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ON THE THEORY OF REACTIONS IN CONTINUOUS MIXTURES

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CONTENTS

A mixture with a very large number of components approaches the condition of a continuous mixture in which the components are not distinguished by a discrete index but by a continuous variable. Such a mixture can be described by distributions of concentration and is capable of sustaining an infinite number of reactions. Polymerization and cracking reactions can be treated in this way and there may be applications to the very complex processes of biology. The aim of this paper is to lay the foundations for the stoicheiometry, thermodynamics and kinetics of such reactions and to outline several techniques for solving the resulting integro-differential equations. Attention is also paid to the problem of fitting the parameters of such a model to experimental data.

INTRODUCTORY REMARKS AND NOTATION

We wish in this paper to lay the foundation for a theory of reactions in mixtures with infinitely many components. This idea goes back to the work of DeDonder (1931),† who outlined the thermodynamics of mixtures with infinitely many components and phases in which an infinite number of reactions could take place. We shall only be concerned with one phase, but it will become clear that once an infinity of components has been introduced an infinity of reactions must also be considered. This leads to integro-differential equations which are entirely analogous to the differential equations of discrete reactions between discrete species.

The first paragraph is concerned with the definition of a continuous mixture and refers to other applications of this notion that have been made. The three paragraphs following introduce the stoicheiometry, thermodynamics and kinetics of continuous reactions, and it has seemed useful and appropriate to collect some results from elementary functional analysis in § 3 (*a*). In § 5 we explore the application of these ideas to some cases where the solution of the equations is easier to obtain than in the general case, but even in the linear case the techniques involved are not entirely routine. Some of these applications, such as that to polymerization, have already been proved and others hold promise for the study of reactions in very complex systems, such as those that arise in biological contexts. Two of the more difficult problems, those of optimality and stability, are adumbrated in § 6. Finally since, as Courant remarks (1964), flights of abstraction must pay attention to the re-entry problem as well as to take-off, we consider and illustrate the problem of fitting the continuous reaction model to experimental data. A variety of methods is used for the solution of the equations that arise: in § 4 (*a*) an explicit solution is obtained; in § 4 (*b*) iterated kernels and resolvent kernels in closed form are used; in § 4 (*c*) a degenerate kernel with a single term allows explicit solution; the differential reactions in §§ 4 (*d*) and 4 (*e*) give rise to partial differential equations; and in § 7 (*b*) a finite difference method is used to solve the equations numerically.

Notation

The following are the principal symbols used in this paper. Some with slightly restricted use are given with paragraph number and ephemeral notation has been omitted. This should cause no confusion as it will be evident that such usages as F, G, f and g for functionals and functions, A and K for operators in § 5 (*a*) and I_1, etc., for certain integrals in § 5 (*b*), are of purely local bearing.

A_s	sth discrete species
$A(x)$	continuous species of index x
$A(x), B(x)$	paraffin and olefins species respectively (§ 5*c*)
$\mathscr{A}(w)$	reaction affinity distribution
$A(w), A'(w)$	Arrhenius pre-exponential factor distribution (§ 4)
a, b	lower and upper bounds of x

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† We are indebted to Professor R. Defay for drawing our attention to this reference. The work reported here had been completed when we learned of DeDonder's discussion, but little overlap and no conflict of material is found.

C	$\int_a^b c(x)\,\mathrm{d}x$, total molar concentration
C_p	heat capacity of mixture
c, d	lower and upper bounds of w
c_s	molar concentration of A_s, N_s/V
$c(x)$, $c(x,t)$	molar concentration distribution, $N(x)/V$
$c_0(x)$	initial concentration distribution
$c_f(x)$	feed concentration distribution
$c^*(x)$	equilibrium concentration distribution
$\bar{c}(x,s)$	Laplace transform of $c(x,t)$
$E(Z, N(x))$	any extensive property (§ 3)
$\bar{E} = E'_N(Z, N, x)$	corresponding intensive property (§ 3)
$E(w)$, $E'(w)$	activation energy distributions (§ 4)
$G(T, P, N(x))$	Gibbs free energy
$H(S, P, N(x))$	enthalpy
$\bar{H}(x)$	partial molal enthalpy distribution
$J(w)$	$-\Delta H(w)/C_p$
K_p, K_p^*	equilibrium constant and its pre-exponential factor (§ 3 (d))
$K(x,u)$	$k(x,u)\{c^*(x)/c^*(u)\}^{\frac{1}{2}}$ (§ 5 (a))
$k(x,u)$	monomolecular reaction rate kernel
$k(x)$	differential reaction rate (§ 5 (d))
k_n	iterated kernel (§ 5 (b))
M_s	mass of A_s present
$M(x)$	mass distribution
m_s	molecular weight of A_s
$m(x)$	molecular weight distribution
N	total number of moles $= \int_a^b N(x)\,\mathrm{d}x$
N_s	number of moles of A_s present
$N(x)$	distribution of number of moles
$n(x)$	$c(x)/C = N(x)/N$, mole fraction distribution
P	pressure
$P(x)$	partial pressure distribution
$p_1, p(x)$	polymer concentration distributions (§ 5 (e))
Q	heat removal rate (§ 6 (b))
$q(x,t)$	olefin concentration distribution (§ 5(c))
R	gas constant
r	index for discrete reactions
$r(P, T, c(x), w)$	reaction rate
S	entropy
S	number of discrete species
s	index for discrete species
s	$\sigma + \mathrm{i}\tau$, Laplace transform variable (§ 5 (b))
T	temperature

T_f,	feed temperature
t	time
$U(S, V, N(x))$	internal energy
V	volume
$v(x', x)$	paraffin cracking kernel (§ 5 (*c*))
w	index for continuous reactions
$w(x', x)$	olefin cracking kernel (§ 5 (*c*))
x	index for continuous species
z_j, $z(x, t)$	experimental data (§ 7)
Z	thermodynamic variables (§ 3)
α_s, α_{rs}	stoicheiometric coefficient of A_s (in *r*th reaction)
$\alpha(x)$	stoicheiometric coefficient distribution for a single reaction
$\alpha(w, x)$, $\alpha(w, w', x)$	stoicheiometric coefficient distributions in continua of reactions
$\alpha(w)$	$\int_a^b \alpha(w, x)\,\mathrm{d}x$
$\beta(w, x)$, $\gamma(w, x)$	order of reaction distributions
$\gamma(x, t)$	$c(x, t)/\{c^*(x)\}^{\frac{1}{2}}$
$\Delta G^0(w)$	standard free energy of reaction distribution
$\Delta H(w)$	heat of reaction distribution
$\zeta(t)$	incompatibility variable (§ 6 (*b*))
$\eta(x, t, \theta)$	adjoint function (§ 6 (*a*))
θ	duration of reaction (§ 6 (*a*)), or holding time (§ 6 (*b*))
$\kappa(x)$	$\int_a^b k(x, u)\,\mathrm{d}u$
λ	eigenvalue
μ_s	chemical potential of A_s
$\mu(x)$	chemical potential distribution
ν_r	multiplier in definition of independence of reactions (§ 2)
$\nu(w)$, $\nu(w, w')$	multiplying distributions in definition of independence of continuous reactions (§ 2)
ξ, ξ_r	extent of reaction, or of *r*th reaction
$\xi(w, t)$, $\xi(w, w', t)$	extent distribution functions for continuous reactions
ρ_s	density of $A_s = M_s/V$
$\rho(x)$	density distribution of $A(x)$

1. Mixtures

In the conventional mixture of chemical substances it is possible to distinguish a finite number of distinct chemical species. These may be denoted by A_s, where s is an integer $1 \leqslant s \leqslant S$. In rare cases it may be possible to express the chemical formulae of the species as functions of s, as with contiguous members of an homologous series (e.g. C_sH_{2s+2}), but in general the A_s suffice as symbols and their chemical meaning must be recorded in a table. In such a mixture, which will be referred to as a discrete mixture when necessary, we can speak of the mass, M_s, of A_s being present in any particular region, and, if V be the volume of that region, of A_s having a mean mass concentration of $\rho_s = M_s/V$. Similarly, if m_s is the molecular weight of A_s, the mass M_s will correspond to $N_s = M_s/m_s$ moles of A_s and we can define a molar concentration by $c_s = N_s/V$.

All these notions have immediate analogues if we allow ourselves to consider a mixture with infinitely many components. The 'species' present in such a mixture may be denoted by $A(x)$, where x is a real variable $a \leqslant x \leqslant b$. It is no longer possible to speak of the mass of $A(x)$ present, but only of the mass distribution† function $M(x)$, which is such that $M(x)\,\mathrm{d}x$ is the mass of the cut of species $A(x')$, $x \leqslant x' < x+\mathrm{d}x$, present. If $M(x)$ is a non-negative piecewise continuous function of x in the open interval (a, b) we shall speak of a continuous mixture (a, b) with this mass distribution function. If $m(x)$ is the molecular weight associated with $A(x)$ then $N(x) = M(x)/m(x)$ is a molar distribution function; $m(x) > 0$ if the species $A(x)$ exists so that the function $N(x)$ is defined and non-negative. Similarly, mass and molar concentration distributions may be defined by $\rho(x) = M(x)/V$ and $c(x) = N(x)/V$ respectively.

Such a concept is not as far fetched as it may at first appear. In practice the chemist may have to deal with extremely complex mixtures (e.g. of hydrocarbons) of which no precise analysis is possible. In such a case he often has recourse to this type of description and speaks of the fraction boiling between temperatures x and $x+\delta x$, or having a retention time on the chromatographic column of x to $x+\delta x$. Indeed the analytical apparatus may actually produce a record of $c(x)$ or some function of it as a continuous curve. The fact that the separation theory of such mixtures can be carried over from the discrete case has been known for some time (Bowman 1949) and a full discussion of their distillation is given by Acrivos & Amundson (1955). Harbert (1947) and Bowman (1951) have shown how the distribution functions may be obtained from experimental data when x is a variable related to the vapour pressure. The justification for this treatment of separation processes lies in the fact that a rather fine gradation of physical properties is found in such complex mixtures. If we are to study the theory of chemical reaction in such mixtures we must assume that there is a similarity or gradation of chemical properties. But this is often the case, for complex systems are rarely without some ordering principle. In polymerization or cracking there is an obvious ordering property and in complex enzyme systems there may be a natural sequencing by function. From a mathematical point of view reactions in continuous mixtures are worth considering as the limiting case and it may be hoped that the behaviour that we observe may have some light to shed on that of very large systems of reactions.

If we admit generalized functions we may discuss mixtures with both continuous and discrete species. Thus, if we use the so-called Dirac delta function, the expression

$$M(x) + \sum_{s=1}^{S} M_s \delta(x - x_s) \tag{1}$$

includes both the mass distribution function for the continuous part of the mixture and the masses of the discrete species, where x_s is the value of the real variable x that should be associated with the species A_s. The generalized molar distribution function is

$$N(x) + \sum_{s=1}^{S} N_s \delta(x - x_s) = \{M(x)/m(x)\} + \sum_{s=1}^{S} \{M_s/m_s\}\,\delta(x - x_s) \tag{2}$$

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† The term 'distribution' will be reserved for such functions and the class of functions called 'distributions' by L. Schwartz will be referred to as 'generalized functions'.

and, dividing by the volume, we can define mass and molar concentration distributions:

$$\rho(x)+\sum_{s=1}^{S}\rho_s\,\delta(x-x_s), \tag{3}$$

$$c(x)+\sum_{s=1}^{S}c_s\,\delta(x-x_s). \tag{4}$$

If x has the range (a, b) and this includes all the points x_s then the total number of moles is

$$N=\int_a^b N(x)\,\mathrm{d}x+\sum_{s=1}^{S}N_s. \tag{5}$$

Another important measure of concentration is the mole fraction distribution

$$n(x)+\sum_{s=1}^{S}n_s\,\delta(x-x_s)=\{N(x)/N\}+\sum_{s=1}^{S}\{N_s/N\}\,\delta(x-x_s). \tag{6}$$

This clearly has the property that

$$\int_a^b n(x)\,\mathrm{d}x+\sum_{s=1}^{S}n_s=1. \tag{7}$$

By insisting that all functions should remain integrable we could, if we wished, adopt $a=0$ as a standard lower limit and let $b\rightarrow\infty$. It will be convenient to let these equations stand for reference with both continuous and discrete parts, but in what follows we shall be largely concerned with the continuous part only. Since all quantities of physical interest will involve integrals of the distribution functions we could have started from cumulative distribution functions like

$$Y(x)=\int_a^b\{y(x')+\Sigma y_s\,\delta(x'-x_s)\}\,\mathrm{d}x'$$

and interpret such integrals as $\int_a^b f(x)\,\mathrm{d}Y(x)$ as Riemann–Stieltjes integrals.

2. Reactions

A single reaction between the set of discrete species A_s $(s=1,2,\ldots,S)$ may be denoted by

$$\sum_{s=1}^{S}\alpha_s A_s=0, \tag{8}$$

where the real numbers α_s are known as stoicheiometric coefficients. The coefficient α_s is proportional to the number of molecules of A_s taking part in the reaction and may be taken to be positive if the species is a product of the reaction. Simultaneous reactions may be denoted by

$$\sum_{s=1}^{S}\alpha_{rs}A_s=0\quad(r=1,2,\ldots,R). \tag{9}$$

Such a reaction is only proper if it is balanced in the atomic species and this implies that

$$\sum_{s=1}^{S}\alpha_{rs}m_s=0\quad(r=1,2,\ldots,R). \tag{10}$$

All this suggests that the mathematical foundations of stoicheiometry lie in the theory of linear vector spaces, an idea which has been explored elsewhere (Aris 1965).

The analogue for continuous mixtures would seem to be the reaction

$$\int_a^b \alpha(x)\, A(x)\, \mathrm{d}x = 0, \tag{11}$$

where $\alpha(x)$ has the property that

$$\int_a^b \alpha(x)\, m(x)\, \mathrm{d}x = 0. \tag{12}$$

We shall find, however, that we need to consider more than just a single reaction. Simultaneous, discrete reactions can be written

$$\int_a^b \alpha_r(x)\, A(x)\, \mathrm{d}x = 0 \quad (r = 1, 2, \ldots, R) \tag{13}$$

with

$$\int_a^b \alpha_r(x)\, m(x)\, \mathrm{d}x = 0 \quad (r = 1, 2, \ldots, R). \tag{14}$$

Such reactions are independent if the only set of multipliers ν_r such that

$$\sum_1^R \nu_r \alpha_r(x) = 0 \quad (a \leqslant x \leqslant b) \tag{15}$$

is the trivial set $\nu_r = 0$.

In the discrete mixture an extent of reaction $\xi(t)$ or $\xi_r(t)$ may be defined and the change in concentration by reaction is given by

$$\Delta c_s = c_s(t) - c_s(0) = \alpha_s \xi(t) \quad \text{or} \quad \sum_{r=1}^R \alpha_{rs} \xi_r(t). \tag{16}$$

The stoicheiometric coefficient function for the continuous mixture can be used in the same way and

$$\Delta c(x) = c(x, t) - c(x, 0) = \alpha(x)\, \xi(t) \quad \text{or} \quad \sum_{r=1}^R \alpha_r(x)\, \xi_r(t). \tag{17}$$

The derivatives $\mathrm{d}\xi/\mathrm{d}t$ and $\mathrm{d}\xi_r/\mathrm{d}t$ are respectively the rate of the single reaction and the rate of the rth reaction of the set.

The question now arises, Can we have a continuum of reactions? Let w be a continuous variable in the interval (c, d) and $\alpha(w, x)$ a piecewise continuous function such that

$$\int_a^b \alpha(w, x)\, m(x)\, \mathrm{d}x = 0. \tag{18}$$

Then

$$\int_a^b \alpha(w, x)\, A(x)\, \mathrm{d}x = 0 \quad (c \leqslant w \leqslant d), \tag{19}$$

is a continuum of reactions over the interval (c, d). With the elementary interval $(w, w + \mathrm{d}w)$ is associated an extent $\xi(w, t)\, \mathrm{d}w$ and

$$\Delta c(x) = c(x, t) - c(x, 0) = \int_c^d \alpha(w, x)\, \xi(w, t)\, \mathrm{d}w. \tag{20}$$

$\xi(w, t)$ is a distribution of extent in reaction space. If we allow $\alpha(w, x)$ to be a generalized function and associate discrete reactions with discrete points w_r of (c, d), then we can subsume the general discrete reaction under this formalism. Thus let

$$\alpha(w, x) = \sum_{r=1}^R \sum_{s=1}^S \alpha_{rs}\, \delta(w - w_r)\, \delta(x - x_s) \tag{21}$$

and the reaction continuum will be

$$\sum_{s=1}^{S} \sum_{r=1}^{R} \alpha_{rs} A_s \delta(w-w_r) = 0,$$

which localizes the rth reaction at the point w_r. The independence condition (15) becomes the condition that the only solution $\nu(w)$ of

$$\int_c^d \nu(w)\,\alpha(w,x)\,\mathrm{d}w = 0 \quad (a \leqslant x \leqslant b), \tag{22}$$

is the trivial function $\nu(w) \equiv 0$ $(c \leqslant w \leqslant d)$. This condition is necessary or the extent distribution function could not be defined, since if there is a nontrivial $\nu(w)$, the function $\xi(w,t)+\nu(w)\,\eta(t)$ would give the same concentration changes as $\xi(w,t)$ for any $\eta(t)$.

