6.337 Modelling Project

The Radioactive Decay of ^{210}Pb.

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INTRODUCTION

Most elements occurring in nature are said to be stable; that is, once formed, these elements do not change in their fundamental composition. However, this is not true of all elements. Some elements, known as radioactive elements, undergo radioactive disintegration or decay in which the original atom, called the parent, emits either an alpha or beta particle. The new element, called the daughter, also might be unstable and subject to further decay. Such a chain of parent elements and daughter elements is called a radioactive series.

The analysis of radioactive series plays an important part in the dating of geological deposits and anthropological artifacts. With the rates

at which the elements decay known, the age of a sample can be estimated by comparing the abundance of the parent element to that of a daughter element. Widely used techniques include Uranium-238 dating, potassium-dating, cabon-14 dating, and lead dating. The focus of this project is on lead dating.

Lead-210, a daughter of the uranium-238 series, is an unstable isotope that decays and eventually forms stable lead-206. The lead series is depicted in figure 1. Lead-210 (a.k.a. radium D) decays to form bismuth-210 (radium E). Bismuth-210, being unstable, decays into two different isotopes: 99.99999% of the atoms decay into polonium-210 (radwn F), while the remaining 0.00001% decay into thallium-206. Both of these daughters are unstable and decay into

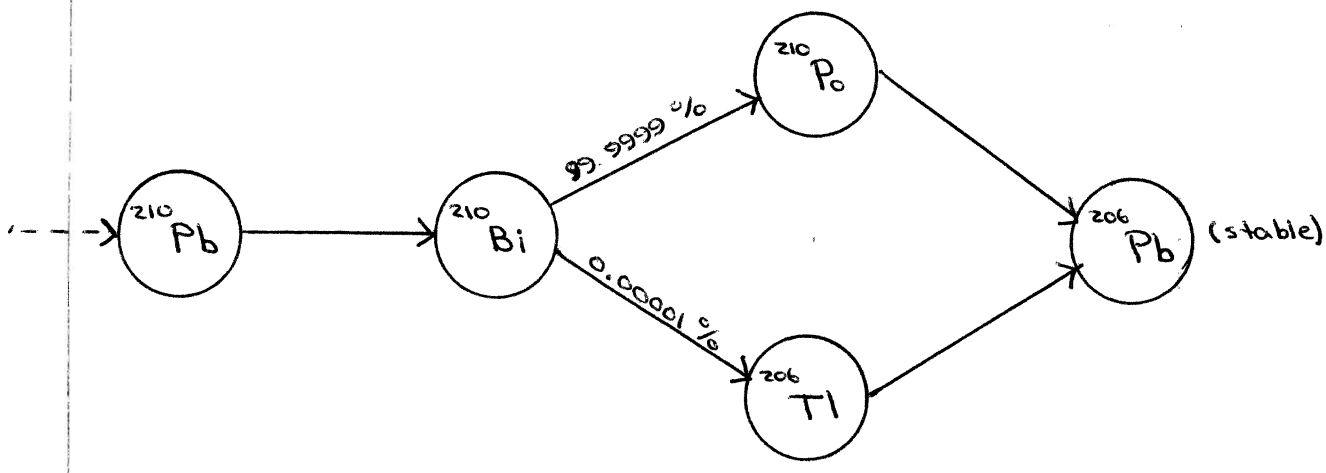


Figure 1. The lead-210 series.

stable lead-206. The purpose of this project is to formulate and analyze a mathematical model that represents this radioactive series. Based upon a set of assumptions, a general model is formulated and analyzed. Then the model is simplified by making assumptions regarding the initial conditions, and applied to the problem of lead-210 decay. Finally, a critique of the model is presented.

ASSUMPTIONS

1. Lead-210 decay obeys the Radioactive Decay law.

The Radioactive Decay law states that "the decrease in the number of radioactive nuclei over a given interval of time is directly proportional to the length of the time interval and to the number of nuclei present at the start of the interval"[1]. Mathematically stated: $\frac{dN(t)}{dt} = -KN$, where K is a positive constant. The Radioactive Decay law has been experimentally proved for many elements and provides the basis for most, if not all, of the models for radioactive decay. Therefore, it is extremely unlikely that the law does not hold "true" for the decay of lead-210.

2. The number of nuclei present is large.

Because the number of nuclei, N, is a discrete variable, the differential equation for the

good

Radioactive Decay law is only an approximation. For large N, the decay of a single nucleus is relatively insignificant and N can be considered as a continuous variable. Also, the constant of proportionality, K, represents physically the average rate of "decay" of a nucleus. Although a single nucleus is likely to decay at a rate different than K, for large N the law of averages holds and the use of an average rate in the model is justifiable. The assumption of a large N is valid because the number of nuclei, even in a small sample, is extremely large.

good

3. ^{210}Pb is not being produced.

In nature, ^{210}Pb is continuously being formed during radioactive decay of the uranium-238 series. For the sake of simplicity, it is assumed

that the initial quantity of ^{210}Pb decays according to the chain shown in figure 1, and that no new ^{210}Pb is formed from external sources. This assumption requires the sample to contain a relatively high amount of ^{210}Pb so that the amount of ^{210}Pb formed from uranium decay is insignificant.

4. Mass is conserved.

good

Radioactive isotopes are unstable and reactive. A nucleus either decays to form a different isotope or reacts with an external element to form some other product. This model assumes that no external reactions occur; that is, the entire initial mass of ^{210}Pb is accounted for within the radioactive chain. Although in reality, some mass is likely lost through external reactions, the amount that is lost

is insignificant and can be ignored.

GENERAL MODEL

The two basic equations that are used in the model are the Radioactive Decay law and the Conservation of Mass equation. The Radioactive Decay law states that $\frac{dN}{dt} = -KN$, $K>0$. However, this is nothing more than the Malthusian model with negative growth rate. The solution to this equation is: $N(t) = N_0 e^{-kt}$; N_0 = initial "population" size, and $K>0$. To obtain a physical interpretation of K, the concept of a half-life is introduced. A half-life, denoted T, is the time required for half of the collection of nuclei to decay. Because the half-lives of the isotopes are frequently quoted in physics, it is desirable to express the rate constant K in terms of T. Consider an element

undergoing decay into a single daughter isotope:

$$N(t) = N_0 e^{-kt}$$

$$N(T) = N_0 e^{-kT}$$

but $N(T) = \frac{1}{2} N_0$, by definition of T.

$$\therefore \frac{1}{2} N_0 = N_0 e^{-kT}$$

$$e^{-kT} = \frac{1}{2} \rightarrow -kT = \ln\left(\frac{1}{2}\right)$$

$$k = \frac{\ln\left(\frac{1}{2}\right)}{-T} \rightarrow k = \frac{\ln(2)}{T}$$

This relationship is valid for any nonbranching decay. For braching decay, such as that of ^{210}Bi in the lead series, the equation must be modified to account for the relative amount in each branch. If a% of an element decays into element A, then $k_A = \frac{a}{100} k$, where k is as defined above.

The conservation of mass equation can be written as ~~the~~ following rate equation:

Net rate of change of mass = production rate −|decay rate|

The model is formulated by applying this equation to each isotope. To avoid confusion with subscripts and superscripts, consider the following series where v denotes ^{210}Pb, w denotes ^{210}Bi, x denotes ^{210}Po, y denotes ^{206}Tl, and z denotes ^{206}Pb.

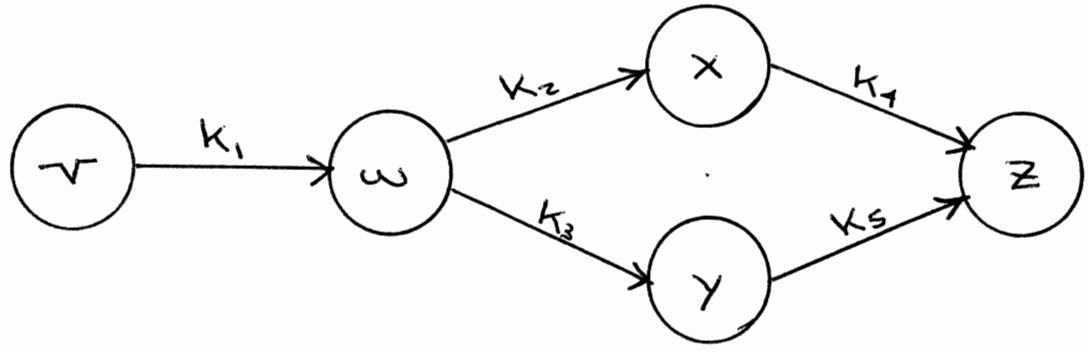


Figure 2. A simplified lead series.

Now, apply the conservation of mass rate equation at each "node".

At v: $v' = 0 - |v_D'|$ where v_D' = decay rate.

