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Some mathematical properties of the Lindemann mechanism

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ABSTRACT. In the first part several mathematical properties of the non-linear mechanism are shown which have not been reported before. In particular it is shown that the traditional interpretation of the experimental slope in terms of the constants of the mechanism corresponds to the slope at an inflection point where the system is not asymptotically near equilibrium. In the second part, with the help of the method of fast variables elimination, the linear and the quadratic rate laws, which are identified with the experimental rate laws, are shown to be approximations when the initial concentration of the reactant is high or low, respectively, compared to combinations of the constants of the mechanism. The interpretation of the linear rate law as emerging because measurements are not near equilibrium and a different interpretation for the constant of the linear rate law in terms of the constants of the mechanism are presented.

RESUMEN. En una primera parte, se exhiben varias propiedades del mecanismo nolineal que no han sido reportadas previamente. En particular se muestra que la interpretación tradicional de la pendiente experimental en términos de las constantes del mecanismo corresponde a la pendiente del punto de inflexión donde el sistema no está asintóticamente cerca de equilibrio. En una segunda parte se muestra, con ayuda del método de eliminación de variable rápida, que las leyes lineal y cuadrática, que se identifican con las leyes de rapidez experimentales, son aproximaciones que ocurren cuando la concentración del reactante es alta o baja, respectivamente, comparada con combinaciones de las constantes del mecanismo. Se presenta la interpretación de que la ley de rapidez lineal emerge porque las mediciones no han sido realizadas cerca del equilibrio y se ofrece una interpretación distinta para la constante de la ley de rapidez experimental lineal en términos de las constantes del mecanismo.

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1. INTRODUCTION

Since the beginning of this century, after the work of Michaelis and Menten in enzymatic reactions [1] and that of Lindemann [2] in gaseous decompositions, it has been a practice,

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when coming across with reactions whose phenomenological rate law does not comply in one way or another either to the Guldberg-Waage kinetic equation form [3,4], or to the expectations of collision theory for chemical reactions, to postulate a mechanism formed by several reaction steps each one of them obeying the Guldberg and Waage law, but involving one or several intermediate species that are not directly observed at the time scale at which the product of the reaction is measured and the rate law observed. The connection between the set of differential equations implied by the mechanism and the phenomenological rate law, a different differential equation, has been traditionally established by postulating that at all times during the evolution of the reaction, the rate of change of the intermediates is zero. When the substitution of the ensuing "steady" reactant concentrations on the equation of the rate of product formation is made, if the resulting equation is of the same form as the experimental rate law, the mechanism is thought to be the kinetic explanation of the reaction. Furthermore, as a consequence, the experimental Arrhenius constant can be interpreted in terms of the reaction constants of the mechanism, thus lending them physical meaning. This procedure is called the pseudo-steady-state hypothesis [3,4].

The pseudo-steady-state hypothesis is considered successful in the sense that the slope of the rate law it predicts as the reaction approaches the equilibrium coincides with the one numerically predicted from the mechanism, for example the Lindemann's and Michaelis-Menten cases [5]. It is also considered successful, at least in the case of gaseous decompositions [6], because of the good agreement between the value of the global rate constant predicted by the statistical mechanical Rice-Ramsberger-Kassel-Marcus and Slater theories [4,7] and the experimental rate constant identified in terms of the constants of the mechanism [7–9]. However, from the point of view of mathematics, *the procedure* followed by the pseudo-steady state-hypothesis to obtain the rate law from the mechanism is objectionable, and to apply it with the belief that it must correspond to some sort of approximation of the equations of the mechanism in a perturbative method when certain parameters are small, without knowing which they are, is to miss information on the applicability and predictive capability of the mechanism, to say the least.

The pseudo-steady-state hypothesis was first criticized within the context of the simple Michaelis-Menten mechanism and related enzymatic reactions, and the form of the rate law justified from the postulated mechanism, by showing that it is the degenerate solution of a singular perturbation method of approximation of the independent equations when certain parameter, chosen from the particular experimental circumstances, is small [10]. In this particular case as in many others the smallness parameter makes evident the existence of two different time scales associated with the reaction, one characterizing the evolution of the intermediate species, called the fast variable, and the other characterizing the evolution of one of the other reactants called the slow variable. The method to obtain from a system of differential equations representing any type of physical process, the one equation that will approximately fit its behaviour near a stable fixed point has been systematized under the name of fast variable elimination [11]. However the selection of the smallness parameter, depends on extra information.

In most of the instances of rate laws that have been mathematically justified using perturbative methods, the smallness parameter is chosen either from particular experimental conditions [10], by deducing it from the pseudo steady state hypothesis itself [8], or by trying relations between magnitudes of the several constants involved. This last way of selection of the smallness parameter is fruitful to obtain the rate law of complex reactions; like that of the formation of hydrogen bromide that has been justified from the mechanism by choosing the smallness parameter from considerations on the relative magnitude the involved rate constants ought to have, given that the intermediates concentrations are to be fast variables since they are absent from the rate law [12]. Several other complex reactions have been studied from the point of view of other perturbation methods [13].

