

# ORIGIN OF THE ASYMMETRY OF BIOMOLECULES AND WEAK INTERACTION

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## 1. Introduction

Living matter on Earth exhibits the quite characteristic phenomenon that if the composing molecules are in an optically active form such as amino acids, sugars, then of the two possible (L-, and D)isomers only one can be found. Living systems contain L-amino acids and D-sugars although there are exceptions, e.g. some antibiotics contain D-amino-acids. An excellent review of the natural distribution of optical isomers has been given by Ulbricht (1962).

The asymmetry of biomolecules starting from its discovery in the last century by Pasteur (1861) has always been a puzzle. In experiments to synthesize optically active molecules racemic mixtures are always obtained. The well-known Miller-type experiments to produce amino acids from inorganic precursors resulted in racemic compositions (Miller, 1973). Nature somehow selected one of the isomers with which to build up life.

Two recent reviews have dealt with the question of the origin of the asymmetry of biomolecules (Thiemann, 1974a.; Ulbricht, 1975).

This review has been written with the aim of discussing just one selected topic of the possible explanations, i.e. to review and to analyse the theoretical and experimental results concerning the correlation between the asymmetry of biomolecules and the fundamental asymmetry of weak interactions discovered by Lee and Yang (1956).

After briefly summarizing the different ideas about the origin of asymmetry (Section 2) the theoretical background of the weak interaction will be reviewed (Section 3). This is followed by a detailed and critical discussion of the experimental work that has already been performed in this field (Section 4). Section 5 contains a summary of experimental results. In Section 6 a simple estimation is outlined to illuminate the quantitative aspects of the problem, viz. has there been enough radioactivity and/or has there been sufficient time during evolution to produce asymmetry by weak interaction? In Section 7 the conclusions of this review will be summarized.

## 2. Ideas About the Origin of Asymmetry

The present data about the origin of life indicate that organisms such as bacteria and blue-green algae existed  $3.2-3.3 \times 10^9$  yr ago (Schopf, 1975). The age of the oldest rocks

are  $3.8 \times 10^9$  yr, the chemical evolution of biomolecules also originated around this time.

So far as is known, living systems can only exist in asymmetric form. During polymerization, L-molecules have a greater probability of combining with L-molecules; D-molecules with D-molecules. If there are mixed polymers they break more easily at the junctions of L- and D-molecules. In this way, over a period of time, pure L- and D-polymers – and eventually, optically pure systems – are produced (Noyes and Bonner, 1974). One can expect that from symmetric starting matter two living systems evolve which exist in parallel, forming two virtually separate but interpenetrating L- and D-biospheres without disturbing each other.

Ideas about the origin of asymmetry can be classified into two main groups:

- that asymmetry has evolved by chance;
- there was some physical reason for asymmetry.

Whereas the ideas in group (a) always deal solely with some autocatalytic process involving growth, ideas grouped under (b) try to find processes which caused asymmetry in the starting matter to have more molecules of one isomer. In this way asymmetry had to be produced during chemical evolution, i.e. between  $3.8$  and  $3.2 \times 10^9$  yr ago.

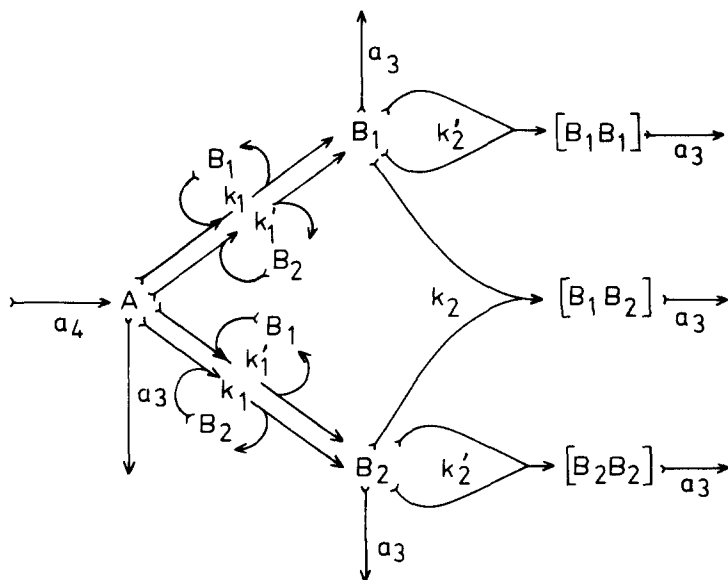


Fig. 1. Reaction scheme of a bistable open system which should produce preferentially one of two antipodes. A substrate  $A$  is delivered into the system at constant rate  $a_4$ . Two enantiomeric compounds  $B_1$  and  $B_2$  react with  $A$ , each preferentially catalysing its own formation, with reaction constants  $K_1 = a_1(1 + b_1)$  and  $K'_1 = a_1(1 - b_1)$  respectively.  $1 > b_1 > 0$  represents the stereoselectivity of the two 'competitive' reactions,  $A + B_1 \rightarrow B_1 + B_1$  and  $A + B_2 \rightarrow B_2 + B_2$ , over the corresponding 'parasitic' reactions  $A + B_1 \rightarrow B_2 + B_1$  and  $A + B_2 \rightarrow B_1 + B_2$  which impair the scope of bistable behaviour.  $B_1$  and  $B_2$  are supposed to neutralize each other by a second order reaction  $K_2 = a_2(1 + b_2)$  for unequal reactants,  $B_1 + B_2 \rightarrow$ ; and  $K'_2 = a_2(1 - b_2)$  for equal reactants,  $B_1 + B_1$  and  $B_2 + B_2$ .  $1 > b_2 > 0$  represents the stereoselectivity of the 'aggressive' reaction between enantiomers over its 'parasitic' reaction between compounds of equal chirality.  $A$ ,  $B_1$  and  $B_2$  are withdrawn from the system by overflow or by some first order reactions with a reaction constant  $a_3$  (Decker, 1973).

Some purely representative examples are given from both groups.

(a) Seelig and Rössler (1972) and, Decker (1973) independently suggested an autocatalytic process, the scheme of which is given in Figure 1. From the optically inactive inflow, autocatalytic processes with  $k_a = k_b$  rate constants produce active matter. These mutually inhibit each other's growth. If one analyses the differential equations of the system one gets — with specified parameters — a solution which describes an unstable equilibrium state. A small fluctuation in one direction causes this side to grow exponentially and the other to die out. A very exhaustive treatment of this type of process has been published by Hochstim (1975). A critique of these ideas is due to be published in the near future (Czégé and Fajsz, 1976).

Harrison (1973) holds the view that living systems were able to produce L- and D-colonies separated territorially. He assumes that after this separation a localized catastrophe destroyed many more systems of one type colony.

According to the theory of Ageno (1972) the asymmetry evolved after the formation of sexuality among living organisms. He was able to construct a coupled differential equation system assuming that the number of entities grows when L males and L females mate and the mating is sterile between L and D couples. On introducing again a small fluctuation the system develops in the direction of the given fluctuation while the opposite part dies out.

(b) There are three important physical possibilities of producing asymmetry in biomolecules:

- (i) adsorption of biomolecules on asymmetric surfaces;
- (ii) synthesis or decomposition of biomolecules by circularly polarized light;
- (iii) effects on biomolecules of the asymmetry of weak interaction.

(i) There are many minerals on the Earth (clay, quartz, etc.) which exhibit optical activity in crystalline form. Many papers have dealt with observation of asymmetric adsorption of optically active molecules on such optically active crystals. The work of Bonner and coworkers (1974) is a representative study in this field. They measured the adsorption of L, D-alanine by L, and D-quartz polycrystals. Their results, reproduced in Table I, clearly show that L-alanine is adsorbed with greater probability on L-quartz than on D-quartz and oppositely. The extent of preferential adsorption is 1–1.8%. In this way, nature could have produced asymmetry if it had produced asymmetry among quartz crystals.

The general criticism of the adsorption ideas is that the problem is only shifted to find the cause of asymmetry in the materials for adsorption.

(ii) It has long been known (Kuhn, and Knopf, 1930) that circularly polarized light is able to produce asymmetric distribution of molecules in synthesis from nonactive precursors and in decomposition when racemic mixtures are irradiated. Two modern investigations should be mentioned in this context. Bernstein *et al.* (1972a) synthesized 1% more L-hexahelicene from its precursor (by light which was 100% left circularly polarized); Kagan *et al.* (1974) obtained about 20% asymmetry in a contrasting experiment by decomposing racemic hexahelicene to 99.9% by circularly polarized light.

TABLE I  
Absorption of alanine by D- and L-quartz. DA is the differential absorption  
(Percentage by L - percentage by D-quartz) (Bonner *et al.*, 1974)

Form	Percentage ( $\pm$ S.D.) adsorption by		DA <sup>a</sup>	Weighted average of DA
	L-quartz	D-quartz		
L	29.35 $\pm$ 0.43	28.33 $\pm$ 0.47	1.02 $\pm$ 0.64	
L	28.35 $\pm$ 0.82	26.60 $\pm$ 0.53	1.75 $\pm$ 1.00	1.2 $\pm$ 0.4
L	22.21 $\pm$ 0.42	21.03 $\pm$ 0.45	1.18 $\pm$ 0.62	
D	29.08 $\pm$ 0.59	30.38 $\pm$ 0.81	-1.30 $\pm$ 1.00	-1.13 $\pm$ 0.68
D	25.92 $\pm$ 0.63	26.88 $\pm$ 0.66	-0.96 $\pm$ 0.95	

<sup>a</sup>The S.D. (standard deviation) for the data in column DA are recalculated from the S.D. values of the numbers using the following equation:

$$\text{S.D. (DA)} = \sqrt{(\text{SD}_L)^2 + (\text{SD}_D)^2}$$

In the latter experiment, the remaining 0.1% of nondestroyed hexahelicene showed the 20% asymmetry. (In Section 4 we return to the simple theoretical background of the difference between synthesis and decomposition-type experiments.) It is therefore clear that circularly polarized light could have been effective in producing the asymmetry of biomolecules. However, the problem remains unsolved because in spite of these well established facts the light from the Sun does not have a measurable amount of circularly polarized light. Attempts to find some mechanism by combining the magnetic field of the Earth (Byk, 1904; Mörtberg, 1971) fail because of the periodic change in the direction of the magnetic field.

(iii) The possibility that the asymmetry of biomolecules has been generated by the fundamental asymmetry of the weak interaction has been a constantly returning experimental and theoretical challenge since it was first suggested by Vester (1957). Since this particular subject is the main topic of the present review it will be dealt with more comprehensively in the next sections.

### 3. Weak Interaction

#### 3.1. PARTICLES AND INTERACTIONS

Matter — living and non-living — is constituted from elementary or subatomic particles. The subatomic zoo contains many particles: some appear very often in experiments, others are deeply hidden and can be detected only by using high energy bombardment. There is some order in this zoo. The particles can be divided into three groups: photons, leptons and hadrons. Leptons are the electrons (positive and negative), the neutrinos that appear in  $\beta$ - and meson decays, and the muons, hadrons are the mesons ( $\pi$ -mesons, K-mesons, . . .) and the baryons: protons, neutrons, which are called nucleons, and the particles heavier than nucleons. The subatomic particles may have spins. The unit of spin of subatomic particles is  $\hbar$ , this being the Planck constant divided by  $2\pi$ .

TABLE II

Interactions and subatomic particles. The entries in the table are not always unambiguous. The photon, for instance, behaves at high energy as if it could interact both hadronically and weakly

Particle	Type	Weak	Electro-magnetic	Hadronic
Photon	Boson	no	yes	no
Leptons				
Neutrino	Fermion	yes	no	no
Electron	Fermion	yes	yes	no
Muon	Fermion	yes	yes	no
Hadrons				
Mesons	Bosons	yes	yes	yes
Baryons	Fermions	yes	yes	yes

The present description follows closely the presentation of Frauenfelder and Henley (1974) in their excellent book *Subatomic Physics*. The particles are classified according to their spin too: particles having integer number of spins are bosons, those having a half-integer number are fermions.

The subatomic particles interact with each other. There are four basic interactions: the hadronic (or strong) interaction, the electromagnetic interaction, the weak interaction and the gravitational interaction. The last is very weak among the subatomic particles and is ignored in the present discussion. The different particles do not take part in all interactions, as is illustrated in Table II.

The nominations of the interactions may be understood from Figure 2. Here the interaction cross-sections of the different particles are given as a function of the energy. At the energies where the comparison of the coupling strengths was performed (namely at few GeV ( $10^3$  MeV)), the hadronic cross-section is of the order of the geometrical cross-section of the proton, i.e.  $\sim 3 \times 10^{-26}$  cm<sup>2</sup>. If the proton were transparent to the incident neutron, we would expect the cross-section to be much smaller than the geometrical cross-section. Nearly every neutron which comes within 'reach' of a scattering centre suffers an interaction. In this sense the hadronic interaction is indeed strong.

The cross-section for electromagnetic interaction ( $\gamma, p$ ) is about 100 times smaller, and the ( $\nu, N$ ) interaction is really very weak, it is  $\sim 10^{12}$  times smaller than the hadronic interaction. Note that in the case of weak interaction a neutrino ( $\nu$ ) interacts with a nucleus ( $N$  atomic nucleus composed of protons and neutrons) – and not another lepton, say an electron. This is because the electron and nucleus interact, due to their electric charge, also by electromagnetic interaction, which is much stronger than the weak interaction. It would be very difficult to detect the weak interaction in an ( $e, N$ ) reaction which is mixed to the electromagnetic one in a ratio of  $\sim 10^{-10}$ .