The continuum of reactions can be extended to a larger number of dimensions and we shall have occasion to consider the two-dimensional continuum

$$\int_a^b \alpha(w,w',x)\,A(x)\,\mathrm{d}x = 0, \tag{23}$$

where the point (w,w') lies in a domain D of the w, w' plane. Then for the reaction continuum to be proper

$$\int_a^b \alpha(w,w',x)\,m(x)\,\mathrm{d}x = 0 \quad ((w,w') \text{ in } D) \tag{24}$$

and there are no nontrivial solutions of

$$\iint_D \nu(w,w')\,\alpha(w,w',x)\,\mathrm{d}w\,\mathrm{d}w' = 0 \quad (a \leqslant x \leqslant b). \tag{25}$$

Then an extent distribution function can be defined in D such that

$$\Delta c(x) = \iint_D \alpha(w,w',x)\,\xi(w,w')\,\mathrm{d}w\,\mathrm{d}w'. \tag{26}$$

As examples we may consider the generalized monomolecular reaction

$$A(w)-A(w') = 0 \quad (a \leqslant w < w' \leqslant b), \tag{27}$$

for which

$$\alpha(w,w',x) = \delta(x-w)-\delta(x-w'). \tag{28}$$

For this

$$\Delta c(x) = \int_a^b \{\xi(x,w')\,\mathrm{d}w' - \xi(w,x)\,\mathrm{d}w\}. \tag{29}$$

The cracking reaction

$$A(w)+A(w')-A(w+w') = 0 \quad (a \leqslant w \leqslant w' \leqslant w+w' \leqslant b), \tag{30}$$

is given by

$$\alpha(w,w',x) = \delta(x-w)+\delta(x-w')-\delta(x-w-w'). \tag{31}$$

Thus

$$\Delta c(x) = \int_a^b \{\xi(x,w')\,\mathrm{d}w' + \xi(w,x)\,\mathrm{d}w - \xi(w,x-w)\,\mathrm{d}w\}. \tag{32}$$

The discrete sequential reaction can be written $A_r - A_{r-1} = 0$ and gives a limiting form $A(w)-A(w-\delta w) = 0$ or symbolically $A'(w) = \partial A(w)/\partial w = 0$. This can be represented by the generalized function

$$\alpha(w,x) = \delta'(w-x), \tag{33}$$

for which
$$\int_a^b \delta'(w-x)\,A(x)\,\mathrm{d}x = A'(w) = 0. \tag{34}$$

Then
$$\Delta c(x) = \int_a^b \xi(w)\,\delta'(w-x)\,\mathrm{d}w = -\xi'(x). \tag{35}$$

3. Thermodynamics of continuous mixtures

There is no difficulty in applying the zero, first and second laws of thermodynamics to continuous mixtures, but some points of interest arise in connexion with the calculation of extensive properties and chemical equilibria. However, we shall need some elementary results from functional analysis and it will be convenient to give them briefly here.

(a) *Results from functional analysis*

Consider a set U of a linear vector space V, whose typical member will be denoted by $u(x)$, $a \leqslant x \leqslant b$. A functional is a mapping from U into the reals; it may also depend on one or more parameters of which it is an ordinary function. If the space V is normed and the norm of $u(x)$ is denoted by $\|u\|$, we can define differentiability of functionals. A functional $F(u)$ is differentiable at an interior point u of U, if for all h sufficiently small in norm
$$F(u+h) = F(u) + \mathrm{d}F(u,h) + R(u,h), \tag{36}$$
where $\lim\limits_{\|h\|\to 0} \dfrac{R(u,h)}{\|h\|} = 0$. The linear functional $\mathrm{d}F(u,h)$ is called the Frechet differential of F and in many cases it may be represented in the form
$$\mathrm{d}F(u,h) = \int_a^b f(x)\,h(x)\,\mathrm{d}x, \tag{37}$$
where $f(x)$ depends on u and x but not on h. Then
$$f(x) = F'_u(u;x) \tag{38}$$
is called the functional derivative; it induces a mapping from $u \in U$ to $\mathrm{d}F(u,h)$, a linear functional of h. In current mathematical terminology this mapping is called the gradient of the functional, but it will cause no difficulty here if we use the terms gradient and functional derivative interchangeably. The Riesz representation theorem asserts that if $u \in L_p[a,b]$ and F is differentiable then representation (37) obtains and $F'_u(u;x) \in L_q[a,b]$, $(1/p)+(1/q) = 1$. When the Frechet differential exists it may be calculated by
$$\mathrm{d}F(u,h) = \left[\frac{\mathrm{d}}{\mathrm{d}\lambda}F(u+\lambda h)\right]_{\lambda=0}, \tag{39}$$
but the converse is not always true. The rules of differentiating a sum, product and function of a functional are immediate extensions of the elementary ones. If $F(u) = G(v)$ where $v(x) = H(u;x)$ is a functional of u depending parametrically on x then
$$F'_u(u;x) = \int_a^b G'_v(v;s)\,H'_u(u;s;x)\,\mathrm{d}s. \tag{40}$$

Finally we notice that since
$$\mathrm{d}F(u,h) = [\mathrm{d}F(u+\lambda h)/\mathrm{d}\lambda]_{\lambda=0}$$
then
$$\begin{aligned}\mathrm{d}F(u+\kappa h,h) &= [\mathrm{d}F(u+\kappa h+\lambda h)/\mathrm{d}\lambda]_{\lambda=0}\\ &= \mathrm{d}F(u+\kappa h)/\mathrm{d}\kappa.\end{aligned} \tag{41}$$

Thus

$$\begin{aligned} F(u+h)-F(u) &= \int_0^1 \frac{\mathrm{d}}{\mathrm{d}\kappa} F(u+\kappa h)\,\mathrm{d}\kappa \\ &= \int_0^1 \mathrm{d}\kappa \int_a^b F_u'(u+\kappa h;x)\,h(x)\,\mathrm{d}x \\ &= \int_a^b h(x)\left[\int_0^1 F_u'(u+\kappa h;x)\,\mathrm{d}\kappa\right]\mathrm{d}x. \end{aligned} \tag{42}$$

(*b*) *Extensive and intensive properties*

An arbitrary extensive property of a continuous mixture will be denoted by $E(Z;N(x))$, where Z denotes a pair of thermodynamic variables such as P, the pressure, and T, the temperature, is a linear functional of the molar density function $N(x)$. Thus

$$E(Z;\kappa N(x)) = \kappa E(Z;N(x)) \tag{43}$$

and

$$\begin{aligned} (\kappa-1)\,E(Z;N(x)) &= E(Z;\kappa N(x)) - E(Z;N(x)) \\ &= \mathrm{d}E(Z;N;(\kappa-1)\,N) + o(\kappa-1) \\ &= (\kappa-1)\int_a^b N(x)\,E_N'(Z;N;x)\,\mathrm{d}x + o(\kappa-1). \end{aligned}$$

Hence dividing by $(\kappa-1)$ and letting $\kappa\to 1$ we have

$$E(Z;N(x)) = \int_a^b N(x)\,E_N'(Z;N;x)\,\mathrm{d}x. \tag{44}$$

Thus the gradient

$$\bar{E}(Z;x) = E_N'(Z;N;x) \tag{45}$$

may be defined as the partial molal property. It is an intensive variable for replacing $N(x)$ by $\kappa N(x)$ in equation (44) shows that

$$E_N'(Z;\kappa N;x) = E_N'(Z;N;x). \tag{46}$$

In particular if Z is the pair of variables, P, the pressure and T, the temperature and E the Gibbs free energy of the system $G(P,T;N(x))$, we have a definition of the density of chemical potential in the functional derivative

$$\bar{G}(x) = G_N'(P,T;N(x);x) = \mu(x) \tag{47}$$

and

$$G(P,T;N(x)) = \int_a^b \mu(x)\,N(x)\,\mathrm{d}x. \tag{48}$$

The calculation of other extensive properties proceeds similarly and in the usual thermodynamic identities the discrete mixture term $\Sigma\delta N_i\bar{E}_i$ is replaced by $\int\delta N(x)\,\bar{E}(x)\,\mathrm{d}x$. For example

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \int_a^b \mu(x)\,\delta N(x)\,\mathrm{d}x, \tag{49}$$

where $\delta N(x)$ is any differential perturbation of $N(x)$. Similarly,

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \int_a^b \mu(x)\,\delta N(x)\,\mathrm{d}x. \tag{50}$$

(*c*) *Ideal gases and mixtures*

The perfect gas is a fluid satisfying the equation of state

$$P = CRT, \tag{51}$$

where

$$C = \int_a^b c(x)\,\mathrm{d}x. \tag{52}$$

If we let

$$n(x) = c(x)/C = N(x)/CV \tag{53}$$

be the mole fraction distribution, the chemical potential in a continuous perfect gas may be written

$$\mu(x) = \mu^0(x) + RT\ln P + RT\ln n(x), \tag{54}$$

where $\mu^0(x)$ is independent of pressure. Thus

$$\begin{aligned} G(T,P;N(x)) &= \int_a^b N(x)\,\mu^0(x)\,\mathrm{d}x + RT\ln P\int_a^b N(x)\,\mathrm{d}x + RT\int N(x)\ln n(x)\,\mathrm{d}x \\ &= V\int_a^b c(x)\,\mu^0(x)\,\mathrm{d}x + CVRT\ln P + VRT\int_a^b c(x)\ln[c(x)/C]\,\mathrm{d}x. \end{aligned} \tag{55}$$

Since the free energy of one mole of pure 'x' is $\mu^0(x) + RT\ln P$, the last term

$$CVRT\int_a^b n(x)\ln n(x)\,\mathrm{d}x$$

is the free energy of mixing.

For the ideal solution we write

$$\mu(x) = \mu^*(x) + RT\ln n(x), \tag{56}$$

where $\mu^*(x)$ may be a function of both T and P, and observe that (54) is also of this form.

In his work on affinity, referred to in our opening remarks, DeDonder (1931) discusses the perfect gas at some length. He defines a partial pressure distribution

$$P(x) = Pn(x) = c(x)\,RT$$

and carries out detailed computation of internal energy, entropy and affinity.

(*d*) *Equilibrium in continuous mixtures*

Chemical equilibrium at a given temperature and pressure is attained when the Gibbs free energy is a minimum. From equation (50) the condition for equilibrium is thus

$$\int_a^b \mu(x)\,\delta N(x)\,\mathrm{d}x = 0.$$

But if a single reaction

$$\int_a^b \alpha(x)\,A(x)\,\mathrm{d}x = 0$$

is taking place, the perturbation $\delta N(x)$ in $N(x)$ will be proportional to $\alpha(x)$ for

$$\delta N(x) = V\Delta c(x) = V\alpha(x)\,\xi.$$

Thus the condition for equilibrium becomes

$$\int_a^b \alpha(x)\,\mu(x)\,\mathrm{d}x = 0.$$

For a perfect gas mixture we may define $P(x) = Pn(x)$ to be the partial pressure density function and with $\mu(x) = \mu^0(x) + RT \ln P(x)$ we have

$$RT \int_a^b \alpha(x) \ln P(x)\, \mathrm{d}x = -\int_a^b \alpha(x)\, \mu^0(x)\, \mathrm{d}x. \tag{57}$$

For the ideal solution $$RT \int_a^b \alpha(x) \ln n(x)\, \mathrm{d}x = -\int_a^b \alpha(x)\, \mu^*(x)\, \mathrm{d}x. \tag{58}$$

Equation (57) may be modified to give

$$RT \int_a^b \alpha(x) \ln c(x)\, \mathrm{d}x = -\int_a^b \alpha(x)\, \{\mu^0(x) + RT \ln RT\}\, \mathrm{d}x. \tag{59}$$

The case of simultaneous reactions may be treated by considering the one dimensional continuum of reactions

$$\int_a^b \alpha(w, x)\, A(x)\, \mathrm{d}x.$$

For this we have $$\delta N(x) = V \int_c^d \delta\xi(w)\, \alpha(w, x)\, \mathrm{d}w$$

and hence the equilibrium condition

$$\int_a^b \mathrm{d}x \int_c^d \mathrm{d}w\, \delta\xi(w)\, \alpha(w, x)\, \mu(x) = 0. \tag{60}$$

It is clear that this implies a definite restriction on the function $\mu(x)$ at equilibrium for by the condition (22) we know that there is no possible $\delta\xi(w)$ such that

$$\int_c^d \delta\xi(w)\, \alpha(w, x)\, \mathrm{d}w = 0$$

for all x. But writing the relation

$$\int_c^d \delta\xi(w)\, \mathrm{d}w \int_a^b \alpha(w, x)\, \mu(x)\, \mathrm{d}x = 0$$

and asserting that this should hold for arbitrary displacements $\delta\xi(w)$ from equilibrium, implies that

$$\int_a^b \alpha(w, x)\, \mu(x)\, \mathrm{d}x = 0. \tag{61}$$

This expresses the principle of microscopic reversibility or detailed balancing, that at equilibrium each reaction of the set or continuum must be at equilibrium.

In the case of a perfect gas we may write

$$RT \int_a^b \alpha(w, x) \ln P(x)\, \mathrm{d}x = -\int_a^b \alpha(w, x)\, \mu^0(x)\, \mathrm{d}x = -\Delta G^0(w)$$

and $$\int_a^b \alpha(w, x) \ln P(x)\, \mathrm{d}x = \ln K_p(w), \tag{62}$$

where $$K_p(w) = \exp\left(-\Delta G^0(w)/RT\right).$$

Now $$\frac{\mathrm{d}}{\mathrm{d}T} \frac{\mu^0(x)}{T} = -\frac{\bar{H}(x)}{T^2},$$

where $\bar{H}(x)$ is the partial molal enthalpy distribution. Hence

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}T}[\ln K_p(w)] &= -\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}T}\int_a^b \alpha(w,x)\frac{\mu^0(x)}{T}\,\mathrm{d}x\\ &= \frac{1}{RT^2}\int_a^b \alpha(w,x)\,\bar{H}(x)\,\mathrm{d}x\\ &= \Delta H(w)/RT^2.\end{aligned}$$

Integrating we obtain
$$K_p(w) = K_p^*(w)\exp\left(-\Delta H(w)/RT\right), \tag{63}$$

where $\Delta H(w)$ is the distribution of the heat of reaction.

$$\mathscr{A}(w) = -\int_a^b \alpha(w,x)\,\mu(x)\,\mathrm{d}x \tag{64}$$

is the distribution of affinity in the reaction space.

As an example of equilibrium conditions consider the cracking reaction (30). Then

$$\int_a^b \alpha(w,w',x)\,\mu(x)\,\mathrm{d}x = \mu(w)+\mu(w')-\mu(w+w')$$

or
$$\frac{P(w)\,P(w')}{P(w+w')} = K_p(P,T;w,w'), \tag{65}$$

where
$$-RT\ln K_p(w,w') = \mu^0(w)+\mu^0(w')-\mu^0(w+w'). \tag{66}$$

4. Kinetics of continuous reactions

We shall not attempt to say too much in general terms about the kinetics of continuous reactions, preferring to illustrate the matter with definite examples where some solutions can be obtained. The subject may be treated using a one-dimensional continuum of reactions, the changes to single or discrete reactions or to continua of more than one dimension being trivial.

