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**CHIRAL-SYMMETRY-BREAKING IN NONEQUILIBRIUM
CHEMICAL SYSTEMS: THE RACEMIZATION
INFLUENCE**

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CHIRAL-SYMMETRY-BREAKING IN NONEQUILIBRIUM CHEMICAL SYSTEMS:

THE RACEMIZATION INFLUENCE

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Abstract

The open chemical nonequilibrium model, proposed by Kondepudi and Nelson to study the chiral-symmetry-breaking phenomenon, is analysed by the inclusion of the racemization process responsible for the interconversion of left- and right-enantiomers. We study the steady states of the chemical system as a function of the matter pumping and of the racemization rate.

1. Introduction

As is well known,¹ Earth's biochemistry is overwhelmingly dissymmetric or chiral. Living organisms are characterized by the presence of optically active and enantiomerically pure molecules. Proteins are composed of L-amino acids while nucleic acids only contain D-sugars. The transition from racemic geochemistry to homochiral biochemistry remains a major problem of chemical evolution. Plausible mechanisms have been demonstrated for synthesizing,² under primitive terrestrial conditions, most of the racemic monomers required for the assembly of the chiral biopolymers, and for the production of diastereomeric mixture of macromolecules needed by the living cells. But a testable mechanism for the natural selection of the L-amino acids and D-sugars, remains to be demonstrated. Many mechanisms have been proposed³⁻⁵ to explain how the "one-handedness" of biomatter came into play on the Earth. Classical mechanisms like adsorption or surface catalysis by enantiomorphous mineral crystals, such as quartz, the differential circular photolysis of racemates by reflected solar radiation, or the Coriolis force due to the rotation of the Earth, which differ in the two hemispheres, might equally

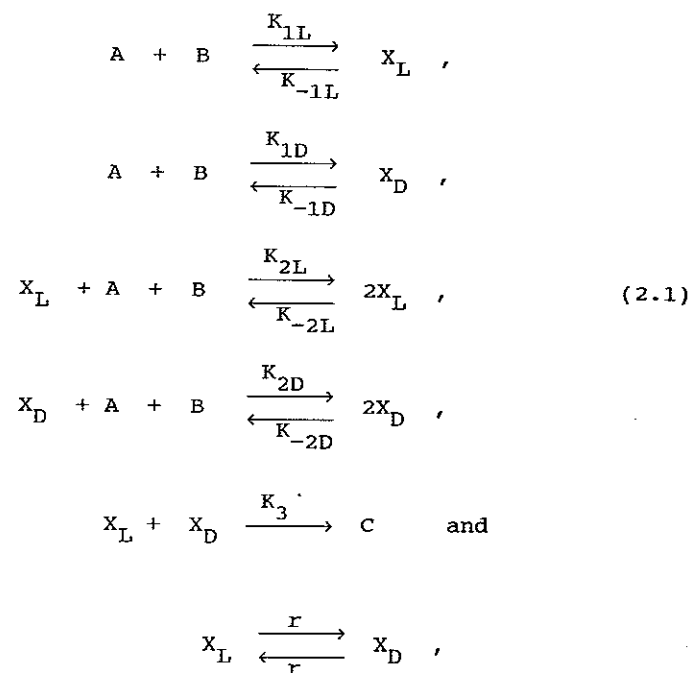
generate an initial enantiomer excess of D-amino acids or L-sugars. So, the particular outcome, L or D handed sugars or amino acids is viewed generally as a "matter of chance".² Theoretical models have been proposed^{4,5} consisting of general kinetic schemes involving stages of autocatalysis and mutual inhibitions. The kinetic behaviors are analysed in terms of concepts drawn from non-linear chemical dynamics.^{6,7} It is shown that under certain conditions the racemate state is unstable. Thus, during a critical period the course of evolution of the system is particularly sensitive to small external perturbations. With the discovery of Parity Violation in Weak Interactions many attempts have been made to show the interrelation of this effect with the homochiral dominance.³⁻⁵ Amazing results have been obtained recently by Kondepudi and Nelson^{8,9} and Tennakone^{10,11} considering the parity violation effect in open nonequilibrium model chemical systems. It was demonstrated that the very small neutral weak currents (WNC) suffices to break the chiral symmetry of racemic reaction sequences in an open nonequilibrium systems. It was shown^{8,9} that if these reactions occur in a system where the net effect of random fluctuations can be taken as very small perturbations, the production of L-enantiomers will be enhanced since the weak forces favors the left-handed enantiomers. Thus, chirally asymmetric life could evolve in these chemical systems.

