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Full Length Research Paper

A possible hypothesis for correcting the radiocarbon age of the Shroud of Turin

Francisco Alconchel-Pecino

Department of Applied Physics, Superior Technical School of Industrial Engineering, Polytechnic University of Madrid, Spain. E-mail: fanti@unipd.it.

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Three methods of calculation in Chemical Physics are used to study how the isotopic exchange could affect the radiocarbon age of the Shroud of Turin. The basic hypothesis is that a fire in the year 1532 caused an isotopic exchange reaction between the air and the fabric of linen. According to this model, molecules of carbon dioxide from the air exchanged isotopes ^{14}C by isotopes ^{12}C with the monomers of cellulose of linen. This would be the reason why the dating laboratories have measured a radiocarbon age of 600 years instead of 2000 years.

Key words: Shroud of Turin, physics, radiocarbon, hypothesis.

INTRODUCTION

In 1988, the three laboratories of Tucson, Oxford and Zurich dated the fabric of the Shroud of Turin (Damon et al., 1989). These teams found that the radiocarbon age was about 600 years old. According to these laboratories the linen of the Shroud of Turin is medieval, between the years A.D. 1260-1390. However, other scientists claim that this cloth was probably used to wrap Christ's body (Jumper et al., 1984). As a result a controversy exists about the authenticity of this relic. To try to clarify this controversy, we begin with three fundamental facts: a fire and two contradictory experiments.

In the year 1532 the Shroud of Turin was in a fire (Siliato, 1985; Cardot, 1934). The cloth was in the chapel of the ducal castle in the French city of Chambéry, it had been kept in a silver covered wooden reliquary. This reliquary was kept inside a wooden closet when a fire began in the wooden pews of the choir on the night of December 4th.

When the wooden closet was burning, the people who had gone to save the Shroud of Turin flooded the reliquary with water. Inside the reliquary the temperature reached about 200°C, since at this temperature the linen changes tonality and it turns to the characteristic bone color which the Shroud of Turin currently has (Petrosillo and Siliato, 1996).

In 1993 the scientist Kist from Uzbekistan informs that he exposed samples of linen cloth to an atmosphere enriched in carbon-14 dioxide. The samples were placed into sealed glass tubes containing 9% by volume of carbon-14 dioxide with an activity of $8.3\times10^{7}(Bq)$ for 120 h. After exposure, the samples were washed by potassium hydroxide for 26 h to eliminate the remains of carbon dioxide according to the reaction

$$CO_2+2KOH\rightarrow K_2CO_3+H_2O$$

This scientist reports that there was an observable change in the activity of linen cloth, and therefore, an evidence for the possibility of carbon isotope exchange between atmospheric carbon dioxide and linen cloth. As a result, this experiment could serve as demostration of the fact that the carbon isotope exchange may not be negligible in radiocarbon dating.On the other hand, in 1995 the scientific American team formed by Jull, Donahue and Damon (Jull et al., 1996) informs that they exposed a sample of old linen cloth to an atmosphere containing modern CO_2 gas.

The old linen cloth was taken from the archaeological location of En Gedi in Israel, which was originally dated to about 2000 years B.P. The sample was put into a Pyrex tube containing CO_2 gas at 1.9 (atm-cm^3) and at 25°C. The tube was sealed and heated to 200°C for 15.5 h.

These scientists report that there was no observable change in the ${}^{14}C$ age.

ISOTOPIC EXCHANGE REACTION

The isotopic exchange reactions are well known from the first half of the 20th century. As of 1947, Bigeleisen and Mayer investigated the reactions of isotopic exchange of the isotopes of the hydrogen, silicon and tin

$${}^{1}H_2+2\,{}^{2}H\,I\leftrightarrow{}^{2}H_2+2\,{}^{1}H\,I$$

$${}^{28}Si\,F_4+{}^{30}Si\,F_6^{=}\leftrightarrow{}^{30}Si\,F_4+{}^{28}Si\,F_6^{=}$$

$${}^{120}Sn\,Cl_4+{}^{118}Sn\,Cl_6^{=}\leftrightarrow{}^{118}Sn\,Cl_4+{}^{120}Sn\,Cl6_6^{=}$$

In particular for the stable isotopes of the carbon, in 1944 Brandner and Urey (1945) investigated the reaction between carbon monoxide and carbon dioxide in gaseous phase

$${}^{13}C\,O_2+{}^{12}C\,O\leftrightarrow{}^{12}C\,O_2+{}^{13}C\,O$$

The carbon isotope exchange is also possible in liquid phase, as Szaram (1997) has investigated in the reaction of hydratation of carbon dioxide

$$C\,O_2+H_2O\leftrightarrow H_2C\,O_3\leftrightarrow H^{+}+H\,C\,O_3^{-}$$

which leads to carbon isotope exchange between $C\,O_2$ and $H\,C\,O_3^{-}$

$${}^{13}C\,O_2+H\,{}^{12}C\,O_3^{-}\leftrightarrow{}^{12}C\,O_2+H\,{}^{13}C\,O_3^{-}$$

Also Thorstenson and Parkhurst (2004) have reported a complex isotopic reaction between calcium carbonate and carbonate ion

$$Ca\,{}^{12}C\,{}^{16}O_{3aq}^{0}+{}^{13}C\,{}^{18}O_{3aq}^{-2}\leftrightarrow Ca\,{}^{13}C\,{}^{18}O_{3aq}^{0}+{}^{12}C\,{}^{16}O_{3aq}^{-2}$$

Moreover, the isotopic exchange reactions can occur between substances in different phases. As an example, Kawabe (1979) has investigated the heterogeneous isotopic equilibrium between quartz and water vapor

$$\frac{1}{6}\left(Si_3\,{}^{16}O_6\right)_{qtz}+H_2\,{}^{18}O_{(v)}\leftrightarrow\frac{1}{6}\left(Si_3\,{}^{18}O_6\right)_{qtz}+H_2\,{}^{16}O_{(v)}$$

in which the isotopes of the oxygen ${}^{16}O$ and ${}^{18}O$ are exchanged. Nowadays the isotopic exchange reactions are widely used in different investigation fields. For example, as Hoefs (1997) indicates, the geologists use the isotopic equilibrium between the calcite and water

$$Ca\,C\,{}^{16}O_3+3H_2\,{}^{18}O\leftrightarrow Ca\,C\,{}^{18}O_3+3H_2\,{}^{16}O \qquad (1)$$

for the study of the paleotemperatures in Geochemistry, since the fractionation factor depends on the temperature. This fractionation factor is at 25°C

$$\alpha_{Ca\,C\,O_3-H_2O}=\frac{\left({}^{18}O/{}^{16}O\right)_{Ca\,C\,O_3}}{\left({}^{18}O/{}^{16}O\right)_{H\,O_2}}=1.031 \qquad (2)$$

with $\left({}^{18}O/{}^{16}O\right)$ the isotopic ratio.

Based on the existence of isotopic reactions, we suppose, as a work hypothesis, that is possible a ${}^{14}C$ isotope exchange reaction between carbon dioxide and linen cloth. We will develop a theoretical model to study how an isotopic exchange reaction could influence the ${}^{14}C$ age of the Shroud of Turin. To that purpose we begin with our fundamental hypothesis: In the 1532 Chambéry fire, an isotopic reaction occurred between the CO_2 of the smoke from the fire and the monomer of cellulose $C_6H_{10}O_5$ of the linen. We propose the reaction

$${}^{14}C\,O_2+{}^{12}C_6H_{10}O_5\leftrightarrow{}^{12}C\,O_2+{}^{14}C\,{}^{12}C_5H_{10}O_5 \qquad (3)$$

in which one isotope ${}^{14}C$ is exchanged by another isotope ${}^{12}C$. As the ${}^{14}C$ is so scarce, we will suppose that a monomer only exchanges one isotope. The Equation (3) has never been verified before and the results presented in the paper are all based on this supposition.

The fibers of the linen fabric are formed by microscopic hollow tubes in which the air penetrates; therefore we can suppose that the linen and the air are mixed homogeneously.

When the linen is in equilibrium with the air, the equilibrium constant of the reaction (3) is

$$K=\frac{\left[{}^{12}C\,O_2\right]\cdot\left[{}^{14}C\,{}^{12}C_5H_{10}O_5\right]}{\left[{}^{14}C\,O_2\right]\cdot\left[{}^{12}C_6H_{10}O_5\right]} \qquad (4)$$

We can put the quotient of concentrations of the dioxide of carbon as the isotopic ratio of the air, that is (Brandner and Urey, 1945)

$$\frac{\left[{}^{12}C\,O_2\right]}{\left[{}^{14}C\,O_2\right]}=\frac{1}{\left({}^{14}C/{}^{12}C\right)_{air}}=\frac{1}{\left({}^{14}C/{}^{12}C\right)_0} \qquad (5)$$

where $\left({}^{14}C/{}^{12}C\right)_0 = (1.176 \pm 0.010)\times 10^{-12}$ is the standard isotopic ratio (Karlen and Olsson, 1968). Similarly for the linen we have

$$\frac{\left[{}^{14}C\,{}^{12}C_5 H_{10} O_5\right]}{\left[{}^{12}C_6 H_{10} O_5\right]} = \left({}^{14}C/{}^{12}C\right)_{linen} \equiv \left({}^{14}C/{}^{12}C\right) \tag{6}$$

With (5) and (6) we can put the equilibrium constant (4) as

$$K = \frac{\left({}^{14}C/{}^{12}C\right)}{\left({}^{14}C/{}^{12}C\right)_0} \tag{7}$$

The equilibrium constant (4) depends on the temperature T in the form (Broecker and Oversby, 1971)

