

RATES OF CHEMICAL REACTIONS: THEIR MEASUREMENT AND MATHEMATICAL EXPRESSIONS

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Summary

Following a definition of the typical expressions of chemical kinetics, simple reactions at constant temperature and their rate equations are considered. Then complex reactions (opposing, parallel, or consecutive) and the main types of reaction promoted by catalysis (homogeneous, enzymatic, and heterogeneous) are dealt with. It is explained briefly how the rate of reaction depends on temperature. Methods for measuring the rates are indicated for both slow and fast reactions, considering the use of batch or continuous reactors.

1. Reaction Rate, Kinetic Equation, Catalysis

1.1. Definitions

A chemical system, unless it is already in equilibrium, tends to evolve towards this state and does so at a specific velocity, which is called the *reaction rate*. Reaching equilibrium may take a fraction of a second or several years, but in all cases it takes time. How long it takes depends on the reaction and on the circumstances under which it takes place. The branch of chemistry that studies these facts is called *chemical kinetics*.

The reaction rate (r) is usually defined as the number of moles of a given reactant that react per unit time and per unit volume:

$$r = \frac{\text{moles reacted}}{\text{time} \times \text{volume}}$$

Since some reactions occur on surfaces it is possible, in these cases, to define the reaction rate as the number of moles reacting per unit time and per unit surface. However, the material that forms the reaction surface will be probably enclosed within a volume, so even in these cases the reaction rate r defined above is a reasonable reference.

The variables that affect the reaction rate are essentially the concentration of the reactant(s) and the temperature. In the case of gas-phase reactions, the former variable may usefully be expressed as partial pressure of the reactant(s).

The mathematical expression indicating how r depends on the variables is termed the *rate equation*. It contains at least one kinetic coefficient (k), but may also contain other coefficients. The simplest example is a rate equation of the form:

$$r = k C_A \tag{1}$$

where C_A is the molar concentration of a reactant A.

It is often useful, and sometimes even necessary, to accelerate the reactions using *catalysts*. These are substances that modify one or more reactants, thus facilitating the reaction, but they are released during the process itself and are not present in the reaction product(s). As a result, they do not appear in the overall stoichiometry of the reaction, which is the same as for the uncatalyzed reaction. Catalysts appear in the rate equations, however, because the rate is usually proportional to the quantity of the catalyst.

Some catalysts are present in the same phase as the reactants: usually a liquid phase, such as a solution. This process is called *homogeneous catalysis*, and is characterized by the existence of the variable “catalyst concentration” in addition to the concentration of the reactant(s). The rate equation in these cases contains the catalyst concentration (C_{cat}): usually the rate is proportional to C_{cat} . In the simplest cases the rate equation can have the following form:

$$r = k_{cat} C_A C_{cat} \quad (2)$$

Many acids and bases are soluble in water and are able to give homogeneous catalysis (*acid catalysis*, *base catalysis*) in aqueous solutions of the appropriate reactants: these are protonated by acids or deprotonated by bases, thus assuming a form more favorable to reaction than the original reactant was.

A very important kind of catalysis is provided by enzymes—large molecules with the chemical nature of proteins and able to exist in water as solutions or suspensions—giving rise to *enzymatic catalysis*. In this case a concentration of the catalyst can also be defined, and this appears in the rate equation (see Section 1.4.2).

Sometimes the reaction product itself (or one of the reaction products) is able to catalyze the reaction. This phenomenon is called *autocatalysis* and has its own typical rate equations, where the concentration of the relevant product appears together with the concentration of the reactant(s). In the simplest case, the equation may have the form:

$$r = k C_A C_P \quad (3)$$

where P is the product that acts as autocatalyst.

Finally, some catalysts occur in a different phase from that of the reacting system: a typical example is provided by a solid catalyst in contact with fluid (gaseous or liquid) reactants. In this case *heterogeneous catalysis* takes place. The reaction occurs on the surface of the solid; here there are active centers that are able to bind and modify one or more reactants, thus permitting a fast reaction instead of the slow one that would be given by the original reactants. Since the surface of the catalyst is the actual site of the reaction, in principle the reaction rate could be expressed with reference to this surface. It is usual, however, to refer to the quantity of the catalyst, which of course is proportional to its surface area. If the catalyst quantity present in the unit volume of the reacting system is taken as a density variable, reference can then be made to the system volume as usual.

