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# Chemical Reaction Rate from a (Semiempirical) Dynamical Point of View

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**Abstract:** The aim of the present paper is to check - or better to confirm - the mathematical validity of chemical reaction rate, faced as a set of differential equations. Firstly one - way elementary reactions are considered, in the most general case. Secondly the same thing is done with two-way (opposing) elementary reactions. At this stage, we show that the two - way reaction, as we mean it, is compatible with the reduction of the total Gibbs energy as expected in every natural process. As an example of a two way elementary reaction of a completely solvable problem we give the hydrolysis of sucrose to glucose and fructose, where the “inversion” of sucrose is examined not only with the initial linear reaction of “Wilhelmy” (1850), but also with the two way nonlinear reaction introduced. Finally the validity of the mathematical model is checked for more complex cases such as the Michaelis-Menten mechanism or reactions in solution, where it is found that the two cases, apparently are four - dimensional while in reality are two - dimensional (after the “subtraction” of the constraints of “motion”) and naturally cannot exhibit chaotic behavior. In all cases the treatment is not one-hundred-percent mathematically austere but it has also arbitrary although reasonable hypotheses.

**Keywords:** Chemical Reaction Rate, Physical Chemistry, Sucrose, Chaos

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## 1. Introduction

For closed chemical systems of reactants and products when they are kept at constant temperature and/or constant pressure, there is experimental evidence that their components tend to constant values as time goes to infinity. [1-4]. Once this is observed, at least for simple systems of reactions, one faces the challenge to try to prove the above fact from the general equations that can be written for the reactions in question. The idea is that this behavior is inherent in the equations and the way they are written.

However, as we shall see, one can find the number of degrees of freedom (i.e., the number of independent functions describing the system) that a system of reactions, or a single reaction is associated with, and when this is  $n = 1$  or  $n = 2$ , it is straightforward to prove the above property (i.e., that  $\lim_{t \rightarrow \infty} c_i(t) = c_{i\infty} = \text{const.} \geq 0$ ). This asymptotic behavior is also supported by the solutions of the chemical reaction rate differential equations, either real or hypothetical, that can

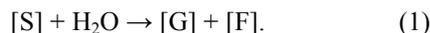
be found in various systems. [1-4].

Moreover, the constants  $c_{i\infty}$  are non-negative and, as expected, this can be proved, by proving that  $c_i(t) \geq 0$  for every  $t \geq 0$  from the system of differential equations, provided that  $c_i(0) \geq 0$ . When the number of degrees of freedom is  $n \geq 3$  (i.e., an autonomous system of three differential equations), the dynamics may not necessarily lead, in principle, to constant asymptotic behavior of the concentrations as  $t \rightarrow +\infty$ , since now oscillations of the reactants and/or products as well as possible chaotic behavior may appear.

However, we believe that for closed systems, even in the case  $n \geq 3$ , the asymptotic behavior tends to constant values, although we do not have the relevant mathematical machinery to prove this by the set of the differential equations of the chemical reactions.

An example of a completely solvable problem of a two-

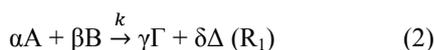
way elementary reaction is the hydrolysis of sucrose forming glucose and fructose:



This reaction which can take place in an enzyme or acid environment is usually taken to be an one-way reaction starting from sucrose and is detected by using standard techniques of polarimetry, since all the species S, G, and F, are optically active with sucrose and glucose being dextrorotatory and fructose levorotatory. [3, 4]. The above two-way elementary reaction, can be shown that it is actually one-way elementary reaction when the initial concentration of sucrose is small enough. However, for larger values of sucrose initial concentration, the inverse reaction probably becomes important too, and it has to be taken into account. In this case a "method" is given for the calculation of both rate constants  $k_1$  and  $k_{-1}$ . Finally, the point of the inversion of sucrose is examined and it is found that for large initial concentration of sucrose the phenomenon may not hold, as it is expected.

## 2. One-way Elementary Reactions

Suppose that we have the one-way elementary reaction



where  $[A] = a$ ,  $[B] = b$ ,  $[\Gamma] = c$ ,  $[\Delta] = d$ , and  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are integers whose greatest common divisor is 1. Defining the molecularity of  $(R_1)$  as the number of molecules coming together to give a successful conversion to products then this is  $\alpha + \beta$ . Furthermore, if we suppose that the order of the reaction is  $p$  with respect to  $[A]$  and  $q$  with respect to  $[B]$ , then we have the following set of differential equations describing the formation of products and the consumption of reactants

$$-\frac{1}{\alpha} \frac{da}{dt} = -\frac{1}{\beta} \frac{db}{dt} = \frac{1}{\gamma} \frac{dc}{dt} = \frac{1}{\delta} \frac{dd}{dt} = k a^p b^q \quad (3)$$

Obviously the overall order is  $p + q$ . We also suppose that  $p \geq 1$  and  $q \geq 1$  or if  $p = 0$  then  $q \geq 1$  and vice versa, an assumption the importance of which will become clear later. The quantities  $a$ ,  $b$ ,  $c$ ,  $d$  are functions of time while  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $k$ ,  $p$ ,  $q$ , are parameters of the system of differential equations (3).

Supposing that the concentration functions  $a(t)$ ,  $b(t)$ ,  $c(t)$ ,  $d(t)$  are continuous (or even more, differentiable) functions of time, we expect the solutions of the system of Eqs. (3) to have the following properties

$$a(t) = a(t_c) + (t - t_c)\dot{a}(t_c) + \dots + \frac{1}{n!} (t - t_c)^n \dot{a}^{(n)}(t_c) + \dots \quad (10)$$

We further suppose that the radius of convergence  $r$  of the series is greater than  $t_c$ :  $r > t_c$ . Using equation (9) and its derivatives and then calculating them at  $t_c$  we have:

$$a(t_c) = \dot{a}(t_c) = \ddot{a}(t_c) = \dots = a^{(n)}(t_c) = 0. \quad (11)$$

This implies that  $a(t) = 0$  inside the radius of convergence, which in turn is a contradiction since  $a(0) = a_0 > 0$  and  $a(t)$  has been considered to be continuous.

- (1)  $a(t)$ ,  $b(t)$ ,  $c(t)$ ,  $d(t)$  to be always positive definite for every  $t \geq 0$ .
- (2) Starting with  $a_0 > 0$ ,  $b_0 > 0$ ,  $c_0 = 0$ ,  $d_0 = 0$ , where  $a_0 \equiv a(t = 0)$ , etc.,  $a$  and  $b$  will be decreasing and  $c$ ,  $d$  increasing functions of time.
- (3)  $\lim_{t \rightarrow +\infty} a(t) = a_\infty$  for  $a(t)$ ,  $b(t)$ ,  $c(t)$ ,  $d(t)$  to reach constant values as  $t \rightarrow +\infty$ . More precisely we expect that if  $\frac{a_0}{\alpha} < \frac{b_0}{\beta}$  then  $\lim_{t \rightarrow +\infty} a(t) = a_\infty = 0$  and  $\lim_{t \rightarrow +\infty} b(t) = b_\infty = b_0 - \frac{\beta}{\alpha} a_0$  or the reverse.

In what follows we will try to prove properties  $P_1$ ,  $P_2$  and  $P_3$  from the system of differential equations (3). The "generalization" to other cases, for instance when only one reactant is present, or more than two, or something similar for the products, follows immediately following the same steps.

