

# INVESTIGATIONS ON THE STABILITY OF TUBULAR REACTORS\*

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This lecture deals with investigations on the stability (as well as on the dynamics, in simple cases) of tubular reactors which fulfil the conditions.

(1) The reactor is homogeneous, the chemical reaction takes place throughout the entire volume (not only on the wall) of the reactor.

(2) Changes in pressure, temperature and velocity within the reactor are negligibly small.

(3) The diameter of the reactor is negligibly small (thus the parameters are functions of only one of the location coordinates: of the longitudinal one).

(4) The diffusion constant may be regarded as a true constant in the reactor.

## I. Description of the discussed cases

The operation of isothermal continuous tubular reactors are described by a partial differential equation when the inductorily listed conditions are fulfilled:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - f(c) \quad (1)$$

where  $c$  = concentration of the reacting substance,

$t$  = time of reaction,

$D$  = diffusion constant,

$x$  = location coordinate (longitudinal),

$v$  = velocity of flow,

$f(c)$  = rate of reaction

$k$  = rate of reaction coefficient which, according to Arrhenius' law, is related to temperature as follows:

$$k = Ae^{-\frac{\Delta H^x}{RT}} = A \exp[-\Delta H^x/RT] \quad (2)$$

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where  $A$  = action constant,

$\Delta H^\ddagger$  = energy of activation,

$R$  = universal gas constant,

$T$  = absolute temperature.

Investigations are conducted on simple reactions of the first and  $n$ th order, on reactions leading to equilibrium, consecutive reactions, parallel reactions and those of the previous equilibrium, all of these reactions being chain and polymerization reactions. Stability is investigated only for reactions leading to equilibrium, on consecutive reactions and for those of the first and

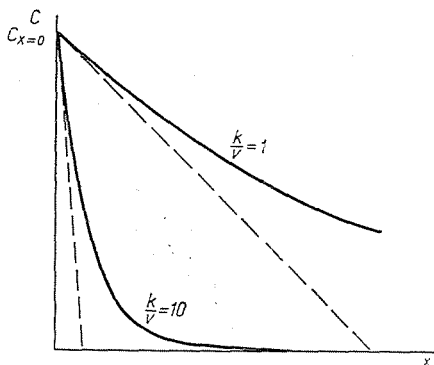


Fig. 1

$n$ th order. A general discussion of chain reactions must be foregone since the individual chain reactions are described by equations of their own on account of the complicated reaction mechanisms. From the chain reactions, only one of the most studied will, therefore, be subjected to investigation although this reaction (the synthesis of water) is of no significance in industry. Similarly as chain reactions, polymerization reactions cannot be investigated either in a general way. Only the radical polymerization of vinyl compounds will be dealt with in consequence. This mechanism is characteristic for such important substances as PVC, polystyrene and (although of different mechanism but of identical type of equation) polyethylene.

The dynamics of the system is also investigated with simple reactions of the first order, whenever the effect of diffusion can be neglected.

## 2. Simple first order reactions

### 2.1. Diffusionless case

In this case, the steady state condition is described by the equation

$$0 = -v \frac{\partial c}{\partial x} - kc. \quad (3)$$

The solution of the equation is

$$c = c_{x=0}(t) \exp \left[ -\frac{k}{v} x \right]. \quad (4)$$

Let the dependence of the steady state condition on location and temperature be investigated, i.e. let it be established whether the diagrams of bifurcation (1) drawn with the two parameters mentioned above possess points of bifurcation.

First, let the dependence on location of the state of equilibrium, described by (4), be investigated.

Since the exponential function is monovalent curves do not possess points of bifurcation.

Investigation of the dependence on temperature of the steady state condition is somewhat more involved, it can be effected by the joint application of (2) and (3). It can be established that the bifurcation diagram possesses no point of bifurcation.

The dynamic system is investigated on the basis of (1)

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} - kc. \quad (4)$$

After subjecting (4) to a Laplace transformation and arranging it, the following inhomogeneous partial differential equation is obtained:

$$\frac{\partial C(s)}{\partial x} = \frac{-(k+s)C(s)}{v} + \frac{c_{t=0}(x)}{v}. \quad (5)$$

The homogeneous equation obtained from (5)

$$\frac{\partial C(s)}{\partial x} = \frac{-(k+s)}{v} C(s)$$

whose the general solution is

$$C_{\text{hom}}(s) = C_{x=0}(s) e^{-\frac{(k+s)}{v} x}.$$

For the investigation of stability, the member causing inhomogeneity (steady state condition) need not be taken into account.

The system subject to investigation thus has dead time and

$$A_h = \exp[-kx/v] = 1$$

$$T_h = x/v,$$

where  $A_h$  is the transfer coefficient,  $T_h$  being the dead time. At point  $x = 0$ , where  $A_h = 1$ ,  $T_h = 0$ ; the system is a proportional element without dead time at this point.