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \tag{8}$$

where $P = 1$ (atm) is the environmental pressure, ΔH the enthalpy of reaction of (3) and

$$R = 8.314\left(\frac{J}{mole \cdot K}\right)$$

is the universal gas constant. We will estimate ΔH by means of an approximate calculation. We put this heat of reaction as the sum of the increases of enthalpy of the gas plus that of the cellulose, that is to say

$$\Delta H = \Delta H_{CO_2} + \Delta H_{C_6 H_{10} O_5} \tag{9}$$

First we calculate the increment ΔH_{CO_2} when a mole of ${}^{14}CO_2$ is transformed to ${}^{12}CO_2$

$$\Delta H_{CO_2} = \Delta U_{CO_2} + \Delta(PV) \tag{10}$$

where U_{CO_2} is the internal energy and V the volume. Since in the isotopic exchange there is no increment in the number of molecules and the environmental pressure P remains constant, the term $\Delta(PV)$ is null, therefore

$$\Delta H_{CO_2} = \Delta U_{CO_2} = U_{{}^{12}CO_2} - U_{{}^{14}CO_2} \tag{11}$$

In our approach we put as internal energy of the dioxide of carbon the sum of the kinetic translational energy, the kinetic rotational energy and the vibrational energy (Alonso and Finn, 1968), that is

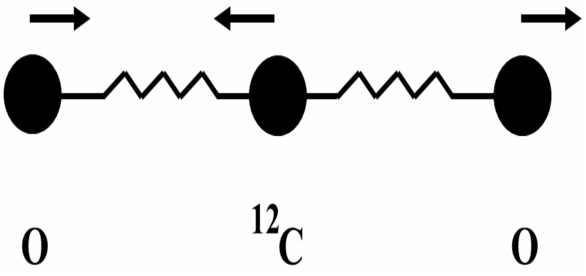

Figure 1. Longitudinal asymmetric mode.

$$U_{CO_2} = U_{tra} + U_{rot} + U_{vib} \tag{12}$$

where

$$U_{tra} = \frac{3}{2} N_A kT \quad ; \quad U_{rot} = N_A kT \tag{13}$$

with $N_A = 6.023\times 10^{23}\left(\frac{particles}{mole}\right)$ the Avogadro number and $k = 1.381\times 10^{-23}\left(\frac{J}{K}\right)$ is the Boltzmann constant. As we can see, the mass of the molecule CO_2 does not appear in (13). So these terms do not change in the transformation ${}^{14}CO_2 \rightarrow {}^{12}CO_2$. Therefore we write (11) as

$$\Delta H_{CO_2} = \Delta U_{vib} \tag{14}$$

As shown in the Figure 1, the molecule of ${}^{12}CO_2$ is linear and it has an asymmetric longitudinal vibrational mode. In this mode the oxygen atoms vibrate in phase and the atom of carbon vibrates in opposite phase. If we approach this vibration like a harmonic oscillator, the vibrational energy according to Goldstein (1959) is

$$U^{l}_{vib} = \frac{1}{2} N_A \hbar \omega_l + \frac{N_A \hbar \omega_l}{\exp(\hbar \omega_l / kT) - 1} \tag{15}$$

where $\hbar = 1.055\times 10^{-34}(J \cdot s)$ is the Planck constant. The frequency of longitudinal vibration ω_l according to Goldstein (1959) is

$$\omega_l = \sqrt{\frac{k_l}{\mu}} \tag{16}$$

where k_l is the spring constant and μ the reduced mass

$$\mu = \frac{2 \cdot m_{{}^{12}C} \cdot m_O}{m_{{}^{12}C} + 2 \cdot m_O} \tag{17}$$

where

$$m_{^{12}C} = 1.994\times10^{-26}(kg) \quad and \quad m_O = 2.657\times10^{-26}(kg)$$

are the masses of the atoms ^{12}C and O respectively. Also, the value $\omega_l = 4.426\times10^{14}(s^{-1})$ is known from the experimental measures of infrared spectroscopy (Alonso and Finn, 1968). In this case, it is clear that the mass of the isotope ^{12}C is involved in the vibrational energy (15), so this term changes in the transformation $^{14}CO_2 \rightarrow {}^{12}CO_2$.

During the 1532 Chambéry fire, inside the reliquary the temperature reached about 200°C $=T_2$. For this temperature the vibrational partition function according to Broecker and Oversby (1971) is

$$q = \frac{\exp(-\hbar\omega_l/2kT_2)}{1-\exp(-\hbar\omega_l/kT_2)} = 2.809\times10^{-2} \tag{18}$$

The energy of the ground state of the harmonic oscillator is $E_0 = \frac{1}{2}\hbar\omega_l = 2.335\times10^{-20}(J)$. Then the fraction of molecules which are in the ground state is

$$\frac{\exp(-E_0/kT_2)}{q} = 0.9988 \tag{19}$$

therefore almost 100% of the molecules are in the ground state, hence in our approach we take (15) as

$$U^l_{vib} \approx \frac{1}{2}N_A\hbar\omega_l \tag{20}$$

As shown in the Figure 2, the molecule of $^{12}CO_2$ has a second symmetric longitudinal vibrational mode. In this mode the atom of carbon does not vibrate, and therefore we do not take into account this mode.

As shown in the Figure 3, there is a transverse vibrational mode. For this mode the frequency is $\omega_t = 1.257\times10^{14}(s^{-1})$ (Alonso and Finn, 1968). Also for this mode we do take into account only the energy of ground state and write

$$U^t_{vib} \approx \frac{1}{2}N_A\hbar\omega_t \tag{21}$$

With (20) and (21) we put the vibrational energy of $^{12}CO_2$ as

$$U_{vib} = U^l_{vib} + U^t_{vib} = \frac{1}{2}N_A\hbar(\omega_l + \omega_t) \tag{22}$$

In a similar way for the isotopic molecule $^{14}CO_2$ we have

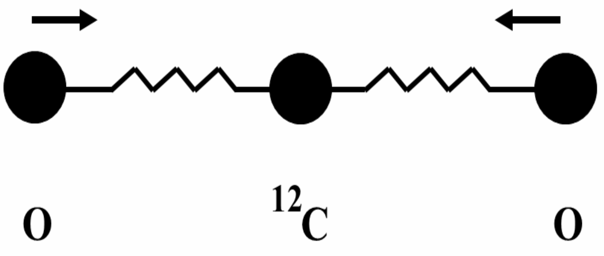

Figure 2. Longitudinal symmetric mode.

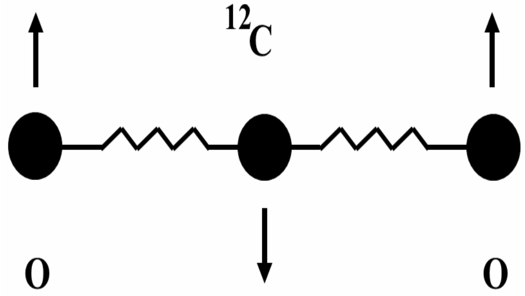

Figure 3. Transverse mode.

$$U'_{vib} = \frac{1}{2}N_A\hbar(\omega'_l + \omega'_t) \tag{23}$$

where ω'_l and ω'_t are the corresponding frequencies. For ω'_l we have a similar form as (16)

$$\omega'_l = \sqrt{\frac{k_l}{\mu'}} \tag{24}$$

with μ' the reduced mass

$$\mu' = \frac{2\cdot m_{^{14}C}\cdot m_O}{m_{^{14}C} + 2\cdot m_O} \tag{25}$$

where $m_{^{14}C} = 2.325\times10^{-26}(kg)$. Then dividing (24) by (16) and with (17) and (25) we calculate

$$\omega'_l = \omega_l\sqrt{\frac{m_{^{12}C}\cdot(m_{^{14}C} + 2\cdot m_O)}{m_{^{14}C}\cdot(m_{^{12}C} + 2\cdot m_O)}} = 4.191\times10^{14}(s^{-1}) \tag{26}$$

and in the same way we obtain

$$\omega'_t = \omega_t\sqrt{\frac{m_{^{12}C}\cdot(m_{^{14}C} + 2\cdot m_O)}{m_{^{14}C}\cdot(m_{^{12}C} + 2\cdot m_O)}} = 1.19\times10^{14}(s^{-1}) \tag{27}$$

With the values (26) y (27) we can already calculate (14) using (22) and (23)

$$\Delta H_{CO_2} = \Delta U_{vib} = U_{vib} - U'_{vib} = 959.5\left(\frac{J}{mole}\right) \tag{28}$$

To finish the calculation of the heat of reaction ΔH in (9), now we will estimate the increase of enthalpy of the cellulose $\Delta H_{C_6H_{10}O_5}$. To make an approximate calculation we will suppose that the linen fabric is a solid constituted by monomers of cellulose and we will apply the Einstein theory of the heat capacity. In accordance with this model, we treat the linen like a group of coupled harmonic oscillators which oscillate with an average frequency

$$\omega = \sqrt{\frac{\kappa}{m}} \tag{29}$$

where m is the mass of the monomer ${}^{12}C_6H_{10}O_5$ and κ is the constant of the springs which unite these masses. With the mass of the hydrogen $m_H = 1.674\times10^{-27}(kg)$ we obtain $m = 2.692\times10^{-25}(kg)$. The Einstein heat capacity at T_2 is, (Kittel, 1953)

$$C_v = 3R\left(\frac{\hbar\omega}{kT_2}\right)^2 \frac{\exp(\hbar\omega/kT_2)}{[\exp(\hbar\omega/kT_2)-1]^2} \tag{30}$$

For a poliatomic solid the geologists take for C_v the heat capacity per atom (Broecker and Oversby, 1971); here we will also use this criterion, that is

$$C_v = \frac{C}{n} \tag{31}$$

where C is the heat capacity of the cellulose and $n = 21$ is the number of atoms of the monomer of cellulose. Then with (30) and (31) we obtain

$$\frac{C}{3nR}[\exp(\hbar\omega/kT_2)-1]^2 = \left(\frac{\hbar\omega}{kT_2}\right)^2 \exp(\hbar\omega/kT_2) \tag{32}$$

