LA-3875

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Reaction Kinetics in Concentration Space

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

Printed in the United States of America. Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Report written: January 1968

Report distributed: March 15, 1968

Reaction Kinetics in Concentration Space

by

C. J. Everett

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

REACTION KINETICS IN CONCENTRATION SPACE

by

C. J. Everett

Introduction. A "global" view of a reversible reaction governed by the law of mass action is obtained by regarding all its possible histories as trajectories in a space of concentrations. Processes at constant volume and at constant pressure are studied in some detail, and appear to present features of mathematical as well as physico-chemical interest. The picture obtained is one of a space separated into two components by a hypersurface of equilibrium points, toward which all points of these components flow, on a family of trajectories simply covering the space.

1. The space C of concentrations. We consider a homogeneous system of particles, of types A_i and B_j , at constant temperature T , participating in the reversible reaction

(a_i, b_j positive integers). Such a system S may be characterized at any instant by its volume V , and a point $p = (x_i, y_j)$ whose mn coordinates $x_i, y_j \geq 0$ are the corresponding A_i, B_j particle densities (numbers per unit volume). The set C of all such points forms a "space of concentrations" in which the course of a reaction appears as a trajectory emanating from its initial point p^* . The present section is devoted to the geometry of this space.

It is convenient to define, for every point $p \in C$, the minima

$$X = \min x_i \geq 0, \quad Y = \min y_j \geq 0$$

and in terms of these, the sets

$$B_Y = \{p; X > 0, Y = 0\},$$

$$B_O = \{p; X = 0, Y = 0\},$$

$$B_X = \{p; X = 0, Y > 0\}$$

of boundary points of C , and the set

$$I = \{p; X > 0, Y > 0\}$$

of its interior points. (Fig. 3 depicts all sets in simplest form.)

There is a purely geometric relation between the subsets B_X, I, B_Y of $C - B_O$, which may be displayed most simply in the following way. With each point $p_O = (x_1^O, y_j^O)$ of B_X ($X^O > 0, Y^O = 0$) we associate a line segment

$$\lambda(p_O) = \{p; x_1 = x_1^O - \zeta; y_j = y_j^O + \zeta; 0 \leq \zeta \leq X^O\} \quad (2)$$

which extends from the boundary point $p_O \in B_X$ to a second boundary point $p_1 \in B_Y$, all intermediate points lying in I . These parallel segments $\lambda(p_O)$, $p_O \in B_X$, "simply cover" the set $C - B_O$. For, if $p^* = (x_1^*, y_j^*)$ is an arbitrary point of the latter, then

$$p_O = (x_1^* + Y^*, y_j^* - Y^*)$$

has $X^O = X^* + Y^* > 0$, $Y^O = Y^* - Y^* = 0$, and so belongs to B_X . Moreover, the segment $\lambda(p_O)$ from this point contains p^* at $\zeta = Y^*$, where $0 \leq Y^* \leq X^O$. It follows that, as p_O ranges over B_X the end point p_1 of $\lambda(p_O)$ ranges over all of B_Y , while its interior sweeps out the whole of I , without duplication.

We shall assume the reaction (1) to be governed by the law of mass action, which asserts that the net number (≥ 0) of "forward" reactions, per unit volume and time, is given by the function

$$r(p) = f_1(p) - f_2(p) = k_1 \pi x_i^{a_i} - k_2 \pi y_j^{b_j} \quad (k_1, k_2 > 0) \quad (3)$$

where $p = (x_i, y_j)$ is the instantaneous concentration

point of the system, and f_1, f_2 represent the individual forward and backward rates.

The sign of the rate function $f(p)$ serves to partition the space C into the sets S^+ , S^0 , S^- on which $f(p) \gtrless 0$. At points of S^+ , the net reaction is forward, at those of S^- , backward, while at points of S^0 , called equilibrium points, the two opposing rates exactly balance.

Clearly then we have the set inclusions

$$B_x \subset S^+, \quad B_0 \subset S^0, \quad B_y \subset S^-.$$

The points of B_0 are "static" equilibria with $f_1 = f_2 = 0$; all other equilibrium points are "dynamic," with $f_1 = f_2 > 0$, and form a set

$$D \equiv S^0 - B_0 \subset I.$$

Moreover, there is exactly one point $\bar{p}$ of (dynamic) equilibrium on each segment $\lambda(p_0)$. For, on the segment $\lambda(p_0)$ in (2), the rate function $f(p)$ in (3) is a polynomial in ζ , namely

$$f(p) \equiv F(\zeta) = k_1 \pi(x_1^0 - \zeta)^{a_1} - k_2 \pi(y_j^0 + \zeta)^{b_j};$$

$$0 \leq \zeta \leq X^0$$

which is clearly decreasing from $f(p_0) = F(0) > 0$ (since $p_0 \in B_x \subset S^+$) to $f(p_1) = F(X^0) < 0$ (since $p_1 \in B_y \subset S^-$). Hence $F(\zeta)$ has a unique zero $\bar{\zeta}$, $0 < \bar{\zeta} < X^0$, and the corresponding point $\bar{p} = (\bar{x}_1, \bar{y}_j) = (x_1^0 - \bar{\zeta}, y_j^0 + \bar{\zeta}) \in D$ is the unique equilibrium point on $\lambda(p_0)$.

Thus the segment $\lambda(p_0)$ is split by $\bar{p}$ into two half-open subsegments $\lambda^+(p_0)$, $\lambda^-(p_0)$, and it appears that S^+ is the union of all $\lambda^+(p_0)$, S^- that of all $\lambda^-(p_0)$, $p_0 \in B_x$. We note here the one-one correspondences

$$B_x \sim D \sim B_y$$

and the two basic partitions

$$B_x \cup I \cup B_y = C - B_0 = S^+ \cup D \cup S^-$$

the first purely geometric, the second imposed by the sign of the rate function $f(p)$.

In this way we obtain a geometric picture of the concentration space C for the reaction (1), composed of the set B_0 of static equilibria, and of its complement $C - B_0$, consisting of the two components $S^+ \supset B_x$, $S^- \supset B_y$, which are separated by an $m - 1$

dimensional hypersurface $D \subset I$ of dynamic equilibria, namely the set of all points $\bar{p}$ of I for which

$$f(\bar{p}) = k_1 \pi \bar{x}_1^{a_1} - k_2 \pi \bar{y}_j^{b_j} = 0$$

or, equivalently,

$$\pi \bar{y}_j^{b_j} / \pi \bar{x}_1^{a_1} = k_1 / k_2 \equiv K$$

where $K = K(T)$ is the "equilibrium constant" for the reaction (1) at the temperature considered.

Allowing an infinite ratio formally, one may say that a point p of $C - B_0$ is in S^+ , D , S^- as

$$\pi y_j^{b_j} / \pi x_1^{a_1} \lessgtr K$$

so that a knowledge of K alone suffices to indicate the direction of net reaction at p .

2. The loci of trajectories. As a preliminary to the following sections some orienting remarks are appropriate. The space C , and the simple covering of its subsets B_x , I , B_y by the segments $\lambda(p_0)$, are purely geometric in character. The sign of the rate function $f(p)$ determines the subsets S^+ , S^0 , S^- of C , based on the direction of net reaction at their points, and the geometric segments $\lambda(p_0)$ afford the simplest means of displaying the separation of S^+ and S^- by D . This much is a completely general background for the reaction (1).

Now it is a purely arithmetic consequence of (1) that a system S^* of volume V^* and concentrations p^* must, after a total net number Z of forward reactions, result in a system S of volume V and concentrations p such that

$$Vx_1 = V^*x_1^* - a_1 Z, \quad Vy_j = V^*y_j^* + b_j Z. \quad (4)$$

However, specification of Z is clearly insufficient to determine the parameters V, p without the imposition of some "constraint" on the system. We shall consider, in what follows, only the two most important cases arising in practice, and our objective now is to indicate the nature of the spatial trajectories in those cases.

A. In §3 we impose the condition that the volume of S remain constant ($V \equiv V^*$), which dictates, via (4), that its concentrations lie on the line

$$x_1 = x_1^* - a_1 z, \quad y_j = y_j^* + b_j z \quad (5)$$

where $z = Z/V^*$ denotes the net number of forward reactions per unit volume from S^* to S .

B. In §4, the constraint imposed is (mathematically) that of constant total particle density

$$s = \sum x_i + \sum y_j \equiv x + y > 0. \quad (6)$$

(This is equivalent to constant total pressure in the case of perfect gases, for which the corresponding partial pressures are $P_i = x_i kT$, $Q_j = y_j kT$.) Specification of the sum constant s singles out a particular partial hyperplane π_s , consisting of all points $p = (x_i, y_j)$ satisfying (6), to which the trajectory emanating from any point p^* on it is confined. The planes π_s , $s > 0$, being parallel and so disjoint, we will limit ourselves to a particular one, which of course consists of its boundary points

$$B_x \cap \pi_s \subset S^+, \quad B_o \cap \pi_s \subset S^0, \quad B_y \cap \pi_s \subset S^-$$

and the set $I \cap \pi_s$ of its interior points.