Determining the time function of the dynamic member by an inverted Laplace transformation,

$$L^{-1} [Y/s] = y(t) = \frac{c(t)}{c_{x=0}(t)} = A_h 1(t - T_h) = e^{-\frac{k}{v}t} 1\left(t - \frac{x}{v}\right).$$

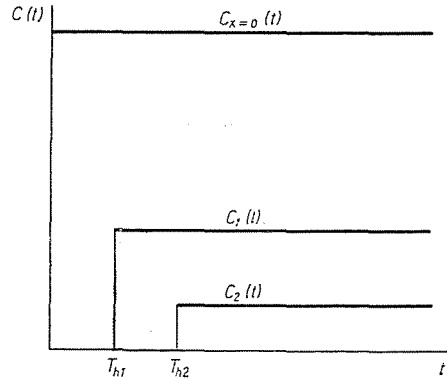


Fig. 2

The time function shown in Fig. 2 is obtained if

$$C_{x=0}(t) = 1(t).$$

### 2.2. General case

The transfer function cannot even be determined by means of the method described in the preceding subparagraph since the shape of the Laplace transform is the following:

$$C_{\text{hom}}(s) = Ae^{-q_1x} + Be^{-q_2x}$$

where

$$A = \frac{\left(\frac{\partial C(s)}{\partial x}\right)_{x=0} + C_{x=0}(s) \left[ \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}} + \frac{v}{2D} \right]}{2 \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}}}$$

$$B = C_{x=0}(s) - \frac{\left(\frac{\partial C(s)}{\partial x}\right)_{x=0} + C_{x=0}(s) \left[ \frac{v}{2D} + \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}} \right]}{2 \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}}}$$

$$q_1 = \frac{v}{2D} - \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}}$$

$$q_2 = \frac{v}{2D} + \sqrt{\left(\frac{v}{2D}\right)^2 - \frac{s+k}{D}}$$

a very complicated expression. Stability must, therefore, be investigated by means of the phase plane methods. This investigation will constitute the investigation on the stability of the state of equilibrium.

Let the state of equilibrium be  $c_e$ . Then, in the vicinity of the state of equilibrium

$$c = c_e + \Delta c.$$

By substituting it into (1)

$$\frac{\partial(c_e + \Delta c)}{\partial t} = -D \frac{\partial^2(c_e + \Delta c)}{\partial x^2} - v \frac{\partial(c_e + \Delta c)}{\partial x} - k(c_e + \Delta c).$$

In the state of equilibrium

$$-D \frac{\partial^2 c_e}{\partial x^2} - v \frac{\partial c_e}{\partial x} - k c_e = \frac{\partial c_e}{\partial t} = 0$$

thus

$$-D \frac{\partial^2(\Delta c)}{\partial x^2} - v \frac{\partial(\Delta c)}{\partial x} - k \Delta c = \frac{\partial(\Delta c)}{\partial t}.$$

Since the signs of every member of the left-hand side are identical, it is sufficient to investigate the sign of a single member to the right and left of the state of equilibrium (along axis  $c$ ).

Next, let the third member be investigated. Since  $c, k$  are always positive and at the left-hand side of the state of equilibrium

$$\Delta c < 0$$

whereas at the right-hand side

$$\Delta c > 0$$

therefore, at the left-hand side of the state of equilibrium

$$-k \Delta c > 0$$

and at the right-hand side

$$-k \Delta c < 0$$

therefore, according to Ljapunov's criterion, the system is stable [1].

### 3. Investigation of the stability in the case of complex reactions

#### 3.1. Simple reaction of the $n$ th order

Since the sign of the first partial derivative with respect to concentration of the rate of reaction

$$\frac{\partial f}{\partial c} = nk c_e^{(n-1)}$$

does not differ from that of the first partial differential quotient according to concentration of the rate of reaction of a simple reaction of the first order, the investigation and its result are indetical.

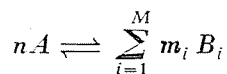
#### 3.2. Reactions leading to equilibrium

##### 3.2.1. Both reactions are of the first order

This case can be reduced to the one discussed under the caption of simple reaction of the first order by means of a simple coordinate transformation.

##### 3.2.2. Reaction not being of the first order

Let the stoichiometric equation be



and let  $n > 1$ .

Denoting the concentration of the raw material by  $c$  and the rate constant of the so-called lead reaction by  $k$ , the concentration of equilibrium

$$f(c) = k [c^n - (c^0)^n].$$

##### 3.2.2.1. Steady state condition. Let

$$k(c^0)^n \equiv a$$

thus

$$\frac{\partial c}{\partial x} = -\frac{k}{v} c^n + \frac{a}{v}. \quad (6)$$

The system bifurcates at the point where the value of the differential quotient becomes infinite or where the differential quotient of the inverted function is zero.