We must note, however, that in the reaction schemes proposed by Kondepudi and Nelson^{8,9} and by Tennakone^{10,11} the interconversion of the left- and right-handed enantiomers due to racemization effects is not taken into account. In this paper the Kondepudi and Nelson⁸ model will be reanalysed including the racemization effects. We will not analyse here what happens when the chemical process occurs in a randomly fluctuating environment. This case, when the amplitude of the chiral dissymmetry would obey a stochastic (Langevin) equation,⁹ will be studied in a forthcoming paper.

2. Chiral-Symmetry-Breaking Chemical Systems

We analyze the chiral-symmetry-breaking phenomenon in an auto-catalytic chemical model where matter is continuously introduced and removed from the system at different rates. This model is based on the open reaction scheme proposed by Kondepudi and Nelson,^{8,9} where substrate molecules A and B, which have no chirality, combine to produce chiral molecules, X_L (left-handed) or X_D (right-handed), X_L and X_D react to form a substance C irreversibly. We must note that, in this scheme, the racemization effect $X_L \xrightleftharpoons[r]{r} X_D$, where r is the racemization rate, was not taken into account. Only the racemization produced by circularly ultraviolet light was considered, assumed as a small fluctuating perturbation, and estimated by using a stochastic (Langevin) equation.⁹ However, we know¹² that L- and D-amino acids and sugars, regardless of their state, gas, in liquid solutions or in solid state, tend to racemize. Although detailed theories¹³⁻¹⁵ and experimental results¹² about racemization are lacking, we know that, for many substances, the racemization rates r strongly increases when the temperature is raised. Substances that are protected from racemization over long periods of time at temperatures below 30°C show substantial rates of racemization for higher temperatures. Thus, depending on the physical

conditions of the chemical system and of the chiral molecules, X_L and X_D , that are being produced, the reversible interconversion of the D and L enantiomers cannot be neglected. So, we study, in this paper, the chiral symmetry breaking phenomena in chemical systems including in the reaction scheme the racemization equation $X_L \xrightleftharpoons[r]{r} X_D$. Thus, considering this effect, the reaction scheme of Kondepudi and Nelson^{8,9} will now be given by



where K_1 , K_{-1} , K_2 , K_{-2} and K_3 are the kinetic coefficients of the reactions. The kinetic coefficients K and the racemization rate r are measured in s^{-1} . In this model the concentrations of the reactants A, B and C are assumed to be maintained constant.

Let us indicate by X_L , X_D , A and B the concentrations of the reactants. Using the law of mass action, the variation in time of the concentrations X_L and X_D , according to Eqs. (2.1), will be given by

$$dX_L/dt = K_{1L}\lambda - K_{-1L}X_L + K_{2L}\lambda X_L - K_{-2L}X_L^2 - K_3X_LX_D - r(X_L - X_D), \quad (2.2)$$

$$dX_D/dt = K_{1D}\lambda - K_{-1D}X_D + K_{2D}\lambda X_D - K_{-2D}X_D^2 - K_3X_DX_L - r(X_D - X_L), \quad (2.3)$$

where $\lambda = AB$.

It is important to remark that Eqs. (2.2) and (2.3) contain the two essential aspects of auto catalysis and competition (or mutual destruction) which seem to be necessary in any chemical system that is to break chiral symmetry. From the theoretical analysis of Kondepudi and Nelson^{8,9} we see that it is possible for the parity violating WNC interaction to become the selector of molecular chirality. However, the difficult of the above chemical model is that the complete sequence of reactions,

described by Eqs. (2.1), seems to be a highly improbable event in a prebiotic medium. Up to now, no experiment has demonstrated spontaneous chiral symmetry breaking directly or indirectly. But, as pointed out by Kondepudi and Nelson,⁸ looking at the current wealth of chiral chemistry, it seems entirely possible, in a near future, to realize such a chemical system.

In next section we will obtain the steady state solutions, symmetric and asymmetric, of the Eqs. (2.2) and (2.3), showing that for $\lambda = \lambda_C$ occurs a bifurcation. We determine how these steady solutions and the critical parameter λ_C depends on the racemization rate r .

As is shown in this work, the critical concentration parameter that defines the bifurcation phenomenon in the Kondepudi and Nelson scheme,^{8,9} is a sensitive function of the racemization rate. Thus, our analysis is important in the sense that it permit us to establish more accurately in what experimental conditions we must expect an enhancement in the L-enantiomers production.