It so happens that little attention has been paid to the mathematical properties of mechanisms. A systematic study of the mathematical properties of a mechanism, as far as it is feasible, can help in the identification of a smallness parameter and to clarify the approximation under which the experimental slope can be equated to the predicted slope. But not only this, a study of the properties of a mechanism might lead to the direct identification of one or more of its constants with experimentally measured quantities in addition of giving information on interesting properties. No one knows what surprises remain hidden if one simply applies the-pseudo-steady-state hypothesis without having shown what the properties of the mechanism are, and which is the approximation, in terms of the constants of the mechanism and of the experiment, that leads to it. That is, other than assuming the rate of formation of intermediate species zero at all times.

Although the study of the non-linear Lindemann mechanism is already a rather old subject [4, 6, 14], we think that proper attention has not been paid to the basic and most simple of its mathematical properties and the approximations under which its associated rate law is obtained. In the present paper we study them. Our central goal, besides getting information, is to find out the circumstances under which the traditional identification of the experimental slope k_{exp} [3, 4, 7], of the linear rate law with a combination of the constants of the mechanism is valid, without having recourse to the pseudo steady state hypothesis. In a second part we show which are the smallness parameters that will yield from the mechanism the linear and quadratic laws that have been observed in gaseous decompositions for which the Lindemann mechanism has been applied. In this second part we use the method of elimination of fast variables [11]. We end the paper with a section of comments on the new results obtained and conclusions.

2. GENERAL PROPERTIES

In this section we prove several properties of the non-linear Lindemann mechanism. They are mostly associated with the slopes at different points of curves of different coordinates. The spaces considered are those pertinent to the relation of the mechanism to the experimental results.

The unimolecular decomposition of reactant R, to yield the products P and Q, through its transformation into the vibrationally exited species C, is represented by the following mechanism:

$$R + R \xrightarrow{k_1} C + R, \tag{1}$$

$$C + R \xrightarrow{k_2} R + R, \tag{2}$$

$$C \xrightarrow{k_3} P + Q, \tag{3}$$

where the k_i represent the rate constants. If we denote the concentrations by the lower-case letters associated to the species represented by capitals, the mass action law applied to the mechanism gives the following equations for the time rate of change of the concentrations:

$$\dot{r} = -k_1 r^2 + k_2 cr, \tag{4}$$

$$\dot{c} = k_1 r^2 - k_2 cr - k_3 c, \tag{5}$$

$$\dot{p} = k_3 c, \tag{6}$$

$$\dot{q} = \dot{p}, \tag{7}$$

where the dot above the symbol denotes the time derivative. We notice that there is one constant of motion since $\dot{r} + \dot{c} + \dot{p} = 0$, and therefore that there are only two independent equations of motion. Upon choosing for the initial time $t = 0$, the following initial values for the concentrations:

$$r(t=0) = r_0, \tag{8}$$

$$c(t=0) = 0, \tag{9}$$

$$p(t=0) = 0; \tag{10}$$

the constant of motion is given by

$$r_0 = r + c + p. \tag{11}$$

We choose as the independent concentrations the set (c, p) and have as a consequence the following independent equations of motion:

$$\dot{c} = k_1(r_0 - c - p)^2 - k_2 c(r_0 - c - p) - k_3 c \tag{12}$$

$$\dot{p} = k_3 c. \tag{13}$$

We obtain, after applying the initial conditions given in (8), (9), and (10) to the independent Eqs. (12) and (13) that the rate of product formation is

$$\dot{p}(t=0) = 0, \tag{14}$$

and that the rate of formation of the intermediate species is

$$\dot{c}(t=0) = k_1 r_0^2. \tag{15}$$

On the other hand calling Ω the time at which equilibrium is achieved, both defining equilibrium conditions,

$$\dot{p}(t=\Omega) = 0 \tag{16}$$

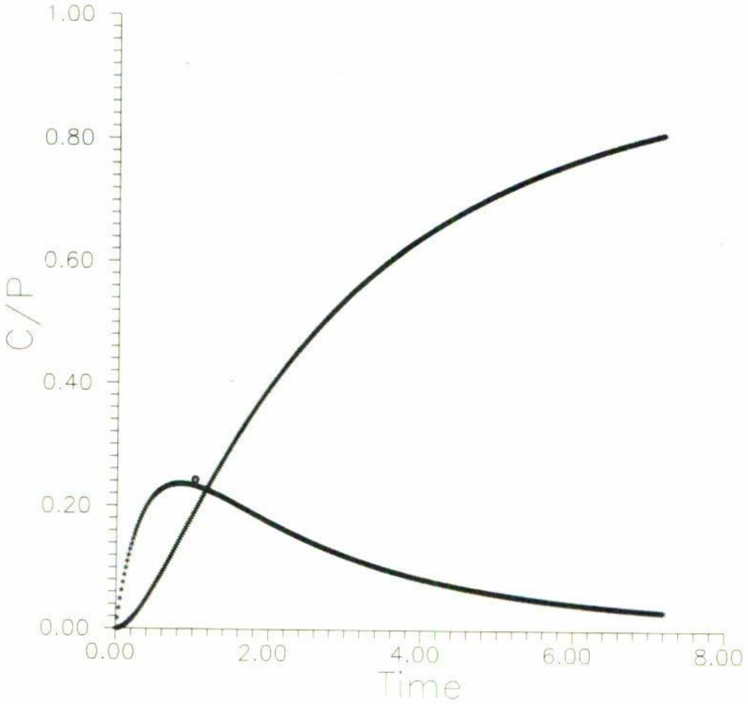

FIGURE 1. Curves $c = c(t)$ and $p = p(t)$, with $k_1 = k_2 = k_3 = 1.00$ and $r_0 = 1.00$, according to equations (12) and (13).