By the kinetics of a continuum of reactions

$$\int_a^b \alpha(w,x)\,A(x)\,\mathrm{d}x = 0,$$

we mean an expression for the time derivative of $\xi(w)$ which is a function of the thermodynamic variables and a functional of the concentration distribution, i.e.

$$\dot{\xi}(w,t) = r(T,P;c(x);w). \tag{67}$$

(A dot will be used to denote derivatives with respect to time.) By differentiating equation (20) with respect to time we have

$$\dot{c}(x,t) = \int_c^d \alpha(w,x)\,r(T,P;c(x);w)\,\mathrm{d}w, \tag{68}$$

which provides an integro-differential equation for $c(x,t)$. Alternatively substituting from (20) into (67) give an integro-differential equation for $\xi(w,t)$, namely

$$\dot{\xi}(w,t) = r\left[T,P;c(x,0)+\int_c^d \alpha(w',x)\,\xi(w',t)\,\mathrm{d}w';w\right]. \tag{69}$$

An immediate generalization of the homogeneous kinetics of discrete mixtures is the following kinetic expression

$$r(T;c(x);w) = \exp\left\{\ln A(w) - \frac{E(w)}{RT} + \int_a^b \beta(w,x)\ln c(x)\,\mathrm{d}x\right\} - \exp\left\{\ln A'(w) - \frac{E'(w)}{RT} + \int_a^b \gamma(w,x)\ln c(x)\,\mathrm{d}x\right\}. \qquad (70)$$

At equilibrium

$$\int_a^b [\gamma(w,x)-\beta(w,x)]\ln c(x)\,\mathrm{d}x = \ln[A(w)/A'(w)] - \frac{E(w)-E'(w)}{RT}. \qquad (71)$$

But comparing this with the equilibrium relationships (62) and (63)

$$\int_a^b \alpha(w,x)\ln P(x)\,\mathrm{d}x = \ln K_p^*(w) - \frac{\Delta H(w)}{RT}$$

we see that the two equations can differ only by one being a multiple of the other. Without loss of generality we can take this multiplier to be one and set

$$\left.\begin{aligned} \gamma(w,x)-\beta(w,x) &= \alpha(w,x), \\ A(w)/A'(w) &= K_p^*(w)\,(RT)^{-\alpha(w)}, \\ \Delta H(w) &= E(w)-E'(w), \\ \text{where}\qquad \alpha(w) &= \int_a^b \alpha(w,x)\,\mathrm{d}x. \end{aligned}\right\} \qquad (72)$$

If

$$\left.\begin{aligned} \beta(w,x) &= \tfrac{1}{2}\{|\alpha(w,x)|-\alpha(w,x)\}, \\ \gamma(w,x) &= \tfrac{1}{2}\{|\alpha(w,x)|+\alpha(w,x)\}, \end{aligned}\right\} \qquad (73)$$

which clearly satisfies the first of the relations (72) then the kinetics are called simple.

It is clear that integro-differential equations of the form of (68) or (69) with r given by (70) will be complex things at the best of times and we turn to some specific examples where solutions may be obtained and actual reaction systems considered. It should be noted however that such equations obtain only for the isothermal batch reaction of a continuous mixture. For a completely mixed reactor of holding time θ and feed composition $c_f(x)$, a mass balance over each elementary cut $(x, x+\mathrm{d}x)$ gives

$$\theta\dot{c}(x,t) = c_f(x) - c(x,t) + \theta\int_c^d \alpha(w,x)\,r(w)\,\mathrm{d}w, \qquad (74)$$

which in the steady state reduces to an integral equation, though in general a nonlinear one.

If a reaction is carried out at constant enthalpy so that

$$\dot{H} = \frac{\mathrm{d}}{\mathrm{d}t}\int_a^b \overline{H}(x)\,c(x,t)\,\mathrm{d}x = 0,$$

we have

$$\left[\int_a^b \frac{\partial\overline{H}(x)}{\partial T}\,c(x,t)\,\mathrm{d}x\right]\frac{\mathrm{d}T}{\mathrm{d}t} + \int_a^b \overline{H}(x)\,\dot{c}(x,t)\,\mathrm{d}x = 0,$$

since for a perfect gas the partial derivative with respect to pressure vanishes and the functional derivative term vanishes because $\overline{H}(x)$ is an intensive quantity. But the term in the first bracket is the specific heat at constant pressure of the mixture, C_p, and substituting from (68) into the second gives

$$\int_a^b \overline{H}(x)\,\mathrm{d}x \int_c^d \alpha(w,x)\,r(w)\,\mathrm{d}w = \int_c^d \Delta H(w)\,r(w)\,\mathrm{d}w.$$

Hence for adiabatic operation at constant pressure

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{-1}{C_p}\int_c^d \Delta H(w)\,r(w)\,\mathrm{d}w. \tag{75}$$

5. First order systems

(a) *Reversible monomolecular systems*

A chemical reaction system is called monomolecular if the coupling between each pair of species is by first order reaction only. Such systems have importance both in reality (isomerization) and as approximations near equilibrium. They have been comprehensively treated by Wei & Prater (1962) in the discrete case and it is shown that the three assumptions: (i) mass is conserved, (ii) no negative concentrations exist, (iii) the rate of change of each concentration is a linear function of the concentrations, together with Brouwer's fixed point theorem, imply the existence of at least one equilibrium point.

In the continuous analogue we shall speak of a monomolecular system if in a closed isothermal system the concentration distribution satisfies

$$\dot{c}(x,t) = Ac(x,t), \tag{76}$$

where A is a linear operator and the conditions (i) and (ii) obtain. By contrast to the discrete case these conditions are not sufficient to ensure the existence of an equilibrium distribution $c^*(x)$ for which $Ac^* = 0$, for Schauder's fixed point theorem is not applicable and further restrictions have to be introduced.

In the continuous system

$$\int_a^b \alpha(w,w',x)\,A(x)\,\mathrm{d}x = 0 \quad (a \leqslant w < w' \leqslant b), \tag{77}$$

we have the analogue of the discrete case $A_i - A_j = 0$ if

$$\alpha(w,w',x) = \delta(x-w) - \delta(x-w'). \tag{28 bis}$$

The system is monomolecular if

$$\begin{aligned}\dot{c}(x,t) &= -\int_a^b k(x,u)\,c(x,t)\,\mathrm{d}u + \int_a^b k(u,x)\,c(u,t)\,\mathrm{d}u\\ &= -\kappa(x)\,c(x,t) + \int_a^b k(u,x)\,c(u,t)\,\mathrm{d}u,\end{aligned} \tag{78}$$

where

$$\kappa(x) = \int_a^b k(x,u)\,\mathrm{d}u. \tag{79}$$

We observe in passing that these kinetics are simple in the sense of equation (73). The conditions (i) and (ii) are satisfied by this system. For, if the reactions are proper

$$\int_a^b \alpha(w, w', x)\, m(x)\, \mathrm{d}x = 0,$$

namely $m(w) = m(w')$, and the total mass will be proportional to

$$\int_a^b c(x, t)\, \mathrm{d}x,$$

which is constant. Again, provided the initial distribution $c(x, 0)$ is positive, $c(x, t)$ can never become negative.

We may now prove the following theorem concerning the equilibrium distribution.

THEOREM 1. *If the kernel* $k(x, u)$ *is such that* $k(u, x)/\kappa(x) \in L_2[D]$, D *being the rectangle* $a \leqslant x,\ u \leqslant b$, *then the system* (78) *has at least one equilibrium distribution.*

Proof. Consider the inhomogeneous integral equation

$$-c^*(x) + \int_a^b \frac{k(u, x)}{\kappa(x)}\, c^*(u)\, \mathrm{d}u = \frac{h(x)}{\kappa(x)}. \tag{80}$$

The Fredholm alternative theorem states that: either equation (80) has a unique solution for any $h(x)$ such that $h(x)/\kappa(x) \in L_2[a, b]$, or the homogeneous equation with $h = 0$ has a nontrivial solution. But the first alternative cannot obtain, for multiplying by $\kappa(x)$ and integrating, we see that

$$\int_a^b h(x)\, \mathrm{d}x = 0.$$

It follows that the homogeneous equation has a nontrivial solution $c^*(x)$, for which

$$-\kappa(x)\, c^*(x) + \int_a^b k(u, x)\, c^*(u)\, \mathrm{d}u = 0. \tag{81}$$

The time-independent solution of (78), $c(x, t) = c^*(x)$, is the required equilibrium distribution.

The questions of the uniqueness and stability of the equilibrium state require a more detailed study of the spectrum of the operator. We shall not pursue this in the most general case but assert the principle of microscopic reversibility, that, at equilibrium, each elementary reaction must be in equilibrium. This means that not only is equation (81) true but

$$k(x, u)\, c^*(x) = k(u, x)\, c^*(u) \tag{82}$$

for all x, u in D. This allows us to symmetrize the equation by the change of variable

$$\gamma(x, t) = c(x, t)/\{c^*(x)\}^{\frac{1}{2}}, \tag{83}$$

for which

$$\dot{\gamma}(x, t) = -\kappa(x)\, \gamma(x, t) + \int_a^b K(x, u)\, \gamma(u, t)\, \mathrm{d}u. \tag{84}$$

The kernel

$$K(x, u) = K(u, x) = k(u, x) \left\{\frac{c^*(u)}{c^*(x)}\right\}^{\frac{1}{2}} = k(x, u) \left\{\frac{c^*(x)}{c^*(u)}\right\}^{\frac{1}{2}} \tag{85}$$

is now symmetric by virtue of equation (82).

This leads us to

THEOREM 2. *The principle of microscopic reversibility implies that the monomolecular system has a unique, stable equilibrium distribution.*

Proof. Multiply equation (84) by $\gamma(x,t)$ and integrate over the range (a,b) giving

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\int_a^b \gamma^2(x,t)\,\mathrm{d}x = -\int_a^b \kappa(x)\,\gamma^2(x,t)\,\mathrm{d}x + \int_a^b\int_a^b K(x,u)\,\gamma(x,t)\,\gamma(u,t)\,\mathrm{d}x\,\mathrm{d}u. \tag{86}$$

Now by (79) and (85) the first integral on the right hand side is

$$\int_a^b \gamma^2(x,t)\,\mathrm{d}x\int_a^b k(x,u)\,\mathrm{d}u = \int_a^b \mathrm{d}x\int_a^b \mathrm{d}u\,K(x,u)\left\{\frac{c^*(u)}{c^*(x)}\right\}^{\frac{1}{2}}\gamma^2(x,t) \tag{87}$$

$$= \int_a^b \mathrm{d}u\int_a^b \mathrm{d}x\,K(u,x)\left\{\frac{c^*(x)}{c^*(u)}\right\}^{\frac{1}{2}}\gamma^2(u,t), \tag{88}$$

by interchange of the ciphers x and u. But $K(x,u) = K(u,x)$ so that writing equation (86), first with (87) substituted and then with (88) substituted, and adding we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_a^b \gamma^2(x,t)\,\mathrm{d}x = -\int_a^b \mathrm{d}x\int_a^b \mathrm{d}u\,K(x,u)\left[\left\{\frac{c^*(u)}{c^*(x)}\right\}^{\frac{1}{4}}\gamma(x,t) - \left\{\frac{c^*(x)}{c^*(u)}\right\}^{\frac{1}{4}}\gamma(u,t)\right]^2. \tag{89}$$

It follows that

$$\int_a^b \gamma^2(x,t)\,\mathrm{d}x$$

is a constantly decreasing function and, since it cannot become negative nor can $\gamma(x,t)$ be zero, almost everywhere its derivative must tend to zero or

$$\left\{\frac{c^*(u)}{c^*(x)}\right\}^{\frac{1}{4}}\gamma(x,t) \to \left\{\frac{c^*(x)}{c^*(u)}\right\}^{\frac{1}{4}}\gamma(u,t)$$

for all x and u as $t\to\infty$. But this implies that

$$c(x,t) \to c^*(x) \tag{90}$$

and the equilibrium state is unique.

Let K denote the operator

$$Kf = \int_a^b K(x,u)\,f(u)\,\mathrm{d}u, \tag{91}$$

and A the operator with the added diagonal term

$$Af = -\kappa(x)\,f(x) + Kf. \tag{92}$$

Then the operator A is symmetric and must have real eigenvalues. But for any eigenvalue λ with corresponding eigenfunction f,

$$\lambda = (Af,f)/(f,f) < 0,$$

since $2(Af,f)$ is the right hand side of equation (89) and so negative. This establishes the theorem.

Before exploring the spectrum of the operator A further it will be useful to give an example showing that other eigenvalues do exist, for most of the general theorems apply to completely continuous operators and A has a part, the diagonal operator $\kappa(x)$, which is not completely continuous. Consider

$$k(x,y) = \tfrac{2}{3}xy + \tfrac{3}{7}x^2y^2 \quad (a = 1,\ b = 2), \tag{93}$$

for which

$$Af = -(x+x^2)f(x) + \tfrac{2}{3}x\int_1^2 yf(y)\,\mathrm{d}y + \tfrac{3}{7}x^2\int_1^2 y^2f(y)\,\mathrm{d}y. \tag{94}$$

The eigenvalue problem is $Af = \lambda f$ whence

$$f(x) = \{\tfrac{2}{3}f_1x + \tfrac{3}{7}f_2x^2\}/\{\lambda + x + x^2\}, \tag{95}$$

where

$$f_k = \int_1^2 y^kf(y)\,\mathrm{d}y \quad (k = 1, 2).$$

To find the f_k we multiply (95) by x and x^2 respectively and integrate to give the homogeneous algebraic system

$$\left[\frac{2}{3}\int_1^2 \frac{x^2}{\lambda+x+x^2}\,\mathrm{d}x - 1\right]f_1 + \left[\frac{3}{7}\int_1^2 \frac{x^3}{\lambda+x+x^2}\,\mathrm{d}x\right]f_2 = 0,$$

$$\left[\frac{2}{3}\int_1^2 \frac{x^3}{\lambda+x+x^2}\,\mathrm{d}x\right]f_1 + \left[\frac{3}{7}\int_1^2 \frac{x^4}{\lambda+x+x^2}\,\mathrm{d}x - 1\right]f_2 = 0.$$

The condition that this system should have a nontrivial solution is the vanishing of the determinant of these equations, which gives

$$\{\lambda F(\lambda) - 1\}\{2\lambda F(\lambda) + 2G(\lambda) + 1\} + 2\lambda G^2(\lambda) = 0, \tag{96}$$

where

$$F(\lambda) = \frac{1}{\nu}\ln\frac{25 + 14\lambda + 2\lambda^2 + (7 + 2\lambda)\nu}{24 + 16\lambda + 2\lambda^2},$$

$$G(\lambda) = \tfrac{1}{2}\ln\frac{\lambda+6}{\lambda+3} - \tfrac{1}{2}F(\lambda),$$

$$\nu = \{1 - 4\lambda\}^{\frac{1}{2}}.$$

Equation (96) has a simple root at $\lambda = -1{\cdot}4212$ approximately, with corresponding eigenfunction

$$f = \{2{\cdot}648x - 0{\cdot}42857x^2\}/\{x^2 + x - 1{\cdot}4212\}.$$

In general it is to be expected that some non-degenerate kernels will induce transformations with an infinite number of eigenvalues. If $\kappa(x)$ is bounded above, any accumulation point of the eigenvalues must lie in the range of $-\kappa(x)$. If $\kappa(x)$ is merely a measurable function then each accumulation point must be a point of density of $-\kappa(x)$. For if λ_i and f_i $(i = 1, 2, 3, \ldots)$ are the eigenvalues and orthonormalized eigenfunctions of the bounded operator A, we have shown that the set of λ is bounded above by zero. To obtain a lower bound let $\bar{\kappa} = \max \bar{\kappa}(x)$, $a \leqslant x \leqslant b$, then

$$\lambda_j = \frac{(Af_j, f_j)}{(f_j, f_j)} = \frac{-(\kappa f_j, f_j) + (Kf_j, f_j)}{(f_j, f_j)} \geqslant -\|K\| - \bar{\kappa}$$

where

$$\|K\| = \int_a^b\int_a^b K(x,u)\,\mathrm{d}x\,\mathrm{d}u.$$

Since $k \in L_2[D]$, it follows from Fubini's theorem that $\int K^2(x,y)\,\mathrm{d}y$ exists for almost all x and by Bessel's inequality

$$\sum_j \left[\int K(x,y) f_j(y)\,\mathrm{d}y\right]^2 = \sum_j \{\lambda_j + \kappa(x)\}^2 f_j^2(x) \leqslant \int K^2(x,y)\,\mathrm{d}y.$$

Thus, integrating with respect to x gives

$$\sum_j \int \{\lambda_j + \kappa(x)\}^2 f_j^2(x)\,\mathrm{d}x \leqslant \int\int K^2(x,y)\,\mathrm{d}x\,\mathrm{d}y < \infty$$

and for an infinite number of eigenvalues the series on the left converges. Hence

$$\int_a^b \{\lambda_j + \kappa(x)\}^2 f_j^2(x)\,\mathrm{d}x \rightarrow 0 \quad \text{as} \quad j \rightarrow \infty. \tag{97}$$

Now if λ_0 is a limit point of the λ_j and is not in the range of $-\kappa(x)$, we can bound $\lambda_j + \kappa(x)$ away from zero for all sufficiently large j. But this contradicts equation (97) and hence λ_0 must belong to the range of $-\kappa(x)$.

