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Report TW 72

On a non-linear differential equation occurring in the theory of thermo-diffusion in a ternary mixture of gases

by

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1. The differential equation

The state of equilibrium of a mixture of three gases with relative concentrations $x_{1,2,3}$ ($\sum_i x_i = 1$) depends on the temperature of the mixture. The concentrations satisfy the set of differential equations:

$$\frac{dx_i}{dt} = - \sum_{j=1}^{3} \alpha_{ij} x_i x_j \ , \quad (i=1,2,3), \tag{1.1}$$

where t denotes the logarithm of the temperature T (t=ln T). The coefficients α_{ij} depend on the concentrations x_i and the temperature; moreover, since $\sum_i x_i = 1$ they are submitted to the condition

$$\alpha_{ij} + \alpha_{ji} = 0 \ . \tag{1.2}$$

In order to obtain some knowledge of the behaviour of the concentrations x_i as functions of the temperature, the coefficients α_{ij} will be taken as constants, which may be assumed to hold approximately in a not too large range of the temperature.

Putting

$$\begin{aligned} \alpha_{12} &= -\alpha_{21} = \alpha, \\ \alpha_{13} &= -\alpha_{31} = \alpha_1, \\ \alpha_{23} &= -\alpha_{32} = \alpha_2, \end{aligned} \tag{1.3}$$

and using the identity

$$x_1 + x_2 + x_3 \equiv 1 \ , \tag{1.4}$$

the system (1.1) can be reduced to:

$$\frac{dx_1}{dt} = x_1 \{ \alpha_1 x_1 + (\alpha_1 - \alpha) x_2 - \alpha_1 \} \ , \tag{1.5}$$

$$\frac{dx_2}{dt} = x_2 \{ (\alpha_2 + \alpha) x_1 + \alpha_2 x_2 - \alpha_2 \} \ . \tag{1.6}$$

Finally by substituting

$$\begin{aligned} \alpha t &= \tau, \\ \frac{\alpha_1}{\alpha} &= \beta_1, \\ \frac{\alpha_2}{\alpha} &= \beta_2, \end{aligned} \tag{1.7}$$

we get rid of one parameter and the system (1.5), (1.6) becomes

$$\frac{dx_1}{d\tau} = x_1 \{ \beta_1 x_1 + (\beta_1 - 1) x_2 - \beta_1 \} \ , \tag{1.8}$$

$$\frac{dx_2}{d\tau} = x_2 \{ (\beta_2 + 1) x_1 + \beta_2 x_2 - \beta_2 \} \ . \tag{1.9}$$

Hence the concentrations x_1 and x_2 are determined by a set of non-linear differential equations with some initial conditions, e.g.

$$x_1(\tau_0) = x_1^{\,0}, \; x_2(\tau_0) = x_2^{\,0}. \qquad (1.10)$$

On account of physical considerations we may assume for the coefficients β_1 and β_2:

i) β_1 and β_2 are of the same sign.
ii) $|\beta_1| > 1$ and $|\beta_2| > 1$.
iii) the quantity $\bar{\beta} = 1 - \beta_1 + \beta_2$, which will appear later on, may be as well positive as negative.

2. Solution of the system of differential equations

In general it is quite difficult to give explicit solutions of systems of non-linear differential equations of the type (1.8), (1.9). In order to obtain a trajectory in the (x_1,x_2) plane, passing through the point $(x_1^{\,0},x_2^{\,0})$, one resorts often to a graphical device by using the method of isoclines.
The equations (1.8), (1.9) yield immediately the curves in the (x_1,x_2) plane, along which the slope , $\frac{dx_2}{dx_1}$, of the trajectories remains constant.
By drawing a sufficient number of isoclines one can easily construct graphically the path of any trajectory passing through some point $(x_1^{\,0},x_2^{\,0})$.
This graphical method, however, involves complications when we are interested in the path of some trajectory in the neighbourhood of a singular point of the system (1.8), (1.9), i.e. a point where the right hand sides of (1.8) and (1.9) both vanish. In such a point vanish both $\frac{dx_1}{d\tau}$ and $\frac{dx_2}{d\tau}$ and hence the slope of the trajectory is quite undetermined.
When we conceive the variable   as a time variable the set of differential equations (1.8), (1.9) correspond to the behaviour of some dynamical system.
It can be shown (see e.g. lit.1) that the singular points of systems of ordinary differential equations of the type (1.8), (1.9) correspond to the points of equilibrium of the dynamical system; this means that the singular points are approached along some trajectory asymptotically for $\tau \to +\infty$ or $\tau \to -\infty$ or for both $\tau \to +\infty$ and $\tau \to -\infty$.
In the case of our problem the singular points are approached for $T \to 0$ or for $T \to +\infty$ or for both $T \to 0$ and $T \to +\infty$.

The system of equations (1.8), (1.9) has four singularities; they are located in the points

A $x_1=0,\ x_2=0,$

B $x_1=1,\ x_2=0,$

C $x_1=0,\ x_2=1,$

D $x_1=\frac{\beta_2}{\bar\beta},\ x_2=-\frac{\beta_1}{\bar\beta}$ with $\bar\beta=1-\beta_1+\beta_2$.

Since we are only interested in positive values of x_1 and x_2 with $0<x_1+x_2<1$, we need only to consider those parts of the trajectories which lie within the triangle with the singular points A, B and C as vertices.

Since β_1 and β_2 have the same sign, the singular point D lies always outside the triangle ABC and so we do not need to investigate the singularity corresponding with point D.

When $(x_{1,s},x_{2,s})$ are the coordinates of the singular point, the behaviour of the trajectories in the neighbourhood of the singular point can be obtained according to the theorem of Liapounoff by writing the right hand sides of (1.8) and (1.9) as polynomials of the second degree in $(x_1-x_{1,s})$ and $(x_2-x_{2,s})$ and retaining consecutively the linear terms only (see lit.1, Chapter III).

By applying the theorem of Liapounoff we shall investigate the behaviour of the trajectories in the neighbourhood of the points A,B and C. When this behaviour is known one can construct quite easily the trajectory, passing through some point $(x_1^{\,o},x_2^{\,o})$ and lying within the triangle ABC by aid of the graphical method of isoclines. In the next section we shall give a short description of the classification of the singularities, which may occur in systems of differential equations of a more general type than that of equations (1.8) and (1.9); moreover, we shall also formulate the condition under which the above mentioned theorem of Liapounoff is valid.

