

## CONTRIBUTION TO THE GENERAL KINETICS OF MATERIAL TRANSFORMATIONS.

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F. JÜTTNER<sup>1</sup> has given a general discussion of the differential equations of chemical dynamics, in so far as they apply to a single chemical reaction taking place in accordance with the law of mass action.

A certain interest attaches to a still more general treatment which should make us independent of the law of mass action, and which should cover the wider field of concurrent reactions of various types. Such a treatment is therefore given below.

The systems with which we have to deal comprise a number of components  $S_1 S_2 \dots S_n$ , whose mass at any instant may be denoted by  $X_1 X_2 \dots X_n$ . Observational data furnish directly or indirectly a system of differential equations<sup>2</sup>

$$\left. \begin{array}{l} \frac{dX_1}{dt} = F_1(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_j) \\ \frac{dX_2}{dt} = F_2(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_j) \\ \dots \dots \dots \\ \frac{dX_n}{dt} = F_n(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_j) \end{array} \right\} \quad (1)$$

<sup>1</sup> Zeitschr. f. phys. Chemie, 1911, v. 77, p. 735. See also R. Marcellin, Ann. de Phys. 1895, v. 3, p. 120.

<sup>2</sup> The system of equations (1) although very general, does not, however, cover cases in which geometric factors (e. g. diffusion effects) play a dominant rôle. Such cases are therefore excluded from our present considerations. Certain reactions in heterogeneous systems, nevertheless, do fall within the scope of this discussion, namely those the velocity of which is small as compared with the rate of diffusion, so that the course of the reaction is determined practically by the reaction velocities alone, irrespective of diffusion velocity.

A class of reactions which, perhaps, may not always fall within the scope of equations of the type (1) and (2) are so-called induced, sympathetic or coupled reactions. In such cases it may be that the velocities  $\frac{dX}{dt}$  can not be represented as functions of the  $X$ 's alone, but that the velocities  $\frac{dX}{dt}$  themselves must appear explicitly in these functions.

The quantities  $P_1 P_2 \dots P_j$  which occur in (1) are certain parameters, such as for example the volume and the temperature<sup>3</sup> of the system in course of transformation. The case commonly considered is that in which these parameters  $P$  are kept constant (or, as in radio-active transformations, the case in which pressure, temperature, etc. are without influence upon the transformation). We shall for the present at any rate, adopt this customary convention, which in point of fact represents the case of prime interest both in theory and in practice. The parameters  $P$  being constant, we may, for our present purposes, omit them from the functional parentheses in (1), so that we have, in effect,

$$\left. \begin{array}{l} \frac{dX_1}{dt} = F_1(X_1, X_2, \dots, X_n) \\ \frac{dX_2}{dt} = F_2(X_1, X_2, \dots, X_n) \\ \dots \dots \dots \\ \frac{dX_n}{dt} = F_n(X_1, X_2, \dots, X_n) \end{array} \right\} \quad (2)$$

It is expedient to introduce new variables as follows:

Putting

$$F_1 = F_2 = \dots = F_n = 0 \quad (3)$$

we obtain<sup>4</sup>

$$\begin{aligned} X_1 &= C_1 \\ X_2 &= C_2 \\ \dots \dots \dots \\ X_n &= C_n \end{aligned} \quad (4)$$

We will write

$$x_i = X_i - C_i \quad (5)$$

and introduce  $x$  in place of  $X$  in (2).

We then have:

$$\frac{dx_i}{dt} = f_i(x_1, x_2, \dots, x_n) \quad (6)$$

<sup>3</sup> The choice of the parameters  $P$  is more or less arbitrary, but in any case the general form of the equations (1), (2) is independent of the particular choice made.

<sup>4</sup> This system of equations will in general have a number of solutions, corresponding to so many different states of equilibrium. In the cases ordinarily considered in physical chemistry, however, one of these solutions is of special or sole interest.

In the expansion of the right-hand member of (6) by Taylor's theorem the absolute term must be zero, in view of (5), hence

$$\left. \begin{aligned} \frac{dx_1}{dt} &= a_{11} x_1 + a_{12} x_2 + \dots + a_{1n} x_n + \dots \\ \frac{dx_2}{dt} &= a_{21} x_1 + a_{22} x_2 + \dots + a_{2n} x_n + \dots \\ \dots & \\ \frac{dx_n}{dt} &= a_{n1} x_1 + a_{n2} x_2 + \dots + a_{nn} x_n + \dots \end{aligned} \right\} \quad (7)$$

