Critical analysis of the thermodynamics of reaction kinetics

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ABSTRACT

Our objective is to show the weakness of the recent thermodynamics of chemical reactions. We show that such a thermodynamic theory of chemical reactions, which could be similar to the generalized Onsager's theory in thermodynamics, is not reality at the moment.

Keywords

Reaction kinetics; equilibrium thermodynamics

SUBJECT CLASSIFICATION

Thermodynamics; reaction-kinetics

INTRODUCTION

The thermodynamics of the reaction kinetics is presently limited on the theory of ideal gases or their mixtures. Consequently it describes the reality to the same degree as the ideal gas describes it. However, complex biological phenomena can be described [i], [ii] and some approaches give realistic results despite this general simplification [iii].

The law of mass action, which is the basis of the chemical reaction kinetics, is not generally valid. It is true that the constitutive equation of reaction speed is approximated well by the product of the power of concentrations, but the the stoichiometric ratio as the power of the concentration does not surely fit to reality. Additionally the law of mass action is a non-linear constitutive equation which does not fit the generalized Onsager's symmetry relations. This is because Onsager's theory is based on constitutive equations of the exchange of current fluxes and their interactions with thermodynamic forces [iv]. However the chemical reactions are based on sources and products of balance equations. Because the resulting values satisfy the mass-conservation rules, and therefore include both negative and positive terms, this excludes the existence of the dissipative potential.

THE BASIS OF REACTION KINETICS

We study a system having multiple chemical components which could interact in stoichiometric chemical reactions. Let the number of the reactions be R. The molar number of chemical reactions derived from two sources: the environmental in- and ex-fluxes and internal sources, counting the chemical components that are used up and those that are produced. Consequently the molar number has a balance equation:
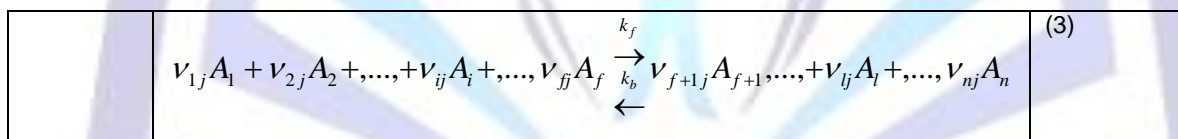
$$\frac{dn_i}{dt} = \frac{dn_i^{(e)}}{dt} + \frac{dn_i^{(i)}}{dt}, \quad (i = 1,2,...,n) \tag{1}$$

where $\dfrac{dn_i^{(e)}}{dt}$ is the molar flux (environmental sources) of the i-th component and $\dfrac{dn_i^{(i)}}{dt}$ is the molar change from the internal sources of the i-th component, called the molar-number production. Because the number of reactions in the system is R, the complete molar number is the superposition of the partial numbers:

$$\frac{dn_i^{(i)}}{dt} = \sum_{j=1}^{R} \frac{dn_{ij}^{(i)}}{dt}, \quad (i = 1,2,...,n) \tag{2}$$

where $\dfrac{dn_{ij}^{(i)}}{dt}$ is the molar-number production of the i-th chemical component in the j-th chemical reaction.

The equations of the stoichiometric reactions are:

$$\nu_{1j}A_1 + \nu_{2j}A_2 +,....,+\nu_{ij}A_i +,...,\nu_{fj}A_f \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \nu_{f+1j}A_{f+1},....,+\nu_{lj}A_l +,...,\nu_{nj}A_n \tag{3}$$

where A_i is the symbol of the i-th component and ν_{ij} is the stoichiometric coefficient of the i-th chemical component in the j-th reaction. By convention, the left to right forward reactions have negative $\nu_{ij}, (i = 1,2,...,f)$ coefficients while the $\nu_{lj}, (l = f+1,2,...,n)$ coefficients are positive; however in the backward reactions from right to left the signs are opposite to those in the forward case.

According to Equation (3), in every step of the j-th reaction in the case of the forward reaction from $\nu_{ij}, (i = 1,2,...,f)$ molar quantities of component A_i, $\nu_{lj}, (l = f+1,2,...,n)$ molar quantities of component A_l are produced, while in the backward reactions the opposite occurs.

Denoting the number of reaction steps by $d\xi_j$ during time dt in the j-th reaction, the molar-number production of the i-th component A_i is:

$$dn_{ij}^{(i)} = \nu_{ij}d\xi_j \tag{4}$$

Hence the balanced molar-number production term of (1) is

$$\frac{dn_i^{(i)}}{dt} = \sum_{j=1}^{R} \frac{dn_{ij}^{(i)}}{dt} = \sum_{j=1}^{R} v_{ij} \frac{d\xi_j}{dt} \tag{5}$$

where ξ_j is the j-th reaction coordinate and $\dfrac{d\xi_j}{dt}$ is its reaction speed.

The mass-conservation principle is of course valid in the chemical reactions too. In our case, this means that the consequent mass balance of all the reactions must not have a source, so:

$$\sum_{i=1}^{n} M_i \frac{dn_i}{dt} = \sum_{i=1}^{n} M_i \frac{dn_i^{(e)}}{dt} + \sum_{i=1}^{n} M_i \frac{dn_i^{(i)}}{dt} \rightarrow \sum_{i=1}^{n} M_i \frac{dn_i^{(i)}}{dt} =$$
$$= \sum_{i=1}^{n} M_i \sum_{j=1}^{R} \frac{dn_{ij}^{(i)}}{dt} = \sum_{i=1}^{n} \sum_{j=1}^{R} M_i v_{ij} \frac{d\xi_j}{dt} = 0 \tag{6}$$

where M_i is the molar-mass of the i-th components.

HOMOGENEOUS SYSTEMS

Chemistry works with concentrations, so we use these too temporarily.

When the system has volume V, the molar concentration of the i-th components is $c_i = \dfrac{n_i}{V}$. Consequently the balance equation (1) will have the form

$$\frac{dc_i}{dt} = \frac{d^{(e)}c_i}{dt} + \frac{d^{(i)}c_i}{dt}, \quad (i = 1,2,...,n)$$
$$\frac{d^{(e)}c_i}{dt} := \frac{1}{V} \frac{dn_i^{(e)}}{dt}, \quad \frac{d^{(i)}c_i}{dt} := \frac{1}{V} \frac{dn_i^{(i)}}{dt} = \sum_{j=1}^{R} \frac{d^{(i)}c_{ij}}{dt} = \sum_{j=1}^{R} v_{ij} \frac{1}{V} \frac{d\xi_j}{dt} = \sum_{j=1}^{R} v_{ij} \omega_j$$
$$\omega_j := \frac{1}{V} \frac{d\xi_j}{dt}, \quad \frac{d^{(i)}c_{ij}}{dt} := \frac{1}{V} \frac{dn_{ij}^{(i)}}{dt} \tag{7}$$

This equation must be completed by constitutive equations to determine the time-dependence of the reactions.

THE CONSTITUTIVE EQUATIONS

The constitutive equation for the concentration flux $\dfrac{d^{(e)}c_i}{dt}$

These equations describe the boundary transports so we have to fit the boundary conditions.

