs are proportional to the partial amounts n_t or n_b and not $(n_t + n_b)$. It is believed that this procedure represents an improvement in the theoretical model.

The authors, in conclusion, wish to thank Professor Gerald Wasserburg for many helpful discussions and Dr. Harmon Craig for suggestions regarding carbon distribution data. They are also indebted to Professor Harrison Brown for his interest in this study.

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CARBON-14 PRODUCTION FROM NUCLEAR EXPLOSIONS

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The increase in the carbon-14 content of the atmosphere as a consequence of nuclear explosions is of such magnitude that it is readily detectable.[1,2] Nearly all the neutrons which escape from a nuclear bomb into the atmosphere are captured in nitrogen to produce carbon-14. The best estimate of the neutron escape efficiency as given by Libby[2] is 2.5 neutrons per 200 Mev of energy release. This figure corresponds to 0.5 moles of carbon-14 per kiloton of bomb yield.

We have listed all the nuclear explosions made to date by the U.S., the U.K., and the U.S.S.R., together with estimates of the yields. The amount, A_i, in moles of carbon-14 produced by the i'th explosion is

$$A_i = 0.5 Y_i f_i, \tag{1}$$

where Y_i is the yield in kilotons, and f_i is the factor which gives the fraction of the yield which contributes to the production of exchangeable carbon-14. We have taken $f_i = 1$ for an air-burst or tower shot, $f_i = \frac{1}{2}$ for a surface or barge shot, and $f_i = 0$ for a subsurface shot.