The relationship  $-\frac{1}{\alpha} \frac{da}{dt} = -\frac{1}{\beta} \frac{db}{dt}$  when integrated gives

$$b = \frac{\beta}{\alpha} (a - a_0) + b_0, \quad (4)$$

where  $a_0 = a(t = 0)$  and  $b_0 = b(t = 0)$ . Eq. (3) can be written in a similar way as

$$b = \frac{\beta}{\alpha} a + \sigma_0, \quad (5)$$

where

$$\sigma_0 = b_0 - \frac{\beta}{\alpha} a_0. \quad (6)$$

Now without loss of generality we can assume that

$$\frac{a_0}{\alpha} < \frac{b_0}{\beta}, \quad (7)$$

From which we have

$$\sigma_0 > 0. \quad (8)$$

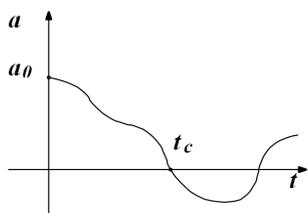
Substituting Eqs. (5) and (6) into Eq. (3), we get

$$\frac{da}{dt} = -k \alpha a^p \left( \sigma_0 + \frac{\beta}{\alpha} a \right)^q, \quad (9)$$

where we recall that  $p \geq 1$  and  $q \geq 1$ . We will firstly prove that if  $a_0 > 0$  then  $a(t) > 0$  for every  $t \geq 0$ . Suppose that there is a  $t_c \in (0, +\infty)$  such that  $a(t_c) = a_c = 0$  (Figure 1). Next we consider the Taylor expansion of the solution  $a(t)$  around  $t_c$  as follows assuming that the function is analytic with respect to time:

The above result means that the solution  $a(t)$  cannot have roots (like at  $t_c$ ) and since the solution is continuous (and since  $a_0 > 0$ ) it must be always positive definite ( $a(t) > 0$  for all times). Secondly we will prove that  $a(t)$  is a decreasing function of its argument (time):

From Eq. (9) and the fact that  $a(t) > 0$  as well as that  $\sigma_0 > 0$ , we have that  $\frac{da}{dt} < 0$  which



**Figure 1.** A hypothetical curve, for the time evolution of a reactant “a”, which reaches the value zero at a finite time  $t_c$  (Impossible!).

means exactly that  $a(t)$  is a decreasing function of time. From a well-known theorem of analysis we know that if a function is bounded from below and decreasing then it converges to a constant value. Finally we will prove that if  $\frac{a_0}{\alpha} < \frac{b_0}{\beta}$  then  $\lim_{t \rightarrow +\infty} a(t) = 0$ . Equation (9) can be written as follows:

$$\frac{da}{dt} = -k\alpha a^p b^q. \quad (12)$$

For  $t \rightarrow +\infty$  we have that

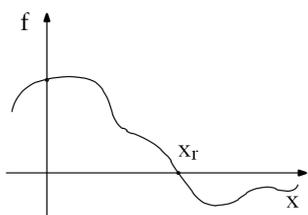
$$\lim_{t \rightarrow +\infty} a(t) = a_{\infty} = \text{constant}$$

$$\lim_{t \rightarrow +\infty} b(t) = b_{\infty} = \text{constant}$$

$$\lim_{t \rightarrow +\infty} \left(\frac{da}{dt}\right) = 0.$$

Substituting these equations into Eq. (12) we have

$$a_{\infty}^p b_{\infty}^q = 0 \Rightarrow a_{\infty} = 0 \text{ or } b_{\infty} = 0. \quad (13)$$



**Figure 2.** The function  $f(x)$  which displays a single root  $x_r$  ( $f(x_r) = 0$ ) with negative slope  $f'(x_r) < 0$ .

From Eqs. (4)-(6) we have

$$b_{\infty} = \frac{\beta}{\alpha} a_{\infty} + b_0 - \frac{\beta}{\alpha} a_0 \quad (14)$$

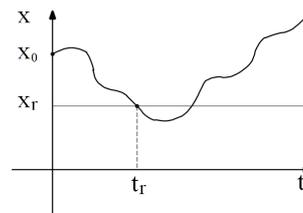
If we suppose  $a_{\infty} = 0$  then  $b_{\infty} = b_0 - \frac{\beta}{\alpha} a_0 > 0$ , while if we suppose  $b_{\infty} = 0$  then  $a_{\infty} = a_0 - \frac{\alpha}{\beta} b_0 < 0$ , which is in contradiction since  $a(t) > 0$  for every  $t \geq 0$ . Therefore, if  $\frac{a_0}{\alpha} < \frac{b_0}{\beta} \Rightarrow a_{\infty} = 0$  and  $b_{\infty} = b_0 - \frac{\beta}{\alpha} a_0 > 0$ .

### 3. Two-Way (Opposing) Elementary Reactions

Before we begin the presentation of this subject we prove first the following Lemma:

Lemma:

Suppose the initial value problem  $\dot{x} = f(x)$ ,  $x \in \mathbb{R}$  and  $x(t = 0) = x_0$ . Suppose further that the function  $f(x)$  has a single root  $x_r$  for which  $f'(x_r) < 0$ . Then  $\lim_{t \rightarrow +\infty} x(t) = x_r$  (Figure 2). Proof: Let us suppose that a probable scenario for the solution  $x(t)$  is the following (Figure 3)



**Figure 3.** A hypothetical curve  $x(t)$  for the time evolution of the differential equation  $\dot{x} = f(x)$ ,  $x(0) = x_0 > x_r > 0$ . The scenario displayed in the figure is impossible.

We will prove that this scenario is impossible, i.e., we will prove, the most rigorously we can, there is no  $t_r$  such that  $x(t_r) = x_r$ . Let us take the Taylor expansion of the solution  $x(t)$  around  $t_r$ , that is

$$x(t) = x(t_r) + (t - t_r)\dot{x}(t_r) + \frac{1}{2}\ddot{x}(t_r)(t - t_r)^2 + \dots, \quad (15)$$

and the only assumption made is that such an expansion exists and the radius of convergence  $r_1$  is  $r_1 \geq t_r$ . Since the differential equation is  $\dot{x} = f(x)$ , we have

$$\dot{x}(t_r) = f(x(t_r)) = f(x_r) = 0.$$

Furthermore,  $\ddot{x} = f'(x)\dot{x} = f(x)f'(x)$ , which implies that  $\ddot{x}(t_r) = f(x_r)f'(x_r) = 0$ . Provided that the derivatives of the function  $f(x)$  are not infinite at  $x = x_r$ , we have finally

$$x^{(n)}(t_r) = 0, \text{ for every } n \geq 1. \quad (16)$$

Equations (15) and (16) can be combined to yield  $x(t) = x_r$  for every  $t \geq 0$ , which is in contradiction since  $x(0) = x_0 > x_r$  in the general case and  $x(t)$  is a continuous function of  $t$ . In other words: Let us suppose that  $x_0 > x_r$ .  $x(t)$  cannot intersect  $x = x_r$  and this means that it is bounded from below since it must be connected smoothly with the initial value  $x(0) = x_0 > x_r$  (requirement of continuity). Similar results can be obtained when  $x_0 < x_r$ , at this time the solution is bounded from above.

Now we return to the case  $x_0 > x_r$ . Given that  $f(x_r) = 0$  and  $f'(x_r) < 0$  (since  $x_r$  is a single root), we have that  $f(x) > 0$  when  $x < x_r$  and  $f(x) < 0$  when  $x > x_r$ . We have shown above that when  $x_0 > x_r$  we are in the region  $x > x_r$  which by itself implies that  $\dot{x} = f(x) < 0$  and this in turn means that  $x(t)$  is a decreasing function of time.