$\therefore v' = -K_1 v$ by the Radioactive Decay law. $K_1 > 0$

Similarly,

At w: $w' = K_1 v - K_2 w - K_3 w$

$w' = K_1 v - (K_2 + K_3) w$; $K_1, K_2, K_3 > 0$

At x: $x' = k_2 w - k_4 x$; $k_2, k_4 \geq 0$

At y: $y' = k_3 w - k_5 y$; $k_3, k_5 > 0$

At z: $z' = k_4 x + k_5 y$; $k_4, k_5 > 0$

Therefore, the radioactive series can be represented by the following system of differential equations:

$$\frac{dv}{dt} = -k_1 v \quad , v(0) = v_0$$

$$\frac{dw}{dt} = k_1 v - (k_2 + k_3) w \quad , w(0) = w_0$$

$$\frac{dx}{dt} = k_2 w - k_4 x \quad , x(0) = x_0$$

$$\frac{dy}{dt} = k_3 w - k_5 y \quad , y(0) = y_0$$

$$\frac{dz}{dt} = k_4 x + k_5 y \quad , z(0) = z_0$$

$$k_1, k_2, k_3, k_4, k_5 > 0$$

Clearly, this is a first-order, linear system of differential equations. Moreover, it is a cascade system: the equations are only weakly coupled and can be solved successively by using the solutions to the previously solved equations. The system has the following solution, which is derived in the

Appendix :

1. $$v(t) = v_0 e^{-k_1 t}$$

2. $$\omega(t) = \omega_0 e^{-(k_2+k_3)t} + \frac{k_1 v_0}{(k_2+k_3-k_1)}\left[e^{-k_1 t} - e^{-(k_2+k_3)t}\right]$$

3. $$x(t) = x_0 e^{-k_4 t} + \frac{k_2 \omega_0}{(k_4-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right]$$
$$+ \frac{k_1 k_2 v_0}{(k_2+k_3-k_1)}\left\{\frac{1}{k_4-k_1}\left[e^{-k_1 t} - e^{-k_4 t}\right] - \frac{1}{(k_4-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right]\right\}$$

4. $$y(t) = y_0 e^{-k_5 t} + \frac{k_3 \omega_0}{(k_5-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]$$
$$+ \frac{k_1 k_3 v_0}{(k_2+k_3-k_1)}\left\{\frac{1}{k_5-k_1}\left[e^{-k_1 t} - e^{-k_4 t}\right] - \frac{1}{(k_5-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]\right\}$$

5. $$z(t) = z_0 + x_0\left[1 - e^{-k_4 t}\right] + y_0\left[1 - e^{-k_5 t}\right]$$
$$+ \omega_0\left\{\frac{k_2 k_4 (k_5-k_2-k_3) + k_3 k_5 (k_4-k_2-k_3)}{(k_4-k_2-k_3)(k_5-k_2-k_3)(k_2+k_3)}\left[1 - e^{-(k_2+k_3)t}\right]\right.$$
$$\left. - \frac{k_2}{(k_4-k_2-k_3)}\left[1 - e^{-k_4 t}\right] - \frac{k_3}{(k_5-k_2-k_3)}\left[1 - e^{-k_5 t}\right]\right\}$$
$$+ v_0\left\{\frac{k_2 k_4 (k_5-k_1) + k_3 k_5 (k_4-k_1)}{(k_2+k_3-k_1)(k_4-k_1)(k_5-k_1)}\left[1 - e^{-k_1 t}\right]\right.$$
$$- \frac{k_1 k_2 k_4 (k_5-k_2-k_3) + k_1 k_3 k_5 (k_4-k_2-k_3)}{(k_2+k_3-k_1)(k_5-k_2-k_3)(k_4-k_2-k_3)(k_2+k_3)}\left[1 - e^{-(k_2+k_3)t}\right]$$
$$\left. + \frac{k_1 k_2}{(k_4-k_2-k_3)(k_4-k_1)}\left[1 - e^{-k_4 t}\right] + \frac{k_1 k_3}{(k_5-k_2-k_3)(k_5-k_1)}\left[1 - e^{-k_5 t}\right]\right\}$$

subject to : $k_1 \neq k_2 + k_3$
$k_4 \neq k_2 + k_3$
$k_4 \neq k_1$
$k_5 \neq k_2 + k_3$
$k_5 \neq k_1$

A SPECIAL CASE

For the sake of simplicity, it is assumed that at time $t=0$, only the parent isotope is present. Mathematically stated;

$$V(0)=V_0 \; ; \; W(0)=X(0)=Y(0)=Z(0)=0.$$

Thus, the presence of the daughter isotopes is due solely to the decay of the initial quantity of the parent isotope. The simplified model is:

1. $V(t) = V_0 e^{-k_1 t}$

2. $W(t) = \frac{k_1 V_0}{(k_2+k_3-k_1)}\left[e^{-k_1 t} - e^{-(k_2+k_3)t}\right]$

3. $X(t) = \frac{k_1 k_2 V_0}{(k_2+k_3-k_1)}\left\{\frac{1}{(k_4-k_1)}\left[e^{-k_1 t} - e^{-k_4 t}\right] - \frac{1}{(k_4-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right]\right\}$

4. $Y(t) = \frac{k_1 k_3 V_0}{(k_2+k_3-k_1)}\left\{\frac{1}{(k_5-k_1)}\left[e^{-k_1 t} - e^{-k_5 t}\right] - \frac{1}{(k_5-k_2-k_3)}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]\right\}$

5. $Z(t) = V_0\left\{\frac{k_2 k_4 (k_5-k_1) + k_3 k_5 (k_4-k_1)}{(k_2+k_3-k_1)(k_4-k_1)(k_5-k_1)}\left[1-e^{-k_1 t}\right]\right.$

$$-\frac{k_1 k_2 k_4 (k_5-k_2-k_3) + k_1 k_3 k_5 (k_4-k_2-k_3)}{(k_2+k_3-k_1)(k_5-k_2-k_3)(k_4-k_2-k_3)(k_2+k_3)}\left[1-e^{-(k_2+k_3)t}\right]$$

$$\left.+\frac{k_1 k_2}{(k_4-k_2-k_3)(k_4-k_1)}\left[1-e^{-k_4 t}\right] + \frac{k_1 k_3}{(k_5-k_2-k_3)(k_5-k_1)}\left[1-e^{-k_5 t}\right]\right\}$$

Clearly, at time $t=0$, $V(t)=V_0$ and $W(t)=X(t)=Y(t)=Z(t)=0$ as required. Similarly

because $e^{-at} \to 0$ as $t \to \infty$, $v(t), w(t), x(t)$ and $y(t)$ all approach zero as $t \to \infty$. Again, this is required, since all the material must eventually end up as the stable daughter element. Now consider $z(t)$ as $t \to \infty$. As $t \to \infty$, $e^{-at} \to 0$, and therefore $(1 - e^{-at}) \to 1$. Thus, as $t \to \infty$,

$$z(t) \to v_0 \left[\frac{k_2 k_4 (k_5 - k_1) + k_3 k_5 (k_4 - k_1)}{(k_2 + k_3 - k_1)(k_4 - k_1)(k_5 - k_1)} - \frac{k_1 k_2 k_4 (k_5 - k_2 - k_3) + k_1 k_3 k_5 (k_4 - k_2 - k_3)}{(k_2 + k_3 - k_1)(k_5 - k_2 - k_3)(k_4 - k_2 - k_3)(k_2 + k_3)} \right.$$

$$\left. + \frac{k_1 k_2}{(k_4 - k_2 - k_3)(k_4 - k_1)} + \frac{k_1 k_3}{(k_5 - k_2 - k_3)(k_5 - k_1)} \right]$$

To prove that $z(t) \to v_0$ as $t \to \infty$ requires a great amount of algebraic work and is not done here. However, by means of a numerical example, the likelihood that this occurs is stressed. Let $k_1 = 1$, $k_2 = 1$, $k_3 = 2$, $k_4 = 4$, and $k_5 = 5$. These values met the requirements listed earlier.

$$\therefore z(t) \to v_0 \left[\frac{(1)(4)(4) + (2)(5)(3)}{(2)(3)(4)} - \frac{(1)(1)(4)(2) + (1)(2)(5)(1)}{(2)(2)(1)(3)} + \frac{(1)(1)}{(1)(3)} + \frac{(1)(2)}{(2)(4)} \right]$$

$$z(t) \to v_0 \left[\frac{16 + 30}{24} - \frac{8 + 10}{12} + \frac{1}{3} + \frac{2}{8} \right]$$

$$z(t) \to v_0 \left[\frac{46}{24} - \frac{36}{24} + \frac{8}{24} + \frac{6}{24} \right] = v_0 \left[\frac{24}{24} \right] = v_0$$

Although this by no means proves that $z(t) \to v_0$ as $t \to \infty$, it does suggest that the model is acting appropriately insofar as mass appears to be conserved.