Generally speaking the hadronic interactions keep the protons and neutrons together

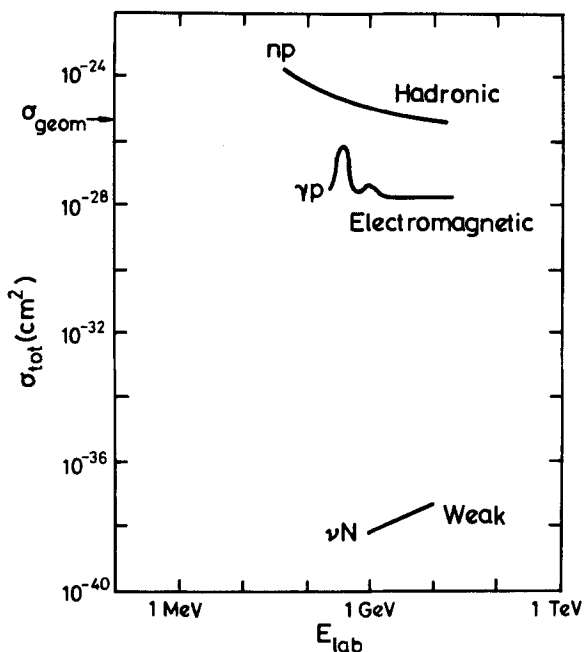


Fig. 2. Comparison of the total cross-section for hadronic, electromagnetic and weak processes on nucleons.  $\sigma_{\text{geom}}$  indicates the geometrical cross-section of a nucleon. ( $p$  = proton,  $n$  = neutron,  $\gamma$  = photon,  $\nu$  = neutrino,  $N$  = nucleus, which is composed from nucleons.) (Frauenfelder and Henley, 1974.)

in the atomic nucleus. The electromagnetic interaction is responsible for the atomic shell, i.e. it determines how the electrons move around the nucleus. When the atoms form molecules and polymers the electromagnetic interaction dominates. The covalent, ionic, hydrophobic, hydrogen bonds and the van der Waals forces are all electromagnetic in origin. It can be stated that in chemistry and biology the electromagnetic interaction plays the leading role. The hadronic and weak interactions are always present but their direct contribution does not, at first glance, seem to be determining. The weak interaction, however, may play a determining role in the origin of asymmetry of biomolecules.

### 3.2. DETAILS OF WEAK INTERACTION

To illustrate the weak interaction, the  $\beta$ -decay of a neutron is considered. A free neutron decays by the emission of an electron and an antineutrino ( $\bar{\nu}$ ) to a proton\*. This can be

\* Every particle has its antiparticle. The antiparticle of an electron is the positron, that of a proton is the anti-proton. . . . In the case of charged particles the antiparticles have the same mass, spin, etc., but the sign of their charge is opposite. The neutron, neutrino are neutral; in such cases the charge cannot serve for discrimination. They are characterized by the general rule: particle and antiparticle annihilate if they meet. Further, the spin of  $\bar{\nu}$  points in the direction of its movement, the spin of  $\nu$  points in the opposite direction.

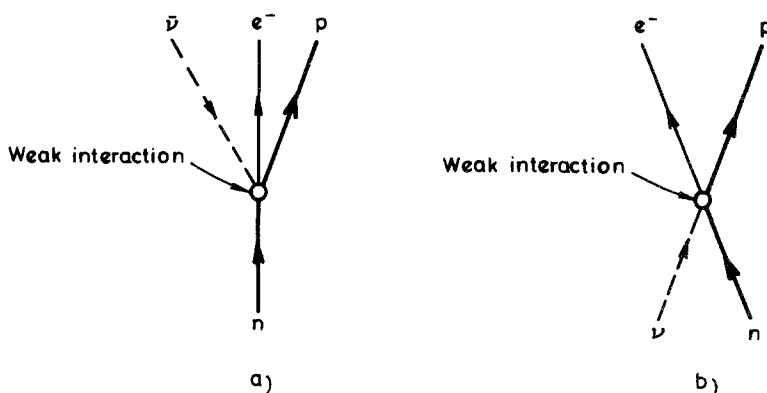


Fig. 3. Neutron decay and neutrino absorption.

visualized with a simple diagram such as that shown in Figure 3a. The half-life of the neutron  $\beta$ -decay is 12 min.

In the decay an antineutrino is emitted which can be considered as a particle going backward in time. It is reasonable that it can be replaced in the scheme by an incoming particle, in this case a neutrino (Figure 3b). In this way the neutron decay and the neutrino absorption by a neutron are considered to be similar processes.

This simple transformation is needed just to illustrate how the theory of weak interaction has been formulated using the analogy of electromagnetic interaction. In Figure 4a the interaction of two moving charges, i.e. two electromagnetic currents  $j_{em}$  and  $j'_{em}$  is illustrated. The interaction is mediated by a virtual photon  $\gamma$ , which makes the connection between the two vertices  $e$ . The strength of the interaction is proportional to the square of the charge. It is said that in the electromagnetic interaction a virtual photon is exchanged between the two currents. In Figure 4b, the neutrino absorption is given

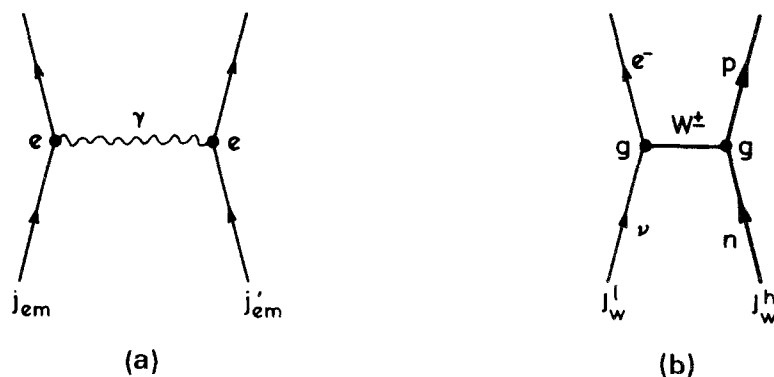


Fig. 4. Comparison of the electromagnetic and the weak interactions. The superscripts  $l$  and  $h$  indicate the weak currents of leptons and hadrons, respectively.

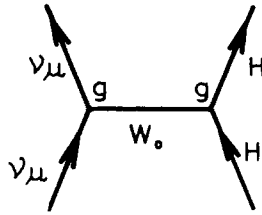


Fig. 5. Diagram of interaction of muon neutrino and hadron.

analogously. The leptonic current ( $j_w^l$ , neutrino and electron) and the hadronic current ( $j_w^h$ , neutron and proton) interact via a virtual boson  $W_{\pm}$ . The coupling constant is replaced by the weak coupling constant which is much smaller than  $e$ . It is very important that the weak currents in both vertices change the value of the electric charge by one unit (i.e. from the neutral neutrino, a charged electron and from a neutron charged proton arises). Such a change of electric charge – which involved the intermediate boson to be charged ( $W_{\pm}$ ), since the electric charge must have been conserved – was quite generally observed in all weak interaction processes until 1973 when weak interactions of neutral currents were detected (Hasert *et al.*, 1973). The process is shown in the diagram of Figure 5. High energy muon neutrinos (originating from the decay of  $\mu$ -mesons) interact with hadrons. There is no change in the electric charge at the vertices and the intermediate boson is a neutral one ( $W_0$ ). Searches for  $W_{\pm}$  and  $W_0$  have been unsuccessful until now or, in other words, it is possible to establish only a lower limit for the mass of these bosons. Because the mass of the particle is inversely related to the range of the force, an upper limit can be given for it, viz.  $R_W < 10^{-14}$  cm, which means that the weak force works between particles only if they are very near to each other.

### 3.3. PARITY

The left hand is the mirror image of the right hand, the screw with the left hand thread is the mirror image of the screw with the right hand thread, the left amino acids and sugars are the mirror images of the right ones, etc. The object and the mirror image are symmetric under an interchange between left and right. This interchange is called mirror reflection or space inversion. Until 1956 it was generally accepted that the laws of physics were symmetric under space inversion. It meant, in other words, that processes would go the same way in space but in their inverted form.

It can easily be seen that symmetry in everyday life would exist only if the number of left-handed people were as great as of right-handed people, if the number of left-handed screws were equal to the number of right-handed screws, if living organisms contained equal numbers of L- and D-molecules, etc. Everyday life – as we see it – is more or less asymmetric.

There are other important examples of asymmetry too. The Earth revolves around the Sun and rotates around its axis in one fixed direction. The sense for revolution and



rotation never changes. This is in spite of the fact that according to physics the gravitational force which drives the Earth is symmetric.

The explanation of this situation is simple: the mirror symmetry of the gravitational force does not also mean that the boundary conditions had to be mirror symmetric; in the case of the Earth those boundary conditions existed when its movement originated.

Nevertheless the symmetry is a strong argument and people are also inclined to believe that the boundary conditions must be symmetric in that sense that in another, independent, solar system the opposite directions of revolution and rotation must exist.

The strong belief of symmetry under space inversion and the concept of parity of elementary particles and microsystems traces back its origin to atomic spectroscopy in the 1920s when Laparte discovered that atoms have two different classes of levels, though he was unable to explain their existence. Wigner (1927) then showed that the two classes follow from invariance of the wave function of the atom under space reflection.

The particles and microsystems are described by wave functions in quantum mechanics. The wave function  $\psi(x, t)$  describes the behaviour of the system in space and time. We are interested only in the space behavior, therefore we omit the time coordinate. On applying the parity operation  $P$  (space inversion or mirror reflection) to a wave function

$$P\psi(x) = \psi(-x). \quad (1)$$

The parity operation changes the sign of the coordinates.

If  $P$  is applied the second time

$$P^2 \psi(x) = \psi(x), \quad (2)$$

and the original wave function is regained.

The energy values of the system whose wave function is  $\psi(x)$  can be obtained from the Schrödinger equation

$$H \psi(x) = E \psi(x), \quad (3)$$

where  $H$  is the Hamiltonian of the interactions in the system (electromagnetic in the case of atoms), and  $E$  is the energy. Let us operate with  $P$  on Equation (3):

$$P H \psi(x) = H P \psi(x) = E P \psi(x). \quad (4)$$

Here  $H$  and  $P$  were assumed to be interchangeable, i.e.  $HP = PH$ . The content of Equation (4) can be written as

$$H \psi'(x) = E \psi'(x), \quad (5)$$

where

$$\psi'(x) = P \psi(x).$$

$\psi(x)$  and  $P \psi(x)$  satisfy the same Schrödinger equation, therefore they must describe the

same physical situation if the eigenvalues are not degenerated. They must therefore be proportional to each other:

$$P \psi(x) = \pi \psi(x). \quad (6)$$

$\pi$  must be  $+1$  or  $-1$  according to Equation (2). The wave function of a physical system can change its sign under parity operation

$$P \psi(x) = -\psi(-x), \quad (7)$$

or can have the same sign

$$P \psi(x) = \psi(-x). \quad (8)$$

In the former case the wave function has *negative parity*, the wave function is odd; in the latter it has *positive parity*, the wave function is even. Examples of the two types of wave function are given in Figure 6.

The parity of a system is a completely quantum mechanical concept; it has no classical analogue. The symmetry of the system is easily seen: the probability of finding quantum-mechanical systems in space is proportional to  $\psi(x)^2$ , which is symmetric under space inversion (Figure 6) for both types of wave functions (odd and even). The parity conservation is included in Equation (4). If  $H$  and  $P$  are interchangeable, then the parity

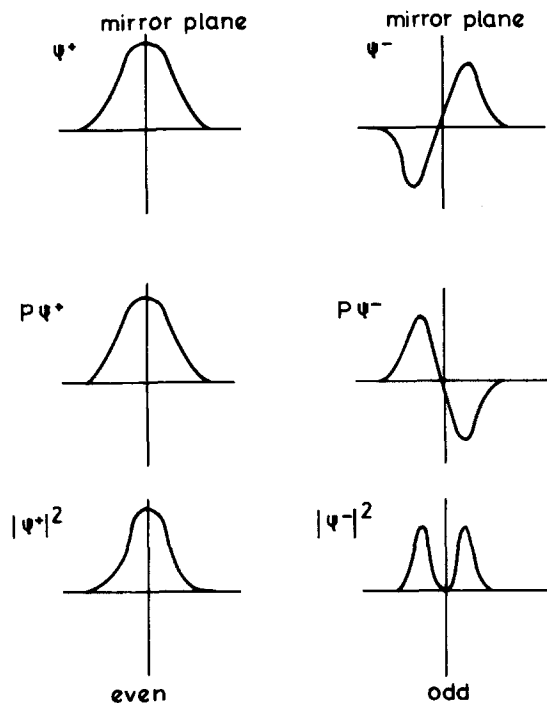


Fig. 6. Even and odd wave functions, their mirror reflected forms and square of absolute values.

of the system is conserved during any interaction described by  $H$ . This rule, which evolved from the experiences of atomic spectroscopy, has proved to be extremely fruitful in many applications and it has become a dogma; the natural laws of interactions were thought to be invariant under any space inversion.