In this approximate calculation for the heat capacity of the cellulose we use the experimental law for wood (Poon, 2003)

$$C\left(\frac{kJ}{kg\cdot K}\right) = 1.125 + 0.00452\cdot T({}^0C) \tag{33}$$

With (33) and the molecular weight of the monomer of cellulose $0.1621\left(\frac{kg}{mole}\right)$ we calculate at $T_2 =$ 200°C the value $C = 328.9\left(\frac{J}{mole\cdot K}\right)$. Putting this value in (32), we write the transcendent equation

$$0{,}6279\cdot\left(e^{\xi}-1\right)^2 = \xi^2 e^{\xi} \tag{34}$$

where $\xi = \hbar\omega/kT_2$. With a scientific calculator TI-92 we obtain the solution $\xi = 2.418$, which allows us to obtain

$$\omega = 1.498\times10^{14}\left(s^{-1}\right) \tag{35}$$

For the other isotopic species ${}^{14}C\,{}^{12}C_5H_{10}O_5$ of mass $m' = 2.725\times10^{-25}(kg)$, the corresponding frequency is

$$\omega' = \sqrt{\frac{\kappa}{m'}} \tag{36}$$

and then with (29) and (36) we have

$$\omega' = \omega\sqrt{\frac{m}{m'}} = 1.489\times10^{14}\left(s^{-1}\right) \tag{37}$$

Then using (35) and (37), according to Einstein's model, the internal energies of a mole of fabric of linen are, for the two isotopic species (Kittel, 1953)

$$U_{{}^{12}C_6H_{10}O_5} = \frac{3N_A\hbar\omega}{\exp(\hbar\omega/kT_2)-1} = 2791\left(\frac{J}{mole}\right) \tag{38}$$

$$U_{{}^{14}C\,{}^{12}C_5H_{10}O_5} = \frac{3N_A\hbar\omega'}{\exp(\hbar\omega'/kT_2)-1} = 2819\left(\frac{J}{mole}\right) \tag{39}$$

Therefore, with (38) and (39), the increase of enthalpy of the linen is

$$\Delta H_{C_6H_{10}O_5} = U_{{}^{14}C\,{}^{12}C_5H_{10}O_5} - U_{{}^{12}C_6H_{10}O_5} = 28\left(\frac{J}{mole}\right) \tag{40}$$

which is quite smaller (28).
Finally putting in (9) the data (28) and (40) we find the heat of reaction

$$\Delta H = \Delta H_{CO_2} + \Delta H_{C_6H_{10}O_5} = 987.5\left(\frac{J}{mole}\right) \tag{41}$$

As $\Delta H > 0$, the isotopic exchange reaction (3) is endothermic. Remembering (8), this means that when the temperature is increased the equilibrium constant in (7) increases. Therefore, when during the 1532 Chambéry fire the temperature and the dioxide increased in the air, probably, if the isotopic exchange taken place, the linen fabric could increase the isotopic ratio $\left({}^{14}C/{}^{12}C\right)$.

As the carbon has another natural isotopes ${}^{13}C$, besides the reaction (3) is possible another isotopic exchange reaction

$$ {}^{13}CO_2 + {}^{12}C_6H_{10}O_5 \leftrightarrow {}^{12}CO_2 + {}^{13}C\,{}^{12}C_5H_{10}O_5 $$

with equilibrium constant

$$ K' = \frac{\left[{}^{12}CO_2\right]\cdot\left[{}^{13}C\,{}^{12}C_5H_{10}O_5\right]}{\left[{}^{13}CO_2\right]\cdot\left[{}^{12}C_6H_{10}O_5\right]} $$

Then the fractionation factor between carbon dioxide and cellulose is

$$ \alpha_{CO_2-C_6H_{10}O_5} = \frac{\left({}^{14}C/{}^{12}C\right)_{CO_2}}{\left({}^{14}C/{}^{12}C\right)_{C_6H_{10}O_5}} = \frac{\dfrac{\left[{}^{14}CO_2\right]}{\left[{}^{12}CO_2\right]}}{\dfrac{\left[{}^{14}C\,{}^{12}C_5H_{10}O_5\right]}{6\left[{}^{12}C_6H_{10}O_5\right]+5\left[{}^{13}C\,{}^{12}C_5H_{10}O_5\right]}} $$

From (4) and K' we obtain

$$ \frac{\left[{}^{14}CO_2\right]}{\left[{}^{12}CO_2\right]} = \frac{\left[{}^{14}C\,{}^{12}C_5H_{10}O_5\right]}{K\left[{}^{12}C_6H_{10}O_5\right]} $$

$$ \left[{}^{13}C\,{}^{12}C_5H_{10}O_5\right] = \frac{K'\left[{}^{13}CO_2\right]\cdot\left[{}^{12}C_6H_{10}O_5\right]}{\left[{}^{12}CO_2\right]} $$

and substituting in the equation for $\alpha_{CO_2-C_6H_{10}O_5}$, and rearranging terms, we have

$$ \alpha_{CO_2-C_6H_{10}O_5} = \frac{6\left[{}^{12}CO_2\right]+5K'\left[{}^{13}CO_2\right]}{K\left[{}^{12}CO_2\right]} $$

In isotopic exchange reactions the equilibrium constants K and K' are near to the unit, and as in the Nature $\left[{}^{12}CO_2\right]\approx 100\left[{}^{13}CO_2\right]$, we consider negligible $\left[{}^{13}CO_2\right]$ in the numerator of last equation for $\alpha_{CO_2-C_6H_{10}O_5}$ and we write

$$ \alpha_{CO_2-C_6H_{10}O_5} \approx \frac{6\left[{}^{12}CO_2\right]}{K\left[{}^{12}CO_2\right]} = \frac{6}{K} $$

Therefore in this approach the fractionation factor between carbon dioxide and cellulose is dominated by the constant K; hence only we have used the isotopic exchange reaction (3) in our approximate model.

INCREASE OF RADIOCARBON

Now we will calculate how the isotopic exchange could affect the radiocarbon age which the Dating Laboratories of Tucson, Oxford and Zurich measured in 1988 (Damon et al., 1989). To that end we will commence with the hypothesis that the fabric of the Shroud of Turin was made at the beginning of the 1st century A.D. In the beginning, the fabric should be in equilibrium with the air in accordance with the isotopic reaction (3). So the initial concentrations were

$$ \frac{\left[{}^{14}CO_2\right]}{\left[{}^{12}CO_2\right]} = \left({}^{14}C/{}^{12}C\right)_0 \quad ; \quad \frac{\left[{}^{14}C\,{}^{12}C_5H_{10}O_5\right]}{\left[{}^{12}C_6H_{10}O_5\right]} = \left({}^{14}C/{}^{12}C\right)_{ini} \tag{42} $$

where $\left({}^{14}C/{}^{12}C\right)_{ini}$ was the initial isotopic ratio of the linen, when it was made. Because the isotope ${}^{14}C$ is unstable, this ratio diminished throughout the history until the year 1532. Let us nominate n_{01}, n_{02}, n_{03} and n_{04} as the initial quantities of moles of the isotopic species ${}^{14}CO_2$, ${}^{12}C_6H_{10}O_5$, ${}^{12}CO_2$ and ${}^{14}C\,{}^{12}C_5H_{10}O_5$ respectively in the year 1532 just before the fire

$$ \begin{array}{cccc} {}^{14}CO_2 & {}^{12}C_6H_{10}O_5 & {}^{12}CO_2 & {}^{14}C\,{}^{12}C_5H_{10}O_5 \\ n_{01} & n_{02} & n_{03} & n_{04} \end{array} \tag{43} $$

As we have already said, n_{04} does not correspond to the equilibrium due to the radioactivity of the isotope ${}^{14}C$. The quantity of ${}^{14}C\,{}^{12}C_5H_{10}O_5$ diminished due to the radioactivity and it did not recover because the reaction (3) is endothermic, since $\Delta H > 0$, and it does not progress toward the right while heat is not given to the system. When the fire begins the system receives heat, the reaction (3) progresses toward the right in the sense of increasing the products, and therefore the quantity of ${}^{14}C\,{}^{12}C_5H_{10}O_5$ increases due to the isotopic exchange. Then if y moles react, the new quantities are $n_1 = n_{01} - y$, $n_2 = n_{02} - y$, $n_3 = n_{03} + y$ and $n_4 = n_{04} + y$

$$ \begin{array}{cccc} {}^{14}CO_2 + & {}^{12}C_6H_{10}O_5 \rightarrow & {}^{12}CO_2 + & {}^{14}C\,{}^{12}C_5H_{10}O_5 \\ n_{01}-y & n_{02}-y & n_{03}+y & n_{04}+y \end{array} \tag{44} $$

Let us nominate x_1, x_2, x_3 and x_4 as the mole fractions

$$ x_1 = \frac{n_1}{n_1+n_2+n_3+n_4} \; ; \; x_2 = \frac{n_2}{n_1+n_2+n_3+n_4} \tag{45} $$

$$x_3 = \frac{n_3}{n_1+n_2+n_3+n_4}\,;\, x_4 = \frac{n_4}{n_1+n_2+n_3+n_4}$$

With this notation the chemical potential of each component at any temperature T and standard pressure $P = 1$ (atm) is

$$\mu_i = \mu_i^0 + RT\ln x_i \quad ; \quad i = 1,2,3,4 \tag{46}$$

where μ_i^0 is the standard chemical potential of each component, that is to say its Gibbs free energy per mole at standard pressure P and temperature T (Broecker and Oversby, 1971). Then the change in chemical potential as the reaction proceeds is

$$\sum_{products}\mu_i - \sum_{reagents}\mu_i = \mu_3 + \mu_4 - \mu_1 - \mu_2 \tag{47}$$