So totally we have  $x(t)$  bounded from below and decreasing ( $x_0 > x_r$ ). By a well-known theorem of analysis this implies that the function tends to a constant value  $x_{\infty}$  for which  $x_0 \geq x_{\infty} \geq x_r$ . Furthermore, we have  $\dot{x} = f(x)$ , and since  $\lim_{t \rightarrow \infty} [x(t)] = x_{\infty} = \text{constant} \Rightarrow \lim_{t \rightarrow \infty} [\dot{x}(t)] = 0$ . Now we have

$$\lim_{t \rightarrow \infty} [\dot{x}(t)] = \lim_{t \rightarrow \infty} [f(x(t))] \Rightarrow 0 = f(x_{\infty}),$$

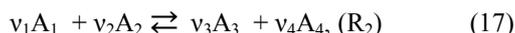
since

$$\lim_{t \rightarrow \infty} f(x(t)) = f(\lim_{t \rightarrow \infty} [x(t)]) = f(x_{\infty}) = 0$$

continuous.) Finally  $f(x_{\infty}) = 0$  and  $f(x_r) = 0$  (single root)  $\Rightarrow x_{\infty} = x_r$  and the theorem is proved.

We return now to the problem of a two way opposing reaction. We suppose that we have a reaction of two “reactants” and two “products”: (the generalization to one or

more than two species is straightforward)



where the  $v_i$ 's,  $i = 1, 2, 3, 4$  are integers whose greatest common divisor is unity (1). Obviously,  $v_i \geq 1$ .

When an experiment of chemistry takes place such as the reaction Eq. (R<sub>2</sub>) at constant temperature and pressure then the change of the total Gibbs energy (of the whole system) is negative ( $\delta G < 0$ ). Then we can write

$$\delta G = \mu_1 \delta n_1 + \mu_2 \delta n_2 + \mu_3 \delta n_3 + \mu_4 \delta n_4, \quad (18)$$

where  $\delta n_i$  is the change in moles of the [particular]  $i$ -th species and  $\mu_i$  the corresponding chemical potential. Taking into account the stoichiometry of the reaction Eq. (R<sub>2</sub>) we have

$$-\frac{\delta n_1}{v_1} = -\frac{\delta n_2}{v_2} = +\frac{\delta n_3}{v_3} = +\frac{\delta n_4}{v_4} = \delta \xi. \quad (19)$$

Introducing the earlier equation into Eq. (18) we get

$$\delta G = (\Delta_r G) \delta \xi, \quad (20)$$

and

$$\Delta_r G = v_3 \mu_3 + v_4 \mu_4 - v_1 \mu_1 - v_2 \mu_2, \quad (21)$$

where  $\Delta_r G$  is the reaction Gibbs energy change. From Eqs. (20) and (21), one can deduce that if  $d\xi > 0$  there is a displacement of R<sub>2</sub> to the right (from "reactants" to "products") while the opposite happens when  $d\xi < 0$ .

Now the crucial point is that for both cases  $\delta G < 0$ , the change in the Gibbs energy is negative (since both processes can be natural processes) and from Eq. (20) we have that

$\Delta_r G < 0$ : displacement to the "products" (right).

$\Delta_r G > 0$ : displacement to the "reactants" (left).

Using the usual expressions of  $\mu_i$ 's, at least for gases, we have that

$$\Delta_r G = \Delta_r G_0 + RT \ln Q_c, \quad (22)$$

where  $Q_c = \frac{c_3^{v_3} c_4^{v_4}}{c_1^{v_1} c_2^{v_2}}$ ,  $\Delta_r G$  is the change of the reaction Gibbs energy, and  $\Delta_r G_0$  is the change in the reaction Gibbs energy at the same temperature and  $P^0 = 1$  atm. Obviously when equilibrium is achieved then  $\Delta_r G = 0$  and  $Q_c = K_c$ , where  $K_c = k_1/k_{-1}$ , which implies that

$$0 = \Delta_r G_0 + RT \ln K_c. \quad (23)$$

Combining Eqs. (22) and (23), we get

$$\Delta_r G = RT \ln \frac{Q_c}{K_c}. \quad (24)$$

$$\frac{1}{v_1} \frac{d_z}{dt} = k_1 (c_{10} - z)^{v_1} (c_{20} - \frac{v_2}{v_1} z)^{v_2} - k_{-1} (c_{30} + \frac{v_3}{v_1} z)^{v_3} (c_{40} + \frac{v_4}{v_1} z)^{v_4}, \quad (31)$$

or equivalently

$$\dot{z} = f(z), \quad (32)$$

where

From the earlier equation it is deduced that if

$Q_c < K_c \Rightarrow$  displacement to the products (right).

$Q_c > K_c \Rightarrow$  displacement to the reactants (left).

We will now prove that the above results are reproduced exactly by the reaction rate of

R<sub>2</sub>:

$$-\frac{1}{v_1} \frac{dc_1}{dt} = -\frac{1}{v_2} \frac{dc_2}{dt} = \frac{1}{v_3} \frac{dc_3}{dt} = \frac{1}{v_4} \frac{dc_4}{dt} = k_1 c_1^{v_1} c_2^{v_2} - k_{-1} c_3^{v_3} c_4^{v_4}, \quad (25)$$

from which we have

$$\text{"reaction rate"} = k_1 c_1^{v_1} c_2^{v_2} (1 - \frac{Q_c}{K_c}), \quad (26)$$

where  $Q_c = \frac{c_3^{v_3} c_4^{v_4}}{c_1^{v_1} c_2^{v_2}}$ , and  $K_c = \frac{k_1}{k_{-1}}$ . We now suppose that  $Q_c < K_c$  then the left-hand-side of Eq. (26) is positive which implies that  $c_1$  and  $c_2$  decrease while  $c_3$  and  $c_4$  increase giving a displacement of the equation R<sub>2</sub> to the right. The reverse happens if  $Q_c > K_c$ .

One more result is worth noticing, i.e., if  $Q_c \ll K_c$ , then obviously the reaction not only "turns" to the right but it also becomes one-way reaction.

Returning to the reaction (R<sub>2</sub>) and considering the dynamics of the related differential Eqs. (R<sub>2</sub>) and (25) we expect that its solutions will be differentiable (and therefore continuous) and furthermore:

- (i)  $c_i$ 's:  $i=1,2,3,4$  positive definite
- (ii) they tend to constant values  $c_{i\infty}$  as  $t \rightarrow \infty$  ( $\lim_{t \rightarrow \infty} c_i(t) = c_{i\infty}$ ), and
- (iii) they satisfy the following relation  $K_c = \frac{c_{3\infty}^{v_3} c_{4\infty}^{v_4}}{c_{1\infty}^{v_1} c_{2\infty}^{v_2}}$ .

Supposing again reaction (R<sub>2</sub>) having initial concentrations  $c_{i0}$ ,  $i = 1, 2, 3, 4$ . Let us suppose also that without loss of generality  $Q_{c0} = \frac{c_{30}^{v_3} c_{40}^{v_4}}{c_{10}^{v_1} c_{20}^{v_2}} < K_c$ . Since  $Q_{c0} < K_c$ ,  $c_1$  and  $c_2$  will, at least initially, decrease and  $c_3$  and  $c_4$  will increase. If at time  $t$  the concentration of  $c_i(t)$  has become lesser to an amount  $z(t)$ , then we have

$$c_1(t) = c_{10} - z(t), \quad (27)$$

$$c_2(t) = c_{20} - \frac{v_2}{v_1} z(t), \quad (28)$$

$$c_3(t) = c_{30} + \frac{v_3}{v_1} z(t), \quad (29)$$

$$c_4(t) = c_{40} + \frac{v_4}{v_1} z(t), \quad (30)$$

Substituting Eqs. (27)-(30) into Eq. (25) we get

$$f(z) = v_1 k_1 (c_{10} - z) v_1 (c_{20} - \frac{v_2}{v_1} z)^{v_2} - v_1 k_{-1} (c_{30} + \frac{v_3}{v_1} z)^{v_3} (c_{40} + \frac{v_4}{v_1} z)^{v_4} \quad (33)$$

Writing

$$z_m = \min \{c_{10}, \frac{v_1}{v_2} c_{20}\}, \quad (34)$$

$$z_M = \min \{\frac{v_1}{v_3} c_{30}, \frac{v_1}{v_4} c_{40}\}, \quad (35)$$

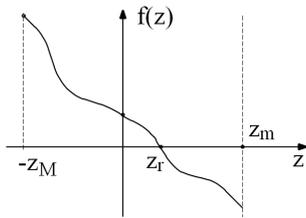
we limit our analysis in the interval  $-z_M \leq z \leq z_m$  and we observe that in this interval all the parentheses of Eq. (33) are greater or equal to zero.