The solution curves are highly dependent upon the relative magnitude of the decay constants. Consider the solution for $v(t) = v_0 e^{-k_1 t}$. For a relatively small decay rate, the solution curve is very shallow; for a high decay constant, the curve becomes very steep. This is illustrated in figure 3.

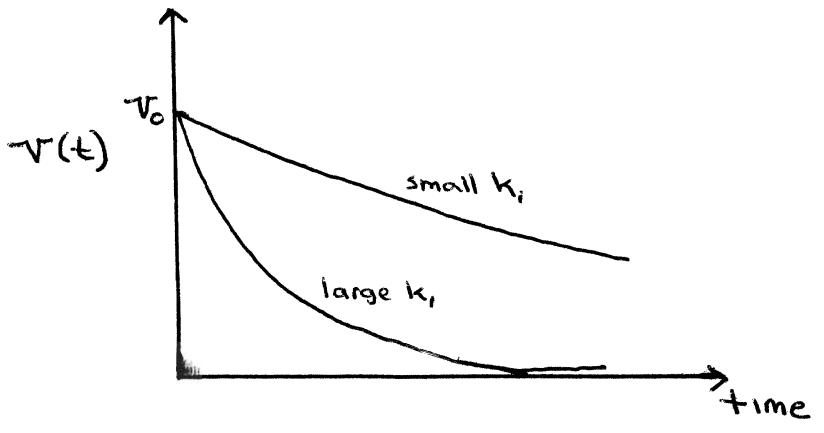


Figure 3. The solution curve for $v(t)$.

The solution curve for $v(t)$ is predicted easily - it is simply the Malthusean curve for negative growth. However, the solution curve for $w(t)$ is not so easy to predict. The shape of the curve depends upon the relative magnitudes of K_1 and (K_2+K_3). The three possible cases are presented in figure 4.

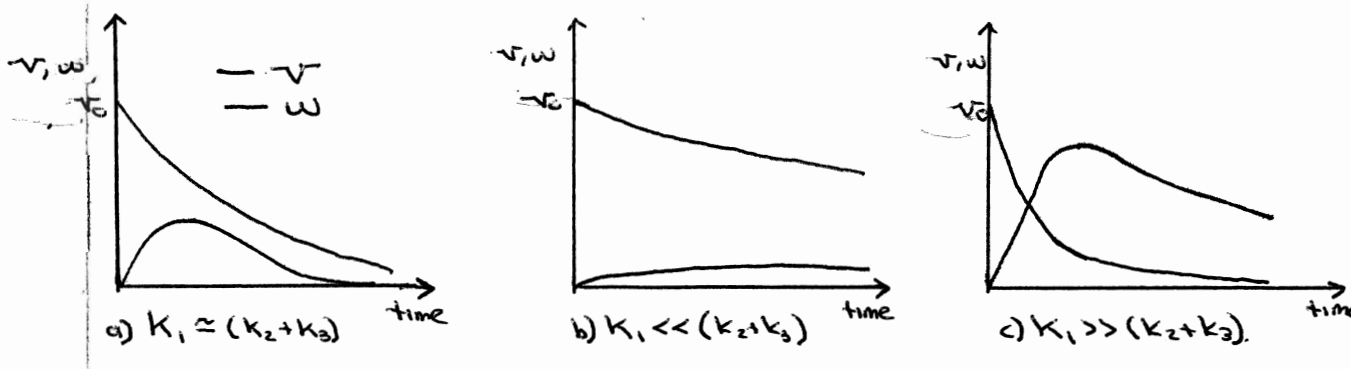


Figure 4. The solution curves for $w(t)$.

In case (a), $w(t)$ increases with time until $v(t) \simeq \frac{v_0}{2}$. At that time, $w(t)$ reaches a maximum, after which time the two isotopes follow similar decay curves. In case (b), isotope v decays so much slower that, what little amount of w is produced, readily decays into something else. The result is a "dominant"

v-decay process; the decay into isotope w becomes less and less significant to the series as K_1 becomes relatively smaller and smaller. The opposite relationship is shown in case (c). Here, v decays relatively quickly. Because w decays at a much slower rate, the result is an accumulation of isotope w followed by a slow decay. The decay of isotope w dominates the series.

A similar analysis on $x(t)$ and $y(t)$ can be performed, although more cases must be considered. However, only three cases will be analyzed, and the results of the others will be inferred. Figure 5 shows the three cases of interest. In case (a), the rates K_1, (K_2+K_3), and K_4 (or K_5) are relatively the same. The result is that no dominant decay process emmerges, but

rather all three decay processes contribute significantly to the overall length of time required to complete the conversion to z. Case (b) represents a system in which one isotope other than x or y dominates. In this scenerio, k_1 is relatively small compared to all of the other rates of decay. In this case, the amount of isotope x or y at any given time is small, and the total length of time required to complete the radioactive chain does not depend significantly on the decay of x or y. Case (c) represents the other extreme, where the decay of x or y is relatively slow and dominates

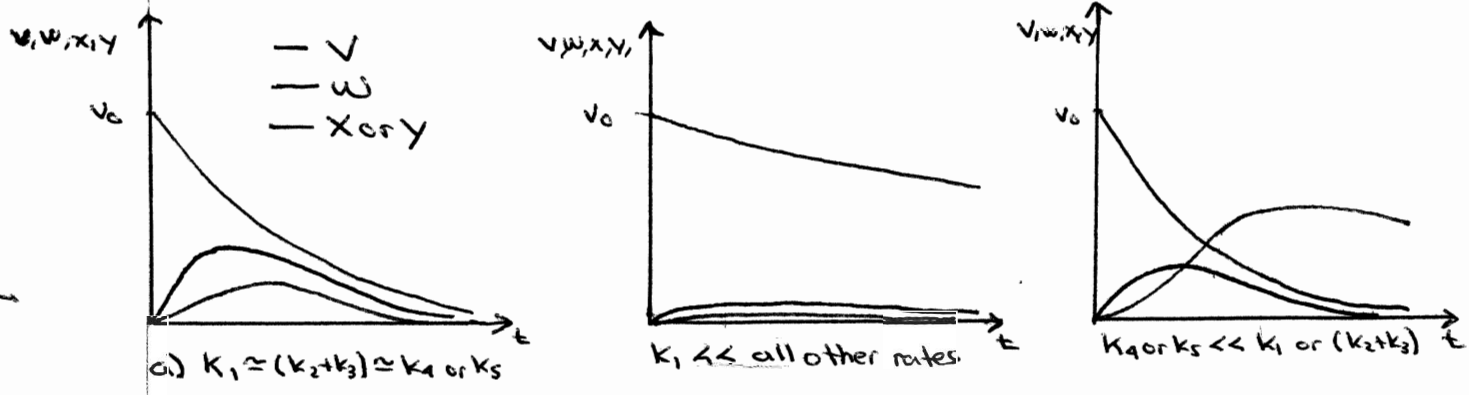
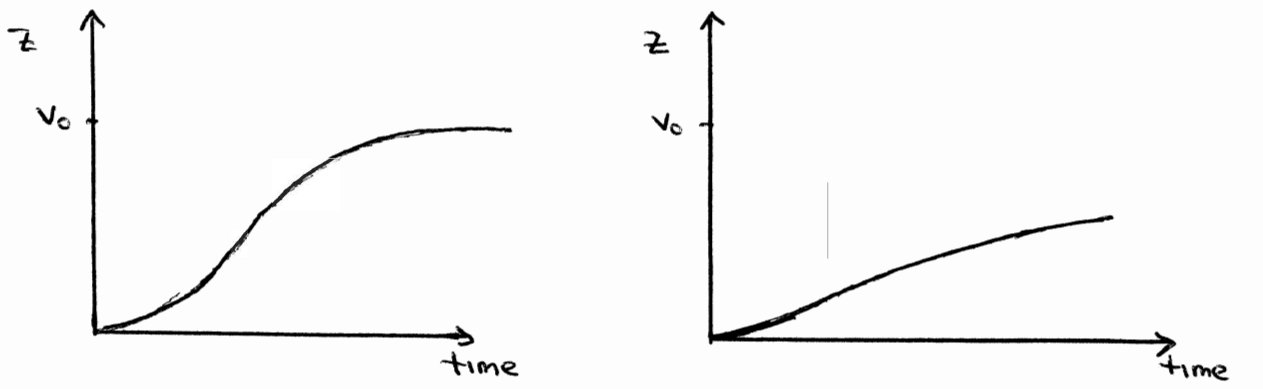


Figure 5. Solution curves for x(t) and y(t).

the process. The X or y isotope accumulates as the others decay and then slowly undergoes a "net decay" when no more of the isotope is formed.