Optically active molecules are asymmetric in space. The steric scheme of L- and D-alanine is represented in Figure 7a and b. The quantum-mechanical interpretation of the asymmetric positions of atoms which determine the optical activity is illustrated below the schemes (Figure 7c and d). The horizontal line gives the position of the atoms, the vertical one the wave function. The isomers alone are asymmetric. Let us apply the law of parity|conservation| to the synthesis of alanine from optically inactive precursors. The synthesis is supposed to go through the interaction of electrons in the electronic shells of the constituent atoms. The interaction is electromagnetic, its Hamilton  $H$  can be interchanged with the parity operator  $P$ , therefore the parity of the starting inactive system which may either be positive or negative must have been conserved during synthesis; this means that the final system has to have the same parity as the starting one, the final system must also be symmetric, i.e. L-, or D-molecules cannot be synthesized

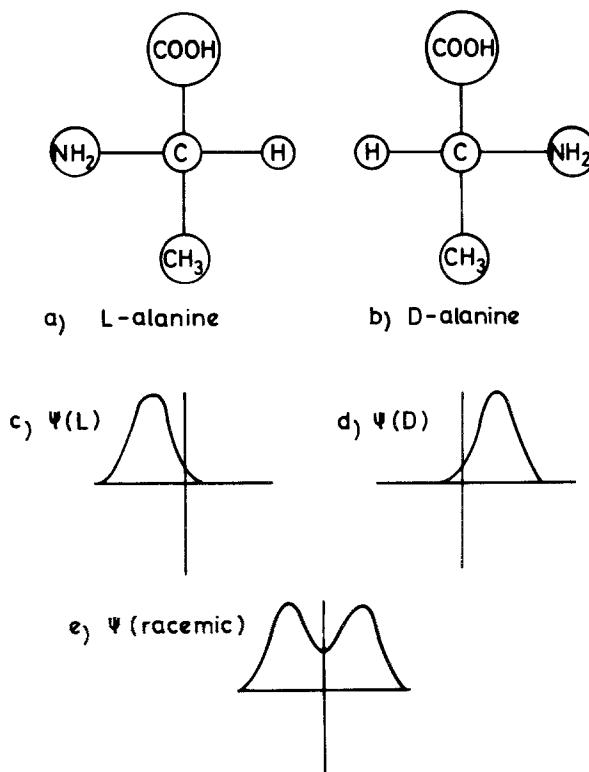


Fig. 7. Scheme of the molecular structure of L- and D-alanine. Illustration of the wave function of the molecules and of their racemic mixture.

separately in such processes. Racemic mixtures, the wave function of which is symmetric (Figure 7e), must be the result of such syntheses. This was found to be true in Miller's experiment (Miller, 1973).

#### 3.4. PARITY NONCONSERVATION IN WEAK INTERACTION

All the experimental facts were in favour of the parity conservation principle until 1956. At that time it became quite clear that 'two' strange particles existed which had the same mass, production cross-section, spin and charge but they could decay either to two  $\pi$ -mesons or to three  $\pi$ -mesons. Because the parity operation is multiplicative and the parity of  $\pi$ -mesons is negative the 'two' particles had to have positive and negative parities respectively, i.e. they had to be different. However, Lee and Yang (1956) thought differently. They considered that the decay has a long lifetime which means that it is caused by weak interaction. Moreover, they realized that one factor had been overlooked; viz. that the parity conservation had been checked only in strong and electromagnetic interactions and not in the weak interaction. Assuming the identity of the 'two' particles they gave up the idea of parity conservation in weak interaction. The consequences of this idea could have been checked in the  $\beta$ -decays which also proceed under the influence of weak interaction.

The first convincing experiment was the observation of the asymmetric emission of  $\beta$ -particles from oriented  $^{60}\text{Co}$  nuclei (Wu *et al.*, 1957). The  $^{60}\text{Co}$  nuclei were oriented through their magnetic moments by an external magnetic field at very low temperature. It was observed that the orientation was lost as the sample warmed up. If the direction of the external field ( $B$ ) is varied up and down, the direction of the orientation changes too. The number of  $\beta$ -particles emitted was different in the two cases. The difference disappeared after warming up (Figure 8). The  $\beta$ -decay of  $^{60}\text{Co}$  nuclei is asymmetric. The experiment was a clear demonstration that parity is not conserved, or in other words, parity is violated in weak interaction.

A further consequence – which seems to be of primary importance concerning the connection between the asymmetry of weak interaction and the asymmetry of biomolecules – is the spin polarization of  $\beta$ -particles. The direction of spin of  $\beta$ -particles is opposite to the direction of their movement and of  $\beta^+$ -particles points in the same direction (Figure 9) with rather high probability. The probability is equal to  $v/c$ , where  $v$  is the velocity of the particle,  $c$  that of the light. In the case of  $\beta$ -particles of some hundreds of keV energy,  $v/c \approx 1$ .

It has to be emphasized that the polarization takes place during the emission of  $\beta$ -particles, i.e. during the action of weak forces, and  $v$  is the starting velocity of the particles. In the material around the source the  $\beta$ -particles slow down and lose their velocity although they do keep, however, a rather substantial part of their original polarization. In the majority of energy-losing collisions the particles lose energy, and change direction, but their direction of spin remains more or less the same as it was with the original probability. The only process in which it is highly likely that the polarization

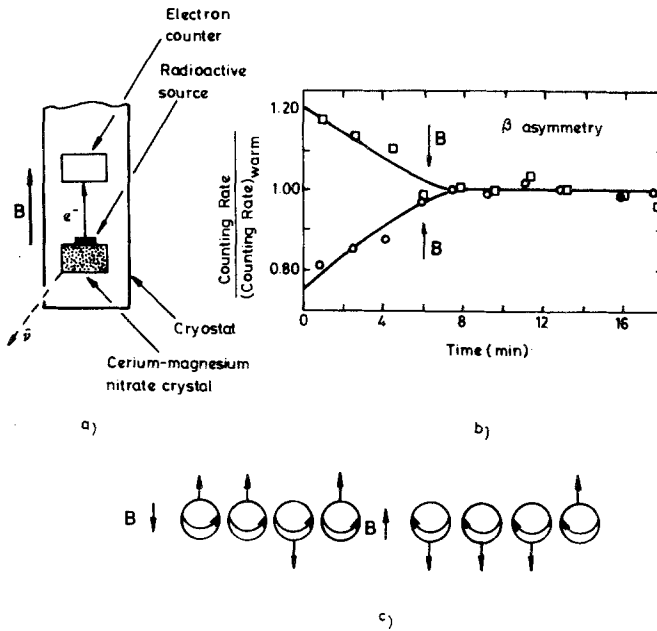


Fig. 8a-c. (a) Arrangement to measure beta-emission from polarized  $^{60}\text{Co}$  nuclei. (b) Result of the earliest experiment showing parity non-conservation (Wu *et al.*, 1957). (c) Scheme of  $\beta$ -decaying polarized  $^{60}\text{Co}$  nuclei.

is lost is the production of high energy bremsstrahlung, which emerges with the circular polarization. Problems connected with the circular polarization of bremsstrahlung will be discussed in Section 4.2. If the parity were not conserved in an interaction among the particles of a system then the wave function would be the superposition of a positive and negative parity wave function:

$$\psi(x) = a\psi^+(x) + b\psi^-(x), \tag{9}$$

where

$$(a)^2 + (b)^2 = 1.$$

Applying the parity operation

$$P\psi(x) = a\psi^+(x) - b\psi^-(x), \tag{10}$$

$\psi(x)$  changes under space inversion.  $\psi(x)^2$  is asymmetric.  $\psi(x)$ ,  $P\psi(x)$  and  $\psi(x)^2$  are

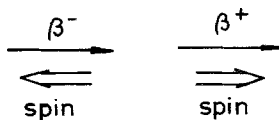


Fig. 9. Polarization of negative ( $\beta^-$ ) and positive ( $\beta^+$ )  $\beta$ -particles.

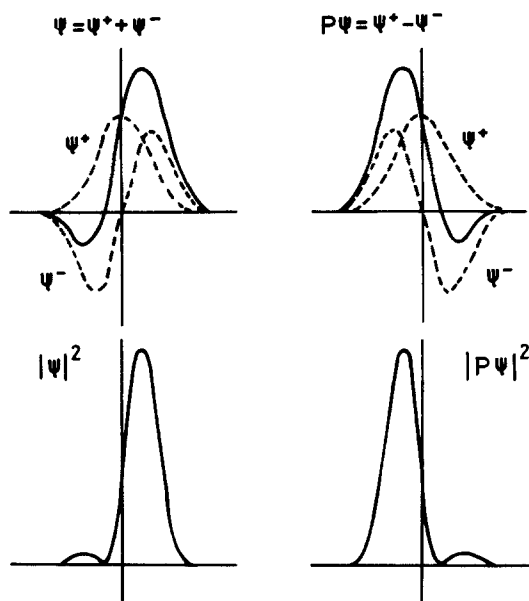


Fig. 10. Superposition of positive and negative parity wave functions, the space inverted form, and square of absolute values.

illustrated in Figure 10 in the case of  $b/a = |F| = 1$ .  $|F|$  is the degree of parity nonconservation.

Let us determine the energy of optically active molecules. The wave function is like that in Equation 9 with  $a = b = 1/\sqrt{2}$ . The operator is  $H + V$ , where  $H$  is interchangeable with the parity operator  $P$

$$PH = HP.$$

This is not true of  $V$  which is parity violating:

$$PV = -VP. \quad (11)$$

For L-molecules

$$H(\psi^+ + \psi^-) = E(\psi^+ + \psi^-) \quad (12)$$

Equation (12) is multiplied by  $\sqrt{2}$ .

On applying  $P$ , the equation for D-molecules is obtained:

$$H(\psi^+ - \psi^-) = E(\psi^+ - \psi^-).$$

To get the energy of the systems, Equation (12) has to be multiplied from the left by  $(\psi^+ + \psi^-)$ , Equation (13) by  $(\psi^+ - \psi^-)$  and integrated for the whole space; then

$$\langle \psi^+ + \psi^- | H | \psi^+ + \psi^- \rangle = E, \quad (14)$$

$$\langle \psi^+ - \psi^- | H | \psi^+ - \psi^- \rangle = E. \quad (15)$$

The energy of L- and D-molecules is the same. Calculating the energy of the parity violating interaction for L-molecules

$$V(\psi^+ + \psi^-) = E_p(\psi^+ + \psi^-),$$

and for D-molecules

$$PV(\psi^+ + \psi^-) = -V(\psi^+ - \psi^-) = E_p(\psi^+ - \psi^-).$$

With similar procedures

$$\langle \psi^+ + \psi^- | V | \psi^+ + \psi^- \rangle = E_p,$$

$$\langle \psi^+ - \psi^- | V | \psi^+ - \psi^- \rangle = -E_p.$$

The result is that the energy of the two systems (L- and D-molecules) is different. A usual expression of the energy in each case is

$$\begin{aligned} E(L) &= E(1 + \epsilon), \\ E(D) &= E(1 - \epsilon), \end{aligned} \tag{16}$$

where  $\epsilon = E_p/E$ .

The parity violating  $V$  potential has recently been determined, taking into account the neutral weak current too. Rein (1974a,b) estimated the value of  $E_p$  for alanine, and found it to be  $\sim 10^{-13}$  eV. Because it is good only for order of magnitude we may take  $\epsilon = 10^{-13}$  for the optically active organic molecules not containing heavy elements. (The value of  $E_p$  increases with  $Z^2$ ,  $Z$  being the atomic number.)

## 4. Analysis of Experiments

### 4.1. CLASSIFICATION

Experiments to verify the connection between the asymmetry of biomolecules and weak interaction can be divided into two classes:

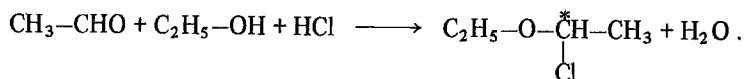
(i) Experiments in which  $\beta$ -particles are used for the irradiation of symmetric precursor molecules to synthesize asymmetric molecules, to degrade racemic mixtures, or to obtain crystallization from racemic solution in the presence of  $\beta$ -particles. In these experiments the role of the weak interaction is simply to produce the spin polarized  $\beta$ -particles. Their interaction with the optical isomers is controlled by the electromagnetic interaction.

(ii) Experiments in which the contribution of the parity violating weak interaction between the electron and proton in the atomic shell plays a role. Experiments of this kind are polymerization or crystallization from racemic mixtures. In such cases the weak interaction is a small effect compared with the electromagnetic interaction which controls the polymerization or crystallization. The experiments in Sections 4.2–4.12 belong to class (i), those in sections 4.13–4.15 to class (ii).

## 4.2. THE EXPERIMENTS OF 'KRAUCH, VESTER, AND ULBRICHT'

The first experiments were reported by Krauch and Vester (1957), Vester *et al.* (1959), Ulbricht (1959), and Ulbricht and Vester (1962). The most detailed description of these early experiments can be found in the paper of Ulbricht and Vester (1962). Ten different types of material were irradiated. Here we discuss two of them only which are characteristic.

The product of the following synthesis type reaction has been studied:



The left side contains only symmetric molecules, at the right side the C atom noted by the asterisk is an asymmetric C atom. The product under  $\beta$ -irradiation from the radioactive nuclei of  $^{32}\text{P}$ ,  $^{90}\text{Sr}$ ,  $^{152}\text{Eu}$  has been measured for optical activity. The observed rotation was generally within the quoted experimental error, and was not greater than 0.02% of the rotation for the pure isomer.

Racemic D,L-alanine was irradiated with a rather high dose of  $\beta^-$ -radiation. The alanine in this case was mixed with silver powder and put into a nuclear reactor. The neutrons produced strong  $^{108}\text{Ag}/^{110}\text{Ag}$   $\beta$ -activity. The alanine was almost completely (96%) decomposed. The rotation in this case was found to be in degrees  $+0.016 \pm 0.008$ . This means a relative surplus of L-molecules of  $6 \times 10^{-3}$  after irradiation (Ulbricht, 1974).