If to the general relations (4) we now add the condition that the system S have concentrations p on the plane π_s containing p^* ,

$$\text{i.e.,} \quad x + y = s = x^* + y^*$$

we obtain, by summing (4) on i and j , the equation

$$Vs = V(x+y) = V^*(x^*+y^*) - (a-b)Z = V^*s - (a-b)Z \quad (7)$$

$$\text{or} \quad V = V^*\{1 - \rho(Z/V^*)\} \quad (8)$$

where we have set

$$a = \sum a_i, \quad b = \sum b_j, \quad (9)$$

and

$$\rho = (a-b)/s \geq 0 \quad (10)$$

is a fundamental constant for the plane. Substitution of (8) in (4) then shows the concentration point p to have coordinates

$$x_i = \frac{x_i^* - a_i(Z/V^*)}{1 - \rho(Z/V^*)}, \quad y_j = \frac{y_j^* + b_j(Z/V^*)}{1 - \rho(Z/V^*)}. \quad (11)$$

Thus the volume V and concentrations p of the system S resulting from S^* , under the present constraint, after a total of Z such reactions are uniquely determined as

$$V = V^*(1 - \rho z) \quad (12)$$

$$\text{and } p: \quad x_i = \frac{x_i^* - a_i z}{1 - \rho z}, \quad y_j = \frac{y_j^* + b_j z}{1 - \rho z} \quad (13)$$

in terms of the parameter $z = Z/V^*$, which here denotes the net number of forward reactions, from S^* to S , per unit initial volume. Just as (5) defines the locus of the trajectory from p^* in the case of

constant volume, so do the equations (13) define the locus in the present case, which is a line lying in the plane π_s through p^* .

In either case, we shall show that the necessary forms (5), (13) of these loci, dictated by the "arithmetic" of the reaction (1), together with the actual values of the rate function $f(p)$ (not involved until now) suffice to determine the trajectories in time lying on these loci.

Note 1. The parameter $z = Z/V^*$ in part B is not so arbitrary as it may appear. For suppose that the system S of volume V and concentrations p , referred to there, subsequently undergoes Z' additional reactions under the same constraint. One easily verifies the physically obvious fact that the result must be a system S' , of volume

$$V' = V - \rho Z' = V^* - \rho(Z+Z') = V^*\{1 - \rho(Z+Z')/V^*\}$$

and concentrations p' , having

$$x'_i = \frac{x_i - a_i(Z'/V)}{1 - \rho(Z'/V)} = \frac{x_i^* - a_i(Z+Z')/V^*}{1 - \rho(Z+Z')/V^*}$$

and the analogous result for y'_j . This shows that the transformation $T_Z(V^*, p^*) = (V, p)$ of (8), (11) has the "group property," in the sense that, if also $T_{Z'}(V, p) = (V', p')$, then $T_Z, T_{Z'}(V^*, p^*) =$

$T_{Z'+Z}(V^*, p^*)$, i.e.,

$$T_Z, T_{Z'} = T_{Z'+Z}.$$

Since only the "number Z of reactions per unit initial volume" appears in each transformation, it is clear that this is a consistent parameter for the description of trajectories.

Note 2. In both §3 and §4 the minima for a point $p \in C$ which are appropriate are

$$\xi = \min x_i/a_i \geq 0, \quad \eta = \min y_j/b_j \geq 0,$$

and this notation (with suitable superscripts) is used throughout. Note that, in the original definitions of the sets B_x , B_o , B_y , I in §1, the X , Y are replaceable by ξ, η indifferently.

3. The "constant volume" trajectories. We study first the simpler case in which the system is maintained at constant volume.

A. We have seen in §2A that the trajectory from a point p^* must lie on a line of form $x_i = x_i^* - a_i z$, $y_j = y_j^* + b_j z$, where z is the net

number of forward reactions per unit volume, counted from p^* .

B. We therefore define formally, for every p^* of $C - B_0$ ($\xi^* + \eta^* > 0$, as in §2, Note 2), the line segment

$$\sigma(p^*) = \{p; x_1 = x_1^* - a_1 z, y_j = y_j^* + b_j z; -\eta^* \leq z \leq \xi^*\} \quad (14)$$

which extends from a point of B_x to a point of B_y , passes through p^* at $z = 0$, and contains the trajectory from p^* .

C. As a special case, we obtain for every $p_0 \in B_x$ the segment

$$\sigma(p_0) = \{p; x_1 = x_1^0 - a_1 \zeta, y_j = y_j^0 + b_j \zeta; 0 \leq \zeta \leq \xi^0\} \quad (15)$$

extending from $p_0 \in B_x \subset S^+$ to $p_1 \in B_y \subset S^-$.

D. These segments $\sigma(p_0)$, $p_0 \in B_x$ simply cover $C - B_0$. In view of §1, we need only note that the point

$$p_0 = (x_1^0, y_j^0) = (x_1^* + a_1 \eta^*, y_j^* - b_j \eta^*) \quad (16)$$

is in B_x , since $\xi^0 = \xi^* + \eta^* > 0$, $\eta^0 = \eta^* - \eta^* = 0$; and moreover, for this p_0 , the segment $\sigma(p_0)$ of (15) contains p^* at $\zeta = \eta^*$, where $0 \leq \eta^* \leq \xi^0 = \xi^* + \eta^*$, as required.

E. There is a unique equilibrium point $\bar{p}$ on each $\sigma(p_0)$. For the rate function $f(p)$ on the segment $\sigma(p_0)$ is a polynomial

$$f(p) = P(\zeta) = k_1 \pi (x_1^0 - a_1 \zeta)^{a_1} - k_2 \pi (y_j^0 + b_j \zeta)^{b_j}; \quad 0 \leq \zeta \leq \xi^0 \quad (17)$$

which is decreasing from $f(p_0) = P(0) > 0$ to

$f(p_1) = P(\xi^0) < 0$. Hence there is a unique

$\bar{p} = (x_1^0 - a_1 \bar{\zeta}, y_j^0 + b_j \bar{\zeta})$ on $\sigma(p_0)$ such that

$$f(\bar{p}) = P(\bar{\zeta}) = 0, \bar{p} \in D, 0 < \bar{\zeta} < \xi^0.$$

Thus $\bar{p}$ splits $\sigma(p_0)$ into $\sigma^+(p_0) \subset S^+$, $\sigma^-(p_0) \subset S^-$, and S^+ and S^- are the unions of all the corresponding half-open subsegments, for $p_0 \in B_x$. This provides a second geometric view of the space C , relevant for the present trajectories. (It of course coincides with that of §1 when all $a_i = b_j = 1$ in (1).)

F. The segment $\sigma(p^*)$ in (14) is identical with the unique $\sigma(p_0)$ containing p^* , as defined in D. For we have the identities

$$x_1^0 - a_1 \zeta = (x_1^* + a_1 \eta^*) - a_1 \zeta = x_1^* - a_1 (\zeta - \eta^*) \equiv x_1^* - a_1 z \quad (18)$$

$$y_j^0 + b_j \zeta = (y_j^* - b_j \eta^*) + b_j \zeta = y_j^* + b_j (\zeta - \eta^*) \equiv y_j^* + b_j z$$

where $z = z(\zeta) = \zeta - \eta^*$ ranges from $-\eta^*$ to ξ^* as ζ ranges from 0 to $\xi^0 = \xi^* + \eta^*$.

G. With these still geometric preliminaries, we turn now to the trajectories in time. Let p^* be an arbitrary point of $S^+ \cup S^-$, defining the densities of a constant volume system at time $t = 0$. Then the densities at time $t \geq 0$ are given by the point

$$p(t): x_1 = x_1^* - a_1 z, y_j = y_j^* + b_j z \quad (19)$$

of $\sigma(p^*)$, where now $z = z(t)$ denotes the net number of forward reactions per unit volume which have occurred up to time t .