Finally, there are two basic solution curves for $z(t)$. First, in the absence of a dominant chain, the curve for $z(t)$ represents a typical "S" curve of a cumulative distribution function. Initially, very little of the element is formed; then the rate of production increases; and eventually the rate decreases again. The second case occurs when a dominant chain is present. The curve can take many shapes, depending upon which chain is dominant; however, ultimately the curve approaches its horizontal asymptote very gradually. In all cases, the asymptote is the line $z(t) = V_0$. These two curves are shown in figure 6.



a) no dominant chain

b) at least one dominant chain

Figure 6. Solution curves for $z(t)$.

Figures 7, 8, and 9 represent scaled plots of the solution curves. Figure 7 is a plot of the case where no dominant chain is present. In figure 8, K_1 is relatively small and the v-chain dominates. Finally, in figure 9, K_4 is relatively small and the x-chain dominates in the radioactive series.

Figure 7

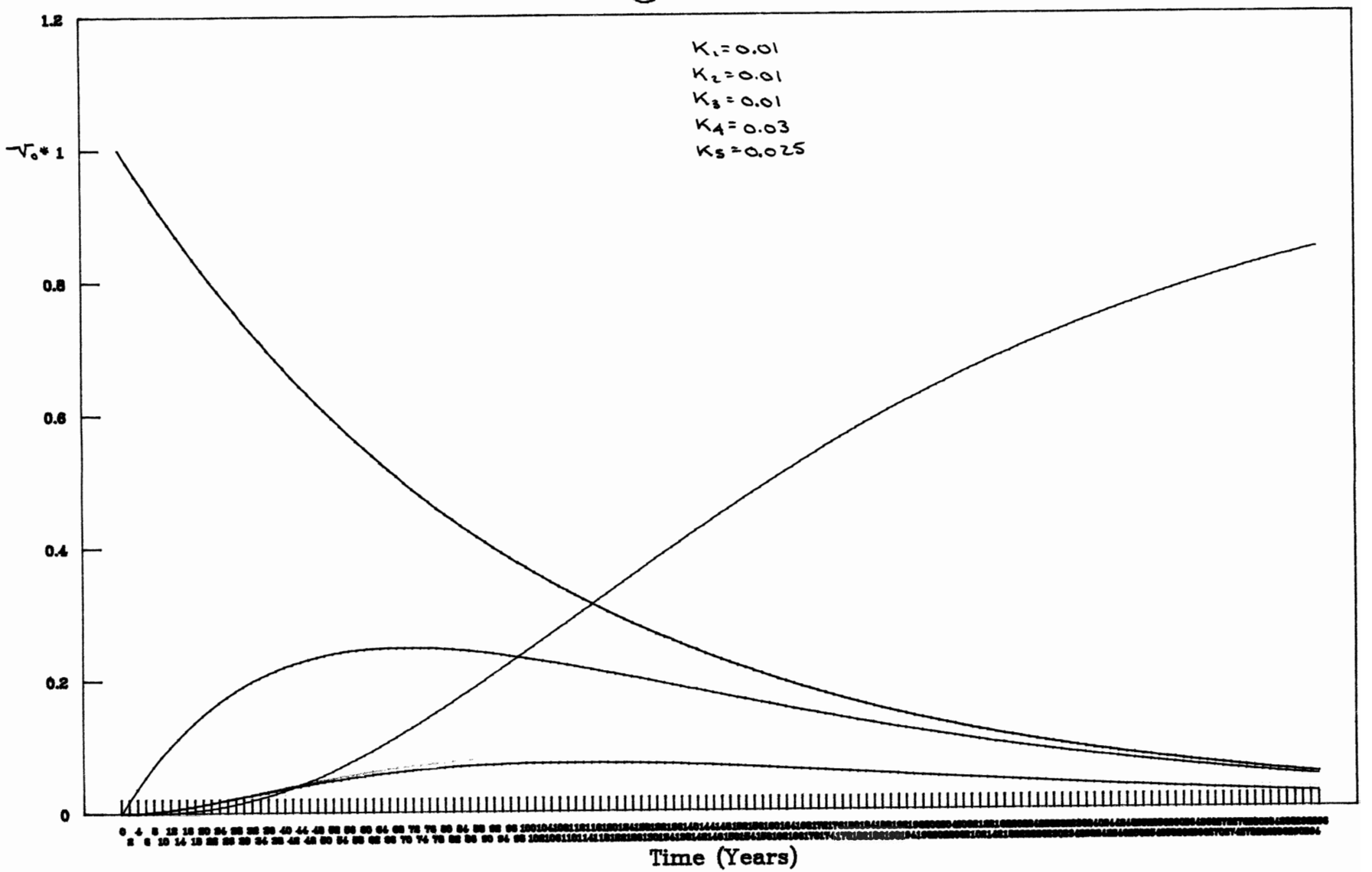

$K_1 = 0.01$
$K_2 = 0.01$
$K_3 = 0.01$
$K_4 = 0.03$
$K_5 = 0.025$
$-V_0 * 1$
1.2
0.8
0.6
0.4
0.2
0
Time (Years)
V
W
X
Y
Z