The spectrum of A is not exhausted by the eigenvalues as we may see by introducing the limit points of the spectrum. These are the points of the continuous spectrum, limit points of the eigenvalues and eigenvalues of infinite multiplicity. Riesz & Nagy (1955) give the theorem that the addition of a completely continuous operator to a bounded operator does not change the set of limit points of the spectrum of the latter. Now $Af = -\kappa f + Kf$ and K is completely continuous. But the spectrum of the bounded, diagonal operator $-\kappa f$ coincides with the range of $-\kappa(x)$, which therefore belongs to the spectrum of A. This discussion may be expressed in the form of

THEOREM 3. *The spectrum of* $A = -\kappa(x) + K$ *consists of the range of* $-\kappa(x)$ *and of a bounded set of eigenvalues with accumulation points, if any, in the range of* $-\kappa(x)$.

The whole of the foregoing discussion may be summarized in the following table which compares the discrete and continuous systems.

TABLE 1. DISCRETE AND CONTINUOUS FIRST ORDER SYSTEMS

Assumptions	Results for discrete systems	Results for continuous systems
(i) conservation of mass (ii) no negative concentrations (iii) rates of change of concentrations linearly dependent on concentration.	The differential system $\dot{\mathbf{c}} = \mathbf{A}\mathbf{c}$ has at least one equilibrium point.	The integro-differential equation $\dot{c}(x,t) = Ac$ may not have any equilibrium points.
(i), (ii), (iii) and (iv) each species connected to every other one by reaction.	The solutions of the equations $\dot{c}_i(t) = -c_i(t)\sum_j k_{ij} + \sum_j k_{ji} c_j(t)$ converge to an unique equilibrium point; namely, **A** has a simple zero eigenvalue and the rest have negative real parts.	The equation $\dot{c}(x,t) = -\kappa(x)\,c(x,t) + \int k(u,x)\,c(u,t)\,\mathrm{d}u$ has at least one equilibrium point; information about its uniqueness and stability are incomplete.
(i), (ii), (iii), (iv) and (v) the principle of microscopic reversibility.	At equilibrium $c_i^* k_{ij} = c_j^* k_{ji}$; the nonzero eigenvalues of **A** are real and negative.	At equilibrium $c^*(x)\,k(x,u) = c^*(u)\,k(u,x)$; the equation $\dot{c} = Ac$ has an unique, stable equilibrium point. The spectrum of A is given by theorem 3.

(*b*) *Solution by means of the Laplace transformation*

The Laplace transformation can be used to solve the equation

$$\dot{c}(x,t) = Ac = -\kappa(x)\,c(x,t) + \int_a^b k(u,x)\,c(u,t)\,\mathrm{d}u. \tag{78 bis}$$

Let
$$\bar{c}(x,s) = \int_0^\infty \mathrm{e}^{-st} c(x,t)\,\mathrm{d}t \tag{98}$$

and
$$c(x,0) = c_0(x), \tag{99}$$

then the equation transforms to

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\kappa(x)} + \frac{1}{s+\kappa(x)} \int_a^b k(u,x)\,\bar{c}(u,s)\,\mathrm{d}u. \tag{100}$$

The solution of this equation has the form

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\kappa(x)} + \int_a^b H(x,u,s)\,\frac{c_0(u)}{s+\kappa(u)}\,\mathrm{d}u, \tag{101}$$

where $H(x,u,s)$ is the resolvent of the kernel $k(u,x)/\{s+\kappa(x)\}$. There are several possible methods for the solution of this equation depending on the nature of the kernel. If $k(u,x)$ is degenerate and takes the form $U(u)\,X(x)$ then the resolvent kernel can be obtained in closed form. If the kinetics are represented by a Pincherle–Goursat kernel, i.e. of the form $\sum_1^n U_k(u)\,X_k(x)$ the resolvent kernel may again be determined. A general kernel may sometimes be approximated by a Pincherle–Goursat kernel, or a formal solution obtained as a series of iterated kernels. Let us look first at this last technique.

The resolvent kernel may be expressed as a series

$$H(x,u,s) = \sum_1^\infty k_n(x,u,s), \tag{102}$$

where
$$\left.\begin{aligned} k_1(x,u,s) &= k(u,x)/\{s+\kappa(x)\},\\ k_n(x,u,s) &= \int_a^b k_1(x,u',s)\,k_{n-1}(u',u,s)\,\mathrm{d}u'. \end{aligned}\right\} \tag{103}$$

It follows that $\bar{c}(x,s)$ has a representation of the form

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\kappa(x)} + \Sigma \overline{Q}_n(x,s), \tag{104}$$

where
$$\overline{Q}_n(x,s) = \int_a^b \frac{k_n(x,u,s)\,c_0(u)}{s+\kappa(u)}\,\mathrm{d}u. \tag{105}$$

Each of the functions $\overline{Q}_n(x,s)$ has a logarithmic discontinuity across the range of $-\kappa(x)$ and is unbounded at the eigenvalues of the operators A. To invert the transform we observe that, by setting $u_0 \equiv x$ for symmetry, $\overline{Q}_n$ may be written in the form

$$\begin{aligned} \overline{Q}_n(u_0,s) &= \int_a^b \mathrm{d}u_1 \int_a^b \mathrm{d}u_2 \ldots \int_a^b \mathrm{d}u_n \frac{k(u_1,u_0)\,k(u_2,u_1)\ldots k(u_n,u_{n-1})}{\{s+\kappa(u_0)\}\{s+\kappa(u_1)\}\ldots\{s+\kappa(u_n)\}}\,c_0(u_n)\\ &= \int_a^b \mathrm{d}u_1 \ldots \int_a^b \mathrm{d}u_n \prod_1^n k(u_k,u_{k-1}) \prod_0^n \frac{1}{\{s+\kappa(u_k)\}}\,c_0(u_n)\\ &= \int_a^b \mathrm{d}u_1 \ldots \int_a^b \mathrm{d}u_n \prod_1^n k(u_k,u_{k-1}) \sum_0^n \left[\frac{1}{\{s+\kappa(u_k)\}} \Big/ \prod_{\substack{m=1\\ m\neq k}}^n \{\kappa(u_m)-\kappa(u_k)\}\right] c_0(u_n). \end{aligned}$$

Inverting term by term we have

$$c(x,t) = c_0(x)\,\mathrm{e}^{-\kappa(x)\,t} + \Sigma Q_n(x,t), \tag{106}$$

where

$$Q_n(u_0,t) = \int_a^b \mathrm{d}u_1 \dots \int_a^b \mathrm{d}u_n \prod_1^n k(u_k,u_{k-1}) \sum_0^n \left[\frac{\exp\left(-\kappa(u_k)\,t\right)}{\prod\limits_{\substack{m=1\\ m\neq k}}^{n} \{\kappa(u_m)-\kappa(u_k)\}}\right]. \tag{107}$$

The integrals must of course be given their Cauchy principal values and the convergence of the series assured by direct test.

We shall show the technique of inverting the transform when the resolvent kernel is given in closed form, by treating an elementary example. This will provide a concrete case for studying the singularities of the kernel. Let $a = 1$, $b = 2$, $k(x,u) = xu$ so that

$$\kappa(x) = \int_a^b k(x,u)\,\mathrm{d}u = \tfrac{3}{2}x.$$

Then

$$\dot{c}(x,t) - = -\tfrac{3}{2}xc(x,t) + x\int_1^2 uc(u,t)\,\mathrm{d}u \tag{108}$$

and

$$c(x,0) = c_0(x).$$

Taking the Laplace transformation of this gives the equation

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\frac{3}{2}x} + \frac{x}{s+\frac{3}{2}x}\int_1^2 u\bar{c}(u,s)\,\mathrm{d}u. \tag{109}$$

Multiplying this by x and integrating gives an equation for

$$\bar{g}(s) = \int_1^2 u\bar{c}(u,s)\,\mathrm{d}u,$$

namely

$$\bar{g}(s) = \frac{9}{4}\int_1^2 \frac{uc_0(u)}{s+\frac{3}{2}u}\,\mathrm{d}u \bigg/ \left\{s - \tfrac{2}{3}s^2 \ln\frac{s+3}{s+\frac{3}{2}}\right\}. \tag{110}$$

Thus substituting back in equation (109) gives

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\frac{3}{2}x} + \frac{9}{4}\,\frac{x}{s(s+\frac{3}{2}x)}\int_1^2 \frac{uc_0(u)\,\mathrm{d}u}{s+\frac{3}{2}u} \bigg/ \left\{1 - \tfrac{2}{3}s\ln\frac{s+3}{s+\frac{3}{2}}\right\}, \tag{111}$$

and the most convenient way of inverting this is to invert $g(s)$ and use the convolution integral.

The singularities of $\bar{g}(s)$ are at $s = 0$ and along the line segment $-3 \leqslant s \leqslant -\frac{3}{2}$. The behaviour of the integral near this line segment is given by the Plemelj formulae (see, for example, Muskhelishvili 1953). These formulae concern the Cauchy integral

$$J(s) = \int_a^b \frac{f(y)}{s+y}\,\mathrm{d}y, \tag{112}$$

to which we must advert for a moment. This is a holomorphic function everywhere except on the line segment $(-b, -a)$ where it is discontinuous, with one-sided limits

$$\left.\begin{aligned} J^+(\sigma) &= \lim_{\epsilon\to 0+} J(\sigma+\mathrm{i}\epsilon) = \int_a^{b^*} \frac{f(y)\,\mathrm{d}y}{\sigma+y} - \mathrm{i}\pi f(-\sigma),\\ J^-(\sigma) &= \lim_{\epsilon\to 0-} J(\sigma+\mathrm{i}\epsilon) = \int_a^{b^*} \frac{f(y)\,\mathrm{d}y}{\sigma+y} + \mathrm{i}\pi f(-\sigma), \end{aligned}\right\} \tag{113}$$

where $\sigma = \mathscr{R}(s)$ and the asterisk denotes the Cauchy principal value. Similar formulae can be developed for integrals of the form

$$I(s) = \int_a^b \frac{f(y)\,\mathrm{d}y}{s+\kappa(y)}. \tag{114}$$

Assuming first that $\kappa(y)$ is differentiable and monotonic we may change the variable of integration by setting

$$z = \kappa(y), \quad y = \tilde{\kappa}(z), \tag{115}$$

giving

$$I(s) = \int_{\kappa(a)}^{\kappa(b)} \frac{f(\tilde{\kappa}(z))\,\tilde{\kappa}'(z)}{s+z}\,\mathrm{d}z$$

and

$$\begin{aligned} I^+(\sigma) &= \int_{\kappa(a)}^{\kappa(b)*} \frac{f(\tilde{\kappa}(z))\,\tilde{\kappa}'(z)}{\sigma+z}\,\mathrm{d}z - \mathrm{i}\pi f(\tilde{\kappa}(-\sigma))\,\tilde{\kappa}'(-\sigma) \\ &= \int_a^{b*} \frac{f(y)\,\mathrm{d}y}{\sigma+\kappa(y)} - \mathrm{i}\pi f(\tilde{\kappa}(-\sigma))\,\tilde{\kappa}'(-\sigma), \end{aligned} \tag{116}$$

with $I^-(\sigma) = \overline{I^+(\sigma)}$, the complex conjugate. If $\kappa(y)$ is differentiable but not monotonic then the interval must be broken up into subintervals of monotonicity, giving rise to similar formulae.

After this diversion we may return to our example for which the integral in the numerator is

$$\frac{9}{4}\int_1^{2*} \frac{uc_0(u)}{\sigma+\frac{3}{2}x}\,\mathrm{d}u \pm \mathrm{i}\pi\sigma c_0(-\tfrac{2}{3}\sigma) \tag{117}$$

for $-3 \leqslant \sigma \leqslant -\frac{3}{2}$. Similarly, the denominator approaches

$$\sigma\left\{1-\tfrac{2}{3}\sigma\ln\left|\frac{\sigma+3}{\sigma+\frac{3}{2}}\right| \pm \mathrm{i}\tfrac{2}{3}\pi\sigma\right\}, \tag{118}$$

as s approaches the segment from above and below. Substituting from equations (117) and (118) into equation (110) gives

$$\bar{g}^+(\sigma) = \frac{\dfrac{9}{4\sigma}\left[I+\mathrm{i}\left(\dfrac{4\pi\sigma}{9}\right)c_0(-\tfrac{2}{3}\sigma)\right]\left[1-\tfrac{2}{3}\sigma\ln\left|\dfrac{\sigma+3}{\sigma+\frac{3}{2}}\right| - \mathrm{i}\tfrac{2}{3}\pi\sigma\right]}{\left\{1-\tfrac{2}{3}\sigma\ln\left|\dfrac{\sigma+3}{\sigma+\frac{3}{2}}\right|\right\}^2 + \tfrac{4}{9}\pi^2\sigma^2}, \tag{119}$$

with $\bar{g}^-(\sigma)$ its complex conjugate, and I is the Cauchy principal value of

$$I = \int_1^2 \frac{uc_0(u)\,\mathrm{d}u}{\sigma+\frac{3}{2}u}. \tag{120}$$

Consider now the contour, C, of figure 1 which contains a simple pole of $\bar{g}(s)$ at $s = 0$ and no other singularity.

$$\frac{1}{2\pi\mathrm{i}}\int_C \bar{g}(s)\,\mathrm{e}^{st}\,\mathrm{d}s = (\text{residue of } \bar{g}(s) \text{ at } s=0) = \frac{3}{2}\int_1^2 c_0(u)\,\mathrm{d}u. \tag{121}$$

But the integral around C is also the sum of the integrals along the segments $A'A$, ABD, $D'B'A'$, DE, $E'D'$, EF and FE', which we will denote by I_1, I_2, I_2', I_3, I_3', I_4 and I_4' respectively. As we let M and N tend to infinity and $\epsilon \to 0$ we obtain

$$I_1 \to \frac{1}{2\pi\mathrm{i}}\int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \bar{g}(s)\,\mathrm{e}^{st}\,\mathrm{d}s = g(t), \tag{122}$$

$$I_2 \to 0, \quad I_2' \to 0, \quad I_3 + I_3' \to 0$$

and

$$I_4 + I_4' \to \frac{1}{2\pi i}\int_{-3}^{-\frac{3}{2}} \{\bar{g}^{+}(\sigma)\,\mathrm{e}^{\sigma t} - \bar{g}^{-}(\sigma)\,\mathrm{e}^{\sigma t}\}\,\mathrm{d}\sigma$$

$$= \int_{-3}^{-\frac{3}{2}} \frac{\left\{1-\frac{2}{3}\sigma\ln\left|\dfrac{\sigma+3}{\sigma+\frac{3}{2}}\right|\right\} c_0\left(-\dfrac{2\sigma}{3}\right) - \frac{3}{2}I}{\left\{1-\frac{2}{3}\sigma\ln\left|\dfrac{\sigma+3}{\sigma+\frac{3}{2}}\right|\right\}^2 + \frac{4}{9}\pi^2\sigma^2}\,\mathrm{e}^{\sigma t}\,\mathrm{d}\sigma$$

$$= \frac{3}{2}\int_{1}^{2} \frac{\left\{1+\sigma'\ln\left|\dfrac{2-\sigma'}{1-\sigma'}\right|\right\} c_0(\sigma') + \displaystyle\int_1^2 \frac{u c_0(u)}{\sigma'-u}\,\mathrm{d}u}{\left\{1+\sigma'\ln\left|\dfrac{2-\sigma'}{1-\sigma'}\right|\right\}^2 + \pi^2\sigma'^2}\,\mathrm{e}^{-\frac{3}{2}\sigma' t}\,\mathrm{d}\sigma'$$

$$= \frac{3}{2}\int_1^2 \{W_0(\sigma')/D(\sigma')\}\,\mathrm{e}^{-\frac{3}{2}\sigma' t}\,\mathrm{d}\sigma', \tag{123}$$

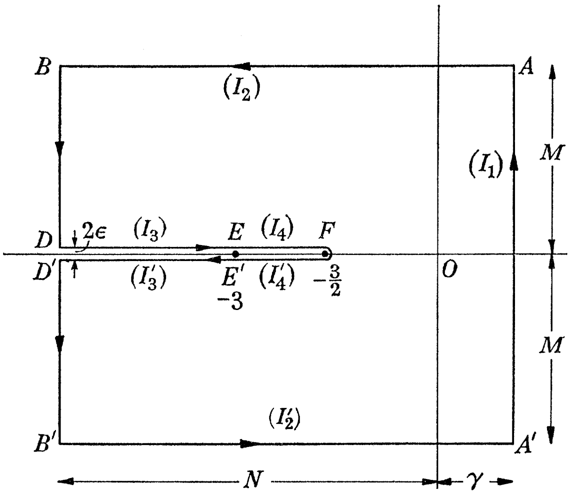

FIGURE 1. Contour for the inversion of $\bar{g}(s)$, equation (110).

where $W_0(\sigma')$ depends on $c_0(\sigma')$ in the manner shown and the change of variable $\sigma' = -\frac{2}{3}\sigma$ has been used to obtain the final form. Combining equations (121), (122) and (123) to give $g(t)$ and taking the convolution of this with $\mathrm{e}^{-\frac{3}{2}t}$, we have

$$c(x,t) = \int_1^2 c_0(u)\,\mathrm{d}u + \left[c_0(x) - \int_1^2 c_0(u)\,\mathrm{d}u\right]\mathrm{e}^{-\frac{3}{2}xt} + x\int_1^2 \frac{\mathrm{e}^{-\frac{3}{2}\sigma' t} - \mathrm{e}^{-\frac{3}{2}xt}}{\sigma'-x}\,\frac{W_0(\sigma')}{D(\sigma')}\,\mathrm{d}\sigma'. \tag{124}$$

As $t \to \infty$, $c(x,t) \to \int_1^2 c_0(u)\,\mathrm{d}u$ as it should.