We now point out the essential difference in producing optically active material in *synthesis* and in *decomposition*. The differential equations for the asymmetric synthesis from symmetric material are the following (we neglect any secondary interactions and suppose that the asymmetric molecules are formed from two components: the concentration of the first is  $N_0$ , that of the second is very large compared with  $N_0$ ):

$$\begin{aligned} \dot{N}_L &= \epsilon_-(L)\phi_-(N_0 - N_L - N_D), \\ \dot{N}_D &= \epsilon_-(D)\phi_-(N_0 - N_L - N_D), \end{aligned} \quad (17)$$

where  $N_0$  is the starting number of symmetric molecules,  $N_L$  and  $N_D$  the number of produced asymmetric molecules,

$$\begin{aligned} \epsilon_-(L) &= \epsilon(1 - Y), \\ \epsilon_-(D) &= \epsilon(1 + Y), \end{aligned} \quad (18)$$

are the rate constants to produce asymmetric molecules from symmetric ones.  $\phi_-$  is the incoming flux of, in this case, backward polarized electrons. If the electrons are forward polarized then

$$\begin{aligned} \epsilon_+(L) &= \epsilon(1 + Y), \\ \epsilon_+(D) &= \epsilon(1 - Y), \end{aligned} \quad (19)$$

$2Y$  expresses the relative difference of rate constants for the synthesis of L-, and D-molecules. The solution of the coupled differential Equations (17) is



$$\begin{aligned}
 N_L(t) &= N_0 \frac{\epsilon_-(L)}{\epsilon_-(L) + \epsilon_-(D)} (1 - e^{-(\epsilon_-(L) + \epsilon_-(D))\phi_- t}), \\
 N_D(t) &= N_0 \frac{\epsilon_-(D)}{\epsilon_-(L) + \epsilon_-(D)} (1 - e^{-(\epsilon_-(L) + \epsilon_-(D))\phi_- t}).
 \end{aligned}
 \tag{20}$$

The relative difference in the number of L- and D-molecules does not depend on time

$$\Delta_{\text{syn}} = \frac{N_L(t) - N_D(t)}{N_L(t) + N_D(t)} = -Y.
 \tag{21}$$

The differential equations for the asymmetric destruction of a racemic mixture are:

$$\begin{aligned}
 \dot{N}_L &= -\tau_-(L)\phi_- N_L, \\
 \dot{N}_D &= -\tau_-(D)\phi_- N_D.
 \end{aligned}
 \tag{22}$$

The same notations are used as in Equation (17) except for  $\tau_-$ .

By analogy

$$\begin{aligned}
 \tau_-(L) &= \tau_-(1 + Z), \\
 \tau_-(D) &= \tau_-(1 - Z),
 \end{aligned}
 \tag{23}$$

where  $\tau_-$  is the mean rate of decomposition for backward polarized electrons,  $Z$  the relative difference for L- and D-molecules. The solutions of the independent Equations (22) are

$$\begin{aligned}
 N_L(t) &= N_{OL} e^{-\tau_-(L)\phi_- t}, \\
 N_D(t) &= N_{OD} e^{-\tau_-(D)\phi_- t},
 \end{aligned}
 \tag{24}$$

Here  $N_{OL} = N_{OD}$  because of the racemic mixture. The relative difference between the number of L- and D-molecules is

$$\Delta_{\text{dec}} = \frac{N_L(t) - N_D(t)}{N_L(t) + N_D(t)} = -Z \ln \frac{1}{1 - F},
 \tag{25}$$

where  $F$  is the decomposed part of the starting material after irradiation\*

$$F = \frac{F_L + F_D}{2}.$$

It can be seen that the result of asymmetric decomposition depends on  $F$  and through  $F$  on the irradiation time. If  $F > 0.63$ , then  $\Delta_{\text{dec}}$  can be larger than  $Z$ .

\* Equation (25) is an approximation. It is satisfactory if  $Z = 0.5$  for  $F < 0.6$ , if  $Z = 0.1$  for  $F < 0.999$ , if  $Z = 0.01$  for  $F < 0.9999$ . Generally  $Z$  and  $t$  have to be calculated from the following equations

$$\begin{aligned}
 \ln(1 - F) &= -\tau t + \ln[e^{-\tau Z t} + e^{+\tau Z t}] - \ln 2, \\
 \Delta_{\text{dec}} &= \tanh(-\tau Z t).
 \end{aligned}$$

To summarize the above results: in synthesis type experiments one never obtains greater relative differences in the number of molecules than  $Y$ , which is given by the relative difference of production rate of asymmetric molecules from symmetric ones; in decomposition type experiments the relative difference can be increased by having  $F > 0.63$ . Consequently, to observe a real difference between the interaction of polarized  $\beta$ -particles and optical isomers the decomposition type experiments must be favoured. It is now possible to understand the experimental results described in Section 4.2.

In the above discussion the polarization of the bombarding radiation was assumed to be  $P = 1$ . To get  $Y$  and  $Z$  in cases where  $P < 1$ , the right side of Equations (21) and (25) must be multiplied by  $P$ . In most experiments the asymmetry is measured through the optical activity (optical rotatory dispersion or circular dichroism) and the result is expressed in percentage of the optical activity of one of the pure isomers. This percentage divided by 100 gives  $\Delta_{\text{syn}}$  or  $\Delta_{\text{dec}}$ .

In the decomposition type experiment of L,D-alanine the result was  $\Delta_{\text{dec}} \leq 6.10^{-3}$  (Ulbricht, 1974). From this, with  $F = 0.96$ ,  $PZ \leq 9.10^{-4}$  is obtained. Assuming a direct interaction of  $\beta$ -particles with the material when  $P \approx 1$ , it can be stated that  $Z < 10^{-3}$ . In the synthesis type experiments  $\Delta_{\text{syn}} \leq 2.10^{-4}$ , which means that  $PY \leq 10^{-4}$ . The present author is not, however, completely convinced that he correctly interpreted the quoted optical activity as 0.02%. This value coincides with the error of the average rotation in the table of rotation of Ulbricht and Vester (1962), and it is not definitely indicated that this value was compared with the rotation of the pure isomer to get the percentage of the optical activity. This may not, however, have changed the upper limits to any great extent.

#### 4.3. IDEAS CONCERNING THE MECHANISM OF INTERACTION

In spite of the negative result of these first experiments it seems to be worthwhile discussing the ideas concerning the mechanism of the asymmetric interactions of Ulbricht and Vester (1962).

Five possibilities were mentioned. (The order of the presentation here does not follow the original order).

(i) *Entropy exchange.* The reaction mixture together with the beam of radiation absorbed by it may be regarded as a closed system in which entropy exchange takes place between two processes: (a) formation of product, and (b) absorption of radiation, such that the state of order of the molecules increases (i.e. optical activity is produced), while the state of order of the  $\beta$ -electrons decreases (depolarization). This entropy exchange must be very small because the energy difference between  $\beta$ -particles and molecules is very large.

(ii) *Non-energetic interaction.* Since optical isomers have the same content (neglecting the small difference due to the intramolecular weak interaction), whether or not one of the two mirror-images is formed is a matter of probability (i.e. entropy). In the presence of polarized  $\beta$ -radiation (a state of low probability), the entropy  $S$  of the system expressed as

$$S = k \cdot \ln P + \text{const},$$

(where  $k$  is the Boltzmann constant,  $P$  represents probability) will be lower than that of a similar system with unpolarized electrons. The order of magnitude of such an interaction between molecules and  $\beta$ -particles would be independent of their energies. What is required is a transmission of information, analogous to the exchange 'forces' of quantum physics. Such a transmission is not known.

(iii) *Magnetic effect*. According to the authors such an effect (spin-orbit interaction between the  $\beta$ -particles and the helical electrons of matter) would be extremely small because of the large difference between the energy of the  $\beta$ -particles and the molecular electrons. Nothing would be gained by using  $\beta$ -radiation of low energy since the degree of asymmetry of the  $\beta$ -rays is proportional to  $v/c$ . But — as has been emphasized in Section 3.4 — the polarization is retained to a considerable extent during slowing down of the particles, and in such a way electrons of small  $v$  can have large polarization. This point will be discussed later in Section 4.10.

(iv) *Secondary electrons*. In slowing down, the  $\beta$ -rays produce secondary electrons ( $\delta$ -rays, Auger electrons). No measurement has been made to determine their polarization. If they are not polarized, their effect would be to diminish that of any other mechanism operating. If they are polarized, however, they could contribute to any overall effect.

(v) *Bremsstrahlung*. It has been shown that the longitudinally polarized  $\beta$ -radiation gives rise to circularly polarized bremsstrahlung even at relatively low energies. Since it has already been demonstrated (Section 3.2) that circularly polarized light could produce optical activity, an evident mechanism existed for the route from polarized  $\beta$ -particles to molecular asymmetry. The degree of circular polarization of low energy bremsstrahlung of 10–100 eV which is comparable to the energy of optical photons is, however,  $P = 10^{-4}$ , according to the following equation (McVoy, 1957):

$$P = \frac{R - L}{R + L} = 1 - \frac{(E_0 - W)(EE_0 + (mc^2)^2)}{hv[(E_0 - W)(E + E_0 + W) + hvE] + (E_0 - W)(EE_0 + (mc^2)^2)} \quad (26)$$

where  $E_0$  is the total (kinetic + rest) energy of  $\beta$ -particles in MeV,  $hv$  is the energy of the emitted bremsstrahlung,  $E = E_0 - hv$ ,

$$W = \sqrt{E^2 - (mc^2)^2},$$

$mc^2 = 0.51$  MeV is the rest energy of the electron,  $R$  and  $L$  are the intensities of right and left circularly polarized bremsstrahlung respectively. If equation (26) is analysed it can be seen that the circular polarization is, in order of magnitude, proportional to  $\alpha \times hv$ , if  $hv < 0.1$  MeV.  $\alpha$  is between 1–2.5 for  $E_0 < 3$  MeV if  $hv$  is expressed in MeV.

In 1962, i.e. at the time of the experiments of Ulbricht and Vester, there were no data on  $Y$  or  $Z$  (Equations (18) and (23)) for the interaction of low energy bremsstrahlung and optical isomers. In a recent measurement (Keszthelyi and Vincze, 1975), an upper limit was established for the difference in the absorption coefficient of  $P \simeq \pm 1$   $\gamma$ -radiation of

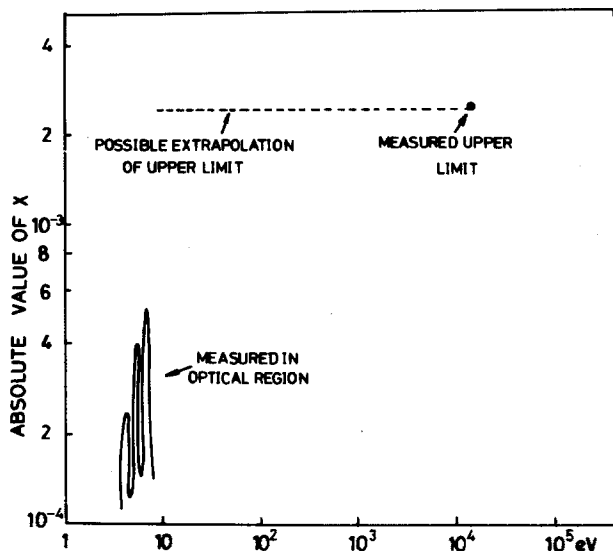


Fig. 11. Absolute values of asymmetry parameter  $X$  in dependence of radiation energy for tryptophane molecules (Keszthelyi and Vincze, 1975).

14.4 keV energy. Using the possibilities of Mössbauer effect to produce circularly polarized  $\gamma$ -radiation, L- and D-tyrosine and L- and D-tryptophane have been studied as absorbers. Expressing the absorption coefficients similarly to Equations (18) and (23)

$$\begin{aligned} \sigma_-(L) &= \sigma(1 + X), & \sigma_+(L) &= \sigma(1 - X), \\ \sigma_-(D) &= \sigma(1 - X), & \sigma_+(D) &= \sigma(1 + X), \end{aligned} \quad (27)$$

where  $\sigma$  is the mean absorption coefficient, + and - represent right and left circular polarization, respectively,  $X$  is the relative difference of the absorption. The upper limit for  $|X|$  was  $4.4 \times 10^{-3}$  for tyrosine and  $2.4 \times 10^{-3}$  for tryptophane. A graphical representation of the result for tryptophane is shown in Figure 11. Though the results concern only the difference in absorption it is certain that  $X \approx Z$ , for decomposition, and it is also safe to assume that  $X \approx Y$ . Because  $P \approx 10^{-4}$ , and for the low energy bremsstrahlung  $X \leq 10^{-3}$ ,  $\Delta_{\text{syn}}$  and  $\Delta_{\text{dec}}$  in the above experiments ought to be smaller than  $10^{-6} - 10^{-7}$ , assuming that the synthesis or decomposition were caused by bremsstrahlung. As for the measurements giving an upper limit of  $2 \times 10^{-4}$ , except for the case of alanine where it was  $6 \times 10^{-3}$ , the experiments were not decisive in favour of the bremsstrahlung hypothesis — as was also stated by the authors themselves.

#### 4.4. BREMSSTRAHLUNG EXPERIMENTS OF 'BONNER'

In a very thorough and detailed series of investigations Bonner (1974) did not find any induced optical activity under the influence of bremsstrahlung of  $^{90}\text{Sr}$ – $^{90}\text{Y}$  radioactivity.

A 61.7 KCi  $^{90}\text{Sr}$ - $^{90}\text{Y}$   $\beta$  - emitting source produced via bremsstrahlung -  $1-4 \times 10^8$  rad at the samples (D-leucine, L-leucine, D,L-leucine, etc.). The decomposed quantity ( $F$  in Equation (25)) had a range of 0.03-0.16. In this way the possible difference of the decomposition rates ( $Z$ ) had to be multiplied by a number  $<1$  to obtain  $\Delta_{\text{dec}}$ . The results were evaluated by observing the optical rotation of the irradiated racemic mixture or by measuring the quantity of L- and D-isomers remaining after irradiation by gas chromatography. From both types of evaluations, differences smaller than the experimental error were obtained. From the optical rotation measurement  $Z < 0.06$  (using  $F = 0.04$ , and  $\Delta_{\text{dec}} = 0.04^\circ/16^\circ = 0.0025$ ), and from the gas chromatographic evaluation  $Z < 0.03$  ( $\Delta_{\text{dec}} = 0.24\%/50\% = 0.005$ , and  $F = 0.14$ ).

This upper limit for  $Z$  is valid under the assumption of  $P=1$  polarization of bremsstrahlung. The low energy bremsstrahlung (say  $<50$  keV energy) could not penetrate to the samples through the water shielding and the wall of the sample container. For higher energy radiation  $P \approx 0.5-1$ ; thus, in an order of magnitude estimation  $Z \approx 0.03-0.06$  could be considered as an upper limit for the relative difference between decomposition rates of L- and D-amino acids under the influence of high energy ( $>0.5-1$  MeV) circularly polarized bremsstrahlung. One important result of these experiments was that  $\Delta E \approx 30$  eV of energy was necessary to decompose one amino acid molecule.