Putting the estequiometric coefficient of the reaction (44) $\nu_1 = \nu_2 = -1$ and $\nu_3 = \nu_4 = 1$ we can write (47) as

$$\sum_{products}\mu_i - \sum_{reagents}\mu_i = \sum_{i=1}^{4}\nu_i\mu_i \tag{48}$$

Using (46) in (48) we have

$$\sum_{i=1}^{4}\nu_i\mu_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\sum_{i=1}^{4}\nu_i\ln x_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{x_3x_4}{x_1x_2} \tag{49}$$

In (49) the quotient x_3/x_1 is the isotopic ratio of the air during the fire, that is

$$\frac{x_3}{x_1} = \frac{1}{\left({}^{14}C/{}^{12}C\right)_{air\ with\ smoke}} \tag{50}$$

We will suppose that the wood of the church pews was not very old, and therefore we will take for the air with smoke the isotopic ratio standard

$$\frac{x_3}{x_1} \approx \frac{1}{\left({}^{14}C/{}^{12}C\right)_0} \tag{51}$$

The other quotient x_4/x_2 in (49) is the isotopic ratio of the linen during the fire

$$\frac{x_4}{x_2} = \left({}^{14}C/{}^{12}C\right)_{linen\ in\ fire} \tag{52}$$

With (51) we write (49) as

$$\sum_{i=1}^{4}\nu_i\mu_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{x_4}{x_2} - RT\ln\left({}^{14}C/{}^{12}C\right)_0 \tag{53}$$

from (45) we have

$$\frac{x_4}{x_2} = \frac{n_4}{n_2} = \frac{n_{04}+y}{n_{02}-y} = \frac{n_{04}/n_{02} + y/n_{02}}{1 - y/n_{02}} \tag{54}$$

As the isotope ${}^{14}C$ is very scarce, $y/n_{02} << 1$, we can make the approach

$$\frac{x_4}{x_2} \approx \frac{n_{04}}{n_{02}} + \frac{y}{n_{02}} \tag{55}$$

and write

$$\ln\frac{x_4}{x_2} = \ln\left(\frac{n_{04}}{n_{02}} + \frac{y}{n_{02}}\right) \tag{56}$$

Now we nominate $x_0 = n_{04}/n_{02}$ and $\Delta x = y/n_{02}$, and with this we put (56) as

$$\ln\frac{x_4}{x_2} = \ln\left(x_0 + \Delta x\right) \tag{57}$$

It is not difficult to calculate that an increase of 18% of ${}^{14}C$ would be enough to diminish the radiocarbon age of a sample by 1400 years. For that reason we will suppose that the increment Δx which took place during the fire is small compared with x_0. Hence we apply to (57) a Taylor expansion

$$\ln\left(x_0 + \Delta x\right) \approx \ln x_0 + \left(\frac{d\ln x}{dx}\right)_{x_0}\Delta x = \ln x_0 + \frac{\Delta x}{x_0} \tag{58}$$

and with (58) we can approximate (57) in the form

$$\ln\frac{x_4}{x_2} \approx \ln x_0 + \frac{\Delta x}{x_0} = \ln\frac{n_{04}}{n_{02}} + \frac{y n_{02}}{n_{02}n_{04}} = \ln\frac{n_{04}}{n_{02}} + \frac{y}{n_{04}} \tag{59}$$

Then putting (59) in (53) we have

$$\sum_{i=1}^{4}\nu_i\mu_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\left(\ln\frac{n_{04}}{n_{02}} + \frac{y}{n_{04}}\right) - RT\ln\left({}^{14}C/{}^{12}C\right)_0 \Rightarrow \tag{60}$$

$$\sum_{i=1}^{4}\nu_i\mu_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{n_{04}/n_{02}}{\left({}^{14}C/{}^{12}C\right)_0} + \frac{RT\,y}{n_{04}} \tag{61}$$

Remembering (42) and using the law of radioactive disintegration, we can put

$$\frac{n_{04}}{n_{02}} = \left({}^{14}C/{}^{12}C\right)_{ini}\exp\left(-\frac{t\ln 2}{\tau}\right) \tag{62}$$

where $t = 1532$ years and $\tau = 5730$ years is the half life of the isotope ${}^{14}C$. With (62) we have

$$\ln\frac{n_{04}/n_{02}}{\left({}^{14}C/{}^{12}C\right)_0} = \ln\frac{\left({}^{14}C/{}^{12}C\right)_{ini}}{\left({}^{14}C/{}^{12}C\right)_0} - \frac{t\ln 2}{\tau} \tag{63}$$

Putting (63) in (61) we write

$$\sum_{i=1}^{4}\nu_i\mu_i = \sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{\left({}^{14}C/{}^{12}C\right)_{ini}}{\left({}^{14}C/{}^{12}C\right)_0} + \frac{RT\,y}{n_{04}} - \frac{RT\,t\ln 2}{\tau} \tag{64}$$

In (64) the sum

$$\sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{\left({}^{14}C/{}^{12}C\right)_{ini}}{\left({}^{14}C/{}^{12}C\right)_0} \tag{65}$$

is the change in chemical potential of the reaction (3) when the concentrations were those of equilibrium in the 1st century before the radioactive decay.

This sum in (65) is null because the Gibbs free energy is minimum in the equilibrium (Broecker and Oversby, 1971), that is

$$\sum_{i=1}^{4}\nu_i\mu_i^0 + RT\ln\frac{\left({}^{14}C/{}^{12}C\right)_{ini}}{\left({}^{14}C/{}^{12}C\right)_0} = 0\left(\frac{J}{mole}\right) \tag{66}$$

Therefore using (66) in (64) we have

$$\sum_{i=1}^{4}\nu_i\mu_i = RT\left(\frac{y}{n_{04}} - \frac{t\ln 2}{\tau}\right) \tag{67}$$

If we suppose that during the fire the reaction (44) reached the equilibrium, then the change in chemical potential in (67) became null, and hence we calculate

$$\frac{y}{n_{04}} = \frac{t\ln 2}{\tau} = 0.1853 \tag{68}$$

With (54), (55) and (68) the quotient of concentrations of the linen is

$$\frac{n_4}{n_2} \approx \frac{n_{04}}{n_{02}}\left(1 + \frac{y}{n_{04}}\right) = \frac{n_{04}}{n_{02}}\left(1 + \frac{t\ln 2}{\tau}\right) \tag{69}$$

The quotient of concentrations n_4/n_2 in (69) is the isotopic ratio which the linen reached after the 1532 Chambéry fire; we nominate this quotient as

$$\frac{n_4}{n_2} = \left({}^{14}C/{}^{12}C\right)_1 \tag{70}$$

The other quotient n_{04}/n_{02} in (69) is the isotopic ratio which the linen had in the year 1532 just before the fire. Then remembering (62) and taking the approach $\left({}^{14}C/{}^{12}C\right)_{ini} \approx \left({}^{14}C/{}^{12}C\right)_0$ we can write

$$\frac{n_{04}}{n_{02}} \approx \left({}^{14}C/{}^{12}C\right)_0 \exp\left(-\frac{t\ln 2}{\tau}\right) \tag{71}$$

Putting (70) and (71) in (69) we obtain

$$\left({}^{14}C/{}^{12}C\right)_1 = \left({}^{14}C/{}^{12}C\right)_0\left(1 + \frac{t\ln 2}{\tau}\right)\exp\left(-\frac{t\ln 2}{\tau}\right) = 1.158\times10^{-12} \tag{72}$$

From the year 1532 until the year 1988, when the laboratories dated the fabric of the Shroud of Turin, the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_1$ has decayed due to radioactivity down to the value

$$\left({}^{14}C/{}^{12}C\right)_2 = \left({}^{14}C/{}^{12}C\right)_1\exp\left(-\frac{t_h\ln 2}{\tau}\right) = 1.096\times10^{-12} \tag{73}$$

where $t_h = 1988 - 1532 = 456$ years. Comparing the isotopic ratio (73) with the standard $\left({}^{14}C/{}^{12}C\right)_0$ we calculate the corresponding radiocarbon age t_r

$$\left({}^{14}C/{}^{12}C\right)_2 = \left({}^{14}C/{}^{12}C\right)_0\exp\left(-\frac{t_r\ln 2}{\tau}\right) \Rightarrow \tag{74}$$

$$t_r = \frac{\tau}{\ln 2}\ln\frac{\left({}^{14}C/{}^{12}C\right)_0}{\left({}^{14}C/{}^{12}C\right)_2} = 582.4 \approx 582\ years \tag{75}$$

To this radiocarbon age t_r corresponds a calendar age t_c

$$t_c = 1988 - 582 = A.D. 1406 \tag{76}$$

The Dating Laboratories of Tucson, Oxford and Zurich dated the fabric of the Shroud of Turin between the years A.D. 1260-1390 (Damon et al., 1989). Our calculation is outside of this interval by 1406-1390=16 years only. Therefore, we could affirm that a process of isotopic exchange between the smoke of the fire and the linen fabric can affect the radiocarbon age by more than one millennium. As a result, the Shroud of Turin would be 2000 years old, in spite of only presenting an ${}^{14}C$ age of 600 years.