3. Classification of the singularities according to Poincaré and the theorem of Liapounoff

The differential equation of the trajectory in the (x_1,x_2) plane is given by the formula:

$$\frac{dx_2}{dx_1}=\frac{x_2\{(\beta_2+1)x_1+\beta_2x_2-\beta_2\}}{x_1\{\beta_1x_1+(\beta_1-1)x_2-\beta_1\}}\,, \qquad (3.1)$$

or in parameter form:

$$\dot{x}_1 = x_1\{\beta_1 x_1+(\beta_1-1)x_2-\beta_1\}\ , \tag{1.8}$$

$$\dot{x}_2 = x_2\{(\beta_2+1)x_1+\beta_2 x_2-\beta_2\}, \tag{1.9}$$

where the dots denote differentiation with respect to τ.

We consider the more general system

$$\frac{dx_2}{dx_1} = \frac{g(x_1,x_2)}{f(x_1,x_2)}\ , \tag{3.2}$$

or in parameter form:

$$\begin{aligned} \dot{x}_1 &= f(x_1,x_2), \\ \dot{x}_2 &= g(x_1,x_2), \end{aligned} \tag{3.3}$$

where f and g are arbitrary polynomials in x_1 and x_2.

Taking the singular point of the differential equation as the origin of the (x_1,x_2) plane and retaining in f and g the linear terms only equations (3.2) and (3.3) reduce to:

$$\frac{dx_2}{dx_1} = \frac{cx_1+dx_2}{ax_1+bx_2} \tag{3.4}$$

and

$$\begin{aligned} \dot{x}_1 &= ax_1+bx_2, \\ \dot{x}_2 &= cx_1+dx_2, \end{aligned} \tag{3.5}$$

where a,b,c and d are constants.

By means of a linear transformation of variables

$$\begin{aligned} \xi_1 &= \alpha x_1+\beta x_2\ , \\ \xi_2 &= \gamma x_1+\delta x_2 \end{aligned} \tag{3.6}$$

with

$\begin{vmatrix} \alpha & \beta \\ \gamma & \delta \end{vmatrix} \neq 0$ the system (3.5) can be reduced to the canonical form:

$$\begin{aligned} \dot{\xi}_1 &= S_1\ \xi_1\ , \\ \dot{\xi}_2 &= S_2\ \xi_2\ , \end{aligned} \tag{3.7}$$

where S_1 and S_2 are constants.

It can easily be shown that S_1 and S_2 are the roots of the quadratic equation:

$$S^2-S(a+d)+(ad-bc) = 0. \tag{3.8}$$

This equation is called the characteristic equation of the system (3.5) and it is the base of the classification of the singularities of the system (3.5), which may occur for various values of the constants a,b,c and d.
It follows from the canonical form (3.7) that the following criteria for the kind of the singularity can be given:

1. If the roots S_1 and S_2 of the characteristic equation are real and negative, one has a stable nodal point.
2. If S_1 and S_2 are real and positive, one has an unstable nodal point.
3. If S_1 and S_2 are real and of opposite sign, one has a saddle point.
4. If S_1 and S_2 are conjugate complex with $Re(S_{1,2}) < 0$ one has a stable focal point.
5. If S_1 and S_2 are conjugate complex with $Re(S_{1,2}) > 0$ one has an unstable focal point.

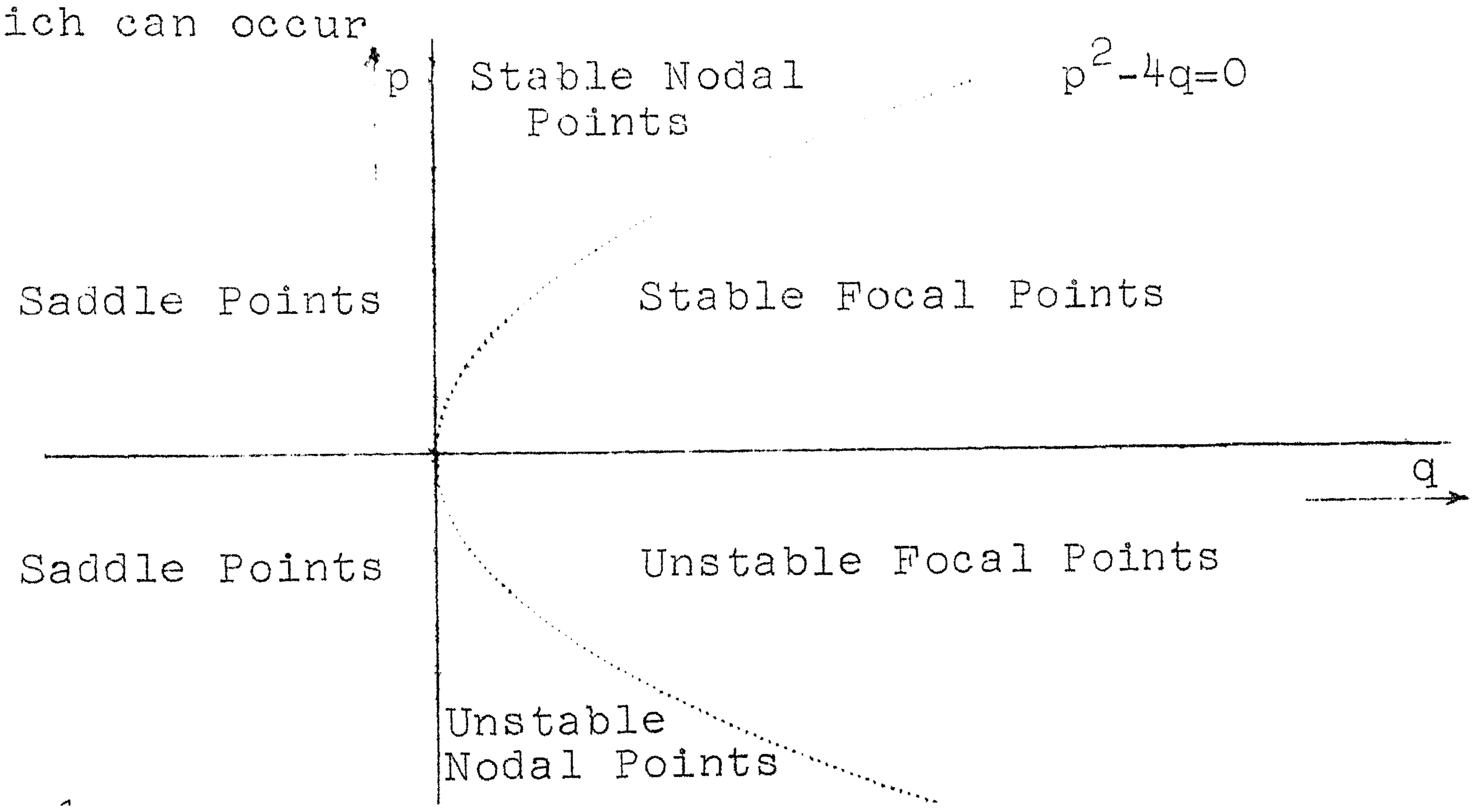
The singularity is called stable if the representative point (x_1,x_2) approaches the singular point (0,0) asymptotically for $\tau \to +\infty$ and is called unstable if the representative point approaches the singular point asymptotically for $\tau \to -\infty$.
Putting $p=-(a+d)$,