and

$$\dot{c}(t = \Omega) = 0, \tag{17}$$

lead to the equilibrium concentrations

$$c(t = \Omega) = 0 \tag{18}$$

and

$$p(t = \Omega) = r_0. \tag{19}$$

Taking into account that the variables are restricted to semipositive values because they are concentrations, we find from Eq. (12) that $c(t)$ has a maximum $c(t = t_0) \equiv c_{\mathrm{m}}$. This maximum is simultaneous with an inflection point for $p(t = t_0) \equiv p_i$ because of Eq. (13). These features are illustrated in Fig. 1 where we have plot $c(t)$ and $p(t)$. The relation among the values c_{m} and p_i, from Eq. (12), is given by

$$k_1(r_0 - c_{\mathrm{m}} - p_i)^2 = k_2 c_{\mathrm{m}}(r_0 - c_{\mathrm{m}} - p_i) + k_3 c_{\mathrm{m}}. \tag{20}$$

Up to now we have information concerning the values of the variables and of the slopes of the curves $c(t)$ and $p(t)$ at selected points, namely at the initial time, at time t_0 where the maximum of c occurs and at the equilibrium time as predicted by the mechanism. We now want to use this information to find out the slope of the functions $\dot{p}(r)$ and $\dot{p}(r+c)$ at those same times. The space $(r, \dot{p})$ is the one relevant for the discussion of the relation between the mechanism and the rate law and space $(r+c, \dot{p})$ will show itself useful in the next section. To obtain the information we want, it is most helpful to find first the slope of the curve in the phase space (p, c). The reason is that from the rules of calculus, the slopes we are looking for are most easily expressed in terms of the slope in (p, c). In fact, we have first that

$$\frac{dc}{dp} = \frac{\dot{c}}{\dot{p}}. \tag{21}$$

Then, using the constant (11) into the expression $d\dot{p}/dr$, we find also from calculus that

$$\frac{d\dot{p}}{dr} = -\frac{\ddot{p}}{\dot{p}+\dot{c}}$$

and with the use of Eq. (13) that

$$\frac{d\dot{p}}{dr} = -\frac{k_3\frac{\dot{c}}{\dot{p}}}{1+\frac{\dot{c}}{\dot{p}}}. \tag{22}$$

In an analogous fashion we also obtain from the expression $d\dot{p}/d(r+c)$ the equality

$$\frac{d\dot{p}}{d(r+c)} = -k_3\frac{\dot{c}}{\dot{p}}. \tag{23}$$

We now proceed to the evaluation of the slope in coordinates (p, c) given by $\frac{\dot{c}}{\dot{p}}$ for the few selected points, of initial time, maximum of c and equilibrium. Its explicit expression can immediately be written down from Eqs. (12) and (13). It is the following one,

$$\frac{\dot{c}}{\dot{p}} = \frac{k_1(r_0-c-p)^2 - k_2c(r_0-c-p) - k_3c}{k_3c}. \tag{24}$$

We find, upon substitution of the initial conditions (9) and (10) in Eq. (24), that its value at the origin in (p, c) or initial time is

$$\lim_{t\to 0}\frac{\dot{c}}{\dot{p}} = \frac{k_1}{k_3}\left\{\frac{r_0^2}{\lim_{t\to 0} c} - \frac{k_2r_0}{k_1} - \frac{k_3}{k_1}\right\} = \infty. \tag{25}$$

This result carries over, with the help of relations (22) and (23), to the following initial time slopes, respectively:

$$\lim_{t\to 0}\frac{d\dot{p}}{dr} = -k_3\lim_{t\to 0}\frac{1}{1+\frac{\dot{p}}{\dot{c}}} = -k_3 \tag{26}$$

and

$$\lim_{t\to 0}\frac{d\dot{p}}{d(r+c)}=\infty.$$

It is verified, with the use of (20), that in (p,c) there is a maximum, since

$$\left\{\frac{dc}{dp}\right\}_{P_i,c_m}=0. \tag{27}$$

Also, because of relations (22) and (23) we find that Eq. (27) implies the presence of a maximum also in coordinates $(r,\dot{p})$ and $(r+c,\dot{p})$.

With respect to the value of the slope at equilibrium, let us denote for expediency,

$$\mathcal{P}\equiv\lim_{t\to\Omega}\frac{\dot{c}}{\dot{p}}, \tag{28}$$

and then apply the equilibrium values given by (18) and (19) to Eq. (24). The result is

$$\mathcal{P}=\frac{k_1}{k_3}\left(\lim_{t\to\Omega}\frac{r_0^2+p^2-2r_0p}{c}-\frac{k_3}{k_1}\right). \tag{29}$$

After applying L'Hôpital's rule to resolve the indetermination, we have that,

$$\mathcal{P}=\frac{k_1}{k_3}\left(\frac{\lim_{t\to\Omega}2(p-r_0)}{\mathcal{P}}-\frac{k_3}{k_1}\right). \tag{30}$$