(6) does not become infinite when  $c$  is finite. Whether  $c$  can become infinite when  $x$  is finite and positive must be subjected to investigation. This investigation can be performed by means of a minorating and of a majorating function. Let  $c_{x=0} = C_{1,x=0}$  and

$$\frac{dC_1}{dx} = -\frac{k}{v} C_1^n \quad (7)$$

(7) minorates (6).

From (7)

$$C_1 = \sqrt[n-1]{\frac{1}{(1-n) \left[ \frac{1}{1-n} \frac{1}{c_{x=0}(n-1)} - \frac{k}{v} x \right]}}$$

which is finite in the investigated domain because the denominator is zero at the value

$$x = \frac{v}{k} \frac{1}{C_{x=0}(n-1)} \frac{1}{1-n} < 0.$$

Let  $c_{x=0} = C_{2,x=0}$  and

$$\frac{dC_2}{dx} = \frac{k}{v} (c^0)^n \quad (8)$$

(8) majorates (6).

From (8)

$$C_2 = \frac{k}{v} (c^0)^n x$$

which is finite as well.

Since both the minorating and the majorating functions remain finite, so does (6). Therefore there is no point of bifurcation.

*3.2.2.2. Effect of the temperature.* Since the rate constant remains finite in the case of finite temperature, (6) will not become infinite, as a consequence, even if the temperature is changed.

*3.2.2.3. Investigation on dynamics.* The investigation thus resembles the one performed with reactions of the  $n$ th order since the member (a) causing inhomogeneity fails when differences are examined.

### 3.3. Consecutive reactions

The first reaction is not affected by the subsequent ones, therefore, the investigation of stability does not differ from that of simple reactions.

### 3.4. Reactions in parallel

When investigation is performed by the method described in paragraph (3.2.2), parallel reactions will also be found to be stable.

## 3.5. Chain reactions

From among chain reactions, only that of oxyhydrogen gas will be treated. This is due to the following cause: Chain reactions cannot be investigated, in general, since

- (1) the mechanism of most chain reactions is unclarified,
- (2) chain and simple mechanisms occur jointly in many cases,
- (3) the chain reactions of known mechanism are described by differential equations of various types,
- (4) changes in the parameters often change the form of the differential equation defining the reaction.

It must be noted, however, that other chain reactions can be investigated by a similar method if the mechanism of the reaction is known (as in the present case).

In the synthesis of water [2]

$$f(c_{\text{H}_2\text{O}}) = \frac{k_0 c_{\text{H}_2} c_M \left( \frac{1 \cdot 5 k_7 + 2 k_5 c_{\text{H}_2}}{k_7 + k_5 c_{\text{H}_2}} \right)}{1 - 2 \frac{k_3}{\Sigma k_1 c_M} - \frac{k_5 c_{\text{H}_2}}{k_7 + k_5 c_{\text{H}_2}}}$$

and

$$c_{0,\text{H}_2} - c_{\text{H}_2} = c_{\text{H}_2\text{O}} - c_{0,\text{H}_2\text{O}}$$

that is

$$f(c_{\text{H}_2\text{O}}) = \frac{dc_{\text{H}_2\text{O}}}{dt} = - \frac{dc_{\text{H}_2}}{dt} \equiv \frac{dc}{dt} = -f(c).$$

When substituting it into (1)

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} - \frac{k_0 c_M c \left( \frac{1 \cdot 5 k_7 + 2 k_5 c}{k_7 + k_5 c} \right)}{1 - 2 \frac{k_3}{\Sigma k_1 c_M} - \frac{k_5 c}{k_7 + k_5 c}}. \quad (9)$$

Henceforth, the concentration of substance  $M$  used for the stabilization of  $\text{H}_2\text{O}$  is assumed to be constant.

## 3.5.1. Steady state condition

From (9) in the steady state condition

$$\frac{\partial c}{\partial x} = - \frac{1}{v} \frac{k_0 c_M c \left( \frac{1 \cdot 5 k_7 + 2 k_5 c}{k_7 + k_5 c} \right)}{1 - 2 \frac{k_3}{\Sigma k_1 c_M} - \frac{k_5 c}{k_7 + k_5 c}}.$$



After arrangement and integration by the method of partial fractions, then arranging again and taking the initial conditions into account,

$$x = \frac{v}{3 k_0 C_M} \left[ 2 \ln \frac{c_{x=0}(3 k_7 + 4 k_5 c)}{c(3 k_7 + 4 k_5 c_{x=0})} + \frac{k_3}{\Sigma k_1 c_M} \ln \frac{c^4(3 k_7 + 4 k_5 c_{x=0})}{c_{x=0}^4(3 k_7 + 4 k_5 c)} \right]. \quad (10)$$

The system possesses a point of bifurcation where the denominator of (10) is zero.