We also have

$$f(z_m) = -v_1 k_{-1} (c_{30} + \frac{v_3}{v_1} z_m)^{v_3} (c_{40} + \frac{v_4}{v_1} z_m)^{v_4} < 0, \quad (36)$$

$$f(-z_M) = v_1 k_1 (c_{10} - z_M) v_1 (c_{20} - \frac{v_2}{v_1} z_M)^{v_2} > 0, \quad (37)$$

$$\begin{aligned} f(0) &= v_1 k_1 C_{10}^{v_1} C_{20}^{v_2} - v_1 k_{-1} C_{30}^{v_3} C_{40}^{v_4} \\ &= v_1 k_1 C_{10}^{v_1} C_{20}^{v_2} (1 - \frac{Qc_0}{Kc}) > 0 \end{aligned} \quad (38)$$



**Figure 4.** An approximate graph of the function  $f(z)$  given by the reactions Eqs. (33) to (35).

Taking the derivative of the function  $f(z)$  with respect to  $z$  we have

$$\begin{aligned} f'(z) &= -k_1 v_1^2 (c_{10} + z) v_1 - 1 (c_{20} - \frac{v_2}{v_1} z)^{v_2} \\ &\quad - k_1 v_2^2 (c_{10} + z) v_1 (c_{20} - \frac{v_2}{v_1} z)^{v_2 - 1} \\ &\quad - k_{-1} v_3^2 (c_{30} + \frac{v_3}{v_1} z)^{v_3 - 1} (c_{40} + \frac{v_4}{v_1} z)^{v_4} \\ &\quad - k_{-1} v_4^2 (c_{30} + \frac{v_3}{v_1} z)^{v_3} (c_{40} + \frac{v_4}{v_1} z)^{v_4 - 1} \end{aligned} \quad (39)$$

we have obviously

$$f'(z) < 0, \text{ for every } z \in (-z_M, z_m). \quad (40)$$

Combining the information of Eqs. (36)-(40) we have the following portrait of the function (shown in Figure 4) Since  $f(0) > 0$  and  $f(z_m) < 0$ , as well  $f'(z) < 0$ , combining Bolzano's and Rolle's theorems we find that there is a unique root of  $f(z)$  such that:  $0 < z_r < z_m$  for which we also have  $f'(z_r) < 0$ . Now applying the proved lemma, we find that the function  $f(z)$  has the property  $0 < z < z_r$  and  $\lim_{t \rightarrow +\infty} z(t) = z_r = \text{const.}$  Now we have

$$c_{1\infty} = \lim_{t \rightarrow +\infty} c_1(t) = c_{10} - z_r = \text{const.}$$

$$c_{2\infty} = \lim_{t \rightarrow +\infty} c_2(t) = c_{20} - \frac{v_2}{v_1} z_r = \text{const.}$$

$$c_{3\infty} = \lim_{t \rightarrow +\infty} c_3(t) = c_{30} + \frac{v_3}{v_1} z_r = \text{const.}$$

$$c_{4\infty} = \lim_{t \rightarrow +\infty} c_4(t) = c_{40} + \frac{v_4}{v_1} z_r = \text{const.}$$

So far we have proved that the final concentrations of  $c_i$ 's are constant. We still have to prove that they are positive definite. Obviously we have

$$0 \leq z(t) \leq z_r < z_m$$

from which it is straightforward that  $c_3(t) = c_{30} + \frac{v_3}{v_1} z(t) > 0$  and similarly for  $c_4(t)$ .  $c_1$  and  $c_2$  are a little bit more problematic:

$$\begin{aligned} 0 \leq z(t) \leq z_r < z_m &\Rightarrow 0 \geq -z(t) \geq -z_r > -z_m \\ &\Rightarrow c_1(t) = c_{10} - z(t) \geq c_{10} - z_r > c_{10} - z_m \geq 0 \end{aligned}$$

The last inequality hold since  $z_m = \min \{c_{10}, \frac{v_1}{v_2} c_{20}\} \rightarrow c_1(t) > 0$  for all  $t \geq 0$ . Similarly,

$$\begin{aligned} c_2(t) &= c_{20} - \frac{v_2}{v_1} z(t) \geq c_{20} - \frac{v_2}{v_1} z_r \\ &> c_{20} - \frac{v_2}{v_1} z_m = \frac{v_2}{v_1} (\frac{v_1}{v_2} c_{20} - z_m) \geq 0 \\ &\rightarrow c_2(t) > 0 \end{aligned} \quad (41)$$

for all  $t \geq 0$ . As  $t \rightarrow \infty$  then

$$\lim_{t \rightarrow +\infty} Q_c = K_c \Rightarrow K_c = \frac{(c_{30} + \frac{v_3}{v_1} z_r)^{v_3} (c_{40} + \frac{v_4}{v_1} z_r)^{v_4}}{(c_{10} - z_r)^{v_1} (c_{20} - \frac{v_2}{v_1} z_r)^{v_2}},$$

which determines the exact unique value of  $z_r$  and consequently of  $c_i$ 's.

In the case where  $Qc_0 > Kc$ , then  $z_r$  is negative and the whole analysis is very similar to the first case. If  $Qc_0 = Kc$  then  $z_r = 0$  and the "system" does not evolve at all.

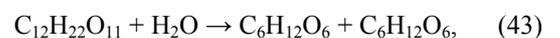
One more thing has to be mentioned. If instead of Eq. (25) we have the more general equation

$$-\frac{1}{v_1} \frac{dc_1}{dt} = -\frac{1}{v_2} \frac{dc_2}{dt} = \frac{1}{v_3} \frac{dc_3}{dt} = \frac{1}{v_4} \frac{dc_4}{dt} = k_1 C_1^{\rho_1} C_2^{\rho_2} - k_{-1} C_3^{\rho_3} C_4^{\rho_4}, \quad (42)$$

where now the  $\rho_i$ 's are real positive numbers as well, then a similar analysis can be carried out and similar conclusions can come forward although now the link to "simple" chemistry has been lost.

## 4. The Hydrolysis of Sucrose [9-11]

"The first known example of a detailed study of the progress of a chemical reaction was the work of Wilhelmy in 1850 on the hydrolysis of sucrose in acid solution using a polarimeter". In this work it was found that the reaction rate is proportional to the first power of the sucrose concentration: 3



or



However the condition of the experiment is such that, initially, only sucrose is present, while there is almost complete absence of G and F ( $[S](t=0) = \sigma_0 > 0$ ,  $[G](t=0) = 0$ ,  $[F](t=0) = 0$ ). Therefore it is doubtful, if one finds the simple law, that the reaction rate is proportional to the first power of the sucrose concentration, when the reaction has proceeded further and the inverse reaction

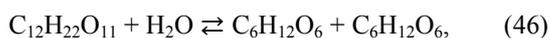


starts to take place.

