

On Thermodynamics, Variational Principles and Stability in Chemical Reaction Systems. * Towards a Rational Thermodynamics. IV

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In thermodynamics one would like to develop variational principles in order to test the stability or instability of non-equilibrium stationary states in analogy to the methods devised by Gibbs to study phase transitions. Gibbs used exergy (available energy) as a Lyapounov function, but exergy cannot be used away from thermodynamic equilibrium. Entropy production (or dissipation) is a Lyapounov function close to equilibrium, which means that stationary states in the Onsager region are always stable. However, entropy production (or surplus entropy production) cannot be used for stability test far from equilibrium.

Prigogine and Glansdorff have suggested another thermokinetic criterion. The idea is to investigate the sign of the quadratic form corresponding to the so-called excess entropy production. We formulate the P.G. criterion especially for homogeneous, chemical reaction systems and apply it rigorously to two chemical reaction models known to be able to show instabilities in the form of limit cycles: The Brusselator and the Oregonator. We conclude that the P.G. criterion is much more difficult to use than linear stability criteria. Simultaneously, the P.G. criterion is much less conclusive. It may be indeterminate in both stable and unstable regions. Therefore, the problem of devising thermodynamically founded stability criteria in nonequilibrium systems has still not been solved.

The systematic exploration of instabilities, catastrophes, bifurcations and chaos in a multitude of nonlinear systems of interest for physicists, chemists, biologists, engineers and many others has been much in fashion during the last decade. Refs. 1–9 are but a small selection from the flourishing literature. However, only a few researchers have attempted to interpret instabilities in terms of the language of thermodynamics. Most notably this angle of attack is characteristic of the “Brussels school of thermodynamics” under the leadership of Ilya Prigogine.

Prigogine and coworkers have focussed on the second variation of the entropy and its time derivative, since the principle of minimum entropy production is no longer valid in far-from-equilibrium situations. The time derivative of the second variation of entropy is named the *excess entropy production*. This quantity is a quadratic form in the deviations

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from the nonequilibrium stationary state considered. If the excess entropy production is positive definite, the stability of the stationary state is warranted. This will be the case in the Onsager-region of linear, irreversible thermodynamics close to equilibrium, where also the theorem of minimum entropy production holds. Furthermore, the excess entropy production will be positive definite in a certain extension beyond the Onsager region (the so-called "thermodynamic branch"). By the stability theorem of Lyapounov, we are still able to guarantee stability on the thermodynamic branch. However, at some distance from equilibrium, the stationary states need not to be stable anymore. Marginal states of stability may conveniently be found by linear stability theory (small perturbations) or by catastrophe or bifurcation theory (finite perturbations). Thermodynamically, there may be certain "directions" in which the deviations are "dangerous" in the sense that the excess entropy production becomes negative. Then, instability is *possible*, but the system needs not to be unstable.

It has some relevance to ask whether the thermodynamic (or rather thermokinetic) stability criterion of Glansdorff and Prigogine is really useful in the sense, that it is simpler to use than for example linear stability theory and that it furnishes us with reasonable, approximate stability boundaries in the space of system parameters. In order to investigate this question, we shall study two relatively simple model reaction systems which are known to be unstable under appropriate conditions: The Brusselator and the Oregonator. Both model systems may exhibit limit cycle behaviour, and the outbreak of this behaviour is correctly predicted by linear stability theory (Hopf bifurcation).

In order to motivate the reader to search for thermodynamic criteria of stability, we shall commence by resuming the results of a largely neglected, early paper of J.W. Gibbs,¹⁰ in which he uses the available energy (or exergy) of a system as a Lyapounov-function to explore the stability boundaries of the cusp catastrophe of liquid-gas phase transition. The analysis was made in the year 1873, 19 years before the pioneering work of Lyapounov¹¹ and some 100 years before the general exploration of the "elementary catastrophes" by René Thom.¹² Although the paper of Gibbs is concerned with the stability of equilibrium states, the concepts are useful also for the attempts to construct thermodynamic criteria of stability for nonequilibrium stationary states.

1. THE EXERGY OF GIBBS AS LYAPOUNOV FUNCTION

In the second paper on thermodynamics by J.W. Gibbs¹⁰ a method of geometrical representation of thermodynamic properties of substances by means of $E(S,V)$ surfaces is introduced. Such topics as the stability of a superheated liquid or an undercooled vapor are discussed in terms of the curvature of the energy surface and in terms of an available energy (exergy) function corresponding to a given temperature (T_0) and pressure (p_0). The function used by Gibbs is given by:

$$\Phi = E - T_0 S + p_0 V \quad (1)$$

Actually, this function may be seen as a generalization of the function named "Gibbs free energy". Notice, that whereas E, S and V are respectively the total energy, the total entropy and the total volume of the *system*, the system needs not to have the temperature T_0 and the pressure p_0 . The system may indeed possess many different temperatures and pressures. If the system is allowed to communicate entropy and volume (but not substance)

with a surrounding reservoir with temperature T_0 and pressure p_0 , then the maximum amount of work which can be done by system+surroundings (the conditional exergy) is given by:

$$Ex = \Phi - \Phi_{eq} \quad (2)$$

In eqn. (2), Φ_{eq} is the value of Gibbs' Φ -function, when the system is in internal equilibrium and also in external equilibrium with the surroundings, *i.e.* $T=T_0$ and $p=p_0$. For a discussion of the exergy concept in a broader context, see for example Refs. 13–15.

By means of the first and second law of thermodynamics, Gibbs showed that the function Φ never increases:

$$\partial\Phi/\partial t = \partial Ex/\partial t \leq 0 \quad (3)$$

If we consider a given amount of substance (some water, say), then we may plot E as a function of S and V in a three dimensional $E-S-V$ space. If the water is at rest (no whirlpools) and in internal equilibrium, we may draw the lowest possible energy surface: The *surface of dissipated energy* (Gibbs' expression). It is easy to find the temperature (T) and the pressure (p) on each point of the dissipated energy surface $E(S, V)$ by means of the osculating tangent plane at (S, V) . The slope of this plane in the S -direction is simply T , whereas the slope in the V -direction is $-p$. On the other hand, we may search for states on the $E(S, V)$ plane in *external* equilibrium with a reservoir (T_0, p_0) . We just draw the plane $P_0: (T_0 S - p_0 V)$ through $(S, V) = (0, 0)$ and seek the osculating planes on $E(S, V)$ which are parallel to P_0 . Then, the vertical distance between the surface of dissipated energy and the plane P_0 is the Φ -function given by eqn. (1).

We envisage different parts of the dissipated energy surface $E(S, V)$ which correspond to liquid water, vapor and ice, respectively. Coexisting phases are determined by having common osculating planes. Three coexisting phases fix completely the tangent plane (the triple point), whereas two coexisting phases have one degree of freedom, since the osculating plane "slides and rolls" on the two corresponding parts of the surface of dissipated energy. In this way a relation between p and T can be derived, *e.g.* the equation of Clapeyron. The lines connecting $E(S_1, V_1)$ of pure phase No. 1 and $E(S_2, V_2)$ of pure phase No. 2 may be regarded as mixtures of the two phases, and the relative quantities of the two phases can be found by the lever rule. Those "tie lines" trace off the true surface of dissipated energy in the case of mixtures of two phases.