A general solution of this system (7) is <sup>5</sup>

$$\left. \begin{aligned} x_1 &= \alpha'_1 e^{\lambda_1 t} + \alpha'_2 e^{\lambda_2 t} + \dots + \alpha'_n e^{\lambda_n t} \\ &\quad + \alpha'_{11} e^{2\lambda_1 t} + \alpha'_{22} e^{2\lambda_2 t} + \dots + \alpha'_{nn} e^{2\lambda_n t} \\ &\quad + \alpha'_{12} e^{(\lambda_1+\lambda_2)t} + \dots \\ x_2 &= \alpha''_1 e^{\lambda_1 t} + \alpha''_2 e^{\lambda_2 t} + \dots \end{aligned} \right\} \quad (8)$$

where  $\lambda_1, \lambda_2, \dots, \lambda_n$  are the  $n$  roots <sup>5a</sup> of the equation of  $n^{\text{th}}$  degree

$$\left| \begin{array}{ccccc} a_{11} - \lambda & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22} - \lambda & a_{23} & \dots & a_{2n} \\ \dots & & & & \\ a_{n1} & a_{n2} & \dots & \dots & a_{nn} - \lambda \end{array} \right| = \Delta(\lambda) = 0 \quad (9)$$

<sup>5</sup> See Picard, *Traité d'Analyse*, 1908, v. 3, p. 14; Forsyth, *Theory of Differential Equations*, 1900, v. 3, pp. 2, 8, 9; Königsberger, *Lehrbuch der Theorie der Linearen Differentialgleichungen*, 1889, p. 283.

<sup>5a</sup> The quantities  $\lambda$  in (8), (9) are subject to certain restrictions. See Picard, loc. cit., pp. 9, 10; 17, 18. The method of determination of certain of the constants  $a$  in (8) also breaks down in the special case that two or more of the roots of (9) are equal, or differ only by an integral factor.

We shall not here discuss the case of multiple roots of equations (9), which presents no particular difficulty (see Königsberger loc. cit.; Lotka, *Zeitschr. f. Phys. Chemie*, 1912, v. 80, p. 161); nor the case in which the series in the right hand members of (7) contain no terms of the first degree. This case does not appear to admit of general treatment. Certain special cases have been treated by Picard, Poincaré, Dulac, Bendixon, Jordan. (See Dulac, *Jl. Ec. Polytechn. IX cahier* 1904; *Bul. Soc. Math.* 1906; Bendixon, *Acta Math.* 24; Jordan, *Jl. Math.* 1906). It should be noted that if the series (8) begin with the terms of second degree, for example, a change in sign only of all the variables  $x$  leaves the velocities  $\frac{dx}{dt}$  unaltered, for small displacements.

Such a state of affairs does not correspond to the nature of the physical systems and processes here under discussion. This special case which presents certain mathematical difficulties, is therefore also a case of no practical interest for our present discussion.

The law of expansion of the determinant  $\Delta(\lambda)$  is readily recognized if we use Cauchy's notation, in which a determinant is defined by writing down the terms of its dexter diagonal enclosed in parentheses. In the case that  $n = 4$ , for example, we have<sup>6</sup>

$$\begin{aligned} \lambda^4 - & \{a_{11} + a_{22} + a_{33} + a_{44}\}\lambda^3 \\ & + \{(a_{11}a_{22}) + (a_{11}a_{33}) + (a_{11}a_{44}) + (a_{22}a_{33}) + (a_{22}a_{44}) + (a_{33}a_{44})\}\lambda^2 \\ & - \{(a_{11}a_{22}a_{33}) + (a_{11}a_{22}a_{44}) + (a_{11}a_{33}a_{44}) + (a_{22}a_{33}a_{44})\}\lambda \\ & + (a_{11}a_{22}a_{33}a_{44}) = 0 \end{aligned} \quad (10)$$

To determine the coefficients  $\alpha'_i, \alpha''_i, \dots$  we substitute in (7)

$$\left. \begin{array}{l} x_1 = \alpha'_i e^{\lambda_i t} \\ x_2 = \alpha''_i e^{\lambda_i t} \\ \dots \dots \dots \end{array} \right\} \quad (11)$$

Equating coefficients of homologous terms we then obtain

$$\left. \begin{array}{l} \alpha'_i(a_{11} - \lambda_i) + \alpha''_i a_{12} + \alpha'''_i a_{13} + \dots = 0 \\ \alpha'_i a_{21} + \alpha''_i (a_{22} - \lambda_i) + \alpha'''_i a_{23} + \dots = 0 \\ \alpha'_i a_{31} + \alpha''_i a_{32} + \alpha'''_i (a_{33} - \lambda_i) + \dots = 0 \\ \dots \dots \dots \end{array} \right\} \quad (12)$$

The equations (12) are not independent, seeing that  $\Delta(\lambda)$  vanishes according to (9).