#### 4.5. EXPERIMENT OF 'GOLDANSKII AND KHRAPOV'

Fourteen different organic compounds were irradiated by polarized radioactive  $\beta$ -particles and with accelerated unpolarized electrons (Goldanskii and Khrapov, 1962). Large doses of radiation from radioactivity (150-15000 Mrads) and from accelerated electrons (30-500 Mrads) were absorbed by samples of L- and D-amino acid and racemates of them. No optical rotation was observed in any of the racemates and the decomposition of L- and D-material had the same rate. There are no quantitative data in the paper for estimating  $Z$ .

#### 4.6. GARAY'S EXPERIMENT

In the first positive experiment, reported by Garay (1968), solutions of L-tyrosine and D-tyrosine were separately irradiated by  $^{90}\text{Sr}$ - $^{90}\text{Y}$   $\beta$ -radiation. The compositions of the samples are given in Table III. The irradiations were made in alkaline solution and in acidic solution prepared by replacing NaOH by HCl. In a control experiment, inactive  $^{89}\text{SrCl}$  was added to the solutions.

The changes in the number of tyrosine molecules were followed by observing their u.v. absorption. Figure 12 shows the results for alkaline, Figure 13 for acidic solution for a time span of 18 months. It is clearly seen that the D-tyrosine decomposed more quickly in the alkaline solution, and no decomposition took place in the acidic solution. The spectra did not change in the presence of inactive  $^{89}\text{SrCl}_2$  salt.

A different presentation of the data of Figure 12 is given in Figure 14 where the peak heights of the absorption curves are given in terms of the time. The data cannot be

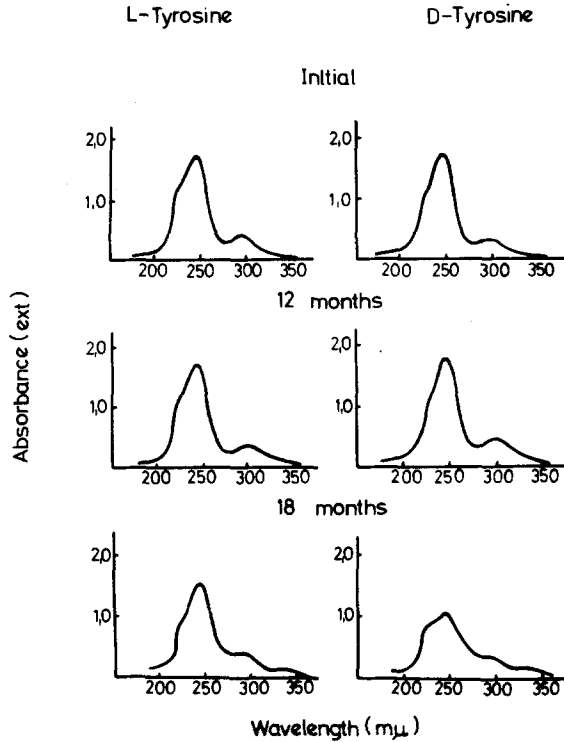


Fig. 12. Decomposition of L- and D-tyrosine (as shown by the absorbance in ultraviolet light) in the presence of  $^{90}\text{Sr}$  during 18 months. Alkaline solution (Garay, 1968).

described by a simple exponential decomposition as in Equation (24). It has to be assumed that the molecules which were decomposed by the primary action of  $\beta$ -particles decompose more molecules in secondary reactions. The differential equation for L-molecules and  $\beta$ -particles is

$$\dot{N}_L(t) = -\tau_{-}(L)\phi_{-}N_L - \lambda_L(N_{OL} - N_L) \cdot N_L, \quad (28)$$

TABLE III  
Composition of samples in Garay's experiment (Garay, 1968) (alkaline solution)

Material	Quantity
H <sub>2</sub> O	3.2 ml
Ethanol	2.0 ml
NaOH	1.6 mg
NaCl	24.0 mg
L- or D-tyrosine	2.0 mg
SrCl <sub>2</sub>	0.25 mg

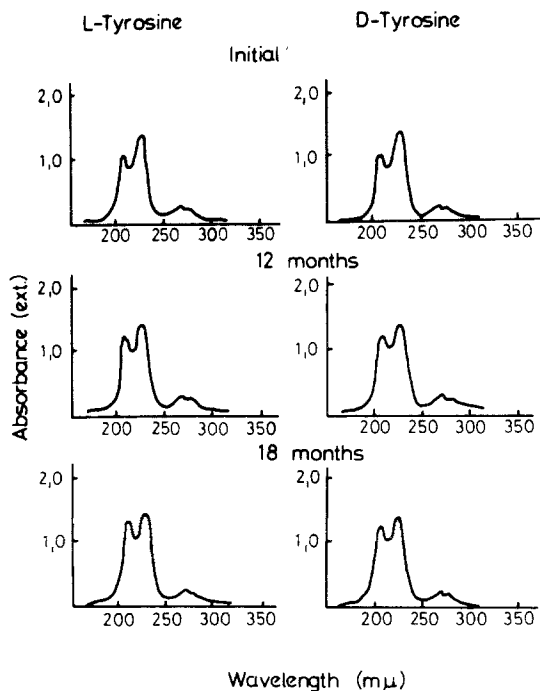


Fig. 13. Decomposition of L- and D-tyrosine in acidic solution. No difference has been found (Garay, 1968).

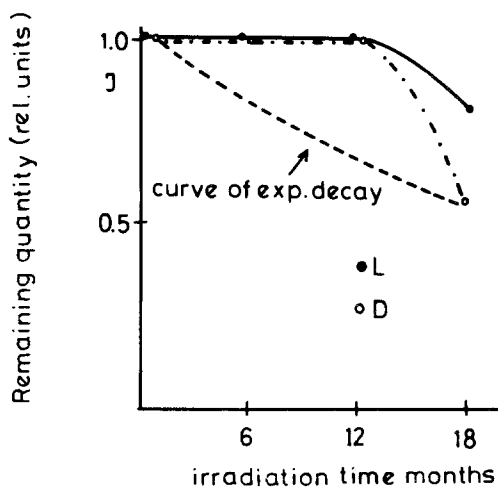


Fig. 14. Dependence of the remaining quantity of L- and D-tyrosine from time in Garay's experiment.

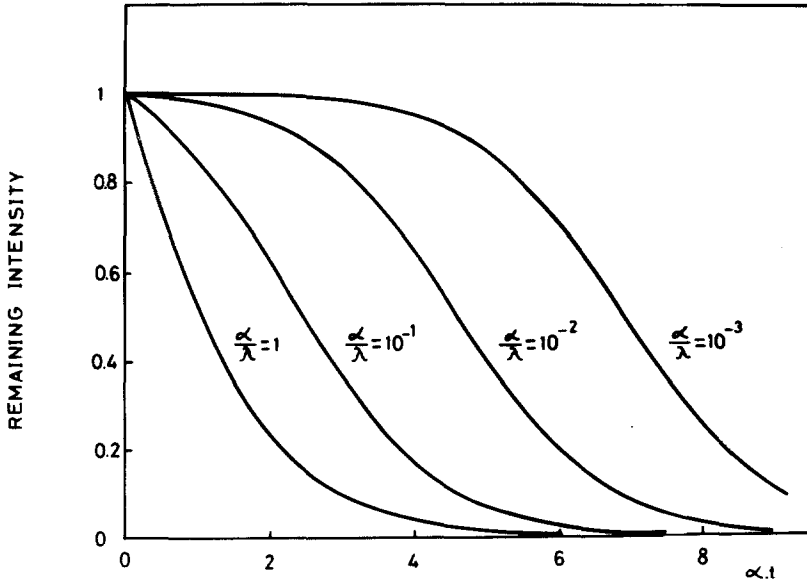


Fig. 15. Remaining intensity vs. normalized time in case of secondary reaction (Equation 29).

where  $\tau_{-}(L)$  and  $\phi_{-}$  have the same meaning as in Equation (22),  $N_0$  is the number of molecules at  $t = 0$ , and  $\lambda_L$  expresses the rate of secondary reaction. The solution of this equation is

$$N_L(t) = N_0 \frac{\frac{\lambda_L}{\alpha_L} + 1}{\frac{\lambda_L}{\alpha_L} + e^{(\alpha_L + \lambda_L)t}}, \quad (29)$$

where the notation  $\tau_{-}(L)\phi_{-} = \alpha_L$  was used. The function  $N_L(t)/N_0$  is represented for different parameters of  $\alpha_L/\lambda_L$  depending on  $\alpha t$  (Figure 15). The function approaches the shape of the experimental curve in Figure 14 with decreasing parameter  $\alpha_L/\lambda_L$  or  $\alpha_D/\lambda_D$ . As a rough estimation the curves with  $\alpha/\lambda \approx 10^{-3}$  coincide with the experimental ones. This means that one decomposed molecule ought to decompose many more molecules in Garay's experiment.

One possible mechanism of this secondary process could be – as the author mentions in his paper – that the spontaneous decomposition rate of tyrosine molecules sensitively depends on the pH in alkaline solutions. The products of decomposition have changed the pH in the direction of increasing spontaneous decomposition. There is no possibility to check this hypothesis from the published data. The absence of any observable decomposition in the case of the acidic solution supports it.

The main difficulty in the understanding of the experimental data lies in the great difference of the remaining L- and D-molecules (80% and 55% respectively). If the above reasoning is accepted the factor  $\lambda$  is responsible for an amplification. There is no reason to think that  $\lambda_L$  and  $\lambda_D$  should be different. The effect ought to be caused by the primary interaction, i.e.  $\alpha_L$  and  $\alpha_D$ , or what is equivalent,  $\tau_{-}(L)$  and  $\tau_{-}(D)$  (Equation



23) must be different. The analysis of the curves of Figure 14 gives  $Z \approx -0.4$  meaning that  $\tau_{-}(D)$  is greater by  $\approx 80\%$  than  $\tau_{-}(L)$ .

Even the 'primary' interaction has to be discussed. It is well known that in aqueous solutions the radiolysis goes mainly through radicals of water produced by the radiation. The main radicals are  $e_{aq}$  and OH. Their  $G$  values (number of radicals for 100 eV absorbed energy) are 2.5 and 2.4 respectively. In 1 ml solution  $1.15 \times 10^{20}$  eV energy was absorbed from the  $1.2 \times 10^{14}$   $\beta$ -particles during 18 months therefore the number of radicals  $R_0 = 2.8 \times 10^{18}$ . The radicals are scavenged by the molecules and ions in the solution. To get the ratio for tyrosine the equation

$$R_{tyr} = \frac{K_{tyr}[M]_{tyr}}{\sum K_i[M]_i} \quad (30)$$

has to be used, where  $K_i$  is the rate constant of the reaction of radicals with the  $i$ th material in litre mole  $s^{-1}$ ,  $[M]_i$  is the concentration of the  $i$ th substance. In Table IV values of  $K_i$ ,  $M_i$ , and  $R_i$  are collected. ( $[M]_{O_2}$  for oxygen is taken to be the usual  $O_2$  concentration in water since the author does not mention the deoxygenation of the samples.) The  $K_i$ 's are given for pH = 7 in the majority of cases though they may be a little different for pH = 8 of the samples. Nevertheless,  $R_{tyr} \approx 10^{-2}$  is obtained for  $e_{aq}$ , and  $\approx 10^{-3}$  for OH radicals. This means that  $R_{tyr} \cdot R_0 = 2.8 \times 10^{16}$  tyrosine molecule  $ml^{-1}$  could have been destroyed by the radicals. The ratio of direct encounter of  $\beta$ -particles with tyrosin molecules to the water molecules is approximately the ratio of their number/ml :  $1.1 \times 10^{18} / 2 \times 10^{22} = 4.6 \times 10^{-5}$ , which means that by direct interaction the  $\beta$ -particles decomposed  $\approx 1.6 \times 10^{14}$  tyrosine molecules  $ml^{-1}$  (assuming that 30 eV is needed for decomposing one molecule). Therefore in the 'primary' interaction only 1% decomposition has been caused by the direct interaction. This fact increases the value of  $Z$  because it cannot be accepted that the polarization of  $\beta$ -particles is transferred through the radicals (Bernstein *et al.*, 1972b). We can accept  $Z = 0.4$  only as a lower limit from this experiment.

TABLE IV  
Radiolysis of the tyrosine containing solution. Only the most important components are given. The  $K$ -values are given in the liter mole $^{-1}$  s $^{-1}$

Component [M]	Concentration mole lit. $^{-1}$	$K_{e_{aq}}$	$[M]K_{e_{aq}}$	$K_{OH}$	$[M]K_{OH}$
Ethanol	6.6	$10^5$	$6.6 \times 10^5$	$1.1 \times 10^9$	$7.3 \times 10^9$
$O_2$	$2 \times 10^{-3}$	$2 \times 10^{10}$	$4 \times 10^7$	—	—
Tyrosine	$2 \times 10^{-3}$	$2 \times 10^8$	$4 \times 10^5$	$5 \times 10^9$	$10^7$

#### 4.7. EXPERIMENT OF 'BERNSTEIN *et al.*'

The idea of the experiment was that the laboratory had a considerable stock of  $^{14}C$  labelled crystalline DL-amino acids that were synthesized 12–24 years ago (Bernstein *et*

TABLE V  
Amino acid  $^{14}\text{C}$ -exposure data, the upper limits for  $2Z$ , and energy available to decompose one molecule

DL-amino acid	Radiation dose Rads ( $\times 10^{-7}$ )	% decomp.	Limit for $ 2Z $	eV/ molecule
Norvaline	7.0	3	4	21
Alanine	3.5	26	0.08	1.4
DOPA	2.5	3	17.0	8
Aspartic Acid	4.2	75–80	0.007	0.5
Methionine	10.4	59	0.5	17

*al.*, 1972b). During the ensuing years these amino acids have been subjected to the effect of their own polarized  $\beta^-$ -particles. The radiation dose of the different samples varied between  $2-10 \times 10^7$  rads (Table V). In the experiments the percentage decomposition ( $F \times 100$  of Equation (25)) and the optical activity (after dissolving some amount in water) was measured. From these measurements the differential decomposition  $2(K_D - K_L)/(K_D + K_L)$ , where  $K_D$  and  $K_L$  are the decomposition rates for D and L molecules respectively, were determined. With our notation this quantity equals  $2Z$  from Equations (23) and (25). The results are collected in Table V. In the measurements no rotations were found within the sensitivity of the spectropolarimeter ( $0.002^\circ$ ), therefore the obtained data of  $2Z$  are only upper limits.\*

The main problem with this experiment however, lies in the fact that because the radiation energy for one decomposed molecule was always smaller than the necessary 30 eV; a substantial number of secondary reactions ought to occur which were surely not asymmetric. This increases the limit  $2Z$  even further. In the best case, viz. aspartic acid, the upper limit of  $2Z$  would be 0.9.