$q=ad-bc$,

the characteristic equation becomes

$$S^2+pS+q=0. \qquad (3.9)$$

Figure 1 shows a graphical description of the various cases, which can occur



The theorem of Liapounoff, mentioned in section 2, states: If the real parts of the roots of the characteristic equation corresponding to the equations (3.5), which are obtained by linearization of the equations (3.3), are different from zero, the linearized equations determine the stability of the non-linear system (3.3). In the case that the roots S_1 and S_2 of the characteristic equation are purely imaginary or zero the coefficient p in equation (3.9) equals zero, while the coefficient q is larger than or equal to zero.
Hence this exceptional case corresponds for the linearized system to a "branch-point" of equilibrium, namely the positive q-axis divides the stable and unstable focal points and one cannot give without further comment a right answer to the question of stability. For literature on this subject the reader is referred to lit.1, 2 and 3.

4. Investigation of the trajectories near the singular points

4.1. The singular point A

The differential equations(1.8) and (1.9) reduce after linearization in the neighbourhood of the origin to the form

$$\frac{dx_1}{d\tau} = -\beta_1 x_1 ,$$
$$\frac{dx_2}{d\tau} = -\beta_2 x_2 . \tag{4.1}$$

Hence in the neighbourhood of the origin the trajectories are given by the equations

$$x_1 = C_1 e^{-\beta_1\tau},$$
$$x_2 = C_2 e^{-\beta_2\tau}, \tag{4.2}$$

or

$$x_2 = C\, x_1^{\frac{\beta_2}{\beta_1}} , \tag{4.3}$$

where C_1 and C_2 are integration constants, varying from trajectory to trajectory and $C=C_1^{-\frac{\beta_2}{\beta_1}} C_2$.
From (4.2) it follows immediately that the origin is a nodal point and when β_1 and β_2 are positive the nodal point is a stable point for the equilibrium of the dynamical system corresponding to the equations (1.8) and (1.9).
When β_1 and β_2 are negative the nodal point is an unstable one. Assuming the parameter α positive the concentrations x_1 and x_2

decrease monotonely to zero for increasing values of the temperature T, when β_1 and β_2 are positive; when β_1 and β_2 are negative the concentrations x_1 and x_2 increase monotonely in the neighbourhood of the origin for increasing values of the temperature.
In the former case the origin is reached for $T=+\infty$ and in the latter case for T=0.
When the parameter α should be negative the direction in which the trajectory is passed along by the representative point (x_1,x_2) for increasing values of the temperature T will be reversed. Since the sign of the parameter α determines only the direction of the trajectory we assume henceforth that α will be positive. When $|\beta_1| < |\beta_2|$ the slope of all trajectories at the origin is zero, when $|\beta_1|>|\beta_2|$ the slope of all trajectories at the origin is infinite. When $\beta_1=\beta_2$ the slope of the trajectories at the origin equals C and it has for various trajectories different values.

4.2. The singular point B

The singular point B has coordinates (1,0).
Putting

$$x_1=1-\xi_1, \quad x_2=\xi_2, \tag{4.4}$$

one obtains after substitution into (1.8) and (1.9) the differential equations:

$$\frac{d\xi_1}{d\tau} = (1-\xi_1)\{\beta_1\xi_1-(\beta_1-1)\xi_2\}, \quad \frac{d\xi_2}{d\tau} = \xi_2\{1-(\beta_2+1)\xi_1+\beta_2\xi_2\}. \tag{4.5}$$

After linearization we get finally:

$$\frac{d\xi_1}{d\tau} = \beta_1\xi_1-(\beta_1-1)\xi_2, \quad \frac{d\xi_2}{d\tau} = \xi_2. \tag{4.6}$$

The characteristic equation becomes:

$$S^2-(\beta_1+1)S+\beta_1 = 0 \tag{4.7}$$

and the roots are $S_1=+1$, $S_2=+\beta_1$.

If β_1 is positive the singular point is an unstable nodal point; this means that the point (x_1,x_2), representative of the concentrations x_1 and x_2, approaches the point (1,0) asymptotically for $T \rightarrow 0$ and that the point (x_1,x_2) goes away from the point (1,0) for increasing values of T.
If β_1 is negative the singular point is a saddle point and hence the singular point is an unstable point.
Solving equations (4.6) we obtain:

$$1-x_1 = C_1 e^{\beta_1 \tau} + C_2 e^{\tau} ,$$
$$x_2 = C_2 e^{\tau} , \tag{4.8}$$

where C_1 and C_2 are integration constants, varying from trajectory to trajectory.
The equation of the trajectories in the neighbourhood of the point (1,0) can also be given by

$$(1-x_1) = C\, x_2^{\beta_1} + x_2 , \tag{4.9}$$

with $C=C_1 . C_2^{-\beta_1}$.
From the equations (4.8) and (4.9) it follows immediately, that the point (1,0) is an unstable nodal point if β_1 is positive (α is assumed positive) and, since $\beta_1 > 1$, the slope of the trajectories at the point (1,0) equals -1.
If, however, β_1 is negative, the point (1,0) is a saddle point and the asymptotic trajectories in the neighbourhood of (1,0) are the lines $x_2=0$ and $x_1+x_2=1$.