The trivial solution (13)

$$\alpha'_i = \alpha''_i = \alpha'''_i = \dots = 0 \quad (13)$$

of (12) is of no interest. The existence of other solutions is assured by the vanishing of  $\Delta(\lambda)$  according to (9). One of the constants  $\alpha'_i, \alpha''_i, \dots$  remains arbitrary, and the proportion  $\alpha'_i: \alpha''_i: \alpha'''_i: \dots$  is then determined in the well-known manner by the homogeneous linear system of equations (12). That is to say, if we form the determinant of the coefficients of  $\alpha'_i, \alpha''_i, \alpha'''_i, \dots$  in the left-hand members of (12), and if we denote by  $\Delta_{\alpha'_i}, \Delta_{\alpha''_i}, \Delta_{\alpha'''_i}, \dots$  the minors of the coefficients of  $\alpha'_i, \alpha''_i, \alpha'''_i, \dots$  in any one selected row, then

$$\alpha'_i: \alpha''_i: \alpha'''_i: \dots : : \Delta_{\alpha'_i}: \Delta_{\alpha''_i}: \Delta_{\alpha'''_i}: \dots \quad (14)$$

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<sup>6</sup> See, for example, Czuber, Einführung in die höhere Mathematik, p. 178. The symbols enclosed in round parentheses denote the determinants of which these symbols form the dexter diagonal.

The coefficients  $\alpha'_{ii}, \alpha''_{ii}, \dots$  of the terms of second and higher degree are determined in analogous manner.

Equations (3), which have so far been introduced merely as a mathematical auxiliary, have an obvious physical significance. They represent the conditions for a steady state or an equilibrium.

Now, if  $X_1, X_2, \dots, X_n$  are entirely independent, it will be seen that (3) completely determines the equilibrium. Physically this means that in such a case, when the values of the parameters  $P$  (e. g. volume, temperature) were once fixed, there would then be no further freedom whatever in fixing the equilibrium. This latter would then, for example be wholly independent of the masses of the several components of the system.

This does not correspond to the actual conditions ordinarily met with in cases of concrete interest. In such cases there are commonly given, in addition to the differential equations (1), which express the general kinetics of the system, a further set of *equations of constraint*<sup>7</sup> of the form

$$\Phi(X_1, X_2, \dots, X_n) = 0 \quad (15)$$

In physico-chemical systems the equations of constraint are commonly derived directly from the *reaction equations*, of which, according

<sup>7</sup> Ordinarily the equations of constraint derived from the reaction equation contain the stoichiometric constants of those equations. However, in the case of certain simultaneous reactions, in which the products of the several reactions are formed in constant proportion, the function  $\Phi$  will contain also certain other constants defining this proportion and not themselves defined by the stoichiometric properties of the system.

In the case most frequently dealt with in physical chemistry, the case of a system of constant total mass, one of the equations of constraint takes the form

$$\Sigma X = \text{const.}$$

Furthermore, the immutability of the chemical elements (in ordinary reactions) furnishes for each element  $e$  an equation of constraint.

$$\Sigma m_e = \text{constant}$$

where  $m_e$  denotes the total mass of the element  $e$  present in the system.

In special cases there may be constraints of entirely different character. Thus, in certain technical processes a stream of gas is passed over a catalytic substance in such manner that an approximately constant mass of the products of reaction issue per unit of time.

In such case, in addition to equations of type (1) there will be given one or more equations of the form

$$\frac{dX}{dt} = \text{constant} = F(C_1, C_2, \dots, C_n)$$

where  $C_1, C_2, \dots, C_n$  are the (constant) concentrations of the substances  $S_1, S_2, \dots, S_n$  entering the reaction chamber.

Cases of this kind do not fall within the scope of our present reflection. Their theoretical and practical treatment presents, however, no particular difficulties.

to circumstances, there may be one or more applying to the system under consideration. They commonly involve the initial values  $A_1, A_2, \dots, A_n$  of  $X_1, X_2, \dots, X_n$  as parameters, so that they are of the general form

$$\Phi(X_1, X_2, \dots, X_n; A_1, A_2, \dots, A_n) = 0 \quad (16)$$

The effect of such equations of restraint is to cause the determinant  $\Delta(0)$  to vanish.<sup>8</sup>

For, in view of (2), (5), and (7) we may write (15) in the form

$$\varphi(\dot{x}_1, \dot{x}_2, \dots, \dot{x}_n) = 0 \quad (17)$$

which implies that

$$J = \frac{\partial(\dot{x}_1, \dot{x}_2, \dots, \dot{x}_n)}{\partial(x_1, x_2, \dots, x_n)} = 0 \quad (18)$$

But inspection of (7) shows that

$$a_{rs} = \left( \frac{\partial \dot{x}_r}{\partial x_s} \right)_o \quad (19)$$

and that therefore

$$\Delta(0) = J_o = 0 \quad (20)^9$$

That is to say, the existence of equations of constraint causes the determinant  $\Delta(0)$  to vanish, as was stated above.

Furthermore, the vanishing of  $\Delta(0)$  means that at least one of the roots  $\lambda$  of (9) is zero. Since the left-hand members of (8) can not contain an absolute term, it follows that at least one of the coefficients  $\alpha$  is thus no longer arbitrary, but is fixed at the value 0.

This loss of an arbitrary constant in (8) must be in some way compensated. This compensation is effected by the equation of constraint (15), which introduces as an arbitrary constant the initial value  $A$  of one of the variables  $X$ .