#### 4.8. EXPERIMENT OF 'DARGE *et al.*'

In an experiment whose principle was very similar to Garay's, Darge *et al.* (1976) observed a greater decomposition of D-tryptophane than L-tryptophane under irradiation by  $^{32}\text{P}$   $\beta^-$ -radiation. 0.1 mg D,L-tryptophane was dissolved in 2 ml water and 5 mCi  $^{32}\text{P}$  was added. From sixteen samples 8 had activities, 8 were for control purposes. The samples were kept at  $-25^\circ\text{C}$  for 12 weeks. The energy absorbed during this period in the samples was  $1.9 \times 10^{20}$  eV. After the irradiation the quantity of decomposed material  $F$  was determined by optical absorption and the angle of rotation of 220 nm light was measured ( $\Delta_{\text{dec}}$ ). The results were  $F = 0.33$ ,  $\Delta_{\text{dec}} = 0.19 \pm 0.11$ . Using Equation (25) we obtain  $Z = +0.47 \pm 0.27$ . (The + sign means, according to Equation (23), that the

\* ( $2Z > 2$  values, which are impossible according to their definition, are partly connected with the fact that Equation (25) (the equivalent of which has been used by the authors) is an approximation, and partly with the very small decomposition.

decomposition rate is higher for L-tryptophane.) The size of  $Z$  agrees surprisingly well with the result of Garay's experiment on tyrosine; its sign, however, is opposite. Approximately  $10^{17}$  tryptophane molecules have to be decomposed during the irradiation. The available energy was shared by water molecules and tryptophane molecules. The ratio of their numbers is  $4.4 \times 10^{-3}$  (in calculating the ratio of the energy to tryptophane its larger size – possibly a factor of 10 – must be taken into account). In this way the energy for one decomposed tryptophane molecule could be between 9.5 and 95 eV. The molecules could have been destroyed by the direct action of the radiation. The radiolytic effect of the water radicals may have been frozen in at  $-25^\circ\text{C}$ .

Therefore  $Z = +0.47 \pm 0.27$  can be accepted as the result of this experiment for the relative difference of the decomposition rates.

#### 4.9. EXPERIMENT WITH ARTIFICIALLY POLARIZED ELECTRONS

In an experiment carried out by Bonner *et al.* (1975) an artificially polarized electron beam was used to irradiate L,D-leucine. The advantage of this type of electron source is that the irradiation can be performed by naturally (antiparallel) and antinaturally (parallel) polarized electrons. The possible effect should change its sign by varying the direction of polarization of electrons.

This was in fact observed (see Table VI). In the experiment the energy of electrons was 120 keV, the target thickness  $\approx 20 \text{ mg cm}^{-2}$ , i.e. just equal to the range of the electrons. The irradiated samples were analysed for the differential decomposition by measuring the undecomposed leucine by gas chromatography. On analysing the data given in Table VI it is possible to calculate the average energy spent by the electrons to decompose a single leucine molecule ( $\Delta E$ ) and to calculate  $2Z$  the relative difference of the decomposition rates. In Table VII,  $F$ ,  $\Delta_{\text{dec}}$  which is the same as the enantiomeric selectivity given in the paper and the degree of polarization of the beam  $P$  are given as data for calculating  $\Delta E$  and  $2Z$ .

The fact that  $\Delta E = 29 \text{ eV}$  for three cases is remarkable and shows that Equation (24) is well applicable in the analysis. The value of  $\Delta E$  coincides with the same value in the case of bremsstrahlung irradiation (Bonner, 1974). The values of  $2Z$  show a broader spread.

TABLE VI  
Irradiation of DL-leucine with longitudinally polarized electrons (Bonner *et al.*, 1975)

Polarization of electrons	Irradiation		Sample decomposition (%)	Composition of sample			Enantiomeric selectivity (%L - %D)
	Percentage excess	(nA h)		%D	%L	$\pm$	
Antiparallel	20	331	52.9	49.29	50.71	0.20	1.42
Antiparallel	17-23	498	50.9	49.57	50.43	0.14	0.86
Parallel	11-17	795	73.9	50.40	49.60	0.12	-0.80
Parallel	10-17	860	75.6	50.37	49.63	0.14	-0.74

TABLE VII  
Analysis of the asymmetric degradation of DL-leucine

No. of expt.	Polarization of electron $P$	Decomposition $F$	Energy/ decomposed molecule in eV	$\Delta_{\text{dec}}$	$2Z$	Weighted average
1	+0.2	0.529	29.3	+1.42	$0.189 \pm 0.039$	
2	+/0.17-0.23/	0.509	55	+0.86	$0.129 \pm 0.030$	$0.151 \pm 0.024$
3	-/0.11-0.17/	0.739	29	-0.80	$0.085 \pm 0.015$	
4	-/0.10-0.17/	0.756	29	-0.74	$0.074 \pm 0.020$	$0.081 \pm 0.012$

This, and the large value of  $\Delta E$  in experiment 2, may be understood by taking into account the remarks of the authors that the control of many experimental parameters of the polarized electron source was rather difficult. Even so, it is felt that the value  $2Z \approx 10\%$  may be accepted.

The authors did not know whether the asymmetric degradations were caused by the longitudinally polarized electrons themselves or by their bremsstrahlung. A short discussion is presented here which clearly shows that the degradations could not have been caused by bremsstrahlung (Keszthelyi, 1976a).

The energy of the incoming electrons is lost in the sample by ionization and radiation; the latter is the bremsstrahlung. The fraction of the incident energy which is converted into bremsstrahlung in a thick target is with a good approximation (Evans, 1955)

$$\frac{I}{E} = 7ZE \times 10^{-4} \quad (31)$$

where  $Z$  (not to be confused with  $Z$  of Equation (23)) is the atomic number of the bombarded material ( $Z \approx 7$  in the case of leucine), and  $E$  is the energy of electrons in MeV.

Even if the whole energy of the bremsstrahlung had been absorbed in the sample, less than 0.1% of the molecules would have been degraded by bremsstrahlung. If the low degree of polarization  $P \approx 10^{-3}$  and the low upper limit for  $Z$  in the case of radiation ( $Z < 3 \cdot 10^{-3}$ ) (Keszthelyi and Vincze, 1975) were also taken into account, the upper limit of enantiomeric selectivity would be  $\approx 10^{-6}\%$ . This is surely in contradiction with the obtained value of  $\approx 1\%$ .

#### 4.10. POSITRON EXPERIMENTS

As has been pointed out in Section 3.4 the  $\beta^+$ -particles, the positrons, are polarized parallel to their direction of movement. The asymmetric phenomena – if they exist – must also appear in positron–amino acid interactions.

The experiments discussed above were all product-oriented, i.e. the product after irradiation was analysed. In the case of positrons, process-oriented experiments were

performed, that is, the interaction process itself was studied (Garay *et al.*, 1973, 1974) by measuring the lifetime spectra of positron annihilation in amino acids.

In condensed materials, energetic positrons ( $\approx 10^5$  keV) slow down within  $10^{-12}$  s to energies of about 10 eV before annihilation. This may happen in two ways: either (a) by annihilation of free electrons which takes place in  $\approx 2 \cdot 10^{-10}$  s; or (b) by formation of positronium (Ps), i.e. positron-electron atom. In the latter case the Ps atoms are formed in both singlet (spin = 0) and triplet (spin = 1) states, in the relative proportion of 1:3, but whereas the singlet Ps has a lifetime of  $\tau_s = 3 \times 10^{-10}$  s, the triplet Ps generally takes longer to annihilate, having a lifetime of  $\tau_t = (5-40) \times 10^{-10}$  depending on the material. In the free, and in the singlet annihilation two 0.51 MeV  $\gamma$ -radiations are emitted in opposite directions, in the true triplet annihilation 3  $\gamma$ -quanta emerge. The true triplet Ps annihilation happens only very rarely in condensed matter because the triplet state is converted (by pick-off process, i.e. by exchanging the electron with parallel spin to an electron with antiparallel spin) into the singlet state. The above-mentioned lifetime of triplet Ps is really the lifetime of its conversion into singlet Ps, which annihilates very rapidly ( $3 \times 10^{-10}$  s). The probability of Ps production depends on the electronic structure of the molecules (Goldanskii, 1967). Because a number of experiments (Hanna, 1958; Dick, 1963) have shown that positrons emitted in radioactive decay partly retain their longitudinal polarization during slowing down and Ps formation, a difference in the annihilation of positrons in L- and D-amino acids could be expected. In fact these positron experiments (Hanna, 1958; Dick, 1963) gave the basis for the discussion in Section 3.4.

Positron lifetime spectra were measured in 5 different compounds. A short-living and a long-living component were clearly seen. After computer evaluation the lifetime and the relative intensity of the long living (triplet) component were determined and L/D ratios of these values calculated. The data are collected in Figure 16. The triplet intensity in D-molecules was by  $20 \pm 6\%$  greater than in L-molecules.

The authors were careful enough not to accept the result as a clear demonstration of the asymmetric interaction of polarized positrons and amino acids. Because the positrons are very sensitive to impurities, to surface effects in polycrystalline materials, etc., the difference could originate even from such sources. Nevertheless, a piece of theoretical work has been done; the details of this work were published by Hrsakó (1973). According to this so called 'helical electron gas model' the electrons of an optically active medium (at least those which take part in forming the molecules) move on a helical path inducing a magnetic field in the axis of the helix which tries to turn the spin of the electron in the direction of the axis. In this way the isotropic matter (the optically active molecules are not oriented) may be characterized by the scheme given in Figure 17. It has to be assumed that the incoming  $\beta$ -particles interact with the electrons of the matter moving parallel to them with greater probability than with electrons moving in the opposite direction. This leads directly to observe more interactions with parallel spin in the case of D-matter (triplet state) and positrons and with opposite spins (i.e. singlet interaction) in the case of D-matter and negative  $\beta^-$ -particles. This makes the greater intensity of triplet

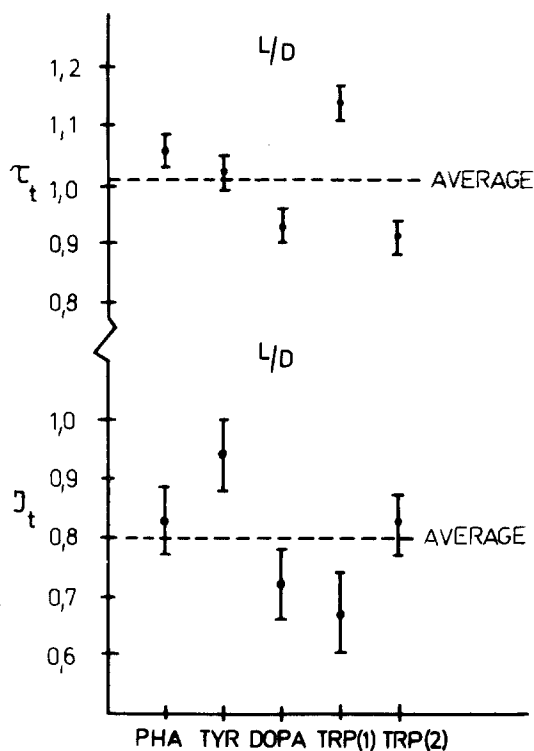


Fig. 16. Ratios of triplet lifetimes and triplet intensity in L- and D-amino acids.

Ps for D-matter understandable. Farther, since it is known from general principles that the singlet interaction is more probable than the triplet between negative electrons, the greater decomposition rate of D-matter by negative electron irradiation is understandable too.

The theory does not, however, give any result for the size of the effect. The general feeling is that though the above-mentioned effects surely exist their extent is very small.

In a recent paper Rich (1976) called the attention to some theoretical calculation which show that electrons lose their original direction after traveling some distance in material. The so-called diffuse scattering of electrons – where the number of forward and backward moving electrons is equal – steps in according to calculations at an energy of  $\approx 3$  keV, which is greater than the energy of positron formation. If this is so then the positrons do not have ‘helicity’, i.e. their velocity and spin is not correlated, which is needed to explain the experiments.

Following this work (Garay, 1973) the results of three more positron lifetime studies in optical isomers have been reported. Two of them dealt with measurements in polycrystalline L- and D-amino acids (Dézsi, 1974; Brandt *et al.*, 1976).