This result shows there are two possible values for $\mathcal{P}$. If condition

$$\frac{k_3}{k_1}=\frac{\lim_{t\to\Omega}2(p-r_0)}{\mathcal{P}} \tag{31}$$

is met, the value of the equilibrium slope is

$$\mathcal{P}=0, \tag{32}$$

but if not, we may evaluate first the limit in the right-hand side of Eq. (30) and then find

$$\mathcal{P}=-1. \tag{33}$$

These two values for the equilibrium slope $\mathcal{P}$, (32) and (33), bring by virtue of the transformation (22) the prediction of two values for the experimental equilibrium slope, in $(r,\dot{p})$, the space of the rate law; they are the following ones:

$$\lim_{t\to\Omega}\frac{d\dot{p}}{dr}=0, \tag{34}$$

corresponding to value the $\mathcal{P} = 0$ (32); and

$$\lim_{t\to\Omega} \frac{d\dot{p}}{dr} = \infty, \tag{35}$$

corresponding to the value $\mathcal{P} = -1$ (33). As the equilibrium slope in $(r+c, \dot{p})$ is concerned, two values are also predicted, corresponding to $\mathcal{P} = 0$ and to $\mathcal{P} = -1$; they are, respectively

$$\lim_{t\to\Omega} \frac{d\dot{p}}{d(r+c)} = 0 \tag{36}$$

and

$$\lim_{t\to\Omega} \frac{d\dot{p}}{d(r+c)} = k_3. \tag{37}$$

Taking into account the information from experiments, we shall discard the set of equilibrium slopes coming from $\mathcal{P} = -1$, (35) and (36), since one of them, prediction

$$\lim_{t\to\Omega} \frac{d\dot{p}}{dr} = \infty$$

up to our knowledge, has never been observed. This consideration leaves us with only the set of equilibrium slopes equal to zero, coming from the value $\mathcal{P} = 0$, namely (34) and (36). Thus we conclude that the mechanism predicts a zero value for the slope at equilibrium as was to be expected since the Lindemann's mechanism has a bimolecular step which will lead to a quadratic rate law. If such is the case, how can we then reconcile an experimental slope $k_{\text{exp}} \neq 0$ and $k_{\text{exp}} \neq \infty$ in $(r, \dot{p})$ with the mechanism?

An obvious and immediate consequence of zero equilibrium slope is that, because there is also a maximum, there must be an inflection point. We now look for the slope of the tangent line at the inflection point in the rate law coordinates $(r, \dot{p})$, or for that matter, as Eq. (13) shows, in coordinates (r, c). Thus with the help of Eqs. (4) and (5) and taking into account that

$$\frac{dc}{dr} = \frac{\dot{c}}{\dot{r}},$$

we obtain the general expression for the slope $\frac{dc}{dr}$ valid at all points of the curve $c = c(r)$, namely

$$\frac{dc}{dr} = \frac{k_1 r^2 - k_2 cr - k_3 c}{-k_1 r^2 + k_2 cr}. \tag{38}$$

From here, after taking the second derivative with respect to r, equating it to zero and rearranging it we obtain the value of the slope at the inflection point. It is given by

$$\left(\frac{dc}{dr}\right)_{\text{inflection}} = \frac{2k_1 cr - k_2 c^2}{k_1 r^2} \tag{39}$$

Now, we notice that at the inflection point the equality between the expressions (38) and (39) must hold, yielding the following condition the coordinates (r, c) must satisfy at that point. It reads as

$$\frac{2k_1 r - k_2 c}{k_1 r} c = \frac{k_1 r^2 - k_2 c r - k_3 c}{-k_1 r + k_2 c}. \tag{40}$$

From here we see that in the approximation when

$$k_2 r c \gg k_3 c,$$

that is, when the system has not arrived to equilibrium since still $r \neq 0$, the equality (40) is satisfied with value zero if $k_1 r = k_2 c$ or, what amounts to the same thing when

$$\left(\frac{dc}{dr}\right)_{k_2 r \gg k_3} = \frac{k_1}{k_2} \tag{41}$$

or, taking into account Eq. (13), when

$$\left(\frac{d\dot{p}}{dr}\right)_{k_2 r \gg k_3} = \frac{k_1 k_3}{k_2}. \tag{42}$$

This last value for the slope is the one the hypothesis of the pseudo steady state assignes to the maximum possible value of k_{exp}. Here we have shown from the mechanism that the slope

$$\frac{k_3 k_1}{k_2} \tag{43}$$

coincides with the tangent at the inflection point *if the approximation* $k_2 r c \gg k_3 c$ *holds*, since in this approximation Eq. (41) satisfies the equality (40).

In Fig. 2 the curve $c = c(p)$ is shown, for the sake of illustration of the features given by Eq. (25) and the maximum. In Fig. 3, the curve $\dot{p}(r)$ is shown; in it we illustrate Eq. (26) and the inflection point, located, within the precision of the graph, at $(r = 0.36, c = 0.13)$ for the k_i used, namely $k_1 = k_2 = k_3 = 1.0$. With these values for the coordinates of the inflection point, Eq. (39) yields a slope of 0.59, clearly not $k_1 k_3 / k_2 = 1$, as it must be since in this case $k_2 r < k_3$, however still with $r \neq 0$.

In other words one finds a linear rate law in coordinates $(r, \dot{p})$ when the experiment has not gone all the way towards the equilibrium. This occurs either because condition $k_2 r \gg k_3$ is met in whose case the slope is $k_1 k_3 / k_2 = 1$, or because the experimental measurements are located near the inflection point on the flat part of the curve between the maximum and the equilibrium.