Figure 8

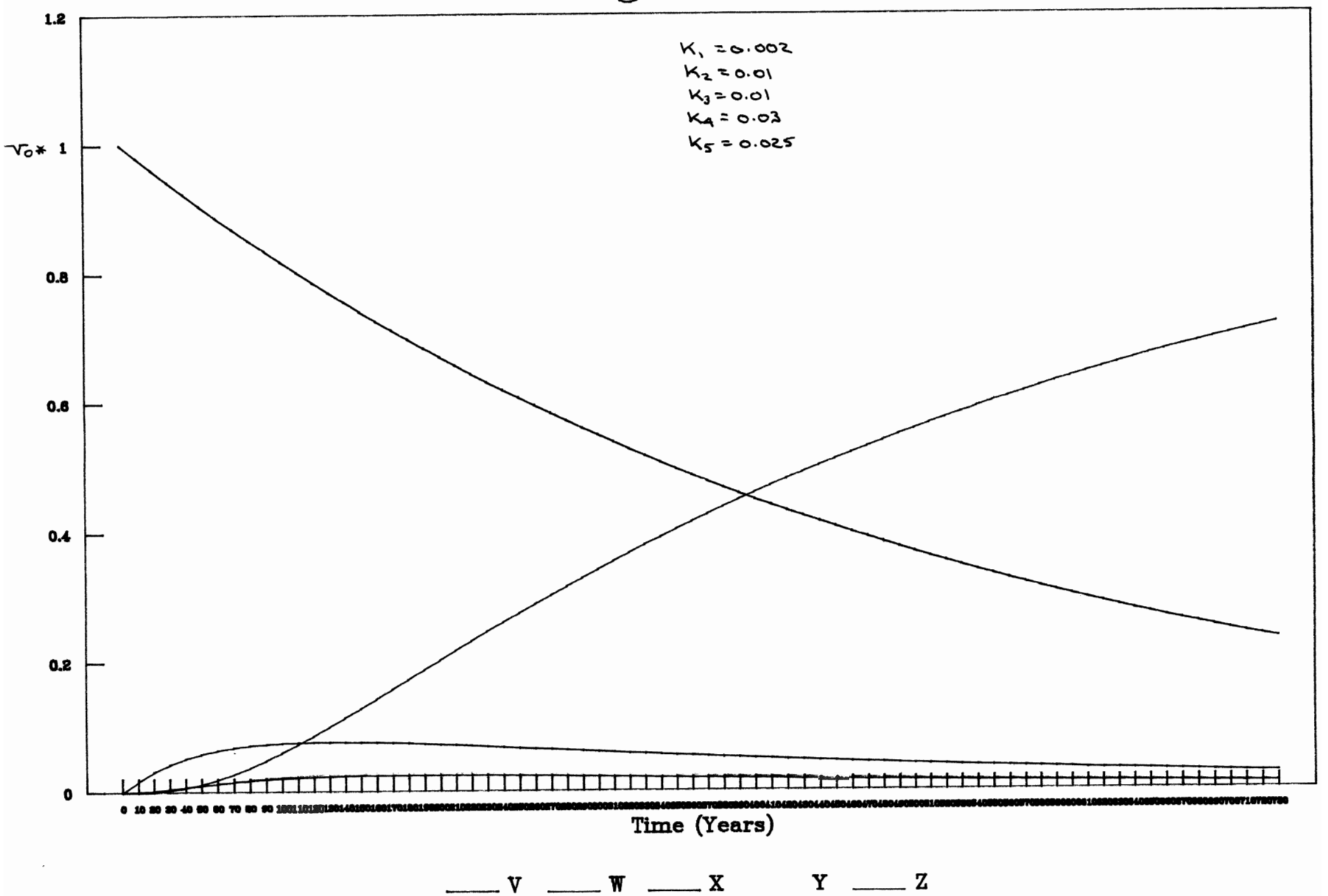
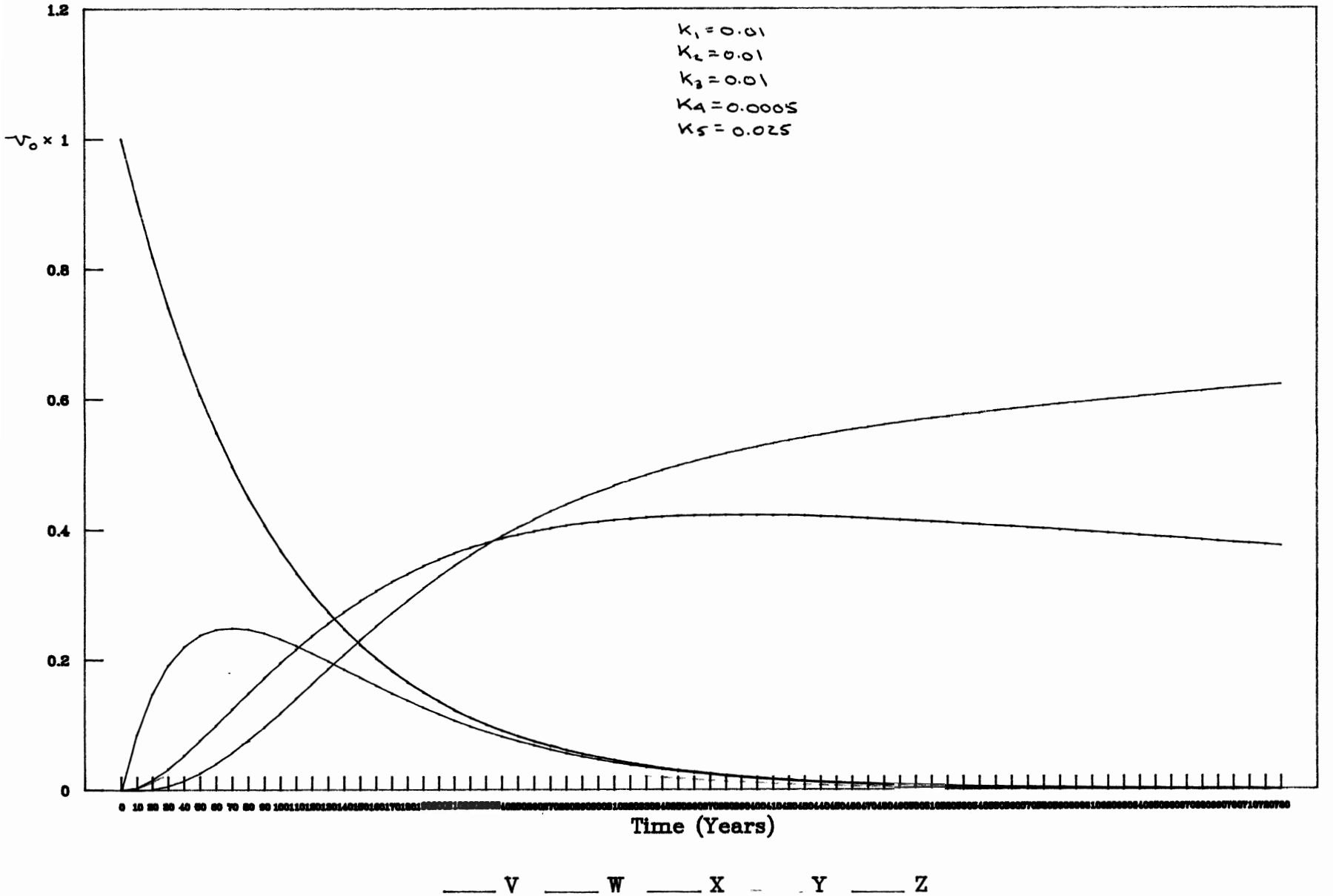

1.2
V_0* 1
0.8
0.6
0.4
0.2
0
$K_1 = 0.002$
$K_2 = 0.01$
$K_3 = 0.01$
$K_4 = 0.03$
$K_5 = 0.025$
0 10 20 30 40 50 60 70 80 90
Time (Years)
V
W
X
Y
Z

Figure 9


$k_1 = 0.01$
$k_2 = 0.01$
$k_3 = 0.01$
$k_4 = 0.0005$
$k_5 = 0.025$
$V_o \times 1$
1.2
0.8
0.6
0.4
0.2
0
Time (Years)
V
W
X
Y
Z

THE LEAD-210 SERIES.

Recalling that v denoted ^{210}Pb, w denoted ^{210}Bi, X denoted ^{210}Po, y denoted ^{206}Tl, and Z denoted ^{206}Pb; the model can now be applied to the ^{210}Pb series. The half-lives of the four unstable isotopes are given in Table 1.

Table 1. Half-lives for isotopes in the lead series.

Element	T
^{210}Pb	19.4 years
^{210}Bi	2.6×10^6 years[2], 5.04 days[3]
^{210}Po	138.4 days
^{206}Tl	4.20 minutes.

Clearly there is a major discrepency in the half-life of ^{210}Bi. For the remainder of this project, the latter value given will be used. The rationale behind this choice is as follows: If the half-life of 2.6×10^6 years was used, virtually all of the ^{210}Pb would decay into ^{210}Bi before any other daughter

isotopes could be formed. It would be impossible to compare the ratio of ^{206}Pb to ^{210}Pb because virtually all of the ^{210}Pb would be gone before any ^{206}Pb formed. Thus, the half-life of 5.04 days is used. The decay constants are found as follows:

$$K_1 = \frac{\ln(2)}{19.4} = 0.0357 \text{ years}^{-1}$$

$$K_2 = \frac{\ln(2)}{5.04}\cdot(365)\cdot\left(\frac{99.999994}{100}\right) = 50.20 \text{ years}^{-1}$$

$$K_3 = \frac{\ln(2)}{5.04}(365)\left(\frac{1\times10^{-5}}{100}\right) = 5.02\times10^{-6} \text{ years}^{-1}$$

$$K_4 = \frac{\ln(2)}{138.4}(365) = 1.838 \text{ years}^{-1}$$

$$K_5 = \frac{\ln(2)}{4.20}(60)(24)(365) = 86742 \text{ years}^{-1}$$

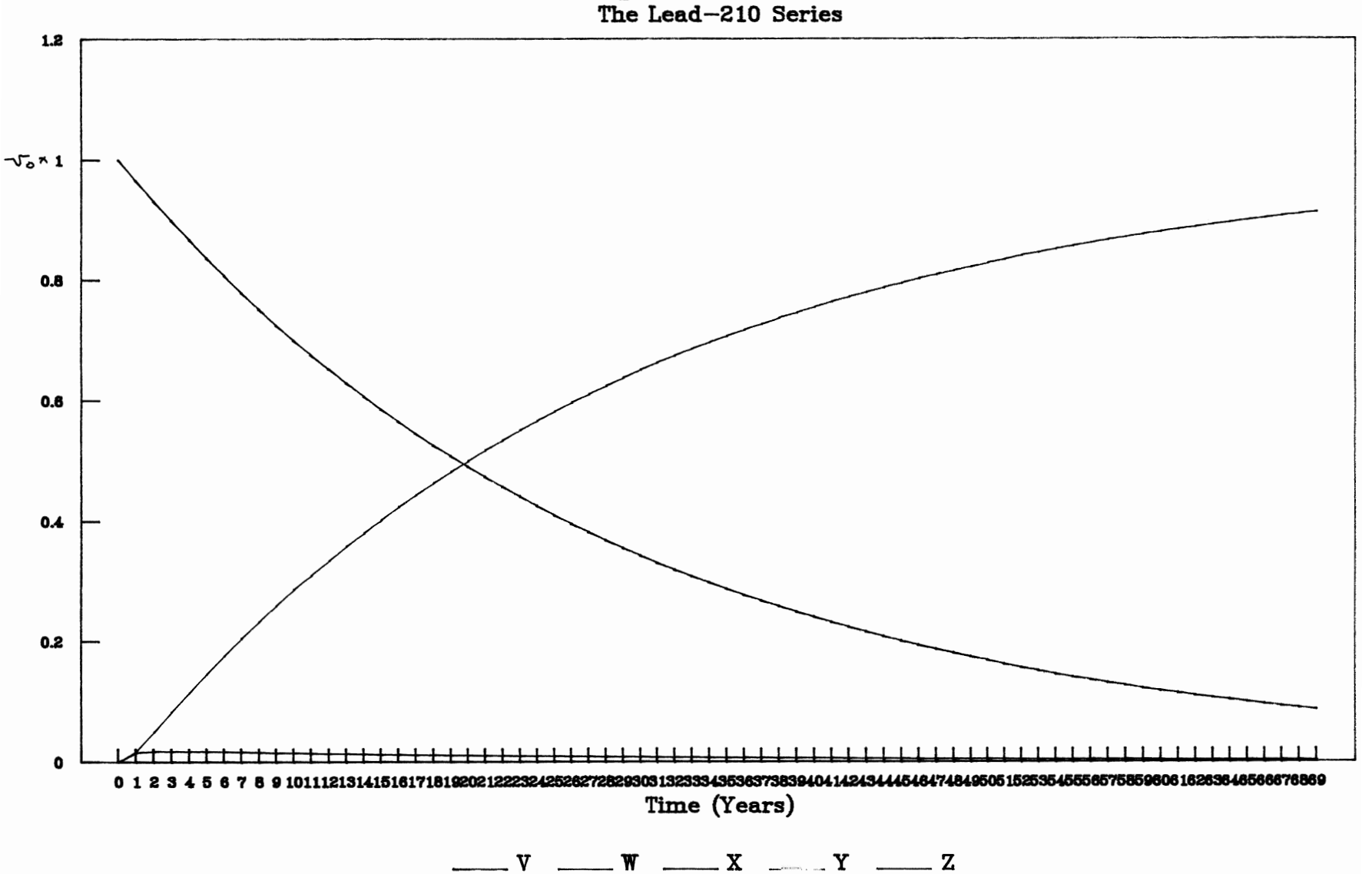
At first glance, it appears that the extremely small value of K_3 will results in a ^{210}Bi-dominant decay. However, it is the sum of K_2 and K_3 that must be considered. Clearly $K_1 << (K_2+K_3)$, or any rate for that matter. Therefore, the series is dominated by ^{210}Pb decay. ^{210}Pb, having a half-life of about 20 years, remains in the environment