Similarly it can be seen that  $m$  equations of constraint (15) cause the appearance of  $m$  zero roots in (9) and of  $m$  arbitrary constants in the form of initial values of variables  $X$ .

<sup>8</sup>  $\Delta(0)$  is the determinant obtained by putting  $\lambda = 0$  in the right-hand member of (9).

<sup>9</sup> The subscript  $o$  in equation (19) and (20) signifies that the values of  $\frac{dx}{dt}$  to be taken are those corresponding to the origin  $x_1 = x_2 = \dots = x_n = 0$

In such case, then, the equilibrium or steady state is no longer fixed by (1) as soon as the values of the parameters  $P_1, P_2, \dots, P_j$  are given, but the equilibrium further requires, for its definition, the statement of the initial values  $A_1, A_2, \dots, A_m$  of the variables  $X_1, X_2, \dots, X_m$ . That is to say, the equations of equilibrium (3) take the form

$$\left. \begin{aligned} & F_1 (A_1, A_2, \dots, A_m; X_{m+1} \dots X_n) \\ & = F_2 (A_1, A_2, \dots, A_m; X_{m+1} \dots X_n) \\ & = \dots \dots \dots \dots \dots \dots \dots \\ & = F_n (A_1, A_2, \dots, A_m; X_{m+1} \dots X_n) = 0 \end{aligned} \right\} \quad (21)$$

the  $X_1, X_2, \dots, X_m$  having been eliminated by virtue of the equations of constraint (15), with introduction, in their place, of the initial constants  $A_1, A_2, \dots, A_m$ . Equilibrium is now free to be influenced by the arbitrary selection of the initial values of  $m$  of the masses  $X$  of the components of the system. This is the case of common interest in physico-chemical transformations.

It has been shown that, in the case where equations of constraint exist between the variables  $X$ , the polynomical  $\Delta(\lambda)$  contains the factor  $\lambda$ , the determinant  $\Delta(0)$  vanishing. In fact, it is evident that the differential equation of  $n^{th}$  order in  $x$  which can be derived in well-known manner<sup>10</sup> from the system (7), after rejection of all terms of higher degree than the first, is reducible to an order as much lower than  $n$  as there are zero roots for the equation  $\Delta(\lambda) = 0$ .

However, in practice, instead of operating in this manner upon the primitive system (1) or its equivalents (2) or (6), it is preferable to eliminate from the start  $m$  of the variables  $X$  by the aid of the equations of constraint (15). There then remain  $(n - m)$  dependent variables, which may be either certain of the original variables  $X$

<sup>10</sup> The elimination of  $(n - 1)$  of the variables  $x_1 x_2 \dots x_n$  in the system (7), discarding the terms of second and higher degree, can be effected at sight according to the plan

$$\Delta \left( \frac{d}{dt} \right) x_i = 0$$

that is to say

$$\left| \begin{array}{cccccc} a_{11} - \frac{d}{dt}, & a_{12}, & \dots & a_{1n} & & \\ a_{21}, & a_{22} - \frac{d}{dt}, & \dots & a_{2n} & & \\ \dots & \dots & \dots & \dots & & \\ a_{n1}, & a_{n2}, & \dots & a_{nn} - \frac{d}{dt} & & \end{array} \right| x_i = 0$$

themselves, or certain other variables which it may be convenient to introduce in their stead, and which serve equally to define the state of the system.

Let  $Y_1, Y_2, \dots, Y_\nu$  be such variables given that

$$\nu = n - m \quad (22)$$

In place of the primitive system (2) we shall then have a system

$$\left. \begin{array}{l} \frac{dY_1}{dt} = \Psi_1(Y_1, Y_2, \dots, Y_\nu; A_1, A_2, \dots, A_m) \\ \frac{dY_2}{dt} = \Psi_2(Y_1, Y_2, \dots, Y_\nu; A_1, A_2, \dots, A_m) \\ \dots \dots \dots \\ \frac{dY_\nu}{dt} = \Psi_\nu(Y_1, Y_2, \dots, Y_\nu; A_1, A_2, \dots, A_m) \end{array} \right\} \quad (23)$$

the  $A_1, A_2, \dots, A_m$ , initial values of  $X_1, X_2, \dots, X_m$ , functioning as parameters independent of the time  $t$ .

The system (23) yields to a treatment identical with that applied to the system (2) above, and gives under corresponding conditions a general solution of the form (8) containing  $(n - m)$  exponential and  $(n - m)$  arbitrary multiplicative coefficients, as required by the conditions of the problem.

#### CONVERGENCE OF THE SERIES (8) AND STABILITY<sup>11</sup> OF THE SYSTEM AT THE ORIGIN OF THE VARIABLES $x$ .

To simplify the discussion let us write

$$\lambda_j = \mu_j + i\nu_j \quad (24)$$

- If  $\mu_j$  is zero,  $\lambda_j$  is a pure imaginary.