4.3. The singular point C

The singular point C has coordinates (0,1).
Putting

$$x_1 = \xi_1,$$
$$x_2 = 1-\xi_2, \tag{4.10}$$

we obtain after linearization:

$$\frac{d\xi_1}{d\tau} = -\xi_1,$$
$$\frac{d\xi_2}{d\tau} = -(\beta_2+1)\xi_1+\beta_2\xi_2 . \tag{4.11}$$

The characteristic equation becomes

$$S^2-(\beta_2-1)S-\beta_2 = 0 \tag{4.12}$$

and the roots are $S_1=-1$ and $S_2=\beta_2$.
If β_2 is positive the singular point is a saddle point and hence it is an unstable point.
If β_2 is negative the singular point is a stable nodal point; this means that the representative point (x_1,x_2) approaches the point (0,1) asymptotically for $T\rightarrow\infty$.
Solving equations (4.11) we obtain for the trajectories in the neighbourhood of the point (0,1) the equations:

$$\begin{aligned} x_1 &= C_1e^{-\tau}, \\ 1-x_2 &= C_2e^{\beta_2\tau}+C_1e^{-\tau}, \end{aligned} \qquad (4.13)$$

where C_1 and C_2 are again the integration constants, varying from trajectory to trajectory.
The equation of the trajectory in the neighbourhood of (0,1) can also be given by the expression:

$$(1-x_2) = C\ x_1^{-\beta_2}+x_1, \qquad (4.14)$$

where $C=C_1^{+\beta_2}.C_2$.
From the equations (4.13) and (4.14) it follows immediately, that the point (0,1) is a saddle point, if β_2 is positive and the asymptotic trajectories are the lines $x_1=0$ and $x_1+x_2=1$.
If, however, β_2 is negative the point (0,1) is a stable nodal point and, since $\beta_2<-1$, the slope of the trajectories at the point (0,1) equals -1.

4.4. The singular point D

The coordinates of the singular point D are $\left(\frac{\beta_2}{\bar{\beta}},-\frac{\beta_1}{\bar{\beta}}\right)$ with $\bar{\beta}=1-\beta_1+\beta_2$.

Since β_1 and β_2 have the same sign the point D lies always outside the triangle ABC and has consequently no physical meaning for the mixture of the three gases.
However, for the construction of the trajectories we can take advantage of the known location of the point D.
The line BD has the equation $\beta_1x_1+(\beta_1-1)x_2-\beta_1=0$ and so $\frac{dx_1}{dx_2}=0$ along BD; the line CD has the equation $(1+\beta_2)x_1+\beta_2x_2-\beta_2=0$ and so $\frac{dx_2}{dx_1}=0$ along CD.
Hence the slopes of all trajectories are infinite when they cross the line BD and they are zero when they cross the line CD.

For the coordinates (x_1,x_2) of the point D, lying in the second or the fourth quadrant of the (x_1,x_2) plane, the relation holds:

$$1 - x_1 - x_2 = \frac{1}{\bar{\beta}} .$$

Hence the point D lies for all values of β_1 and β_2 with $\bar{\beta} > 0$ at the left hand side of the line $x_1+x_2=1$, and for all values of β_1 and β_2 with $\bar{\beta} < 0$ at the right hand side of the line $x_1+x_2=1$. Although the point D has no physical meaning in our problem it may have a meaning for the dynamical system corresponding to the equations (1.8) and (1.9) (then, τ is conceived as a time variable). For the sake of completeness we shall investigate the question of the stability in the point D.

Putting

$$\begin{aligned} x_1 &= \xi_1 + \frac{\beta_2}{\bar{\beta}} , \\ x_2 &= \xi_2 - \frac{\beta_1}{\bar{\beta}} \end{aligned} \qquad (4.15)$$

and substituting this into the equations (1.8) and (1.9) we obtain after linearization:

$$\begin{aligned} \frac{d\xi_1}{d\tau} &= \frac{\beta_2}{\bar{\beta}} \left\{ \beta_1 \xi_1 + (\beta_1 - 1) \xi_2 \right\} , \\ \frac{d\xi_2}{d\tau} &= - \frac{\beta_1}{\bar{\beta}} \left\{ (\beta_2 + 1) \xi_1 + \beta_2 \xi_2 \right\} . \end{aligned} \qquad (4.16)$$

The characteristic equation becomes:

$$S^2 = \frac{\beta_1 \beta_2}{\bar{\beta}}$$

and the roots are

$$S_{1,2} = \pm \sqrt{\frac{\beta_1 \beta_2}{\bar{\beta}}} .$$

When $\bar{\beta}$ is positive, S_1 and S_2 are real and of opposite sign and the point D is a saddle point.

When, however, $\bar{\beta}$ is negative, S_1 and S_2 are purely imaginary and the condition, under which Liapounoffs theorem is valid, is no longer fulfilled.

In this case wecan not make without further comment a statement regarding the stability in the point D. The point D corresponds for the linearized system with a branch-point of equilibrium.

5. Qualitative description of the trajectories in the (x_1,x_2) plane

Since we have investigated the behaviour of the trajectories in the singular points A,B and C we are now able to construct these trajectories for various values of the parameters β_1 and β_2 by aid of the method of isoclines.

In this section we give a sketch of the trajectories in the (x_1,x_2) plane for the various cases, which are possible with respect to the values of the parameters β_1 and β_2.

The figures are not claimed to be accurate from the quantitative point of view, but they give an idea of the qualitative behaviour of the concentrations x_1 and x_2 for varying temperatures.

The parameter α is assumed to be positive and the direction of the curves denotes increasing temperature; if α is negative the direction of the curves has to be reversed.

As $x_1+x_2+x_3=1$, the value of the concentration x_3 equals $\sqrt{2}$ times the distance from the point (x_1,x_2) to the line $x_1+x_2=1$.

I. $\bar{\beta} > 0$

1. $\beta_1 > 0$, $\beta_2 > 0$

a. $\beta_1 > \beta_2$

Point A: Stable nodal point, $\frac{dx_2}{dx_1} = \infty$.

Point B: Unstable nodal point, $\frac{dx_2}{dx_1} = -1$.

Point C: Saddle point. Asympt.traj. $x_1=0$; $x_1+x_2=1$.

Point D: Fourth quadrant, at left hand side of $x_1+x_2=0$.