Next, we envisage also a smooth transition between the two phases (liquid and gas, say). Such states will be metastable (superheated liquid, supercooled vapor) or hypothetical (impossible). Since such states are not in true equilibrium, they have to be situated *above* the surface of dissipated energy, so that energy may be drawn reversibly from the system at constant S and V . Fig. 1 shows a vertical, plane section through the surface of dissipated energy and through the smooth transition surface. The tie line connecting l_1 and v_1 coexisting at (T_0, p_0) lies as well in the surface of dissipated energy for liquid-vapor mixtures as in the osculating plane $E = T_0 S - p_0 V + \text{const}$.

Now, we take a "test plane" $P(T, p)$ tangent to the $E(S, V)$ surface at a given point (S, V) . The vertical distance between $E(S + \Delta S, V + \Delta V)$ of a neighboring point and the test plane is the conditional exergy of the neighboring state relative to an external reservoir at (T, p) . This exergy is seen to be positive, when the test plane is positioned in any points at the surface of

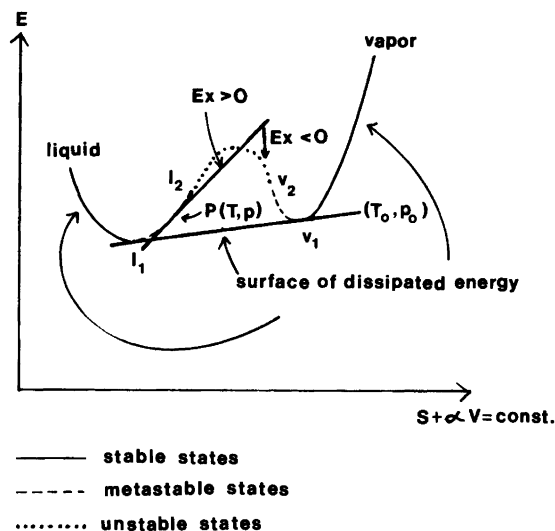


Fig. 1. A section through the $E(S, V)$ surface demonstrating how the curvature of this surface can be used to distinguish between stable, metastable and unstable states. The parameter α denotes a fixed ratio between S and V . It should not be confused with α in Figs. 2, 3 and 4.

dissipated energy for the stable, pure liquid or vapor. This is due to the upward curvature in all directions of the surface of dissipated energy. Since the exergy always decreases during irreversible processes the exergy will always diminish in value, reaching zero asymptotically. In this way stability is always assured.

When the liquid is superheated (dashed line between l_1 and l_2), stability can still be assured for *infinitesimal* perturbations by similar arguments. For *finite* perturbations (such as introducing a bubble of vapor), we need not have stability, however. The test plane drawn Fig. 1 clearly intersects the continuous transition surface. For perturbations above that size we have *negative* values of the exergy. Since the exergy still decreases by the second law of thermodynamics, the value of the exergy will now become more and more negative. The system will never revert to the point of departure with $Ex=0$. Thus, we have only *local stability* on the metastable surfaces. Finally, when the test plane is positioned somewhat on the dotted part of the curve (between l_2 and v_2) we see, that even infinitesimal fluctuations lead to negative exergies. The points on the part of the continuous transition surface with downward curvature in at least one direction are therefore *unstable*, and that part of the surface represents hypothetical states which are not physically possible.

When T_0 (and thereby p_0) is varied, the points l_1 and v_1 trace out curves in space. When these curves are projected on the $S-V$ plane, the *limits of absolute stability* appear. These curves at the same time denote coexisting liquid and vapor, meeting each other in the *critical point*. The projections of the points l_2 and v_2 on the $S-V$ plane similarly trace out the *limits of local stability*, sometimes called the *spinodal curves*. They too meet each other and the coexistence curves at the critical point, and all the curves have a common tangent in this point. The points l_2 and v_2 are characterized by saying, that one of the principal curvatures on the $E(S, V)$ surface changes sign from a positive value to a negative value in those points.

For further details about the geometry in the vicinity of the critical point (the cusp point in the nomenclature of Thom), the reader is referred to Gibbs. (For example he proves that the heat capacity at constant pressure is infinite in the critical point). The purpose of the present section has only been to point to an elegant paradigm given by the master of thermodynamics on how to treat stability problems. Are we able to devise similar variational methods for nonequilibrium systems?

2. LEAST DISSIPATION IN CHEMICAL REACTION SYSTEMS

Unfortunately, exergy (or entropy) cannot be used as Lyapounov function for non-equilibrium stationary states. The reason is, that there is already an exergy content (or entropy deviation) in the stationary state. This is not the case in thermodynamic equilibrium, where the exergy and its time derivative are both zero. In thermodynamic equilibrium, the exergy is a strict minimum, at least when we do not consider degrees of freedom along which reversible transformations occur. The minimum value of the exergy is zero by definition, and the time derivative of the exergy is everywhere negative except at equilibrium, where it is zero. Thus, by Lyapounov's theorem on asymptotic stability (Ref. 16, theorem 4.2) we are sure, that thermodynamic equilibrium is asymptotically stable. This fact should hardly come as a surprise, however.

In a non-equilibrium stationary state, where the thermodynamic variables are maintained constant through flow of energy or matter across the system, we might still define an exergy by momentarily "freezing" the flows in the system and bringing reversibly the system in internal and external equilibrium. This will be possible under the usual "local equilibrium" assumption. This exergy will always be positive outside equilibrium, but it will *not* be zero in a non-equilibrium stationary state. One might attempt to use the "excess exergy" $\Delta Ex = Ex - Ex_{st}$ (Ex_{st} for the exergy in the stationary state) as a Lyapounov function. The problem with this function, however, is that it is an uneven function of the deviations from the stationary state. In the direction towards equilibrium it is negative, whereas it is positive in the opposite direction. Thus, the excess exergy will never have a minimum in a non-equilibrium stationary state. However, there may exist quasi-equilibrium situations, where the (excess) exergy is minimum in certain rapidly relaxing directions.

Now we turn instead to the dissipation (or entropy production) as a candidate for a Lyapounov-function. Since the papers of Onsager^{17,18} we have known, that non-equilibrium stationary states close to equilibrium have least dissipation in comparison to neighboring instationary states, and that this theorem of least dissipation is equivalent to the validity of Onsager's reciprocal relations (ORR) for the transport coefficients. We shall see this here in the special case of chemical reactions between ideally dilute species. At the same time we shall demonstrate the existence of a potential function for the kinetics near equilibrium in the sense required by classical theory of catastrophes.¹² Given n dilute species we write for the dissipation pr. unit volume (Φ_1):

$$\Phi_1 = - \sum_{i=1}^n \dot{c}_i \cdot (\mu_i - \bar{\mu}_i) = - \sum_{i=1}^n RT \ln \left[\frac{c_i}{\bar{c}_i} \right] \cdot \dot{c}_i \quad (4)$$

A dot over a symbol means differentiation with respect to time, μ_i is the chemical potential of species i and $\bar{\mu}_i$ the same at equilibrium. Assuming small deviations from equilibrium ($\Delta c_i/\bar{c}_i \ll 1$) we have:

$$\Phi_1 \equiv -RT \sum_{i=1}^n \dot{c}_i \cdot \Delta c_i / \bar{c}_i \geq 0 \quad (5)$$

The equality sign corresponds to thermodynamic equilibrium. Now, according to conventional irreversible thermodynamics, the dissipation may be written as a product sum of fluxes and corresponding driving forces. Taking \dot{c}_i as the fluxes, the forces (X_i) close to equilibrium become:

$$X_i \equiv -RT \Delta c_i / \bar{c}_i \quad (i=1, n) \quad (6)$$

Close to equilibrium there will also be proportionality between fluxes and driving forces:

$$\dot{c}_i \equiv \sum_{j=1}^n L_{ij} \cdot X_j \quad (i=1, n) \quad (7)$$

Insertion of eqn. (7) into eqn. (5) yields the following expression for the dissipation close to equilibrium:

$$\Phi_1 = (RT)^2 \sum_{i=1}^n \sum_{j=1}^n L_{ij} \cdot \frac{\Delta c_i \cdot \Delta c_j}{\bar{c}_i \cdot \bar{c}_j} \geq 0 \quad (8)$$