VAN'T HOFF APPROACH

Now we will develop another approximate model which can explain the experimental negative result which the American team reported (Jull et al., 1996). To that end we remember that in (41) the term $\Delta H_{C_6H_{10}O_5}$, which depends on the temperature, is much smaller than the other term ΔH_{CO_2} which does not depend on the temperature. Then with the value of (28) we make the approach

$$\Delta H \approx \Delta H_{CO_2} = 959.5\left(\frac{J}{mole}\right) \equiv \Delta H^0 \tag{77}$$

in which the heat of reaction ΔH^0 does not depend on the temperature. Applying (77) to (8) we can calculate the integral

$$\int_{K_1}^{K} d\ln K = \int_{T_1}^{T} \frac{\Delta H}{RT^2} dT \approx \frac{\Delta H^0}{R} \int_{T_1}^{T} \frac{dT}{T^2} \Rightarrow \tag{78}$$

$$\ln\frac{K}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right) \tag{79}$$

(79) is the well-known van't Hoff approach which allows to relate the equilibrium constants K and K_1 corresponding to the respective temperatures T and T_1. If T is the temperature reached by the linen during the fire, then the equilibrium constant K is given in (7) by the quotient of isotopic rations. The night of December 4th of the year 1532 the Shroud of Turin was in the city of Chambéry, which is very near the Alps. Based on this fact, we assume that $T_1 = 0$°C for the temperature just before the fire. Indeed, as previously said, the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_{T_1} = n_{04}/n_{02}$ which the linen had at the temperature T_1 was not of equilibrium due to the radioactive decay during the 1532 years lapsed from the making of the cloth. However we will see that in an approximate calculation we can take this isotopic ratio as if it were of equilibrium. For this we remember the change in chemical potential (67) corresponding to the reaction (44) and we write

$$\frac{1}{RT}\sum_{i=1}^{4} \nu_i \mu_i = \frac{y}{n_{04}} - \frac{t\ln 2}{\tau} \tag{80}$$

Just before the fire, $T = T_1$ and $y = 0$, therefore putting these values in (80) we obtain the approach

$$\frac{1}{RT_1}\sum_{i=1}^{4} \nu_i \mu_i = -\frac{t\ln 2}{\tau} = -0.1853 \approx 0 \tag{81}$$

This means that the change in chemical potential in (81) is approximately null, and therefore the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_{T_1}$ is of equilibrium. Then the equilibrium constant K_1 at the temperature T_1 is the quotient of isotopic ratios

$$K_1 = \frac{\left({}^{14}C/{}^{12}C\right)_{T_1}}{\left({}^{14}C/{}^{12}C\right)_0} \tag{82}$$

Putting (82) and (7) in the van't Hoff approach (79) we have

$$\ln\frac{\left({}^{14}C/{}^{12}C\right)}{\left({}^{14}C/{}^{12}C\right)_{T_1}} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right) \tag{83}$$

We can use (83) to calculate again the increment of ${}^{14}C$ which took place in the fire. To do this we put $T = T_2$, we include a subscript T_2 and with the value (77) we obtain

$$\ln\frac{\left({}^{14}C/{}^{12}C\right)_{T_2}}{\left({}^{14}C/{}^{12}C\right)_{T_1}} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0.1786 \tag{84}$$

To obtain $\left({}^{14}C/{}^{12}C\right)_{T_1}$ we can use again the law of radioactive disintegration as in (71), that is

$$\left({}^{14}C/{}^{12}C\right)_{T_1} = \left({}^{14}C/{}^{12}C\right)_0 \exp\left(-\frac{t\ln 2}{\tau}\right) = 9.771\times10^{-13} \tag{85}$$

Then with the values (84) and (85) we find

$$\left({}^{14}C/{}^{12}C\right)_{T_2} = \left({}^{14}C/{}^{12}C\right)_{T_1} \exp(0.1786) = 1.168\times10^{-12} \tag{86}$$

Later on, due to radioactivity, $\left({}^{14}C/{}^{12}C\right)_{T_2}$ ends up being in the year 1988 the new value

$$\left({}^{14}C/{}^{12}C\right)_{1988} = \left({}^{14}C/{}^{12}C\right)_{T_2} \exp\left(-\frac{t_h\ln 2}{\tau}\right) = 1.105\times10^{-12} \tag{87}$$

From (87) we calculate the corresponding radiocarbon age t_r'

$$t_r' = \frac{\tau}{\ln 2}\ln\frac{\left({}^{14}C/{}^{12}C\right)_0}{\left({}^{14}C/{}^{12}C\right)_{1988}} = 514.8 \approx 515\,years \tag{88}$$

which is similar to the value calculated previously t_r in (75).

Now we will plot the isotopic ratio of the linen $\left({}^{14}C/{}^{12}C\right)$ versus the temperature T. To that end we put (83) in the form

$$\frac{\left({}^{14}C/{}^{12}C\right)}{\left({}^{14}C/{}^{12}C\right)_{T_1}} = \exp\left[\frac{\Delta H^0}{RT_1}\left(1 - \frac{T_1}{T}\right)\right] \tag{89}$$

Doing the changes of variables $f = \left({}^{14}C/{}^{12}C\right)/\left({}^{14}C/{}^{12}C\right)_{T_1}$, $z = T/T_1$ and calculating the numerical value $\Delta H^0/RT_1 = 0.4225$ we obtain from (89) the function

$$f(z) = \exp\left[0.4225 \cdot \left(1 - \frac{1}{z}\right)\right] \quad (90)$$

The function $f(z)$ in (90) is shown by the curve in the Figure 4.

Also in this figure we represent with arrows the thermodynamic diagram which expresses the evolution of the isotopic ratio of the linen during the 1532 Chambéry fire.

Initially the relic was in the point P_1 of the thermodynamic diagram at the temperature T_1 with the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_{T_1}$. During the fire, the combustion of the wood flooded the air of carbon dioxide and increased the temperature. In these circumstances, due to the isotopic exchange, the fabric moves up to the point P_2 where the cloth reaches the temperature T_2 and the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_{T_2}$. At that moment, the people who had gone to save the Shroud of Turin flooded the reliquary with water (Siliato, 1985; Cardot, 1934). This implies two things; First is the sudden cooling from the temperature T_2 to the temperature T_1, and second is that the water covering impedes the isotopic exchange between the air and the fabric. As a result, during this sudden cooling the fabric moves from the point P_2 to the point P_3 supporting the disturbed isotopic ratio $\left({}^{14}C/{}^{12}C\right)_{T_2}$.

On the other hand, it is known that silver is a catalyst for isotopic exchange reactions (Brandner and Urey, 1945). The graph of the function in (90) can also explain the negative result obtained by the American team (Jull et al., 1996). American scientists introduced a piece of old linen in a closed tube containing modern carbon dioxide. They heated the tube at 200°C for 15 h, but without water or silver, and they found no significant change in the isotopic ratio $\left({}^{14}C/{}^{12}C\right)$ of the linen. This could be explained if, after warming, they allowed the linen to cool slowly inside the tube. In that case, as shown in the Figure 5, the isotopic ratio $\left({}^{14}C/{}^{12}C\right)$ of the linen moves from the point P_2 toward the point P_i; that is to say, the reaction (3) displaces toward the left in the sense of increasing the reagents. In this way, at the point P_i the piece of linen recovers the room temperature $T_i = 25$ °C and the isotopic ratio $\left({}^{14}C/{}^{12}C\right)_i$ which it had before the experiment.

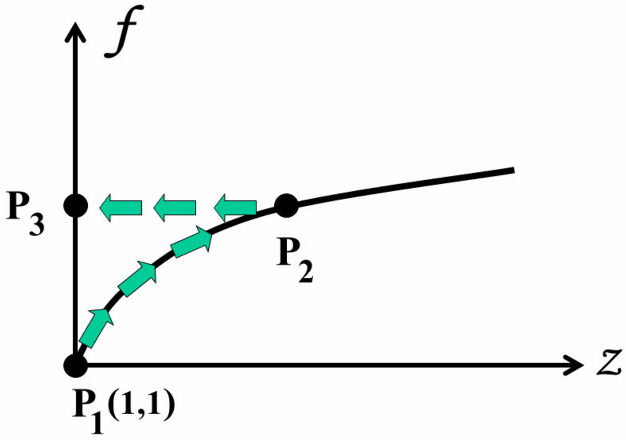

Figure 4. Isotopic ratio as a function of temperature.

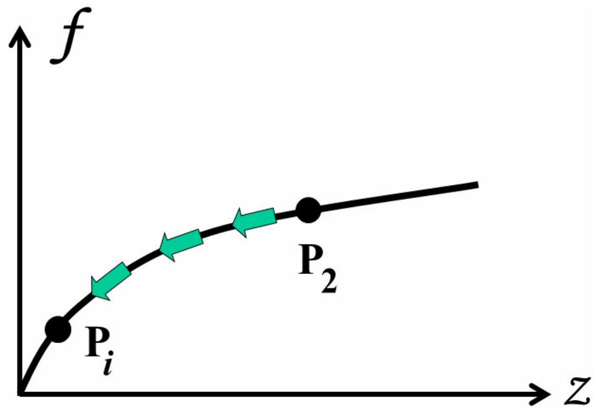

Figure 5. Recovery of the isotopic ratio.

STATISTICAL THERMODYNAMICS

Finally, for the sake of completeness, we will make a third estimate of the disturbance of radiocarbon age using Statistical Thermodynamics. In the middle of last century Urey, Bigeleisen and others established the basis for the calculation of the equilibrium constant for isotopic exchange (Urey, 1946; Bigeleisen and Mayer, 1947). The constant (4) can be written as

$$K = \frac{Q_{{}^{12}CO_2} \cdot Q_{{}^{14}C\,{}^{12}C_5H_{10}O_5}}{Q_{{}^{14}CO_2} \cdot Q_{{}^{12}C_6H_{10}O_5}} \quad (91)$$

where $Q_{{}^{12}CO_2}$ is the partition function of ${}^{12}CO_2$ and so on. For carbon dioxide the partition function is given by the product of three factors

$$Q_{{}^{12}CO_2} = Q^t_{{}^{12}CO_2} \cdot Q^r_{{}^{12}CO_2} \cdot Q^v_{{}^{12}CO_2} \quad (92)$$

where the translational partition function (Broecker and Oversby, 1971) is

$$Q^{t}_{^{12}CO_2}=\left(\frac{2\pi\cdot m_{^{12}CO_2}\cdot kT}{h^2}\right)^{3/2}V \tag{93}$$

and where $m_{^{12}CO_2}$ is the mass of the isotopic molecule $^{12}CO_2$ and $h=6.626\times10^{-34}\,(J\cdot s)$ is the Planck constant. With the same notation, for the other isotopic molecule $^{14}CO_2$ we have

$$Q^{t}_{^{14}CO_2}=\left(\frac{2\pi\cdot m_{^{14}CO_2}\cdot kT}{h^2}\right)^{3/2}V \tag{94}$$

The rotational partition function according to Broecker and Oversby (1971) in (92) is

$$Q^{r}_{^{12}CO_2}=\frac{8\pi^2\mu_r\delta^2kT}{2h^2} \tag{95}$$

In (95) μ_r is the reduced mass of the two oxygen atoms and δ their separation. The factor 2 in the denominator is due to the symmetry of the molecule (Urey, 1946). Obviously $Q^{r}_{^{12}CO_2}=Q^{r}_{^{14}CO_2}$ since the carbon atom is not involved in the rotation of the molecule.