1. In a closed homogeneous system:

$$\frac{d^{(e)}c_i}{dt} = 0 \tag{8}$$

2. In the case of constant flux concentration (e.g. flow reactors):

$$\frac{d^{(e)}c_i}{dt} = \Phi_i = const \tag{9}$$

3. In the case of a material contact reservoir:

$$\frac{d^{(e)}c_i}{dt} = -k_{i0}(c_i - c_{i0}) \tag{10}$$

where k_{i0} is the coefficient of material transfer of the i-th component and c_{i0} is the molar concentration of the i-th component in the reservoir.

Constitutive equations for $\dfrac{d^{(i)}c_i}{dt}$ production of concentration

This law of mass action studies the stoichiometric reactions according to (1). The law of mass action states that the forward reaction proceeds at the rate

$$k_{fj}c_1^{-\nu_{1j}}c_2^{-\nu_{2j}}...c_i^{-\nu_{ij}}..c_f^{-\nu_{fj}} = k_{fj}\prod_{i=1}^{f}c_i^{-\nu_{ij}}, \quad \left(j=1,2,...,R\right)$$	(11)

while the backward reaction proceeds at the rate

$$k_{bj}c_{f+1}^{\nu_{f+1j}}c_2^{\nu_{2j}}...c_l^{\nu_{lj}}..c_n^{\nu_{nj}} = k_{bj}\prod_{l=f+1}^{n}c_l^{\nu_{lj}}, \quad \left(j=1,2,...,R\right)$$	(12)

where c_k is the molar concentration of the k-th chemical component, and k_f and k_b are dimensional constants that must be determined empirically. Note that the concentrations k_f and k_b can depend not only on the temperature but also on the pressure. The general convention is that the ν_{ij} values are positives in (11). Under these conditions, the constitutive equations for the concentration production are:

$$\omega_j = k_{fj}\prod_{i=1}^{f}c_i^{-\nu_{ij}} - k_{bj}\prod_{l=f+1}^{n}c_l^{\nu_{lj}}, \quad \left(j=1,2,...,R\right)$$	(13)

By understanding these principles in more depth, the reaction speed will be connected to a measurable value. Based on

(4) we find a connection between the concentration speed $\dfrac{d^{(i)}c_{ij}}{dt}$ (introduced in (7)) and the reaction speed.

According to (4), the i-th component of the change of speed of the molar-concentration in the j-th reaction is:

$$\frac{d^{(i)}c_{ij}}{dt} = \frac{1}{V}\frac{dn_{ij}^{(i)}}{dt} = \frac{1}{V}\nu_{ij}\frac{d\xi_j}{dt} \rightarrow \frac{1}{V}\frac{d\xi_j}{dt} = \frac{1}{\nu_{ij}}\frac{d^{(i)}c_{ij}}{dt}$$	(14)

from which the constitutive equations are:

$$\omega_j = \frac{1}{V}\frac{d\xi_j}{dt} = \frac{1}{\nu_{ij}}\frac{d^{(i)}c_{ij}}{dt} = k_{fj}\prod_{i=1}^{f}c_i^{-\nu_{ij}} - k_{bj}\prod_{l=f+1}^{n}c_l^{\nu_{lj}}, \quad \left(j=1,2,...,R\right)$$	(15)

For example, let us study a homogeneous system with four components $A_1,...,A_4$, where only a single chemical reaction happens. Then the reaction equation is:

$$\upsilon_1 A_1 + \upsilon_2 A_2 \underset{\underset{\leftarrow}{k_b}}{\overset{\overset{\rightarrow}{k_f}}{}} \upsilon_3 A_3 + \upsilon_4 A_4$$	(16)

This system has four concentration balances, four concentration productions, but only one reaction coordinate and one characteristic reaction speed.

This reaction speed could be expressed with any of the four concentration productions according to (14).

Let us study the concentration production of chemical component A_1. In equilibrium we could derive two kinds of speeds. One reaction speed is in the direction of the upper arrow (forward) while the other one is in the direction of the lower arrow (backward). The mass conservation is valid, so the consequent reaction speed is:

$$\omega = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{v_1}\frac{d^{(i)}c_1}{dt} = k_f c_1^{-v_1} c_2^{-v_2} - k_b c_3^{v_3} c_4^{v_4} \tag{17}$$

Hence the consequent reaction speed is the sum of the forward and backward reactions.

$$\omega = \overset{\rightarrow}{\omega} + \overset{\leftarrow}{\omega} = k_f c_1^{-v_1} c_2^{-v_2} - k_b c_3^{v_3} c_4^{v_4} \tag{18}$$

It is zero in equilibrium, so:

$$k_f c_1^{-v_1} c_2^{-v_2} = k_b c_3^{v_3} c_4^{v_4} \rightarrow \frac{c_3^{v_3} c_4^{v_4}}{c_1^{-v_1} c_2^{-v_2}} = \frac{k_f}{k_b} = K(T,p) \tag{19}$$

where K is the equilibrium constant.

Examples of the reaction kinetics of homogeneous systems.

1. Single-component system without reservoir reaction

In this case, the concentration balance (7) has no production term, only flux, so

$$\frac{dc}{dt} = \frac{d^{(e)}c}{dt} \tag{20}$$

a) In the case of the constant flux $\frac{d^{(e)}c}{dt} = \Phi = const$., the solution of (20) is

$$c(t) = \Phi t + Const \tag{21}$$

b) When the system has a material transfer contact with a reservoir according to (10), then from (20) we get:

$$\frac{dc}{dt} = -k(c - c_0) \tag{22}$$

Its solution is:

$$c(t) = c_0 + (c(t=0) - c_0)e^{-kt} \tag{23}$$

Note that the boundary condition has a definite influence on the result.

2. Production of component A from component X by decay

In this case the system has a reaction:

$$X \underset{k_b}{\overset{k_f}{\underset{\leftarrow}{\rightarrow}}} A \tag{24}$$

The reaction speed according to (13) is $\omega = (k_f c_X - k_b c)$, so the concentration production by (14) is

$\frac{d^{(i)}c}{dt} = (k_f c_X - k_b c)$. Consequently the concentration balance

$$\frac{dc}{dt} = \frac{d^{(e)}c}{dt} + (k_f c_X - k_b c) \tag{25}$$

When the system is closed and $c_X = const$, the solution is:

	(26)
$c(t) = c_0 + \left(c(t=0) - c_0\right)e^{-k_f t},$ $$c_0 = \frac{k_f}{k_b} c_X$$	

When the flux is constant, $\dfrac{d^{(e)}c}{dt} = \Phi = const$, and $c_X = const$, the solution is:

	(27)
$c(t) = c_1 + \left(c(t=0) - c_1\right)e^{-k_f t},$ $$c_1 = \frac{\Phi + k_f c_X}{k_b}$$	

3. Production of component A from X by autocatalytic reaction

In this case the system reacts as follows:

	(28)
$X + A \underset{k_b}{\overset{k_f}{\rightleftarrows}} 2A$	

The reaction speed according to Equation (13) is $\omega = \left(k_f c_X c - k_b c^2\right)$, so the concentration production is $\dfrac{d^{(i)}c}{dt} = \left(k_f c_X c - k_b c^2\right)$ by (14). From here the concentration balance is:

	(29)
$\dfrac{dc}{dt} = \dfrac{d^{(e)}c}{dt} + \left(k_f c_X c - k_b c^2\right)$	

When the system is closed and $c_X = const$, then:

	(30)
$\dfrac{dc}{dt} = \left(k_f c_X c - k_b c^2\right)$	

In equilibrium:

	(31)
$c_0 = \dfrac{k_f}{k_b} c_X$	

Then we get:

	(32)
$\dfrac{dY}{Y} + \dfrac{dY}{1-Y} = d\tau,$ $$Y := \frac{c}{c_0}, \quad d\tau = k_f c_X t$$	

and its solution

	(33)
$Y(\tau) = \dfrac{Y(\tau=0)}{Y(\tau=0) - \left[Y(\tau=0) - 1\right]e^{-\tau}}$	

In a closed system, where $c_X + c = c^0$ is a predetermined constant value, the equilibrium value is: $c_0 = \dfrac{k_f}{k_f + k_b} c_X$.
Introducing this, we again obtain (32) with other parameters as before:

$$\frac{dY}{Y} + \frac{dY}{1-Y} = d\tau,$$

$$Y := \frac{c}{c_0}, \quad d\tau = k_f c^0 t \tag{34}$$

Its solution has the form shown in (33).

4. Population dynamics

The reaction kinetics of autocatalytic systems shown above can be connected to the Volterra-Lotka-Glaser population-

$$X + A \xrightarrow{k_f} 2A$$
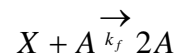
dynamics theory [v]. Its basis is that, in the case of a population of N individuals, the kinetic equation

$$\frac{dN}{dt} = rN$$

generates population growth with a growth rate r. This analogy can be made only when the feeding has infinite capacity. When the capacity is finite, the growth rate decreases by the growth of the number of the given

$$r(N) = r_0(1 - \frac{N}{N_0})$$

population. In this case, , where N_0 is the upper limit of the population size. In this case, the population dynamics could be described by

$$\frac{dN}{dt} = \frac{r_0}{N_0} N(N_0 - N) \tag{35}$$

which has the identical form to (30).

Consequently the population dynamics can be modelled well by Equation (28) of the autocatalytic processes. The challenge however is that Equation (30) was derived while considering at least two independent constitutional conditions, and it is not yet clear how these were fixed here.

5. A Gray-Scott-model

We can show the asymmetry in consequence of the mass conservation. The model investigates the following processes in a homogeneous system [vi]:

$$A + 2B \xrightarrow{k_1} 3B,$$

$$B \xrightarrow{k} P \tag{36}$$
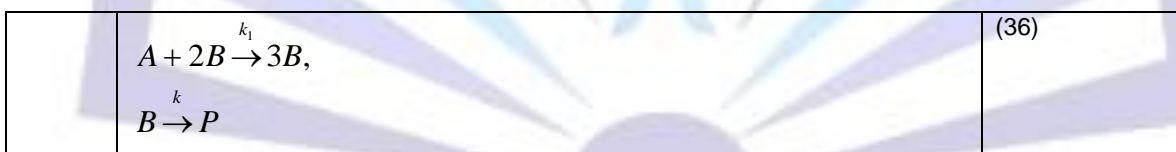
Here the first equation describes the situation when the catalyzer B produces component B from A. The second equation is the degradation of the catalyzer. The balance of P is undetermined so it has no dynamical description. The reaction

speed of the decay of the component A is $\omega_a = -k_1 c_a c_b^2$ according to (13), and so the concentration production of A is

$$\frac{d^{(i)} c_a}{dt} = -k_1 c_a c_b^2$$

according to (14). The reaction speed of the component B catalyzer according to (13) is

$\omega_b = k_1 c_a c_b^2 - k c_b$, so for the concentration production of B we get $\dfrac{d^{(i)} c_b}{dt} = k_1 c_a c_b^2 - k c_b$. Hence the balances of concentration are:

$$\frac{dc_a}{dt} = \frac{d^{(e)}c_a}{dt} - k_1 c_a c_b^2,$$

$$\frac{dc_b}{dt} = \frac{d^{(e)}c_b}{dt} + k_1 c_a c_b^2 - k c_b$$

(37)

We found that one of the productions is opposite to the other one.

a) When the system is in material exchange contact with the reservoir described by (10), then from (20) we get:

$$\frac{d^{(e)}c_a}{dt} = -k_0(c_a - c_{a0}),$$

$$\frac{d^{(e)}c_b}{dt} = -k_0(c_b - c_{b0})$$

(38)

When the parameters of the material transfer are identical, we get the equations of the Gray-Scott model:

$$\frac{dc_a}{dt} = -k_1 c_a c_b^2 - k_0(c_a - c_{a0}),$$

$$\frac{dc_b}{dt} = k_1 c_a c_b^2 - k c_b - k_0(c_b - c_{b0})$$

(39)

which are simply transformed to

$$\frac{da}{dt} = -ab^2 - F(1-a),$$

$$\frac{db}{dt} = ab^2 - (F+k)b$$

(40)

The thermodynamics have not been taken into consideration until this point. Now we give the further development of the thermodynamic reaction kinetics.

THERMODYNAMIC BASIS OF REACTION KINETICS

The first law of thermodynamics is formulated:

$$dU = TdS - pdV + \sum_{k=1}^{n} \mu_k dN_k =$$

$$= TdS - pdV + \sum_{k=1}^{n} \bar{\mu}_k dm_k,$$

$$\bar{\mu}_k = \frac{L}{M_k}, \quad dm_k = dN_k \frac{M_k}{L}$$

(41)

where for the i-th components, $dm_i = dN_i \frac{M_i}{L}$, where M_i is the molar mass, L is the Loschmidt number, and N_i is the number of molecules. From the balance of molecular numbers described in (2), it follows that:

$$dm_1 = dm_1^e - d\xi \upsilon_1 \frac{M_1}{L},..,dm_i = dm_i^e - d\xi \upsilon_i \frac{M_i}{L},..(i = 1,2,3,..f);$$

$$dm_{f+1} = dm_{f+1}^e + d\xi v_{f+1} \frac{M_{f+1}}{L},...,dm_j = dm_j^e + d\xi v_j \frac{M_j}{L},..(j = f+1,...,n)$$

(42)

Due to the chemical reactions of $dm_j^i = d\xi v_j \frac{M_j}{L}$, the formula of mass conservation is:

$$\sum_{i=1}^{f} dm_i^i - \sum_{j=f+1}^{n} dm_j^i = 0, \tag{43}$$

From which

$$\sum_{i=1}^{f} \nu_i \frac{M_i}{L} - \sum_{j=f+1}^{n} \nu_j \frac{M_j}{L} = 0, \rightarrow \sum_{i=1}^{f} \nu_i M_i - \sum_{j=f+1}^{n} \nu_j M_j = 0, \tag{44}$$

From the equations (41) and (42), the first law of thermodynamics is derived:

$$dU = TdS - pdV + \sum_{k=1}^{n} \overline{\mu}_k dm_k^e + \left(\sum_{i=1}^{f} \overline{\mu}_i \upsilon_i \frac{M_i}{L} - \sum_{j=f+1}^{n} \overline{\mu}_j \upsilon_j \frac{M_j}{L} \right) d\xi \tag{45}$$