The function $z(t)$, $t \geq 0$ is uniquely determined by the initial condition $z(0) = 0$, and the law (3), which, in conjunction with (19) yields here the differential equation

$$dz/dt = k_1 \pi (x_1^* - a_1 z)^{a_1} - k_2 \pi (y_j^* + b_j z)^{b_j} \equiv P^*(z). \quad (20)$$

In view of the identities (18), it is clear that

$$P^*(z) \equiv P^*(z(\zeta)) \equiv P(\zeta); -\eta^* \leq z = \zeta - \eta^* \leq \xi^*, \quad 0 \leq \zeta \leq \xi^0 \quad (21)$$

where $P(\zeta)$ is the polynomial in (17). Since $P(\zeta)$ was shown in E to be decreasing, with the unique zero $\bar{\zeta}$, $0 < \bar{\zeta} < \xi^0$, it follows that $P^*(z)$ is decreasing, from $P^*(-\eta^*) > 0$ to $P^*(\xi^*) < 0$, with a unique zero $\bar{z} (= \bar{\zeta} - \eta^*)$ on $-\eta^* < \bar{z} < \xi^*$. ($\bar{z}$ is of course computed directly from $P^*(z)$ in (20), and requires only the value of $K = k_1/k_2$.) Thus $P^*(z)$ is simply the function $P(\zeta)$ viewed from p^* as origin. (Cf. Figs. 1, 2.)

The differential equation (20) may therefore be integrated in the form

$$t = t(z) = \int_0^z \frac{dz}{P^*(z)} \quad (22)$$

where z ranges from $z = 0$ (left or right) to the first singularity $\bar{z}$ of the integrand. (This, and the integral of §4, may be integrated in terms of

elementary functions^[4], the nature of which justifies the properties of $t(z)$ cited below.)

H. Now, since $p^* \in S^+ \cup S^-$, we must distinguish the two cases:

Case 1. $p^* \in S^+$, $P^*(0) > 0$, $\bar{z} > 0$ (Fig. 1). The initial reaction being forward, z begins to increase from $z(0) = 0$, and steadily rises to

$$\lim_{t \rightarrow \infty} z(t) = \bar{z} > 0 \quad (23)$$

as will appear in a moment. The corresponding limiting concentrations are seen from (19) to be

Fig. 1

$$\bar{p} = p(\infty): \bar{x}_1 = x_1^* - a_1 \bar{z} > 0, \bar{y}_j = y_j^* + b_j \bar{z} > 0. \quad (24)$$

(This is of course the unique equilibrium point on the segment $\sigma(p_0)$ containing p^* .) The trajectory therefore covers the part of $\sigma^+(p_0)$ from p^* to $\bar{p}$.

To establish (23), one need only note that the integrand $1/P^*(z)$ in (22) increases from $1/P^*(0) > 0$ to infinity at $z = \bar{z}$, and it being a rational function, $t(z)$ necessarily increases from $t(0) = 0$ to $t(\bar{z}) = \infty$, whence (23) follows for the inverse function $z(t)$.

Case 2. $p^* \in S^-$, $P^*(0) < 0$, $\bar{z} < 0$ (Fig. 2). In a similar way, we find that the net reaction begins backward, with z steadily decreasing from $z(0) = 0$ to

$$\lim_{t \rightarrow \infty} z(t) = \bar{z} < 0$$

the corresponding limiting concentrations (24) being again those of the equilibrium point $\bar{p}$ on the seg-

ment $\sigma(p_0)$ involved. The trajectory traces out the part of $\sigma^-(p_0)$ from p^* to $\bar{p}$. Note that the range of z in (22) is $\bar{z} < z \leq 0$ in this case.

Fig. 2

I. Returning to our geometric picture of C , as it appears in time, for constant volume reactions, we see that the points of B_0 remain static, while all points of S^+ and S^- "flow" on parallel straight line trajectories toward points of the separating equilibrium surface D as limiting concentrations. (Fig. 3.)

J. It is interesting to note that there are basically only two trajectories in time on $\sigma(p_0)$, namely those emanating from its end points p_0 and p_1 . All others are "partial" trajectories of these, with the time scale shifted in the obvious way.

For example, suppose that the given point p^* lies on $\sigma^+(p_0)$ ($0 \leq \eta^* < \bar{\zeta}$) with p_0 and $\sigma(p_0)$ as in (16), (15). We have already observed the spatial identities (18), and the resulting functional identity $P^*(z) \equiv P(\zeta)$ in (21), where $z = z(\zeta) = \zeta - \eta^*$. Let us agree to denote by τ the time on the fundamental trajectory out of p_0 , so that

$$\tau = \tau(\zeta) = \int_0^\zeta \frac{d\zeta}{P(\zeta)}; \quad 0 \leq \zeta < \bar{\zeta} \quad (25)$$

defines $\zeta = \zeta(\tau)$, $0 \leq \tau < \infty$, as a special case of (22). Now, using the formal substitution $z = \zeta - \eta^*$, and the identity (21), we have from (22) for the trajectory out of p^* ,

$$t = \int_0^z \frac{dz}{P^*(z)} = \int_{\eta^*}^{\eta^*+z} \frac{d\zeta}{P(\zeta)} = \tau(\eta^*+z) - \tau(\eta^*). \quad (26)$$

Defining

$$\tau^* = \tau(\eta^*) = \int_0^{\eta^*} \frac{d\zeta}{P(\zeta)}$$

(the time τ to p^*), we see from (26) that

$$\tau(\eta^*+z) = \tau^* + t \quad (27)$$

and by inversion,

$$\eta^* + z = \zeta(\tau^*+t).$$

This means that $z(t) \equiv \zeta(\tau) - \eta^*$ (28)

where $\tau = \tau^* + t$, $t \geq 0$

t being the "local" time on the trajectory out of p^* . It follows that the identities (18) are not only spatial, with $z \equiv \zeta - \eta^*$, but also temporal, with $z = z(t)$, $\zeta = \zeta(\tau)$, and $\tau = \tau^* + t \geq \tau^*$.

An equivalent way of expressing this is the following. In (22) the initial time t at which $z = 0$ was arbitrarily taken as $t = 0$. If we had, just as arbitrarily, taken this initial time as the universal time τ^* from p_0 to p^* on the fundamental trajectory, this would synchronize local and universal time, and the equation (27) would read simply $\tau(\zeta) \equiv t(z)$, where $\zeta = \eta^* + z \geq \eta^*$.

Thus if we consider the trajectories from all points $p_0 \in B_x$, $p_1 \in B_y$, originating at the same instant $\tau = 0$ of universal time τ , we then obtain at one blow, as $\tau \rightarrow \infty$, a picture of all trajectories of the systems 3.

Note. A favorite question in elementary chemistry texts concerns the effect of adding to a (constant volume) solution at equilibrium an additional amount of one of the reactants A_1 . From the above point of view, the rate function at the given equilibrium point $\bar{p}$ is

$$f(\bar{p}) = f_1(\bar{p}) - f_2(\bar{p}) = 0$$

and addition of A_1 increases the value of x_1 above $\bar{x}_1$, shifting the system discontinuously to one at a concentration point p^* for which

$$f_1(p^*) > f_1(\bar{p}), f_2(p^*) = f_2(\bar{p})$$

so that

$$f(p^*) = f_1(p^*) - f_2(p^*) > f_1(\bar{p}) - f_2(\bar{p}) = f(\bar{p}) = 0.$$

Therefore $p^* \in S^+$, and with this as origin, the trajectory approaches a new equilibrium point $\bar{p}$, as in Case 1, at which all $\bar{y}_j = y_j^* + b_j \bar{z} > y_j^* = \bar{y}_j$. As always, $\bar{z}$ and $\bar{p}$ may be computed from $P^*(z) = 0$ in (20), and (24), only the value of K being required. The situation is indicated in Fig. 3.

Example 1. As the simplest, but still hardly trivial example, consider a reaction (such as that between ortho- and para-hydrogen)

for which C is the set of all points (x, y) , $x, y \geq 0$. Then

$$B_x = \{(x, 0); x > 0\}, B_0 = \{(0, 0)\},$$

$$B_y = \{(0, y); y > 0\}, I = \{(x, y), x > 0, y > 0\}.$$

The rate function $f(p) = k_1 x - k_2 y$ defines the sets S^+ , S^0 , S^- of points for which $k_1 x \geq k_2 y$. The hypersurface D is the line $\bar{y}/\bar{x} = K = k_1/k_2$, $\bar{x}, \bar{y} > 0$.

For $p_0 = (x^0, 0) \in B_x$, we have the segment

$$\sigma(p_0) = \{(x, y); x = x^0 - \zeta, y = \zeta; 0 \leq \zeta \leq x^0\}$$

with end point $p_1 = (0, x^0) \in B_y$. The unique equilibrium point $\bar{p}$ on $\sigma(p_0)$ is attained for

$$\bar{\zeta} = k_1 x^0 / (k_1 + k_2), \text{ with } \bar{x} = k_2 x^0 / (k_1 + k_2),$$

$$\bar{y} = k_1 x^0 / (k_1 + k_2).$$

Taking p^0 as initial point, integration of (25) yields $\zeta(\tau) = \bar{\zeta} \{1 - \exp[-(k_1 + k_2)\tau]\}$, the trajectory being $x = x^0 - \zeta(\tau) \rightarrow x^0 - \bar{\zeta} = \bar{x}$, $y = \zeta(\tau) \rightarrow \bar{\zeta} = \bar{y}$. Taking p_1 as initial point, one obtains the oppositely directed trajectory from p_1 to $\bar{p}$.