We need not discuss the case in which the equation  $\Delta(\lambda) = 0$  has zero roots, since these can be eliminated by a change of variables by virtue of the equations of constraint.

There remain to be discussed the following cases:

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<sup>11</sup> A detailed discussion of the question of the existence of series solution of equations of the type (1) will be found in Poincaré's memoir "Sur les Courbes Définies par les Equations Différentielles," Jl. mathém. 1886, Ser. 4, v. 2, chapter XVII. See also Encycl. des Sciences Math. t. II, v. 3, fasc. 1.

1. If all the  $\mu$ 's are negative, the series (8) evidently converge for large values of  $t$ , and the  $x$ 's then approach zero as  $t$  approaches infinity. In this case, then, the point  $x_1 = x_2 = \dots = x_n = 0$  corresponds to a stable condition.

2. If, on the other hand, all the  $\mu$ 's are positive, then the series (8) converge for large values of  $-t$ , and diverge for large values of  $t$ . The origin of the  $x$ 's in this case corresponds to an unstable condition.

3. If some of the  $\mu$ 's are positive, others negative, the series (8) evidently in general converge neither for large values of  $t$  nor for large values of  $-t$ .

However, in this case we can single out a particular solution

$$x_i = \alpha_i e^{\lambda t} + \alpha_{ii} e^{2\lambda t} + \dots \quad (25)$$

in which  $\mu > 0$ ; from which it is evident that the state of the system at the origin of the  $x$ 's is certainly unstable at any rate for certain displacements. Equilibrium at the origin is therefore in this case unstable.

4. If some of the roots  $\lambda$  are pure imaginaries, the presence of even a single positive  $\mu$  will determine the instability of the equilibrium of the origin. If, on the other hand, those  $\mu$ 's which are not zero, are all negative, then the series may converge for large values of  $t$ , and in that case the equilibrium, at the origin of the  $x$ 's, would be in a certain sense stable; for, after an arbitrary displacement, though the system would not in general return to the origin, it would ultimately travel in a periodic path not containing the origin.<sup>12</sup> That is to say, after the lapse of a certain time the point representing the state of the system would thenceforth never be further away from the origin than a certain finite maximum distance  $M$ .

The criterion for the existence of purely imaginary roots is evidently that  $\Delta(\lambda)$  and  $\Delta(-\lambda)$  have one or more common factors of the form  $(\lambda^2 + \rho^2)$ , where  $\rho$  is a real quantity.

5. If all the  $\lambda$ 's are pure imaginaries,<sup>13</sup> (in which case  $\Delta(\lambda)$  contains,

<sup>12</sup> To be more exact, the point  $x_1, x_2, \dots, x_n$  in  $n$ -dimensional space, which represents the state of the system, describes such a path.

<sup>13</sup> The existence of purely imaginary roots  $\lambda$  may perhaps seem of theoretical rather than practical interest, since they could occur only when the coefficients in (7) satisfy very particular conditions, and since it appears improbable that these conditions would be satisfied in nature.

However, the case, in no way improbable *a priori*, that the real part  $\mu$  of  $\lambda$  be very small, in practice will differ but little from the case where  $\mu = 0$ . For, if  $\mu$  is sufficiently small, any accidental disturbance of the system (e.g. any accidental change in one of the parameters  $P$ ) from equilibrium, will set up oscillations with only slight damping, so that the system will be liable to be kept in more or less constant oscillations.

only even powers of  $\lambda$ , with all coefficients of the same sign), then the series (8) may converge for all values of  $t$ . In that case the process would be periodic *ab initio*, and the equilibrium at the origin would be stable in the same sense as in case (4) above.

To recapitulate, we may enunciate two propositions, of which one is the converse of the other:

Given that the series (8) are convergent,

1. If none of the real parts  $\mu$  of the roots  $\lambda$  of the equation  $\Delta(\lambda) = 0$  is positive, the system is in stable equilibrium at the origin of the  $x$ 's.

This stability is absolute if none of the  $\mu$ 's are zero.

It is relative, of the type (4) or (5), if  $\Delta(\lambda) = 0$  has one or more roots in which  $\mu = 0$ .

2. If the system is stable (absolutely or relatively) at the origin of the  $x$ 's, then the equation  $\Delta(\lambda) = 0$  can not have a root  $\lambda$  such that  $\mu > 0$ .

#### SPECIAL CASES.

##### 1. Only one dependent variable.

If  $n - m = 1$ , i. e., if the number of equations of constraint is only one less than the total number of primitive dependent variables  $X$ , then the state of the system at any instant is completely defined by statement of the value of one single variable  $Y$ , given the values of the initial constants  $A_1, A_2, \dots$  and of the parameters  $P_1, P_2, \dots$ . The transformation can in this case be regarded as one single reaction.

The commonest example of this kind is that of one simple chemical reaction, reversible or not, unaccompanied by any simultaneous reaction of any kind (such as side reactions, consecutive reactions, etc.). For the variable  $Y$  we may then employ the mass (or concentration) of an arbitrarily selected component, or any convenient multiple thereof.<sup>14</sup>

In this case, if we omit from the functional parenthesis the parameters  $A_1, A_2, \dots$ , the system of equations (19) reduces to a single equation.