If we differentiate the dissipation with respect to the deviation in the k 'th concentration we obtain:

$$\partial \Phi_1 / \partial \Delta c_k = \frac{2(RT)^2}{\bar{c}_k} \left[L_{kk} \frac{\Delta c_k}{\bar{c}_k} + \frac{1}{2} \sum_{i \neq k} (L_{ki} + L_{ik}) \frac{\Delta c_i}{\bar{c}_i} \right] \quad (9)$$

By comparison between eqn. (7) with $i=k$ and eqn. (9) we observe that if and only if

$$L_{ik} = L_{ki} \text{ (ORR) (all } i \neq k) \quad (10)$$

we have that:

$$\dot{c}_k = -\frac{\bar{c}_k}{2RT} \cdot (\partial \Phi_1 / \partial \Delta c_k) \quad (k=1, n) \quad (11)$$

Eqn. (11) may be written in a more symmetric form introducing the following variables:

$$x_k \equiv \frac{\Delta c_k}{\sqrt{\bar{c}_k / 2RT}} \quad (k=1, n) \quad (12)$$

Then we have:

$$\dot{x}_k = -\partial \Phi_1 / \partial x_k \quad (k=1, n) \quad (13)$$

Eqn. (13) shows that the dissipation (Φ_1) is a true *kinetic potential* in the sense of the word used in catastrophe theory. This will only be the case close to equilibrium, however, when ORR are valid. The physical content of ORR is, that all reactions are in detailed balance at equilibrium, which is easily seen by considering specific, kinetic examples. (For

example the triangular reaction considered by Onsager).

In any stationary state we have $\dot{x}_k=0$ for all k and eqn. (13) shows, that the dissipation has a stationary value with respect to variation in the variables x_k in such a state. The further properties of the dissipation in the neighborhood of the stationary state are then given by the Hessian matrix taken at the stationary point (minimum, maximum or saddle). However, since the Hessian matrix around thermodynamic equilibrium ($L_{ij}/(\bar{c}_i\bar{c}_j)$) is positive definite by the second law of thermodynamics, any local Hessian at a nearby stationary state will be the same. Therefore, Φ_1 and $\Delta\Phi_1=\Phi_1-\Phi_1^{st}$ will have strict minima in the stationary state, and the latter (the "excess dissipation") has a minimum value equal to zero. The time derivative of the excess dissipation is given by:

$$\partial\Delta\Phi_1/\partial t=\partial\Phi_1/\partial t=\sum_{i=1}^n \dot{x}_i \cdot (\partial\Phi_1/\partial x_i)=-\sum_{i=1}^n (\dot{x}_i)^2 \leq 0 \quad (14)$$

It is seen, that the existence of the kinetic potential secures that the time derivative is negative (or zero in the stationary point). In summary, the excess dissipation fulfils the requirement of Lyapounov's theorem, so that the asymptotic stability of near-to-equilibrium stationary states is warranted.

Further from equilibrium, when the dissipation cannot be written in the form of eqn. (8), it also ceases to be a kinetic potential for the reaction system. Therefore, the dissipation is no longer stationary in stationary states. (Notice the difference between the mathematical term "stationary" and the physical term "stationary state". A stationary state is a time-invariant state, whereas a function is "stationary" in minima, maxima or saddle points). Therefore, stationary states are no longer characterized by having minimal dissipation. Furthermore, the time derivative of the dissipation is not necessarily negative as in eqn. (14), since there is not necessarily any kinetic potential. At least the kinetic potential is *not* the dissipation. In special cases, however, there might be another kinetic potential, and by the same arguments as used in eqn. (14) we observe that the time derivative of any such kinetic potential always have to be ≤ 0 . Stability questions may then be answered by looking at the Hessian taken in the stationary state of the kinetic potential itself. Unfortunately, such situations are rare.

The time derivative of the dissipation may be divided into one part, which is due to the time variation of the fluxes ($J_i=\dot{c}_i$) and another part, which is due to the time variation of the forces ($X_i=-RT\ln(c_i/\bar{c}_i)$):

$$\partial_J\Phi_1/\partial t=\sum_i X_i \cdot \dot{c}_i=-RT\sum_i \ln(c_i/\bar{c}_i) \cdot \dot{c}_i \quad (15)$$

$$\partial_X\Phi_1/\partial t=\sum_i \dot{c}_i \cdot \dot{X}_i=-RT\sum_i \frac{(\dot{c}_i)^2}{c_i} \leq 0 \quad (16)$$

$$\partial\Phi_1/\partial t=\partial_J\Phi_1/\partial t+\partial_X\Phi_1/\partial t \quad (17)$$

It is seen that $\partial_X\Phi_1/\partial t$ is always negative except at the stationary state. This result is general and was proved as a "universal evolution criterion" in irreversible thermodynamics by Glansdorff and Prigogine^{1,19,20,21}. Only the usual thermodynamic stability criteria (together with the assumption of local equilibrium) are used in the proof.

Near to thermodynamic equilibrium, each of the two contributions to the dissipation can be shown to be one half of the total dissipation. In that case, eqn. (16) may be used as a

Lyapounov stability criterion. Far from equilibrium, however, $d_X\Phi_1$ cannot normally be written as an exact differential $d\Phi$ of a function of the concentrations only. This would require that:

$$\frac{\partial}{\partial c_j} \left(\frac{\dot{c}_i}{c_i} \right) = \frac{\partial}{\partial c_i} \left(\frac{\dot{c}_j}{c_j} \right) \quad (\text{all } i \neq j) \quad (18)$$

Eqn. (18) imposes a severe restriction on the form of the rate laws. It can be shown, however, that an integrating denominator $\theta(c_1, c_2, \dots, c_n)$ exists, if $d_X\Phi_1=0$ has a solution. The latter will always be true in the case of two variables.²² Then, we have:

$$d\Phi = \frac{d_X\Phi_1}{\theta} \quad (19)$$

In eqn. (19), $d\Phi$ is now an exact differential. Since Φ may be taken as Φ_1 and θ as 1/2 close to equilibrium, there will also be a certain nonlinear region in which θ is positive and $\partial\Phi/\partial t \leq 0$. In such cases, the excess function $\Delta\Phi = \Phi - \Phi_{st}$ might be proposed as a candidate for a Lyapounov test function. However, as we have seen we must also require, that $\Delta\Phi$ has a strict minimum in the stationary state in order to have absolute stability.