In general, all heterogeneous reactions are complex phenomena because they involve mass transfer between different phases. Even when mass transfer can be accelerated to a point where it does not affect the rate of the overall process (*intrinsic kinetics*), heterogeneous catalysis is still a complex phenomenon, as its mechanism requires the formation of special bonds between the active centers on the surface and the reactant(s) present in the fluid phase (in other words, *chemisorption*), followed by reaction on the surface and eventually desorption of products from it. As a result, the rate equations typical of heterogeneously catalyzed reactions are less simple than Eqs. (1)–(3). For example:

$$r = \frac{kC_A}{1 + b_A C_A} \quad (4)$$

where b_A can be interpreted as the adsorption equilibrium constant of reactant A on the surface of the catalyst.

If the number of active sites of a catalyst can be determined reliably, it is possible to substitute the concept of reaction rate r , as here defined, with the concept of *turnover frequency* (TOF): that is, the number of molecules that react per unit time and per unit site. This is a more basic measure of catalytic activity, but its use is made difficult by the requirement for precise knowledge of the number of active sites. In the case of metallic catalysts, active sites are often identified with surface metal atoms, and since these can be measured it is possible to convert rates into turnover frequencies.

1.2. Simple Reactions

Single reactions from one or two reactants to one or two products, occurring within a single phase, are often kinetically simple (see *Molecular Dynamics*). In these cases, the rate equation is commonly a power-law equation, which contains the product of powers of reactants concentrations. For instance, for:



the rate equation can have the form:

$$r = kC_A^{\nu_A}C_B^{\nu_B} \quad (6)$$

where exponent ν_A defines the order of reaction with respect to reactant A and ν_B that with respect to reactant B, while the sum $\nu_A + \nu_B$ defines the overall order of reaction. For gas-phase reactions, the rate equation could just as well be expressed in terms of partial pressures, that is in the form:

$$r = kP_A^{\nu_A}P_B^{\nu_B} \quad (7)$$

Molar concentrations shall be used here, however.

A common situation is that where reactions occur in a discontinuous manner: in other words in batches, with evolution of the system as a function of time, starting from an instant taken as “time zero.” While the temperature could change during the reaction this would complicate the treatment, making it preferable to consider an isothermal situation, and correspondingly to perform kinetic measurements at constant temperature, using appropriate thermostatic equipment.

Due to the definition of reaction rate, the function r can be expressed as follows, for a reaction such as Eq. (5):

$$r = -\frac{1}{V} \frac{dn_A}{dt} = -\frac{1}{V} \frac{dn_B}{dt} = \frac{1}{V} \frac{dn_P}{dt} = \frac{1}{V} \frac{dn_Q}{dt} \quad (8)$$

The derivatives must be used, since r is a function of time. Of course, it is possible to consider either the moles of A (or B) reacted, or the moles of P (or Q) produced, because they are stoichiometrically correlated and (particularly in the case of Eq. 5) numerically equal.

A common situation is that of a system at constant volume: liquids and solids behave (at least approximately) as if their volume was unaffected by chemical transformations within them; gas reactions could involve large variations of volume if the reaction causes a change in the number of moles, but are usually carried out in closed vessels where volume is constant by definition. Only in certain specific cases (Section 3.2) is V a variable during a reaction.

If volume is constant, Eqs. (8) can be written more simply using molar concentrations, as in:

$$r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \frac{dC_P}{dt} = \frac{dC_Q}{dt} \quad (9)$$

It should be noticed that reaction Eq. (5) has the simplest possible stoichiometry, since all components have unit coefficients. In more general terms one should consider a reaction such as Eq. (10), with stoichiometric coefficients a , b , p , and q :



In this case, Eq. (9) would be modified only slightly, assuming the form of:

$$r = -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = \frac{1}{p} \frac{dC_P}{dt} = \frac{1}{q} \frac{dC_Q}{dt} \quad (11)$$

When a power-law rate equation is substituted into one of Eqs. (9), a differential equation is obtained. When more than one reactant is present, it is convenient to refer to the one that is in defect and indicated as the limiting reactant: say A . If the reaction is first-order with respect to A , the differential equation has the form:

$$-\frac{dC_A}{dt} = kC_A \quad (12)$$

and can be integrated into

$$\ln C_A = \ln C_A^\circ - kt \quad (13)$$

which is equivalent to

$$C_A = C_A^\circ e^{-kt} \quad (14)$$

According to Eq. (14) the concentration C_A , like the ratio C_A / C_A° , is an exponentially decreasing function of time, as shown in Figure 1.