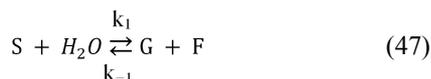
In the analysis that follows we consider the hydrolysis of the sucrose as a two-way elementary reaction and show that one gets essentially the same results as if it were a one-way reaction provided that the sucrose initial concentration  $\sigma_0$  is much less than  $k_1/(4k_{-1})$ , i.e.,  $\sigma_0 \ll \frac{k_1}{4k_{-1}}$ , where  $k_1$  and  $k_{-1}$  are the forward and the inverse rate constants, respectively. The concentrations that satisfy this inequality are not of negligible measure since one expects in general  $k_{-1}$  to be much less than  $k_1$  (expressed in appropriate units) and therefore  $\sigma_0$  can get moderately large values, although  $\sigma_0 \ll \frac{k_1}{4k_{-1}}$  at the same time. At the end of the present analysis a "method" to determine the constants  $k_1$  and  $k_{-1}$  and their links to the experiment, as we imagine it, is given, while at the same time one can easily recognize that the concentrations  $[S](t)$ ,  $[G](t)$ ,  $[F](t)$ , expressed as functions of time, retain the properties (i)-(iii) of Section III.

#### The mathematical model

We consider the hydrolysis of sucrose to glucose and fructose as a two-way reaction:



or symbolically



One can easily derive the following rate equations

$$\frac{d[S]}{dt} = -k_1 [S] + k_{-1} [G][F], \quad (48)$$

$$\frac{d[G]}{dt} = \frac{d[F]}{dt} = +k_1 [S] - k_{-1} [G][F], \quad (49)$$

with the initial conditions, appropriate for only sucrose present initially:

$$[S](0) = \sigma_0 > 0, [G](0) = [F](0) = 0. \quad (50)$$

From Eqs. (48) and (49) with the conditions Eqs. (50) we can easily get the following constraints:

$$[G](t) = [F](t), \quad (51)$$

$$[S](t) + [G](t) = \sigma_0, \quad (52)$$

$$[S](t) + [F](t) = \sigma_0. \quad (53)$$

It is important to notice that the constraints Eqs. (51)-(53)

are also valid in the case where the rate equations are first order in sucrose concentration ( $k_{-1} = 0$ ). Substituting the constraints Eqs. (51)-(53) into Eqs. (48) and (49) and solving the resulting differential equations we have

$$[F](t) = [G](t) = \rho_2 \frac{(1 - e^{-\sqrt{D}t})}{1 + \frac{\rho_2}{|\rho_1|} e^{-\sqrt{D}t}}, \quad (54)$$

$$[S](t) = \frac{(\sigma_0 - \rho_2) + \rho_2 \frac{\sigma_0}{|\rho_1|} e^{-\sqrt{D}t}}{1 + \frac{\rho_2}{|\rho_1|} e^{-\sqrt{D}t}} \quad (55)$$

where

$$\rho_2 = \frac{-k_1 + \sqrt{D}}{2k_{-1}}, |\rho_1| = \frac{k_1 + \sqrt{D}}{2k_{-1}}, \quad (56)$$

with  $\rho_1 < 0 < \rho_2$ , and

$$D = k_1^2 + 4k_1k_{-1}\sigma_0. \quad (57)$$

Unambiguously expression Eq. (54) is positive. The same should be true for Eq. (55) if  $\sigma_0 > \rho_2$  which is straightforward to prove using Eq. (56) and (57). Moreover we have  $[F]_\infty = [G]_\infty = \rho_2 = \text{const.} > 0$  and  $[S]_\infty = \sigma_0 - \rho_2 > 0$  (constant). We observe now that if  $\rho_2/|\rho_1| \ll 1$  the curves corresponding to Eqs. (54) and (55) respectively become the simple equations for exponential growth and decay, respectively.:

$$[F](t) = [G](t) = \rho_2(1 - e^{-\sqrt{D}t}), \quad (58)$$

$$[S](t) \approx (\sigma_0 - \rho_2) + \rho_2 e^{-\sqrt{D}t}. \quad (59)$$

From the expressions of  $|\rho_1|$ ,  $\rho_2$ , we can readily see that the condition  $\rho_2 \ll |\rho_1|$  is equivalent to

$$\sigma_0 \ll \frac{k_1}{4k_{-1}} \quad (60)$$

One more remark, at this limit, is that  $\rho_2 \approx \sigma_0$  and the equations (58) and (59) become completely first order in concentration of sucrose. If one sets  $k = \sqrt{D}$  then one has

$$K = \sqrt{k_1^2 + 4k_1k_{-1}\sigma_0} = k \sqrt{1 + \frac{4k_{-1}\sigma_0}{k_1}} \approx k_{1+2k_{-1}\sigma_0},$$

or

$$k \approx k_1 + 2k_{-1}\sigma_0. \quad (61)$$

Now in principle the constant  $k$  can be measured by a polarimetry experiment for dilute solutions from which plotting  $k$  as a function of  $\sigma_0$  one can get  $k_1$  as the intercept and  $2k_{-1}$  as the slope.

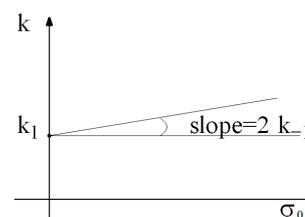


Figure 5. A linear graph of the rate constant  $k$  of the reaction  $S + H_2O \rightleftharpoons G + F$ , at the vicinity  $\sigma_0 \approx 0$  with intercept  $k_1$  and slope  $2k_{-1}$ .

Two comments have to be made: (a) The intercept  $k_1$  cannot be found by setting  $\sigma_0 = 0$  because then no experiment exists but it can be found by extrapolation near  $\sigma_0 = 0$ . (b) The slope is expected to be very small and a variety of  $\sigma_0$  must be taken until one reaches a large  $\sigma_0$ , but not so large to destroy the linear behavior.

#### The inversion of sucrose

(For the present subsection we replace  $[S] = C_s$ ,  $[G] = C_g$ ,  $[F] = C_f$ , to make symbols easier to handle.) It is well known from the 19th century that when polarized light passes through a relatively dilute solution of one optically active substance, then there is a rotation of the plane of the polarized light at an angle  $\alpha$  depending upon: (a) the wavelength of the light source ( $\lambda$ ), (b) the temperature of the solution (T), (c) the length of the optical path in the solution ( $\ell$ ), (d) the nature of the sample (e.g., sugar solution), (e) the concentration of the optically active substance.

Summarizing the above facts we have the law of polarimetry:

$$\alpha = \ell \omega C, \quad (62)$$

where  $\alpha$  is the angle of rotation measured in degrees ( $\circ$ ),  $C$  is the concentration of the optically active substance measured in mol/l or  $\text{g/cm}^3$ ,  $\ell$  is the length of the beam inside the solution measured in dm, and  $\omega$  is the specific rotation which depends both on  $\lambda$  and T which is measured in degrees/(dm/(mol/l)), or in degrees/(dm/(g/cm<sup>3</sup>

$$\omega = \Omega \left( \frac{\text{degrees}}{\text{dm} \frac{\text{mol}}{\text{lt}}} \right) = \Omega' \left( \frac{\text{degrees}}{\text{dm} \frac{\text{g}}{\text{cm}^3}} \right)$$

the two numerical values  $\Omega$  and  $\Omega'$  are related through  $\Omega = \frac{Mr}{1000} \Omega'$ , where  $Mr$  is the molecular weight of the optical substance. A question that naturally arises, is what happens with the angle of rotation, when we have a mixture of optically active substances such as sucrose, glucose, and fructose. Obviously, it is a function of the concentration of each species, having  $\ell$ ,  $\lambda$ , T as parameters, i.e.,

$$\alpha = \Phi(C_s, C_g, C_f; \ell, \lambda, T), \quad (63)$$

where  $C_s$ ,  $C_g$ , and  $C_f$  are the concentrations of sucrose, glucose, and fructose, respectively, and  $\ell$ ,  $\lambda$ , T have the same meaning as above. From the earlier equation we have  $\Phi(0, 0, 0) = 0$ , as well  $\Phi(C_s, 0, 0) = \ell \omega_s C_s$ , and similarly for  $\Phi(0, C_g, 0)$  and  $\Phi(0, 0, C_f)$ , which is a clear sign that the function  $\Phi$  is analytical around  $(0, 0, 0)$  and therefore we can take its Taylor expansion around this point from which we have

$$\alpha \approx 0 + \ell[\omega_s C_s + \omega_g C_g + \omega_f C_f] + 0(C_2). \quad (64)$$

