# CONTRIBUTION TO THE THEORY OF PERIODIC REACTIONS

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It lies in the nature of the law of mass-action that every simple (isothermal) reaction approaches its equilibrium asymptotically. In systems, on the other hand, in which several reactions go on simultaneously, the possibility of other modes of approach to equilibrium (or to a steady state) arises. A case of this kind, which presents some features of special interest, is treated below.

Consider the following series of consecutive reactions, each of which we will suppose to be (practically) irreversible:

$$\text{I.} \quad a \longrightarrow A$$
$$\text{2.} \quad A \longrightarrow B$$
$$\text{3.} \quad B \longrightarrow C.$$
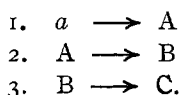
It is to be understood that the capitals refer to substances in the state of "dilute" gas or solution, while the small letter a denotes a saturated vapor or solution in contact with its condensed phase. It is further to be assumed that the conversion of a into A is slow as compared with the establishment of equilibrium between the condensed phase and its vapor or solution, so that the concentration of the latter may be regarded as practically constant, and diffusion effects may be left out of consideration.

Then the equations expressing the rate of change of the concentrations of the substances A and B are:

$$\frac{dc_A}{dt} = H - k_1 c_A \tag{1}$$

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B \tag{2}$$

where H, k_1 and k_2 are constants, and the symbols c_A c_B have the usual meaning.

Now let the substance B influence autocatalytically

its own rate of formation, and let us further assume that this influence follows the simplest possible law, so that we can write for k_1 in (1):

$$k_1 = kc_B \qquad (3)$$

Equations (1) and (2) then become

$$\frac{dc_A}{dt} = H - kc_A c_B \qquad (4)$$

$$\frac{dc_B}{dt} = kc_A c_B - k_2 c_B \qquad (5)$$

The complete solution of equations (4) and (5), giving the entire course of the reaction, presents difficulties. Of the final stages in the process, however, which are of special interest, we can very easily obtain a representation.

Let us first of all simplify equations (4) and (5) by changing the scale of time reckoning, and by fusing some of the constants. We will put

$$T = kt \qquad (6)$$

$$h = \frac{H}{k} \qquad (7)$$

$$K = \frac{k_2}{k} \qquad (8)$$

Making these substitutions in equations (4) and (5), we have

$$\frac{dc_A}{dT} = h - c_A c_B \qquad (9)$$

$$\frac{dc_B}{dT} = (c_A - K)c_B \qquad (10)$$

A further transformation is suggested by the reflection that the system will ultimately settle down to a steady state when

$$\frac{dc_A}{dT} = h - c_A c_B = 0 \qquad (11)$$

$$\frac{dc_B}{dT} = (c_A - K)c_B = 0 \qquad (12)$$

i. e., when

$$c_A = K \tag{13}$$

$$c_A c_B = K c_B = h \tag{14}$$

$$c_B = \frac{h}{K} = L \tag{15}$$

Instead of reckoning with absolute concentrations c_A c_B, let us then reckon with the excess

$$x = c_A - K \tag{16}$$

$$y = c_B - L \tag{17}$$

of the existing over the ultimate concentrations. Introducing these in equations (9) and (10) we thus finally obtain

$$-\frac{dx}{dT} = x\dot{y} + Ky + Lx \tag{18}$$

$$\frac{dy}{dT} = xy + Lx \tag{19}$$

Now in the last stages of the process, when the steady state is nearly reached, x and y are both very small, and we can neglect the product xy. Equations (18) and (19) then finally by elimination of y and x respectively, lead to the differential equations of the second order

$$\frac{d^2x}{dT^2} + L\frac{dx}{dT} + KLx = 0 \tag{20}$$

$$\frac{d^2y}{dT^2} + L\frac{dy}{dT} + KLy = 0 \tag{21}$$

in which we recognize the well-known "damped vibration" type. The reaction is periodic provided that

$$L < 4K.$$

The solution of (20) and (21) in that case, written in the simplest form, is

$$y = y_0 \, e^{-pT} \cos qT \tag{23}$$

$$x = \frac{1}{L}\frac{dy}{dT} = -zy_0 e^{-pT} \sin(\varphi + qT) \tag{24}$$

$$= Me^{-pT} \sin(\varphi + qT) \tag{25}$$

where

$$p = \frac{L}{2} \tag{26}$$

$$q = \frac{\sqrt{4KL - L^2}}{2} \tag{27}$$

$$Lz = \sqrt{p^2 + q^2} \tag{28}$$

$$\sin \varphi = \frac{p}{\sqrt{p^2 + q^2}} \tag{29}$$

$$\cos \varphi = \frac{q}{\sqrt{p^2 + q^2}} \tag{30}$$

The constant y_0 is the value of y at time $T = 0$, as is evident from (23). The origin of time is arbitrarily so chosen that equation (23) contains no sine term.

No reaction is known which follows the above law, and as a matter of fact the case here considered was suggested by the consideration of matters lying outside the field of physical chemistry.[1] It seems interesting, however, also from a purely chemical point of view, to note that in a system in which consecutive reactions take place in the presence of an autocatalytic decomposition-product, we have the requisite conditions for the occurrence of a "periodic" process. And in the simple case here considered we have two consecutive reactions of equal period, each following the law of "damped vibrations," and the one lagging behind the other by an angle depending on certain coefficients characteristic of the reactions, but independent of the initial concentrations.

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[1] The growth of living matter is obviously autocatalytic at least in form. It has been shown by T. Brailsford Robertson (Arch. f. Entwickelungsmech. d. Organismen, 1908, p. 581) that the growth of man and other organisms can be represented with close approximation as the resultant of two components, each following the law of a reversible monomolecular autocatalytic reaction. The rather close agreement of the calculated with the observed values seems rather surprising. For the circumstances which ultimately bring the autocatalytic reaction to a standstill are the decreasing concentration of the substances entering into the reaction, and the increasing concentration of the reaction-products. It is not obvious what are the analogous conditions (if any) which set a limit upon the mass of the full-grown organism.