UNDAMPED OSCILLATIONS DERIVED FROM THE LAW OF MASS ACTION.

By Alfred J. Lotka.

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It was shown by the writer on a former occasion[1] that the course of a chemical reaction, as computed from the laws of chemical dynamics, may, in certain circumstances, assume an oscillatory character.

The case considered led, however, to damped oscillations fading off into equilibrium, not to a continued periodic process; and reflections of a general character on the kinetics of material transformations[2] seemed to make the occurrence of undamped oscillations, in the absence of geometrical causes (surface films, etc.), appear improbable, since it seemed to demand a very special numerical relation between the reaction constants. These, in nature, of course stand generally in no obvious relation.

It is, therefore, somewhat contrary to his first expectations that the writer now finds the conditions for undamped oscillations may occur in the absence of any geometrical causes in a homogeneous system.

A case which leads to such an effect is, for example, the following.

A substance S_0 is present in constant concentration. (This condition may be secured either by providing a large excess, or by using a saturated solution in the presence of undissolved substance. In the former case the system will be homogeneous, in the latter case it will not be. This circumstance has no bearing on the course of the reaction to be considered except insofar as it provides a constant concentration of the substance S_0. If the system is heterogeneous we shall assume, as on a former occasion, that the chemical changes taking place are slow as compared with diffusion effects so that these latter may be left out of account.) In this system let a substance S_1 be formed autocatalytically from the substance S_0. Since the concentration of S_0 is constant, the rate of formation of S_1 will, in the simplest case, be proportional to the quantity X_1 of S_1 actually present, so that we may write

$$\text{mass of } S_1 \text{ formed per unit of time}^3 = a_1X_1. \qquad (1)$$

Let another substance S_2 be formed from S_1 in mono-molecular reaction, so that we may write

$$\text{mass of } S_2 \text{ formed per unit of time} = cX_1. \qquad (2)$$

And furthermore let the substance S_2 also influence its own formation autocatalytically, so that

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[1] A. J. Lotka, *J. Phys. Chem.*, **14**, 271 (1910); *Z. physik. Chem.*, **72**, 508 (1910); **80**, 159 (1912); see also Hirniak, *ibid.*, **75**, 675 (1910); and compare also Lowry and John, *J. Chem. Soc.*, **97**, 2634 (1910); Rakowski, *Z. physik. Chem.*, **57**, 321 (1906).

[2] Lotka, *Phys. Rev.*, **24**, 235 (1912); *Proc. Am. Acad.*, **55**, 137 (1920); see, in particular, footnote 13 on page 145 of the latter reference.

[3] At constant volume; masses being, in that case, proportional to concentrations.

$$c = a_2X_2. \tag{3}$$

Likewise let S_2 decompose in molecular reaction, so that

$$\text{mass of } S_2 \text{ decomposed per unit of time} = b_2X_2. \tag{4}$$

If in the second reaction, S_2 alone is formed from S_1 then we have evidently

$$\frac{dX_1}{dt} = a_1X_1 - a_2X_1X_2 \tag{5}$$

since, in that case, the amount of S_1 decomposed is equal to the mass of S_2 formed.

We may, however, make the more general supposition that along with S_2 any other substances are formed in proportional amounts. In that case we may write

$$\frac{dX_1}{dt} = a_1X_1 - b_1X_1X_2 \tag{6}$$

where b_1 is in general different from (greater than) a_2.

On the other hand, as regards the substance S_2 we have

$$\frac{dX_2}{dt} = a_2X_1X_2 - b_2X_2. \tag{7}$$

The course of events in the system under consideration is now defined by Equations 6 and 7.