3. THE PRIGOGINE-GLANSDORFF STABILITY CRITERION

Another Lyapounov test function has been considered by Glansdorff, Prigogine and Nicolis.^{1,2} The function chosen was the second variation of the entropy. In our case, however, it is more convenient to take the second variation of Gibbs' free energy, which is the appropriate exergy function at constant temperature and pressure. Let g be the free energy density (J/m^3). By a Taylor expansion of g around a stationary state we obtain:

$$g = g_{st} + \delta g + (1/2)\delta^2 g \quad (20)$$

We cannot use δg as a Lyapounov test function away from thermodynamic equilibrium, since it changes sign with the direction of the fluctuation from the stationary state. However, it can be shown that $\delta^2 g$ is always positive, because of the stability conditions for local equilibrium. Thus, in the simple case of ideally dilute species (corresponding to reaction kinetics with constant rate constants) we have:

$$\delta^2 g = \sum_i \sum_j \frac{\partial^2 g}{\partial c_i \partial c_j} \delta c_i \delta c_j = \sum_j \sum_i \left(\frac{\partial \mu_i}{\partial c_j} \right)_{st} \delta c_i \delta c_j \quad (21a)$$

$$\delta^2 g \cong RT \sum_i \sum_j \left(\frac{\partial \ln c_i}{\partial c_j} \right)_{st} \cdot \delta c_i \delta c_j = RT \sum_i \frac{(\delta c_i)^2}{c_i^{st}} \geq 0 \quad (21b)$$

Eqn. (21a) is generally valid, and we have used the fact that $\delta g = \sum_i \mu_i \delta c_i$ at constant T and p . Eqn. (21b) is valid for ideally dilute species, in which case the Hessian matrix is diagonal. Since $\delta^2 g$ has a strict minimum in the stationary state, it may be used as a Lyapounov test function. We then have to distinguish between the following cases:

$$\frac{\partial \delta^2 g}{\partial t} \leq 0 \quad (= \text{only for all } \delta c_i = 0) \quad (22a)$$

$$\frac{\partial \delta^2 g}{\partial t} \leq 0 \quad (= \text{also for some } \delta c_i \neq 0) \quad (22b)$$

$$\frac{\partial \delta^2 g}{\partial t} \geq 0 \quad (= \text{only for all } \delta c_i = 0) \quad (22c)$$

In the first case, the stationary state is asymptotically stable. This means that all deviations from the stationary state vanish asymptotically with time. The case (22b) corresponds to Lyapounov's theorem of stability (Ref. 16, theorem 4.1). Stability means, that any solution starting inside a sphere around the origin (all $\delta c_i = 0$) will remain inside another sphere (maybe with a larger radius) at all subsequent times. The case (22c) is a special case of Chetayev's instability theorem (Ref. 16, theorem 4.3) which is a kind of anti-Lyapounov theorem securing instability. Finally, we also have the indeterminate case:

$$\frac{\partial \delta^2 g}{\partial t} \begin{matrix} \geq 0 \\ < 0 \end{matrix} \quad (22d)$$

In the case (22 d), the time derivative of $\delta^2 g$ is a quadratic form, which is neither convex nor concave, *i.e.* a saddle. In that case, the stationary point may be stable or unstable.

For ideally dilute species we obtain by differentiation of eqn. (21b) with respect to time:

$$\partial \delta^2 g / \partial t = 2RT \sum_i \frac{\delta c_i \cdot \delta \dot{c}_i}{c_i^{st}} \quad (23)$$

When we linearize all the kinetic rate equations around the stationary state we obtain

$$\delta \dot{c}_i = \sum_j A_{ij} \delta c_j \quad (\text{all } i) \quad (24)$$

where A_{ij} is a kinetic matrix. Inserting eqn. (24) into eqn. (23) we obtain:

$$\partial \delta^2 g / \partial t = 2RT \sum_i \sum_j \frac{A_{ij}}{c_i^{st}} \delta c_i \delta c_j \quad (25)$$

Thus, we only have to investigate the quadratic form with the following matrix:

$$B_{ij} \equiv \frac{A_{ij}}{c_i^{st}} \quad (26)$$

In the further investigation it is an advantage to transform the matrix of the quadratic form into a symmetric matrix:

$$B_{ij}^* = \frac{1}{2} \{B_{ij} + B_{ji}\} \quad (27)$$

If the B^* -matrix is *negative definite* (22a), then the stationary is surely asymptotically stable. If it is *negative semi-definite* (22b), then the stationary state is stable in the sense of

Lyapounov. However, there might appear a stable limit cycle surrounding the stationary point (or even a strange attractor). Thus, stability in the Lyapounov sense is *not* equivalent with the stability concept as used by the Brussels school, since the latter refers to the outbreak of a limit cycle as an instability.

When the B^* -matrix is *positive definite* (22c), the stationary state is surely unstable, and we can neither have a stable point attractor, a limit cycle nor a stable torus attractor or a stable strange attractor (chaos), at least not in the linearized neighbourhood of the stationary state. In the *indefinite* case (22d) we cannot safely induce anything about the stability.

4. A SPECIFIC EXAMPLE: THE BRUSSELATOR

In the subsequent sections we shall give some examples concerning the use of the function

$$\Phi_2 \equiv \delta^2 g \quad (28)$$

as a Lyapounov test function in chemical reaction systems. The simplest model chemical system known to be able to produce limit cycle behaviour is the so-called "Brusselator" invented by Prigogine and Lefever in 1968.²³ Here we shall consider a slightly generalized version of this model (with reversible chemical reactions):



The species A, B, D and E appear in "large" concentrations which may be considered as constant parameters in the model. Only the species X and Y need to be followed with regard to concentration vs. time. In *dimensionless variables* the differential equations for those concentrations read as follows:

$$\frac{dx}{d\tau} = \bar{A} - (\bar{B}+1)x + \bar{D}y + x^2y - \frac{x^3}{K_3} \quad (30a)$$

$$\frac{dy}{d\tau} = \bar{B}x - \bar{D} \cdot y - x^2y + \frac{x^3}{K_3} \quad (30b)$$

$$\tau \equiv (k_4 + k_{-1}) \cdot t \quad (\text{dimensionless time}) \quad (31)$$

$$x \equiv \sqrt{\frac{k_3}{k_4+k_{-1}}} \cdot [X] \quad (\text{dimensionless conc.}) \quad (32)$$

$$y \equiv \sqrt{\frac{k_3}{k_4+k_{-1}}} \cdot [Y] \quad (\text{dimensionless conc.}) \quad (33)$$

$$\bar{A} \equiv \sqrt{\frac{k_3}{k_4+k_{-1}}} \cdot \frac{k_1[A]+k_{-4}[E]}{k_4+k_{-1}} \quad (\text{dimensionless conc.}) \quad (34)$$

$$\bar{B} \equiv \frac{k_2}{k_4+k_{-1}} \cdot [B] \quad (\text{dimensionless conc.}) \quad (35)$$

$$\bar{D} \equiv \frac{k_{-2}}{k_4+k_{-1}} \cdot [D] \quad (\text{dimensionless conc.}) \quad (36)$$

$$K_3 \equiv k_3/k_{-3} \quad (\text{equilibrium constant}) \quad (37)$$

The stationary point is easily determined by taking zero time derivatives in eqns. (30a) and (30b):

$$(x_{st}, y_{st}) = \left(\bar{A}, \frac{\bar{B}}{\bar{A}} + \frac{\bar{A}}{K_3} \right) \quad (38)$$

Linearizing the kinetic equations around the stationary point by taking the Jacobian matrix around that point we obtain the following kinetic matrix:

$$A = \begin{bmatrix} \bar{B}(2\alpha-1) - \beta(3-2\alpha) - 1 & \bar{A}^2/\alpha \\ -\bar{B}(2\alpha-1) + \beta(3-2\alpha) & -\bar{A}^2/\alpha \end{bmatrix} \quad (39)$$

$$\alpha \equiv \frac{\bar{A}^2}{\bar{A}^2 + \bar{D}} \quad (0 < \alpha \leq 1) \quad (40)$$

$$\beta \equiv \frac{\bar{A}^2}{K_3} \quad (\beta \geq 0) \quad (41)$$

For the original Brusselator (with all reactions completely irreversible) we have $\alpha=1$ and $\beta=0$. The eigenvalues of the kinetic matrix are found as roots in the second order equation:

$$\lambda^2 - [(2\alpha-1) \cdot \bar{B} - 1 - (\bar{A}^2/\alpha) - \beta(3-2\alpha)]\lambda + (\bar{A}^2/\alpha) = 0 \quad (42)$$