Considering now that we have a dilute sample in all three species (i.e., 'low' concentrations), the dominant term is the linear one, while the quadratic, cubic, etc. give only small corrections and therefore

$$\alpha = \ell[\omega_s C_s + \omega_g C_g + \omega_f C_f], \quad (65)$$

Now, consider the conditions of the experiment performed,

in which only sucrose is initially present. Since the concentrations are functions of time, then  $\alpha$  is also a function of time. Inserting the constraints Eqs. (51)-(53) of the differential equations into Eq. (65) we find that

$$\alpha(t) = \ell [(\omega_s - (\omega_g + \omega_f))C_s(t) + (\omega_g + \omega_f)\sigma_0]. \quad (66)$$

Now it is known that  $\omega_s > 0$ ,  $\omega_g > 0$ ,  $\omega_f < 0$ , and  $\omega_f + \omega_g < 0$ . Initially, only sucrose is present and we have, in the case where the whole process is considered of first order with respect to sucrose concentration,  $C_s(0) = \sigma_0$ , which yields:

$$\alpha_0 = \ell \omega_s \sigma_0 > 0. \quad (67)$$

Finally we have that  $C_s(\infty) = C_{s,\infty} = 0$  and this yields

$$\alpha_\infty = \ell(\omega_g + \omega_f)\sigma_0 < 0. \quad (68)$$

Inserting Eqs. (67) and (68) into Eq. (66) one can get

$$C_s(t) = \sigma_0 \left( \frac{\alpha(t) - \alpha_\infty}{\alpha_0 - \alpha_\infty} \right) \quad (69)$$

Now, what happens in the case  $C_{s,\infty} = \sigma_0 - \rho_2 > 0$ ? Then,  $\sigma_0 - \rho_2$  may be large enough such that the first term in Eq. (66) (positive) may be larger than the second (negative) resulting to  $\alpha_\infty > 0$  and no inversion occurs. We will prove that provided  $k_1/k_{-1}$  is large this happens in unusually large concentrations: Since  $0 < \sigma_0 - \rho_2 < \sigma_0$  we may write

$$(\sigma_0 - \rho_2) = \lambda \sigma_0, \quad 0 \leq \lambda < 1, \quad (70)$$

and respectively

$$\alpha_\infty = \ell[(\omega_s + |\omega_+|)\lambda \sigma_0 - |\omega_+|\sigma_0], \quad (71)$$

with  $\omega_+ = \frac{\omega_g + \omega_f}{1000}$ ,  $\omega_s > 0$ ,  $\omega_+ < 0$ . No inversion can occur when  $\alpha_\infty > 0$  resulting to

$$\lambda_c = \frac{|\omega_+|}{\omega_s + |\omega_+|} < \lambda < 1. \quad (72)$$

Solving Eq. (70) with respect to  $\sigma_0$  we get

$$\sigma_0 = \frac{\lambda}{(1-\lambda)^2} \frac{k_1}{k_{-1}}. \quad (73)$$

The function  $\sigma_0$  with respect to  $\lambda$  is an increasing function of its argument, therefore the concentrations that do not invert sucrose are these for which  $\sigma_0 > \sigma_{0c} = \sigma_0(\lambda_c)$ , or

$$\sigma_0 > \sigma_{0c} = \frac{|\omega_+|}{\omega_s} \left( 1 + \frac{|\omega_+|}{\omega_s} \right) \frac{k_1}{k_{-1}}, \quad (74)$$

where  $\omega = \Omega \frac{\text{degrees}}{\text{dm} \frac{\text{mol}}{\text{lt}}}$ . Having  $\Omega'_+ \approx 39.7\circ$ ,  $\Omega'_s \approx 66.5\circ$ , and  $\Omega = \frac{Mr}{1000} \Omega'$ , we get

$$\sigma_{0c} \approx 0.413 \frac{k_1}{k_{-1}}, \quad (75)$$

where  $\sigma_{0c}$  is in mole/L,  $k_1$  in s<sup>-1</sup>, and  $k_{-1}$  in s<sup>-1</sup>L/mole. in s<sup>-1</sup>L/mole. The critical concentration is probably very large since  $k_{-1}$  is expected to be small, and for sure it is far from the limit of inequality (60), indicating that the inverse reaction  $G + F \rightarrow S + H_2O$  is important too. Although we

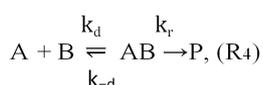
have tried to present our results with the greatest possible accuracy, there are complications which can destroy at least partially the simple and nice view of the phenomenon under investigation:

- For large concentrations of sucrose and/or glucose and fructose Eq. (65) (the simple law of polarimetry) may not be valid anymore, but need to add to it quadratic or cubic terms of the concentrations, the best work done when Eq. (63) is completely known.
- In the whole of our analysis, starting from the differential equations describing the system we have considered that the concentration of water is found in large excess. This is not the case when we have large concentrations of sucrose where the water has to be faced as a reactant, consumed and regenerated.
- The last remark concerns the difficulty in the transference of the polarimeter to visible light, when the concentration of sucrose is very large.

## 5. Reactions in Solution [15]

Reactions in solution happen in a much different way than reactions in the gas phase. Two reactants A and B come together, they form an intermediate complex AB and then dissociate into products P. However, since solvent is always present between A and B the two reactants have to jostle enough before they form the intermediate complex and this makes more difficult the reaction. Furthermore, the solvent molecules do not allow easily the dissociation of AB into P for the same reason. The last effect is known as the cage effect. 2

The whole process is described phenomenologically by the following set of reactions:



where d stands for diffusion and r for reaction. The meaning of the rate constants  $k_d$  and  $k_r$  is straightforward while  $k_{-d}$  expresses the dynamics for which the A and B reactants are reformed from the intermediate complex. The differential equations describing the whole process are the following:

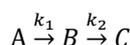
$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_d[A][B] + k_{-d}[AB], \quad (76)$$

$$\frac{d[AB]}{dt} = k_d[A][B] - (k_{-d} + k_r)[AB], \quad (77)$$

$$\frac{d[P]}{dt} = k_r[AB]. \quad (78)$$

The usual route of facing the problem is to apply the steady state approximation [3] (or else principle of stationary states [4]) for the intermediate product (here [AB]) and impose  $\frac{d}{dt}[AB] \approx 0$  and [AB] small enough.

However we know from the simplest case of a problem with an intermediate product



that the steady state approximation is valid only if  $k_1 \gg k_2$ . This means, in our case that may not, for all values of  $k_d$ ,  $k_{-d}$ ,  $k_r$ , the steady state approximation be valid and one has to examine the full model Eqs. (76)-(78) and confirm that it gives reasonable results no matter the values of the rate constants.