Lastly but not least, we find that Eq. (42) predicts, with the help of relations (22) and (23), the following slope at the inflection point in the coordinates $(r + c, \dot{p})$:

$$\left(\frac{d\dot{p}}{d(r + c)}\right)_{k_2 r \gg k_3} = \frac{k_1 k_3}{k_1 + k_2}. \tag{44}$$

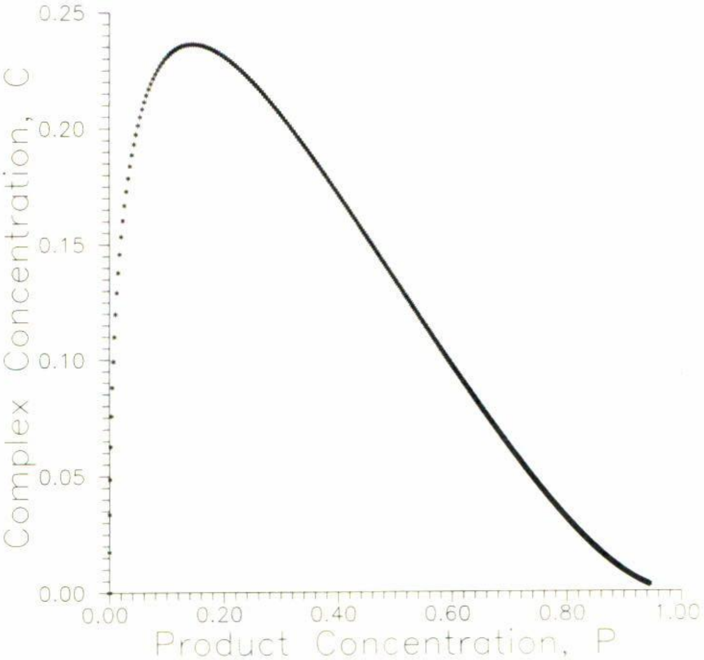

FIGURE 2. Curve $c = c(p)$, with $k_1 = k_2 = k_3 = 1.00$ and $r_0 = 1.00$, from Eq. (24).

3. FAST VARIABLE ELIMINATION

In the present section, we show the form of the rate law predicted from the mechanism by the method of elimination of fast variables for two cases, low initial concentration and high initial concentration of reactant r_0. The method employed is the singular perturbation method [11]. We show that the rate equation derived from the procedure of the pseudo steady state hypothesis, namely

$$-\dot{p} = \dot{r} = -\frac{k_1 k_3 r^2}{k_2 r + k_3}, \tag{45}$$

can be justified as a gross approximation of the rate law obtained in the low initial concentration case; in consequence, we argue that the result for the slope (42) cannot be consistently obtained from (45) by applying to it the approximation $k_2 r \gg k_3$. As for the high initial concentration case, we obtain a linear law that leads to the result (42).

In the first part of this section we show the rate law that is obtained from the independent equations in (c, r) associated to the Lindemann mechanism, Eqs. (4) and (5) under the assumption that the initial concentration of the reactant r_0 and the values of the k_i are such that the intermediate species c, suffers decomposition faster than recombination or formation. This amounts to the definition of the following smallness parameter:

$$\varepsilon_x \equiv \frac{k_x r_0}{k_3} \ll 1, \tag{46}$$

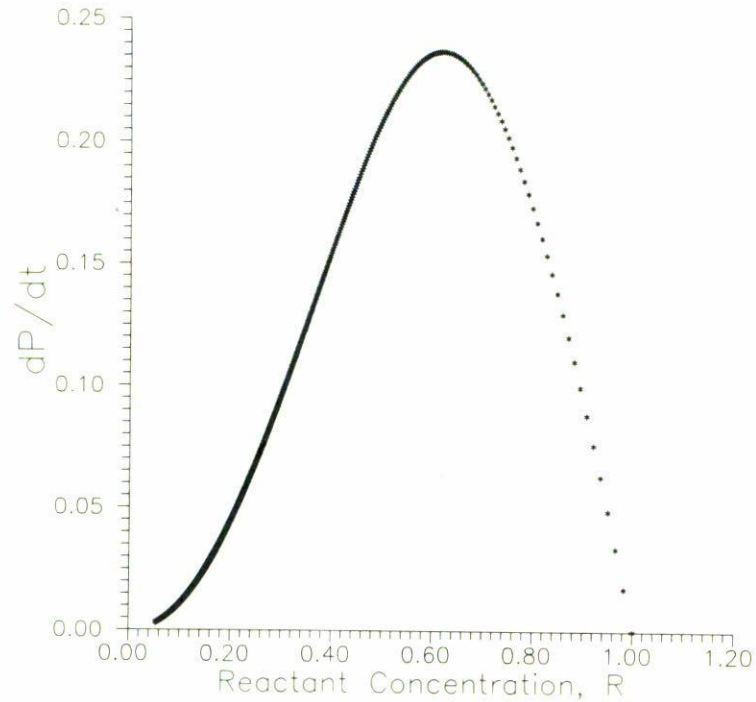

FIGURE 3. $\dot{p} = \dot{p}(r)$, with $k_1 = k_2 = k_3 = 1.00$ and $r_0 = 1.00$ from Eqs. (12)–(13) with the help of Eq. (22).