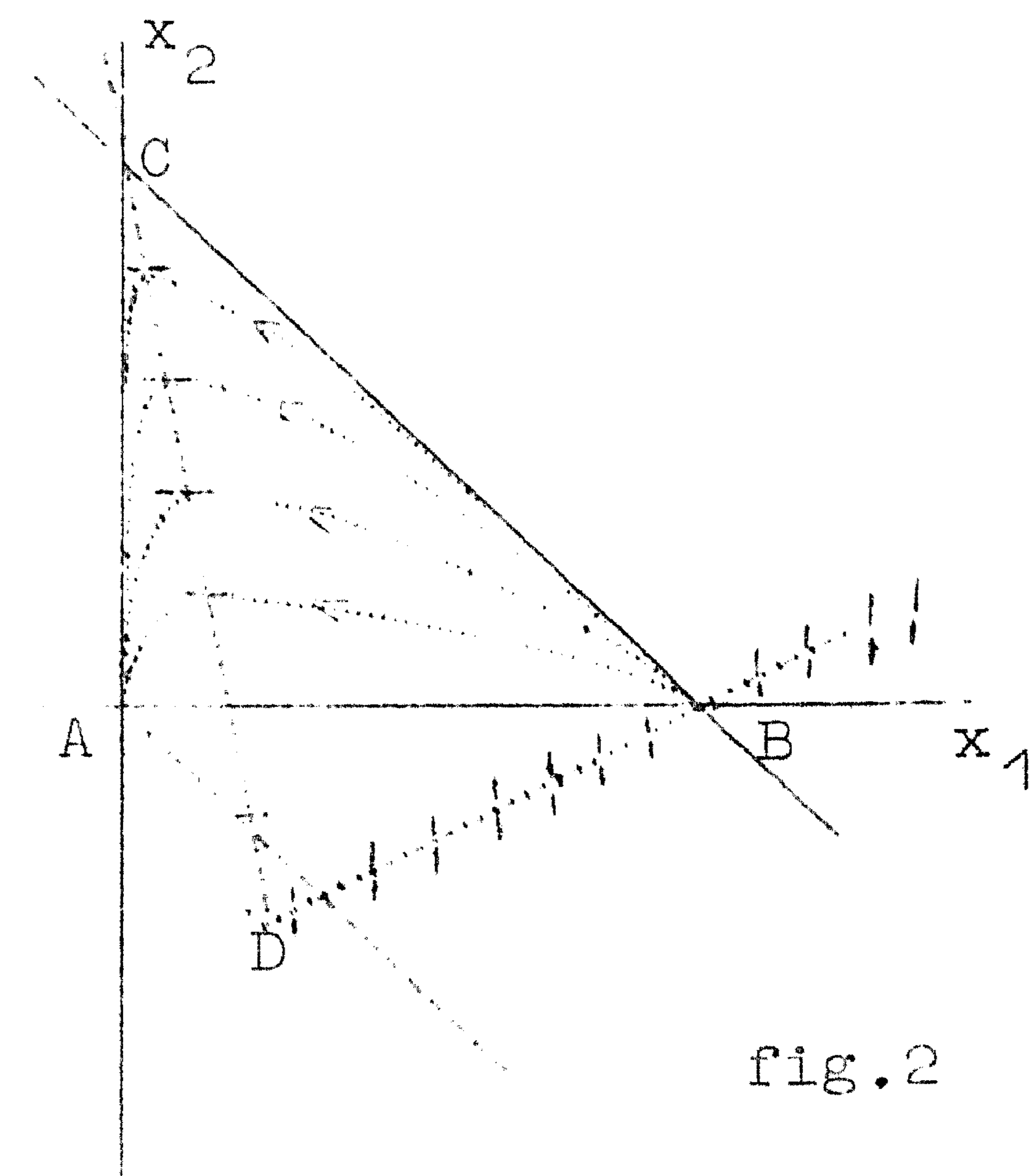


fig.2

b. $\beta_1 < \beta_2$

Point A: Stable nodal point, $\frac{dx_2}{dx_1} = 0$.

Point B: Unstable nodal point, $\frac{dx_2}{dx_1} = -1$.

Point C: Saddle point. Asympt.traj. $x_1=0$; $x_1+x_2=1$.

Point D: Fourth quadrant, at right hand side of $x_1+x_2=0$ and at left hand side of $x_1+x_2=1$.