3. Steady state solutions of the kinetic equations

In this section we obtain the steady state solutions of the kinetic equations (2.2) and (2.3) and the corresponding bifurcation equation where $K_{1L} = K_{1D}$, $K_{2L} = K_{2D}$, etc.⁸ Defining the new variables $\alpha = (X_L - X_D)/2$ and $\beta = (X_L + X_D)/2$, we get from Eqs. (2.2) and (2.3) the following kinetic equations:

$$d\alpha/dt = -K_{-1}\alpha + K_2\lambda\alpha - 2K_{-2}\alpha\beta - 2r\alpha, \quad (3.1)$$

$$d\beta/dt = K_1\lambda - K_{-1}\beta + K_2\lambda\beta - K_{-2}(\alpha^2 + \beta^2) + K_3(\alpha^2 - \beta^2). \quad (3.2)$$

The chemical system described by the above equations evolves in time and eventually it reaches nonequilibrium steady states characterized by constant values of the concentrations X_L and X_D .

The system presents three different steady states. For a fixed value of r , we observe that for low values of λ the stable steady state is one that is called symmetric (S) i.e., $X_L = X_D$ what implies $\alpha_S = 0$. When λ increases, there is a value $\lambda = \lambda_C$ where the symmetric solution becomes unstable and two new asymmetric (A) solutions ($X_L \neq X_D$), with α_A and $-\alpha_A$, arises. For

$\lambda > \lambda_C$ these asymmetric solutions are stable.

The symmetric solutions is obtained placing $\alpha = 0$ in Eqs. (3.1) and (3.2). This procedure gives

$$\alpha_S = 0, \quad (3.3)$$

$$\beta_S = \frac{K_2\lambda - K_{-1} + \sqrt{(K_2\lambda - K_{-1})^2 + 4(K_3 + K_{-2})K_1\lambda}}{2(K_{-2} + K_3)}. \quad (3.4)$$

The asymmetric solutions, obtained from Eqs. (3.1) and (3.2), are given by

$$\alpha_A = \pm \sqrt{\beta_A^2 - (2r\beta_A + K_1\lambda) / (K_3 - K_{-2})}, \quad (3.5)$$

$$\beta_A = \frac{K_2\lambda - 2r - K_{-1}}{2K_{-2}}. \quad (3.6)$$

The transition from the symmetric steady state to one of the asymmetric states, where the bifurcation takes place, occurs when $\alpha_A = \alpha_S = 0$ (that is equivalent to $\beta_A = \beta_S$). So, using Eqs. (3.3) - (3.6), with these conditions, we obtain the

equation for the line of critical points, λ_C versus r , defined by

$$A_1 r^2 + A_2 r \lambda_C + A_3 \lambda_C^2 + A_4 r + A_5 \lambda_C + A_6 = 0, \quad (3.7)$$

where $A_1 = 4(K_3 + K_{-2})$, $A_2 = -4K_3K_2$, $A_3 = K_2^2 (K_3 - K_{-2})$, $A_4 =$

$4K_3K_{-1}$, $A_5 = -2K_{-1} (K_3 - K_{-2}) - 4K_1K_{-2}^2$ and $A_6 = K_{-1}^2 (K_3 - K_{-2})$.

Analysing Eq. (3.7) we verify that, as long as $K_3 > K_{-2}$, λ_C is an increasing function of r . This is shown in Fig. 1, for the particular values of the reaction rates $K_1 = K_3 = 10^{-1}$ and $K_{-1} = K_2 = k_{-2} = 10^{-4}$, adopted by Kondepudi and Nelson.⁸

(I N S E R T F I G. 1)

From the above analysis we conclude that the bifurcation that appears in the Kondepudi and Nelson scheme is not modified by the racemization effect. The racemization only modifies the critical parameter λ_C , that increases as r raises. Fig. 2 illustrates qualitatively the bifurcation when the racemization is taken into account.

(I N S E R T F I G. 2)

The stability of the symmetric and asymmetric solutions of the Eqs. (3.1) and (3.2) are analysed in the appendix.

In next section, assuming that there is a small difference in the energies of the L and D enantiomers, due to the WNC, we obtain the steady states solutions of the kinetic equations (3.1) and (3.2) as a function of the parameters λ and r .

4. Weak Chiral Interaction

The system that evolves in time according to Eqs. (3.1) and (3.2) can go, for $\lambda > \lambda_C$, to a steady state with greater concentration X_L or to a steady state with greater concentration X_D . These are the asymmetric solutions (α_A, β_A) and $(-\alpha_A, \beta_A)$, respectively, given by Eqs. (3.5) and (3.6). The system can attain anyone of these states with equal probability.