If $c_0(x) = x^{-1}$ we have $W_0(\sigma') = \sigma'^{-1}$ and

$$c(x,t) = \ln 2 + \left(\frac{1}{x} - \ln 2\right)\mathrm{e}^{-\frac{3}{2}xt} + x\int_1^2 \frac{\mathrm{e}^{-\frac{3}{2}\sigma' t} - \mathrm{e}^{-\frac{3}{2}xt}}{\sigma'-x}\,\frac{\mathrm{d}\sigma'}{\sigma' D(\sigma')}.$$

Similarly, with $c_0(x) = x$ we have $W_0(\sigma') = -\frac{3}{2}$ and

$$c(x,t) = \tfrac{3}{2} + (x - \tfrac{3}{2})\,\mathrm{e}^{-\frac{3}{2}xt} - \frac{3x}{2}\int_1^2 \frac{\mathrm{e}^{-\frac{3}{2}\sigma' t} - \mathrm{e}^{-\frac{3}{2}xt}}{\sigma'-x}\,\frac{\mathrm{d}\sigma'}{D(\sigma')}.$$

As an example of the use of the generalized Plemelj formulae we may mention

$$k(x,u) = \tfrac{1}{2}\sin x \sin u, \quad a = 0, \quad b = \pi.$$

Here we obtain

$$\bar{c}(x,s) = \frac{c_0(x)}{s+\sin x} + \frac{\sin x}{2(s+\sin x)}\,\bar{g}(s),$$

where
$$\bar{g}(s) = \int_0^\pi \frac{c_0(u)\sin u}{\sin u + s}\,\mathrm{d}u \Big/ \left\{\frac{\pi s}{2} - \frac{s^2}{(1-s^2)^{\frac{1}{2}}}\ln\left[\frac{1+(1-s^2)^{\frac{1}{2}}}{s}\right]\right\}. \tag{125}$$

The logarithm is given its principal determination and the square root determined accordingly. $\bar{g}(s)$ has singularities on $-1 \leqslant s \leqslant 0$. Denote by $f(s)$ and $I(s)$ the functions

$$f(s) = \ln\left[\frac{1+(1-s^2)^{\frac{1}{2}}}{s}\right] \quad \text{and} \quad I(s) = \int_0^\pi \frac{c_0(u)\sin u}{\sin u + s}\,\mathrm{d}u,$$

for which
$$f^{\pm}(\sigma) = \ln\left|\frac{1+(1-\sigma^2)^{\frac{1}{2}}}{\sigma}\right| \mp \mathrm{i}\pi,$$

$$I^{\pm}(\sigma) = \int_0^{\pi *} \frac{c_0(u)\sin u}{\sin u + \sigma}\,\mathrm{d}u \pm \frac{\mathrm{i}\pi\sigma}{(1-\sigma^2)^{\frac{1}{2}}}\,[c_0(-\sin^{-1}\sigma) + c_0(\pi + \sin^{-1}\sigma)].$$

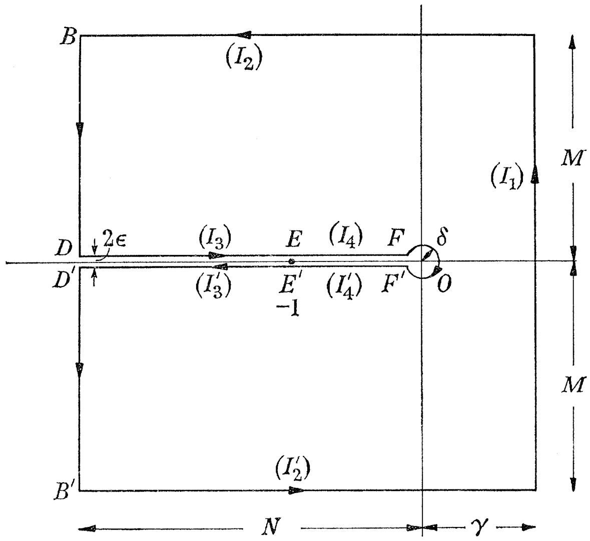

FIGURE 2. Contour for the inversion of $\bar{g}(s)$, equation (125).

As $s \to 0$, $\bar{g}(s)$ becomes unbounded but the singularity is not isolated. However, for purposes of contour integration it has the same effect as a simple pole, for we may write

$$\bar{g}(s) = \frac{2}{\pi s}\int_0^\pi c_0(u)\,\mathrm{d}u + \left\{\bar{g}(s) - \frac{2}{\pi s}\int_0^\pi c_0(u)\,\mathrm{d}u\right\},$$

and the second term is bounded at $s = 0$. Also $\bar{g}(s)$ is $O(|s|^{-2})$ as $s \to \infty$. With this information we can invert the transformation by integrating $\bar{g}(s)\,\mathrm{e}^{st}/2\pi\mathrm{i}$ around the contour shown in figure 2; the contour is broken up into eight parts and the notation, which is entirely similar to the preceding case, should be clear from the figure. The integral along $A'A$, I_1 becomes the inversion integral as $M \to \infty$ and as M and $N \to \infty$ and ϵ and $\delta \to 0$ we can establish the following behaviour

$$I_1 \to g(t), \quad I_2 \to 0, \quad I_2' \to 0, \quad (I_3 + I_3') \to 0, \quad I_5 \to -\frac{2}{\pi}\int_0^{\pi} c_0(u)\,\mathrm{d}u,$$

$$(I_4 + I_4') \to \frac{1}{2\pi \mathrm{i}}\left[\int_{-1}^{0} I^{+}(\sigma)\,\mathrm{e}^{\sigma t}\left\{\frac{\pi\sigma}{2} - \frac{\sigma^2}{(1-\sigma^2)^{\frac{1}{2}}} f^{+}(\sigma)\right\}^{-1} \mathrm{d}\sigma \right.$$
$$\left. + \int_{0}^{-1} I^{-}(\sigma)\,\mathrm{e}^{\sigma t}\left\{\frac{\pi\sigma}{2} - \frac{\sigma^2}{(1-\sigma^2)^{\frac{1}{2}}} f^{-}(\sigma)\right\}^{-1} \mathrm{d}\sigma\right]$$
$$= \int_0^{\frac{1}{2}\pi} [W(\sigma')\{c_0(\sigma') + c_0(\pi - \sigma')\} - J(\sigma')]\,\frac{\mathrm{e}^{-t\sin\sigma'}}{D(\sigma')}\,\mathrm{d}\sigma',$$

where $\sigma = -\sin\sigma'$ and
$$W(\sigma') = \tfrac{1}{2}\pi + \tan\sigma' \ln\{\cot\tfrac{1}{2}\sigma'\},$$
$$D(\sigma') = W^2(\sigma') + \pi^2 \tan^2\sigma',$$
$$J(\sigma') = \int_0^{\pi^*} \frac{c_0(u)\sin u}{\sin u - \sin\sigma'}\,\mathrm{d}u.$$

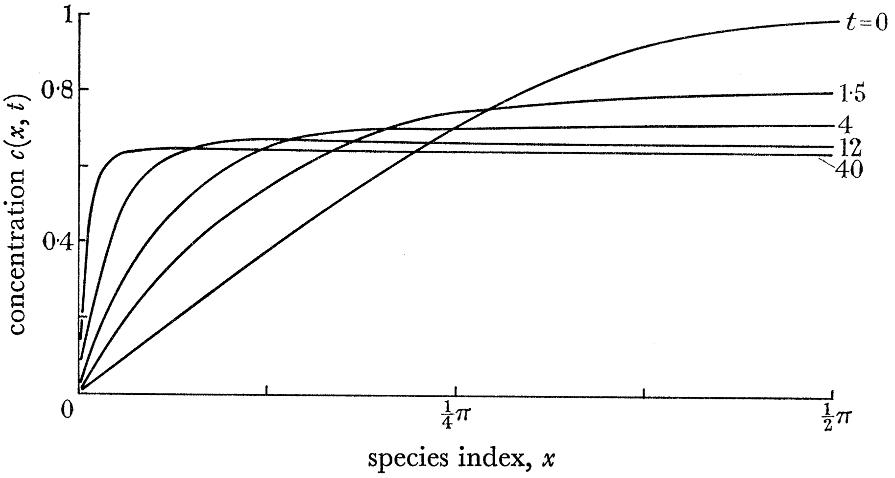

FIGURE 3. The concentration distribution given by equation (126).

This leads, via the convolution integral to the solution

$$c(x,t) = \frac{1}{\pi}\int_0^{\frac{1}{2}\pi} c_0(u)\,\mathrm{d}u + \left[c_0(x) - \frac{1}{\pi}\int_0^{\pi} c_0(u)\,\mathrm{d}u\right]\mathrm{e}^{-t\sin x}$$
$$-\tfrac{1}{2}\sin x \int_0^{\frac{1}{2}\pi} \frac{W(\sigma')\{c_0(\sigma') + c_0(\pi - \sigma')\} - J(\sigma')}{D(\sigma')}\,\frac{\mathrm{e}^{-t\sin\sigma'} - \mathrm{e}^{-t\sin x}}{\sin x - \sin\sigma'}\,\mathrm{d}\sigma'.$$

For example, the initial distribution $c_0(x) = \sin x$ gives the solution

$$c(x,t) = \frac{2}{\pi} + \left(\sin x - \frac{2}{\pi}\right)\mathrm{e}^{-t\sin x} + \sin x \int_0^{\frac{1}{2}\pi} \frac{\mathrm{e}^{-t\sin\sigma'} - \mathrm{e}^{-t\sin x}}{\sin x - \sin\sigma'}\,\frac{\mathrm{d}\sigma'}{D(\sigma')}, \tag{126}$$

and figure 3 shows the distribution for five values of time.

(*c*) *Irreversible systems; cracking by direct fission*

As an example of an irreversible system we shall consider the continuous analogue of the cracking of a mixture of paraffins and olefins by direct fission. It is not suggested that this is the only, or even the dominant, mechanism (free radical reactions are often more important), but it is useful to isolate it for study here. Let $A(x)$ $(0 \leqslant x \leqslant b)$, be a continuous distribution of 'paraffins' and $B(x)$ $(0 \leqslant x \leqslant b)$, a similar distribution of 'olefins'. These are symbolic species of the form C_xH_{2x+2} and C_xH_{2x} respectively and were they to exist they would certainly be capable of cracking according to the equations

$$\left.\begin{aligned} A(x) &\rightarrow A(x')+B(x-x'),\\ B(x) &\rightarrow B(x')+B(x-x'),\end{aligned}\right\} \tag{127}$$

for all x, x', $0 \leqslant x' < x \leqslant b$. Denote the concentration densities of $A(x)$ and $B(x)$ by $c(x,t)$ and $q(x,t)$ respectively. Let the total rate of cracking of $A(x)$ be $\kappa(x)$ and $\lambda(x)$ be that of $B(x)$; let $v(x',x)$ be the fraction of $A(x)$ that cracks to $A(x')$ and $w(x',x)$ the fraction of $B(x)$ that cracks to $B(x')$. The symmetry of the olefinic reaction implies that

$$w(x',x) = w(x-x',x). \tag{128}$$

The fact that v and w are fractions requires that

$$\int_0^x v(x',x)\,\mathrm{d}x' = 1, \quad \int_0^x w(x',x)\,\mathrm{d}x' = 2. \tag{129}$$

The concentration densities are given by

$$\dot{c}(x,t) = -\kappa(x)\,c(x,t)+\int_x^b \kappa(x')\,v(x,x')\,c(x',t)\,\mathrm{d}x', \tag{130}$$

$$\dot{q}(x,t) = -\lambda(x)\,q(x,t)+\int_x^b \kappa(x')\,v(x'-x,x')\,c(x',t)\,\mathrm{d}x'+\int_x^b \lambda(x')\,w(x,x')\,q(x',t)\,\mathrm{d}x'. \tag{131}$$

The integrals represent direct cracking from higher species and give a pair of simultaneous Volterra integro-differential equations. However, the equations are uncoupled and when the first has been solved we can solve the second as an inhomogeneous equation of the same type. We shall therefore concentrate our attention on equation (130).

For this purpose we define the operator

$$Ac = -\kappa(x)\,c(x,t)+\int_x^b \kappa(x')\,v(x,x')\,c(x',t)\,\mathrm{d}x', \tag{132}$$

and supplement the assumptions on κ and v by imposing the conditions

$$\text{(i)}\quad v(x',x) \geqslant 0, \quad \int_0^x v(x',x)\,\mathrm{d}x' = 1, \quad v(x',x) \in L_2[D]; \tag{133}$$

$$\text{(ii)}\quad 0 < g(x) \leqslant \kappa(x) \leqslant M, \quad 0 < x \leqslant b; \quad g(x) \text{ is continuous on } (0,b); \tag{134}$$

where D is the rectangle $(0,b)\times(0,b)$. The first is just a reiteration of equation (129), the second condition ensures that there are no pockets of material that does not crack.

We observe first of all that there is no equilibrium distribution, for if there were $\kappa(x)\,c^*(x)$ would be an eigenfunction of the Volterra equation

$$\phi(x) = \int_x^b v(x,x')\,\phi(x')\,\mathrm{d}x',$$

which is impossible. The eigenvalue problem associated with the operator A is a homogeneous Volterra equation

$$\phi(x) = \int_x^b \frac{\kappa(x')\,v(x,x')}{\lambda+\kappa(x)}\,\phi(x')\,\mathrm{d}x' \tag{135}$$

in the interval (x_0, b) if $\lambda+\kappa(x)$ is bounded away from zero. It follows that the eigenvalues of equation (135) must lie in the set

$$E_{x_0} = \{y : y = -\kappa(x), \quad x_0 \leqslant x \leqslant b\}$$

for all $x_0 < b$. Hence all eigenvalues of A lie in the set

$$E = \bigcap_{0<x_0<b} E_{x_0}$$

and for continuous $\kappa(x)$ the only possible eigenvalue is

$$\lambda = -\kappa(b). \tag{136}$$

The operator A has in addition a continuous spectrum which coincides with the range of $-\kappa(x)$ and the solution of equation (130) can be represented as

$$c(x,t) = -\frac{1}{2\pi \mathrm{i}}\int_C \mathrm{e}^{\lambda t}(A-\lambda I)^{-1}c_0\,\mathrm{d}\lambda,$$

where the contour C encloses the spectrum. To see the behaviour of $c(x_0,t)$ as $t\to\infty$ for any $x_0>0$ we need only consider the function $c(x,t)$ in (x_0,b). In this case the range of $-\kappa(x)$ lies entirely in the left hand plane and the contour C can be taken there also. Thus

$$c(x_0,t)\to 0 \quad \text{as} \quad t\to\infty \quad \text{for all} \quad x_0>0. \tag{137}$$

This is what we expect on physical grounds and, as the convergence is pointwise and neither uniform nor in the mean, the conservation of mass is not violated.