The *marginal* states of stability (according to linear stability theory) are found for the real parts of one of the roots equal to zero. It is easy to see that no physically meaningful solution exists to eqn. (42) with $\text{Re}(\lambda) = \text{Im}(\lambda) = 0$. Thus, there are no stationary, marginal states. To find the oscillatory, marginal states we put $\lambda = i\omega$ in eqn. (42) and obtain:

$$\omega = \frac{\bar{A}}{\sqrt{\alpha}} \quad (43)$$

$$\bar{B}_{cr}(\text{kinetic}) = \frac{1 + \frac{\bar{A}^2}{\alpha} + \beta(3-2\alpha)}{2\alpha-1} \quad (44)$$

The angular frequency given by eqn. (43) is the frequency at the outbreak of the limit cycle (when \bar{B} passes \bar{B}_{cr}) according to the Hopf bifurcation theorem. According to linear stability theory, the stationary state is *asymptotically stable*, when the following condition is met:

$$\text{Re}(\lambda_1) = \text{Re}(\lambda_2) = \frac{1}{2} \cdot \left[(2\alpha-1) \cdot \bar{B} - 1 - \frac{\bar{A}^2}{\alpha} - \beta(3-2\alpha) \right] < 0$$

The condition may be reformulated as:

$$\bar{B} \begin{cases} < \bar{B}_{cr}(\text{kinetic}), & 0.5 < \alpha \leq 1 \\ > \bar{B}_{cr}(\text{kinetic}), & 0 < \alpha < 0.5 \end{cases} \quad \text{(Asymptotic stability)} \quad (45a)$$

$$(45b)$$

In the case (45b), $\bar{B}_{cr}(\text{kinetic}) < 0$ and since \bar{B} is always positive, the inequality (45b) will always be satisfied. Thus, the stationary state is *always* asymptotically stable for $0 < \alpha < 0.5$.

Now, let us turn to the Glansdorff-Prigogine criterion. The matrix of the quadratic form of $\partial\Phi_2/\partial\tau$ close to a stationary state is given by eqns. (26), (27) and (39):

$$B_{11}^* = \frac{\bar{B}(2\alpha-1) - \beta(3-2\alpha) - 1}{\bar{A}} \quad (46a)$$

$$B_{22}^* = \frac{-1}{\alpha^2} \cdot \frac{\bar{A}^3}{\bar{B} + \beta} \quad (46b)$$

$$B_{12}^* = B_{21}^* = \frac{\bar{A}}{2\alpha} \left[1 + \frac{\beta(3-2\alpha) - \bar{B} \cdot (2\alpha-1)}{\bar{B} + \beta} \right] \quad (46c)$$

According to Ref. 22 section 10.16 it is possible to show, that a quadratic form is surely negative definite, if the matrix of the quadratic form is made symmetric and if all the *principal minors* of the matrix are negative as well as the full determinant of the matrix. In the present case (2x2 matrix) we have the following conditions:

$$\Delta_1 \equiv \left. \begin{matrix} B_{11}^* < 0 \\ B_{22}^* < 0 \end{matrix} \right\} \text{diagonal conditions} \quad (47a)$$

$$(47b)$$

$$\Delta_2 \equiv B_{11}^* \cdot B_{22}^* - (B_{12}^*)^2 < 0 \quad \text{cross condition} \quad (47c)$$

The inequality (47b) is always fulfilled, but the diagonal condition (47a) may be violated. The physical reason is that species *X* participates in the *autocatalytic* reaction No. 3 in the scheme (29).

We obtain:

$$\tilde{B} \begin{cases} < \frac{\beta(3-2\alpha)+1}{2\alpha-1} \equiv \tilde{B}_{cr}(\text{diagonal}), 0.5 < \alpha \leq 1 & (48a) \\ > \tilde{B}_{cr}(\text{diagonal}) < 0 & 0 < \alpha < 0.5 & (48b) \end{cases}$$

The case (48b) always leads to fulfilment, so that the only violation of the inequality (47a) possible is one for which $\tilde{B} > \tilde{B}_{cr} > 0$ and $0.5 < \alpha \leq 1$. In that case we have:

$$\tilde{B} > \tilde{B}_{cr}(\text{diagonal}) = \tilde{B}_{cr}(\text{kinetic}) - \frac{\tilde{A}^2}{\alpha} \cdot \frac{1}{2\alpha-1} < B_{cr}(\text{kinetic}) \quad (49)$$

(instability thermodynamically possible, $0.5 < \alpha \leq 1$)

The instability is not thermodynamically sure before also the inequality (47c) is violated. The stationary state may be unstable, when the inequality (49) is fulfilled. We know, however, that the stationary state will not be unstable before $\tilde{B} > \tilde{B}_{cr}(\text{kinetic})$. Thus, there is a zone between $\tilde{B}_{cr}(\text{diagonal})$ and $\tilde{B}_{cr}(\text{kinetic})$, where the Glansdorff-Prigogine criterion is indeterminate.

It can be shown (Ref. 22, section 10.16) that it is possible to perform a variable transformation

$$\begin{pmatrix} \delta x \\ \delta y \end{pmatrix} = Q \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} \quad (50)$$

transforming the quadratic form considered to a diagonal form (congruent transformation):

$$\Delta_1 \cdot \xi_1^2 + (\Delta_2/\Delta_1) \cdot \xi_2^2 \quad (51)$$

Therefore, we now consider the condition (47c). Introducing the variable

$$b \equiv \tilde{B} + \beta \quad (52)$$

instead of \tilde{B} in the matrix elements B_{ij}^* , the inequality (47c) may be written as:

$$\left(\frac{b}{A}\right)^2 \cdot \Delta_2 = -b^2 + \frac{1+2\alpha\beta}{\alpha^2} b - (\beta/\alpha)^2 < 0 \quad (53)$$

Therefore, we have:

$$b_1 = \frac{1}{2\alpha^2} \left[1 + 2\alpha\beta - \sqrt{1 + 4\alpha\beta} \right] \quad (54)$$

$$b_2 = \frac{1}{2\alpha^2} \left[1 + 2\alpha\beta + \sqrt{1 + 4\alpha\beta} \right] \quad (55)$$

$$\Delta_2 < 0 \text{ for } \bar{B} + \beta < b_1 \text{ or } \bar{B} + \beta > b_2 \quad (56)$$

$$\Delta_2 \geq 0 \text{ for } b_1 \leq \bar{B} + \beta \leq b_2 \quad (57)$$

In other words, Δ_2 is zero when $\bar{B} = \bar{B}_{cr,1}^{xy}$ or $\bar{B}_{cr,2}^{xy}$ and Δ_2 is greater than zero between those critical values:

$$\Delta_2 \geq 0 \text{ for } \bar{B}_{cr,1}^{xy} \leq \bar{B} \leq \bar{B}_{cr,2}^{xy} \quad (58)$$

$$\bar{B}_{cr,1}^{xy} \equiv \frac{1}{2\alpha^2} \left[1 - \sqrt{1 + 4\alpha\beta} \right] + \frac{1-\alpha}{\alpha} \cdot \beta \quad (59)$$

$$\bar{B}_{cr,2}^{xy} = \bar{B}_{cr,1}^{xy} + \frac{1}{\alpha^2} \sqrt{1 + 4\alpha\beta} \quad (60)$$

Expanding the square root to the third power in $\alpha\beta$ we obtain for small values of $\alpha\beta$:

$$\bar{B}_{cr,1}^{xy} \equiv -\beta + \beta^2 - 2 \cdot \beta^3 \cdot \alpha \quad (\alpha\beta \ll 1) \quad (61)$$

It is seen that $\bar{B}_{cr,1}^{xy}(\alpha=0)$ is negative for $0 < \beta < 1$ and positive for $\beta > 1$, whereas $\bar{B}_{cr,1}^{xy}(\alpha=1)$ is always negative for $\beta > 0$. For $\beta=0$, $\bar{B}_{cr,1}^{xy}$ is equal to zero for all values of α .