Fig. 3

$$(K = k_1/k_2 = 2/3).$$

Example 2. For the reaction $2A \rightleftharpoons B$ the space C is again that of Ex. 1, but now segments are of form

$$\sigma(p_0) = \{(x, y); x = x^0 - 2\zeta, y = \zeta; 0 \leq \zeta \leq x^0/2\},$$

and the rate function ($k_1 = 1, k_2 = 4$)

$f(p) = x^2 - 4y$ shows that D is a parabola (Fig. 4).

Fig. 4

In particular, for $p_0 = (4, 0) \in B_x$,

$$\sigma(p_0) = \{(x, y); x = 4 - 2\zeta, y = \zeta; 0 \leq \zeta \leq 2\}$$

with end point $p_1 = (0, 2)$, and equilibrium point

$\bar{p} = (2, 1)$ at the unique zero $\bar{\zeta} = 1, 0 < \bar{\zeta} < 2$, of the polynomial $P(\zeta) = (4 - 2\zeta)^2 - 4\zeta = 4(1 - \zeta)(4 - \zeta)$.

For p_0 as initial point, the trajectory is determined via (25):

$$\begin{aligned} \tau(\zeta) &= \int_0^\zeta \frac{d\zeta}{P(\zeta)} = \frac{1}{12} \int_0^\zeta \left\{ \frac{1}{1-\zeta} - \frac{1}{4-\zeta} \right\} d\zeta \\ &= -\frac{1}{12} \log \left\{ \frac{(1-\zeta)}{(1-\zeta/4)} \right\} \end{aligned}$$

$$\text{whence } \zeta(\tau) = \left(1 - e^{-12\tau}\right) / \left(1 - \frac{1}{4} e^{-12\tau}\right) \rightarrow 1 = \bar{\zeta}.$$

To illustrate the "partial trajectory" result of (28), consider the point $p^* = (3, 1/2)$ on $\sigma^+(p_0)$. The segment $\sigma(p^*) (= \sigma(p_0))$ has the form

$$\sigma(p^*) = \{(x, y); x = 3 - 2z, y = \frac{1}{2} + z; -\frac{1}{2} \leq z \leq \frac{3}{2}\},$$

on which the rate function appears as

$$P^*(z) = (3 - 2z)^2 - 4\left(\frac{1}{2} + z\right) = 4\left(\frac{1}{2} - z\right)\left(\frac{7}{2} - z\right).$$

Since $P^*(0) = 7 > 0, \bar{z} = 1/2 > 0$, we have under

Case 1, from (22),

$$t = \int_0^z \frac{dz}{P^*(z)} = -\frac{1}{12} \log \left\{ \frac{(1-2z)}{\left(1 - \frac{2}{7}z\right)} \right\}$$

$$\text{whence } z(t) = \frac{1}{2} \left\{ \frac{(1 - e^{-12t})}{\left(1 - \frac{1}{7} e^{-12t}\right)} \right\} \rightarrow \frac{1}{2}.$$

Now $\eta^* = \frac{1}{2}$ for p^* , so that

$$\begin{aligned} \tau^* = \tau(\eta^*) &= -\frac{1}{12} \log \left\{ \frac{\left(\frac{1}{2}\right)}{\left(\frac{7}{8}\right)} \right\} = -\frac{1}{12} \log \frac{4}{7}, \text{ or} \\ e^{-12\tau^*} &= 4/7. \end{aligned}$$

One then verifies that

$$\zeta(\tau) = \zeta(\tau^* + t) = \left\{ \frac{\left(1 - \frac{4}{7} e^{-12t}\right)}{\left(1 - \frac{1}{7} e^{-12t}\right)} \right\},$$

$$\text{and so } \zeta(\tau) - \eta^* = \zeta(\tau^* + t) - \frac{1}{2}$$

$$= \frac{1}{2} \left\{ \frac{(1 - e^{-12t})}{\left(1 - \frac{1}{7} e^{-12t}\right)} \right\} = z(t)$$

as stated in (28).

Example 3. For comparison with §4, we include a reaction of form $A_1 + A_2 \rightleftharpoons B_1$, for which the space

C of points $p = (x_1, x_2, y_1)$ appears in Fig. 5. The

rate function $f(p) = x_1 x_2 - y_1$ ($k_1 = k_2 = 1$) partitions C into the sets S^+, S^0, S^- , where S^0 is the familiar "saddle surface" (cf. $PV = RT$) consisting of the lines B_0 , and of D , which is that part of the saddle lying in I . The region S^+ lies below the saddle while S^- lies above it in the figure, which shows the segments

$$\sigma(p_0) = \{p; x_1 = x_1^0 - \zeta, y_1 = \zeta; 0 \leq \zeta \leq \xi^0\}$$

for a number of points $p_0 \in B_x$ for which $x_1^0 + x_2^0 = 7$.

These segments being parallel, lie on the plane $x_1/7 + x_2/7 + y_1/(7/2) = 1$. The curve $\bar{c}$ in which the plane cuts the saddle indicates the positions of the equilibrium points $\bar{p}$ on the segments.

Consider in particular the point $p_0 = (3, 4, 0)$, with $\sigma(p_0) = \{p = (3 - \zeta, 4 - \zeta, \zeta); 0 \leq \zeta \leq 3\}$, having end point $p_1 = (0, 1, 3) \in B_y$. Solution of $P(\zeta) \equiv (3 - \zeta)(4 - \zeta) - \zeta = (2 - \zeta)(6 - \zeta) = 0$ gives the unique zero $\bar{\zeta} = 2, 0 < \bar{\zeta} < 3$, and the equilibrium point $\bar{p} = (1, 2, 2)$ on $\sigma(p_0)$.

Integration of (25) yields

$$\begin{aligned} \tau(\zeta) &= \int_0^\zeta \frac{d\zeta}{P(\zeta)} = \frac{1}{4} \int_0^\zeta \left\{ \frac{1}{2-\zeta} - \frac{1}{6-\zeta} \right\} d\zeta \\ &= -\frac{1}{4} \log \left\{ \frac{(1-\zeta/2)}{(1-\zeta/6)} \right\} \end{aligned}$$

which shows that

$$\zeta(\tau) = 2(1 - e^{-4\tau}) / (1 - \frac{1}{3} e^{-4\tau}) \rightarrow 2 = \zeta.$$

The trajectory out of p_0 is therefore

$$x_1 = 3 - \zeta(\tau) \rightarrow 1 = \bar{x}_1, \quad x_2 = 4 - \zeta(\tau) \rightarrow 2, \quad y_2 = \zeta(\tau) \rightarrow 2.$$

In Fig. 6 are shown the trajectories, in the plane π_7 , from the same points p_0 , under the constraint of §4 (cf. Ex. 4).

Note on the irreversible case. If the reverse reaction in (1) is impossible ($k_2 = 0$) we see that S^- is vacuous, $f(p)$ being positive on $B_x \cup I \equiv S^+$, and zero on $B_0 \cup B_y \equiv S^0$. All equilibrium points are therefore "static." For any point p^* of S^+ , the trajectory is given by (19), where now

$\lim_{t \rightarrow \infty} z(t) = \xi^0$, i.e., the segment $\sigma(p_0)$ containing

p^* is traced out from p^* to its end point $p_1 \in B_y \subset S^0$ as limit. Equations (20) and (22) determine $t = t(z)$, where $k_2 = 0$ in $P^*(z)$, and $0 \leq z < \xi^0$.

Since the B_j play no rôle in the reaction, it is more interesting to consider as a concentration space for the A_1 alone the (projection) set C_x of all points $p = (x_1)$, $x_1 \geq 0$. The function $f_1(p)$ in (3) then splits C_x into the sets $S_x^+ = I_x = \{p; \xi > 0\}$, $S_x^0 = B_{x0} = \{p; \xi = 0\}$, on which $f_1(p) > 0$, $f_1(p) = 0$, resp. The trajectory $x_1 = x_1^* - a_1 z(t)$, $0 \leq z \leq \xi^*$ from a point $p^* \in S_x^+$ is the x_1 -part of that above, tracing out a segment from p^* to a limit point $p_1 \in S_x^0 = B_{x0}$ with $x_1^1 = x_1^* - a_1 \xi^*$. It is worth noting that all trajectories are now on infinite segments $\sigma(p_1)$, $p_1 \in B_{x0}$, of form

$$\{p; x_1 = x_1^1 + a_1 \zeta; 0 \leq \zeta < \infty\}$$

and that there is essentially only one trajectory on each $\sigma(p_1)$.