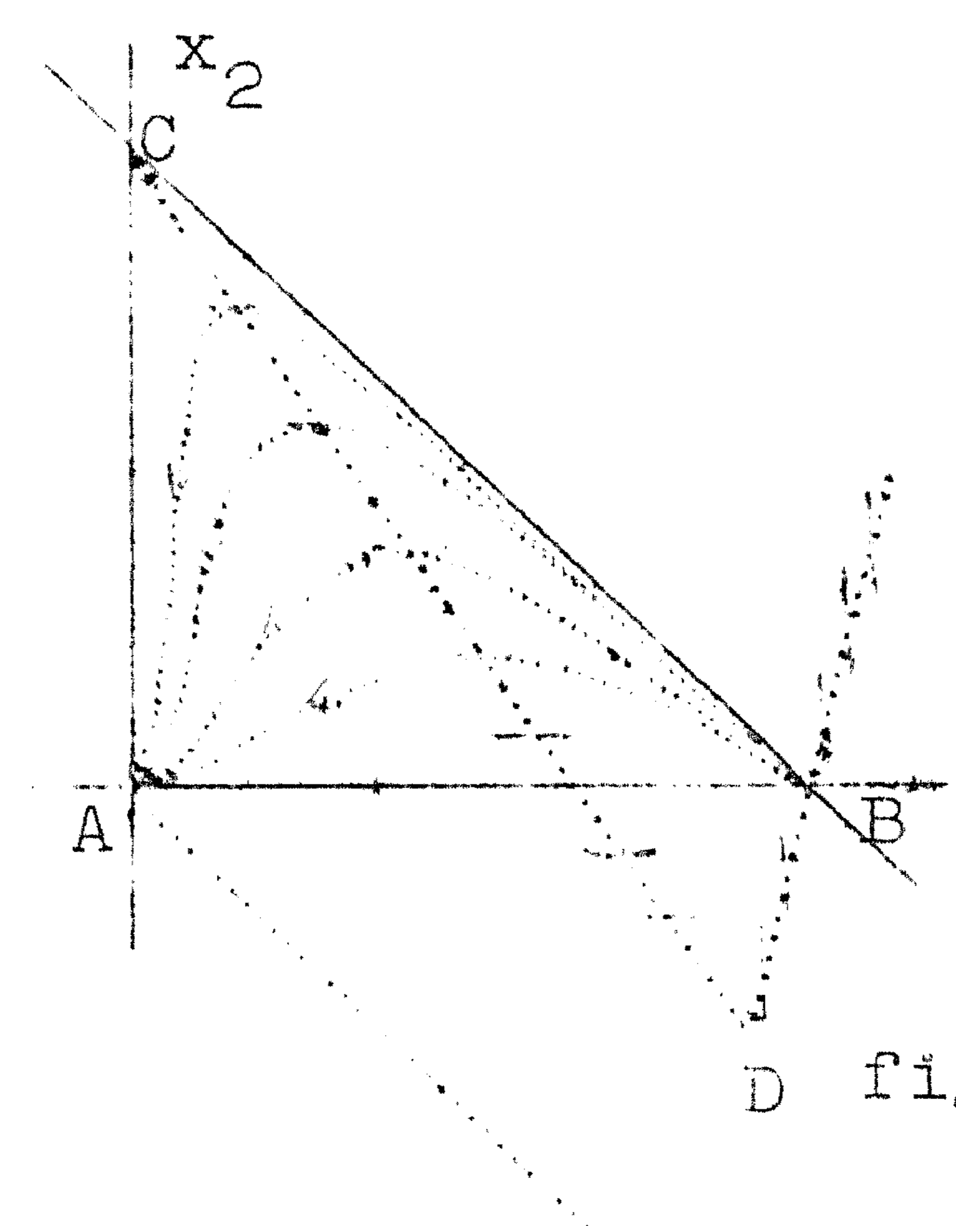


fig.3

2. $\beta_1 < 0$, $\beta_2 < 0$

a. $\beta_1 > \beta_2$

Point A: Unstable nodal point, $\frac{dx_2}{dx_1} = 0$.

Point B: Saddle point. Asympt.traj. $x_2=0$; $x_1+x_2=1$.

Point C: Stable nodal point, $\frac{dx_2}{dx_1} = -1$.

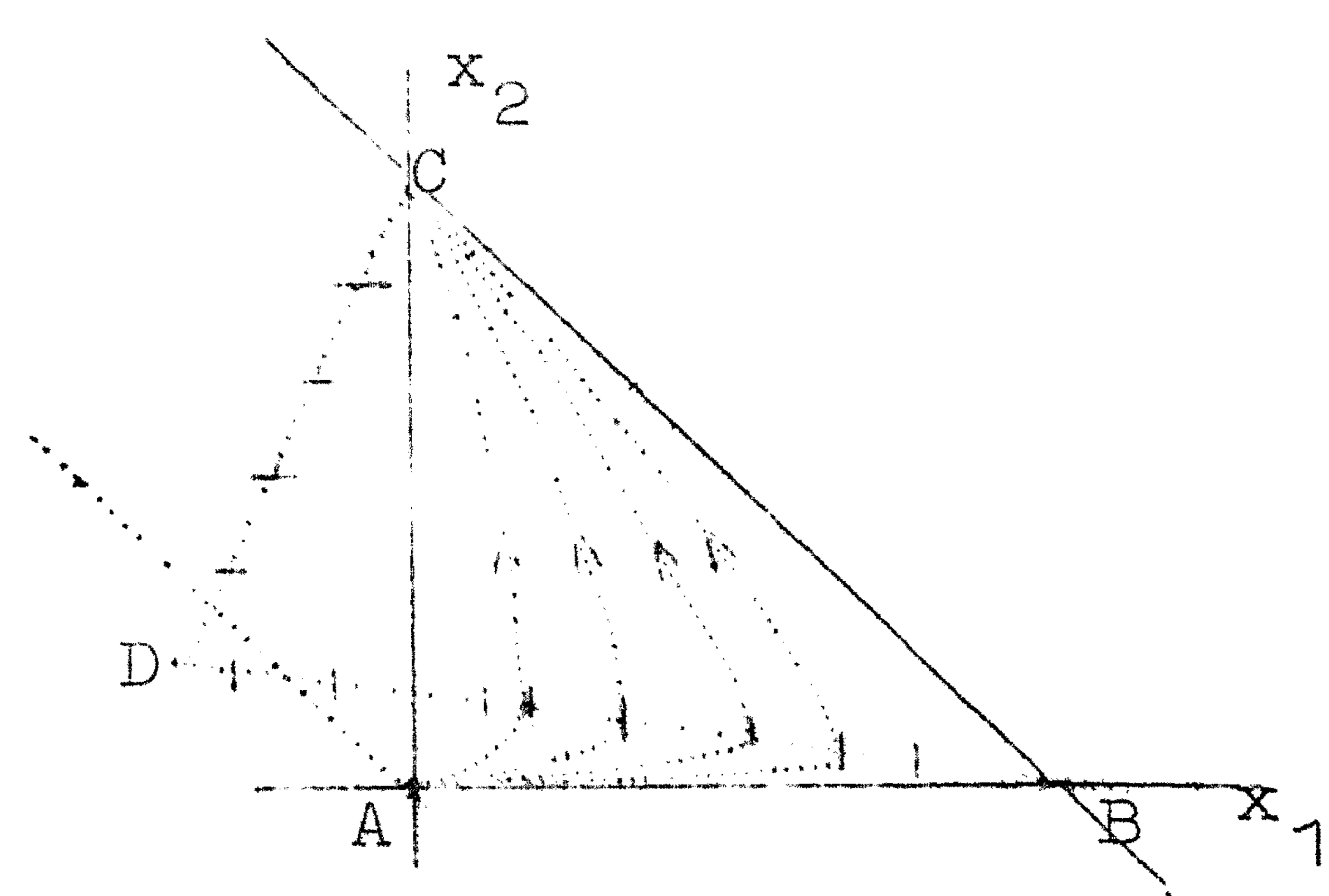


fig.4

Point D: Second quadrant, at left hand side of $x_1+x_2=0$

b. $\beta_1 < \beta_2$

Point A: Unstable nodal point, $\frac{dx_2}{dx_1} = \infty$.

Point B: Saddle point. Asympt.traj. $x_2=0$; $x_1+x_2=1$.

Point C: Stable nodal point, $\frac{dx_2}{dx_1} = -1$.

Point D: Second quadrant, at right hand side of $x_1+x_2=0$ and at left hand side of $x_1+x_2=1$.