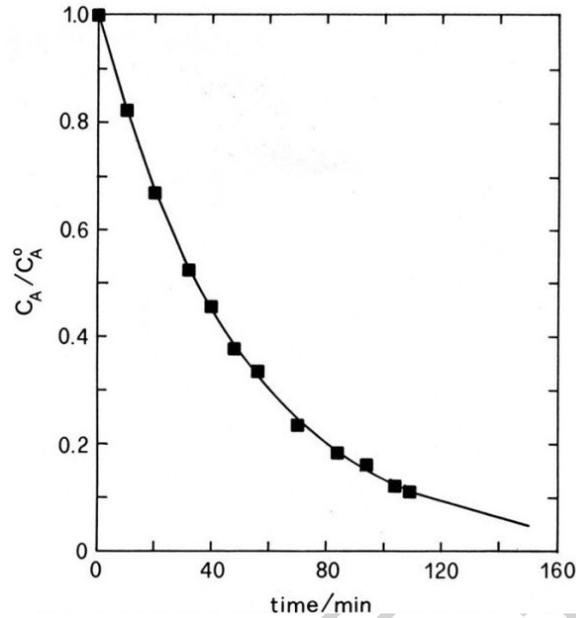


Figure 1. First-order reaction: concentration of the reactant as a function of time for a reaction presenting a kinetic coefficient $k = 0.02 \text{ min}^{-1}$

When a linear representation is preferred, a plot of $\ln C_A$ vs. time, according to Eq. (13), is drawn (Figure 2).

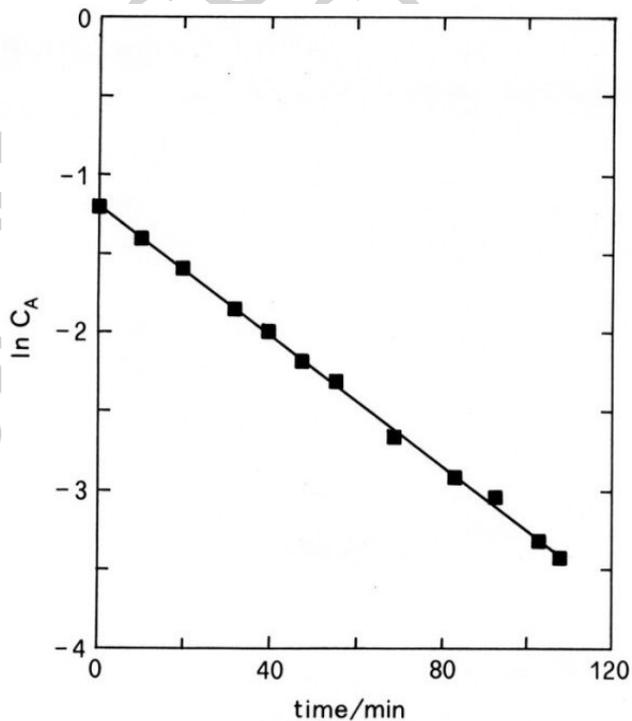


Figure 2. First-order reaction: plot of Eq. (13) for the same experimental points as in Figure 1 ($C_A^\circ = 0.3 \text{ mol l}^{-1}$)

The procedure indicated for a first-order reaction can be applied for any other rate equation, obtaining the corresponding integrated equation which gives the concentration of the limiting reactant as a function of time. A list of the results for the most common cases is given in Table 1, where reaction orders in the range from zero to two are considered.