Dividing (7) by (6) we obtain

$$\frac{dX_2}{dX_1} = \frac{X_2(a_2X_1 - b_2)}{X_1(a_1 - b_1X_2)} \tag{8}$$

or

$$\left(\frac{a_1}{X_2} - b_1\right) dX_2 = \left(a_2 - \frac{b_2}{X_1}\right) dX_1. \tag{9}$$

Integrating,

$$b_2 \log X_1 - a_2X_1 + a_1 \log X_2 - b_1X_2 = K. \tag{10}$$

Let us put

$$X_1 = x_1 + b_2/a_2 = x_1 + p \tag{11}$$

$$X_2 = x_2 + a_1/b_1 = x_2 + q. \tag{12}$$

Then (10) becomes

$$b_2 \log (x_1 + p) - a_2x_1 + a_1 \log (x_2 + q) - b_1x_2 = K'. \tag{13}$$

Expanding the logarithms by Taylor's theorem certain terms are found to cancel out and we have

$$b_2\left(\log p - \frac{x_1^2}{2p^2} + \frac{x_1^3}{3p^3} - \ldots\right) + a_1\left(\log q - \frac{x_2^2}{2q^2} + \frac{x_2^3}{3q^3} - \ldots\right) = K'. \tag{14}$$

In the immediate neighborhood of the origin of x_1, x_2 this reduces to

$$\frac{b_2x_1^2}{p^2} + \frac{a_1x_2^2}{q^2} = 2(b_2 \log p + a_1 \log q - K'). \tag{15}$$

$$= \text{constant} \tag{16}$$

$$= r_2, \text{ say;} \tag{17}$$

from which it is seen that near the origin the integral curves (10) of (8) approach the elliptic form (17).

More generally the integral curves (10), or their equivalent (13), in the positive quadrant of X_1, X_2, are closed curves of some such form as indicated in Fig. 1.

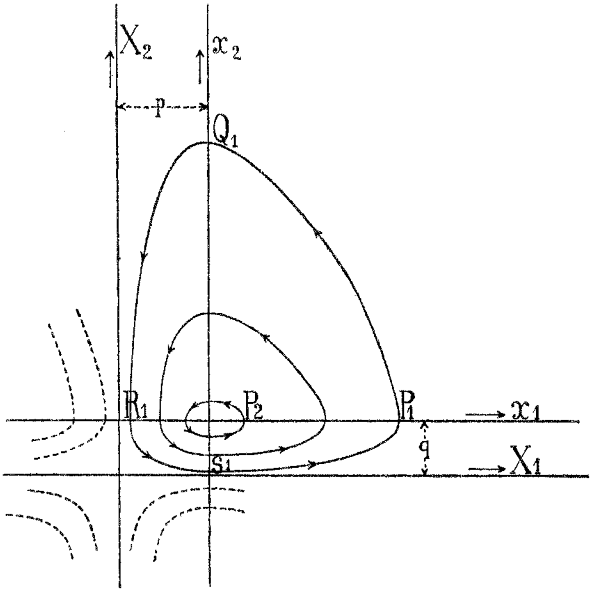

Fig. 1.—Diagram showing general character of the integral curves of Equation 8. In the positive quadrant of X_1X_2 these are closed curves, contained entirely within that quadrant, and intersecting the aces of x_1x_2 orthogonally. Near the origin of x_1x_2 the curves are very nearly elliptical.

The solution (10) enables us to plot X_2 as a function of X_1. We can then plot point for point

$$\varphi(X_1) = \frac{1}{a_1X_1 - b_1X_1X_2} \tag{18}$$

and Equation (6) then takes the form

$$\frac{dX_1}{\varphi(X_1)} = dt \tag{19}$$

$$t = \int \frac{dX_1}{\varphi(X_1)} \tag{20}$$

from which we obtain by simple quadrature (*e. g.*, with the planimeter), an expression for t as a function of X_1, or, say

$$X_1 = \Phi_1(t). \tag{21}$$

In exactly similar manner we obtain

$$X_2 = \Phi_2(t) \tag{22}$$

thus completing our solution of the system of differential Equations 6, 7.

The Character of the Functions Φ.—It has already been observed that within the positive quadrant of X_1X_2 (which alone interests us, since masses cannot be negative) the integral curves (10) are closed curves.