where

$$k_x = k_1,\ k_2,\ (k_1 + k_2) \tag{47}$$

and correspondingly to

$$\varepsilon_x = \varepsilon_1,\ \varepsilon_2,\ \varepsilon_3. \tag{48}$$

We now look for a transformation of the Eqs. (4) and (5) such that with the proposed ε_x, one variable can be considered a slow one and the other a fast one. Let us choose the time scale defined by

$$\tau \equiv k_x r_0 t, \tag{49}$$

and the following dimensionless variables:

$$r \equiv \frac{k_x r_0}{k_y}\sigma, \tag{50}$$

$$c \equiv \frac{k_x r_0}{k_y}\upsilon, \tag{51}$$

where, corresponding to the selection of k_x above, the k_y are to be chosen respectively as

$$k_y = k_2,\ \ k_1,\ \ k_1 \text{ or } k_2.$$

With the help of the transformation (49) to (51) the set of Eqs. (4) and (5) is seen to be transformed into the following one:

$$\frac{d\sigma}{d\tau} = -\frac{k_1}{k_y}\sigma^2 + \frac{k_2}{k_y}\sigma v, \tag{52}$$

$$\frac{dv}{d\tau} = \frac{k_1}{k_y}\sigma^2 - \frac{k_2}{k_y}\sigma v - \frac{v}{\varepsilon_x}. \tag{53}$$

Two time scales become apparent now, the slow one for variable σ and the fast one for variable v, since as $\varepsilon_x \to 0$, the rate $\frac{dv}{d\tau}$ becomes infinite while the rate $\frac{d\sigma}{d\tau}$ remains finite.

Following the well known procedure systematized in Ref. [11] we substitute for the fast variable in Eq. (53) the following series:

$$v = v^{(0)} + \varepsilon v^{(1)} + \varepsilon^2 v^{(2)} + \cdots$$

and require the different orders in ε_x to be equal on both sides of the equation. To order ε_x^{-1} we find that

$$v^{(0)} = 0,$$

and after reverting to the original variables that

$$\dot{r} = -k_1 r^2 \quad \text{and} \quad \dot{p} = 0.$$

To order ε_x^0 we find that

$$v^{(1)} = \frac{k_1}{k_y}\sigma^2,$$

and after reverting to the original variables that

$$\dot{r} = -k_1 r^2 + \frac{k_1 k_2}{k_3} r^3, \quad \text{while} \quad \dot{p} = k_1 r^2.$$

Since one of our goals is to find out the approximation under which the rate law given by Eq. (45) is obtained, we push the calculation to the next order, ε_x, and find that

$$v^{(2)} = \frac{k_1^2}{k_y^2}\sigma^3 \left(2 - \frac{k_2}{k_1} - \frac{2k_2 k_x r_0}{k_y k_3}\sigma \right). \tag{54}$$

Upon reverting to the original variables the resulting rate equations are

$$\dot{r} = -k_1 r^2 \left(1 - \frac{k_2}{k_3} r - \left(2 - \frac{k_2}{k_1}\right) \frac{k_1 k_2}{k_3^2} r^2 + \frac{2 k_1 k_2^2 r_0}{k_y^2} r^3\right) \tag{55}$$

and

$$\dot{p} = k_1 r^2 \left(1 + \frac{k_1}{k_3}\left(2 - \frac{k_2}{k_1}\right) r - 2\frac{k_2 k_1}{k_3^2} r^2\right). \tag{56}$$

At this point, the connection between the rate law predicted by the pseudo steady state hypothesis (45), and Eqs. (55) and (56) can be seen in the following way. Let us keep, in Eq. (55), terms up to order r^3 only, and let us consider the resulting expression as a first order approximation if

$$k_2 r \ll k_3.$$

When we do this, the resulting equation is non other than the equation for $\dot{r}$ in (45). This approximation is a legitimate one, since $k_2 r \ll k_3$ is either, independent from the smallness parameter ε_1, compatible with the smallness parameter ε_2, or compatible with the smallness parameter ε_3, see Eq. (48), anyone of them giving rise to Eq. (55). Notice however, that we can now see that it is incongruous to try to obtain the linear rate law by claiming in Eq. (45) that $k_2 r \gg k_3$ as it is usually done, since Eq. (45) comes as we have shown here from the opposite approximation applied to (55).

It is perhaps worthwhile to point out that the approximation $k_2 r \gg k_3$ applied to Eq. (45) is equivalent to take $r_0 = \infty$. In fact the comparison of

$$k_{\text{exp}} \equiv -\frac{d \ln r}{dt}$$

with Eq. (45) can be written as

$$\frac{1}{k_{\text{exp}}} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1 r}.$$

From here we see that to take the maximum possible value of $k_{\text{exp}} = \frac{k_1 k_3}{k_2}$ amounts to take $\frac{1}{r} = 0$. Nevertheless, the identification of the slope

$$\frac{d\dot{p}}{dr} = \frac{k_1 k_3}{k_2}$$

is justified apart from (45), in a particular approximation, because as we have shown in the previous section, it corresponds to the slope of the tangent at the inflection point between the maximum and the equilibrium minimum, only when $k_2 r \gg k_3$ still holds. Notice also that contrary to what the pseudo steady state hypothesis establishes, see Eq. (45), only to order r^2 is $\dot{p} = -\dot{r}$.