These authors found no differences in the triplet intensity ratio above the experimental error of 4–6%. In the third study, the results of which should at present be

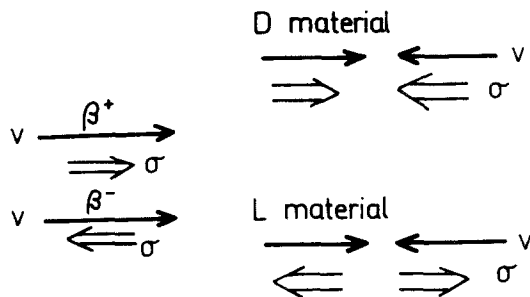


Fig. 17. Scheme of the polarization of electrons in isotrop D- and L-materials according to the helical electron gas model and the polarization of the incoming  $\beta^+$  and  $\beta^-$  particles. Arrow  $v$  shows the direction of the velocity of movement of the electrons. In case of the free electrons the parallel or antiparallel spin state is caused by the weak interactions. In the molecules (D material, L material) the spin is oriented in the direction of  $v$  by the magnetic field of the helical electron path.

considered as preliminary (Ache, 1976), the author intended to avoid the problems of polycrystalline materials and performed the positron lifetime measurements in L- and D-liquids which were carefully purified and deoxygenated. The results are given in Table VIII. The data show differences in all cases (from 3–10%), and what is even more important, the ratio depends on temperature. The ratio increases with decreasing temperature. This is quite plausible because the polarization of the ‘helical electron gas’ should increase with decreasing temperature (the averaging influence of thermal motion cancels).

The evaluation of positron lifetime experiments is very complicated. From the measured spectra many parameters (lifetimes, intensities, background, parameters characterizing the electronics) have to be calculated by computer fitting. All these parameters correlate in calculations and in such a way produce large errors. Further

TABLE VIII  
Ratio of triplet intensities for various optical isomer  $[\alpha]^{20}$  is the specific rotation at 20 °C (Ache, 1976)

Compound	Temp. (°C)	L/D
<u>OCTANOL-2</u>	100	0.957
$\alpha^{20}$ D = +9.79° L = -9.79°	60	0.960
	22	0.955
	-78	0.953
	-196	0.920
<u>2-AMINO-BUTANOL-1</u>	60	0.927
$\alpha^{20}$ D = +15° L = -15°	22	0.996
	-78	0.944
	-196	0.894

improvements in the measuring technique are needed to ascertain that the differences which are surely very small are real.

#### 4.11. $\beta$ -DECAY LIFETIME EXPERIMENT

One of the consequences of the helical electron gas model of optically active material (Hraskó, 1973) is that the lifetime of radioactive decay of nuclei in L- and D-material must be different. The size of the effect:

$$\frac{\lambda_L - \lambda_D}{2\lambda_0} = w \cdot F(x), \quad (32)$$

where  $\lambda_L$  and  $\lambda_D$  are the decay constants  $\lambda = 1/\tau$ ,  $\tau$  is the mean life of the decay,  $F(x)$  is a function depending on the maximal energy of the  $\beta$ -decay (its explicit form is given in Hraskó's paper (Hraskó, 1974)), and  $w$  is a constant factor to be determined from the experiment.

In a careful comparison of the lifetime of  $^{82}\text{Br}$  in L- and D-3,5-dibromtyrosine, Soós and Bagyinka (1976) did not find any difference above the experimental error. From this  $w < 1.5 \times 10^{-5}$ .

#### 4.12. CRYSTALLIZATION EXPERIMENT OF 'KOVÁCS AND GARAY'

A quite different idea from the decomposition type experiments has been attempted by Kovács and Garay (1975). Sixty-three crystallizations of DL-NaNH<sub>4</sub> tartrate were performed in the presence and in the absence of polarized  $\beta^-$ -particles of  $^{32}\text{P}$ , respectively. Below 27 °C, DL-NaNH<sub>4</sub> tartrate crystallizes in racemic conglomerates, that is, D and L crystallization centres form independently and then grow. Any difference between the number of D and L centres has an increasingly marked effect on the optical activity of the conglomerates as crystallization proceeds. The result of this experiment is presented in Figure 18.\* The distribution of optical activity in the control samples (i.e. without  $\beta$ -activity) was symmetric to the zero value, while in the case of irradiation an asymmetric distribution was found.

This experiment seems to be a very important new approach to the problem of the origin of optical activity. The results, however, need further confirmation. Such investigations are necessary: to study the influence of  $\beta$ -particles on the quantity of crystallized material, to see the shift in opposite direction by positron irradiation, to obtain the size of shift in terms of the quantity of the radioactivity to which the solution to be crystallized is subjected, etc. Proceeding along these lines Kovács (1976a) has found that the quantity of crystallized material increased by  $\approx 20\%$  if he mixed 1.7 mCi  $^{32}\text{P}$  into 2 ml of 45% NaNH<sub>4</sub> tartrate solution.

\* The original histogram of the paper (Kovács and Garay, 1975) has been redrawn because it was an incorrect presentation of the data. The axis of optical activity was broken by separating the 0 readings from the other values. Thanks are due to Dr K. L. Kovács for permission to use the raw data.



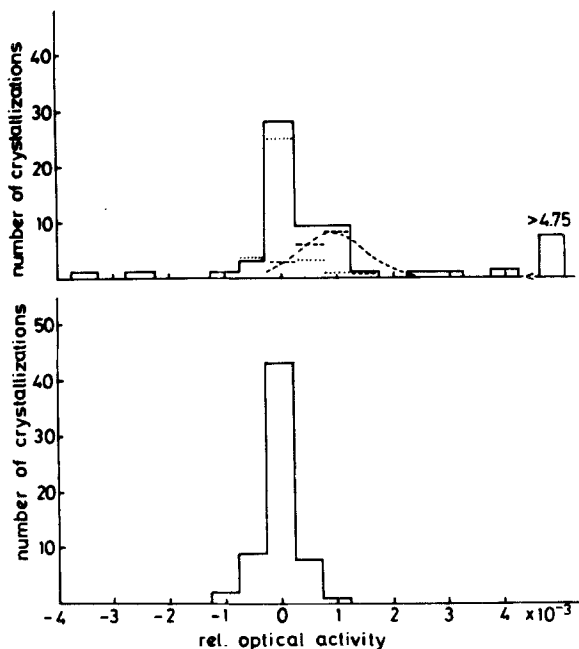


Fig. 18. Distribution of relative optical activity in  $\text{NaNH}_4$ -tartrate samples as crystallized in presence (upper curve) and absence (lower curve), of  $\beta$ -particles. Dashed line possible separation of results into influenced and not influenced crystallizations.

#### 4.13. POLYMERIZATION EXPERIMENTS

In Section 3.4 it has been shown that because of the parity non-conservation in weak interaction the energy content of optical isomers is not equal. This is summarized in Equation (16). We have seen that according to the calculations of Rein (1974a,b),  $\epsilon \approx 10^{-13}$  for alanine. In so far as this result is good only in order of magnitude we may accept it for the usual optical isomers. The second possibility to involve the weak interaction in the origin of the optical purity is based on this small energy difference (Section 4.1).

All the ideas go back to a paper of Yamagata (1966) in which he developed his thesis that the small energy difference could lead to sizeable effect during polymerization.

Let us assume that the polymerization rate for L- and D-molecules is proportional to their energy content

$$\begin{aligned} P_L &= P(1 + \epsilon), \\ P_D &= P(1 - \epsilon), \end{aligned} \quad (33)$$

then to have polymers of  $n$  units

$$\begin{aligned} P_L^n &= P^n(1 + \epsilon)^n, \\ P_D^n &= P^n(1 - \epsilon)^n. \end{aligned} \quad (34)$$

The resulting relative difference

$$2 \frac{P_L^n - P_D^n}{P_L^n + P_D^n} \approx 2n\epsilon, \quad (35)$$

taking the value of  $\epsilon$  to be very small. Equation (35) shows that in such experiments the small value of  $\epsilon$  increases  $n$  times. Since the polymers of living systems may have a large number of units (say in DNA  $n = 10^6 - 10^9$ ), experiments in this direction are worthwhile.

Thiemann and Darge (1974), in a very careful experiment, polymerized racemic D,L-alanine. They were extremely concerned about the real racemic state of the starting monomers (the material was racemized by heat treatment) and about the calibration of their device measuring the optical rotation of light. They observed a net rotation  $-0.84 \pm 0.24$  millidegree of the synthetic poly-alanine, the length of which was  $n = 166$ . They determined the value of  $\epsilon$  to be  $+7.7 \times 10^{-6}$ . ( $\epsilon$  is positive, meaning that the energy content of the L-molecules is higher.) The obtained value of  $\epsilon$  is much higher than theoretically expected.

#### 4.14. CRYSTALLIZATION EXPERIMENTS

The observation of asymmetry in the crystallization of racemic mixtures has been the aim of many experiments since the discovery of the asymmetry of biomolecules. Thiemann (1974a) provides a review of the early experiments. Here only three modern experiments will be dealt with.

In ten independent crystallizations of DL-NaNH<sub>4</sub>-tartrate Thiemann and Wagener (1970) obtained negative optical rotation of  $\approx 1$  millidegree. These authors suggest that this indicates a relative difference in the lattice energy between L- and D-crystals of  $\approx 10^{-5}$ . Because  $n$ , the number of molecules in the crystallites of the polycrystalline material, is not given in the publication, the value of  $\epsilon$  can not be calculated.

In another experiment Thiemann (1974b) used DL-AspNH<sub>2</sub> as a test material to find the consequences of weak interaction in a crystallization experiment. On measuring the optical activity of the crystallized material he observed optical rotation. When the crystallization was performed in the temperature range 0–7.5°C the resulting rotation was negative, from 8° to 12.5°C the sense of rotation changed to positive.\* In the first range the enrichment of D-AspNH<sub>2</sub> was observed.

The contribution of weak interaction to the molecular energy does not depend on the temperature. If the asymmetry had come from it the change at  $\sim 8^\circ\text{C}$  ought to be connected with a change in the crystal structure of AspNH<sub>2</sub>.

\* It should be noted that averaging the ratio of the crystallized L- and D-material ( $C_L/C_D$  in Table I of Thiemann's paper) one gets 10.998/12.000 for the first temperature range and 14.006/14.000 for the second one. As far as this quantity can be considered the real effect, it can be stated that the effect disappeared above 8°C crystallization temperature instead of turning to positive.

It is not possible to estimate the value of  $\epsilon$  from this experiment because  $n$  is not given in the paper.

As a third experiment in this field the control curve of the experiment of Kovács and Garay (1975) may be considered. Because in this case sixty-three different crystallizations were performed and the resulting crystalline material was tested for optical activity to get a distribution curve (Figure 18, lower curve) this result seemed to be well suited for an analysis to get an estimation of  $\epsilon$  (Keszthelyi, 1976c).

A very small spread of optical activity can be observed, the relative width of which is  $\approx 4 \cdot 10^{-4}$ . This spread should have its origin in the finite number of crystallites  $N$  in the crystallization tubes. Taking the relative width as the relative error of the number of crystallites,  $N \approx 6 \cdot 10^6$ . The average weight ( $\approx 1$ g) of the crystallized material in the tube is known, therefore the diameter of the separated crystallites must be  $\approx 50 \mu$ . This average size has recently been observed with an optical microscope (Kovács, 1976b). The number of molecules in a crystallite of such size is  $n \approx 10^{15}$ .

The relative shift of the curve from zero optical activity cannot be larger than  $S < 10^{-4}$ . Before using Equation (35) we have to take into account that the crystals do not grow linearly like the polymers. In most general terms, they grow in three dimensions and then  $\sqrt[3]{n}$ ; or we accept that they grow in planes, then  $\sqrt{n}$  has to be used. This gives  $\epsilon_3 \lesssim 5 \times 10^{-10}$ , or  $\epsilon_2 \lesssim 1.6 \times 10^{-12}$ , respectively. The real upper limit of  $\epsilon$  from this analysis is somewhere between  $\epsilon_3$  and  $\epsilon_2$ . Even  $\epsilon_3$  is a rather small value with only three orders of magnitude above the expected theoretical value. At present this is the smallest upper limit for  $\epsilon$ .

#### 4.15 'MERWITZ'S' EXPERIMENT

Before closing this section, a very curious experiment is discussed (Merwitz, 1976). L-, D-, and LD-phenylalanine labelled by  $^{14}\text{C}$  at the carboxyl group were irradiated by  $^{60}\text{Co}$   $\gamma$ -radiation separately and the liberated radioactive  $^{14}\text{CO}_2$  molecules from radio decarboxylation were counted. The results are summarized in Table IX. Surprisingly, the

TABLE IX  
Counting rates, percentages and dose-dependent G-values for the  $\text{CO}_2$ -cleavage. For  $\epsilon$  see text

	Dose	50	$5 \cdot 10^2$	$5 \cdot 10^3$	$5 \cdot 10^4$	$5 \cdot 10^5$
D	cpm $\text{g}^{-1}$	$1.3 \times 10^4$	$2.4 \times 10^4$	$3.0 \times 10^4$	$4.6 \times 10^4$	$1.5 \times 10^5$
	% $\text{CO}_2$	0.028	0.054	0.067	0.101	0.337
	G( $\text{CO}_2$ )	$3.2 \times 10^4$	$6.3 \times 10^3$	$7.7 \times 10^2$	$1.2 \times 10^2$	39
L	cpm $\text{g}^{-1}$	$5.7 \times 10^3$	$9.0 \times 10^3$	$1.2 \times 10^4$	$2.5 \times 10^5$	$1.3 \times 10^5$
	% $\text{CO}_2$	0.013	0.020	0.026	0.056	0.300
	G( $\text{CO}_2$ )	$1.5 \times 10^4$	$2.3 \times 10^3$	$3.0 \times 10^2$	65	35
$\epsilon$		$1.6 \times 10^{-5}$	$2.1 \times 10^{-4}$	$1.6 \times 10^{-3}$	$6.5 \times 10^{-3}$	$3.1 \times 10^{-3}$

liberated quantity of  $\text{CO}_2$  was different by an average factor of 2 for D- and L-phenylalanine. The factor depended on the dose rate. Because the  $\gamma$ -radiation of  $^{60}\text{Co}$  is not at all circularly polarized, some other explanation was looked for. The G-values of  $\text{CO}_2$  production (number of molecules  $100 \text{ eV}^{-1}$  absorbed energy) were very high (between  $3 \cdot 10^4$ –30), therefore the author assumed that the primary decomposed molecules initiated some chain reaction decomposing more molecules. The asymmetry — say from the difference of energy content of L- and D-molecules — was multiplied, thus resulting in the differences of decomposition. Using Equation (25) and setting  $Z = n\epsilon$  and for  $n$  just the value of  $G$  (it is known that the  $G(\text{CO}_2)$  value of amino acids is  $\approx 1$  (Merwitz, 1976) the values of  $\epsilon$  have been calculated. They are given in the last line of Table IX. It is impossible to accept the results of this experiment because  $\epsilon$  may not depend on the length of the chain.