The Gibbs relation for multicomponent systems is the unification of the first and second principles of thermodynamics. Its formulation with the molar numbers is:

$$dU = TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} + \sum_{k=1}^{n} \mu_k dn_k^{(i)} =$$
$$= TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} + \sum_{j=1}^{R} \left(\sum_{i=1}^{f} \mu_i \nu_i^j - \sum_{l=f+1}^{n} \mu_l \nu_l^j \right) d\xi_j \tag{46}$$

Introducing the following denotations (affinities),

$$A_j = \overset{\leftarrow}{A}_j - \vec{A}_j,$$
$$\overset{\leftarrow}{A}_j = \sum_{l=f+1}^{n} \mu_l \nu_l^j, \quad \vec{A}_j = \sum_{i=1}^{f} \mu_i \nu_i^j \tag{47}$$

we get the form of the first law of thermodynamics formulated by molecular numbers for chemical reactions:

$$dU = TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} - \sum_{j=1}^{R} \left(\vec{A}_j - \overset{\leftarrow}{A}_j \right) d\xi_j =$$
$$= TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} - \sum_{j=1}^{R} A_j d\xi_j \tag{48}$$

where A_j is the affinity of the j-th chemical reaction. The value ξ is the so-called reaction coordinate.

The affinity and the form of the irreversible heat in the next formula (49) were precisely formulated by De Donder [vii]:

$$dQ_{irr} = \sum_{j=1}^{R} A_j d\xi_j \geq 0 \tag{49}$$

In consequence of (49), that the consequent $A_j d\xi_j$ would not be negative in all of the reactions. When only one chemical reaction happens in the system, the affinity A and the character $d\xi$ of the development of the reaction have the same sign and become zero at the same time. When the chemical reaction isobaric and isothermal, then we can introduce the Gibbs free enthalpy [viii] as:

$$dG = d(U - TS + pV) = \sum_{k=1}^{n} \mu_k dn_k^{(e)} - \sum_{j=1}^{R} A_j d\xi_j \tag{50}$$
$$G := U - TS + pV$$

which, in the case of a close system, is:

$$dG = -\sum_{j=1}^{R} A_j d\xi_j \le 0 \tag{51}$$

The free enthalpy G decreases during the chemical reaction and reaches a minimum in equilibrium. The necessary condition of the equilibrium is:

$$\frac{\partial G}{\partial \xi_j} = 0, \; \rightarrow A_j = 0 \rightarrow \vec{A}_j = \overleftarrow{A}_j, \quad (j = 1,2,..,R) \tag{52}$$

Dividing (38) by the volume V of the system and using the balance of molar concentration (7), we get:

$$d\frac{G}{V} = dg = \sum_{k=1}^{n} \mu_k d^{(e)} c_k - \sum_{j=1}^{R} A_j \frac{1}{V} d\xi_j \rightarrow$$

$$\frac{dg}{dt} = \sum_{k=1}^{n} \mu_k \frac{d^{(e)} c_k}{dt} - \sum_{j=1}^{R} A \omega_j, \tag{53}$$

$$\omega_j = \frac{1}{V}\frac{d\xi}{dt}$$

The entropy produced by the chemical reactions is derived from (39):

$$\sigma_{chemreac} := \frac{1}{V}\frac{1}{T}\frac{dQ_{irr}}{dt} = \sum_{j=1}^{R}\frac{A_j}{T}\frac{1}{V}\frac{d\xi_j}{dt} = \sum_{j=1}^{R}\frac{A_j}{T}\omega_j \ge 0 \tag{54}$$

There is a linear connection between the generalized fluxes (in our case ω_j) and forces ($-\dfrac{A_j}{T}$) according to Onsager's principles. For example, for only two variables:

$$\omega_1 = L_{11}\left(-\frac{A_1}{T}\right) + L_{12}\left(-\frac{A_2}{T}\right),$$

$$\omega_2 = L_{21}\left(-\frac{A_1}{T}\right) + L_{22}\left(-\frac{A_2}{T}\right) \tag{55}$$

where the matrix of conduction coefficients (sometimes called chemical conduction) is positive definite. However, unfortunately this is not true in chemical reaction kinetics. In the case of the constitutive equation (15), considering only one chemical reaction, the form is

$$\omega = L\left(e^{\frac{\vec{A}}{RT}} - e^{\frac{\overleftarrow{A}}{RT}}\right) \tag{56}$$

and it can also be proven that it is valid only in the approximation of an ideal gas [ix]. Linearity can be approximated by

$$\omega == L\left(e^{\frac{\vec{A}}{RT}} - e^{\frac{\overleftarrow{A}}{RT}}\right) = Le^{\frac{\overleftarrow{A}}{RT}}\left(e^{-\frac{A}{RT}} - 1\right) \approx \frac{Le^{\frac{\vec{A}}{RT}}}{R}\frac{A}{T} \tag{57}$$

where we suppose that $A << RT$ and so $\left(e^{-\frac{A}{RT}} - 1 \right) \approx -\frac{A}{T}$. Unfortunately even the ideal-gas approximation fails to describe the reactions. The non-linear Onsager's theorem can be constructed by $\left(e^{\frac{\overrightarrow{A_j}}{RT}} - e^{\frac{\overleftarrow{A_j}}{RT}} \right)$ type forces and by

$$\Psi \left(T, p, e^{\frac{\overrightarrow{A_j}}{RT}} - e^{\frac{\overleftarrow{A_j}}{RT}} \right)$$

dissipation potentials, but it also fails due to the differences in the stoichiometric coefficients of these forces. The other theory of the reaction kinetics could be based on Eyring's reaction-rate principle [x], [xi], but it also failed [xii].

CONTINUOUS SYSTEMS – EQUATION OF REACTION DIFFUSION

Morphogenesis is the embryonal development of the structure of an organism. Its principal result is the explanation of the complex structures starting from a single cell. The embryonal development has two additional mechanisms: the movement of the cell and the specialization of its function. These mechanisms are influenced by various chemical components produced in the cell and liberated afterwards. These chemical products are the morphogens. The morphogens diffuse freely from one cell to another through their membranes, and their intracellular concentration affects the development of the cell. The first mathematical model of the morphogenesis was made by Turing [xiii]. His model was made with two morphogens, a and b. Transport of these is defined by their concentration gradient. However the diffusion is not the only mechanism of the variation of morphogen concentration in the cell. The morphogens can chemically react with each other, depending on their intracellular concentrations. The time-variation of morphogens can be described by coupled equations of reaction-diffusion. Study of the system of equations showed that when the diffusion constants differ between the morphogens then the initial perturbation of the morphogen concentration shows a stable periodic pattern.

In the thermodynamic formulation

$$dU = TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} - \sum_{j=1}^{R} \left(\overrightarrow{A}_j - \overleftarrow{A}_j \right) d\xi_j =$$ $$= TdS - pdV + \sum_{k=1}^{n} \mu_k dn_k^{(e)} - \sum_{j=1}^{R} A_j d\xi_j$$	(58)

Introducing the affinities,

$$A = \overrightarrow{A} - \overleftarrow{A},$$ $$\overleftarrow{A} = \sum_{j=f+1}^{n} \mu_j \upsilon_j, \qquad \overrightarrow{A} = \sum_{i=1}^{f} \mu_i \upsilon_i$$	(59)

Let us next calculate the mass balance of the individual components of a static, continuous, multi-phase system. The mass of components can be changed for two reasons:

A mass-current flux exists on the surface of the system. This is only conductive in the static system, which is connected to diffusion.