However, as discussed in section 2, the effect of a weak chiral interaction, can be very relevant in the process of selection of one of the asymmetric solutions. In order to introduce this effect we assume^{8,9} that $K_{1L} = K_1 (1 + g/2)$ and $K_{1D} = K_1 (1 - g/2)$, where $g = \Delta E/kT$, ΔE the small difference in the energies of X_L and X_D , due to a weak chiral interaction, k the Boltzmann constant and T the temperature of the system. The parameter g behaves as a weak chiral symmetry breaking "field". In this approach the kinetic equations are now given by

$$\frac{dX_L}{dt} = K_1(1+g/2) \lambda - K_{-1}X_L + K_2\lambda X_L - K_{-2}X_L^2 - K_3X_LX_D - r(X_L - X_D), \quad (4.1)$$

$$\frac{dX_D}{dt} = K_1(1-g/2) \lambda - K_{-1}X_D + K_2\lambda X_D - K_{-2}X_D^2 - K_3X_DX_L - r(X_D - X_L), \quad (4.2)$$

Using the variables $\alpha = (X_L - X_D)/2$ and $\beta = (X_L + X_D)/2$ the above equations for X_L and X_D are rewritten as

$$d\alpha/dt = K_1\lambda g/2 - K_{-1}\alpha + K_2\lambda\alpha - 2K_{-2}\alpha\beta - 2r\alpha, \quad (4.3)$$

$$d\beta/dt = K_1\lambda - K_{-1}\beta + K_2\lambda\beta - K_{-2}(\alpha^2 + \beta^2) + K_3(\alpha^2 - \beta^2). \quad (4.4)$$

As it can be seen from Eqs. (4.3) and (4.4), the symmetric solution $\alpha_S = 0$ ($X_L = X_D$) is no more a steady state of the system. Only asymmetric steady states are solutions of these equations.

From Eq. (4.4) we obtain for the stationary regime, $d\beta/dt = 0$, the stationary value of β as a function of the stationary value of α :

$$\beta = \frac{K_{-2}\beta_A + r + \sqrt{(K_{-2}\beta_A + r)^2 + (K_3 + K_{-2})(K_1\lambda + (K_3 - K_2)\alpha^2)}}{(K_3 + K_{-2})} \quad (4.5)$$

where $\beta_A = (K_2\lambda - 2r - K_{-1}) / 2K_{-2}$.

Substituting β , given by Eq. (4.5), in Eq. (4.3) we get the following equation for the time evolution of α :

$$\begin{aligned} d\alpha/dt = & K_1 \lambda g/2 + 2K_{-2} \beta_A \alpha - \left[\frac{2K_{-2} \alpha}{K_3 + K_{-2}} \right] \left\{ K_{-2} \beta_A + r + \right. \\ & \left. + \left[(K_{-2} \beta_A + r)^2 + (K_3 + K_{-2}) (K_1 \lambda + (K_3 - K_{-2}) \alpha^2) \right]^{1/2} \right\} \end{aligned} \quad (4.6)$$

Now we study the behaviour of the Eq. (4.6) when α is small. In this case we expand the radical in Eq. (4.6)

$$\begin{aligned} & \left[(K_{-2} \beta_A + r)^2 + (K_3 + K_{-2}) (K_1 \lambda + (K_3 - K_{-2}) \alpha^2) \right]^{1/2} \\ & \cong \left[(K_{-2} \beta_A + r)^2 + (K_3 + K_{-2}) K_1 \lambda \right]^{1/2} \left[1 + \frac{(K_3^2 - K_{-2}^2) \alpha^2}{2 \left[(K_{-2} \beta_A + r)^2 + K_1 \lambda (K_3 + K_{-2}) \right]} \right]. \end{aligned}$$

In these conditions, Eq. (4.6) becomes

$$d\alpha/dt = - \left[\frac{K_{-2} (K_3 - K_{-2})}{\beta_S (K_3 + K_{-2}) - (K_{-2} \beta_A + r)} \right] \alpha^3 + 2K_{-2} (\beta_A - \beta_S) \alpha + \frac{K_1 \lambda g}{2}, \quad (4.7)$$

β_S defined by Eq. (3.4).