The last factor in (92) is the vibrational partition function (Broecker and Oversby, 1971)

$$Q^{v}_{^{12}CO_2}=\frac{\exp(-\hbar\omega_l/2kT)}{1-\exp(-\hbar\omega_l/kT)}\left[\frac{\exp(-\hbar\omega_t/2kT)}{1-\exp(-\hbar\omega_t/kT)}\right]^2 \tag{96}$$

The square in the last bracket of (96) is due to the fact that the transverse vibrational mode ω_t is doubly degenerate (Urey, 1946). For the other isotopic molecule $^{14}CO_2$ we have

$$Q^{v}_{^{14}CO_2}=\frac{\exp(-\hbar\omega_l'/2kT)}{1-\exp(-\hbar\omega_l'/kT)}\left[\frac{\exp(-\hbar\omega_t'/2kT)}{1-\exp(-\hbar\omega_t'/kT)}\right]^2 \tag{97}$$

Then, putting (93), (94), (96) and (97) in (91) we obtain

$$K=\left(\frac{m_{^{12}CO_2}}{m_{^{14}CO_2}}\right)^{3/2}\frac{1-\exp(-\hbar\omega_l'/kT)}{1-\exp(-\hbar\omega_l/kT)}\left[\frac{1-\exp(-\hbar\omega_t'/kT)}{1-\exp(-\hbar\omega_t/kT)}\right]^2 \tag{98}$$

$$\times\left\{\exp\left[\frac{\hbar}{2kT}(\omega_l'+2\omega_t'-\omega_l-2\omega_t)\right]\right\}\frac{Q_{^{14}C\,^{12}C_5H_{10}O_5}}{Q_{^{12}C_6H_{10}O_5}}$$

It is difficult to calculate the partition functions of linen $Q_{^{12}C_6H_{10}O_5}$ and $Q_{^{14}C\,^{12}C_5H_{10}O_5}$. To make an approximate calculation, again we suppose that the linen fabric is a solid which obeys the Einstein theory of the heat capacity. In accordance with this model the partition function only depends on the average frequency. Then, remembering the values (35) and (37), the percentage change is only

$$\frac{(\omega-\omega')\cdot100}{\omega}=0.6\% \tag{99}$$

As this change (99) is small, we neglect the change in the partition function of linen, that is

$$Q_{^{14}C\,^{12}C_5H_{10}O_5}\approx Q_{^{12}C_6H_{10}O_5} \tag{100}$$

With (100) we can write (98) as

$$K=\left(\frac{m_{^{12}CO_2}}{m_{^{14}CO_2}}\right)^{3/2}\frac{1-\exp(-\hbar\omega_l'/kT)}{1-\exp(-\hbar\omega_l/kT)}\left[\frac{1-\exp(-\hbar\omega_t'/kT)}{1-\exp(-\hbar\omega_t/kT)}\right]^2 \tag{101}$$

$$\times\exp\left[\frac{\hbar}{2kT}(\omega_l'+2\omega_t'-\omega_l-2\omega_t)\right]$$

Then, putting the subscripts for the temperatures T_1 and T_2, we can write (101) for the respective equilibrium constants, that is,

$$K_1=\left(\frac{m_{^{12}CO_2}}{m_{^{14}CO_2}}\right)^{3/2} \tag{102}$$

$$\times\frac{1-\exp(-\hbar\omega_l'/kT_1)}{1-\exp(-\hbar\omega_l/kT_1)}\left[\frac{1-\exp(-\hbar\omega_t'/kT_1)}{1-\exp(-\hbar\omega_t/kT_1)}\right]^2$$

$$\times\exp\left[\frac{\hbar}{2kT_1}(\omega_l'+2\omega_t'-\omega_l-2\omega_t)\right]$$

$$K_2=\left(\frac{m_{^{12}CO_2}}{m_{^{14}CO_2}}\right)^{3/2} \tag{103}$$

$$\times\frac{1-\exp(-\hbar\omega_l'/kT_2)}{1-\exp(-\hbar\omega_l/kT_2)}\left[\frac{1-\exp(-\hbar\omega_t'/kT_2)}{1-\exp(-\hbar\omega_t/kT_2)}\right]^2$$

$$\times\exp\left[\frac{\hbar}{2kT_2}(\omega_l'+2\omega_t'-\omega_l-2\omega_t)\right]$$

Again, as we did in the van't Hoff approach, we take the isotopic ratio $\left(^{14}C/^{12}C\right)_{T_1}$ as if it were of equilibrium and we write the equilibrium constants as in (82)

$$K_1=\frac{\left({}^{14}C/{}^{12}C\right)_{T_1}}{\left({}^{14}C/{}^{12}C\right)_0} \tag{104}$$

$$K_2=\frac{\left({}^{14}C/{}^{12}C\right)'_{T_2}}{\left({}^{14}C/{}^{12}C\right)_0} \tag{105}$$

With (104), (105) and dividing (103) by (102) we obtain the value

$$\begin{aligned}\frac{\left({}^{14}C/{}^{12}C\right)'_{T_2}}{\left({}^{14}C/{}^{12}C\right)_{T_1}}&=\frac{1-\exp\left(-\hbar\omega'_l/kT_2\right)}{1-\exp\left(-\hbar\omega_l/kT_2\right)}\\&\times\left[\frac{1-\exp\left(-\hbar\omega'_t/kT_2\right)}{1-\exp\left(-\hbar\omega_t/kT_2\right)}\right]^2\frac{1-\exp\left(-\hbar\omega_l/kT_1\right)}{1-\exp\left(-\hbar\omega'_l/kT_1\right)}\\&\times\left[\frac{1-\exp\left(-\hbar\omega_t/kT_1\right)}{1-\exp\left(-\hbar\omega'_t/kT_1\right)}\right]^2\\&\times\exp\left[\frac{\hbar}{2k}\left(\omega'_l+2\omega'_t-\omega_l-2\omega_t\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]=1.216\end{aligned} \tag{106}$$

and with (85)

$$\left({}^{14}C/{}^{12}C\right)'_{T_2}=\left({}^{14}C/{}^{12}C\right)_{T_1}\cdot1.216=1.188\times10^{-12} \tag{107}$$

Moreover by radioactivity (107) becomes in 1988 the new value

$$\left({}^{14}C/{}^{12}C\right)'_{1988}=\left({}^{14}C/{}^{12}C\right)'_{T_2}\exp\left(-\frac{t_h\ln2}{\tau}\right)=1.124\times10^{-12} \tag{108}$$

From (108) we calculate the corresponding radiocarbon age

$$t''_r=\frac{\tau}{\ln2}\ln\frac{\left({}^{14}C/{}^{12}C\right)_0}{\left({}^{14}C/{}^{12}C\right)'_{1988}}=373.9\approx374\ \textit{years} \tag{109}$$

which is comparable to the other values calculated previously in (75) and (88).

CHEMICAL KINETICS

Thermodynamics does not allow us to calculate how long the isotopic exchange took in increasing the quantity of radiocarbono of the linen. For this purpose we need the Chemical Kinetics.

Brandner and Urey (1945) investigated experimentally the reaction of isotopic exchange between carbon dioxide and carbon monoxide.

$${}^{13}CO_2+{}^{12}CO\leftrightarrow{}^{12}CO_2+{}^{13}CO \tag{110}$$

They used quartz, silver and gold like catalysts in presence of water about 900℃. We will use their experimental data of rate constant of reaction and activation energy to study a rate law for the isotopic exchange reacction (3) between carbon dioxide and cellulose. The mechanism that Brandner and Urey (1945) proposed for the reaction (110) is as follows. To high temperature the water is dissociated in hydrogen and oxygen

$$2H_2O\leftrightarrow2H_2+O_2 \tag{111}$$

The hydrogen with catalyst H_2^* allows the formation of an activate complex, which favours the break of a double bond ${}^{13}C{=}O$ of carbon dioxide

$${}^{13}CO_2+H_2^*\leftrightarrow{}^{13}CO+H_2O^* \tag{112}$$

Based on this idea we propose the three following sequential reactions as a machanism for the isotopic exchange reacction (3). The first step is similar to (112)

$${}^{14}CO_2+H_2^*\leftrightarrow{}^{14}CO+H_2O^* \tag{113}$$

In the 1532 Chambéry fire the water could come from the combustion of the wood and the water used to extinguish the fire. The silver could come from the reliquary which contained the cloth. In the exterior of the reliquary the temperature could reach about 900℃, since in some points the silver melted and it perforated in the fabric of linen 8 holes.

The nuns Clarisas of Chambéry patched these 8 holes in 1534 (Siliato, 1985; Cardot, 1934). This indicates that the fire could reach enough temperature for the dissociation of the water (111). Inside the reliquary the temperature reached about 200℃, since at this temperature the linen changes tonality and it turns to the characteristic bone color which the Shroud of Turin currently has; to superior temperature the linen becomes black (Petrosillo and Siliato, 1996).