4. The "constant pressure" trajectories. We now turn to the more difficult case in which the reaction (1) occurs in a system at constant temperature and constant total particle density

$$s = \sum x_i + \sum y_j = x + y > 0.$$

A. As shown in §2B, the trajectory for such a system, with initial volume V^* , and concentrations p^* on the plane π_6 , must lie on the line (13)

$$x_i = \frac{x_i^* - a_i z}{1 - \rho z}, \quad y_j = \frac{y_j^* + b_j z}{1 - \rho z}$$

in that plane, where $\rho = (a-b)/s$, and z is a parameter denoting the net number of forward reactions per unit initial volume, counted from p^* . Moreover, the volume V after z such reactions is given by (12) as

$$V = V^*(1 - \rho z).$$

It appears from this that the three types of reaction (1) indicated by the relations $a \geq b$ ($\rho \geq 0$) are attended by quite different volume behavior. While the equality $a = b$ implies constant volume ($V = V^*$) and hence a special case of §3, and the nature of either of the remaining cases $a \geq b$ may be inferred from that of the other by interchanging the A_1 and B_j in (1), we will treat all three cases uniformly. The results obtained must therefore reduce to those of §3 when $a = b$, and moreover, one need not be concerned with the gymnastics of interchange in the nontrivial case $a \neq b$.

B. The nature of the trajectory from p^* being indicated in A, we examine more critically, for $p^* \in (C - B_0) \cap \pi_6$, the set

$$\gamma(p^*) = \left\{ p; x_i = \frac{x_i^* - a_i z}{1 - \rho z}, y_j = \frac{y_j^* + b_j z}{1 - \rho z}; -\eta^* \leq z \leq \xi^* \right\}. \quad (29)$$

1. We note first of all that, for every point p^* of π_6 , we have the inequalities

$$1 - \rho \xi^* > 0, \quad 1 + \rho \eta^* > 0. \quad (30)$$

For $\rho = 0$, both are trivial. For $\rho > 0$, the second is trivial, while the first follows from

$$\begin{aligned} 1/\rho &= s/(a-b) > s/a \geq x^*/a = \sum x_i^*/\sum a_i \\ &\geq \min x_i^*/a_i = \xi^*. \end{aligned}$$

For $\rho < 0$, the first is obvious, and the second follows from

$$\begin{aligned} -1/\rho &= s/(b-a) > s/b \geq y^*/b = \sum y_j^*/\sum b_j \\ &\geq \min y_j^*/b_j = \eta^*. \end{aligned}$$

2. From (30) it appears that $1 - \rho z > 0$ for z on the interval in (29), and therefore $x_i \geq 0$, $y_j \geq 0$.

Fig. 5

Fig. 6

Moreover, summing on i and j in (29) shows that

$$x + y = \frac{(x^* + y^*) - (a-b)z}{1-pz} = s$$

so that the points p of $\gamma(p^*)$ are well-defined in π_s .

3. The set $\gamma(p^*)$ is a straight line segment. For the x_i, y_j of (29) may be written in the form

$$x_i = x_i^* - (a_i - \rho x_i^*) \cdot \frac{z}{1-pz} = x_i^* - \alpha_i u$$

$$y_j = y_j^* + (b_j + \rho y_j^*) \cdot \frac{z}{1-pz} = y_j^* + \beta_j u$$

where $u = z/(1-pz)$ is a new parameter, increasing with z .

4. The line $\gamma(p^*)$ obviously extends from a point of $B_x \cap \pi_s$ to a point of $B_y \cap \pi_s$ and must contain the trajectory emanating from p^* at $z = 0$.

C. In particular, for every point $p_0 \in B_x \cap \pi_s$, (29) defines a line segment $\gamma(p_0) \subset \pi_s$, namely

$$\gamma(p_0) = \left\{ p; x_i = \frac{x_i^0 - a_i \zeta}{1-\rho \zeta}, y_j = \frac{y_j^0 + b_j \zeta}{1-\rho \zeta}; \right. \\ \left. 0 \leq \zeta \leq \xi^0 \right\} \quad (31)$$

which originates at $p_0 \in B_x \cap \pi_s \subset S^+$, terminates in a point $p_1 \in B_y \cap \pi_s \subset S^-$, and has all intermediate points in $I \cap \pi_s$. Note that $1 - \rho \zeta > 0$ on the range in (31), by B.2.

D. We now note that the segments $\gamma(p_0)$, $p_0 \in B_x \cap \pi_s$, simply cover the set $(C-B_0) \cap \pi_s$. For one easily verifies that, if p^* is an arbitrary point of the latter set, there exists a unique point $p_0 \in B_x \cap \pi_s$, with components

$$p_0: x_i^0 = x_i^* + (a_i - \rho x_i^*) \zeta^*, y_j^0 = y_j^* - (b_j + \rho y_j^*) \zeta^*; \\ \zeta^* \equiv \eta^*/(1+\rho \eta^*) \geq 0 \quad (32)$$

for which the segment $\gamma(p_0)$ of (31) passes through p^* (at the parameter value $\zeta = \zeta^*$). Here one must observe that, for the p_0 of (32), one has $\xi^0 = (\xi^* + \eta^*)/(1+\rho \eta^*) > 0$, $\eta^0 = 0$, $x^0 + y^0 = s$,

so that $p_0 \in B_x \cap \pi_s$, and moreover $0 \leq \zeta^* \leq \xi^0$ as required in (31). It follows as before that every point of $B_y \cap \pi_s$ is the end point p_1 of a unique $\gamma(p_0)$, and every point of $I \cap \pi_s$ lies on just one $\gamma(p_0)$, $p_0 \in B_x \cap \pi_s$. Note here that the segments $\gamma(p_0)$ need not be parallel (Fig. 6).

E. We show next that there is a unique equilibrium point $\bar{p}$ on each $\gamma(p_0)$. On the segment $\gamma(p_0)$ of (31), the rate function $f(p)$ in (3) appears now as a rational function of ζ :

$$f(p) = R(\zeta) = k_1 \pi \left(\frac{x_i^0 - a_i \zeta}{1-\rho \zeta} \right)^{a_i} - k_2 \pi \left(\frac{y_j^0 + b_j \zeta}{1-\rho \zeta} \right)^{b_j} \\ = R_1(\zeta) - R_2(\zeta); \quad 0 \leq \zeta \leq \xi^0 \quad (33)$$

and certainly $f(p_0) = R(0) > 0$ since $p_0 \in S^+$, while $f(p_1) = R(\xi^0) < 0$ since $p_1 \in S^-$. However, it is not obvious that $R(\zeta)$ is a decreasing function, and this is proved below. It will then follow that there exists a unique $\bar{\zeta}$, $0 < \bar{\zeta} < \xi^0$, at which $R(\bar{\zeta})$ vanishes, the corresponding equilibrium point $\bar{p}$ on $\gamma(p_0)$ being

$$\bar{p}: \bar{x}_i = \frac{x_i^0 - a_i \bar{\zeta}}{1-\rho \bar{\zeta}}, \bar{y}_j = \frac{y_j^0 + b_j \bar{\zeta}}{1-\rho \bar{\zeta}}. \quad (34)$$

The segment $\gamma(p_0)$ is therefore split by the point $\bar{p}$ (where it cuts the hypersurface D) into two half-open subsegments $\gamma^+(p_0) \subset S^+ \cap \pi_s$, $\gamma^-(p_0) \subset S^- \cap \pi_s$, and one sees that S^+ is the union of all the former, S^- that of all the latter subsegments, where $p_0 \in B_x \cap \pi_s$, $s > 0$. This affords a third view of the geometry of the space C , quite apart from the rôle played by the $\gamma(p_0)$ as spatial trajectories in the present case.

We complete the above remarks by proving that, in all cases, $R_1(\zeta)$ is decreasing, while $R_2(\zeta)$ increases, from which it follows that $R(\zeta)$ in (33) is decreasing, as stated. This is obvious for $\rho = 0$.