The nature of the quadratic form $\partial^2 g / \partial t^2$ is now by the expression for its diagonal form (51) determined by the changes of sign of the determinants Δ_1 and Δ_2 . On Figs. 2, 3 and 4 we have shown the various stability limits as a function of α for $\beta=0, 1$ and 2. Only in the case where Δ_1 is negative and Δ_2 is positive will the quadratic form be negative definite, and the stability of the stationary state is guaranteed by the theorem of asymptotic stability of Lyapounov. In the other areas of the diagrams, the Prigogine-Glansdorff criterion is *indeterminate* with one "dangerous direction" and one "stable direction". However, the system needs not to follow along the dangerous direction. This depends on the solutions to the differential equations. Therefore, nothing can be said about the stability or instability of the system in those areas. If both Δ_1 and Δ_2 were found to be positive, *instability* would be predicted safely (at least locally) by means of Chetayev's instability theorem. No such areas are found for the generalized Brusselator, however.

The diagonal condition of stability $\Delta_1 < 0$ leads to $\bar{B} < \bar{B}_{cr}^{xx} \equiv \bar{B}_{cr}(\text{diagonal})$ given by the inequality (48a). This condition corresponds to the linear stability condition as \bar{A} tends towards zero. Thus, the diagonal condition misses the influence of the \bar{A} parameter on the stability of the system. In short, the Prigogine-Glansdorff criterion of stability yields a rather conservative (cautious) estimate of the stability region. It predicts *possibility* of instability in cases where no instability exists. Fig. 4 shows that there may even appear regions deeply inside the region of guaranteed asymptotic stability, wherein the P.G. criterion become indeterminate (lower left corner).

5. ANOTHER EXAMPLE: THE OREGONATOR

We shall briefly investigate still another example, namely the so-called Oregonator proposed by Field and Noyes (from Oregon) in order to model some of the features of the oscillating

Belousov-Zhabotinskii reaction.²⁴ The model has three variable concentrations. Using the quasi-stationarity assumption for one of the variable concentrations (HBrO_2), the model is in effect reduced to the case of a Thomian "cusp catastrophe" with the concentration of Ce^{4+} and a model parameter (q) as control variables and the Br^- concentration as "jump variable". Thus, the quasi-stationarity condition provides a cusp surface on which the phase point of the system slides and jumps, because of the slow variation of the Ce^{4+} concentration governed by two dimensional differential equations in the Br^- and the Ce^{4+} concentrations. For further details about this approximation, the reader is referred to the treatments by Tyson²⁵ or by Sørensen.²⁶ In the present study we shall stay with the three dimensional Oregonator, however, in order to provide an example with one dimension more than possessed by the Brusselator.

The Oregonator contains a "stoichiometric factor" f , for which a plausible experimental value seems to be 0.5 (when defined as in Ref. 26). We therefore fix the value of f to this value. The model is then described by the following three differential equations:

$$dx/d\tau = \frac{1}{\varepsilon} \cdot (x+y-xy-qx^2) \quad (62a)$$

$$dy/d\tau = \frac{1}{q} \cdot z-y-xy \quad (62b)$$

$$dz/d\tau = \frac{q}{p} \cdot x - \frac{1}{p} \cdot z \quad (62c)$$

The variables x, y and z are dimensionless concentrations of HBrO_2 , Br^- and Ce^{4+} , respectively. the dimensionless time is given by τ , and p, q and ε are model parameters determined by the rate constants and the concentration of BrO_3^- .

The stationary solutions to eqns. (62a-c) are readily found to be given by:

$$(x_{st}, y_{st}, z_{st}) = \left(x_{st}, \frac{x_{st}}{1+x_{st}}, q \cdot x_{st} \right) \quad (63a)$$

$$x_{st} = \frac{1}{2} \left\{ \sqrt{\frac{8}{q} + 1} - 1 \right\} \quad (63b)$$

The Jacobian matrix in the stationary point may be written as:

$$\mathbf{A} = \begin{bmatrix} \frac{1}{\varepsilon} \cdot \left(\frac{1}{1+x_{st}} - 2qx_{st} \right) & -\frac{x_{st}}{\varepsilon} & 0 \\ -\frac{x_{st}}{1+x_{st}} & -1-x_{st} & \frac{1}{q} \\ \frac{q}{p} & 0 & -\frac{1}{p} \end{bmatrix} \quad (64)$$

Table 1. Values of x_{st} , A_{11} and the coefficients of the characteristic equation for the Oregonator with $f=0.5$, $\varepsilon=2 \cdot 10^{-4}$ and $p=310$ and various values of q .

q	x_{st}	A_{11}	C_0	C_1	C_2	$C_2C_1 - C_0$
$8.4 \cdot 10^{-6}$	487.5	-30.71	+64.48	-2.417 · 10 ⁶	+5.192 · 10 ²	-1.2550 · 10 ⁹
10^{-5}	446.7	-33.50	+64.48	-2.214 · 10 ⁶	+4.812 · 10 ²	-1.0652 · 10 ⁹
10^{-4}	140.92	-105.69	+64.40	-6.847 · 10 ⁵	+2.476 · 10 ²	-1.6953 · 10 ⁸
10^{-3}	44.22	-331.7	+64.16	-2.012 · 10 ⁵	+3.769 · 10 ²	-7.585 · 10 ⁷
0.01	13.651	-1023.8	+63.42	-4.859 · 10 ⁴	+1.0385 · 10 ³	-5.046 · 10 ⁷
0.1	4.000	-3.000 · 10 ³	+61.29	-9.903 · 10 ¹	+3.005 · 10 ³	-2.976 · 10 ⁶
0.10999125	3.793	-3.129 · 10 ³	+61.15	+1.963 · 10 ⁻²	+3.134 · 10 ³	+0.3711 · 10 ⁹
0.11	3.7932	-3.129 · 10 ³	+61.15	+0.8256 · 10 ⁰	+3.134 · 10 ³	+2.526 · 10 ³
0.12	3.613	-3.252 · 10 ³	+61.02	+8.617 · 10 ²	+3.256 · 10 ³	+2.806 · 10 ⁶
0.3	2.130	-4.792 · 10 ³	+59.36	+7.768 · 10 ³	+4.795 · 10 ³	+3.725 · 10 ⁷
1.0	1.000	-7.500 · 10 ³	+56.45	+1.252 · 10 ⁴	+7.502 · 10 ³	+9.396 · 10 ⁷
10	0.17082	-1.2812 · 10 ⁴	+50.74	+1.492 · 10 ⁴	+1.2813 · 10 ⁴	+1.9112 · 10 ⁸
100	1.9615 · 10 ⁻²	-1.4712 · 10 ⁴	+48.70	+1.5046 · 10 ⁴	+1.4712 · 10 ⁴	+2.214 · 10 ⁸
10 ⁶	2.000 · 10 ⁻⁶	-1.5000 · 10 ⁴	+48.39	+1.5048 · 10 ⁴	+1.5001 · 10 ⁴	+2.257 · 10 ⁸