There are chemical reactions inside the system, which could be the source or sink of the mass of various components.

In a system which has volume V and a mathematically closed surface we consider the mass dm_k of the k-th component in the volume dV. Then the mass-density of the k-th component is $\rho_k = \frac{dm_k}{dV}$, so the complete mass of that component is $m_k = \int_V \rho_k dV$.

When $\mathbf{J_k}$ is the mass-current density of the k-th component, the mass-current through the surface $d\mathbf{A}$ will be $-\mathbf{J_k} \cdot d\mathbf{A}$ in unit time. Consequently the mass-current through the complete boundary surface will be $-\int_A \mathbf{J_k} \cdot d\mathbf{A}$ in unit time. The negative sign shows the incoming flow, because the normal vector of the surface is directed outside. It was shown above that the molar concentration of the k-th component changes by $\sum_{j=1}^{R} \nu_{kj}\omega_j$ in unit-time when the system has R number of chemical reactions. Consequently the mass concentration of the k-th component changes by $\sum_{j=1}^{R} M_k \nu_{kj}\omega_j$ in unit time. So the production of the k-th component in a system with volume V is $\int_V \sum_{j=1}^{R} M_k \nu_{kj}\omega_j dV$. Hence the global mass balance on the k-th component is:

$$\frac{dm_k}{dt} = \frac{d}{dt}\int_V \rho_k dV = -\int_A \mathbf{J_k} \cdot d\mathbf{A} + \int_V \sum_{j=1}^{R} M_k \nu_{kj}\omega_j dV \tag{60}$$

Applying the Gauss theorem:

$$\int_V \left(\frac{d\rho_k}{dt} + \nabla \cdot \mathbf{J_k} - \sum_{j=1}^{R} M_k \nu_{kj}\omega_j \right) dV = 0 \tag{61}$$

This could be written for any volume V, so the differential mass balance is:

$$\frac{d\rho_k}{dt} + \nabla \cdot \mathbf{J_k} = \sum_{j=1}^{R} M_k \nu_{kj}\omega_j, \quad (k = 1,2,...,n) \tag{62}$$

Introducing the mass concentration $c_k = \dfrac{\rho_k}{\rho}$, we get

$$\rho \frac{dc_k}{dt} + \nabla \cdot \mathbf{J_k} = \sum_{j=1}^{R} M_k \nu_{kj}\omega_j, \quad (k = 1,2,...,n) \tag{63}$$

where $\rho = \sum_{k=1}^{n} \rho_k$ is the mass density of the system.

NON-EQUILIBRIUM THERMODYNAMICS OF MULTICOMPONENT SYSTEMS

For the actual form of the entropy balance, we start from the Gibbs relation:

$$Tds = du + pdv - \sum_{k=1}^{n} \mu_k dc_k \tag{64}$$

Hence the rate of entropy density is

$$\frac{ds}{dt} = \frac{1}{T}\frac{du}{dt} + \frac{p}{T}\frac{dv}{dt} - \sum_{k=1}^{n} \frac{\mu_k}{T}\frac{dc_k}{dt} \tag{65}$$

Additionally we consider the concentration balances form (63), the condition $\rho \dfrac{dv}{dt} = div\mathbf{v}$, and the balance of the internal energy:

$$\rho \frac{du}{dt} + \nabla \cdot \mathbf{J}_q = 0 \tag{66}$$

When the system is incompressible we get $\rho \dfrac{dv}{dt} = div\mathbf{v} = 0$; then the entropy balance is:

$$\rho \frac{ds}{dt} + \nabla \cdot \left(\frac{\mathbf{j}_q}{T} - \sum_{k=1}^{n} \frac{\mu_k}{T} \mathbf{j}_k \right) =$$
$$= \mathbf{j}_q \cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^{n} \mathbf{j}_k \cdot \nabla \left(\frac{\mu_k}{T} \right) - \sum_{j=1}^{n} \omega_j \frac{A_j}{T} \tag{67}$$

from which the entropy current density is:

$$\mathbf{j}_s = \frac{\mathbf{j}_q}{T} - \sum_{k=1}^{n} \frac{\mu_k}{T} \mathbf{j}_k \tag{68}$$

and the entropy production is:

$$\sigma_s = \mathbf{j}_q \cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^{n} \mathbf{j}_k \cdot \nabla \left(\frac{\mu_k}{T} \right) - \sum_{j=1}^{n} \omega_j \frac{A_j}{T} \tag{69}$$

In the case of an isothermal system, two term remains for investigation, of which the term which describes the chemical reactions was discussed above. The term which describes the diffusion is $- \sum_{k=1}^{n} \mathbf{j}_k \cdot \nabla \left(\dfrac{\mu_k}{T} \right)$, which shows that the thermodynamic currents are proportional to the gradient of the thermodynamic currents $\mathbf{j}_k$, while the thermodynamic forces are proportional to the gradients of the chemical potentials: $\nabla \left(-\dfrac{\mu_k}{T} \right)$. Consequently the Onsager's constitutive equations for the diffusion are:

$$\mathbf{j}_i = \sum_{k=1}^{n} L_{ik} \nabla \left(-\frac{\mu_k}{T} \right), \quad (i = 1,2,\ldots,n) \tag{70}$$

REACTION-DIFFUSION EQUATION

For simplicity, let us limit the calculation to two components. We now have two mass current densities and two forces: $\mathbf{j}_1, \mathbf{j}_2, -\dfrac{1}{T}\nabla\mu_1, -\dfrac{1}{T}\nabla\mu_2$. The system is isothermal, so the chemical potentials depend only on the concentrations. Because the chemical reactions were described in the ideal-gas approximation, we apply that here too. Then the chemical potentials of the various components depend only on their own concentrations, while cross-effects are neglected, and using the form $\nabla\mu_i \cong \dfrac{\partial\mu_i}{\partial c_i}\nabla c_i, (i=1,2)$ (70), we get:

$$\mathbf{j}_1 = -\frac{L_{11}}{T}\frac{\partial\mu_1}{\partial c_1}\nabla c_1 = -D_1^*\nabla c_1,$$
$$\mathbf{j}_2 = -\frac{L_{22}}{T}\frac{\partial\mu_2}{\partial c_2}\nabla c_2 = -D_2^*\nabla c_2 \tag{71}$$

Using the concentration balances from (63), the reaction-diffusion equation of the concentrations is:

$$\rho \frac{dc_1}{dt} - \nabla \cdot D_1^* \nabla c_1 = \sum_{j=1}^{2} M_1 \nu_{1j} \omega_j,$$

$$\rho \frac{dc_2}{dt} - \nabla \cdot D_2^* \nabla c_2 = \sum_{j=1}^{2} M_2 \nu_{2j} \omega_j,$$

(72)

Substituting into the terms of concentration production, the right-hand of the equation (72) the constitutive equations (15), we get the function of the concentrations similar to the equations found by Gray-Scott model. Denoting these concentrations as $\sigma_1^*(c_1, c_2)$ and $\sigma_2^*(c_1, c_2)$, we get:

$$\rho \frac{dc_1}{dt} - \nabla \cdot D_1^* \nabla c_1 = \sigma_1^*(c_1, c_2),$$

$$\rho \frac{dc_2}{dt} - \nabla \cdot D_2^* \nabla c_2 = \sigma_2^*(c_1, c_2)$$

(73)