Form of the rate equation	$C = C(t)$
$r = k$ (15)	$C_A = C_A^\circ - kt$ (16)
$r = k C_A^{0.5}$ (17)	$C_A^{0.5} = (C_A^\circ)^{0.5} - 0.5 kt$ (18)
$r = k C_A$ (1)	$C_A = C_A^\circ e^{-kt}$ (14) or $\ln C_A = \ln C_A^\circ - kt$ (13)
$r = k C_A^{1.5}$ (19)	$1/C_A^{0.5} = 1/(C_A^\circ)^{0.5} + 0.5 kt$ (20)
$r = k C_A^2$ (21)	$1/C_A = 1/C_A^\circ + kt$ (22)
$r = k C_A C_B$ (23)	$C_A/C_B = (C_A^\circ/C_B^\circ) \exp[-(C_B^\circ - C_A^\circ) kt]$ (24) or $\left\{ C_A/[C_A + (C_B^\circ - C_A^\circ)] \right\} = (C_A^\circ/C_B^\circ) \exp[-(C_B^\circ - C_A^\circ) kt]$ (25) or $\ln \left\{ C_A/[C_A + (C_B^\circ - C_A^\circ)] \right\} = \ln (C_A^\circ/C_B^\circ) - (C_B^\circ - C_A^\circ) kt$ (26)
In Eqs (25) and (26), it has been considered that $C_B = C_B^\circ - (C_A^\circ - C_A)$	

Table 1. Integrated rate equations, giving the molar concentration of the limiting reactant A as a function of time, for simple reactions such as $A \rightarrow$ products or $A + B \rightarrow$ products

Among the integrated rate equations shown in Table 1, those corresponding to a reaction order lower than one show that C_A becomes zero within a finite amount of time (see Figure 3 for the case $\nu_A = 0.5$), while those for reaction orders equal to or greater than one state that the variable C_A tend asymptotically to zero, reaching this value only for an infinite value of t (see Figure 1 for the case $\nu_A = 1$). In practice, however, C_A can be considered zero even in these cases after sufficient time has elapsed.

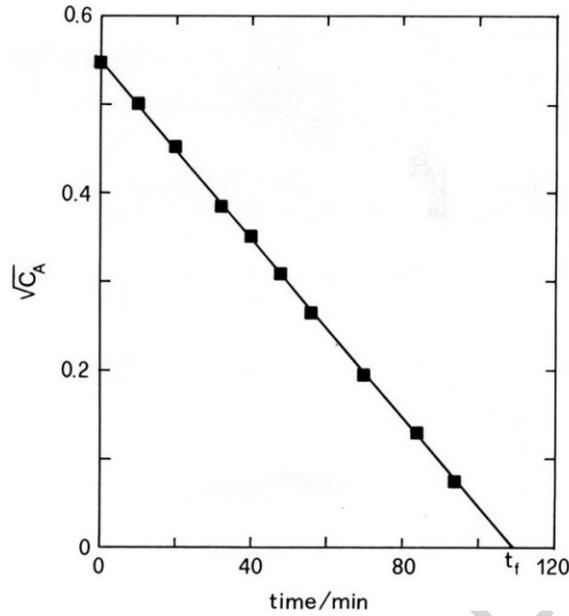


Figure 3. Reaction of order $\nu_A = 0.5$: plot of $C_A^{0.5}$ vs. time for a reaction that presents a kinetic coefficient $k = 0.01 \text{ mol}^{0.5} \text{ l}^{-0.5} \text{ min}^{-1}$ ($C_A^\circ = 0.3 \text{ mol l}^{-1}$); t_f indicates the time for a complete reaction

Several equations in Table 1, besides Eq. (13), allow a linear representation of a simple function of C_A vs. time. For a second-order reaction ($\nu_A + \nu_B = 2$) this is shown in Figure 4.

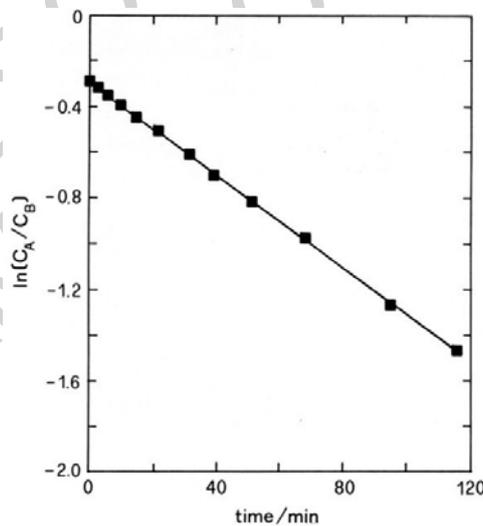


Figure 4. Second-order reaction of the type $\nu_A + \nu_B = 2$: plot of $\ln(C_A/C_B)$ vs time [C_B is obtained as $C_B^\circ - (C_A^\circ - C_A)$]; the reaction has $C_A^\circ = 0.3$ and $C_B^\circ = 0.4 \text{ mol l}^{-1}$; $k = 0.1 \text{ l mol}^{-1} \text{ min}^{-1}$