Thus

$$c_b = \frac{k_7}{k_5} \frac{1 - 2 \frac{k_3}{\Sigma k_1 c_M}}{2 \frac{k_3}{\Sigma k_1 c_M}}$$

$c_b$  is the concentration at the point of bifurcation.

### 3.5.2. Investigation on dynamics

The stability of the system is investigated (on the diagram of bifurcation) by Poincaré's method (1)

Let

$$\frac{\partial c}{\partial t} \equiv F(c, x)$$

exist.

Let us examine what is this positive and negative function.

Let

$$F(c, X) \equiv v \frac{\partial c}{\partial x} - f_e(c)$$

where

$$f_e(c) \equiv \frac{k_0 c_M(1.5 k_7 + 2 k_5 c)}{k_7 \left( 1 - 2 \frac{k_3}{\Sigma k_1 c_M} \right) - 2 \frac{k_3}{\Sigma k_1 c_M} k_5 c}$$

from which

$$\frac{\partial c}{\partial x} > - \frac{f_e(c)}{v}.$$

If

(1)

$$\frac{c(1.5 k_7 + 2 k_5 c)}{k_7 \left( 1 - 2 \frac{k_3}{\Sigma k_1 c_M} \right) - 2 \frac{k_3}{\Sigma k_1 c_M} k_5 c} > 0$$

and

(a) there are two points of bifurcation

$$\left(\frac{1}{2} > \frac{k_3}{\Sigma k_1 c_M}\right)$$

then

$$0 < c < \frac{k_7}{k_5} \frac{1 - 2 \frac{k_3}{\Sigma k_1 c_M}}{2 \frac{k_3}{\Sigma k_1 c_M}} = c_b$$

( $c_b$ ) denotes the value corresponding to the bifurcation lying in the finite.

(b) there is one point of bifurcation, then

$$c > c_b > 0.$$

The solution of the inequality, in both cases (after arrangement, integration rearrangement and substitution of the initial values)

$$x > \frac{v}{3 k_0 c_M} \left[ 2 \ln \frac{c_{x=0}(3 k_7 + 4 k_5 c)}{c(3 k_7 + 4 k_5 c_{x=0})} + \frac{k_3}{\Sigma k_1 c_M} \ln \frac{c^4(3 k_7 + 4 k_5 c_{x=0})}{c^4_{x=0}(3 k_7 + 4 k_5 c)} \right] = g(c) \quad (2)$$

$$\frac{c(1.5 k_7 + 2 k_5 c)}{k_7 \left(1 - 2 \frac{k_3}{\Sigma k_1 c_M}\right) - 2 \frac{k_3}{\Sigma k_1 c_M}} < 0$$

and

(a) there are two points of bifurcation, then

$$c > c_b$$

(b) there is one point of bifurcation

$$c < c_b < 0$$

which is impossible.

In the two cases above

$$x < g(c).$$

At the point subject to investigation, let

$$x = x_e$$

(the lower-case character referring to the steady state condition).

Then

$$\Delta x = x - x_e = 0 \cong g(c) - g(c_e).$$

(The direction of the inequality is the upper one when the first condition is fulfilled.)

From among the solutions figuring in paragraph (3.5.1), the stability of only two shall be investigated on account of the great number of solutions. (It must be noted that the same method can be applied to the other solutions as well.) The following solutions are to be studied:

(with the assumption of  $c_{e,x=0} = c_{x=0}$  in every case)

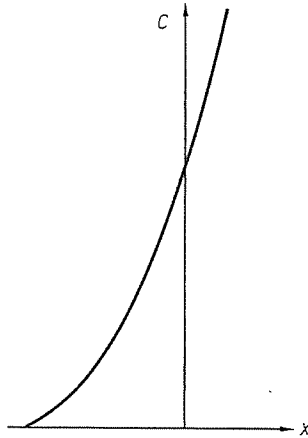


Fig. 3

3.5.2.1. A single point of bifurcation (Fig. 3). Conditions:

$$c_b > c_{x=0},$$

$$k_7 \cong \frac{4}{3} k_5 c_b,$$

$$k_7 \cong \frac{4}{3} k_5 c.$$

That is, the chain-closing reaction is always much faster than the chain-carrier reaction.

Thus

$$\Delta x = 0 > \frac{2v}{3k_0 c_M} \left( 1 - 2 \frac{k_3}{\sum k_1 c_M} \right) \ln \frac{c_e}{c}$$

that is,

$$c_e > c$$

when

$$F(c, x) > 0$$

which indicates that the system is *stable*.