In contrast to the reversible case the convergence of the Neumann series of iterated kernels is assured, but solutions in closed form which were there available for arbitrary degenerate kernels are here only possible for a degenerate kernel with a single term. The following example is one in which a closed form is obtained. Let $\kappa(x) = x^2$, $v(x,x') = 1/x'$, $b = 1$, then

$$\dot{c}(x,t) = -x^2c(x,t) + \int_x^1 x'c(x',t)\,\mathrm{d}x', \quad c(x,0) = c_0(x). \tag{138}$$

Taking the Laplace transform we obtain

$$(s+x^2)\,\bar{c}(x,s) = c_0(x) + \int_x^1 x'\bar{c}(x',s)\,\mathrm{d}x'. \tag{139}$$

By differentiation with respect to x we have

$$\frac{\mathrm{d}\bar{c}}{\mathrm{d}x} + \frac{3x}{s+x^2}\bar{c} = \frac{c_0'(x)}{s+x^2}, \tag{140}$$

and

$$\bar{c}(1,s) = c_0(1)/(1+s),$$

whence

$$\bar{c}(x,s) = \frac{c_0(x)}{x^2+s} + \frac{1}{(x^2+s)^{\frac{3}{2}}}\int_x^1 \frac{x'c_0(x')\,\mathrm{d}x'}{(x'^2+s)^{\frac{1}{2}}}. \tag{141}$$

This holds even when $c_0(x)$ is not differentiable or even continuous and may be inverted to give

$$c(x,t) = c_0(x)\,\mathrm{e}^{-x^2t}+\frac{2}{\pi}\,\mathrm{e}^{-x^2t}\int_x^1 x'c_0(x')\,F(x,x',t)\,\mathrm{d}x',$$

where

$$F(x,x',t) = 2t\int_0^\infty \frac{z^2}{(z^2+1)^2}\exp\left\{\frac{x^2-x'^2}{z^2+1}\,t\right\}\mathrm{d}z. \tag{142}$$

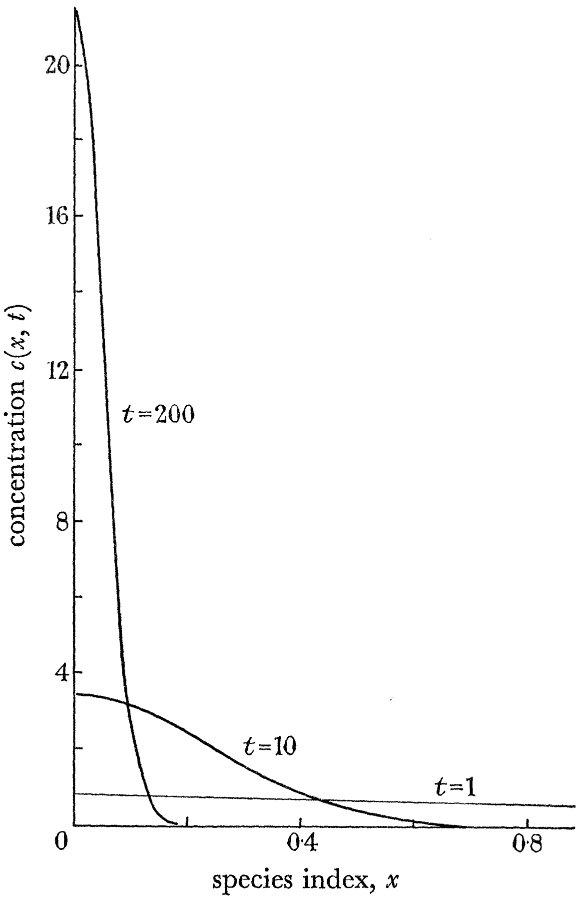

FIGURE 4. The concentration distribution by direct cracking: equation (142).

If the initial distribution is originally concentrated entirely at $x=1$, $c_0(x)=\delta(x-1)$, we have

$$c(x,t) = \delta(x-1)\,\mathrm{e}^{-x^2t}+\frac{2}{\pi}\,\mathrm{e}^{-x^2t}F(x,1,t),$$

and shows, in figure 4, a continuous drift toward the zero species.

(*d*) *The differential reactions*

The generalization of the discrete sequence reaction $A_r-A_{r-1}=0$ has been mentioned above. It may be represented by using the generalized function $\delta'(w-x)$ which, acting on any test function, gives its derivative. Thus we have symbolically

$$\int_a^b \alpha(w,x)\,A(x)\,\mathrm{d}x = \int_a^b \delta'(w-x)\,A(x)\,\mathrm{d}x = A'(w) = 0, \tag{34 bis}$$

and for the concentration change

$$\Delta c(x) = \int_a^b \xi(w)\,\delta'(w-x)\,\mathrm{d}w = -\xi'(x). \tag{35 bis}$$

If we define $\dot{\xi}(x)$, the rate of reaction at x, to be

$$\dot{\xi}(x) = k(x)\,c(x,t) \tag{143}$$

we have for $c(x,t)$ the partial differential equation

$$\dot{c}(x,t) = -[k(x)\,c(x,t)]',$$

or

$$\frac{\partial c}{\partial t}+\frac{\partial}{\partial x}(kc) = \frac{\partial c}{\partial t}+k(x)\frac{\partial c}{\partial x}+k'(x)\,c = 0. \tag{144}$$

This can be solved by the method of characteristics for along a characteristic we have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(x) \qquad (x = x_0,\ t = 0),$$

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k'(x)\,c \qquad (c = c_0(x_0),\ t = 0).$$

Thus

$$t = \int_{x_0}^{x} \frac{\mathrm{d}x'}{k(x')} \tag{145}$$

defines the characteristic and along it $k(c)\,c(x,t)$ is constant, i.e.

$$c(x,t) = \frac{k(x_0)}{k(x)}\,c_0(x_0). \tag{146}$$

If the continuous mixture does not extend beyond a finite range we set $k(x) = 0$ outside that range. Thus if $a = 0$, b finite, $k(x) = \mathrm{e}^{\beta x}$ and $c_0(x) = C/\alpha$, $0 \leqslant x \leqslant \alpha < b$ we have

$$t = \int_{x_0}^{x} \mathrm{e}^{-\beta x'}\,\mathrm{d}x' = \frac{1}{\beta}(\mathrm{e}^{-\beta x_0}-\mathrm{e}^{-\beta x}),$$

or

$$x = \frac{1}{\beta}\ln\{\mathrm{e}^{-\beta x_0}-\beta t\}^{-1}.$$

The non-zero concentration thus moves in a band between the curves

$$\beta t = 1-\mathrm{e}^{-\beta x},$$

and

$$\beta t = \mathrm{e}^{-\alpha\beta}-\mathrm{e}^{-\beta x}.$$

In this region and the open interval $(0,b)$

$$\begin{aligned} c(x,t) &= (C/\alpha)\,\mathrm{e}^{-\beta(x-x_0)} \\ &= \frac{C}{\alpha}\,\frac{\mathrm{e}^{-\beta x}}{\mathrm{e}^{-\beta x}+\beta t}. \end{aligned} \tag{147}$$

However, because of the discontinuity in $k(x)$ at $x = b$ we have $k'(x) = \beta\,\mathrm{e}^{\beta x}-\mathrm{e}^{\beta b}\,\delta(x-b)$, thus at $x = b$ there is built up a delta function distribution

$$\mathrm{e}^{\beta b}\,\delta(x-b)\int_0^t c(b,t)\,\mathrm{d}t = \frac{C}{\alpha\beta}\,\delta(x-b)\ln\left[\frac{\mathrm{e}^{-\beta b}+\beta t}{\mathrm{e}^{-\alpha\beta}}\right]$$

for $(1/\beta)\,(\mathrm{e}^{-\alpha\beta}-\mathrm{e}^{-\beta x}) \leqslant t \leqslant (1/\beta)\,(1-\mathrm{e}^{-\beta x})$. After this latter time the distribution is $C\delta(x-b)$. A more versatile generalization of the sequential reaction, based on the notion of a biochemical sequence with Michaelis–Menten kinetics, would be obtained with

$$\dot{\xi}(x) = k(x)\,c(x,t)/\{1+m(x)\,c(x,t)\} = F(x,c). \tag{148}$$

This also leads to an equation amenable to solution by the method of characteristics

$$\frac{\partial c}{\partial t}+\left(\frac{\partial F}{\partial c}\right)\frac{\partial c}{\partial x}+\frac{\partial F}{\partial x} = 0. \tag{149}$$

Here however the characteristic equations

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\partial F}{\partial c}, \quad \frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{\partial F}{\partial x}$$

call for simultaneous integration.

Another system leading to a partial differential equation is $A'(x)-\beta(x)\,B(x) = 0$, the generalization of $A_{r+1}-A_r-\beta_r B_r = 0$. In this case we may set

$$\dot{\xi}(x) = k(x)\,b(x,t)\,c(x,t), \tag{150}$$

where $b(x,t)$ the concentration density of $B(x)$ changes by irreversible incorporation and so

$$b(x,t) = b_0(x)-\beta(x)\int_0^t c(x,t')\,\mathrm{d}t'. \tag{151}$$

If we introduce the new independent variable

$$\Gamma(x,t) = \int_0^t c(x,t')\,\mathrm{d}t' \tag{152}$$

we obtain the nonlinear hyperbolic equation

$$\frac{\partial^2\Gamma}{\partial t^2}+\{\kappa-\gamma\Gamma\}\frac{\partial^2\Gamma}{\partial x\,\partial t}+\{\kappa'-\gamma'\,\Gamma\}\frac{\partial\Gamma}{\partial t}-\gamma\frac{\partial\Gamma}{\partial t}\frac{\partial\Gamma}{\partial x} = 0, \tag{153}$$

where $\kappa(x) = k(x)\,b_0(x), \quad \gamma(x) = k(x)\,\beta(x),$

and $\Gamma(x,0) = 0, \quad \Gamma_t(x,0) = c_0(x).$

The sequence of reversible first order reactions

$$\dots A_{r-1} \xrightleftharpoons[k_{r,2}]{k_{r-1,1}} A_r \xrightleftharpoons[k_{r+1,2}]{k_{r,1}} A_{r+1} \dots$$

has the equations

$$\begin{aligned}\dot{c}_r &= k_{r+1,\,2}\,c_{r+1}-(k_{r,\,2}+k_{r,\,1})\,c_r+k_{r-1,\,1}\,c_{r-1}\\ &= (k_{r+1,\,2}\,c_{r+1}-2k_{r,\,2}\,c_r+k_{r-1,\,2}\,c_{r-1})+(k_{r,\,2}-k_{r,\,1})\,c_r-(k_{r-1,\,2}-k_{r-1,\,1})\,c_{r-1}.\end{aligned}$$

The generalization of this to a continuous mixture is the second order parabolic partial differential equation

$$\frac{\partial c}{\partial t} = \frac{\partial^2}{\partial x^2}(k_2 c)+\frac{\partial}{\partial x}(k_2-k_1)\,c. \tag{154}$$

We observe that this has an equilibrium distribution $c^*(x)$ for which $\partial c/\partial t = 0$, satisfying

$$\frac{\partial^2}{\partial x^2}(k_2 c)+\frac{\partial}{\partial x}(k_2-k_1)\,c = 0,$$

i.e.

$$\frac{\partial}{\partial x}k_2 c+(k_2-k_1)\,c = \text{constant}.$$

Now by the principle of microscopic reversibility we would have in the discrete system

$$k_{r,1}c_r = k_{r+1,2}c_{r+1} \quad \text{or} \quad (k_{r+1,2}c_{r+1}-k_{r,2}c_r)+(k_{r,2}-k_{r,1})\,c_r = 0.$$

In the continuous analogue this is

$$\frac{\partial}{\partial x}(k_2 c)+(k_2-k_1)\,c = 0,$$

so that the constant is zero and

$$c^*(x) = \frac{c^*(0)\,k_2(0)}{k_2(x)}\exp\int_0^x\left\{\frac{k_1(x')}{k_2(x')}-1\right\}\mathrm{d}x'. \tag{155}$$

Solution of equation (154) by the Laplace transform leads to the linear equation

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}(k_2\bar{c})+\frac{\mathrm{d}}{\mathrm{d}x}(k_2-k_1)\,\bar{c}-s\bar{c} = c_0(x).$$

It may be interpreted as a heat conduction problem in an inhomogeneous medium with heat generation.

(*e*) *Polymerization*

There is little need to say much on the subject of polymerization, since this has been well treated by Amundson and his co-workers (Amundson & Liu 1961 and particularly Amundson & Zeman 1963, 1965). However, it is of interest to cast it into the mould that has been formed here and to exhibit a solution for a simple case. The simplest model for addition polymerization is that of an initiation reaction, $M_1 \rightarrow P_1$, in which the monomer is activated (with rate constant k_i), followed by a propagation reaction, $M_1+P_n \rightarrow P_{n+1}$, by which the active polymer grows (rate contant k_p) and a termination reaction $M_1+P_n \rightarrow M_{n+1}$, by which dead polymer is formed (rate constant k_t). If the rate constants are independent of length, this leads to the following kinetic equations:

$$\left.\begin{aligned}\frac{\mathrm{d}m_1}{\mathrm{d}t} &= -k_i\,m_1-(k_p+k_t)\,m_1\sum_1^\infty p_n, & \frac{\mathrm{d}p_1}{\mathrm{d}t} &= k_i m_1-(k_p+k_t)\,m_1 p_1,\\ \frac{\mathrm{d}p_n}{\mathrm{d}t} &= k_p m_1(p_{n-1}-p_n)-k_t m_1 p_n \quad (n = 2, 3, \ldots), & \frac{\mathrm{d}m_n}{\mathrm{d}t} &= k_t m_1 p_{n-1} \quad (n = 2, 3, \ldots).\end{aligned}\right\} \tag{156}$$

Let us consider that there are two species M_1 and P_1 and two continuous mixtures $M(x)$, $P(x)$, $x > 1$. Then the third and fourth of the above equations can be approximated by partial differential equations for $p(x,t)$ and $m(x,t)$, namely

$$\left.\begin{aligned}\partial p/\partial t &= -k_p m_1\frac{\partial p}{\partial x}-k_t m_1 p,\\ \partial m/\partial t &= k_t m_1\left(p-\frac{\partial p}{\partial x}\right).\end{aligned}\right\} \tag{157}$$

These partial differential equations have to be solved in the region $x > 1$, $t > 0$ with the boundary conditions $p(1, t) = p_1(t)$, $m(1, t) = m_1(t)$, $p(x, 0) = m(x, 0) = 0$. It is convenient to transform these to linear equations by taking

$$\tau = \int_0^t k_i m_1(t')\,\mathrm{d}t', \quad \varpi(t) = p_1(t) + \int_1^\infty p(x, t)\,\mathrm{d}x \tag{158}$$

and putting
$$\kappa_p = k_p/k_i, \quad \kappa_t = k_t/k_i, \quad \kappa = k_p/k_t. \tag{159}$$

Also we take $p_1(0) = 0$, $m_1(0) = 1$, by normalization of concentrations, then

$$\left.\begin{aligned} \frac{\mathrm{d}m_1}{\mathrm{d}\tau} = -\{1 + (\kappa_p + \kappa_t)\,(\varpi - p_1)\}, \quad \frac{\mathrm{d}p_1}{\mathrm{d}\tau} = 1 - (\kappa_p + \kappa_t)\,p_1, \\ \frac{\partial p}{\partial \tau} + \kappa_p \frac{\partial p}{\partial x} = -\kappa_t\,p, \quad \frac{\partial m}{\partial \tau} = -\kappa_t \frac{\partial p}{\partial x} + \kappa_t\,p. \end{aligned}\right\} \tag{160}$$

By integrating the equation for $p(x, \tau)$ from 1 to ∞

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \int_1^\infty p(x, \tau)\,\mathrm{d}x = \kappa_p p_1(\tau) - \kappa_t \int_1^\infty p(x, \tau)\,\mathrm{d}x$$

and adding the equation for p_1, we have

$$\mathrm{d}\varpi/\mathrm{d}\tau = 1 - \kappa_t \varpi. \tag{161}$$

The equations for p_1 and ϖ can be integrated immediately to give

$$p_1 = \{1 - \mathrm{e}^{-(\kappa_p + \kappa_t)\tau}\}/(\kappa_p + \kappa_t) \tag{162}$$

$$\varpi = \{1 - \mathrm{e}^{-\kappa_t \tau}\}/\kappa_t. \tag{163}$$

The equation for m_1 may be integrated by quadratures and the relation between t and τ is given by

$$k_i t = \int_0^\tau \frac{\mathrm{d}\tau'}{\mathrm{d}m_1(\tau')}.$$

To obtain $p(x, \tau)$ we integrate along the characteristic paths $\tau = \tau_0 + (x - 1)/\kappa_p$ to give

$$\begin{aligned} p(x, \tau) &= \{\mathrm{e}^{-(x-1)/\kappa} - \mathrm{e}^{x-1-(\kappa_p + \kappa_t)\tau}\}/(\kappa_p + \kappa_t) \quad (1 \leqslant x \leqslant 1 + \kappa_p \tau), \\ &= 0 \quad (x > 1 + \kappa_p \tau), \end{aligned} \tag{164}$$

and
$$\begin{aligned} m(x, \tau) &= (\tau/\kappa)\,\mathrm{e}^{-(x-1)/\kappa} \quad (1 < x \leqslant 1 + \kappa_p \tau), \\ &= 0 \quad (x > 1 + \kappa_p \tau). \end{aligned} \tag{165}$$

The method may be adapted to the case when rate constants depend on the polymer length without difficulty. Since this and other cases have been well treated by Amundson & Zeman (1963), we need not pursue them further here.