The evolution of a chemical system may also be followed in terms of fractional conversion of the limiting reactant (x_A), which is defined as the ratio of the moles of A converted into products to the moles of A initially present:

$$x_A = (C_A^\circ - C_A) / C_A^\circ = 1 - (C_A / C_A^\circ) \quad (27)$$

This is obviously

$$C_A = C_A^\circ (1 - x_A) \quad (28)$$

and it is possible to express the integrated rate equations using the variable x_A instead of C_A . The results for the most common cases are given in Table 2.

Form of the rate equation	$x_A = x_A(t)$
$r = k$ (15)	$x_A = kt / C_A^\circ$ (29)
$r = k C_A^{0.5}$ (17)	$(1 - x_A)^{0.5} = 1 - (0.5 kt) / (C_A^\circ)^{0.5}$ (30)
$r = k C_A$ (1)	$x_A = 1 - e^{-kt}$ (31) or $\ln [1 / (1 - x_A)] = kt$ (32)
$r = k C_A^{1.5}$ (19)	$1 / (1 - x_A)^{0.5} = 1 + 0.5 (C_A^\circ)^{0.5} kt$ (33)
$r = k C_A^2$ (21)	$1 / (1 - x_A) = 1 + C_A^\circ kt$ (34)
$r = k C_A C_B$ (23)	$(1 - x_A) / (1 - Mx_A) = \exp[-(C_B^\circ - C_A^\circ) kt]$ (35) or $\ln [(1 - Mx_A) / (1 - x_A)] = (C_B^\circ - C_A^\circ) kt$ (36)
In Eqs (35) and (36) $M = C_A^\circ / C_B^\circ$	

Table 2. Integrated rate equations, giving the fractional conversion of the limiting reactant A as a function of time, for the same cases as in Table 1

A useful kinetic concept is that of *half-time*, or the time required for reaching a fractional conversion of 0.5 (= 1/2): this is usually indicated as $t_{1/2}$. The formulae for the values of $t_{1/2}$ may be derived for various reaction orders by putting $x = 0.5$ into the relevant equations of Table 2. The results are given in Table 3.

Form of the rate equation	$t_{1/2}$
$r = k$ (15)	$t_{1/2} = 0.5 C_A^\circ / k$ (37)

$r = k C_A^{0.5}$ (17)	$t_{1/2} = 0.5858 (C_A^{\circ})^{0.5} / k$ (38)
$r = k C_A$ (1)	$t_{1/2} = 0.6931 / k$ (39)
$r = k C_A^{1.5}$ (19)	$t_{1/2} = 0.8284 / k(C_A^{\circ})^{0.5}$ (40)
$r = k C_A^2$ (21)	$t_{1/2} = 1 / kC_A^{\circ}$ (41)
$r = k C_A C_B$ (23)	$t_{1/2} = [\ln (2-M)] / k(C_B^{\circ}-C_A^{\circ})$ (42)
In Eq. (42) $M = C_A^{\circ}/C_B^{\circ}$	

Table 3. Half-lives for simple reactions (the same cases as in Table 1)

It can be seen that knowledge of $t_{1/2}$, associated with that of the initial concentrations (C_A° and, if required, C_B°), allows easy evaluation of the kinetic coefficient k . For a first-order reaction, Eq. (39) shows that even knowledge of C_A° is unnecessary: in this case, if (for instance) $t_{1/2} = 100$ s, one can immediately calculate $k = 0.6931/100 = 0.006931 \text{ s}^{-1}$. Of course, it is possible to define any fractional lifetime other than $t_{1/2}$; for instance, the value $t_{0.85}$ would indicate the time required to reach a fractional conversion of 0.85.