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<sup>14</sup> In chemical dynamics it is customary to employ for the variable  $Y$  in a single reaction the change in concentration, from the origin of time to the instant  $t$ , of one or more, chosen arbitrarily, of the components. The relation between the  $X$ 's, the  $A$ 's and the  $Y$ 's, at constant volume, is then

$$Y = A - X.$$

A somewhat different convention is followed by Jüttner loc. cit. See also Mellor, Chemical Statics and Dynamics, 1904, pp. 85, 86; 91, 92.

$$\frac{dY}{dt} = F(Y) \quad (26)$$

or, shifting the origin after the manner of (5), (6),

$$\frac{dy}{dt} = f(y) \quad (27)$$

and hence, by the same procedure as in the case of (7)

$$\frac{dy}{dt} = ay + by^2 + \dots \quad (28)$$

The solution (8) in this case takes the form

$$y = \alpha_1 e^{\lambda t} + \alpha_{11} e^{2\lambda t} + \alpha_{111} e^{3\lambda t} + \dots \quad (29)$$

where

$$\lambda = a \quad (30)$$

$$= \frac{\partial y}{\partial t} \quad (31)$$

Now if the equilibrium at  $y = 0$  is stable, it is evident that we must have

$$\left. \begin{array}{l} \frac{\partial y}{\partial t} < 0 \\ a < 0 \\ \lambda < 0 \end{array} \right\} \quad (32)$$

Hence we conclude that

1. The series (29) converges for large values of  $t$ .
2. The variable  $y$  ultimately approaches zero asymptotically, since the coefficient  $a$ , from the nature of things, can not be complex.

A proof of this asymptotic approach to equilibrium has been given by Jüttner, for the case of a single-chemical reaction following the law of mass action. The proof given above is independent of the law of mass action and applies to all cases satisfying only the broad condition that the equilibrium corresponding to  $y = 0$  is stable.

#### SPECIAL CASES (continued).

2. If  $n - m > 1$  the transformation can not be regarded as one single reaction. The state of the system at any instant, for given values of the parameters  $P$  and  $A$  requires for its definition  $(n - m)$

$= \nu$  variables  $Y_1, Y_2, \dots, Y_\nu$ . The process can in this case be regarded as the resultant of  $(n - m)$  single transformations proceeding simultaneously, and the state of the system, and in particular the velocities  $\frac{dX}{dt}$ , are fully defined when we are given the values of the parameters  $P$ ; the initial values  $A_1, A_2, \dots, A_m$  of the variables  $X$  (masses of the several components); and the values of the variables  $Y_1, Y_2, \dots, Y_\nu$ , which tell us how far each reaction has proceeded.

#### CONSECUTIVE TRANSFORMATIONS.

A special case arises if the  $(n - m)$  "single" transformations whose resultant is the actual transformation can be so arranged in order, that the velocity of the first depends solely on  $Y_1$ , that of the second on both  $Y_1$  and  $Y_2$ , in general that of the  $j^{\text{th}}$  on  $Y_1 Y_2 \dots Y_j$ . This is the case of what might be termed *purely consecutive* reactions.

The system of equations (7) in this case takes the form:

$$\left. \begin{aligned} \frac{dy_1}{dt} &= a_{11} y_1 + \dots \\ \frac{dy_2}{dt} &= a_{21} y_1 + a_{22} y_2 + \dots \\ &\dots \dots \dots \\ \frac{dy_\nu}{dt} &= a_{\nu 1} y_1 + a_{\nu 2} y_2 + \dots + a_{\nu \nu} y_\nu + \dots \end{aligned} \right\} \quad (33)$$

The solution of (33) is here also given by (8); however, it takes on a simplified form owing to certain special properties of the exponential constants  $\lambda$  and the coefficients  $a$ , as follows:

#### A. EXPONENTIAL CONSTANTS.

1. It will be seen that in (33), as compared with (7), every coefficient  $a_{rs}$  for which  $s > r$  is zero. In consequence of this  $\Delta(\lambda)$  reduces to the dexter diagonal, and hence

$$\lambda_i = a_{ii}$$

2. Inasmuch as the coefficients  $a$  are essentially real, it follows that the  $\lambda$ 's also are all real. If therefore equilibrium is established,

the approach to it must be ultimately asymptotic, the presence of trigonometric terms in (8) being excluded by the reality of all the  $\lambda$ 's.

Indeed, the purely successive character of the reactions, as defined above, excludes reversible reactions, so that the final mass of certain of the components, when in equilibrium, is zero. Oscillations beyond the equilibrium point are therefore excluded by the physical nature of the variables  $X$  (masses), which do not admit of negative values.