for a number of years. However, the other three unstable isotopes have very short half-lives and do not remain in the environment for very long. The result, shown in figure 10, is the "slow" decay of ^{210}Pb almost directly into ^{206}Pb. The curves for the other isotopes are indistinguishable from the horizontal axis.

The ratio of ^{206}Pb to ^{210}Pb in a sample can be used to estimate the samples age. The dating technique assumes that only ^{210}Pb existed at the time the sample was created and that all ^{206}Pb was formed from the ^{210}Pb. Let R denote the ratio of ^{206}Pb to ^{210}Pb. Because ^{210}Pb decays almost directly into ^{206}Pb, the quantity of ^{206}Pb at any time t is approximately:

$$^{206}Pb = {}^{210}Pb_0[1 - e^{-k_1 t}]$$

Figure 10


The Lead-210 Series
1.2
0.8
0.6
0.4
0.2
0
$V_o \times 1$
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69
Time (Years)
V
W
X
Y
Z

and the quantity of ^{210}Pb at any time t is:

$$^{210}Pb = {}^{210}Pb_0 e^{-k_1 t}$$

$$\therefore R = \frac{1 - e^{-k_1 t}}{e^{-k_1 t}} = e^{k_1 t} - 1$$

$$e^{k_1 t} = R + 1 \rightarrow k_1 t = \ln|R+1| \qquad R \geq 0.$$

$$\therefore t = \frac{\ln(R+1)}{k_1} = \frac{\ln(R+1)}{0.0357} \quad \text{in years.}$$

To estimate the maximum age that can be determined using this technique, assume that it is technically feasible to measure R values up to 10,000. Then

$$t_{max} = \frac{\ln(10000)}{0.0357} \approx 260 \text{ years.}$$

Although this limit for R was assumed, it is not unreasonable to assume such technology exists. The answer $t_{max} \approx 260$ years seems very reasonable - lead dating is used to determine the age of paintings that are a few hundreds of years old!

CRITIQUE OF THE MODEL.

In general, the model is a good one. It applies two simple laws, the Radioactive Decay law and the conservation of mass law, which result in a first-order, linear cascade system of differential equations. The system is solved easily by solving the equations successively.

The only two problems with the model relate to its parameters - the initial values or conditions, and the rates of decay. As for the former, the model assumes that the initial quantity of each isotope can be determined. It is extremely unlikely that this information would be known with any degree of certainty. In the simplified model, the initial values were assumed to be zero for all isotopes save the parent. While this assumption makes the analysis

simpler, it may not be any more justifiable than the first assumption. The second problem relates to the estimation of the half-lives, and therefore, to the estimation of the decay rates. There is bound to be some uncertainty in every estimate of the half-lives, especially for those half-lives in the order of millions of years. The half-life of ^{210}Bi has been estimated to be as low as 5.04 days to as high as 2.6×10^6 years. Clearly, the model is extremely sensitive to uncertainties of this order of magnitude.

Possible improvements in the model include incorporating a "sink" node in the chain to account for mass loss. However, this would complicate the model and require an estimation of the loss rate. Because of the low loss rate and the relatively

high uncertainty ~~[illegible]~~ regarding the rate, it is unlikely that the improvement would be significant.

In conclusion, the model appears to represent the physical problem well. In the case of lead-210 decay, a simpler model based only on ^{210}Pb decaying into ^{206}Pb could probably yield comparable results. However, for a radioactive decay series that is not dominated by one decay chain, it is not likely that a simpler model could represent the problem as well.

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APPENDIX

1 $\frac{dv}{dt} = -k_1 v \longrightarrow \frac{dv}{v} = -k_1 dt \longrightarrow \ln(v) = -k_1 t + C_1$

$v = C_2 e^{-k_1 t}$ with $C_2 = e^{C_1} > 0$

$v(0) = v_0 = C_2(1)$

$\therefore \underline{v(t) = v_0 e^{-k_1 t}}$

2. $\frac{dw}{dt} = k_1 v - (k_2 + k_3) w$

$\frac{dw}{dt} + (k_2 + k_3) w = k_1 v$ - first order, linear d.e.

Using the integration factor $e^{(k_2+k_3)t}$:

$w = e^{-(k_2+k_3)t} \left[\int_0^t k_1 v e^{(k_2+k_3)s} ds + C \right]$

$w = C e^{-(k_2+k_3)t} + e^{-(k_2+k_3)t} \int_0^t k_1 v_0 e^{-k_1 s} e^{(k_2+k_3)s} ds$

$w = C e^{-(k_2+k_3)t} + e^{-(k_2+k_3)t} \int_0^t k_1 v_0 e^{(k_2+k_3-k_1)s} ds.$

$w = C e^{-(k_2+k_3)t} + e^{-(k_2+k_3)t} \left(\frac{k_1 v_0}{k_2+k_3-k_1} \right) \left[e^{(k_2+k_3-k_1)s} \right]_0^t$

$w = C e^{-(k_2+k_3)t} + \left(\frac{k_1 v_0}{(k_2+k_3-k_1)} \right) e^{-(k_2+k_3)t} \left[e^{(k_2+k_3-k_1)t} - 1 \right]$

$w = C e^{-(k_2+k_3)t} + \frac{k_1 v_0}{k_2+k_3-k_1} \left[e^{-k_1 t} - e^{-(k_2+k_3)t} \right]$

$w(0) = w_0 = C(1) + \frac{k_1 v_0}{k_2+k_3-k_1}(1-1) \longrightarrow C = w_0$

Defining $k_7 = k_2 + k_3 - k_1 \neq 0 \longrightarrow k_1 \neq k_2 + k_3$:

$\underline{w(t) = w_0 e^{-(k_2+k_3)t} + \frac{k_1 v_0}{k_7} \left[e^{-k_1 t} - e^{-(k_2+k_3)t} \right]}$

3. $\frac{dx}{dt} = k_2 w - k_4 x \longrightarrow \frac{dx}{dt} + k_4 x = k_2 w$

$$\frac{dx}{dt} + k_4 x = k_2\left\{w_o e^{-(k_2+k_3)t} + \frac{k_1 v_o}{k_7}\left[e^{-k_1 t} - e^{-(k_2+k_3)t}\right]\right\}$$

$$x = e^{-k_4 t}\left\langle \int_0^t k_2\left\{w_o e^{-(k_2+k_3)s} + \frac{k_1 v_o}{k_7}\left[e^{-k_1 s} - e^{-(k_2+k_3)s}\right]\right\} e^{k_4 s}\, ds + c \right\rangle$$

$$x = ce^{-k_4 t} + k_2 e^{-k_4 t}\int_0^t \left\{w_o e^{-(k_2+k_3)s} + \frac{k_1 v_o}{k_7}\left[e^{-k_1 s} - e^{-(k_2+k_3)s}\right]\right\} e^{k_4 s}\, ds$$

$$x = ce^{-k_4 t} + k_2 e^{-k_4 t}\int_0^t \left\{w_o e^{(k_4-k_2-k_3)s} + \frac{k_1 v_o}{k_7}\left[e^{(k_4-k_1)s} - e^{(k_4-k_2-k_3)s}\right]\right\} ds$$

$$x = ce^{-k_4 t} + k_2 w_o e^{-k_4 t}\int_0^t e^{(k_4-k_2-k_3)s}\, ds + \frac{k_1 k_2 v_o}{k_7} e^{-k_4 t}\int_0^t e^{(k_4-k_1)s}\, ds - \frac{k_1 k_2 v_o}{k_7} e^{-k_4 t}\int_0^t e^{(k_4-k_2-k_3)s}\, ds$$

$$x = ce^{-k_4 t} + \frac{k_2 w_o}{(k_4-k_2-k_3)} e^{-k_4 t}\left[e^{(k_4-k_2-k_3)s}\right]_0^t + \frac{k_1 k_2 v_o}{k_7(k_4-k_1)} e^{-k_4 t}\left[e^{(k_4-k_1)s}\right]_0^t$$

$$- \frac{k_1 k_2 v_o}{k_7(k_4-k_2-k_3)} e^{-k_4 t}\left[e^{(k_4-k_2-k_3)s}\right]_0^t$$