When ρ is positive, $R_2(\zeta)$ is increasing, since each of its factors $y_j(\zeta)$ is obviously increasing. However, differentiation of $x_i(\zeta)$ shows that $dx_i/d\zeta \leq 0$ as $x_i^0/a_i \leq 1/\rho$, and it is not necessary that all factors of $R_1(\zeta)$ decrease. (Example: $a_1 = 2$, $a_2 = 1$, $b_1 = 1$; $x_1^0 = 1$, $x_2^0 = 2$, $y_1^0 = 0$.) Surely all those x_i for which $x_i/a_i < 1/\rho$ do so (and

there is at least one $x_1/a_1 = \xi^0 < 1/\rho$) but any others must be nondecreasing. To see that $R_1(\zeta)$ itself is nevertheless decreasing (hence also $R(\zeta)$) we write

$$R_1(\zeta) = k_1 \frac{\pi(x_1^0 - a_1 \zeta)^{a_1}}{(1 - \rho \zeta)^a} = k_1'' \frac{\pi(\xi_1^0 - \zeta)^{a_1}}{(\rho' - \zeta)^a} \equiv k_1'' Q_1(\zeta)$$

where $\xi_1^0 \equiv x_1^0/a_1$, $\rho' \equiv 1/\rho > 0$, $k_1'' > 0$, and show that $Q_1'(\zeta) < 0$ on $0 \leq \zeta < \xi^0$. Using "Leibniz's rule", one finds that

$$(\rho' - \zeta)^{2a} Q_1'(\zeta) = (\rho' - \zeta)^a \sum_i (-a_i) (\xi_1^0 - \zeta)^{a_i - 1} \prod_{h \neq i} (\xi_h^0 - \zeta)^{a_h} + a(\rho' - \zeta)^{a-1} \pi(\xi_1^0 - \zeta)^{a_1} = (\rho' - \zeta)^a \pi(\xi_1^0 - \zeta)^{a_1} \left\{ - \sum \frac{a_i}{\xi_1^0 - \zeta} + \frac{a}{\rho' - \zeta} \right\}.$$

Since $\zeta < \xi^0 = \min \xi_1^0 < 1/\rho = \rho'$, it remains to prove

$$\frac{1}{\rho' - \zeta} < \sum \frac{a_i/a}{\xi_1^0 - \zeta} = \sum \alpha_i (\xi_1^0 - \zeta)^{-1}$$

or

$$\rho' - \zeta > \left\{ \sum \alpha_i (\xi_1^0 - \zeta)^{-1} \right\}^{-1}$$

where we have set $\alpha_i = a_i/a > 0$, with $\sum \alpha_i = 1$. But

$$\rho' = s/(a-b) > s/a \geq \sum x_1^0/a = \sum (a_i/a)(x_1^0/a_i) = \sum \alpha_i \xi_1^0$$

and therefore

$$\rho' - \zeta > \sum \alpha_i (\xi_1^0 - \zeta) \geq \left\{ \sum \alpha_i (\xi_1^0 - \zeta)^{-1} \right\}^{-1}$$

which suffices. (The final relation is the classical inequality^[1,3] for the arithmetic and harmonic means of the numbers $\xi_1^0 - \zeta > 0$ weighted by the $\alpha_i > 0$ of unit sum.)

In considering the case $\rho < 0$, one sees that $R_1(\zeta)$ is obviously decreasing, while $R_2(\zeta)$ is proved to be increasing by invoking the same classical inequality for $\sum \beta_j (\eta_j^0 + \zeta) \geq \left\{ \sum \beta_j (\eta_j^0 + \zeta)^{-1} \right\}^{-1}$, where $\beta_j \equiv b_j/b$, $\eta_j^0 \equiv y_j^0/b_j$.

While we are about it, we prove here the additional result, cited below in part G, that the related function

$$U(\zeta) \equiv (1 - \rho \zeta) R(\zeta); \quad 0 \leq \zeta \leq \xi^0$$

is also decreasing, and, since $1 - \rho \zeta > 0$, has the same unique zero $\bar{\zeta}$ as $R(\zeta)$, $0 < \bar{\zeta} < \xi^0$. For $\rho = 0$, this is trivial. For $\rho > 0$, we note that $1 - \rho \zeta$ is decreasing, hence $(1 - \rho \zeta) R_1(\zeta)$ is decreasing, whereas $(1 - \rho \zeta) R_2(\zeta) = k_2 \pi(y_j^0 + b_j \zeta)^{b_j} / (1 - \rho \zeta)^{b-1}$ is increasing, since the numerator obviously is, and we have $b-1 \geq 0$ in the denominator. Similarly, when $\rho < 0$, $1 - \rho \zeta$ is increasing, hence $(1 - \rho \zeta) R_2(\zeta)$ is increasing, while

$(1 - \rho \zeta) R_1(\zeta) = k_1 \pi(x_1^0 - a_1 \zeta)^{a_1} / (1 - \rho \zeta)^{a-1}$ decreases, since the numerator does, and $a-1 \geq 0$ in the denominator.

F. Let p^* be an arbitrary point of $(C-B_0) \cap \pi_s$, $\gamma(p^*)$ the segment (29), $\gamma(p_0)$ the unique segment containing it, with $p_0 \in B_x \cap \pi_s$, as defined in (31), (32), and discussed in part D. We show that $\gamma(p^*)$ is simply a reparameterization of the identical segment $\gamma(p_0)$. For, we easily verify the relations

$$x_1 = \frac{x_1^0 - a_1 \zeta}{1 - \rho \zeta} = \frac{x_1^* + (a_1 - \rho x_1^*) \zeta^* - a_1 \zeta}{1 - \rho \zeta} = \frac{(1 - \rho \zeta^*) x_1^* - a_1 (\zeta - \zeta^*)}{1 - \rho \zeta} \\ = \frac{x_1^* - a_1 (\zeta - \zeta^*) / (1 - \rho \zeta^*)}{(1 - \rho \zeta) / (1 - \rho \zeta^*)} \equiv \frac{x_1^* - a_1 z}{1 - \rho z}$$

with the analogous result

$$y_j = \frac{y_j^0 + b_j \zeta}{1 - \rho \zeta} \equiv \frac{y_j^* + b_j z}{1 - \rho z}$$

where $z = z(\zeta) = (1 + \rho \eta^*) \zeta - \eta^*$. (35)
(One need only recall the definition $\zeta^* = \eta^* / (1 + \rho \eta^*)$ from (32).)

Since z in (35) ranges from $-\eta^*$ to ξ^* as ζ ranges from 0 to $\xi^0 = (\xi^* + \eta^*) / (1 + \rho \eta^*)$, it appears that $\gamma(p^*) \equiv \gamma(p_0)$.

G. We are ready once more to consider the time dependent trajectories. Let V^* be the volume, and $p^* \in (S^+ \cap \pi_s) \cup (S^- \cap \pi_s)$ the concentrations of a

system S^* at time $t = 0$, and V, p the corresponding parameters of the system S resulting from it, under the present constraint, after a total net number $Z(t)$ of forward reactions counted up to time $t \geq 0$. We know from §2B that V and p are given by the equations

$$V = V(t) = V^*(1-pz) \quad (36)$$

$$p(t): x_i = \frac{x_i^* - a_i z}{1-pz}, \quad y_j = \frac{y_j^* + b_j z}{1-pz}$$

where $z = z(t) = Z(t)/V^*$, and $p(t)$ is on the segment $\gamma(p^*)$.

From the definition of the rate function $f(p)$ in (3), as the instantaneous net number of forward reactions per unit time and volume, it seems clear that we should write

$$dz/dt = Vf(p) = V^*(1-pz)f(p) \quad (37)$$

for the time rate of change of the total number Z at time t . Thus (37) and (36) lead to the differential equation

$$\begin{aligned} dz/dt &= (1-pz) \left\{ k_1 \pi \left(\frac{x_i^* - a_i z}{1-pz} \right)^{a_i} - k_2 \pi \left(\frac{y_j^* + b_j z}{1-pz} \right)^{b_j} \right\} \\ &\equiv (1-pz)R^*(z) \equiv U^*(z) \end{aligned} \quad (38)$$

which, together with the initial condition $z(0) = 0$, uniquely determines the function $z(t)$, $t \geq 0$.

Since we have identified the segment $\gamma(p^*)$ carrying the trajectory (36) with the segment $\gamma(p_0)$ containing p^* , under the substitution (35):

$$z = z(\zeta) = (1+p\eta^*)\zeta - \eta^*$$

it is clear that we have also the functional identity

$$\begin{aligned} U^*(z) &= (1-pz(\zeta))R^*(z(\zeta)) \equiv \frac{1-pz(\zeta)}{1-p\zeta} (1-p\zeta)R(\zeta) \\ &\equiv (1+p\eta^*)U(\zeta) \end{aligned} \quad (39)$$

between the function $U^*(z)$ in (38), and the function $U(\zeta)$ defined on $\gamma(p_0)$ and discussed at the end of part E. It was shown there that $U(\zeta)$ is decreasing, with the unique zero $\bar{\zeta}$ of $R(\zeta)$, $0 < \bar{\zeta} < \xi^0$. Since $1+p\eta^* > 0$, it follows from (39) that $U^*(z)$ is decreasing on $\gamma(p^*)$, from $U^*(-\eta^*) > 0$ to $U^*(\xi^*) < 0$, with a unique zero $\bar{z}$ ($= z(\bar{\zeta})$) on $-\eta^* < \bar{z} < \xi^*$. (Again, $\bar{z}$ is computed directly, from $R^*(z) = 0$).