Due to the incompressibility, (73) can be divided by the densities; hence:

$$\frac{dc_1}{dt} - \nabla \cdot D_1 \nabla c_1 = \sigma_1(c_1, c_2),$$

$$\frac{dc_2}{dt} - \nabla \cdot D_2 \nabla c_2 = \sigma_2(c_1, c_2)$$

$$D_i = \frac{D_i^*}{\rho}, \sigma_i(c_1, c_2) = \frac{\sigma_i^*(c_1, c_2)}{\rho}, \quad (i = 1,2)$$

(74)

When the diffusion constants are independent from the concentrations we get the reaction-diffusion equations proposed by Turing [xiv]:

$$\frac{dc_1}{dt} = \sigma_1(c_1, c_2) + D_1 \Delta c_1$$

$$\frac{dc_2}{dt} = \sigma_2(c_1, c_2) + D_2 \Delta c_2$$

(75)

These equations are completed with the boundary conditions (such as the concentrations on the boundaries, concentration of the current densities on the boundaries, or a combination of these). These equations are subject to intensive mathematical investigations although they are the result of a very high level of simplification and neglect of components during their development.

We have some critical notes at this step:

1.   In the Gray-Scott model we considered the boundary conditions. Further anticipation of boundary conditions is useless.

2.   The diffusion of morphogens is performed in gel-like media, which are far from the ideal gas.

3.   Unfortunately the diffusion "constants" are not constants even in the case of an ideal gas.

4.   The morphogenesis starts from division of a single cell and then the number grows. The volume and the boundary of this system change over time. The complete theory neglects this.

ELEMENTS OF THE MATHEMATICAL STUDY OF THE GRAY-SCOTT EQUATION

The Gray-Scott equation is formed from the Turing equation (75) combined with the concentration production term from equation (40):

$$\frac{dc_1}{dt} = -c_1 c_2^2 + F(1 - c_1) + D_1 \Delta c_1$$

$$\frac{dc_2}{dt} = c_1 c_2^2 - (F + k)c_2 + D_2 \Delta c_2$$

(76)

1. Homogenous equilibrium solution

When (76) exists then the solutions satisfy the equations:

$$0 = -c_1 c_2^2 + F(1 - c_1)$$
$$0 = c_1 c_2^2 - (F + k)c_2$$
(77)

which have a trivial solution of $c_1 = 1$ and $c_2 = 0$. It is also a simple consequence that

$$c_{1+} = \frac{1}{2} - \sqrt{\frac{1}{4} - \alpha}, \ c_{1-} = \frac{1}{2} + \sqrt{\frac{1}{4} - \alpha}$$
$$\delta c_{2+} = \frac{1}{2} + \sqrt{\frac{1}{4} - \alpha}, \ \delta c_{2-} = \frac{1}{2} - \sqrt{\frac{1}{4} - \alpha},$$
$$\alpha = F\delta^2, \quad \delta = \frac{F + k}{F} = 1 + \frac{k}{F} > 1$$
(78)

The α is a bifurcation parameter that drastically changes the character of the solution at the point $\alpha_c = 1/4$, accompanied by a critical value k_c connected to F:

$$k_c = \frac{\sqrt{F}}{2} - F = \frac{1}{16} - \left(f - \frac{1}{4}\right)^2,$$
$$f := \sqrt{F}$$
(79)

The $k_c(f)$ function is a parabola, and the condition $\alpha \le \alpha_c = 1/4$ involves the relation $k \le k_c$.

1.   Kinetic stability and Andronov-Hopf bifurcation

We study the stability of the homogeneous time-dependent solution of the Gray-Scott-equation in the vicinity of the equilibrium of the linear approximation of the following equation:

$$\frac{dc_1}{dt} = -c_1 c_2^2 + F(1 - c_1)$$
$$\frac{dc_2}{dt} = c_1 c_2^2 - (F + k)c_2$$
(80)

The Jacobi matrix of the right side of the equation system is:

$$\mathbf{J} = \begin{pmatrix} -c_1^2 - F & -2c_1 c_2 \\ c_2^2 & 2c_1 c_2 + (F + k) \end{pmatrix}$$
(81)

and from the values of the parameters at the equilibrium point we get:

$$c_1 \delta c_2 = \alpha, \quad (\delta c_2)^2 - \delta c_2 + \alpha = 0$$
(82)

Hence the Jacobi matrix is:

$$\mathbf{J} = \frac{1}{\delta^2} \begin{bmatrix} -\delta c_2 & -2\alpha\delta \\ \delta c_2 - \alpha & \alpha\delta \end{bmatrix}$$
(83)

Its trace-determinant is:

$$tr(\delta^2 \mathbf{J}) = \alpha\delta - \delta c_2, \quad Det(\delta^2 \mathbf{J}) = \alpha\delta(\delta c_2 - 2\alpha)$$
(84)

so $tr(\delta^2\mathbf{J})$ and $Det(\delta^2\mathbf{J})$ have the same sign as

$\alpha\delta - \delta c_2, \quad \delta c_2 - 2\alpha$	(85)

These values will be the coefficients in the characteristic polynomial. The c_{1+} and c_{2+} solutions of (78) will have

condition $\delta c_{2+} - 2\alpha > 0$, because $\delta c_{2+} > \dfrac{1}{2}$ and $2\alpha < \dfrac{1}{2}$.

So $Det(\mathbf{J}) > 0$ in case of the c_{1+} and c_{2+} solutions. The Hopf bifurcation [xv] starts at $tr(\mathbf{J}) = 0$ or when $\alpha\delta - \delta c_{2+} = 0$. From this, the critical value of δ is:

$\delta_c(\alpha) = \dfrac{\delta c_{2+}}{\alpha} = \dfrac{1}{\alpha}\left(\dfrac{1}{2} - \sqrt{\dfrac{1}{4} - \alpha}\right)$	(86)

Consequently at $\alpha < \alpha_{krit} = \dfrac{1}{4}$, that is, any solution where δ crosses the $\delta_c(\alpha)$ curve, the value of $tr(\mathbf{J})$ at the solution of c_{1+}, c_{2+} changes from negative to positive, and, as we prove in the following, it makes the solution instable.