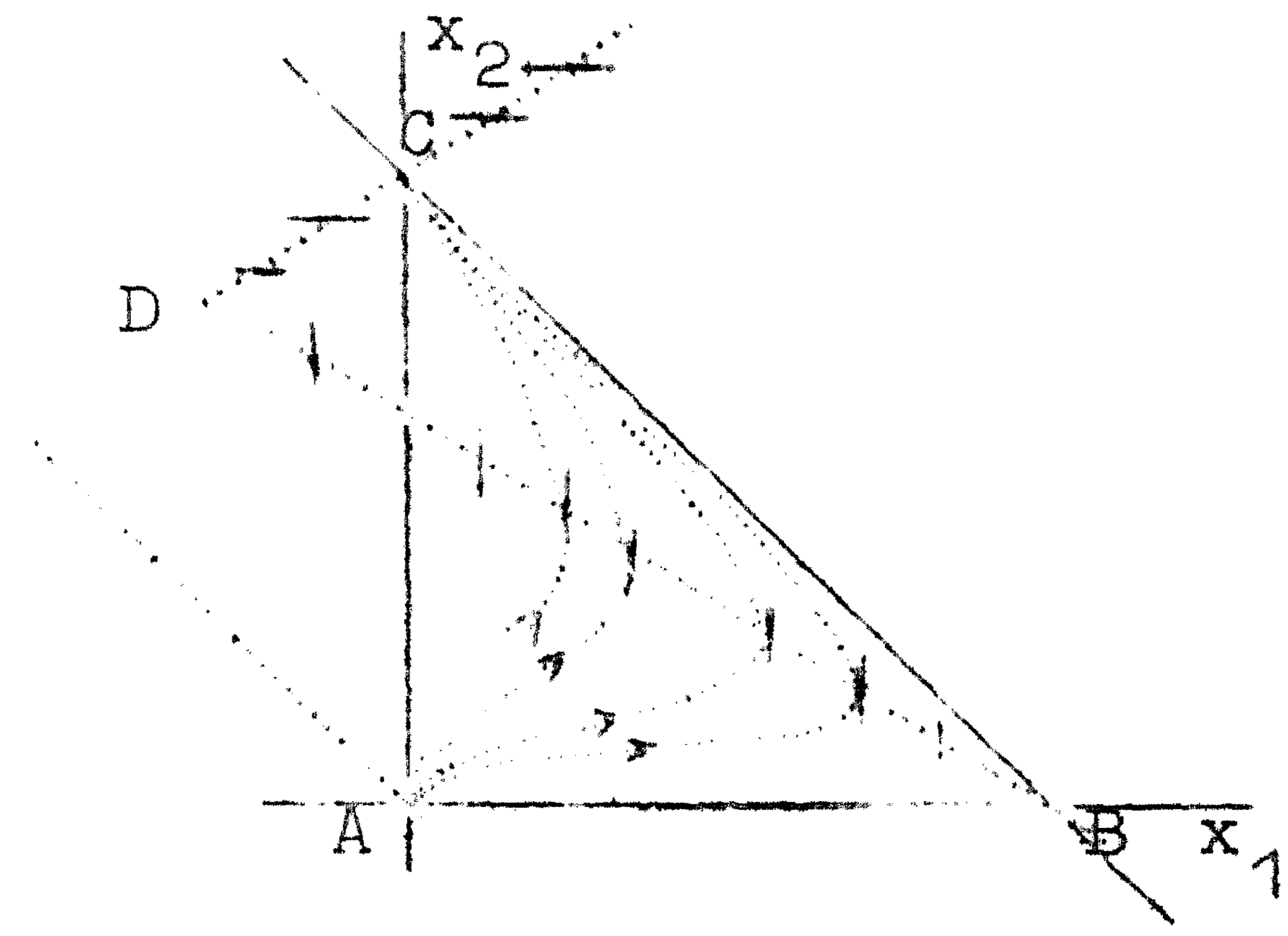


fig.5

II $\bar{\beta} < 0$

1. $\beta_1 > 0$, $\beta_2 > 0$; thus $\beta_1 > \beta_2$

Point A: Stable nodal point, $\frac{dx_2}{dx_1} = \infty$.

Point B: Unstable nodal point, $\frac{dx_2}{dx_1} = -1$.

Point C: Saddle point, Asympt.traj. $x_1=0$; $x_1+x_2=1$.

Point D: Second quadrant, at right hand side of $x_1+x_2=1$.