6. Reactions under nonisothermal conditions

The solutions obtained so far have been for isothermal conditions the only variables being the concentration distributions. We have, however, mentioned the temperature variation that would ensue from adiabatic reaction

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \int_c^d \frac{-\Delta H(w)}{C_p}\, r(w)\,\mathrm{d}w, \tag{75 bis}$$

which would give an equation for temperature to be solved simultaneously with equation (68) or equation (69). However, since $r(w) = \mathrm{d}\xi(w)/\mathrm{d}t$ we have for adiabatic reaction

$$T = T_0 + \int_c^d \frac{-\Delta H(w)}{C_p}\, \xi(w)\, \mathrm{d}w.$$

Substituted in equation (68), or (69), this no longer requires the simultaneous solution of an ordinary differential equation, but certainly introduces an additional element of nonlinearity.

If the temperature is specified as a function of time then the reaction rate will become an explicit function of time and the equations no longer autonomous. A problem of considerable interest is the determination of a temperature programme or history which is in some sense optimal. We shall not attempt this in any great generality, but will obtain a maximum principle for the cracking equations.

(a) *The optimal temperature variation in the cracking reaction*

For the cracking reaction we have the integro-differential equation

$$\dot{c}(x,t) = -\kappa(x)\, c(x,t) + \int_x^b \kappa(x')\, v(x,x')\, c(x',t)\, \mathrm{d}x', \qquad (130\ bis)$$

with

$$c(x,0) = c_0(x)$$

and certain conditions, (133), on the cracking pattern, $v(x,x')$. If we assume that the cracking pattern is independent of temperature T, but that the rate distribution function $\kappa(x)$ is $\kappa(x,T)$, then we may ask for the optimal temperature programme, $\overline{T}(t)$, which maximizes the functional

$$G(\theta;T) = \int_0^b g(x)\, c(x,\theta)\, \mathrm{d}x \qquad (166)$$

of the final state $c(x,\theta)$ at time $t=\theta$.

Let us denote $c(x,t)$ as a functional of $T(t)$ by $F(x,t;T(t))$ and the functional derivative of F with respect to T at $t=s$ by

$$F'_T(x,t;T;s) = h(x,t,s).$$

Then the functional derivative of G is

$$G'_T(\theta;T;s) = \int_0^b g(x)\, h(x,\theta,s)\, \mathrm{d}x. \qquad (167)$$

Now if $f(x,T(t))$ denotes the right hand side of equation (130) and f_T its partial derivative with respect to T, then functional differentiation of this equation with respect to T gives

$$\left.\begin{aligned} \dot{h}(x,t,s) &= -\kappa(x,T(t))\, h(x,t,s) + \int_x^b \kappa(y,T(t))\, v(x,y)\, h(y,t,s)\, \mathrm{d}y + f_T(x,T(t))\, \delta(s-t), \\ h(x,0,s) &= 0. \end{aligned}\right\} \qquad (168)$$

Consider now the adjoint function $\eta(x,t,\theta)$ satisfying

$$\left.\begin{aligned} \dot{\eta} &= \kappa(x,T(t)) \left[\eta(x,t,\theta) - \int_0^x v(y,x)\, \eta(y,t,\theta)\, \mathrm{d}y\right], \\ \eta(x,\theta,\theta) &= g(x). \end{aligned}\right\} \qquad (169)$$

By rearrangement of the integrals we see that

$$\begin{aligned} G'_T(\theta; T; s) &= \int_0^b \eta(x,\theta,\theta)\,h(x,\theta,s)\,\mathrm{d}x \\ &= \int_0^b \mathrm{d}x \int_0^\theta \mathrm{d}t(\dot{\eta}h+\dot{h}\eta) \\ &= \int_0^b \eta(x,s,\theta)\,f_T(x,\,T(s))\,\mathrm{d}x. \end{aligned} \tag{170}$$

Now if $G(\theta;\,T)$ is truly a maximum for $T = \bar{T}$ then

$$G(\theta;\,\bar{T}+\lambda\tau)-G(\theta;\,\bar{T}) \leqslant 0$$

for an arbitrary function τ and sufficiently small λ. If $\bar{T}$ lies entirely within the permitted domain of temperature this implies that $G'_T(\theta;\,\bar{T};s) = 0$ for all s, $0 \leqslant s \leqslant \theta$. But more generally if the permitted domain of temperature is a convex set, so that when $\bar{T}$ and $\bar{T}+\tau$ belong to it so do all the functions $\bar{T}+\lambda\tau$, $0 \leqslant \lambda \leqslant 1$, then, by an application of equation (42),

$$G(\theta;\,\bar{T}+\tau)-G(\theta;\,\bar{T}) = \int_0^\theta \tau(s)\,\mathrm{d}s \int_0^1 G'_T(\theta;\,\bar{T}+\lambda\tau;s)\,\mathrm{d}\lambda \leqslant 0.$$

If now $\tau(s)$ is zero outside the interval $(t-\delta,\,t+\delta)$ and is a constant c in this interval we have

$$c\int_0^1 \mathrm{d}\lambda \int_{t-\delta}^{t+\delta} G'_T(\theta;\,\bar{T}+\lambda\tau;s)\,\mathrm{d}\lambda \leqslant 0.$$

If G'_T is continuous this implies that for sufficiently small δ

$$c\int_0^1 G'_T(\theta;\,\bar{T}+\lambda\tau;t)\,\mathrm{d}\lambda \leqslant 0.$$

But by introducing equation (170) for G' and performing the integration with respect to λ we have

$$\int_0^b \eta(x,t,\theta)\,\{f(x,\,\bar{T}(t)+c)-f(x,\,\bar{T}(t))\}\,\mathrm{d}x \leqslant 0.$$

In other words $\bar{T}$ is such that it maximizes the Hamiltonian

$$\int_0^b \eta(x,t,\theta)\,f(x,\,T(t))\,\mathrm{d}x \tag{171}$$

at every point of the path. The Hamiltonian may be written

$$\int_0^b \eta(x,t,\theta)\left\{-\kappa(x,\,T)\,c(x,t)+\int_x^b \kappa(x',\,T)\,v(x,x')\,c(x',t)\,\mathrm{d}x'\right\}\mathrm{d}x,$$

and the necessary condition that it should be maximized at each point is analogous to the maximum principle of Pontryagin for simultaneous differential equations. The solution of equations (130), (169) and (171) is clearly a matter of considerable difficulty. Probably it is best to try an iterative technique assuming a temperature history and integrating (130) from 0 to θ and (169) from θ to 0 and then readjusting the temperature to maximize the Hamiltonian. Methods of this sort have proved successful with other forms of Pontryagin's principle.

(*b*) *Transient behaviour in a stirred tank*

The equation given above, (74), for the stirred tank must be augmented by a heat balance equation if the non-isothermal behaviour of the system is to be discussed. Thus we have the equations

$$\theta\dot{c}(x,t) = c_f(x) - c(x,t) + \theta\int_c^d \alpha(w,x)\,r(w,c,T)\,\mathrm{d}w, \tag{74 bis}$$

$$\theta\dot{T}(t) = T_f - T(t) + \theta\int_c^d J(w)\,r(w,c,T)\,\mathrm{d}w - Q, \tag{172}$$

where $J(w) = -\Delta H(w)/C_p$, Q is proportional to the rate of removal of heat and θ is the holding time of the reactor. To obtain the complete behaviour of the reactor these equations have to be integrated starting from the initial conditions

$$c(x,0) = c_0(x), \quad T(0) = T_0. \tag{173}$$

The equation for the concentration distribution can be written in terms of extents of reaction. Let

$$c(x,t) = c_f(x) + \int_c^d \alpha(x,w)\,\xi(w,t)\,\mathrm{d}w + \{c_0(x) - c_f(x)\}\,\zeta(t), \tag{174}$$

then the initial condition is $\xi(w,0) = 0$, $\zeta(0) = 1$. If the initial and feed compositions are related by

$$c_0(x) = c_f(x) + \int_c^d \alpha(x,w)\,\xi_0(w)\,\mathrm{d}w, \tag{175}$$

then we can let $\xi(w,0) = \xi_0(w)$ and set $\zeta(t) = 0$, but this is a special circumstance that may not obtain. Substituting (174) into equation (74) we have

$$\int_c^d \alpha(x,w)\,[\theta\dot{\xi}(w,t) + \xi(w,t) - \theta r(w,\xi,\zeta,T)]\,\mathrm{d}w + \{c_0(x) - c_f(x)\}\,[\theta\dot{\zeta} + \zeta] = 0.$$

Now since the reactions are independent there is no nontrivial function $\nu(w)$ such that $\int\alpha(x,w)\,\nu(w)\,\mathrm{d}w = 0$, and if, in addition, no relation such as equation (175) exists then we must have

$$\theta\dot{\xi}(w,t) = -\xi(w,t) + \theta r(w,\xi,\zeta,T) \tag{176}$$

and

$$\theta\dot{\zeta} = -\zeta. \tag{177}$$

The solution to the second of these equations is immediate, namely

$$\zeta(t) = \mathrm{e}^{-t/\theta} \tag{178}$$

and shows that the initial incompatibility of composition is merely 'washed out' of the reactor in the same way as a non-reacting substance. If the feed composition were variable in time, $c_f = c_f(x,t)$, it would probably be better to work with the equation for $c(x,t)$ rather than that for $\xi(w,t)$.

Whilst the solution of equations (172) and (176) calls for numerical work immediately, something may be said about the stability of the reactor. The steady state distribution, $c_s(x)$, and temperature, T_s, are given by

$$c_s(x) = c_f(x) + \int_c^d \alpha(w,x)\,\xi_s(w)\,\mathrm{d}w, \tag{179}$$

$$\xi_s(w) - \theta r(w, \xi_s(w), T_s) = 0, \tag{180}$$

$$T_f - T_s + \theta \int_c^d J(w)\, r(w, \xi_s(w), T_s)\, \mathrm{d}w - Q_s = 0. \tag{181}$$

Let
$$\xi(w,t) = \xi_s(w) + \psi(w,t), \quad T(t) = T_s + \chi(t), \tag{182}$$

then linearizing equations (172) and (176) we have

$$\theta\dot{\psi}(w,t) = -\psi(w,t) + \theta \int_c^d \psi(w',t)\, r'_\xi(w, \xi_s, T_s; w')\, \mathrm{d}w' + \theta\chi(t)\, r_T(w, \xi_s, T_s), \tag{183}$$

$$\theta\dot{\chi}(t) = \theta \int_c^d \mathrm{d}w \int_c^d \mathrm{d}w' J(w)\, r'_\xi(w, \xi_s, T_s; w')\, \psi(w',t) - \chi(t) \left[1 + Q'_s - \theta \int_c^d J(w)\, r_T(w, \xi_s, T_s) \right], \tag{184}$$

where Q'_s is the partial derivative of Q with respect to temperature evaluated at steady state. The condition for the asymptotic stability of the steady state is therefore that the spectrum of eigenvalues of the operators in equations (183) and (184) lies in the left hand plane. A necessary, but insufficient, condition for stability can be obtained from the steady state equations. If (180) is treated as a nonlinear integral equation for $\xi_s(w)$ as a function of T_s and its solution substituted in (181), the latter may be written

$$T_s - T_f + Q_s = \theta \int_c^d J(w)\, r(w, \xi_s(w, T_s), T_s)\, \mathrm{d}w = \int_c^d J(w)\, \xi_s(w, T_s)\, \mathrm{d}w,$$

of which the left hand side represents the heat removal rate and is often linear in T_s, and the right hand side the rate of heat generation. A sufficient condition for instability is that the slope of the heat generation curve should be greater than that of the heat removal curve. Denoting the partial derivative of $\xi_s(w)$ with respect to T_s by $\xi'_s(w, T_s)$ this gives the condition

$$\int_c^d J(w)\, \xi'_s(w, T_s)\, \mathrm{d}w > 1 + Q'_s.$$

But by differentiating equation (180) with respect to T_s we have an equation for $\xi'_s(w, T_s)$, namely

$$\xi'_s(w, T_s) - \theta \int_c^d r'_\xi(w, \xi_s, T_s; w')\, \xi'_s(w', T_s) = \theta r_T(w, \xi_s, T_s).$$

If only discrete reactions are involved, the conditions reduce to those for simultaneous reactions; see, for example, Amundson & Aris (1958). Finally we should notice that since r is primarily a function of c and c of ξ, the formula (40) has to be used in evaluating

$$\begin{aligned} r'_\xi(w, \xi, T; w') &= \int_a^b r'_c(w, c, T; x')\, c'_\xi(x', T; w')\, \mathrm{d}x' \\ &= \int_a^b r'_c(w, c, T; x')\, \alpha(w', x')\, \mathrm{d}x'. \end{aligned} \tag{185}$$

7. Determination of kinetics

We must not close without some reference to the determination of kinetic kernels. As always this needs to be informed by a proper understanding of the chemistry of the situation for the mathematician can only contribute a method and random attempts to fit unsuitable functions are inevitably futile. We shall outline two methods and illustrate one of them.

(*a*) *Application of the functional gradient*

The equation for the cracking reaction is

$$\left.\begin{aligned} \dot{c}(x,t) &= -\kappa(x)\,c(x,t)+\int_x^b \kappa(x')\,v(x,x')\,c(x',t)\,\mathrm{d}x', \\ c(x,0) &= c_0(x). \end{aligned}\right\} \tag{186}$$

Suppose that experimental data is given in the form of an observed function $z(x,t)$, $0 \leqslant t \leqslant \theta$, with $z(x,0) = c_0(x)$. We wish to determine the functions $\kappa(x)$ and $v(x,x')$ to give the best fit in the sense of minimizing the functional

$$F(\kappa,v) = \int_0^\theta \int_0^b [c(x,t)-z(x,t)]^2\,\mathrm{d}x\,\mathrm{d}t. \tag{187}$$

F is functionally dependent on $c(x,t)$ by equation (187) and $c(x,t)$ is dependent on $\kappa(x)$ and $v(x,x')$ through equation (186). For convenience we denote the latter dependence by

$$c(x,t) = G(\kappa,v;x,t) \tag{188}$$

and the functional derivatives by

$$\left.\begin{aligned} G'_\kappa(\kappa,v;x,t;\xi) &= \phi(x,t;\xi), \\ G'_v(\kappa,v;x,t;\xi,\xi') &= \psi(x,t;\xi,\xi'). \end{aligned}\right\} \tag{189}$$

A necessary condition for the minimization of F is the vanishing of the gradients

$$F'_\kappa(\kappa,v;\xi) = 2\int_0^\theta \int_0^b [c(x,t)-z(x,t)]\,\phi(x,t;\xi)\,\mathrm{d}x\,\mathrm{d}t = 0, \tag{190}$$

$$F'_v(\kappa,v;\xi,\xi') = 2\int_0^\theta \int_0^b [c(x,t)-z(x,t)]\,\psi(x,t;\xi,\xi')\,\mathrm{d}x\,\mathrm{d}t = 0. \tag{191}$$

The gradients ϕ and ψ satisfy equations obtained by functionally differentiating equation (186); this gives

$$\begin{aligned} \dot{\phi}(x,t;\xi) = &-\delta(\xi-x)\,c(x,t)-\kappa(x)\,\phi(x,t;\xi)+H(\xi-x)\,v(x,\xi)\,c(\xi,t) \\ &+\int_x^b \kappa(x')\,v(x,x')\,\phi(x',t;\xi)\,\mathrm{d}x', \end{aligned} \tag{192}$$

$$\begin{aligned} \dot{\psi}(x,t;\xi,\xi') = &-\kappa(x)\,\psi(x,t;\xi,\xi')+H(\xi'-x)\,\delta(\xi-x)\,\kappa(\xi')\,c(\xi',t) \\ &+\int_x^b \kappa(x')\,v(x,x')\,\psi(x',t;\xi,\xi')\,\mathrm{d}x', \end{aligned} \tag{193}$$

with
$$\phi(x,0;\xi) = 0, \quad \psi(x,0;\xi,\xi') = 0. \tag{194}$$

The function $H(x)$ is the Heaviside step function (the integral of the delta function), $H(x) = 0$, $x < 0$ and $H(x) = 1$, $x > 0$. The set of equations (186), (190) to (194), must be solved simultaneously for the functions $c(x,t), \kappa(x), v(x,x')$, $\phi(x,t;\xi)$, $\psi(x,t;\xi,\xi')$. This is clearly a formidable task and would require the refinement of an initial guess of κ and v by an iterative technique.