In the second step the monoxide exchanges ${}^{14}C$ with the cellulose

$${}^{14}CO+{}^{12}C_6H_{10}O_5\leftrightarrow{}^{12}CO+{}^{14}C\,{}^{12}C_5H_{10}O_5 \tag{114}$$

In the third step the monoxide reacts with the water to give dioxide

$${}^{12}CO+H_2O^*\leftrightarrow{}^{12}CO_2+H_2^* \tag{115}$$

Now we will propose two possible mechanisms for the the second step (114). The chemical structure of one monomer of cellulose is as in Figure 6.

In the first mechanism we suppose that one ${}^{14}CO$ and one not screened hydroxyl group HO constitute a transition state with a carboxyl group $COOH$ in the

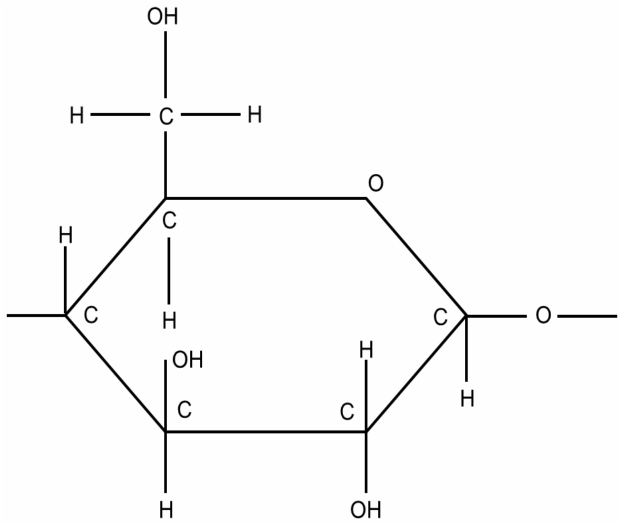

Figure 6. Monomer of cellulose.

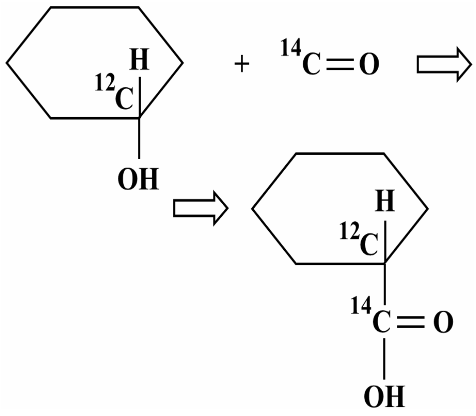

Figure 7. Transition state.

monomer, as is shown in the Figure 7.

During this transition state the isotopes ^{12}C and ^{14}C are united by a bond. The nuclei of these isotopes have an even number of protons and an even number of neutrons. According to a well-known empirical rule of Nuclear Physics this nucleous type has null spin, and therefore they are bosons. Then, we have that the bond $^{12}C{-}^{14}C$ is a compound system with two bosones in quantum different states. Let us nominate estate a to the position in which the nucleus of the ^{12}C forms part of the monomer, and let us nominate estate b to the position in which the nucleus of the ^{14}C forms part of the carboxyl group. Let us designate for $\Psi_a(12)$ and $\Psi_b(14)$ to the wavefunctions which describe to these quantum states. If we obviate the difference of mass, these particles are indisinguishable bosons, therefore the wavefunction Ψ which describes to the compound system should be symmetric with respect to particle interchange, that is

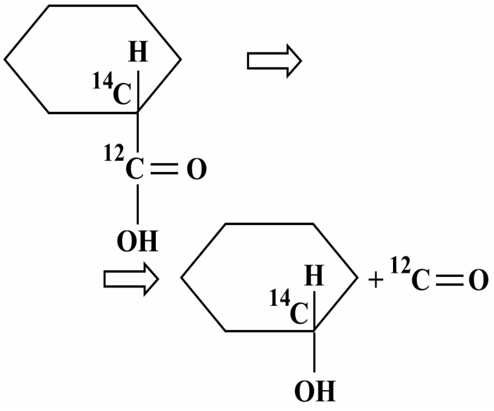

Figure 8. New transition state.

$$\Psi=\frac{1}{\sqrt{2}}\left[\Psi_a(12)\cdot\Psi_b(14)+\Psi_a(14)\cdot\Psi_b(12)\right] \tag{116}$$

where $\Psi_a(14)$ represents to the nucleus of the ^{14}C in the monomer and $\Psi_b(12)$ represents to the nucleus of the ^{12}C in the carboxyl group. Then if $a=b$, (116) is not null since

$$\Psi=\frac{2}{\sqrt{2}}\Psi_a(12)\cdot\Psi_a(14) \tag{117}$$

This means that the nucleuses can approach one to other, and therefore, to exchange their positions. Then now the transition state is as in the Figure 8. After this exchange the transition state disappears and a monomer and a separated ^{12}CO appear.

In the second alternative mechanism we suppose that one ^{14}CO and one not screened H constitute a transition state with a carbonyl group COH in the monomer, as is shown in the Figure 9. The rest of the second mechanism is the same as the first.

Now we will deal with the chemical kinetics of the first two steps (113) and (114), which we write again and we put the forward and back reactions explicitly. For the first step (113) we have

$$^{14}CO_2+H_2^*\rightarrow{}^{14}CO+H_2O^* \quad (K_1) \tag{118}$$

$$^{14}CO+H_2O^*\rightarrow{}^{14}CO_2+H_2^* \quad (K_{-1}) \tag{119}$$

and for the second step (114) we have

$$^{14}CO+{}^{12}C_6H_{10}O_5\rightarrow{}^{12}CO+{}^{14}C\,{}^{12}C_5H_{10}O_5 \quad (K_2) \tag{120}$$

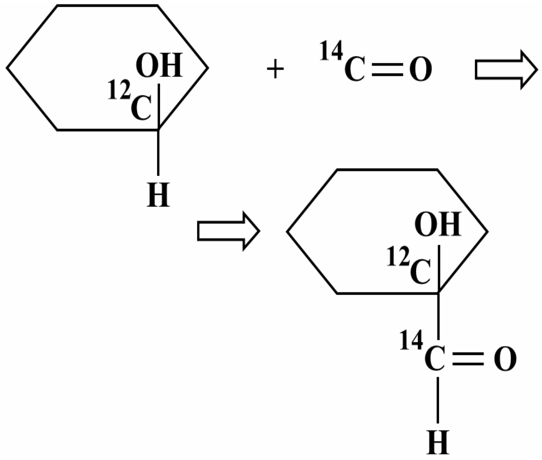

Figure 9. Second alternative mechanism.

where K_1, K_{-1} and K_2 are rate constans of reaction. In (118) it is necessary to break a double bond $^{14}C{=}O$ of carbon dioxide, which has a bond energy about $730\left(\frac{kJ}{mole}\right)$. In the second step (120), as we said before, it is not necessary to break double bond $^{14}C{=}O$ of carbon monoxide, but a single bond $^{12}C{-}OH$ of the monomer, which has a bond energy about only $352\left(\frac{kJ}{mole}\right)$. This allows us to suppose that the activation energy E_{a1} of the first step (118) is greater than activation energy E_{a2} of the second step (120). In the Figure 10 this energy profile is shown.

Therefore in the second step (120) the ^{14}CO would be more reactive than the $^{14}CO_2$ in the first step (118). Then, as the rate constant of reaction is proportional to an exponential in the form $K \propto \exp\left(\frac{-E_a}{RT}\right)$, the rate constant of reaction K_2 of the second step (120) is greater than the rate constant of reaction K_1 of the first step (118).

Therefore, according to this model, the first step (118) would be the rate determining step.

On the other hand, as the bond energy of the bond $O{-}H$ is about $460\left(\frac{kJ}{mole}\right) > 352\left(\frac{kJ}{mole}\right)$, we can also suppose that for the back reaction (119) $E_{a2} < E_{a-1}$ and therefore $K_2 > K_{-1}$. Now we apply the steady-state hypothesis, that is $K_2 >> K_{-1}, K_1$. Then, as the rate of reaction of (120) is much greater that that of (118), the ^{14}CO reacts the moment it is produced.

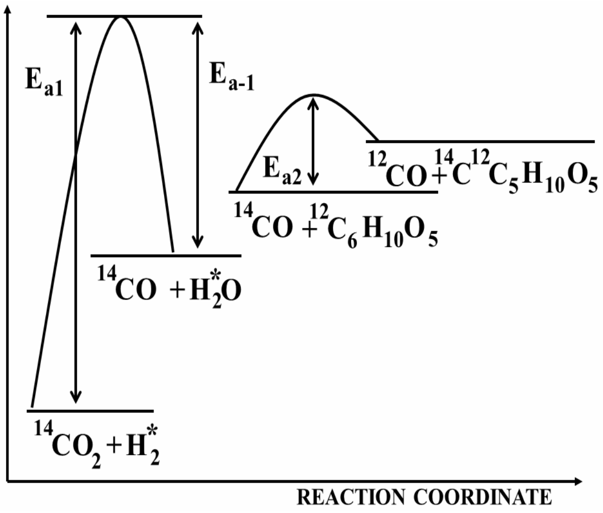

Figure 10. Energy profile.

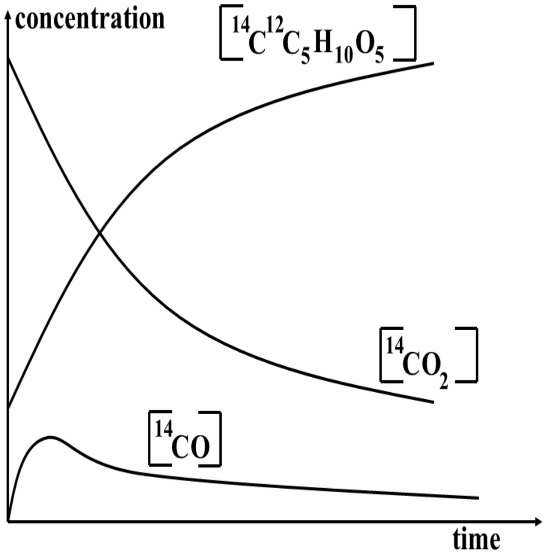

Figure 11. Variation of concentration.