The characteristic equation is given by:

$$\lambda^3 + C_2 \cdot \lambda^2 + C_1 \lambda + C_0 = 0 \quad (65)$$

$$C_0 = \frac{1}{p} \left[\frac{1}{\varepsilon} \cdot \frac{x_{st}}{1+x_{st}} - (1+x_{st}) \cdot A_{11} \right] \quad (66a)$$

$$C_1 = \frac{1+x_{st}}{p} - \frac{x_{st}^2}{\varepsilon(1+x_{st})} - \left(1+x_{st} + \frac{1}{p} \right) \cdot A_{11} \quad (66b)$$

$$C_2 = \left(1+x_{st} + \frac{1}{p} \right) - A_{11} \quad (66c)$$

In eqns. (66a-c), A_{11} is element 11 of the Jacobian matrix (64). The conditions for having (linear) stability with all real parts of the λ -roots negative can now be found from the Hurwitz criterion. For a characteristic equation of third degree, the criterion amounts to the following three inequalities (see for example Ref. 27, chapter 9, section 4):

$$\text{Condition I: } C_2 > 0 \quad (67a)$$

$$\text{Condition II: } C_2 C_1 - C_0 > 0 \quad (67b)$$

$$\text{Condition III: } C_0 \cdot (C_2 C_1 - C_0) > 0 \quad (67c)$$

Table 1 shows the dependence of x_{st} , A_{11} , C_0 , C_1 , C_2 and $C_2 C_1 - C_0$ on the parameter q , fixing the other parameters in the Oregonator to the following values:

$$\varepsilon = 2 \cdot 10^{-4} \quad p = 310 \quad (68)$$

The above values seem plausible from known values of the individual rate constants, but the value $q = 8.4 \cdot 10^{-6}$ in the original Oregonator was pure guesswork, and comparison with experimental oscillations seems to indicate, that q should be many orders of magnitude higher (see Refs. 25 and 26).

Table 1 shows that C_0 and C_2 are always positive, so condition I is never violated. Conditions II and III are violated simultaneously at $q_{cr} = 0.10999125$. (The sensitivity in the determination of the root q_{cr} is great. At the mentioned value of q_{cr} , $C_2 C_1 - C_0$ is found to be +0.3711. At $q = 0.10999122$ one finds $C_2 C_1 - C_0$ to be -8.279). The result of the linear stability analysis for the parameter choice (68) is therefore given by:

$$\text{Linear } \begin{cases} \text{stability} & q > q_{cr} = 0.10999125 \\ \text{instability} & q < q_{cr} \end{cases} \quad (69)$$

Turning now to the Prigogine-Glansdorff criterion, we may form the B -matrix by the rule given by eqn. (26). After symmetrisation we have:

Table 2. Values of Δ_2 and Δ_3 as a function of q for the Oregonator with $f=0.5$, $\varepsilon=2 \cdot 10^{-4}$ and $p=310$.

q	Δ_2	Δ_3
$8.4 \cdot 10^{-6}$	-4969	+10.132
10^{-5}	-4966	+11.043
10^{-4}	-4893	+33.98
10^{-3}	-4653	+98.17
10^{-2}	-3821	+219.7
$7.625 \cdot 10^{-2}$	-1076.3	+1.305 $\cdot 10^{-2}$
$7.626 \cdot 10^{-2}$	-1076.3	-4.667 $\cdot 10^{-2}$
0.1	-312.5	-150.00
0.11010	-2.839 $\cdot 10^{-2}$	-217.8
0.11011	+2.780 $\cdot 10^{-1}$	-217.8
1.0	+25000	-7500

$$B_{11}^* = A_{11}/x_{st} \quad B_{22}^* = -(1+x_{st})^2/x_{st} \quad B_{33}^* = -\frac{1}{pqx_{st}} \quad (70a)$$

$$B_{12}^* = -\frac{1}{2} \cdot \left(1 + \frac{1}{\varepsilon}\right) = B_{21}^* \quad (70b)$$

$$B_{13}^* = \frac{1}{2 \cdot p \cdot x_{st}} = B_{31}^* \quad (70c)$$

$$B_{23}^* = \frac{1+x_{st}}{2 \cdot q \cdot x_{st}} = B_{32}^* \quad (70d)$$

The principal minors are given by:

$$\Delta_1 = B_{11}^* = A_{11}/x_{st} < 0 \text{ for all values of } q \text{ (Table 1)} \quad (71)$$

$$\Delta_2 = B_{11}^* B_{22}^* - (B_{12}^*)^2 = -A_{11} \cdot \left(\frac{1+x_{st}}{x_{st}}\right)^2 - \frac{1}{\varepsilon} \quad (72)$$

$$pq \left(\frac{x_{st}}{1+x_{st}}\right)^2 \cdot \Delta_3 = \frac{A_{11}}{x_{st}} + \frac{1}{\varepsilon} \frac{x_{st}^{-1}}{(1+x_{st})^2} \quad (73)$$

Table 3. Stable and indeterminate regions for the Oregonator with $f=0.5$, $\varepsilon=2 \cdot 10^{-4}$ and $p=310$ from the Prigogine-Glansdorff criterion.

	q	<0.07625	<q	<0.11010	<q
Δ_1	neg.		neg.		neg.
Δ_2	neg.		neg.	0	pos.
Δ_3	pos.	0	neg.		neg.
Δ_2/Δ_1	pos.		pos.	0	neg.
Δ_3/Δ_2	neg.	0	pos.	$\pm \infty$	neg.
P.G. crit.		indeterminate		stability secured	

By a congruent transformation, the quadratic form may be transformed to the following form:

$$\Delta_1 \cdot \xi_1^2 + (\Delta_2/\Delta_1) \cdot \xi_2^2 + (\Delta_3/\Delta_2) \cdot \xi_3^2 \quad (74)$$

For the parameter choice (68), Δ_2 and Δ_3 are shown as functions of q in Table 2. Two critical q -values are found, where Δ_2 respectively Δ_3 change sign. Those values are:

$$q_{cr}^{(2)} = 0.11010 \quad q_{cr}^{(3)} = 0.07625 \quad (75)$$

Table 3 shows the changes of sign of the principal minors and of the coefficients in the diagonalised quadratic form (74). It appears that we have:

$$\begin{aligned} q > q_{cr}^{(2)} = 0.11010 & \quad \text{Stability secured by P.G. criterion} \\ q < q_{cr}^{(2)} = 0.11010 & \quad \text{P.G. criterion indeterminate} \end{aligned} \quad (76)$$

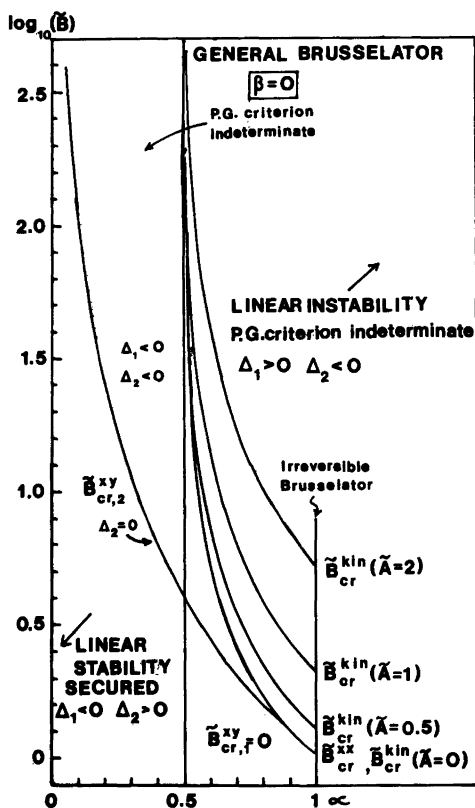


Fig. 2. Critical values of \bar{B} for the general Brusselator for $\beta=0$. \bar{B}_{cr}^{kin} is determined by linear stability analysis for various values of \bar{A} . \bar{B}_{cr}^{xx} is determined by Prigogine-Glansdorff's criterion (diagonal fluctuations in the x -concentration). \bar{B}_{cr}^{xy} are similarly determined from the P.G. criterion allowing for cross fluctuations (simultaneous fluctuations in x and y). The abscissa parameter (α) is the parameter defined by eqn. (40).