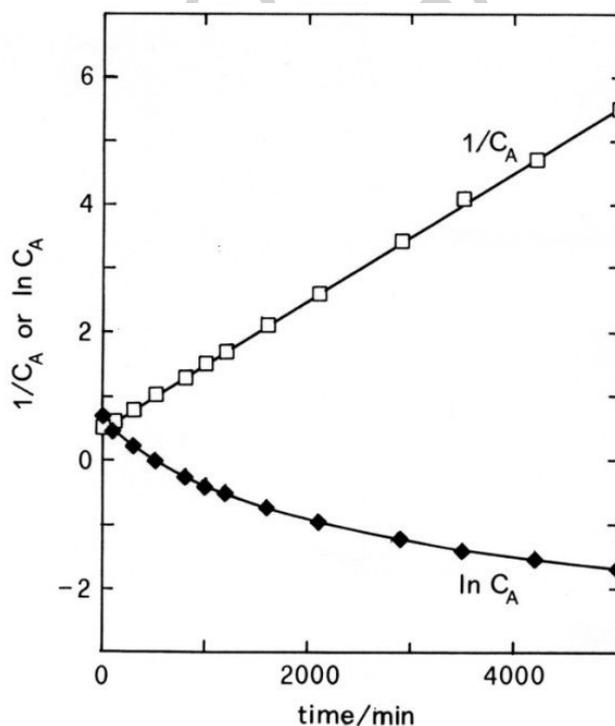


Figure 5. Second-order reaction of the type $\nu_A = 2$, with $C_A^{\circ} = 2.0 \text{ mol l}^{-1}$, $k = 0.001 \text{ l mol}^{-1} \text{ min}^{-1}$; experimental data are represented using both Eqs. (13) and (22), but only the latter gives a linear plot

It is clear from the previous considerations that kinetic coefficients can be determined only when the rate equation is known, in terms of molar concentrations (Table 1), of fractional conversions (Table 2), or in certain cases simply of half-lives (Table 3). Usually one collects experimental data of C_A (or x_A) vs. time and tries to find the appropriate equation for correlating such data. Most commonly, linear forms of the rate equations (for instance, Eqs. (13), (16), (18), (20), (21), and (26) in Table 1) are employed: a successful linear regression will give both the reaction order and the rate coefficient, taking into account (when required) the values of the initial concentrations C_A° and C_B° . It is advisable to support this first determination by performing analogous measurements at different values of the initial concentrations. An example of a search for the correct reaction order is shown in Figure 5, where a second-order reaction is interpreted using rate equations corresponding to $\nu_A = 1$ and $\nu_A = 2$. It is clear that the former interpretation is incorrect because it gives rise to a curved plot.

Since the half-life will have a different dependence on initial concentrations, according to the reaction order, it is also possible to use Eqs (37)–(42) (Table 3) or other similar equations. For example, a zero-order reaction has $t_{1/2}$ proportional to C_A° , a first-order reaction has a $t_{1/2}$ independent of C_A° , and a second-order reaction of rate equation Eq. (21) presents a $t_{1/2}$ inversely proportional to C_A° . The reaction order (and, consequently, the rate coefficient) can be determined by experiments at different values of the initial concentrations.

The reaction rate r is usually a function of time, and this is why it is not measured directly. However, if an evaluation of r is possible, using an approximate procedure (the slope of the experimental curve of C_A vs. time) or by using a continuous reactor operating at steady conditions (see Section 3.2), then experiments at different values of C_A will allow determination of the reaction order using the equation:

$$r = kC_A^{\nu_A} \quad (43)$$

This may be written in logarithmic form as:

$$\ln r = \ln k + \nu_A \ln C_A \quad (44)$$

According to Eq. (44), the reaction order ν_A is the slope of the straight line of $\ln r$ vs. $\ln C_A$.

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Biographical Sketch

Paolo Beltrame was born in Milan, Italy, on December 3, 1930, and graduated in Industrial Chemistry at the University of Milan in 1954. He was assistant professor at the same university from 1955 to 1970 and full Professor at the University of Cagliari, Italy, from 1970 to 1974, and then at the University of Milan, where he worked at the Dipartimento Di Chimica Fisica ed Elettrochimica until retirement in 2006. Thanks to two fellowships, he spent six months at University College London in 1959 and six months at UCLA in 1962. Initially his research was in the field of kinetics and the mechanisms of organic chemistry reactions, but he then expanded into the field of applied chemical kinetics and catalysis. He has contributed about 150 papers to international journals. His teaching activity has been largely connected with chemical kinetics.

He is married, with two daughters and four granddaughters. He enjoys skiing.