The linearized equation from (80) is formed by the (x, y) deviation from the equilibrium point, where x is the deviation of the first component and y is deviation of the second component from the equilibrium value:

$\begin{bmatrix} \dfrac{dx}{dt} \\ \dfrac{dy}{dt} \end{bmatrix} = \mathbf{J}\begin{bmatrix} x \\ y \end{bmatrix} = \dfrac{1}{\delta^2}\begin{bmatrix} -\delta c_{2+} & -2\alpha\delta \\ \delta c_{2+} - \alpha & \alpha\delta \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix}$	(87)

The solution could have the form of:

$\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \end{bmatrix}e^{\lambda t}$	(88)

And so we get the linear homogeneous equation:

$(\lambda\mathbf{I} - \mathbf{J})\begin{bmatrix} x_0 \\ y_0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$	(89)

where $\mathbf{I}$ is the unit matrix. This has a solution when

$Det(\lambda\mathbf{I} - \mathbf{J}) = 0$	(90)

So we have the characteristic polynomial

$Det\begin{bmatrix} \lambda - \dfrac{\delta c_{2+}}{\delta^2} & -\dfrac{2\alpha\delta}{\delta^2} \\ \dfrac{\delta c_{2+} - \alpha}{\delta^2} & \lambda + \dfrac{\alpha\delta}{\delta^2} \end{bmatrix} = \lambda^2$ $= \lambda^2 - \dfrac{1}{\delta^2}(\alpha\delta - \delta c_{2+})\lambda + \dfrac{1}{\delta^2}\alpha\delta(\delta c_{2+} - 2\alpha) = 0$	(91)

and the solution:

$$\lambda = \frac{\left(\alpha\delta - \delta c_{2+}\right) \pm \sqrt{\left(\alpha\delta - \delta c_{2+}\right)^2 - 4\alpha\delta\left(\delta c_{2+} - 2\alpha\right)}}{2\delta^2}$$

(92)

Now it is clearly proven that when the growing δ crosses the $\delta_c(\alpha)$ curve at $\alpha < \alpha_c = \dfrac{1}{4}$, the value of $\left(\alpha\delta - \delta c_{2+}\right)$ becomes positive through zero. In this case the real value of λ also goes through zero to positive, while the argument of the square root is negative, so λ has an imaginary part. Consequently the at first constant oscillation of the amplitude of $\delta_c(\alpha)$ curve, and a growing amplitude appears by growing λ, and after crossing zero an instability appears. This is the Andronov-Hopf bifurcation [xvi].

2. Kinetic stability considering diffusion

The diffusion (as Turing also showed) can cause instability [xvii]. For this we study the linearized equation from (76):

$$\begin{bmatrix} \dfrac{dx}{dt} \\ \dfrac{dy}{dt} \end{bmatrix} = \mathbf{J}\begin{bmatrix} x \\ y \end{bmatrix} = \frac{1}{\delta^2}\begin{bmatrix} -\delta c_{2+} & -2\alpha\delta \\ \delta c_{2+} - \alpha & \alpha\delta \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} + \begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix}\begin{bmatrix} \Delta x \\ \Delta y \end{bmatrix}$$

(93)

Supposing the solution is in the form of

$$\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \end{bmatrix} e^{\lambda t + i\mathbf{m}\cdot\mathbf{r}}$$

(94)

we get the following homogenous linear algebraic equation:

$$\left(\lambda\mathbf{I} - \mathbf{J} + m^2\begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix}\right)\begin{bmatrix} x_0 \\ y_0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

(95)

which, becomes:

$$\left(\lambda\mathbf{I} - \frac{1}{\delta^2}\begin{bmatrix} -\delta c_{2+} + m^2 D_1 & -2\alpha\delta \\ \delta c_{2+} - \alpha & \alpha\delta + m^2 D_2 \end{bmatrix}\right)\begin{bmatrix} x_0 \\ y_0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

(96)

It has a solution when

$$Det\left(\lambda\mathbf{I} - \frac{1}{\delta^2}\begin{bmatrix} -\delta c_{2+} + m^2 D_1 & -2\alpha\delta \\ \delta c_{2+} - \alpha & \alpha\delta + m^2 D_2 \end{bmatrix}\right) = 0$$

(97)

And so we get the characteristic polynomial of the

$$\frac{1}{\delta^2}\begin{bmatrix} -\delta c_{2+} + m^2 D_1 & -2\alpha\delta \\ \delta c_{2+} - \alpha & \alpha\delta + m^2 D_2 \end{bmatrix}$$

(98)

matrix:

$$\lambda^2 - \frac{1}{\delta^2}\left(\alpha\delta - \delta c_{2+} + m^2\left(D_2 + D_2\right)\right)\lambda +$$
$$+ \frac{1}{\delta^2}\left(\alpha\delta\left(\delta c_{2+} - 2\alpha + m^2 D_1\right) - \delta c_{2+} m^2 D_2 + m^4 D_1 D_2\right) = 0$$

(99)

Introducing

$$\alpha_m = \frac{1}{\delta^2}\left(\alpha\delta - \delta c_{2+} + m^2(D_2 + D_2)\right),$$

$$\beta_m = \frac{1}{\delta^2}\left(\alpha\delta(\delta c_{2+} - 2\alpha + m^2 D_1) - \delta c_{2+}m^2 D_2 + m^4 D_1 D_2\right)$$

(100)

the polynomial can be simplified as:

$$\lambda^2 - \alpha_m\lambda + \beta_m = 0$$

(101)

where the index m denotes the wave number of the space pattern.

The transition from the stable $\operatorname{Re}\lambda < 0$ state to the instable $\operatorname{Re}\lambda > 0$ state goes through the value $\lambda = 0$. From (101) and (102), the point of bifurcation is

$$\beta_m = \frac{1}{\delta^2}\left(\alpha\delta(\delta c_{2+} - 2\alpha + m^2 D_1) - \delta c_{2+}m^2 D_2 + m^4 D_1 D_2\right) = 0$$

(102)

When the extreme of this four-ordered function is zero, then the critical wave-number m_c can be determined from the following equation:

$$\frac{d\beta_m}{dm} = \frac{d}{dm}\left[\frac{1}{\delta^2}\left(\alpha\delta(\delta c_{2+} - 2\alpha + m^2 D_1) - \delta c_{2+}m^2 D_2 + m^4 D_1 D_2\right)\right] = 0$$

(103)

From the equation (101) we get:

$$\lambda_{1,2} = \frac{\alpha_m \pm \sqrt{\alpha_m^2 - 4\beta_m}}{2}$$

(104)

The character of the radical can be obtained from the diagram of (β_m, α_m) from the point of view of stability. The the ($\alpha_m = 0,$ and $\beta_m = 0$) axis and the curve by $\alpha_m^2 = 4\beta_m$ determine five domains (see Figure 1):

1. The domain I is determined by $\beta_m < 0$, $\operatorname{Re}\lambda_1 > 0$, and $\operatorname{Re}\lambda_2 < 0$. These are real radicals, and it is a hyperbolic point in an instable state.

2. The domain II is determined by $\alpha_m < 0, \beta_m > 0, |\alpha_m| > 2\sqrt{\beta_m}$, The $\operatorname{Re}\lambda_1 < 0$, and $\operatorname{Re}\lambda_2 < 0$ are real radicals, is a stable fixed point, and is in a stable state.

3. In the domain III characterized by $\alpha_m < 0, \beta_m > 0, |\alpha_m| < 2\sqrt{\beta_m}$. The $\operatorname{Re}\lambda_1 < 0$ and $\operatorname{Re}\lambda_2 < 0$ are complex radicals and it is an attractive focus-point (attractor) in a stable state.

4. In the domain IV, we have $\alpha_m > 0, \beta_m > 0, |\alpha_m| < 2\sqrt{\beta_m}$. The $\operatorname{Re}\lambda_1 > 0$ and $\operatorname{Re}\lambda_2 > 0$ are complex radicals, and it has instable focus in an instable state.