We noted that in this situation, as is shown in Figure 11, during the majority of the time we can assume that the concentration $[^{14}CO]$ is aproximately constant, that is

$$\frac{d[^{14}CO]}{dt} \approx 0 \tag{121}$$

From (118), (119) and (120) we will suppose that for ^{14}CO the rate law is

$$\frac{d[^{14}CO]}{dt} = K_1[^{14}CO_2]\cdot[H_2^*] - K_{-1}[^{14}CO]\cdot[H_2O^*] - K_2[^{14}CO]\cdot[^{12}C_6H_{10}O_5] \tag{122}$$

but due to (121) we have

$$\left[{}^{14}CO\right]=\frac{\mathrm{K}_1\left[{}^{14}CO_2\right]\cdot\left[H_2^*\right]}{\mathrm{K}_{-1}\left[H_2O^*\right]+\mathrm{K}_2\left[{}^{12}C_6H_{10}O_5\right]} \quad (123)$$

From (120) we will suppose that for ${}^{14}C^{12}C_5H_{10}O_5$ the rate law is

$$\frac{d\left[{}^{14}C^{12}C_5H_{10}O_5\right]}{dt}=\mathrm{K}_2\left[{}^{14}CO\right]\cdot\left[{}^{12}C_6H_{10}O_5\right] \quad (124)$$

and putting (123) in (124) we have

$$\frac{d\left[{}^{14}C^{12}C_5H_{10}O_5\right]}{dt}=\frac{\mathrm{K}_1\mathrm{K}_2\left[H_2^*\right]\cdot\left[{}^{14}CO_2\right]\cdot\left[{}^{12}C_6H_{10}O_5\right]}{\mathrm{K}_{-1}\left[H_2O^*\right]+\mathrm{K}_2\left[{}^{12}C_6H_{10}O_5\right]} \quad (125)$$

Now we apply the hypothesis of the stationary state $\mathrm{K}_2>>\mathrm{K}_{-1}$ and we make the approach $\mathrm{K}_{-1}\left[H_2O^*\right]<<\mathrm{K}_2\left[{}^{12}C_6H_{10}O_5\right]$; then (125) becomes

$$\frac{d\left[{}^{14}C^{12}C_5H_{10}O_5\right]}{dt}\approx\mathrm{K}_1\left[H_2^*\right]\cdot\left[{}^{14}CO_2\right] \quad (126)$$

From (118) we will suppose that for ${}^{14}CO_2$ the rate law is

$$\frac{d\left[{}^{14}CO_2\right]}{dt}=-\mathrm{K}_1\left[H_2^*\right]\cdot\left[{}^{14}CO_2\right] \quad (127)$$

As the ${}^{14}CO_2$ is very scarce, we can suppose that $\left[H_2^*\right]>>\left[{}^{14}CO_2\right]$. Then as the reagent H_2^* is in excess with relation to the reagent ${}^{14}CO_2$, we assume that the change in $\left[H_2^*\right]$ is small and we make the approach $\left[H_2^*\right]\approx$ constant. Under these circumstances we nominate $\mathrm{K}_1\left[H_2^*\right]=\mathrm{K}$. With this we can write (126) and (127) as

$$\frac{d\left[{}^{14}C^{12}C_5H_{10}O_5\right]}{dt}=\mathrm{K}\left[{}^{14}CO_2\right] \quad (128)$$

$$\frac{d\left[{}^{14}CO_2\right]}{dt}=-\mathrm{K}\left[{}^{14}CO_2\right] \quad (129)$$

Integrating (129) we find

$$\left[{}^{14}CO_2\right]=\left[{}^{14}CO_2\right]_0\cdot\exp(-\mathrm{K}t) \quad (130)$$

where $\left[{}^{14}CO_2\right]_0$ is the inital concentration at the beginning of the isotopic exchange at $t=0$. Putting (130) in (128) and integrating we find

$$\left[{}^{14}C^{12}C_5H_{10}O_5\right]=\left[{}^{14}C^{12}C_5H_{10}O_5\right]_0+\left[{}^{14}CO_2\right]_0\left[1-\exp(-\mathrm{K}t)\right] \quad (131)$$

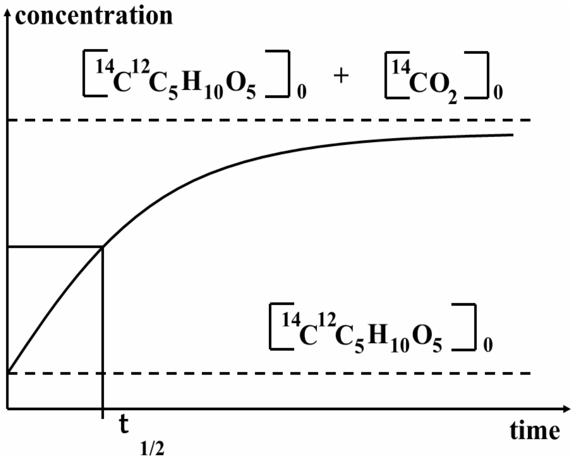

Figure 12. Variation of linen radiocarbon.

where $\left[{}^{14}C^{12}C_5H_{10}O_5\right]_0$ is the concentration of radiocarbon of the linen at the beginning of the Chambéry fire. As is shown in Figure 12, (131) indicates the increase of radiocarbon of the Shroud of Turín.

In this graph

$$\tau_{1/2}=\frac{\ln 2}{\mathrm{K}} \quad (132)$$

is the time that takes the linen in reaching half of increase in radiocarbono.

Now we will estimate the value of K from the experimental data which Brandner and Urey (1945) measured for the isotopic exchange reaction (110). Starting from the machanism (112) they found that the rate law

$$\frac{d\left[{}^{13}CO_2\right]}{dt}=-\mathrm{K}'\left[{}^{13}CO_2\right] \quad (133)$$

was in accord with experimental data. They also saw that the silver is so good catalyst as the quartz. In an experiment carried out to temperature $T'=897^0$C they found the experimental values of activation energy E'_a and rate constant of reaction K'

$$E'_a=112\left(\frac{kcal}{mole}\right) \ ; \ \mathrm{K}'=101\left(min^{-1}\right) \quad (134)$$

To estimate the K of (129) to the temperature $T=200^0$C inside the reliquary during the fire of Chambéry, we use the Arrhenius-Eyring equation (Broecker and Oversby, 1971)

$$\mathrm{K}=\sigma F N_A\sqrt{\frac{8kT}{\mu_{14}}}\cdot\exp\left(-\frac{E_a}{RT}\right) \quad (135)$$

where

$$\sigma = \pi\left[r\left(^{14}CO_2\right) + r\left(H_2^*\right)\right]^2 \qquad (136)$$

being $r\left(^{14}CO_2\right)$ and $r\left(H_2^*\right)$ the radius of the molecules $^{14}CO_2$ and H_2^*. The reduced mass μ_{14} is

$$\mu_{14} = \frac{m\left(^{14}CO_2\right)\cdot m\left(H_2^*\right)}{m\left(^{14}CO_2\right) + m\left(H_2^*\right)} \qquad (137)$$

F is the steric factor which takes account the form of the molecules. For the K' of (133) we use the same obvious notation

$$K' = \sigma F' N_A \sqrt{\frac{8kT'}{\mu_{13}}}\cdot \exp\left(-\frac{E_a'}{RT'}\right) \qquad (138)$$

As in changing from ^{14}C isotope to ^{13}C isotope the radius and the form of the molecules vary very little, we can suppose that $\sigma \approx \sigma'$ and $F \approx F'$. Moreover using the values of the masses in atomic mass unit $m(H) = 1.008$, $m(O) = 15.995$, $m(^{13}C) = 13.003$ and $m(^{14}C) = 14.008$ we found tha $\mu_{14} \approx \mu_{13}$. As we want only the order of magnitude, we consider negligible the variation in activation energy with the isotopic change $^{14}C \rightarrow {}^{13}C$ and with the temperature change $T \rightarrow T'$, that is $E_a \approx E_{a'}$. Then dividing (135) by (138) we have

$$K \approx K'\sqrt{\frac{T}{T'}}\cdot \exp\left[\frac{E_a}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)\right] = 59.82\left(min^{-1}\right) \qquad (139)$$

Putting (139) in (132) we obtain

$$\tau_{1/2} = \frac{\ln 2}{K} = 1.159 \cdot 10^{-2}\left(min\right) \qquad (140)$$

Although this value is only approximate due to the made approaches, the order of magnitude indicates that under the chemical physical conditions during the Chambéry fire, the fabric of the Shroud of Turin could increase its content in radiocarbon quickly.

Conclusion

We have seen how the isotopic exchange reactions could affect the radiocarbon age of a sample. We used three methods of calculation: Gibbs free energy, the Van't Hoff approach and the Urey formulation. These three theories predict that the 1532 Chambéry fire could affect by more than 1400 years the radiocarbon age of a cloth which is 2000 years old; this would apply to the Shroud of Turin. In addition, it explains also the experimental contradictory results which Uzbek scientist and American scientists obtained.

Thus, our theoretical model would put an end to the controversy between the dating laboratories and the experts on the Shroud of Turin. The laboratories did excellent work in having found a mediaeval radiocarbon age. However, the experts give solid reasons to think that the Shroud of Turin dates from the 1st century A.D. Probably the controversy arose because, once more, human innocence was surprised by the subtleties of Mother Nature.

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