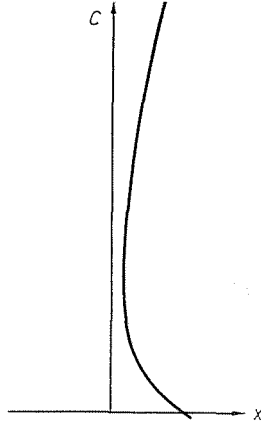


Fig. 4

3.5.2.2. *Two points of bifurcation* (Fig. 4). Conditions:

$$c_b > c_{x=0},$$

$$k_7 \ll \frac{4}{3} k_5 c_b,$$

$$k_7 \ll \frac{4}{3} k_5 c,$$

$$k_7 \ll \frac{4}{3} k_5 c_{x=0}$$

and, at first,  $c_b > c$  while, later,  $c_b < c$ . This indicates that the chain-carrier reaction is much faster than the chain-closure reaction.

Thus

$$\Delta x = 0 > \frac{v}{k_0 c_M} \left( \ln \frac{c_b}{c} \right) \frac{k_3}{\Sigma k_1 c_M}$$

therefore,

$$\frac{c_b}{c} < 1$$

that is

$$c_b < c$$

when  $F|c, x| > 0$

which means that it is unstable after the point of bifurcation, but that it is stable before the point of bifurcation ( $c_b > c$ ). When the system possesses a single point of bifurcation, then it is stable, when it has two points of bifurcation, then it is stable when  $c < c_b$ , and unstable when  $c > c_b$ . The first half of the reactor is definitely stable for, if  $x = 0$ , then  $c = c_{x=0}$ , and, in the case under investigation,  $c_{x=0} < c_b$ .

### 3.5.3. Effect of pressure on the stability of the system

Several of the partial reactions involve changes in mole number wherefore the rates of these partial reactions depend on the pressure.

The values of  $k_7$  and  $\frac{k_3}{\sum k_1 c_M}$  increase significantly by the effect of pressure drop wherefore  $c_b$  turns negative below a certain pressure. When pressure is increased, the values of  $\frac{k_3}{\sum k_1 c_M}$  and  $k_7$  diminish. First,  $k_7$  turns zero ( $c_b = 0$ ), then  $\frac{k_3}{\sum k_1 c_M}$  as well ( $c_b$  is not interpreted in this instance). The latter value

probably lies beyond the domain of interpretation of the initial differential equation. (It was not possible to find the third limit of pressure on account of the limited domain of validity of the initial differential equation.) (Results conform to that obtained by HINSHELWOOD [2] who used other means.)

### 3.5.4. Effect of temperature on stability

The third reaction demands a high activation energy, the first reaction considerably increasing the value of  $\frac{k_3}{\sum k_1 c_M}$ . Thus  $c_b < 0$  over a certain tem-

perature which indicates that the system definitely becomes stable by the effect of increased temperature. (This result conforms to the one obtained by Semenov [2] who used other means.)

## 3.6. Polymerization

A general investigation of polymerization entails even greater difficulties than that of chain reactions since numerous and multifarious side-reactions (chain transfer, retardation, copolymerization etc.) are liable to occur, for which reason only a single type of polymerization will be dealt with in the following, the initiation polymerization of vinyl compounds.

According to the mechanism established by MATHESON [2] (the key of the following notations is also found in [2]):

$$f(c_M) = \frac{k_2}{\sqrt{k_3}} c_I^{(1/2)} c_M \left( \frac{\frac{k_1 k_I}{k_r} c_M}{1 + \frac{k_I}{k_r} c_M} \right)^{1/2} \equiv f_p(c). \quad (11)$$

Henceforth, let  $c_I$  be constant.

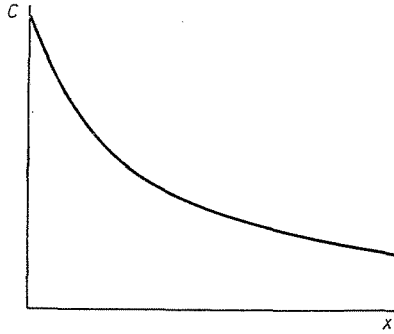


Fig. 5

On the basis of (1) and (11)

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} - f_p(c)$$

where

$$c = c_M.$$

### 3.6.1. Steady state condition

Let

$$a \equiv \frac{k_2}{\sqrt{k_3}} c_I^{1/2}$$

$$b \equiv \left( \frac{k_1 k_I}{k_r} \right)^{0.5}$$

$$d \equiv \frac{k_I}{k_r}.$$

Therefore (Fig. 5)

$$\frac{\partial c}{\partial x} = -\frac{ab}{v} \sqrt{\frac{c^3}{1 + dc}}. \quad (12)$$

The system possesses a point of bifurcation where (1)  $1 + dc = 0$ .