The conditions that have to be fulfilled are the following:

$$(i) \quad 0 \leq [A, B, AB, P] < \text{constant} < +\infty.$$

$$(ii) \quad \lim_{t \rightarrow +\infty} [A](t) = \text{constant} \geq 0,$$

and similarly for [B, AB], and [P] as  $t \rightarrow +\infty$ . From the left-hand-side of Eq. (76) we get

$$[B] = [A] + \delta_0, \quad (79)$$

where

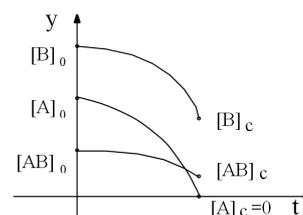
$$\delta_0 = [B]_0 - [A]_0. \quad (80)$$

Without loss of generality we can choose  $\delta_0 \geq 0$ . Otherwise, we interchange the roles of A and B. Adding Eqs. (76), (77), and (78), we have  $\frac{d}{dt}([A] + [AB] + [P]) = 0$  or else

$$[A] + [AB] + [P] = \sigma_0, \quad (81)$$

where

$$\sigma_0 = [A]_0 + [AB]_0 + [P]_0. \quad (82)$$



**Figure 6.** A hypothetical scenario for the time evolution of the concentration of the species [A, AB], and [B]. [A] is reflected toward the y-positive axis when it reaches the t-axis, remaining always positive.

Let's suppose now that starting from positive initial values of  $[A]_0$ ,  $[B]_0$ ,  $[AB]_0$ , one of them let's say the [A] - is the first that reaches the t-axis.

We have then

$$\left(\frac{d[A]}{dt}\right)_c = -k_d[A]_c[B]_c + k_{-d}[AB]_c > 0$$

which implies that [A] is reflected toward the positive y-axis and cannot pass into negative values. If [AB] first reaches the t-axis then from Eq. (77) we have a similar conclusion and therefore [AB] cannot take negative values. If [A] or [AB] attempts for a second time to pass the t-axis, the same thing happens and so on. [B] cannot take negative values because it is larger than [A] and so it is proved that all concentrations are greater than zero. The same is valid for [P]:

$$[P] = [P]_0 + \int_0^t k_r [AB] dt \geq [P]_0 \geq 0,$$

since  $[AB] \geq 0$ . From the positiveness of  $[A, AB, P] \geq 0$  and the condition Eqs. (81) and we get

$$0 \leq [A] \leq \sigma_0, \quad (83)$$

$$0 \leq [AB] \leq \sigma_0, \quad (84)$$

$$0 \leq [P] \leq \sigma_0, \quad (85)$$

$$0 \leq [B] \leq \sigma_0. \quad (86)$$

This means that all concentrations are bounded below from the value zero and above from the value  $\sigma_0$ . Eqs. (76)-(78) is probably impossible to be solved analytically. Although this cannot be done, a discussion can be made that will shed light to the nature of the solutions especially when they tend to infinity. First of all, Eqs. (76)-(78) apparently seem to have four degrees of freedom, exactly as many as they are the concentrations of each species taking part in the three reactions. Such a dynamical problem could even be possible of exhibiting chaotic behaviour or strange oscillations or another exotic behaviour. However, imposing equations (79) and (81) onto Eqs. (76)-(78), the number of degrees of freedom reduces to two.

According to the accepted opinions, an autonomous system of ordinary differential equations with two degrees of freedom cannot exhibit chaotic behavior. Besides ordinary differential equation systems with two degrees of freedom, i.e., ODEs on the plane, have been very well studied and we know that their dynamics is mainly governed by the so-called Poincaré - Bendixson theorem. It is known from the proof of the Poincaré - Bendixson theorem that if the solution remains in a compact set K (which is closed and bounded) for  $t \geq 0$  (and especially as  $t \rightarrow +\infty$ ) enclosing a single fixed point, then the solution finally either tends to the fixed point or to a limit cycle. [5], [6]. As an immediate conclusion of the above theorem is the following corollary:

Corollary

Suppose the initial value problem

$$x' = P(x, y), y' = Q(x, y), x(t=0) = x_0, y(t=0) = y_0$$

which has a single fixed point located at  $(0, 0)$  [without loss of generality], i.e.,  $P(0, 0) = Q(0, 0) = 0$ , and  $|P(x, y)| + |Q(x, y)| > 0$  for  $(x, y) \in \mathbb{R}_2 - (0, 0)$ . Making the substitution  $x = 0 + \xi_1$ ,  $y = 0 + \xi_2$  we take the linearized problem (from a Taylor expansion) keeping only the linear terms:

$$\xi_1' = \sigma_{11}\xi_1 + \sigma_{12}\xi_2 + O(\xi^2),$$

$$\xi_2' = \sigma_{21}\xi_1 + \sigma_{22}\xi_2 + O(\xi^2),$$

where

$$\sigma_{11} = \left(\frac{\partial P}{\partial x}\right)_0, \sigma_{12} = \left(\frac{\partial P}{\partial y}\right)_0,$$

$$\sigma_{21} = \left(\frac{\partial Q}{\partial x}\right)_0, \sigma_{22} = \left(\frac{\partial Q}{\partial y}\right)_0.$$

For the linearized problem to exist we must have  $|\sigma_{11}| + |\sigma_{12}| > 0$ , and / or  $|\sigma_{21}| + |\sigma_{22}| > 0$ . If  $\lambda_1, \lambda_2$  are the eigenvalues of the  $2 \times 2$  matrix with elements  $\sigma_{ij}$ ,  $i, j = 1, 2$ , we have  $\lambda^2 - T\lambda + D = 0$ , where  $T = \lambda_1 + \lambda_2 = \sigma_{11} + \sigma_{22}$ , and  $D = \lambda_1\lambda_2 = \sigma_{11}\sigma_{22} - \sigma_{12}\sigma_{21}$ . Now from the Poincaré -Bendixson theorem we can state the following:

(a) If the solution remains in a compact region K

(enclosing the fixed point), as  $t \rightarrow +\infty$ , then if the eigenvalues of the matrix of the linearized problem are both negative or both have negative real parts then the solution tends to the fixed point as  $t \rightarrow +\infty$ .

(b) If the solution remains in a compact region K (closed and bounded) and at least one eigenvalue is nonnegative then the solution tends to a limit cycle.

(c) If the solution does not remain in a compact region then it finally escapes to infinity. The proof of the above corollary is a natural conclusion of the Poincaré -Bendixson

theorem and the remark that the linearized problem -when it exists - is the most appropriate description of the behavior of the solution as  $t \rightarrow +\infty$ . What we actually want now to prove is that the case of reactions in solution belongs to the case (a) of the corollary which means that we have a limiting behavior tending to constant values, excluding the cases (b) and (c), i.e., this of limit cycle or tending to infinity. Since we are doing dynamics, it should be appropriate (actually for writing shorter expressions) to convert the chemical symbols to other symbols that are common in dynamics, i.e.,  $[A] \rightarrow x$ ,  $[B] \rightarrow y$ ,  $[AB] \rightarrow z$ , and  $[P] \rightarrow w$ . Then, Eqs. (76)-(78) become:

$$x' = y' = -k_dxy + k_{-d}z, \quad (87)$$

$$z' = +k_dxy - (k_{-d} + k_r)z, \quad (88)$$

$$w' = +k_r z, \quad (89)$$

where

$$y = x + \delta_0, x + z + w = \sigma_0, \quad (90)$$

with  $\delta_0, \sigma_0 > 0$ .