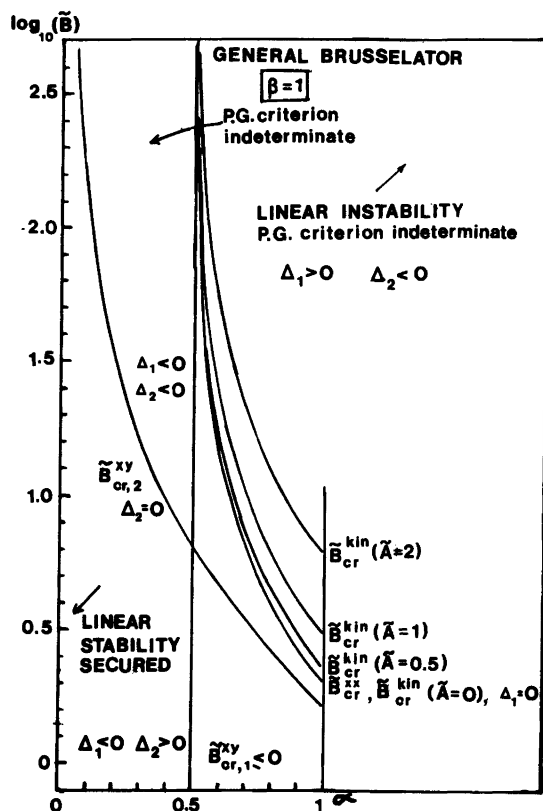


Fig. 3. Critical values of \tilde{B} for the general Brusselator for $\beta=1$. See text below Fig. 2.

When q is less than 0.10999125, the Oregonator is linearly unstable. In this specific case, the P.G. criterion of stability is only slightly more "conservative" than the linear stability criterion. This should be contrasted to the situation found for the general Brusselator. (The difference between $q_{cr}(\text{linear})$ and $q_{cr}^{(2)}$ seems to be real and not just due to numeric error. Also there seems not to be any theoretical reason for the identity of the two critical values).

6. CONCLUSION

The Prigogine-Glansdorff criterion yields a *sufficient* condition for stability. However, the stability limits may be rather conservative in comparison with the linear stability criterion (Figs. 2,3 and 4). The P.G. criterion may be *indeterminate* in *linearly unstable* situations (Figs. 2,3,4 and section 5.). The P.G. criterion may also be *indeterminate* in *stable* situations, not only near the linear stability boundary (Figs. 2,3 and 4) but also in regions deeply buried inside the linearly stable region (Fig. 4). Since the criterion of Glansdorff and Prigogine is *more complicated* to use than linear stability analysis in two-, three- and higher dimensional systems, and since linearisation is involved anyway, there seems to be no real advance in

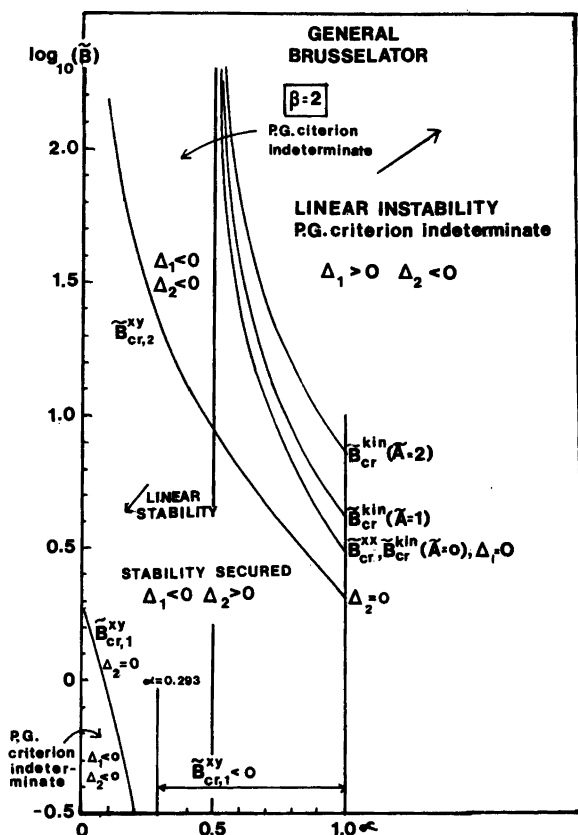


Fig. 4. Critical values of \bar{B} for the general Brusselator for $\beta=2$. See text below Fig. 2.

using their thermokinetic criterion instead of linear stability analysis. Those remarks should apply *a fortiori* for more complex systems (e.g. thermo-hydrodynamical systems, interfacial systems, crystallisation), where the Prigogine-Glansdorff criterion (in some generalized form) has been applied during the course of time.

In a recent paper,²⁸ Rastogi and Shabb have recommended the use of the Prigogine-Glansdorff criterion for the investigation of the stability of nonequilibrium, homogeneous stationary states in chemical reaction systems. However, the examples investigated by Rastogi and Shabb are rather trivial, since they may be grouped in two classes: Either, there is only one reaction kinetic degree of freedom (auto-inhibited reaction, autocatalytic reaction), or only the "diagonal conditions" of the P.G. criterion are investigated (monomolecular triangular reaction, Lotka-Volterra model). This is far from sufficient in systems with more than one dimension. For example, Fig. 2,3 and 4 clearly shows, that the P.G. stability boundary for the Brusselator depends on whether one assumes $\delta Y=0$ or one considers general variations ($\delta X, \delta Y$). Also, section 5 shows, that the Oregonator is not unstable at all, if one considers diagonal fluctuations only. In an earlier paper, Keizer and Fox²⁹ have expressed a similar criticism against the P.G. criterion. The arguments of these authors are somewhat unclear to me, however. Firstly, they show some region, where the

simple, reversible and autocatalytic reaction $X + Y \rightleftharpoons 2X$ should have a possibility for being unstable according to the P.G. criterion, but is not in the sense of Laypounov. However, the P.G. criterion is seemingly applied on a closed and instationary system, which is against the intention of the P.G. principle. (In the present context it is obvious, that linear stability and P.G. stability are completely coincident when there is only one element in the kinetic A -matrix and one element in the B -matrix of the P.G. principle). Secondly, Keizer and Fox analyze the Brusselator, but consider only fluctuations in X and not simultaneous fluctuations in X and Y as done in the present paper. In summary, it is quite safe to conclude, that thermokinetic criteria of stability and instability for nonequilibrium stationary states analogous to the exergy method of Gibbs (Fig. 1) have still not been successfully developed.

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