The main problem lies in the heat treatment of the samples to drive out the  $^{14}\text{CO}_2$  molecules. Even at room temperature  $10^3 \text{ cpm g}^{-1}$  comes from volatilization. At  $160$ – $190^\circ\text{C}$  the volatilized quantity surely increases. There is no description of any control experiment in which the author sublimed unirradiated samples at these elevated temperatures. The high G-values are certainly the result of sublimation and not of the chain reaction after irradiation. (Not any trace of chain reaction has been found in the experiment of Bonner *et al.* (1976).) The identity of UV-spectra and optical rotation of sublimed and non-sublimed phenylalanine may not be considered to be any control because the decomposed part was only 0.3 per cent in the best case which cannot be detected by conventional technique. The difference between L- and D-material could be the consequence of, say, different crystal sizes of the polycrystalline samples.

## 5. Summary of Experimental Results

### 5.1 DECOMPOSITION TYPE EXPERIMENTS

Having surveyed the experiments, the main effort in this review has been to determine the quantity  $2Z$  of Equation (25), which is the relative difference of the decomposition rates

TABLE X  
Relative differences of decomposition rates for L- and D- molecules ( $2Z$ , from Equation (25))

Amino acid	$2Z$	Note	Ref.
Alanine	$<2 \times 10^{-3}$	Upper limit, no sign of $2Z$	Ulbricht (1962)
Tyrosine	-0.8	0.8 is a lower limit for $ 2Z $	Garay (1968)
Leucine	$-0.10 \pm 0.02$	With artificially polarized electrons	Bonner (1975)
Tryptophane	$+0.94 \pm 0.54$	Opposite sign	Darge (1976)
Leucine	$<0.06$	Bremsstrahlung ( $E \sim 0.5$ – $1 \text{ MeV}$ )	Bonner (1974)

for L- and D-molecules under  $\beta$ -irradiation.  $2Z$  must have a finite value and must be negative to obtain less D- than L-molecules. Values of  $2Z$  are collected in Table X. It can be seen that

- (1) there are no independent studies on the same amino acid with the same irradiation,
- (2) values of  $2Z$  have extreme spread,
- (3) the two greatest values were obtained in water solutions,
- (4) the sign of  $2Z$  is wrong in the case of tryptophane.

As a conclusion it can be stated that the experimental situation is contradictory in this field.

## 5.2 POLYMERIZATION-CRYSTALLIZATION TYPE EXPERIMENTS

The value of  $\epsilon$ , the contribution of parity-violating forces to the relative energy difference between L- and D-molecules as defined in Equation (35), is the value to be determined from such experiments. There are two values  $\epsilon = 7.7 \times 10^{-6}$  and  $\epsilon < 10^{-10}$ . The first value (Thiemann, 1974) is in contradiction with theory.

The found asymmetry – if the measurements were correct – is most likely the result of some other physical agent.

## 6. Quantitative Aspects

In spite of the quite active research outlined above there is only one published estimation of the quantitative aspects of the problem (Keszthelyi, 1976b): The questions taken into consideration were:

- (1) Could the radioactivity or cosmic radiation on the Earth have produced a real difference in the number of surviving L- and D-biomolecules which could finally have led to the asymmetric biosphere on the Earth?
- (2) Could the small energy difference of L- and D-molecules due to the contribution of weak forces have caused large enough concentration differences through polymerization and/or crystallization?

Only the first of these problems has been dealt with in Keszthelyi's paper (Keszthelyi, 1976b). The estimation was based on the following set of input data:

(a) the quantity of biomolecules having originated from abiotic interactions  $n_L = n_D$ . The data were taken from a paper of Sagan and Khare (1971), the number of amino acid molecules synthesized by the u.v. light of the Sun in the primordial atmosphere  $2\alpha = 2.4 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ .

(b) the number of energy of  $\beta$ -particles from radioactive nuclei and of cosmic ray particles. An analysis of the existing data showed the role of cosmic radiation to be negligible, the effect could come mainly from the  $\beta^-$ -decay of  $^{40}\text{K}$ .

(c) the size of asymmetry of the interaction of  $\beta^-$ -particles with L- and D-molecules,

i.e.  $2Z$  from Equation (23). Because no acceptable value of  $2Z$  exists at present, it has been used as a parameter.

As a basic principle it was considered that the difference  $n_L(t) - n_D(t)$  must be greater than the statistical fluctuation of the number of molecules:  $\sqrt{n_L(t) + n_D(t)}$ .

A simple model was constructed to describe the change in the number of molecules and the time  $T$  when the difference surpassed the statistical fluctuation was calculated. The result for molecules having fallen into sea water

$$T_V = \left( \frac{2}{V} \frac{l}{\alpha} \frac{1}{2\tau_V(2Z)^2} \right)^{1/3}, \quad (36)$$

and for molecules having fallen on the land surface

$$T_F = \left( \frac{2}{F} \frac{1}{\alpha} \frac{1}{2\tau_F(2Z)^2} \right)^{1/3}. \quad (37)$$

Here  $V/F$  is the volume (surface) considered,  $l$  is the depth of the sea,  $\tau_V(\tau_F)$  the mean decomposition rate in sea water (land surface),

$$\tau_V = \frac{E_V}{\Delta E} \times 3 \times 10^{-26},$$

$$\tau_F = \frac{E_F}{\Delta E} \times 5 \times 10^{-22},$$

where  $E_V/E_F$  is the energy of  $\beta$ -radiation in unit time and in unit volume (surface) and  $\Delta E$  is the energy spent for decomposition of one molecule (30 eV). Setting  $V = 1$  litre,  $l = 10$  metres,  $2Z = 10^{-2}$ ,  $E_V = 530$  MeV litsec $^{-1}$ ,  $F = 1$  cm $^2$ ,  $E_F = 0.4$  MeVcm $^2$  gsec $^{-1}$ ,  $T_V = 1.4 \times 10^2$  yr,  $T_F = 10^2$  yr have been obtained. In the case of  $2Z = 10^{-5}$ ,  $T_V = 1.4 \times 10^4$  yr,  $T_F = 10^4$  yr.

These times are very short compared with the time span of chemical evolution ( $\approx 6 \times 10^8$  yr). There is another problem, however, which is that of the spontaneous racemization of amino acids. For  $2Z = 10^{-5}$  the  $T$  times are in the same order of magnitude as the racemization half-lives (Bada and Schröder, 1975).

The influence of spontaneous racemization has been taken into account accurately by Fajszai and Czégé (1976).

According to their calculations a lower limit exists in the values of  $2Z$  (Equation 23) to grow out from statistical fluctuation. This depends on the half-life of racemization ( $T_R$ )

$$Z_{\min} = 4.3 \times 10^{-4} (T_R) \text{ in year.}$$

For  $T_R = 10^4$  yr,  $Z_{\min} \approx 4.10^{-8}$ . If  $Z$  is smaller than  $Z_{\min}$ , the difference never will exceed the statistical fluctuations.

Another more interesting question is raised: for which values of  $2Z$  will the concentration difference reach the level of statistical fluctuation in a given time  $T$ ?

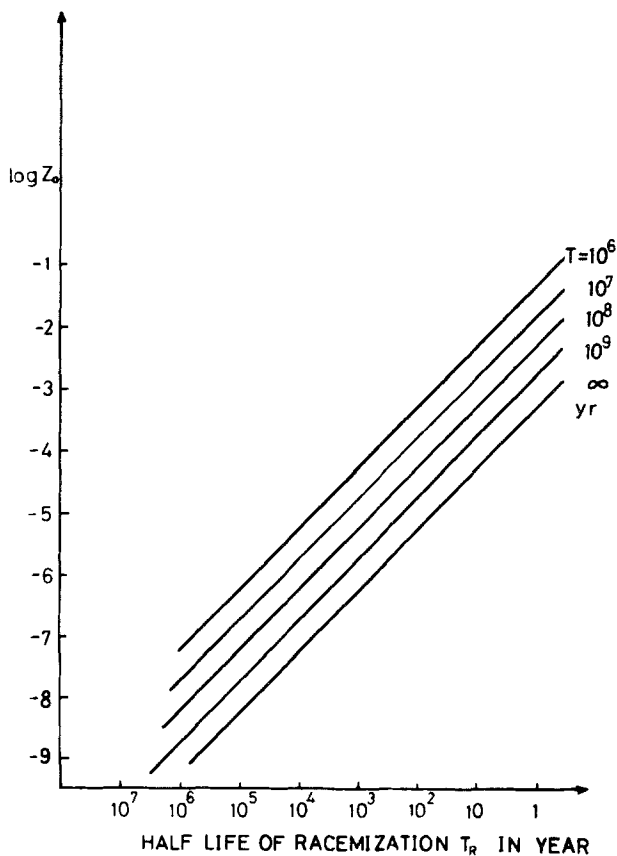


Fig. 19. Dependence of  $2Z_0$  on  $T_R$  for several values of  $T$ . The concentration difference overgrows the level of statistical fluctuations in a period of time not longer than  $T$ , if and only in case of  $2Z > 2Z_0$ , the limiting value of the relative difference of rate constants for decomposing L- and D-molecules by  $\beta$ -particles (Fajszki and Czégé, 1976).

Figure 19 shows the result of these calculations. For  $T_R = 10^4$  yr and  $T = 10^8$  yr, the value of  $Z_{\min}$  increases to  $\approx 10^{-6}$ .

The simple calculation of Keszthelyi and the more refined ones of Fajszki and Czégé show that the concentration differences may surpass the statistical fluctuations; though the relative differences themselves are very small they are never greater than  $2Z$ .

We now try to estimate the concentration difference of L- and D-molecules caused by the energy difference of molecules due to the direct contribution of weak forces. This estimation is more safe than the previous one because the energy difference surely exists from theoretical reasons and the calculation of  $\epsilon$  is good at least in order of magnitude (Rein, 1974b). Only amino acids will be dealt with.

Let us suppose that the molecules fall into a lagoon of  $l = 10$  m deep. With the above  $2\alpha = 2 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , about  $10^6$  years are needed to get a sizeable

concentration for crystallization. This is short compared with the time period of chemical evolution ( $\approx 6 \times 10^8$  yr). For the crystallization Equation (35) may be used;  $n$  may be calculated from the weight  $w$  (in gram) of crystallites. Assuming the molecular weight of an average amino acid to be 100,  $n_3 = 2.1 \times 10^7 \times \sqrt[3]{w}$ ,  $n_2 = 10^{11} \times \sqrt{w}$ . With  $w = 1\text{g}$ , and  $\epsilon = 10^{-13}$ , the relative differences  $(RD)_3 = 4.2 \times 10^{-6}$ ,  $(RD)_2 = 2 \times 10^{-1}$ . (Index '3' relates to the cubic, '2' to surface crystal growth.)

If some mechanism repeated the process (if the solution were driven away, then fresh water came and dissolved the crystallized material, and through evaporation the solution again became saturated and then new crystallization occurred) the relative difference would grow (though the quantity of material would diminish).

## 7. Conclusions

In this paper an attempt was made to give a comprehensive picture of the possible connection between the optical asymmetry of biomolecules and the parity-violating weak interaction. It was pointed out that two ways can be thought out for this connection:

- (1) that of the asymmetric synthesis or decomposition of optically active molecules by spin polarized  $\beta$ -particles,
- (2) the asymmetric polymerization or crystallization of optically active molecules because their energy content is different due to the contribution of weak forces to the intramolecular forces.

The main conclusions of this paper regarding (1) are the following:

- asymmetry in the synthesis-type of experiment has not yet been found;
- evaluation of the results of the decomposition-type of experiments leads to very different values being calculated for the difference of elementary interaction ( $2Z$ );
- measurements and calculations have demonstrated that circularly polarized bremsstrahlung could not play any role in producing optical purity;
- the helical electron gas model is the only existing theoretical undertaking to explain the results of experiments. It is, however, qualitative. The size and sign of  $2Z$  cannot be predicted from it; the remaining helicity of electrons or positrons after slowing down must be reconsidered;
- the crystallization experiment of Kovács and Garay is very promising but it needs further confirmation.

Evaluating the efforts in this field we think that to make progress the following experimental and theoretical studies are needed:

- to measure  $2Z$  in process-oriented experiments;
- to repeat the 'successful' decomposition experiments in such a way that the radiation dose should be different by a factor of 5–10 in the same laboratory with the same measuring system;
- to have data on the same amino acids;
- to work out a theory for the interaction of spin polarized electrons and optically active molecules, perhaps by using the potential described by Karl (1975). It must be



pointed out that practically nothing is known about the cross-sections for decomposition and ionization of amino acids even with circularly polarized light.

Regarding (2) it may be stated that

- optically active molecules have a different energy content due to weak interaction, but this is extremely small;
- this energy difference has not yet been demonstrated experimentally. The polymerization and crystallization experiments of Thiemann *et al.* give too great values, which cannot be explained by the weak interaction.

Further work is also needed in this field. To measure  $\epsilon$ , careful crystallization experiments are needed. To increase its effect and facilitate the correct evaluation, the crystallization of optically active molecules containing high *Z*-elements seems to be necessary. Even the theory of the amplification of this very small difference in biological processes has to be worked out.

Until now two physical interactions have been suggested to explain the origin of optical purity. Circularly polarized light produces optical activity but a suitable source of this light is not known. The weak interaction is asymmetric but the connection with biomolecules has not yet been verified in a convincing way.

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