Defining $k_8 = k_4 - k_2 - k_3 \neq 0 \longrightarrow k_4 \neq k_2 + k_3$:

$$x = ce^{-k_4 t} + \frac{k_2 w_o}{k_8} e^{-k_4 t}\left[e^{(k_4-k_2-k_3)t} - 1\right] + \frac{k_1 k_2 v_o}{k_7(k_4-k_1)} e^{-k_4 t}\left[e^{(k_4-k_1)t} - 1\right]$$

$$- \frac{k_1 k_2 v_o}{k_7 k_8} e^{-k_4 t}\left[e^{(k_4-k_2-k_3)t} - 1\right]$$

$$x = ce^{-k_4 t} + \frac{k_2 w_o}{k_8}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right] + \frac{k_1 k_2 v_o}{k_7(k_4-k_1)}\left[e^{-k_1 t} - e^{-k_4 t}\right] - \frac{k_1 k_2 v_o}{k_7 k_8}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right]$$

$$x = ce^{-k_4 t} + \frac{k_7 k_2 w_o - k_1 k_2 v_o}{k_7 k_8}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right] + \frac{k_1 k_2 v_o}{k_7(k_4-k_1)}\left[e^{-k_1 t} - e^{-k_4 t}\right]$$

$$x(0) = x_o = c + 0 + 0 \longrightarrow c = x_o$$

$$\underline{x(t) = x_o e^{-k_4 t} + \frac{k_7 k_2 w_o - k_1 k_2 v_o}{k_7 k_8}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right] + \frac{k_1 k_2 v_o}{k_7(k_4-k_1)}\left[e^{-k_1 t} - e^{-k_4 t}\right]}$$

$$x(t) = x_o e^{-k_4 t} + \frac{k_2}{k_8} w_o\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right]$$

$$+ \frac{k_1 k_2}{k_7} v_o\left\{\frac{-1}{k_8}\left[e^{-(k_2+k_3)t} - e^{-k_4 t}\right] + \frac{1}{(k_4-k_1)}\left[e^{-k_1 t} - e^{-k_4 t}\right]\right\}$$

4. $\frac{dy}{dt} = k_3\omega - k_5 y \longrightarrow \frac{dy}{dt} + k_5 y = k_3\omega$

$$\frac{dy}{dt} + k_5 y = k_3\left\{\omega_0 e^{-(k_2+k_3)t} + \frac{k_1 v_0}{k_7}\left[e^{-k_1 t} - e^{-(k_2+k_3)t}\right]\right\}$$

$$y = e^{-k_5 t}\left\langle \int_0^t k_3\left\{\omega_0 e^{-(k_2+k_3)s} + \frac{k_1 v_0}{k_7}\left[e^{-k_1 s} - e^{-(k_2+k_3)s}\right]\right\} e^{k_5 s}\, ds + C \right\rangle$$

$$y = Ce^{-k_5 t} + k_3 e^{-k_5 t}\int_0^t \left\{\omega_0 e^{-(k_2+k_3)s} + \frac{k_1 v_0}{k_7}\left[e^{-k_1 s} - e^{-(k_2+k_3)s}\right]\right\} e^{k_5 s}\, ds.$$

$$y = Ce^{-k_5 t} + k_3 e^{-k_5 t}\int_0^t \left\{\omega_0 e^{(k_5-k_2-k_3)s} + \frac{k_1 v_0}{k_7}\left[e^{(k_5-k_1)s} - e^{(k_5-k_2-k_3)s}\right]\right\} ds$$

$$y = Ce^{-k_5 t} + k_3\omega_0 e^{-k_5 t}\int_0^t e^{(k_5-k_2-k_3)s}\, ds + \frac{k_1 k_3 v_0}{k_7} e^{-k_5 t}\int_0^t e^{(k_5-k_1)s}\, ds - \frac{k_1 k_3 v_0}{k_7} e^{-k_5 t}\int_0^t e^{(k_5-k_2-k_3)s}\, ds$$

$$y = Ce^{-k_5 t} + \frac{k_3\omega_0}{k_5-k_2-k_3} e^{-k_5 t}\left[e^{(k_5-k_2-k_3)s}\right]_0^t + \frac{k_1 k_3 v_0}{k_7(k_5-k_1)} e^{-k_5 t}\left[e^{(k_5-k_1)s}\right]_0^t$$

$$- \frac{k_1 k_3 v_0}{k_7(k_5-k_2-k_3)} e^{-k_5 t}\left[e^{(k_5-k_2-k_3)s}\right]_0^t$$

Defining $k_9 = k_5 - k_2 - k_3 \neq 0 \longrightarrow k_9 \neq k_2 + k_3$:

$$y = Ce^{-k_5 t} + \frac{k_3\omega_0}{k_9} e^{-k_5 t}\left[e^{(k_5-k_2-k_3)t} - 1\right] + \frac{k_1 k_3 v_0}{k_7(k_5-k_1)} e^{-k_5 t}\left[e^{(k_5-k_1)t} - 1\right]$$

$$- \frac{k_1 k_3 v_0}{k_7 k_9} e^{-k_5 t}\left[e^{(k_5-k_2-k_3)t} - 1\right]$$

$$y = Ce^{-k_5 t} + \frac{k_3\omega_0}{k_9}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right] + \frac{k_1 k_3 v_0}{k_7(k_5-k_1)}\left[e^{-k_1 t} - e^{-k_5 t}\right] - \frac{k_1 k_3 v_0}{k_7 k_9}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]$$

$$y = Ce^{-k_5 t} + \frac{k_7 k_3\omega_0 - k_1 k_3 v_0}{k_7 k_9}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right] + \frac{k_1 k_3 v_0}{k_7(k_5-k_1)}\left[e^{-k_1 t} - e^{-k_5 t}\right]$$

$$y(0) = y_0 = C + 0 + 0 \longrightarrow C = y_0$$

$$y(t) = y_0 e^{-k_5 t} + \frac{k_7 k_3\omega_0 - k_1 k_3 v_0}{k_7 k_9}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right] + \frac{k_1 k_3 v_0}{k_7(k_5-k_1)}\left[e^{-k_1 t} - e^{-k_5 t}\right]$$

$$y(t) = y_0 e^{-k_5 t} + \frac{k_3}{k_9}\omega_0\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]$$

$$+ \frac{k_1 k_3}{k_7} v_0\left\{\frac{1}{k_5-k_1}\left[e^{-k_1 t} - e^{-k_5 t}\right] - \frac{1}{k_9}\left[e^{-(k_2+k_3)t} - e^{-k_5 t}\right]\right\}$$

5. $\frac{dz}{dt} = k_4 x + k_5 y \longrightarrow z = \int_0^t k_4 x\,ds + \int_0^t k_5 y\,ds + C.$

First, consider $\int_0^t k_4 x\,ds$:

$$\int_0^t k_4 x\,ds = \int_0^t k_4 x_0 e^{-k_4 s}\,ds + \int_0^t k_4\left[\frac{k_7 k_2 w_0 - k_1 k_2 v_0}{k_7 k_8}\right]\left[e^{-(k_2+k_3)s} - e^{-k_4 s}\right]ds + \int_0^t k_4\left[\frac{k_1 k_2 v_0}{k_7(k_4-k_1)}\right]\left[e^{-k_1 s} - e^{-k_4 s}\right]ds$$