In order to see how the branch selection occurs for $\alpha > 0$ and $\alpha < 0$, we investigate the behaviour of α as a function of λ near to λ_C (given by Eq. (3.7)), for a fixed value of r . In this case we expand the coefficient, $\beta_A - \beta_S$, that multiplies α in eq. (4.7) up to linear terms in $\lambda - \lambda_C$ and consider $\beta_A = \beta_A^*$, where $\beta_A^* = \beta_A(\lambda_C)$. The remaining coefficients will be calculated for $\lambda = \lambda_C$ and $\beta_S = \beta_A^*$. Thus, near to $\lambda = \lambda_C$, Eq. (4.7) becomes

$$d\alpha/dt = -U_0 \alpha^3 + V_0 (\lambda - \lambda_C) \alpha + W g, \quad (4.8)$$

where

$$U_0 = \frac{2K_{-2}^2 (K_3 - K_{-2})}{K_3 (K_3 \lambda_C - K_{-1} - 2r) - 2K_{-2} r}$$

$$\begin{aligned} V_0 = & \left(\frac{\beta_A^*}{\beta_A^* - r/K_3} \right) \left[K_2 - (K_2 K_{-2} / K_3) \left(1 + \frac{r K_3}{K_{-2} \beta_A^* (K_3 + K_{-2})} \right) + \right. \\ & \left. (K_1 / K_2 \beta_A^*) \right] \end{aligned}$$

and $W = K_1 \lambda_C / 2$.

Thus, in the vicinity of the critical point $\lambda = \lambda_C$, the stationary value of α is a solution of the equation

$$-U_0 \alpha^3 + V_0 (\lambda - \lambda_C) \alpha + Wg = 0. \quad (4.9)$$

A solution with $\alpha > 0$ is always a stable solution of Eq. (4.9). For $\lambda = \lambda_C$ the only solution of this equation is that with $\alpha > 0$. Thus, we see that when the parameter λ is increased from λ_C the system will attain a steady state with $\alpha > 0$, i.e. a solution where the amount of L molecules is greater than the amount of D molecules. When $\lambda = \lambda_1$, where $\lambda_1 = \lambda_C + (3U_0/4V_0) (4Wg/U_0)^{2/3}$, two new solutions with $\alpha < 0$ appear. One of them, the greater in intensity, is always stable and the other is always unstable. The α branches as function of $(\lambda - \lambda_C) / \lambda_C$ are shown in Fig. 3 for $r = 0$ and $r = 10^{-4}$, taking $K_1 = K_3 = 10^{-1}$, $K_2 = K_{-1} = K_{-2} = 10^{-4}$ and $g = 10^{-17}$.

(I N S E R T F I G. 3)

When the racemization increases, since it tends to equalize the X_L and X_D populations, the chiral selection of the L-enantiomers is inhibited if the reagent concentration $\lambda = AB$ is maintained constant. This inhibition effect can be calculated integrating, for given values of λ and r , the set of ordinary equations (4.3) and (4.4) from an initial state, up to the final steady state with $\alpha > 0$. In Fig. 4, where the steady state value of α is plotted as function of λ , for $r = 0$ and $r = 10^{-4}$, the inhibition effect due to the racemization is clearly shown. To obtain Fig. 4 we have used the same kinetic coefficients and g adopted in Fig. 3.

(I N S E R T F I G. 4)

Acknowledgements

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APPENDIX. Linear Analysis of Stability

Here we study the stability of the kinetic equations (3.1) and (3.2).

Let us perform the linear stability analysis of the Eqs. (3.1) and (3.2) defining the small deviations $\xi(t) = \alpha(t) - \alpha^*$ and $\eta(t) = \beta(t) - \beta^*$, where β^* and α^* are stationary values of the referred equations. In this way, the equations for $\xi(t)$ and $\eta(t)$, up to linear terms in $\xi(t)$ and $\eta(t)$, are given by

$$d\xi/dt = M_{11}\xi + M_{12}\eta, \quad (\text{A.1})$$

$$d\eta/dt = M_{21}\xi + M_{22}\eta, \quad (\text{A.2})$$

where $M_{11} = (\partial F/\partial\alpha)_{\alpha=\alpha^*, \beta=\beta^*}$, $M_{12} = (\partial F/\partial\beta)_{\alpha=\alpha^*, \beta=\beta^*}$, $M_{21} = (\partial G/\partial\alpha)_{\alpha=\alpha^*, \beta=\beta^*}$, $M_{22} = (\partial G/\partial\beta)_{\alpha=\alpha^*, \beta=\beta^*}$ and $F(\alpha, \beta)$, $G(\alpha, \beta)$ are the right hand side of the Eqs. (3.1) and (3.2), respectively.