(*b*) *Approximation by degenerate kernels*

Suppose that the kernel in equation (186) can be approximated by a finite sum

$$v(x,x') = \Sigma a_i(x)\,b_i(x'). \tag{195}$$

We consider that no hydrocarbons with less than two carbon atoms are formed and hence that the lower bound of x is 2. Then the condition corresponding to equation (133) is

$$\int_2^{x'} v(x,x')\,\mathrm{d}x = \Sigma b_i(x') \int_2^{x'} a_i(x)\,\mathrm{d}x = 1, \tag{196}$$

which may be satisfied by

$$b_i(x') = c_i\left\{\int_2^{x'} a_i(x)\,\mathrm{d}x\right\}^{-1}, \quad \Sigma c_i = 1.$$

Inspection of the data given below suggests trying $a_i(x) = x^{1-i}$. The data in table 2 is taken from Fabuss *et al.* (1962), who considered the rapid cracking of n-hexadecane. The accuracy probably does not justify more than two terms and we therefore consider a kernel

$$v(x,x') = \frac{\alpha}{x'-2} + \frac{1-\alpha}{x \ln \frac{1}{2}x'} \tag{197}$$

where, in order to ensure that v is positive, $0 \leqslant \alpha \leqslant 1{\cdot}42$. Following the suggestion of Voge & Good (1949) we take $\kappa(x)$ proportional to $(x-1)\,(1{\cdot}57x-3{\cdot}9)$ and absorb the constant of proportionality into the time to give

$$\dot{c}(x,t) = -(x-1)\,(1{\cdot}57x-3{\cdot}9)\,c(x,t) + \alpha\int_x^{16} \frac{(x'-1)\,(1{\cdot}57x'-3{\cdot}9)}{x'-2}\,c(x',t)\,\mathrm{d}x'$$
$$+\frac{1-\alpha}{x}\int_x^{16} \frac{(x'-1)\,(1{\cdot}57x'-3{\cdot}9)}{\ln\frac{1}{2}x'}\,c(x',t)\,\mathrm{d}x'. \tag{198}$$

This equation was solved numerically on an IBM 7094 computer. The interval $2 \leqslant x \leqslant 16$ was divided into 56 parts and Simpson's rule used for the integrals. An Adams–Moulton predictor-corrector formula was used for the integration in the time direction with a step of $\Delta t = 0{\cdot}04$. To approximate the initial condition of pure hexadecane, the initial condition was taken

$$c_0(x) = \begin{cases} 200x - 3000 & (15 \leqslant x \leqslant 16), \\ 0 & (2 \leqslant x \leqslant 15). \end{cases}$$

No stability problems were encountered and some results are shown in figure 5.

To calculate the best value of α, the weighted sum of squares

$$Q = \sum_{\substack{x_i=2\\ x_i\neq 4}}^{13} [c(x_i,t) - \tilde{c}(x_i)]^2 M_i \tag{199}$$

was minimized. Here $\tilde{c}(x_i)$ is the data, for which $x_i = 4$ is lacking, and M_i the molecular weight, $14x_i+2$. The value of t was chosen to give the same total fraction cracked. Q was computed for $\alpha = 0(0{\cdot}2)1{\cdot}4$, but, being found insensitive to α, the minimizing value was not refined beyond $\alpha = 0{\cdot}6$.

The results are shown in table 2 and it is clear that, whilst the trend is reasonable, the fit is far from good; one case is shown in figure 6. The inaccuracy of the data makes it difficult to decide how adequate the linear equations are at high conversions. The kernel with $a_1 = x^{-1}$ and $a_2 = x^{-2}$ was also tried and found inferior, so that a three-term kernel with $a_i = x^{1-i}$ is not likely to be an improvement on (197). To account for the secondary maximum in the neighbourhood of $x_i = 6$ a much more elaborate kernel would seem to be needed.

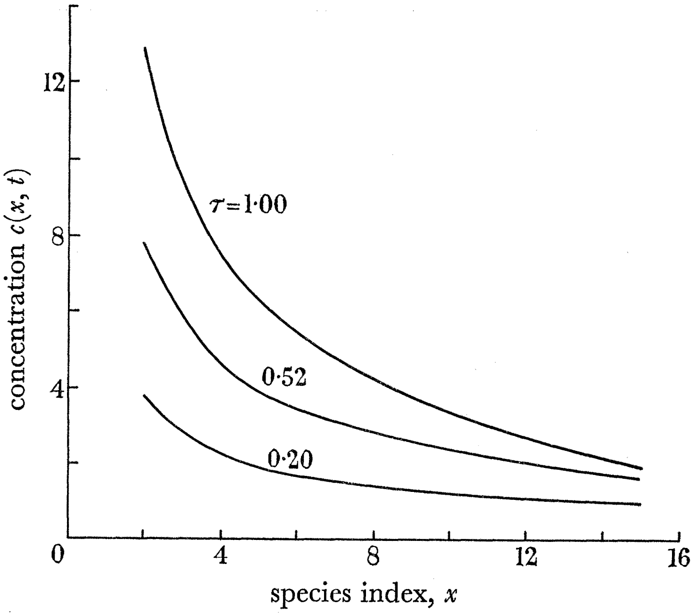

FIGURE 5. Concentration distribution for cracking of hexadecane using the kernel (197).

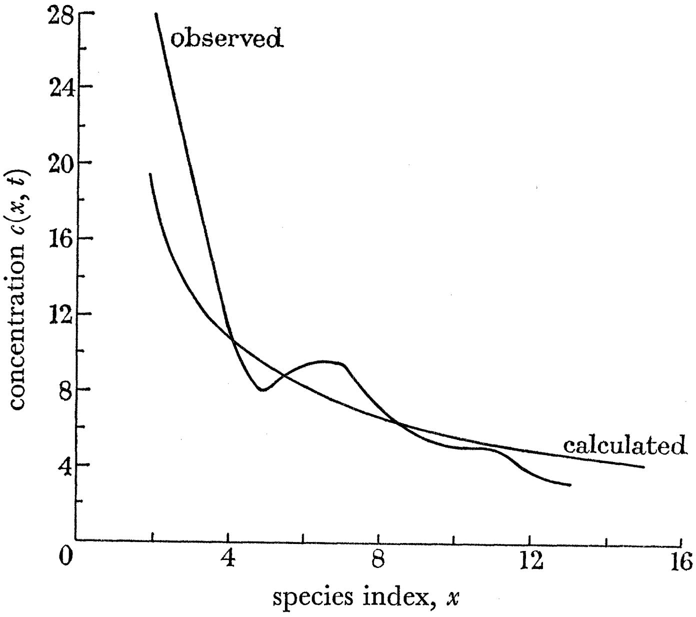

FIGURE 6. Comparison of experimental distribution with that calculated for the second run in table 2.

TABLE 2. EXPERIMENTAL AND CALCULATED RESULTS FOR HEXADECANE CRACKING

temperature (°C) ...	610		593·3		610		610	
fraction cracked ...	0·276		0·296		0·510		0·688	
time, t ...	0·32		0·35		0·71		1·16	
moles per 100 moles of $C_{16}H_{34}$ cracked	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
C_2H_6	14·1	18·64	27·7	18·72	26·7	19·78	56·4	21·05
C_3H_8	10·4	13·47	19·8	13·52	16·9	14·29	29·8	15·20
C_4H_{10}	—	10·84	—	10·88	—	11·45	—	12·12
C_5H_{12}	6·7	9·23	8·1	9·26	6·3	9·68	7·7	10·15
C_6H_{14}	7·4	8·13	9·4	8·15	7·2	8·43	8·0	8·74
C_7H_{16}	8·0	7·32	9·5	7·34	7·5	7·49	5·8	7·63
C_8H_{18}	6·3	6·69	7·1	6·69	5·8	6·73	4·2	6·72
C_9H_{20}	5·0	6·17	5·7	6·16	3·2	6·09	3·1	5·95
$C_{10}H_{22}$	4·6	5·74	5·1	5·72	3·8	5·53	2·4	5·27
$C_{11}H_{24}$	3·6	5·36	5·2	5·34	3·2	5·04	2·2	4·67
$C_{12}H_{26}$	3·3	5·03	3·9	5·00	2·7	4·60	2·0	4·13
$C_{13}H_{28}$	2·6	4·73	3·2	4·69	1·3	4·20	1·6	3·64
$C_{14}H_{30}$	—	4·45	—	4·40	—	3·83	—	3·21
$C_{15}H_{32}$	—	4·20	—	4·15	—	3·49	—	2·81

(c) *Least squares estimation of parameters*

The general problem of fitting the best values of a set of parameters in a kernel of given form may be formulated as follows. Let us consider the general reaction governed by the equation

$$\dot{c}(x,t) = \int_c^d \alpha(w,x)\, r(c(x',t)\,; w\,; \beta_1, \dots, \beta_p)\,\mathrm{d}w, \tag{200}$$

where $\beta_1, \dots, \beta_p$ are a set of adjustable parameters in a reaction rate expression of given form. Let us further suppose that the only quantities that can be measured are certain linear functionals of the concentration distribution at certain instants, i.e. the quantities

$$z_j = \int_a^b h_j(x)\, c(x, t_j)\,\mathrm{d}x \tag{201}$$

can be measured. Suppose these observations are a set of numbers ζ_j $(j = 1, 2, \dots, n > p)$, then we may estimate the parameters $\beta_1, \dots, \beta_p$ by choosing them so that the sum of squares

$$Q = \sum_{j=1}^{n} (z_j - \zeta_j)^2 \tag{202}$$

is minimum. The method to use is clearly a hill-climbing technique in which, starting from some initial guess at the β's, the p estimated values are successively adjusted to reach the minimum of Q. Quite sophisticated techniques are available for this; see, for example, the text and references in Rosenbrock & Storey (1966), whose approach to the estimation problem we follow here. A best set of parameters, $\bar{\beta}_1, \dots, \bar{\beta}_p$, may always be found, but it does not follow that this set has any real meaning. As always the function r needs to be informed by a knowledge of the chemistry of the situation. Moreover there is no guarantee that the set of parameters so found is unique and even if unique the values of the β_i may be very sensitive due to the suppression of information implicit in equation (201). It follows that with every estimate of the β one should associate an estimate of reliability.

We shall assume that the estimates $\bar{\beta}_i$ of the parameters are close enough to the true values β_i^* that wholesale linearization of the equations is permissible. If the parameter values

$$\beta_i = \bar{\beta}_i + \beta_i' \tag{203}$$

lead to a solution
$$c(x,t) = \bar{c}(x,t) + c'(x,t) \tag{204}$$

differing only by $c'(x,t)$ from the solution $\bar{c}(x,t)$ obtained with the values $\bar{\beta}_i$, then linearization gives

$$\dot{c}'(x,t) = \int_c^d \alpha(w,x)\left[\int_a^b \Phi(\bar{c};w;u)\,c'(u,t)\,\mathrm{d}x + \sum_{i=1}^p \Psi_i(\bar{c},w)\,\beta_i'\right]\mathrm{d}w, \tag{205}$$

where $\Phi(\bar{c};w;u)$ is the functional derivative of r with respect to c evaluated on $c = \bar{c}$ and Ψ_i the partial derivative of r with respect to β_i. If we may interchange the order of integration we have

$$\dot{c}'(x,t) = \int_a^b \bar{\Phi}(x,u)\,c'(u,t)\,\mathrm{d}u + \sum_{i=1}^p \bar{\Psi}_i(x)\,\beta_i', \tag{206}$$

where
$$\bar{\Phi}(x,u) = \int_c^d \alpha(w,x)\,\Phi(\bar{c};w;u)\,\mathrm{d}w, \tag{207}$$

$$\bar{\Psi}_i(x) = \int_c^d \alpha(w,x)\,\Psi_i(\bar{c},w)\,\mathrm{d}w, \tag{208}$$

the overbar being a reminder of the functional dependence on $\bar{c}$. The linear system (206) allows us to use the adjoint equation to show the effect of β_i' on the observed quantities z_j.

Let $\gamma_j(x,t)$ satisfy the equation

$$\dot{\gamma}_j(x,t) = -\int_a^b \gamma_j(u,t)\,\bar{\Phi}(u,x)\,\mathrm{d}u \tag{209}$$

$$\gamma_j(x,t_j) = h_j(x). \tag{210}$$

Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_a^b c'(x,t)\,\gamma_j(x,t)\,\mathrm{d}x = \int_a^b \gamma_j(x,t)\,\mathrm{d}x \int_a^b \bar{\Phi}(x,u)\,c'(u,t)\,\mathrm{d}u$$
$$+\sum_{i=1}^p \int_a^b \gamma_j(x,t)\,\bar{\Psi}_i(x)\,\beta_i'\,\mathrm{d}x - \int_a^b c'(x,t)\,\mathrm{d}x \int_a^b \bar{\Phi}(u,x)\,\gamma_j(u,t)\,\mathrm{d}u,$$

and by integrating from $t = 0$ to $t = t_j$ we have

$$z_j' = \int_a^b h_j(x)\,c'(x,t_j)\,\mathrm{d}x = \sum_{i=1}^p \bar{\Gamma}_{ji}\beta_i', \tag{211}$$

where
$$\bar{\Gamma}_{ji} = \int_0^{t_j}\mathrm{d}t \int_a^b \gamma_j(x,t)\,\bar{\Psi}_i(x)\,\mathrm{d}x. \tag{212}$$

The $\bar{\Gamma}_{ji}$ are thus the partial derivatives of z_j with respect to β_i and may be calculated from solutions of the adjoint equations.

Now let us suppose that the observations ζ_j differ from

$$\bar{z}_j = \int_a^b h_j(x)\,\bar{c}(x,t_j)\,\mathrm{d}x$$

by an error η_j so that
$$z_j - \zeta_j = \bar{z}_j + z_j' - \bar{z}_j - \eta_j = z_j' - \eta_j.$$

Then

$$\frac{1}{2}\frac{\partial Q}{\partial \beta_i} = \frac{1}{2}\frac{\partial}{\partial \beta_i}\sum_{j=1}^{n}\{z'_j-\eta_j\}^2 = \sum_{j=1}^{n}\bar{\Gamma}_{ji}\left(\sum_{k=1}^{p}\bar{\Gamma}_{jk}\beta'_k-\eta_j\right)$$

to the first order in small quantities. If the value of Q is minimum, these derivatives will be zero and we have a relation between the small variations in the β and the observational inaccuracy,

$$\sum_{k=1}^{p}\left(\sum_{j=1}^{n}\bar{\Gamma}_{ji}\bar{\Gamma}_{jk}\right)\beta'_k = \sum_{j=1}^{n}\bar{\Gamma}_{ji}\eta_j. \tag{213}$$

If the matrix $\bar{\mathbf{\Gamma}}^*\bar{\mathbf{\Gamma}}$ is nonsingular we may write this in an obvious matrix notation as

$$\boldsymbol{\beta}' = (\bar{\mathbf{\Gamma}}^*\bar{\mathbf{\Gamma}})^{-1}\mathbf{\Gamma}^*\eta. \tag{214}$$

Now if the errors $\boldsymbol{\eta}$ are random Gaussian deviates with zero mean and covariance matrix

$$E(\boldsymbol{\eta}\boldsymbol{\eta}^*) = \mathbf{M}, \tag{215}$$

then within the range of linearity the covariance matrix of the parameter estimates is

$$E(\boldsymbol{\beta}'\boldsymbol{\beta}'^*) = \mathbf{P} = (\bar{\mathbf{\Gamma}}^*\bar{\mathbf{\Gamma}})^{-1}\bar{\mathbf{\Gamma}}^*\mathbf{M}\bar{\mathbf{\Gamma}}(\bar{\mathbf{\Gamma}}^*\bar{\mathbf{\Gamma}})^{-1}. \tag{216}$$

In particular the variance of the estimate of β_i is $\sigma_i^2 = P_{ii}$, and at a 95 % confidence level

$$\bar{\beta}_i - 1\cdot96\sigma_i \leqslant \beta_i \leqslant \bar{\beta}_i + 1\cdot96\sigma_i. \tag{217}$$

In obtaining equation (211) we have assumed that $c(x,0)$ is known perfectly, so that $c'(x,0) = 0$. If there is an error in the initial observation of composition this will transmit a contribution of

$$\int_a^b \gamma_j(x,0)\,c'(x,0)\,\mathrm{d}x$$

to z'_j and this must be allowed for in the subsequent calculation. Since we have allowed for the $h_j(x)$ being different there is no greater generality in introducing a diagonal matrix of weighting factors. The more general case of minimizing

$$Q = \sum_{j=1}^{n}\sum_{k=1}^{n} W_{jk}(z_j-\zeta_j)\,(z_k-\zeta_k),$$

where the weights W_{jk} are elements of a positive definite matrix, can be treated exactly as above.

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