In the second part of this section we apply the singular perturbation method again. This time let us assume that the intermediate species c, suffers recombination and formation faster than decomposition; this assumption disqualifies c as a short lived variable. This situation is taken into account through the following smallness parameterλ_x, and time scale θ:

$$\begin{aligned} \lambda_x &\equiv \frac{k_3}{k_x r_0} \ll 1, \\ \theta &\equiv \lambda_x t. \end{aligned} \tag{57}$$

Here, the k_i are the same as in (47) and, correspondingly,

$$\lambda_x = \lambda_1,\ \lambda_2,\ \lambda_3,$$

Let us start once more from the independent equations (4) and (5) but this time, since we have shown in the previous section that a linear rate law is to be expected when not near equilibrium, that is when $c \neq 0$ is still valid, let us apply to them, the following change of variable:

$$(c, r) \longrightarrow (Y \equiv c + r,\ r).$$

The result is the set formed by

$$\dot{Y} = -k_3(Y - r) \tag{58}$$

and

$$\dot{r} = -k_1 r^2 + k_2 r(Y - r). \tag{59}$$

In the time scale θ, the set of evolution Eqs. (58) and (59) is seen to be transformed into the pair for the slow variable Y, and the fast one r, given next,

$$\frac{dY}{d\theta} = -(Y - r)k_x r_0, \tag{60}$$

$$\frac{dr}{d\theta} = \frac{1}{\lambda_x}(-k_1 r^2 + k_2 r(Y - r)). \tag{61}$$

The substitution of the series

$$r = r^{(0)} + \lambda_x r^{(1)} + \lambda_x^2 r^{(2)} + \cdots$$

into the fast variable equation (61) and the application, as before, of the well known method [9], leads, to the first order in the smallness parameter λ^{-1}, to two solutions,

$$r^{(0)} = \frac{k_2 Y}{k_1 + k_2} \quad \text{and} \quad r^{(0)} = 0,$$

which in their turn yield respectively the following equations:

$$\frac{d(r+c)}{dt} = \frac{k_1 k_3}{k_1 + k_2}(r+c)$$

and

$$\frac{d(r+c)}{dt} = k_3(r+c)$$

To the next order, λ_x, we find essentially the same results, that is the straight lines

$$\frac{d(r+c)}{dt} = \frac{k_1 k_3}{k_1 + k_2}(r+c) - \frac{k_1 k_3^2}{(k_1 + k_2)^2} \tag{62}$$

$$\frac{d(r+c)}{dt} = k_3(r+c). \tag{63}$$

We immediately recognize this rate laws as the ones giving slopes we have already calculated. In fact, Eq. (62) has the inflection point slope, Eq. (44), that is consistent with the slope (42); whereas Eq. (63) has the near equilibrium slope given in the Eq. (37) which we have discarded on the grounds of no experimental evidence for it.

With respect to Eq. (62) an approximation similar to the one employed for (55) can be devised if one insists in an equation of the form predicted by the pseudo steady state hypothesis. In fact, expressing

$$\frac{k_1 k_3 (r+c)}{k_1 + k_2}$$

as common factor in Eq. (62) and looking upon the resulting expression as an approximation when in addition of (57) the more stringent requisite

$$\frac{k_3}{(k_1 + k_2)(r+c)} \ll 1$$

is still satisfied, it can be written as

$$\dot{p} = \frac{k_1 k_3 (r+c)^2}{(k_1 + k_2)(r+c) + k_3}. \tag{64}$$

It might be argued that Eq. (62) does not correspond to a true rate law because it contains the variable $r + c$ and c is a concentration that is not the one traditionally measured. However, in the case of gaseous decompositions, the intermediate species invoked by the Lindemann's mechanism is not a chemically different species from the reactant r as is the case of the intermediate in the Michaelis-Menten mechanism for example. The Lindemann's mechanism postulates species c to be the same as species r, only that having some of its internal degrees of freedom enriched in energy; thus when the concentration of

r is thought to be the measured one, it could be the concentration corresponding to $r+c$. If this is the experimental case, we may conclude that the real linear rate law found is the one given by (62) and the linear experimental slope k_{exp} must be equated with

$$\frac{k_1 k_3}{k_1 + k_2}, \tag{65}$$

corresponding to Eq. (44), rather than with

$$\frac{k_1 k_3 r}{k_2 r + k_3}.$$

We must stress the fact that whether this is the case for a particular experiment or not, it does not affect the validity of Eq. (42). In any case, we are in the physical situation that the occurrence of a constant experimental slope comes from the fact that the experimental measurement of the reactant concentration r has not been made when asymptothically near the equilibrium.

Finally let us point out that it is inconsistent to apply the approximation

$$k_3 \gg (k_2 + k_1)(r + c)$$

with the goal of obtaining the quadratic law form in expression (64) because it is the opposite of the approximation that leads to Eq. (64) in the first place.