Defining by ω_1 and ω_2 the eigenvalues of the matrix M_{ij} , the general solutions for $\xi(t)$ and $\eta(t)$ are written in the form

$$\xi(t) = a_1 e^{\omega_1 t} + a_2 e^{\omega_2 t},$$

$$\eta(t) = b_1 e^{\omega_1 t} + b_2 e^{\omega_2 t}.$$

So, if the real part of ω_1 or ω_2 are positive or negative, the solutions are unstable or stable, respectively.

For the symmetric solution we verify that $\omega_1 = 2K_{-2} (\beta_A - \beta_S)$ and $\omega_2 = K_2\lambda - K_{-1} - 2\beta_S (K_{-2} + K_3)$. As ω_2 is always negative, for feasible values of λ the symmetric solution is stable as long as $\beta_A < \beta_S$, with β_S and β_A defined by Eqs. (3.4) and (3.6), respectively. This occurs for $\lambda < \lambda_C$, as is shown in Fig. 5. In these figures for $r = 0$ and $r = 10^{-4}$, β_A and β_S have been calculated, as a function of λ , taking $K_1 = K_3 = 10^{-1}$ and $K_{-1} = K_2 = K_{-2} = 10^{-4}$, in agreement with Kondepudi and Nelson.⁸ When $\lambda = \lambda_C$, $\beta_A = \beta_S$ and $\omega_2 = 0$. For $\lambda > \lambda_C$ the symmetric solution becomes unstable. Adopting the same procedure to find the eigenvalues corresponding to the asymmetric solutions, we verify that for $\lambda > \lambda_C$ the asymmetric solutions are indeed stable. The scheme of fixed points and their stability is qualitatively illustrated in Fig. 6.

(I N S E R T F I G . 5 A N D F I G . 6)

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FIGURE CAPTIONS

- Fig. 1 - The critical parameter λ_C as a function of the racemization rate r .
- Fig. 2 - The steady state α values as a function of λ , for different values of r .
- Fig. 3 - α/α_0 , where $\alpha_0 = \alpha(\lambda_C)$, as a function of $(\lambda - \lambda_C)/\lambda_C$, for $r = 0$ and $r = 10^{-4}$.
- Fig. 4 - The positive α branch as a function of λ , for $r = 0$ and $r = 10^{-4}$. Solid lines (—) are stable and dashed lines (----) are unstable.
- Fig. 5 - β_S and β_A versus λ for $r = 0$ and $r = 10^{-4}$.
- Fig. 6 - The scheme of stability of fixed points of Eqs. (3.1) and (3.2) for: (a) $\lambda < \lambda_C$ and (b) $\lambda > \lambda_C$. S is the fixed point corresponding to the symmetric solution, I is a fixed point with no physical meaning. A_1 and A_2 are the two fixed points corresponding to the asymmetric solutions.