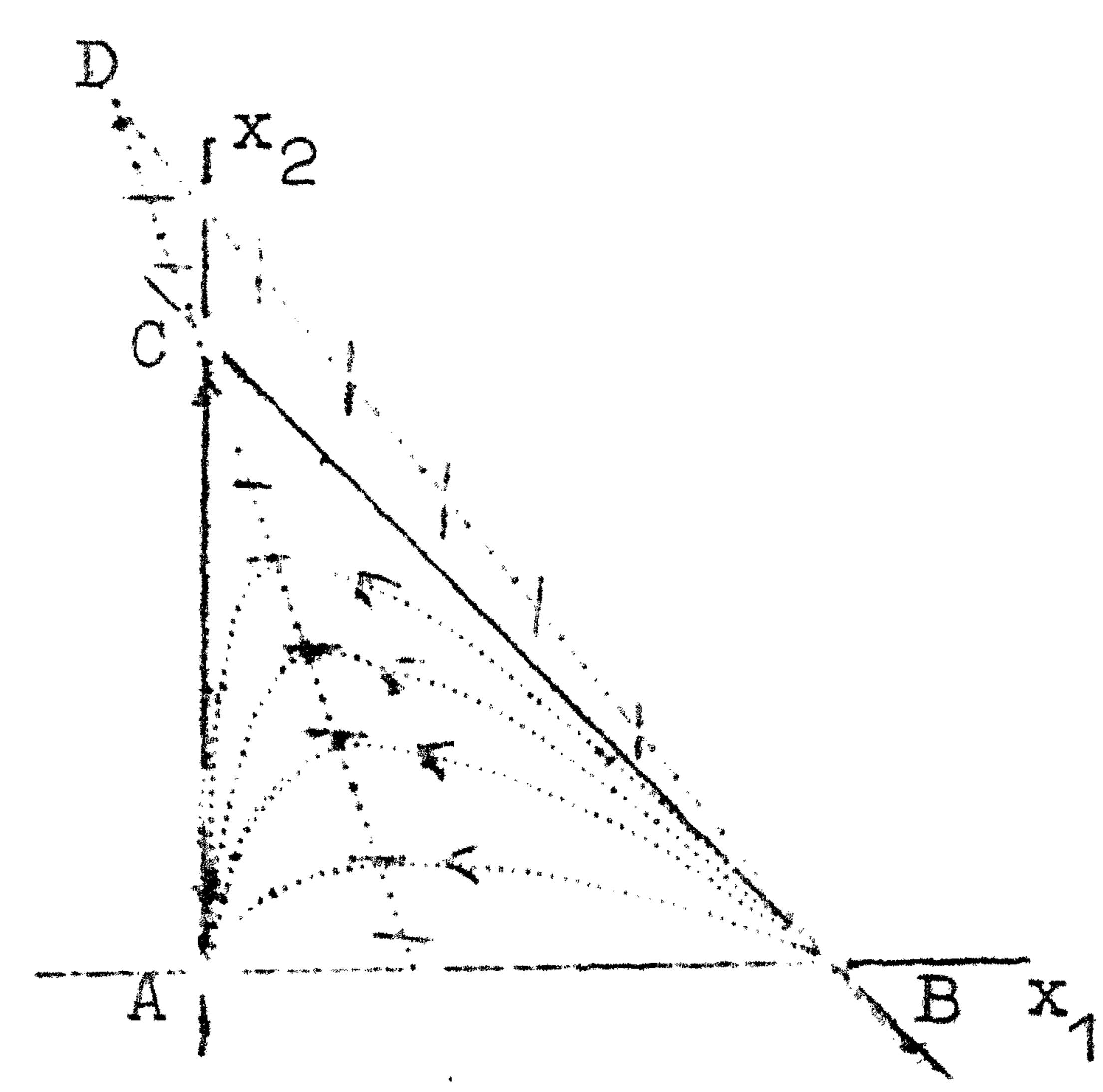


fig.6

2. $\beta_1 < 0$, $\beta_2 < 0$; thus $\beta_1 > \beta_2$

Point A: Unstable nodal point, $\frac{dx_2}{dx_1} = 0$.

Point B: Saddle point, Asympt.traj. $x_2=0$ and $x_1+x_2=1$.

Point C: Stable nodal point, $\frac{dx_2}{dx_1} = -1$.

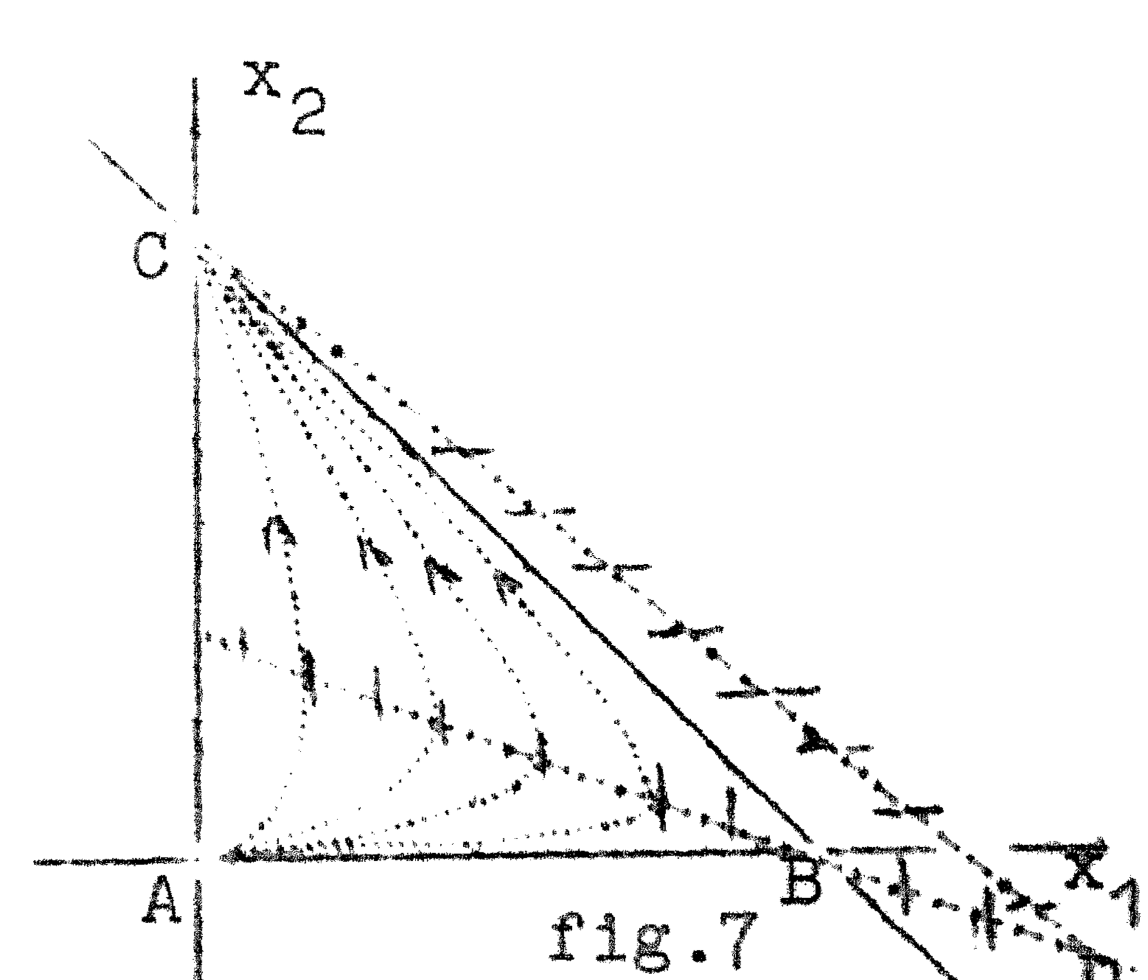


fig.7

Point D: Fourth quadrant, at right hand side of $x_1+x_2=1$.

As to the figures 2,3 and 6 it may be remarked that on the one hand the line segment AB and on the other hand the "curve" consisting of the line segments AC and BC are also trajectories; they are obtained by taking the integration constants equal to zero or infinity.

The same remark can be made "mutatis mutandis" for the figures 4,5 and 7.

It may be mentioned finally that there are some particular cases, where it is possible to integrate the system of equations (1.8) and (1.9) exactly; e.g. when $\beta_1 = \beta_2$ or when $\bar{\beta} = 0$.

5. Literature

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