(The pertaining  $c$  is negative since  $d > 0$ , which is impossible.)

$$(2) \quad (a;b) \rightarrow \infty \\ (a) \quad a \rightarrow \infty$$

if

$$(A)$$

$$\frac{k_2}{\sqrt{k_3}} \rightarrow \infty$$

(i.e. chain increase becomes infinite in reference to chain closure)

$$(B) \quad c_I \rightarrow \infty \text{ (an impossibility)}$$

$$(b) \quad b \rightarrow \infty$$

if

$$\frac{k_1 k_I}{k_r} \rightarrow \infty .$$

Therefore

$$(A)$$

$$\frac{k_1}{k_r} \rightarrow \infty$$

(indicating the total dissociation of the initiator)

$$(B)$$

$$\frac{k_I}{k_r} \rightarrow \infty$$

(indicating that from among the possible reactions of the dissociated initiator — recombination or initiation — only the latter can occur).

(3)

$$c \rightarrow \infty .$$

In the first two cases, the solution does not depend on  $c$  but only on temperature and, sometimes, on pressure (however, these functions are generally unknown wherefore dependence on pressure and temperature will not be dealt with).

For investigating the third case, let us solve (12). After arrangement of (12), integrating it, rearranging it and taking the initial conditions into account,

$$x = \frac{v}{ab} \left\{ 2 [\sqrt{d + (1/c)} - \sqrt{d + (1/c_{x=0})}] + \right. \\ \left. + \ln \frac{[\sqrt{d + (1/c)} - \sqrt{d}] [\sqrt{d + (1/c_{x=0})} + \sqrt{d}]}{[\sqrt{d + (1/c_{x=0})} - \sqrt{d}] [\sqrt{d + (1/c)} + \sqrt{d}]} \right\} = g(c) \quad (13)$$

is obtained. Based on (13)

$$\lim_{c \rightarrow \infty} x \rightarrow \infty.$$

In the second case

$$\lim_{(a; b) \rightarrow \infty} x = 0.$$

Summarization: *The system always possesses one point of bifurcation pertaining to which either  $c_b \rightarrow \infty$  or  $0 < c_b < \infty$ .*

(3.6.2) *Investigation on dynamics*

Let

$$F(c; x) = -v \frac{\partial c}{\partial x} - ac \left( \frac{bc}{1 + dc} \right)^{1/2} > 0$$

then

$$\frac{\partial c}{\partial x} > -\frac{ab}{v} \sqrt{\frac{c^3}{1 + dc}} = h(c).$$

When

$$(1) \quad h(c) > 0$$

that is

$$(a) \quad (a; b) > 0$$

$$(b) \quad (a; b) < 0 \text{ (impossible)}$$

(There is no other case since the quantity under the root sign is always positive)

then  $x < g(c)$

$$(2) \quad h(c) < 0$$

that is

either  $a$  or  $b$  is negative (which is impossible)

Let

$$c_{e; x=0} = c_{x=0}.$$

Then

$$\Delta x \equiv x - x_e = 0 < \frac{v}{ab} \left\{ 2 \left[ \sqrt{\bar{d} + (1/c)} - \sqrt{\bar{d} + (1/c_e)} \right] + \right. \\ \left. + \ln \frac{[\sqrt{\bar{d} + (1/c)} - \sqrt{\bar{d}}][\sqrt{\bar{d} + (1/c_e)} + \sqrt{\bar{d}}]}{[\sqrt{\bar{d} + (1/c_e)} - \sqrt{\bar{d}}][\sqrt{\bar{d} + (1/c)} + \sqrt{\bar{d}}]} \right\}.$$

When

$$1/c > 1/c_e$$

then the first member is positive and the second one is also since if

$$y = a \frac{x - b}{x + b}$$



where

$$a \equiv \frac{\sqrt{\bar{d} + (1/c_e)} + \sqrt{\bar{d}}}{\sqrt{\bar{d} + (1/c_e)} - \sqrt{\bar{d}}}$$

$$b \equiv \sqrt{\bar{d}}$$

$$x \equiv \sqrt{\bar{d} + (1/c)}$$

and, if  $x$  increases then  $y$  does so as well (Fig. 6).

Then

$$F(c; x) > 0$$

when

$$c < b_b$$

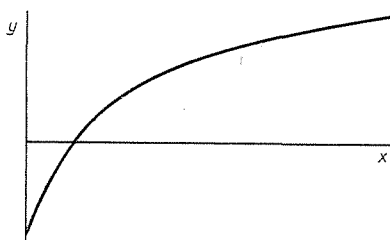


Fig. 6

which means that it is stable. (The stability of the system cannot be determined by this method when  $0 \leq c_b < \infty$  since every point may constitute a point of bifurcation.)

Summing up: Except for special cases, the polymerization reaction is stable.