Letting $A = \frac{k_7 k_2 w_0 - k_1 k_2 v_0}{k_7 k_8}$ and $B = \frac{k_1 k_2 v_0}{k_7(k_4-k_1)}$:

$$\int_0^t k_4 x\,ds = \frac{k_4}{-k_4} x_0\left[e^{-k_4 s}\right]_0^t + \frac{k_4}{-(k_2+k_3)} A e^{-(k_2+k_3)s}\Big]_0^t - \frac{k_4}{-k_4} A e^{-k_4 s}\Big]_0^t + \frac{k_4}{-k_1} B e^{-k_1 s}\Big]_0^t - \frac{k_4}{-k_4} B e^{-k_4 s}\Big]_0^t$$

$$\int_0^t k_4 x\,ds = -x_0\left[e^{-k_4 t} - 1\right] - \frac{k_4 A}{(k_2+k_3)}\left[e^{-(k_2+k_3)} - 1\right] + A\left[e^{-k_4 t} - 1\right] - \frac{k_4 B}{k_1}\left[e^{-k_1 t} - 1\right] + B\left[e^{-k_4 t} - 1\right]$$

$$\int_0^t k_4 x\,ds = x_0\left[1 - e^{-k_4 t}\right] + \frac{k_4 A}{(k_2+k_3)}\left[1 - e^{-(k_2+k_3)}\right] - A\left[1 - e^{-k_4 t}\right] + \frac{k_4 B}{k_1}\left[1 - e^{-k_1 t}\right] - B\left[1 - e^{-k_4 t}\right]$$

$$\int_0^t k_4 x\,ds = (x_0 - A - B)\left[1 - e^{-k_4 t}\right] + \frac{k_4 A}{(k_2+k_3)}\left[1 - e^{-(k_2+k_3)}\right] + \frac{k_4 B}{k_1}\left[1 - e^{-k_1 t}\right]$$

Now consider $\int_0^t k_5 y\,ds$:

$$\int_0^t k_5 y\,ds = \int_0^t k_5 y_0 e^{-k_5 s}\,ds + \int_0^t k_5\left[\frac{k_7 k_3 w_0 - k_1 k_3 v_0}{k_7 k_9}\right]\left[e^{-(k_2+k_3)s} - e^{-k_5 s}\right]ds + \int_0^t k_5\left[\frac{k_1 k_3 v_0}{k_7(k_5-k_1)}\right]\left[e^{-k_1 s} - e^{-k_5 s}\right]ds$$

Letting $D = \frac{k_7 k_3 w_0 - k_1 k_3 v_0}{k_7 k_9}$ and $E = \frac{k_1 k_3 v_0}{k_7(k_5-k_1)}$:

$$\int_0^t k_5 y\,ds = \frac{k_5}{-k_5} y_0 e^{-k_5 s}\Big]_0^t + \frac{k_5 D}{-(k_2+k_3)} e^{-(k_2+k_3)s}\Big]_0^t - \frac{k_5 D}{-k_5} e^{-k_5 s}\Big]_0^t + \frac{k_5 E}{-k_1} e^{-k_1 s}\Big]_0^t - \frac{k_5 E}{-k_5} e^{-k_5 s}\Big]_0^t$$

$$\int_0^t k_5 y\,ds = -y_0\left[e^{-k_5 t} - 1\right] - \frac{k_5 D}{(k_2+k_3)}\left[e^{-(k_2+k_3)t} - 1\right] + D\left[e^{-k_5 t} - 1\right] - \frac{k_5 E}{k_1}\left[e^{-k_1 t} - 1\right] + E\left[e^{-k_5 t} - 1\right]$$

$$\int_0^t k_5 y\,ds = y_0\left[1 - e^{-k_5 t}\right] + \frac{k_5 D}{k_2+k_3}\left[1 - e^{-(k_2+k_3)}\right] - D\left[1 - e^{-k_5 t}\right] + \frac{k_5 E}{k_1}\left[1 - e^{-k_1 t}\right] - E\left[1 - e^{-k_5 t}\right]$$

$$\int_0^t k_5 y\,ds = (y_0 - D - E)\left[1 - e^{-k_5 t}\right] + \frac{k_5 D}{k_2+k_3}\left[1 - e^{-(k_2+k_3)}\right] + \frac{k_5 E}{k_1}\left[1 - e^{-k_1 t}\right]$$

$$Z = \int_0^t K_4 X\,ds + \int_0^t K_5 Y\,ds + C.$$

$$Z = (X_0 - A - B)\left[1 - e^{-k_4 t}\right] + \frac{k_4 A}{(k_2+k_3)}\left[1 - e^{-(k_2+k_3)t}\right] + \frac{k_4 B}{k_1}\left[1 - e^{-k_1 t}\right]$$

$$+ (Y_0 - D - E)\left[1 - e^{-k_5 t}\right] + \frac{k_5 D}{(k_2+k_3)}\left[1 - e^{-(k_2+k_3)t}\right] + \frac{k_5 E}{k_1}\left[1 - e^{-k_1 t}\right] + C.$$

$$Z(0) = Z_0 = 0 + 0 + 0 + 0 + 0 + 0 + C \longrightarrow C = Z_0.$$

$$Z(t) = Z_0 + (X_0 - A - B)\left[1 - e^{-k_4 t}\right] + (Y_0 - D - E)\left[1 - e^{-k_5 t}\right] + \frac{k_4 A + k_5 D}{(k_2+k_3)}\left[1 - e^{-(k_2+k_3)t}\right]$$

$$+ \frac{k_4 B + k_5 E}{k_1}\left[1 - e^{-k_1 t}\right]$$

Consider: $\underline{X_0 - A - B} = X_0 - \frac{k_7 k_2 w_0 - k_1 k_2 v_0}{k_7 k_8} - \frac{k_1 k_2 v_0}{k_7 (k_4 - k_1)}$

$$= \frac{k_7 k_8 (k_4 - k_1) X_0 - (k_4 - k_1) k_7 k_2 w_0 + (k_4 - k_1) k_1 k_2 v_0 - k_8 k_1 k_2 v_0}{(k_4 - k_1) k_7 k_8}$$

$$= X_0 - \frac{k_2}{k_8} w_0 + \left(\frac{k_1 k_2}{k_7 k_8} - \frac{k_1 k_2}{(k_4 - k_1) k_7}\right) v_0$$

$$\underline{Y_0 - D - E} = Y_0 - \frac{k_7 k_3 w_0 - k_1 k_3 v_0}{k_7 k_9} - \frac{k_1 k_3 v_0}{k_7 (k_5 - k_1)}$$

$$= Y_0 - \frac{k_3}{k_9} w_0 + \left[\frac{k_1 k_3}{k_7 k_9} - \frac{k_1 k_3}{k_7 (k_5 - k_1)}\right] v_0$$

$$\underline{\frac{k_4 A + k_5 D}{(k_2+k_3)}} = \frac{k_4 k_7 k_2 w_0 - k_1 k_2 k_4 v_0}{k_7 k_8 (k_2+k_3)} + \frac{k_5 k_7 k_3 w_0 - k_1 k_3 k_5 v_0}{k_7 k_9 (k_2+k_3)}$$

$$= \left[\frac{k_2 k_4 k_9 + k_3 k_5 k_8}{k_8 k_9 (k_2+k_3)}\right] w_0 - \left[\frac{k_1 k_2 k_4 k_9 + k_1 k_3 k_5 k_8}{k_7 k_8 k_9 (k_2+k_3)}\right] v_0$$

$$\underline{\frac{k_4 B + k_5 E}{k_1}} = \frac{k_4 k_1 k_2 v_0}{k_1 k_7 (k_4 - k_1)} + \frac{k_5 k_1 k_3 v_0}{k_1 k_7 (k_5 - k_1)} = \left[\frac{k_2 k_4 (k_5 - k_1) + k_3 k_5 (k_4 - k_1)}{k_7 (k_4 - k_1)(k_5 - k_1)}\right] v_0$$

Substituting these equations and gathering terms yields:

$$z(t) = z_0 + x_0\left[1 - e^{-k_4 t}\right] + y_0\left[1 - e^{-k_5 t}\right]$$

$$+ \omega_0 \left\{ \frac{k_2 k_4 k_9 + k_3 k_5 k_8}{k_8 k_9 (k_2 + k_3)}\left[1 - e^{-(k_2+k_3)t}\right] - \frac{k_2}{k_8}\left[1 - e^{-k_4 t}\right] - \frac{k_3}{k_9}\left[1 - e^{-k_5 t}\right] \right\}$$

$$+ v_0 \left\{ \frac{k_2 k_4 (k_5 - k_1) + k_3 k_5 (k_4 - k_1)}{k_7 (k_4 - k_1)(k_5 - k_1)}\left[1 - e^{-k_1 t}\right] - \frac{k_1 k_2 k_4 k_9 + k_1 k_3 k_5 k_8}{k_7 k_8 k_9 (k_2 + k_3)}\left[1 - e^{-(k_2+k_3)t}\right] \right.$$

$$\left. + \frac{k_1 k_2}{k_8 (k_4 - k_1)}\left[1 - e^{-k_4 t}\right] + \frac{k_1 k_3}{k_9 (k_5 - k_1)}\left[1 - e^{-k_5 t}\right] \right\}$$