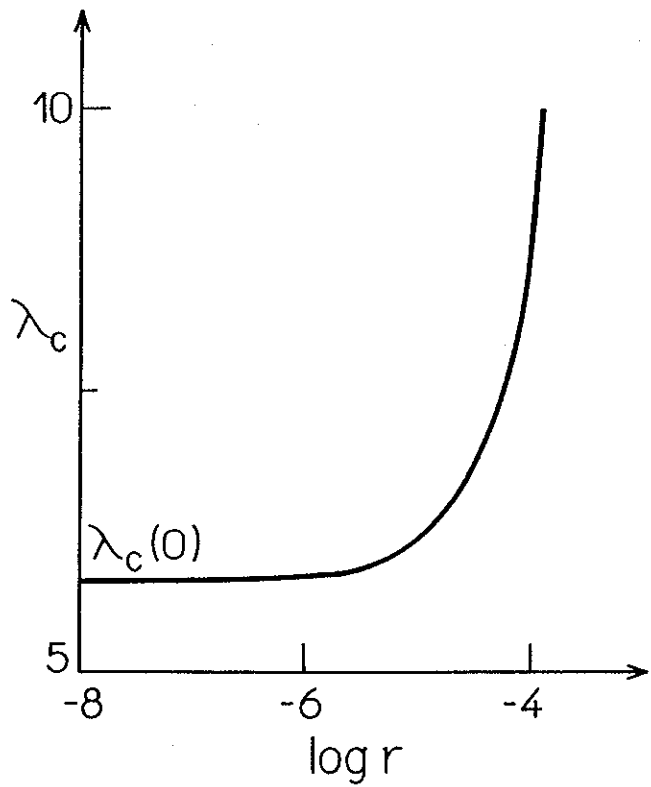


Fig. 1

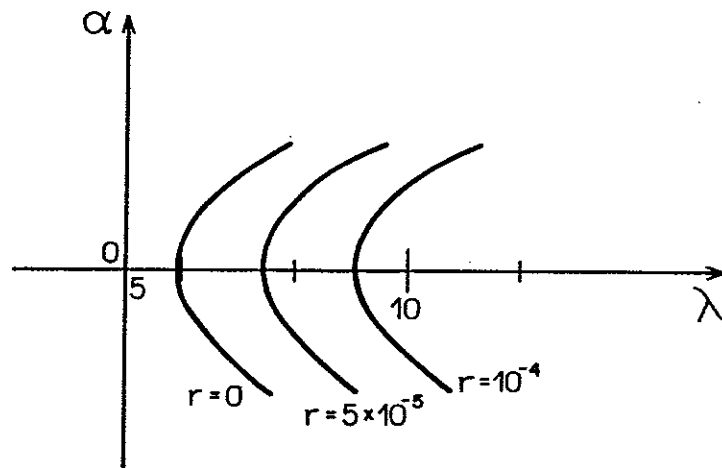


Fig. 2

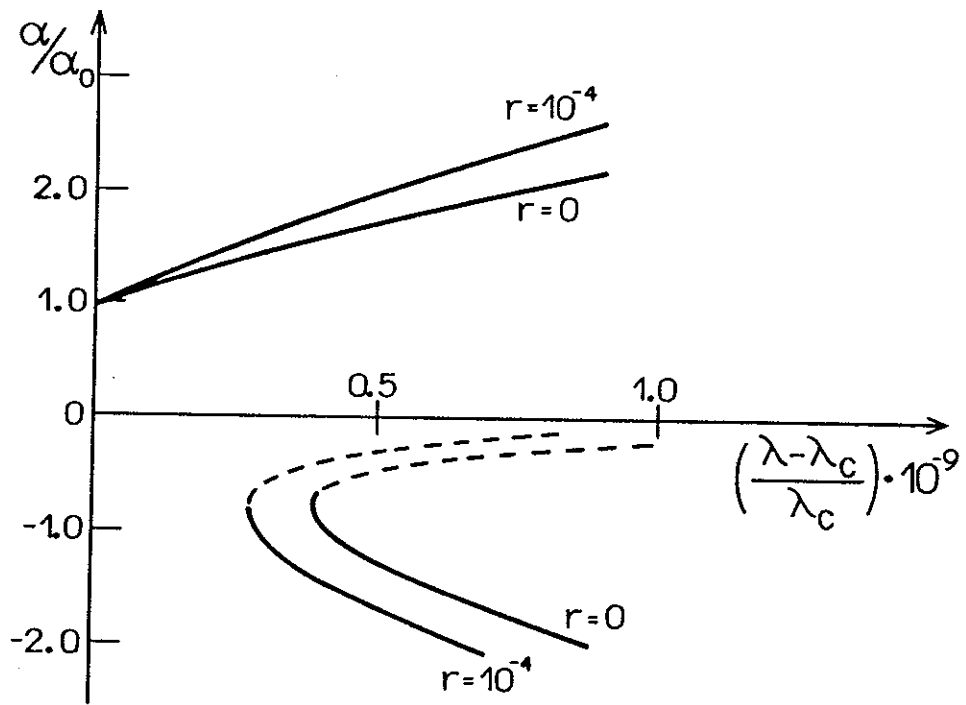


Fig. 3

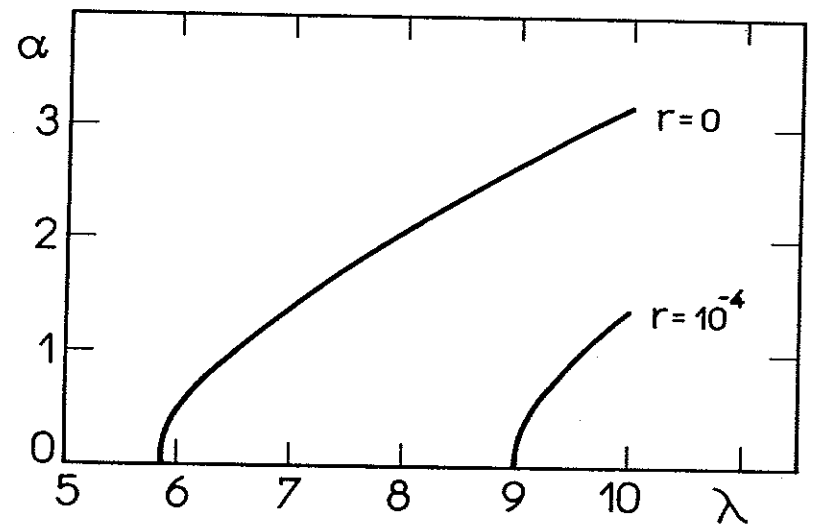