Furthermore, it can be seen by inspection of (6) that

$$\frac{dX_1}{dt} \begin{matrix} > \\ = \\ < \end{matrix} 0 \tag{23}$$

according as

$$X_2 \begin{matrix} < \\ = \\ > \end{matrix} \frac{a_1}{b_1} \tag{24}$$

that is to say, by (12), according as

$$x_2 \begin{matrix} < \\ = \\ > \end{matrix} 0. \tag{25}$$

A glance at Fig. 1 shows that this means the point X_1X_2 travels in counter clockwise direction around the integral curves as the process represented by (6), (7) takes its course.

From this, again, it is plain that $\Phi_1(t)$, $\Phi_2(t)$ are periodic functions of t. We may, therefore, expand them into Fourier's series.

$$\left.\begin{aligned} X_1 = \Phi_1(t) = A_0 &+ A_1 \cos nt + B_1 \sin nt \\ &+ A_2 \cos 2nt + B_2 \sin 2nt \\ &+ \ldots \end{aligned}\right\} \tag{26}$$

$$\left.\begin{aligned} X_2 = \Phi_2(t) = A'_0 &+ A'_1 \cos nt + B'_1 \sin nt \\ &+ A'_2 \cos 2nt + B'_2 \sin 2nt \\ &+ \ldots \end{aligned}\right\} \tag{27}$$

The constants n, A, B may be evaluated by substituting (26), (27) in (6), (7) and equating coefficients of homologous terms.

We thus find, in particular, for n

$$n = \pm \sqrt{a_1b_2} \tag{28}$$

that is to say, the reaction is oscillating, with a period

$$T = \frac{2\pi}{\sqrt{a_1b_2}}. \tag{29}$$

It is interesting to observe that the amplitude of the oscillation, as defined by the constants A, B, A', B', depends on the initial masses X_1, X_2, but the period of oscillation T is independent of these. Hence if two systems of the kind here considered be started off simultaneously, but from different initial concentrations, they will forever after keep time with each other, although one may be making much greater excursions than the other. In terms of Fig. 1 this means, for example, that if one system starts from point P_1 at a given instant, the other from point P_2, they will periodically pass through P_1 and P_2 simultaneously, though one travels in one cycle around the large circuit $P_1Q_1R_1S_1P_1$ the other one around the small (nearly) elliptical circuit P_2.

Two Types of Equilibrium.—It is interesting to note the topography of the integral curves about the two equilibrium points. These curves have been drawn in dotted lines also in the negative and mixed quadrants where they have only a geometrical meaning.

Around the point

$$X_1 = \frac{b_2}{a_2} \quad \text{or} \quad x_1 = 0$$

$$X_2 = \frac{a_1}{b_1} \quad \text{or} \quad x_2 = 0$$

the curves form closed contour lines, like those which on a map represent a mountain crest or a trough-shaped valley.

On the other hand near the point

$$X_1 = 0 \quad \text{or} \quad x_1 = -p$$

$$X_2 = 0 \quad \text{or} \quad x_2 = -q$$

the curves follow a course such as the contour lines near a saddle or col in a landscape.

These features are typical of the two kinds of equilibrium. The crest corresponds to a center of oscillation. The saddle point corresponds to a position of unstable equilibrium. For details regarding this feature the reader is referred to a previous publication by the writer.[1]

Rhythmic phenomena are of particular interest in connection with biological systems (*e. g.*, heart-beat). An extension of the method here set forth, in its application to certain biological systems, will appear in a forthcoming issue of the Proceedings of the National Academy of Sciences.

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THE HEATS OF COMBUSTION OF BENZENE, TOLUENE, ALIPHATIC ALCOHOLS, CYCLOHEXANOL, AND OTHER CARBON COMPOUNDS.

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This paper is a continuation of extended researches concerning the physico-chemical properties of typical compounds of carbon. It enumerates the careful quantitative combustion in an adiabatic calorimeter of the following substances, cane sugar, naphthalene, benzoic acid (these 3 taken as standard substances); benzene, toluene, tertiary butyl benzene, cyclohexanol; together with methyl, ethyl, propyl, butyl and isobutyl alcohols. The main features of the present investigation, which lead to the hope that it may be an improvement over earlier

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[1] Lotka, *Science Progress*, 14, 406 (1920).