3. We have seen that the system will be stable at the origin of the  $y$ 's, and at the same time the series (8) will converge, provided that all the  $\mu$ 's are negative, i. e. in the present case, provided that

$$a_{ii} < 0 \quad (i = 1, 2, \dots, \nu) \quad (34)$$

that is to say, provided that each individual transformation taken by itself tends towards a stable equilibrium (see discussion of equation 32).

### B. MULTIPLICATIVE CONSTANTS.

1. The system (33) has the following peculiarity: We may break off at any one of the equations, say the  $j^{th}$ , and leave a self-complete system.

From this it is easily seen that the series (8) for  $y_i$  must in this case break off at the terms in  $\lambda_i = a_{ii}$  or its multiples, and can not, for example contain any terms in  $\lambda_{(j+1)}$ . The coefficients of these further terms must therefore be zero. This also follows directly by (12).

2. Let  $-\lambda_m = -a_{mm}$  be the least of the  $-\lambda$ 's, all the  $\lambda$ 's being negative. Or, in other words, let  $|\lambda_m| = |a_{mm}|$  be the least of the  $|\lambda|$ .

Then it is evident that for sufficiently large values of  $t$  all other terms may be neglected in comparison with those in  $\lambda_m$  and of the first degree. In its last phases the process is therefore represented by

$$\left. \begin{array}{l} y_1 = 0 \\ y_2 = 0 \\ \dots \dots \dots \\ y_{m-1} = 0 \\ y_m = C_o e^{\lambda_m t} \\ y_{m+1} = C_1 e^{\lambda_m t} \\ \dots \dots \dots \\ y_\nu = C_\nu e^{\lambda_m t} \end{array} \right\} \quad (36)$$

so that in the last phases

$$y_1 : y_2 : \dots : y_{m-1} : y_m : y_{m+1} : \dots : y_\nu : 0 : 0 : \dots : 0 : C_o : C_1 : \dots : C_\nu \quad (37)$$

That is to say, the quantities  $y$  are in constant ratio. Furthermore, if  $y_m$  relates to the substance or substances  $S_m$  having the least  $|\lambda|$ , all the substances parent to  $S_m$  are entirely absent in the last stages of the transformation.

We recognize here a well-known property of radioactive equilibria, in which the longest-lived substance (e. g. uranium) heads the series, while the other substances are present in constant ratio. However, from the method by which this conclusion has here been reached, it is evident that this property is independent of the particular form of radioactive transformations, but rests on a broader basis and is common to all systems in which is taking place a series of purely successive transformations according to any law whatever.

#### SPECIAL CASES. (Continued)

##### *Consecutive Reversible<sup>15</sup> Reactions.*

It may be noted in passing that the conclusions of the last section above are still applicable to a broad class of cases of consecutive reactions, including reversible reactions, provided that at least one among them is irreversible. It will suffice here to point out, by the way of example, one such case, that of five consecutive reactions, of which the second and third only are reversible. It is understood that the reactions considered are otherwise purely consecutive, so that the second, for instance, is wholly independent of the progress of the fourth and fifth.

The determinant  $\Delta(\lambda)$  in this case takes the form:

$$\Delta(\lambda) = \begin{vmatrix} a_{11} - \lambda & 0 & 0 & 0 & 0 \\ a_{21} & a_{22} - \lambda & a_{23} & 0 & 0 \\ a_{31} & a_{32} & a_{33} - \lambda & a_{34} & 0 \\ a_{41} & a_{42} & a_{43} & a_{44} - \lambda & 0 \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} - \lambda \end{vmatrix}$$

In this case also it will be found that  $\Delta(\lambda)$  reduces to its dexter diagonal, all the roots for  $\lambda$  being in consequence necessarily real. The approach to equilibrium is therefore in this case also asymptotic,

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<sup>15</sup> The word "reversible" is here of course not understood in its thermodynamical sense.

and the proportion of the  $y$ 's is, during the last stages of the process, constant. This last conclusion applies, in fact to all cases in which all the roots  $\lambda$  are real and negative.

#### GENERAL CASE.

We have considered certain special cases in which  $\Delta(\lambda)$  reduces to its dexter diagonal, so that all the roots  $\lambda$  are real. In general some or all of these roots may be complex, so that in general a more or less complicated series of reactions may give rise to oscillatory phenomena.<sup>16</sup>

In conclusion it may be remarked that the treatment set forth above presents an evident analogy to the theory of small oscillations according to Lagrange. However, in the case of the oscillations of a mechanical system if the number of coordinates is  $n$ , the general solution contains  $2n$  arbitrary multiplicative constants; whereas in the case here studied the number of such constants is equal to the number of variables, namely  $n$ .

This point of difference is not without physical significance:

The multiplicative constants are determined by initial conditions. In the case of an oscillating mechanical system it is necessary, in order completely to determine the motion of the system, to know the  $n$  initial values of the  $n$  coordinates  $X_1, X_2, \dots, X_n$ , and further, the  $n$  initial values of the velocities  $\frac{dX_1}{dt}, \frac{dX_2}{dt}, \dots, \frac{dX_n}{dt}$ .