#### 4. Appendix

##### 4.1. The effect of the parameters on the stability of the system

If the system is described by the following equation:

$$\frac{dx}{dt} = f(x; \lambda)$$

and  $f(x; \lambda)$  is an analytic function of  $x$  and  $\lambda$ , and if

$$\begin{aligned} x &= x_e \\ f(x; \lambda) &= 0 \end{aligned} \tag{14}$$

then, solving eq. (14) for  $x_e$  on the basis of this solution the effect of the parameter on the state of equilibrium can be examined. Fig. 7 shows the so-called diagram of bifurcation [1].

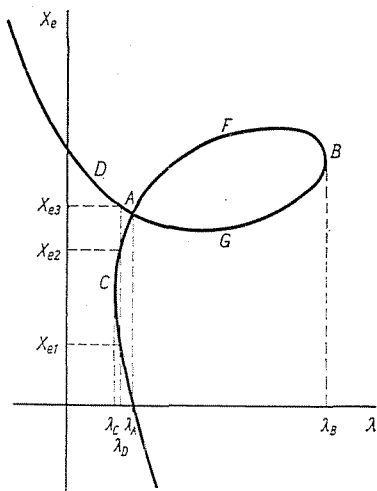


Fig. 7

The curve is intersected by the straight line  $\lambda = \lambda_0$  at three points, thus the three points of equilibrium belong to one single  $\lambda$ . In point  $\lambda_c$   $x_{e1}$  and  $x_{e2}$  coincide, therefore in the cases where  $\lambda < \lambda_c$  only one state of equilibrium can exist, thus the point  $\lambda = \lambda_c$  is a bifurcational value.  $\lambda_A$  and  $\lambda_B$  are similarly bifurcational values.

Differentiating Eq. 14 by  $\lambda$ :

$$\frac{df}{dx_e} \cdot \frac{dx_e}{d\lambda} + \frac{df}{d\lambda} = 0$$

or

$$dx_e/d\lambda = - \frac{f'_\lambda(x_e; \lambda)}{f'_x(x_e; \lambda)}. \quad (15)$$

If in the environment of the point

$$f'_x(x_e; \lambda) \neq 0$$

then the function can be differentiated. If the simultaneous equations

$$\text{and } \left. \begin{aligned} f(x_e; \lambda) &= 0 \\ f'_x(x_e; \lambda) &= 0 \end{aligned} \right\} \quad (16)$$

have no real roots, then the point is not bifurcational.

If Eq. 16 is fulfilled and in these points the simultaneous equations have two, coincidental real roots, consequently where the tangent of the curve is perpendicular, then the system has a bifurcational point. (The case, when

$$f''_{x\lambda}(x_e; \lambda) = 0$$

is not examined now.)

The stability of the singular point  $x = x_e$  is determined by the sign of  $f'_x(x_e; \lambda)$ . The singular point is stabil, if

$$f'_x(x_e; \lambda) < 0.$$

Thus the stability test of the system can be done with the help of the bifurcational diagram. This is done with the method of Poincaré by the following way:

1. First the area

$$f(x; \lambda) > 0$$

is marked on the bifurcational diagram.

2. Now that portion of the bifurcational curve is marked, by which this area is surrounded from below, this is instabil, that from above is stabil. (Above and below means higher and lower values of  $x$ .)

3. The limiting points of the portions are stated, these are bifurcational points.

4. Those points are picked out, that lay between bifurcational points on the straight line

$$f(x_e; \lambda) = 0.$$

5. It must be stated, whether the area  $f(x; \lambda) > 0$  is directly above or below them. (This result is the generalization of Ljapunov's stability-criterion for parametric systems.)

Examine now the hatched area of Fig. 8. Above this area the points show equilibrium states, as here

$$f'_x(x_e; \lambda) < 0.$$

Thus the portion  $\overline{DAFB; CE}$  marked with a heavy line, belongs to stabil points, and portion  $\overline{CAGB}$  to instabil ones. The system is either stabil or instabil between two bifurcational points, the stability of the system changes at the bifurcational points (e.g.  $A, B, C$ ). The number of the states of equilibrium changes in the bifurcational points, generally, by even numbers.

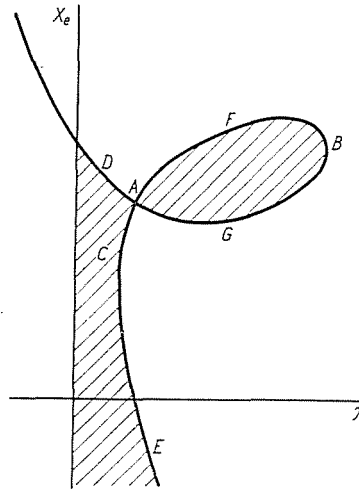


Fig. 3

#### 4.2. Condition of the existence of the bifurcational point

Seeking the place of the bifurcational point. It had been stated when examining the bifurcational diagram, that if the differential equation describing the system is

$$\frac{dx}{dt} = f(x; \lambda)$$

then the derivative

$$\frac{dx}{d\lambda} = - \frac{df/d\lambda}{df/dx}$$

having been deduced by differentiating by  $\lambda$  and arranging the equation

$$f(x; \lambda) = 0$$

becomes infinite or indefinit (zero per zero expression) in the bifurcational points.