The differential equation (38) may therefore be integrated in the form

$$t = t(z) = \int_0^z \frac{dz}{U^*(z)} \quad (40)$$

where z ranges, left or right, to the first singularity $\bar{z}$ of the rational function $1/U^*(z)$.

The remaining parts now follow in strictly analogous fashion to those of §3, and we need only state the results.

H. In Case 1, $p^* \in S^+ \cap \pi_g$, $U^*(0) > 0$, $\bar{z} > 0$, $z(t)$ increases from $z(0) = 0$ to $\lim_{t \rightarrow \infty} z(t) = \bar{z} > 0$,

while in Case 2, $p^* \in S^- \cap \pi_g$, $U^*(0) < 0$, $\bar{z} < 0$, $z(t)$ decreases from 0 to $\lim_{t \rightarrow \infty} z(t) = \bar{z} < 0$. In either

case, $z = z(t)$ is obtained by integration of (40), with $0 \leq z < \bar{z}$, or $\bar{z} < z \leq 0$ respectively, and the trajectories extend on $\gamma(p^*)$ from p^* to the limiting concentrations, given by (36) as

$$\bar{p} = p(\infty): \bar{x}_i = \frac{x_i^* - a_i \bar{z}}{1-p\bar{z}}, \quad \bar{y}_j = \frac{y_j^* + b_j \bar{z}}{1-p\bar{z}} \quad (41)$$

where $\bar{p}$ is the unique equilibrium point on the segment $\gamma(p_0)$ containing p^* . The limiting volume is of course

$$\bar{V} = V^*(1-p\bar{z}). \quad (42)$$

I. The picture of the space C in time in the present case shows all points of S^+ and S^- flowing on the lines $\gamma(p_0)$ (not always parallel) of the planes π_g toward the separating manifold D .

J. We again have only two basic trajectories on a segment $\gamma(p_0)$. Define

$$\tau = \tau(\zeta) = \int_0^\zeta \frac{d\zeta}{U(\zeta)}, \quad 0 \leq \zeta < \bar{\zeta} \quad (43)$$

and $\zeta = \zeta(\tau)$ by inversion, for the trajectory out of $p_0 \in B_x \cap \pi_g$, as a special case of (40). Then, using the substitution

$$z = z(\zeta) = (1+p\eta^*)\zeta - \eta^*$$

of (35), and the corresponding identity (39):

$$U^*(z) \equiv (1+p\eta^*)U(\zeta)$$

we have from (40), for the trajectory out of

$p^* \in \gamma^+(p_0)$, $0 \leq \zeta^* < \bar{\zeta}$,

$$\begin{aligned} t &= \int_0^z \frac{dz}{U^*(z)} = \int_{\zeta^*}^{\zeta^* + \{z/(1+p\eta^*)\}} \frac{d\zeta}{U(\zeta)} \\ &= \tau(\zeta^* + \{z/(1+p\eta^*)\}) - \tau(\zeta^*) \end{aligned}$$

where $\zeta^* \equiv \eta^*/(1+\rho\eta^*)$. Defining

$$\tau^* = \tau(\zeta^*)$$

(the time τ on $\gamma(p_0)$ to p^*), this gives

$$\tau(\zeta^* + \{z/(1+\rho\eta^*)\}) = \tau^* + t$$

and by inversion $\zeta^* + \{z/(1+\rho\eta^*)\} = \zeta(\tau^* + t)$.

This may be written in the form (cf. (35))

$$z(t) = (1+\rho\eta^*)\zeta(\tau) - \eta^* \quad (44)$$

where $\tau = \tau^* + t$

t being the local time out of p^* . In view of the spatial identity of $\gamma(p^*)$ and $\gamma(p_0)$ under the substitution (35), (44) identifies the trajectory out of p^* temporally with the part of the trajectory out of p_0 from p^* to $\bar{p}$. Again local time t may be synchronized with universal time τ by taking $t = \tau^*$ as the initial time τ at $z = 0$ in (40), in place of $t = 0$. Thus, starting from $\tau = 0$ at all points of $B_x \cap \pi_s$, $B_y \cap \pi_s$, $s > 0$, simultaneously, we obtain a total view of all trajectories as $\tau \rightarrow \infty$.

Note 1. The differential equation (37):

$$dz/dt = Vf(p)$$

proposed in part G may be open to dissention, since the situation at this point seems somewhat ambiguous. The alternative

$$\frac{d}{dt} \left(\frac{z}{V} \right) = f(p)$$

leads to the result $dz/dt = (1-\rho z)^2 f(p)$ in place of (38) as adopted above. In this connection, one may note that, for the irreversible ($k_2 = 0$) decay

$A \rightarrow bB$, with $x^0 > 0$, $y^0 = 0$, one finds, using the equation (43) based on (38), that $V_0 x^0 = V_0 x^0 e^{-k_1 t}$

which states that the total decay is independent of volume changes attending the reaction at constant pressure. And this seems as it should be. The decay cited is treated in a way apparently different from both of the above alternatives in [2], which is the closest approach to the question we have been able to find. In any event, the ambiguity, if it exists, affects only the time dependence of trajectories, and not their loci, or the position of equilibrium points.

Note 2. It is important in practice to know how many particles of each kind exist at equilibrium, compared with the numbers initially present. An initial system S^* , having volume V^* and concen-

trations $p^* \in \pi_s$, contains $V^* x_1^*$, $V^* y_j^*$ particles of types A_1, B_j . Its equilibrium volume $\bar{V}$ and concentrations $\bar{p}$ are given by (42), (41) as

$$\bar{V} = V^*(1-\rho\bar{z})$$

$$\bar{p}: \quad \bar{x}_1 = \frac{x_1^* - a_1 \bar{z}}{1-\rho\bar{z}}, \quad \bar{y}_j = \frac{y_j^* + b_j \bar{z}}{1-\rho\bar{z}}$$

where $\bar{z}$ is the unique zero, $-\eta^* < \bar{z} < \xi^*$, of $R^*(z)$ in (38). Hence the corresponding limiting numbers at equilibrium are

$$\bar{V} \bar{x}_1 = V^*(x_1^* - a_1 \bar{z}) \leq V^* x_1^*$$

$$\bar{V} \bar{y}_j = V^*(y_j^* + b_j \bar{z}) \geq V^* y_j^*$$

as $\bar{z} \geq 0$, i.e., as $p^* \in S^+ \cap \pi_s$ (Case 1) or

$p^* \in S^- \cap \pi_s$ (Case 2). Note here that possible mixture of increasing and decreasing behavior in concentrations does not affect the result for total numbers.

Note 3. In connection with the above question, we consider the effect of pressure on equilibrium in a reaction for which $a > b$ ($\rho > 0$). Let S be a system of volume V_0 and concentrations $p_0 \in B_x \cap \pi_s$, hence with particle counts $V_0 x_1^0 > 0$, $V_0 y_j^0 \geq 0$.

The equilibrium volume and concentrations for the system are

$$\bar{V} = V_0(1-\rho\bar{\zeta}); \quad \rho = (a-b)/s > 0, \quad s = x^0 + y^0 > 0$$

$$\bar{p}: \quad \bar{x}_1 = \frac{x_1^0 - a_1 \bar{\zeta}}{1-\rho\bar{\zeta}}, \quad \bar{y}_j = \frac{y_j^0 + b_j \bar{\zeta}}{1-\rho\bar{\zeta}}$$

where $\bar{\zeta}$, $0 < \bar{\zeta} < \xi^0$, is the unique zero of the decreasing function

$$R(\zeta) = \frac{k_1 \pi(x_1^0 - a_1 \zeta)^{a_1}}{(1-\rho\zeta)^a} - \frac{k_2 \pi(y_j^0 + b_j \zeta)^{b_j}}{(1-\rho\zeta)^b}$$

$$\equiv R_1(\zeta) - R_2(\zeta); \quad 0 \leq \zeta \leq \xi^0.$$

The particle counts at equilibrium are therefore (as in Note 2)

$$\bar{V} \bar{x}_1 = V_0(x_1^0 - a_1 \bar{\zeta}), \quad \bar{V} \bar{y}_j = V_0(y_j^0 + b_j \bar{\zeta}).$$