On the other hand, in the case of transformations of the type here considered, not only is it *sufficient* to know the initial values of  $X_1, X_2, \dots, X_n$ , but, when these are given there remains no further freedom of choice for the initial values of the velocities  $\frac{dX}{dt}$ . We have here a characteristic property of *inertia-free* or completely damped systems, in which velocities are completely determined when the values of the generalized coordinates are given, and in which the accelerations vanish with the velocities.<sup>17</sup>

<sup>16</sup> See Lotka, Zeitschrift f. phys. Chem., 1910, v. 72, p. 508; 1912, v. 80, p. 159; Hirniak ibid. 1910, v. 75, p. 675.

<sup>17</sup> By differentiating (7) we obtain

$$\frac{d^2x_1}{dt^2} = a_{11} \frac{dx_1}{dt} + a_{12} \frac{dx_2}{dt} + \dots$$

Hence it is evident, provided none of the coefficients  $a$  are infinite, that the second and all higher derivatives of  $x_1 x_2 \dots x_n$  vanish with the velocities  $\frac{dx}{dt}$ . Compare Buckingham, Thermodynamics, 1900, p. 33.

Furthermore, in the absence of inertia, the velocities being nevertheless finite, these must be held in check by dissipative resistances. The transformations which we have been considering are accordingly typical *irreversible*<sup>18</sup> processes, and the history of the system undergoing such transformation is a typical example of *evolution*. It is, indeed, with a view to preparing the ground for a general investigation of the dynamics of evolution, that the reflections here set forth were conceived along broad and comprehensive lines. Attention may be drawn to the fact that, while we have spoken of the variables  $X$  as the masses of the components of a system in chemical reaction, there is nothing in the method followed to restrict us to such interpretation. The  $X$ 's may be masses of any species of material complexes in any mutual relation of interdependence. For example, they may be the masses of biological species dependent on each other for food and in other ways. The equations developed by Sir Ronald Ross<sup>19</sup> relative to the interdependence of the malaria parasite, the anopheles mosquito and man, fall within the type here considered, and their solution is comprehended in the general solution given above.

### SUMMARY

THE differential equations relating to a physical system undergoing change of state are of the general form

$$\left. \begin{aligned} \frac{dX_1}{dt} &= F_1(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_i) \\ \frac{dX_2}{dt} &= F_2(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_i) \\ \dots & \dots \dots \\ \frac{dX_n}{dt} &= F_n(X_1, X_2, \dots, X_n; P_1, P_2, \dots, P_i) \end{aligned} \right\} \quad (1)$$

where  $X_1, X_2, \dots, X_n$  are the masses of the components of the system and the quantities  $P$  measure certain parameters defining the state of the system (e. g. pressure, temperature).

The functions  $F$  commonly considered in discussions of this subject are those defined by the law of mass action. Some other special cases

<sup>18</sup> In the thermodynamical sense.

<sup>19</sup> Nature, Oct. 5, 1911, p. 466; A. J. Lotka, ibid. Feb. 8, 1912, p. 497.

have also been considered. The most general discussion of the subject is that given by Jüttner, but is restricted to a broad treatment of a somewhat general form of the law of mass action.

In the present paper a very general treatment of the kinetics of material transformations is developed on the sole assumption that the functions  $F$  are analytic in the neighborhood of the equilibrium values of the variables  $X$ .

A general solution is given of the system of differential equations (1) for the case that the parameters  $P$  are held constant during the transformation. This solution is oscillatory or aperiodic according to the nature (complex or real) of the roots  $\lambda$  of a certain determinantal equation  $\Delta(\lambda) = 0$

The effect of equations of constraint is discussed.

Convergence of the series solution is shown to be related to the stability of the system at the equilibrium point.

Several special cases are considered.

1. Single transformation.

2. Consecutive transformations. It is well known that in chains of consecutive radio-active transformations the products are present in constant ratio. This property is now shown to be quite general for the terminal stages of any series of purely consecutive reactions taking place according to any law whatever, provided only that the functions  $F$  are analytic as previously assumed.

3. A similar conclusion applies to all systems in which the process of transformation is aperiodic.

4. In general, in a complicated system, the process is oscillatory.

The entire development set forth presents an analogy to the theory of small oscillations according to Lagrange. However, instead of  $2n$  arbitrary constants, corresponding to  $n$  co-ordinates, as in Lagrange's theory, we have here only  $n$  such constants. This fact stands in close relation to the circumstance that the systems here considered are essentially "inertia-free" or "completely damped," and the transformations accordingly are typically irreversible processes, typical cases of evolution (see for example Chwolson, Textbooks of Physics, German Edition 1905, v. 3, p. 499; J. Perrin, *Traité de Chimie Physique*, 1903, Chapter V). It is on this account, with a view to preparing for the treatment of the general problem of evolution that the reflections here set forth were conceived along broad and comprehensive lines.