Fig. 4

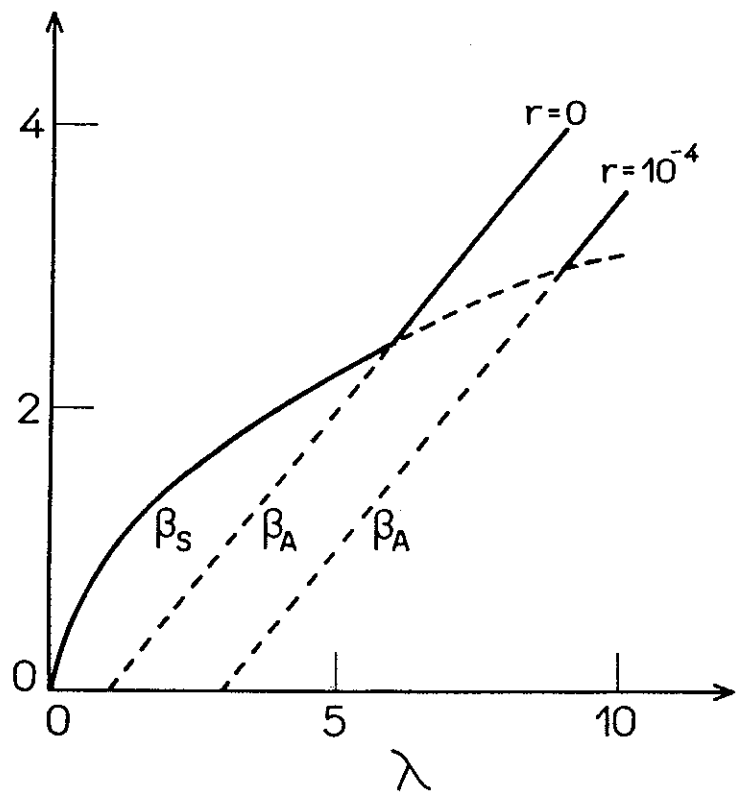


Fig. 5

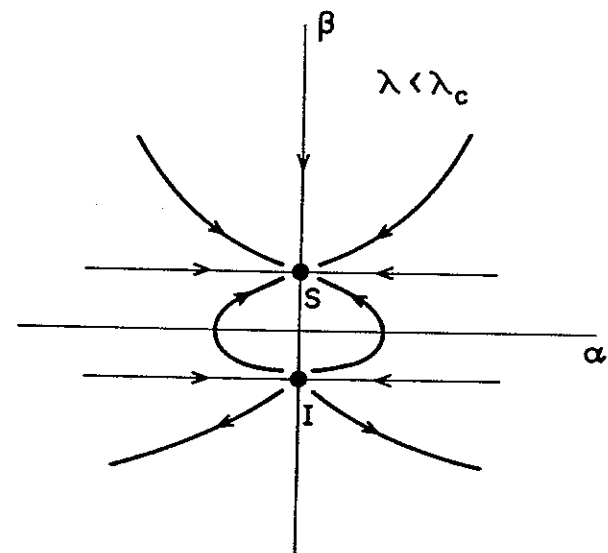


Fig. 6a

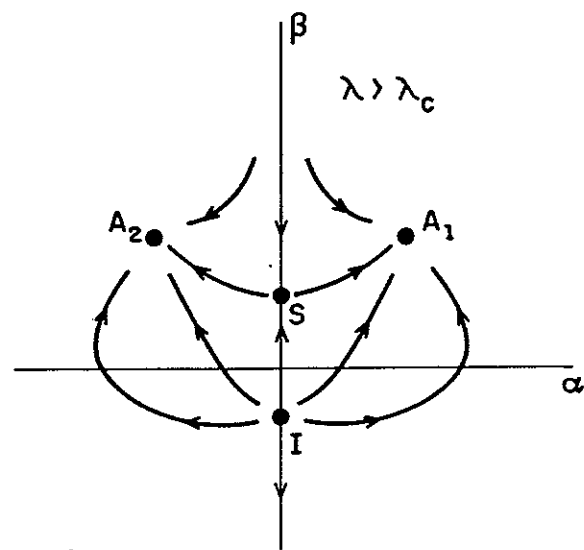


Fig. 6b