For comparison, consider a system of initial volume $V_0 k^{-1}$, and concentrations $k p_0$ ($k > 1$), which therefore contains the same numbers of particles of each type, but lies on a "higher" plane π_{ks} of concentra-

tion (pressure). The equilibrium volume and concentration for this system will be, in terms of the above notation,

$$\bar{V} = V_0 k^{-1} (1 - k^{-1} \rho \bar{\zeta})$$

$$\bar{P}: \quad \bar{x}_1 = \frac{kx_1^0 - a_1 \bar{\zeta}}{1 - k^{-1} \rho \bar{\zeta}}, \quad \bar{y}_j = \frac{ky_j^0 + b_j \bar{\zeta}}{1 - k^{-1} \rho \bar{\zeta}}$$

where $z = \bar{\zeta}$, $0 < \bar{\zeta} < k\xi^0$ is the unique zero of the decreasing function

$$\bar{R}(z) = \frac{k_1 \pi (kx_1^0 - a_1 z)^{a_1}}{(1 - k^{-1} \rho z)^a} - \frac{k_2 \pi (ky_j^0 + b_j z)^{b_j}}{(1 - k^{-1} \rho z)^b},$$

$$0 \leq z \leq k\xi^0.$$

To compare this with $R(\zeta)$, we change variable to $\zeta = z/k$, in terms of which we may write

$$\begin{aligned} \bar{R}(z) &\equiv \bar{S}(\zeta) = k^a R_1(\zeta) - k^b R_2(\zeta) \\ &= k^b \{ k^{a-b} R_1(\zeta) - R_2(\zeta) \}; \quad 0 \leq \zeta = z/k \leq \xi^0 \end{aligned}$$

where $R_1(\zeta)$ and $R_2(\zeta)$ are precisely the component functions of $R(\zeta)$ on the same ζ interval. Since $k > 1$, and $a > b$, we therefore have, at the zero $\bar{\zeta}$ of $R(\zeta)$, where note $R_1(\bar{\zeta}) > 0$,

$$\bar{S}(\bar{\zeta}) = k^b \{ k^{a-b} R_1(\bar{\zeta}) - R_2(\bar{\zeta}) \}$$

$$> k^b \{ R_1(\bar{\zeta}) - R_2(\bar{\zeta}) \} = k^b R(\bar{\zeta}) = 0.$$

It follows that the unique zero of the decreasing function $\bar{S}(\zeta)$ exceeds that of $R(\zeta)$, and therefore $\bar{\zeta}/k > \bar{\zeta}$. Thus the particle counts at equilibrium for the second system are

$$\bar{V} \bar{x}_1 = V_0 (x_1^0 - a_1 \bar{\zeta} k^{-1}) < V_0 (x_1^0 - a_1 \bar{\zeta}) = \bar{V} \bar{x}_1$$

$$\bar{V} \bar{y}_j = V_0 (y_j^0 + b_j \bar{\zeta} k^{-1}) > V_0 (y_j^0 + b_j \bar{\zeta}) = \bar{V} \bar{y}_j.$$

This is the mathematical content of Le Châtelier's principle in this instance, showing that higher pressure favors the formation of products in a reaction for which $a > b$.

5. Comparison of the two cases. Consider a system S of volume V_0 and initial concentrations $p_0 \in B_X$, undergoing a reaction (1) for which $a > b$ ($\rho > 0$), e.g., the synthesis

The initial numbers of particles are therefore

$$V_0 x_1^0 > 0, \quad V_0 y_j^0 \geq 0.$$

Under constant volume $V \equiv V_0$, the equilibrium point $\bar{p}$ approached on $\sigma(p_0)$ is given in §3 as

$$\bar{P}: \quad \bar{x}_1 = x_1^0 - a_1 \bar{\zeta}, \quad \bar{y}_j = y_j^0 + b_j \bar{\zeta}; \quad 0 < \bar{\zeta} < \xi^0$$

where $\bar{\zeta}$ is the unique zero of the decreasing function

$$P(\zeta) = k_1 \pi (x_1^0 - a_1 \zeta)^{a_1} - k_2 \pi (y_j^0 + b_j \zeta)^{b_j} \equiv P_1(\zeta) - P_2(\zeta); \quad 0 \leq \zeta \leq \xi^0.$$

The total numbers at equilibrium are therefore

$$V_0 \bar{x}_1 = V_0 (x_1^0 - a_1 \bar{\zeta}), \quad V_0 \bar{y}_j = V_0 (y_j^0 + b_j \bar{\zeta}).$$

Under constant "pressure", the same initial system has equilibrium volume $\bar{V}$ and concentrations $\bar{p}$ on $\gamma(p_0)$, given in §4 as

$$\begin{aligned} \bar{V} &= V_0 (1 - \rho \bar{\zeta}) \\ \bar{P}: \quad \bar{x}_1 &= \frac{x_1^0 - a_1 \bar{\zeta}}{1 - \rho \bar{\zeta}}, \quad \bar{y}_j = \frac{y_j^0 + b_j \bar{\zeta}}{1 - \rho \bar{\zeta}}; \quad 0 < \bar{\zeta} < \xi^0 \end{aligned}$$

where $\bar{\zeta}$ is the unique zero of the decreasing function $R(\zeta)$ in (33), which we may write here in the form

$$R(\zeta) = \frac{1}{(1 - \rho \zeta)^b} \left\{ \frac{P_1(\zeta)}{(1 - \rho \zeta)^{a-b}} - P_2(\zeta) \right\}; \quad 0 \leq \zeta \leq \xi^0 (< 1/\rho)$$

in terms of the above $P_1(\zeta)$, $P_2(\zeta)$.

Now at the equilibrium value $\bar{\zeta}$, we know (as for any ζ on $0 < \zeta \leq \xi^0$) that

$$0 < 1 - \rho \xi^0 \leq 1 - \rho \bar{\zeta} < 1$$

and, since also $a > b$ and $P_1(\bar{\zeta}) > 0$, it follows that

$$R(\bar{\zeta}) > \frac{1}{(1 - \rho \bar{\zeta})^b} \{ P_1(\bar{\zeta}) - P_2(\bar{\zeta}) \} = \frac{1}{(1 - \rho \bar{\zeta})^b} P(\bar{\zeta}) = 0.$$

Since $R(\zeta)$ is decreasing, its unique zero $\bar{\zeta}$ satisfies $\bar{\zeta} > \bar{\zeta}$ and therefore we have, for the particle counts at equilibrium in the constant pressure case

$$\bar{V} \bar{x}_1 = V_0 (x_1^0 - a_1 \bar{\zeta}) < V_0 (x_1^0 - a_1 \bar{\zeta}) - V_0 \bar{x}_1$$

$$\bar{V} \bar{y}_j = V_0 (y_j^0 + b_j \bar{\zeta}) > V_0 (y_j^0 + b_j \bar{\zeta}) = V_0 \bar{y}_j.$$

Thus, for a reaction with $a > b$, constant pressure favors formation of products in comparison with constant volume.

Example 4. The reaction $A_1 + A_2 \rightleftharpoons B_1$ of Ex. 3,

under the present constraint, has trajectories of the form in Fig. 6, where a few of those lying in the plane π_7 are shown. In particular, for the initial point $p_0 = (3, 4, 0)$, the function

$$R(\zeta) = \frac{(3-\zeta)(4-\zeta)}{(1-\zeta/7)^2} - \frac{\zeta}{(1-\zeta/7)} = \frac{8}{7} \frac{(\zeta-\zeta_1)(\zeta-\zeta_2)}{(1-\zeta/7)^2}$$

$$0 \leq \zeta \leq 3$$

where $\zeta_1 = \bar{\zeta} = (7 - \sqrt{7})/2$, $\zeta_2 = (7 + \sqrt{7})/2$, and one finds upon integration of

$$d\zeta/d\tau = (1-\zeta/7)R(\zeta)$$

$$\text{that } -8\sqrt{7}\tau = (7-\zeta_1)\log\left(1 - \frac{\zeta}{\zeta_1}\right) - (7-\zeta_2)\log\left(1 - \frac{\zeta}{\zeta_2}\right).$$

Although not explicitly expressible, the inverse function $\zeta(\tau)$ exists on $0 \leq \tau < \infty$, and $\lim_{\tau \rightarrow \infty} \zeta(\tau) =$

$$\bar{\zeta} = \frac{1}{2}(7 - \sqrt{7}) = \zeta_1.$$

REFERENCES

1. E. D. Cashwell, C. J. Everett, The means of order t , and the laws of thermodynamics, Amer. Math. Monthly, 74, 1967, pp. 271-274.
2. A. A. Frost, R. G. Pearson, Kinetics and mechanism, John Wiley & Sons, Inc., N.Y., 1935, p. 35.
3. G. H. Hardy, J. E. Littlewood, G. Pólya, Inequalities, Cambridge, 1934, p. 26.
4. W. F. Osgood, Advanced calculus, Macmillan, N.Y., 1925, Ch. I, §8.