The place of the bifurcational points can also by other methods be evaluated.

Derivating by  $x$  and arranging the equation

$$f(x; \lambda) = 0$$

results

$$\frac{df}{dx} = \frac{df}{d\lambda} \cdot \frac{d\lambda}{dx}.$$

The bifurcational point will be that point, where the equation becomes zero or indefinit (zero times infinite). The advantage of this latter method is, that it agrees with the well-known function-test method of extreme-value examination.

By simultaneous utilization of these two methods in many cases the  $x$ ;  $\lambda$  coordinates of the bifurcational point may be determined. It is an interesting case if the two derivatives are not different ones (See Fig. 9). In this case the two methods result in the same equation. Let this result be

$$x = f(\lambda).$$

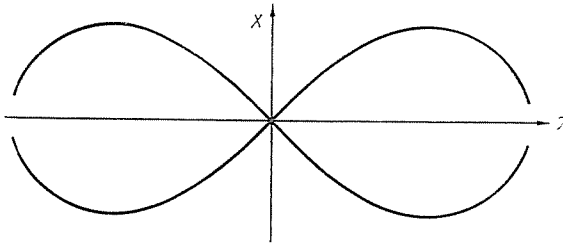


Fig. 9

The other coordinate can now be determined by calculating the inverse function

$$\lambda = g(x)$$

and by simultaneously solving the two equations.

The method, described in this chapter can be used in case of more parameters as well, this is not examined here.

#### 4.3. Satisfactory condition for the non-existing of the bifurcational point

The method is the limit-determination, widely used in mathematics.

Let the examined equation be:

$$f(x; \lambda) = 0$$

and its tangent:

$$\frac{dx}{d\lambda} = g(x; \lambda)$$

then the satisfactory condition for the non-existence of the bifurcational point is the following:

If there is existing at least one such

$$F_1(x; \lambda) = 0$$

equation, for which it is true, that

$$f(x; 0) = F_1(x; 0)$$

and its tangent is

$$\frac{dx}{d\lambda} = G_1(x; \lambda)$$

and it is true, that

$$G_1(x; \lambda) > g(x; \lambda)$$

and there is existing at least one such

$$F_2(x; \lambda) = 0$$

equation, for which it is true, that

$$f(x; 0) = F_2(x; 0)$$

and it is true for its

$$\frac{dx}{d\lambda} = G_2(x; \lambda)$$

tangent, that

$$G_2(x; \lambda) < g(x; \lambda)$$

and the curves belonging to equations

$$F_1(x; \lambda) = 0$$

and

$$F_2(x; \lambda) = 0$$

have no bifurcational point, than the curve, belonging to the treated equation has also none.

In many cases this method gives simple examination process for treating equations which are difficultly treatable and of a complicated form.

#### 4.4. Stability tests with limiting functions

If the system has no bifurcational point, then, according to 4.3 it is satisfactory for determining the stable or unstable state of the system by doing the stability test at an optional parameter-value.

In our case in the differential equation describing the system there is the derivative by the parameter too, but, owing to the constant value of the parameter, it is also constant and has no influence on the stability of the system.

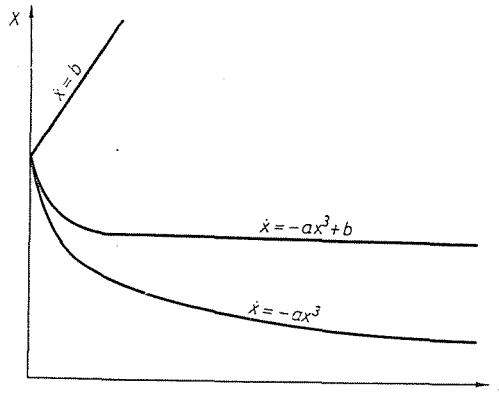


Fig. 10

The stability test with the limiting functions is actually based on a satisfactory condition of the stability, according to which: The system is stable, if the system, belonging to the majorant and minorant of the equation, describing the alteration of the system is stable. Thus the task is to find the limiting functions — if they exist (e.g. Fig. 10).

### Summary

The lecture deals with investigations on the stability of certain tubular reactors in the case of plain and composite (in-parallel, consecutive, equilibrium, chain and polymerization) reactions. (Dynamics are also investigated with plain reactions of the first order). The stable domain of the described reactions is determined as a function of the parameters (tube length, temperature, pressure) by using novel and classical procedures.

The procedures (and also in part the results) are suitable for the description of other types of reactors as well.

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