5. In the domain V the conditions are: $\alpha_m > 0, \beta_m > 0, |\alpha_m| > 2\sqrt{\beta_m}$. The $\operatorname{Re}\lambda_1 > 0$ and $\operatorname{Re}\lambda_2 > 0$ are real radicals, and it is a repulsive node in an instable state.

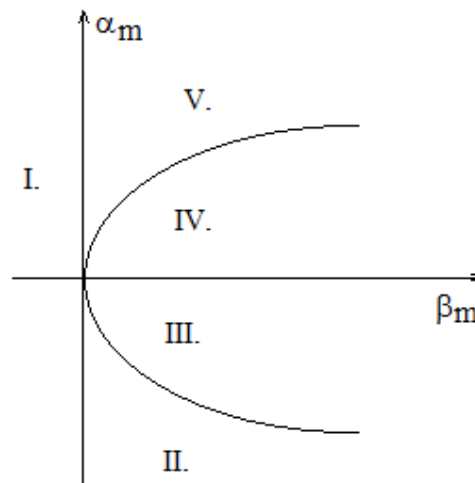**Figure 1. The $\left(\beta_m, \alpha_m\right)$ diagram for the determination of the stability in Turing domains.**

EFFECT OF DIFFUSION ON THE DECOMPOSITION OF HOMOGENEOUS DYNAMIC STABILITY

Turing discovered the phenomenon in which the diffusion can destabilize the dynamic stability of a homogeneous system [xiii]. Starting from a stable homogeneous state, the condition of stability is:

$$\frac{1}{\delta^2}\left(\delta c_{2+} - \alpha\delta\right) < 0,$$

$$\frac{1}{\delta^2}\alpha\delta\left(\delta c_{2+} - 2\alpha\right) > 0$$

(105)

The trace and the determinant expression are modified in the characteristic polynomial by diffusion. With diffusion, the stability conditions are:

$$\frac{1}{\delta^2}\left(\delta c_{2+} - \alpha\delta\right) - m^2\left(D_1 + D_2\right) < 0,$$

$$\frac{1}{\delta^2}\left[\left(\delta c_{2+} - m^2 D_1\right)\left(\alpha\delta - m^2 D_2\right) - 2\alpha^2\delta\right] > 0$$

(106)

Because $m^2\left(D_1 + D_2\right) > 0$, the negativity of the first equation of (106) does not change by diffusion. However in the second equation of (106) the left side is m^2 parabolic, which is open upwards. Under the condition $m^2 = 0$, the left expression is positive (which follows immediately from (105)), and it is positive for large m^2 too. The decomposition of the stability starts when the expression becomes negative. The minimal value of the parabola is determined by the condition

$$\frac{d}{d\left(m^2\right)}\left[\left(\delta c_{2+} - m^2 D_1\right)\left(\alpha\delta - m^2 D_2\right) - 2\alpha^2\delta\right] =$$

(107)

Hence we obtain:

$$m_{\min}^2 = \frac{D_1\alpha\delta + D_2\delta c_{2+}}{2D_1 D_2}$$

(108)

Consequently the minimum is:

$$\delta c_{2+} \alpha\delta - 2\alpha^2\delta - \frac{(D_1\alpha\delta + D_2\delta c_{2+})^2}{4D_1D_2} \qquad (109)$$

This is negative when

$$D_1\alpha\delta + D_2\delta c_{2+} > 2\sqrt{D_1 D(\delta c_{2+}\alpha\delta - 2\alpha^2\delta)} \qquad (110)$$

This is the necessary and sufficient condition of the instability.

Due to the expression in (105), the square-root in (110) is real, and a weaker condition is also valid:

$$D_1\alpha\delta + D_2\delta c_{2+} > 0 \qquad (111)$$

From the first equation of (105) and from (111) the values of δc_{2+} and $\alpha\delta$ have opposite signs. In our present case $\delta c_{2+} > 0$, so in consequence $\alpha\delta < 0$. Introducing the diffusion lengths,

$$l_1 = \sqrt{\frac{D_1}{\delta c_{2+}}\alpha\delta}, \quad l_2 = \sqrt{\frac{D_2}{-\alpha\delta}} \qquad (112)$$

the necessary and sufficient condition of the instability in (110) could be written as

$$m_{min}^2 = \frac{1}{2}\left(\frac{1}{l_1^2} - \frac{1}{l_2^2}\right) > \sqrt{\frac{\delta c_{2+}\alpha\delta - 2\alpha^2\delta}{D_1D_2}} > 0 \qquad (113)$$

This shows that the necessary condition for the instability is that the diffusion length l_2 is longer than the diffusion length l_1; that is, $l_2 > l_1$. In consequence, in our discussed case the chemical component 1 tries to stabilize the system (the stability grows) while the chemical component 2 acts in the opposite way, trying to block the stability. So 1 is an activator and 2 is an inhibitor from the point of view of stability.

Note that these last results are not relevant in the case of a cancerous cell set, because according to the experiments of Lowenstein [xviii] the cancerous cells are not connected but are isolated (autonomic). In this case the diffusion of morphogens has no relevance.

CONCLUSION

In summary, unfortunately the idea of finding such a thermodynamic theory of chemical reactions which could be similar to the generalized Onsager's theory appears to be hopeless. In consequence neither the free enthalpy nor the dissipative potentials could be followed. Hence the offered advantages of these potentials are to construct such non-linear differential equations as were worked out by Poincare, Bendixon, Lyapunov, and others.

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Curriculum Vitae

Andras SZASZ

PERSONAL

1947. November 04. Born in Budapest, Hungary

STUDIES

1967-72	Studies at Eötvös University (Physics) [MS graduation, thesis: Positron annihilation]
1974	Doctor's degree at Eötvös University (Surface physics)
1983	Candidate of Mathematical and Physical Sciences of Russian Academy of Sciences, (Surface physics)
1983	Candidate of Physical Sciences of Hungarian Academy of Sciences (Surface physics)
1996	Habilitation at St.Istvan University (Hungary) (Biophysics)

ACADEMIC APPOINTMENTS

1972-1974:	Assistant professor at Eotvos University Budapest, Hungary
1974-1982:	Associate professor at Eotvos University Budapest, Hungary
1982-1985:	Head of Metalab and Laboratory of Surface Physics in Eotvos University
1985-1986:	Head of Dept. Solid State Physic, Eotvos University Budapest, Hungary
1986-1987:	Research fellow Scottish Surface Centre, Strathclyde University, Glasgow, UK
1988-2004:	Appointed visiting professor to Material Engineering Department of Strathclyde University, Glasgow, UK
1996-cont.	Professor at St. Istvan University, Gödöllö, Hungary, teaching biophysics to PhD students
2012-cont.	Visiting professor appointment, Pazmany Catholic University, teaching bioelectrodynamics to PhD students
2013-cont.	Visiting professor at Chiba University, Japan, teaching fractal physiology to PhD students

PRESENT ADMINISTRATIVE POSITIONS

2000-cont.	Head of Biotechnics Department in St. Istvan University, Faculty of Engineering. Hungary
2001-cont.	CSO of OncoTherm (www.oncotherm.de) (both the Hungarian and German Branches)

SCIENCE AWARD

2000   Dennis Gabor Award (Hungarian Academy of Science)

PUBLICATIONS

Author and co-author of about 700 publications (articles, conference contributions/abstracts), and co-author of eight books.