Setting Eqs. (87)- (89) equal to zero in order to get the fixed points and using Eqs. (90) in addition, we have

$$k_d x_r y_r - (k_{-d} + k_r) z_r = 0,$$

$$-k_d x_r y_r + k_{-d} z_r = 0,$$

$$k_r z_r = 0,$$

where the subscript r stand for the word 'root'. From these and Eqs. (90) we get  $x_r = 0$ ,  $z_r = 0$ ,  $y_r = \delta_0 > 0$ , and  $w_r = \sigma_0 > 0$ . We choose  $x$  and  $z$  as the independent variables and together with Eqs. (90) we make the substitution  $x = x_r + \xi_1 = 0 + \xi_1$ , and  $z = z_r + \xi_2 = 0 + \xi_2$

retaining only the linear terms in Eqs. (87) and (88) getting

$$\xi_1' = -k_d \xi_1 (\xi_1 + \delta_0) + k_{-d} \xi_2, \quad (91)$$

$$\xi_2' = +k_d \delta_0 \xi_1 - (k_{-d} + k_r) \xi_2. \quad (92)$$

The linear equations are

$$\xi_1' = -k_d \delta_0 \xi_1 + k_{-d} \xi_2, \quad (93)$$

$$\xi_2' = +k_d \delta_0 \xi_1 - (k_{-d} + k_r) \xi_2. \quad (94)$$

It is now easy to deduce that the eigenvalues of the linearized problem are given by the following quadratic equation:

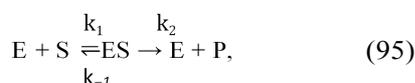
$$\lambda^2 + \lambda[k_{-d} + k_r + k_d\delta_0] + k_r k_d \delta_0 = 0.$$

Since  $k_{-d}$ ,  $k_d$ ,  $k_r$ , and  $\delta_0$  are all positive, the solutions of the quadratic equation are either both negative or have both negative real parts.

Furthermore, both variables  $x$  and  $z$  'live' in the region  $K = [0, \sigma_0] \times [0, \sigma_0]$  which is both closed and bounded, i.e., it is compact. Therefore we are in the case (a) of the corollary and the conditions of the 'usual' chemistry have been proved.

## 6. The Michaelis-Menten Mechanism and More [14]

Another set of chemical reactions which has a linearized problem and it is actually two-dimensional and therefore tractable is the Michaelis-Menten mechanism



where  $E$  stands for the concentration of the enzyme,  $S$  for the substrate,  $ES$  for the intermediate complex and  $P$  for products. The equations describing the above process are the following:

$$\frac{d}{dt}[ES] = +k_1[E][S] - (k_{-1} + k_2)[ES], \quad (96)$$

$$\frac{d}{dt}[E] = -k_1[E][S] + (k_{-1} + k_2)[ES], \quad (97)$$

$$\frac{d}{dt}[S] = -k_1[E][S] + k_{-1}[ES], \quad (98)$$

$$\frac{d}{dt}[P] = k_2[ES]. \quad (99)$$

One can easily produce the following:

$$[ES] + [E] = \sigma_1 = \text{constant} > 0, \quad (100)$$

$$[ES] + [S] + [P] = \sigma_2 = \text{constant} > 0, \quad (101)$$

where  $\sigma_1 = [ES]_0 + [E]_0$  and  $\sigma_2 = [ES]_0 + [S]_0 + [P]_0 = [S]_0$ , assuming that the initial values of the intermediate complex and the products are zero. Equating Eqs. (96) to (99) to zero, in order to find the fixed points, we have that  $[ES]_r = 0$  and  $[E]_r [S]_r = 0$ . From Eq. (100) we have that  $[ES]_0 + [E]_0 = [E]_0 = \sigma_1 = [ES]_r + [E]_r = [E]_r$ , which implies  $[E]_r = \sigma_1 = [E]_0$  and this means that at the end of the whole process we get the same quantities of enzyme as it was in the beginning of the reaction.

Furthermore, we find  $[S]_r = 0$  and  $[P]_r = [S]_0$  which means that the final concentration of products equals the initial concentration of the substrate, which is another result expected to happen.

The above analysis is 'illegal' unless it is proved that the Eqs. (96) and (97) fall into the case (a) of the corollary. Using methods analogous to these of the previous section one can prove that all concentrations are greater than or equal to zero. Then using Eqs. (100) and (101) one can prove that they remain in a compact region  $K$ .

Substituting  $[S] = x$ ,  $[P] = y$ ,  $[E] = z$ ,  $[ES] = w$ , and finding  $x_r = 0$ ,  $y_r = \sigma_2$ ,  $z_r = \sigma_1$ ,

$w_r = 0$  and posing  $x(t=0) = x_0 > 0$ ,  $y(t=0) = 0$ ,  $z(t=0) = z_0 > 0$ ,  $w(t=0) = 0$ , we get:

$$\dot{x} = -k_1(\sigma_1 - \sigma_2 + x + y)x + k_{-1}(\sigma_2 - x - y), \quad (102)$$

$$\dot{y} = +k_2(\sigma_2 - x - y), \quad (103)$$

with  $x(t=0) = x_0 > 0$  and  $y(t=0) = 0$ ,  $x_r = 0$  and  $y_r = \sigma_2$ . Making the new substitution

$x = x_r + \xi_1 = 0 + \xi_1 = \xi_1$  and  $y = y_r + \xi_2 = \sigma_2 + \xi_2$  we get the linearized problem

$$\dot{\xi}_1 = -(k_1\sigma_1 + k_{-1})\xi_1 - k_{-1}\xi_2,$$

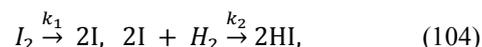
$$\dot{\xi}_2 = -k_2\xi_1 - k_2\xi_2,$$

the eigenvalues of which are given by

$$\lambda^2 + \lambda(k_1\sigma_1 + k_{-1} + k_2) + k_1\sigma_1 k_2 = 0.$$

which are either both negative (real) or have both negative real parts (complex).

A final remark concerns other systems of reactions, which need more effort to come to the same conclusions. Such a system is the reaction of  $I_2$  and  $H_2$  to form  $HI$ . The usual mechanism proposed is the following:



One can proceed by writing the equations for the four species  $I_2$ ,  $I$ ,  $H_2$ , and  $HI$  and it is to derive that there exist two constraints reducing the degrees of freedom from four to two. Therefore the problem belongs into the usual one, of the differential equations on the plane. However the progress with this problem is difficult since (a) the search for the fixed point gives two distinct cases, and (b) there is no linearized problem but instead of it the behavior at infinity is governed by quadratic equations, which are not easy to handle in an analytical manner.

## 7. Conclusions [12, 13]

In conclusion a system of reactions involving  $m$  species (reactants and products) and  $n$  reactions ( $m > n$ ) has  $n$  degrees of freedom, i.e., so many as they are the single and the double arrows of the reaction equation. In any case of  $n$  reactions and  $m$  species one can probably find  $m - n$  constants (integrals of "motion"-constraints) and reduce the number of independent equations from  $m$  to  $n$ .

For instance in the case of paragraph II we have  $m = 4$ ,  $n = 1$  from which we get

$$m - n = 3 \text{ (three independent constraints)}$$

$$\frac{b(t)-b_0}{\beta} = \frac{a(t)-a_0}{\alpha} = \frac{c(t)-c_0}{\gamma} = \frac{d(t)-d_0}{\delta} \quad (105)$$

and the same holds for paragraph III. For paragraph IV we have  $m = 3$  [ $S, G, F$ ] and  $n = 1$  for which  $m - n = 2$

(constraints (51) and (52)). For paragraph V,  $m = 4$  [A,B,AB,P] and  $n = 2$ . Therefore  $m - n = 2$  [Eqs.(79) and (81)] In paragraph VI,  $m = 4$  [E,S,ES,P] and  $n = 2$  implies  $m - n = 2$  [constraints (100),(101)].

From the above paragraph and the accepted opinions about chaos, we understand that the existence of chaos is impossible unless the species that are involved in the chemical process take part in a system of at least three reactions ( $n \geq 3$ ). But even in this case, chemical chaos may not appear since the rate constants (i.e., the  $k$ 's) and/or the initial values of the reactants and/or products (final or intermediate) may not fall into a chaotic region of the full model. However, this is not the case for oscillations that may well appear for  $n \geq 2$ , since nothing prohibits in principle their appearance.

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