4. CONCLUDING REMARKS

Several properties of the non-linear Lindemann mechanism have been demonstrated. They are embodied by the new results expressed among others in Eqs. (26) for the initial slope in the experimental space $(r, \dot{p})$, and particularly the Eqs. (32) and (33), for the near equilibrium slope in the phase space (p, c). These two possible values, predicted by the mechanism, exhibit the existence of two branches of results; one of them, has not, up to our knowledge, being observed in experiments. It is the one given by the set of Eqs. (33), (35) and (37). With respect to the other set of equations for the near equilibrium slopes, given by (32), (34) and (36), and in view of the fact that there exists the maxima implied by Eq. (27) for the spaces $(r, \dot{p})$ and $(r+c, \dot{p})$ we conclude there must exist the corresponding inflection points.

Since according to the mechanism the equilibrium slope in $(r, \dot{p})$ is zero, the idea is advanced that if a constant slope is experimentally found, it is because the experiment has been taking place along the flat part of the curve where the inflection point is to be found, that is, when still $r \neq 0$ and $c \neq 0$ (see Fig. 3). It was next shown that the value of the slope that traditionally has been ascribed to the experimental slope k_{exp} namely the one given by (43) corresponds to the slope of the tangent at the inflection point that occurs, in the $(r, \dot{p})$ curve predicted by the Lindemann's mechanism, when $k_2 r \gg k_3$. This last condition however, is not always realized; given a decomposition reaction, at fixed temperature, the k_i are fixed and if it holds or not will depend on the chosen r_0. In fact, in Fig. 3 the case is exhibited where an approximately flat part is found near the inflection point, whose slope is not the one given by (43) since in this case the approximation $k_2 r \gg k_3$ is not applicable.

The question of finding the approximations that will lead to the linear and the quadratic rate laws from the mechanism, was addressed with the singular perturbation method of approximation known as fast variable elimination method in the second section.

We have shown first than when the nature of the reactant and its initial concentration and temperature are such that the decomposition rate is the fastest process, that is when $k_x r_0 \ll k_3$, the rate law is the polynomial given by either of the Eqs. (55) or (56), its lowest order giving the quadratic law. The rate law predicted by the pseudo steady state hypothesis, namely Eq. (45), is shown to be the cubic order in r approximation of (55), when $k_2 r \ll k_3$. In this way it is exhibited that it cannot be claimed to obtain the linear law $\dot{p}(r)$ in a consistent fashion from Eq. (45) because that requires to ask for the opposite approximation, $k_2 r \gg k_3$. Thus, the identification of the expression (43) with the k_{exp} at high concentration is open to objection. The question remains then of how to obtain a linear rate law from the mechanism. This we addressed next.

We have shown that if a slope is found to be a constant, different from zero, it is because the measurements are not yet near equilibrium, otherwise a zero slope would be found (see (34) and (36)) and c would be zero. According to this fact, we applied the approximation method of elimination of fast variable. The result we found is the prediction of a linear rate law for $\dot{Y}(Y)$, where $Y \equiv r + c$ but not for $\dot{r}(r)$. This result is obtained when the nature of the reactant and the initial concentration are such that $k_3 \ll k_x r_0$, see (57), happens to be. But if such is the physical situation, then, c cannot possibly act as a fast variable. After transformation of the evolution equations to the variables r, and $r + c$, the predicted rate law is the one given in Eq. (62). Its slope being the same as in (44), which is consistent with the result given by Eq. (42). Our comment on this is that because species r and c are chemically the same, their differences coming from the excitation of internal degrees of freedom in c, it might well happen that the true linear rate law experimentally obtained is the one given in Eq. (62) and the experimental slope k_{exp} should then be equated with (44) and not with (42).

Therefore, in opposition to the pseudo steady state hypothesis, Eq. (45), to which both approximations $k_2 r \ll k_3$ and $k_2 r \gg k_3$ have been traditionally applied, we have shown here the following properties of the Lindemann's mechanism. First, the application of the approximation $k_2 r \gg k_3$ to Eq. (45) is inconsistent because Eq. (45) is shown to be obtained when $k_2 r \ll k_3$. As a consequence, the identification of the linear rate law constant k_{exp} with (43) cannot be justified from Eq. (45). Second, a linear rate law is obtained for the sum of concentrations $r + c$ which leads to a different identification of k_{exp}, namely the one given in (65).

If, however, it is sure that the true experimental coordinates are $(r, \dot{p})$, then the linear rate law in coordinates $(r, \dot{p})$ is an experimental approximation along the tangent at the inflection point of the curve predicted by the mechanism. Whatever the case, Eq. (42) remains true because it is a result derived directly from the mechanism itself without having recourse to any particular method or interpretation; however it cannot come from elimination of a fast variable with independent variables (r, c).

Summing up, we have found that for a given reaction, if one starts with an r_0 such that $k_x r_0 \ll k_3$ is met and a linear rate law in $(c, \dot{p})$ is found, k_{exp} cannot possibly be given by (43) but comes from the experiment being realized along the flat part of the curve predicted by the Lindemann mechanism. But if one starts with an r_0 such that $k_x r_0 \gg k_3$ is met and a linear rate law is found, then k_{exp} is given by (44) provided it can be shown that the measured concentration is $r + c$. The question of what is the correct identification of the experimental, constant slope, (43) or (44) depends therefore on which are the true experimental variables, but if Lindemann's mechanism is to be applicable, a constant different from zero slope will emerge because measurements have not been taken up to the equilibrium but lie near the inflection point of $(r, \dot{p})$. The identification of k_{exp}, has an impact on the evaluation of the k_i from the mechanism, but this and further consequences in connection with statistical mechanics theories will be pursued elsewhere.

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