

MICROKINETICS VERSUS MACROKINETICS: THE ROLE OF TRANSPORT PHENOMENA IN DETERMINING REACTION RATES

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Keywords: reaction rate, chemical kinetics, transport phenomena, microkinetics, macrokinetics, multiphase reactions, heterogeneous reactions, fluid–fluid homogeneous reactions, effective reaction rate, effective activation energy, effective reaction order, interphase diffusion, intraphase diffusion, interphase effectiveness, intraphase effectiveness, consecutive reactions, parallel reactions, simultaneous reactions, yield, selectivity, characteristic time, Damköhler number, Hatta number, Thiele modulus, Biot number.

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Summary

After a short account of the main concepts related both to chemical reaction rate and transport phenomena, a simple example is used to introduce the concepts of *microkinetics* and *macrokinetics*. Situations where mass transport and reactions proceed in series are then discussed, with particular reference to fluid–solid interphase diffusion and reactions. In this context, the concepts of interphase effectiveness and of the

Damköhler number are introduced. Moreover, the effects of mass-transfer rate on both yield and selectivity are discussed. Situations where diffusion and reactions proceed simultaneously within a phase are then presented for both particles and drops, introducing both the Thiele modulus and the concept of intraphase effectiveness. Simultaneous external and internal mass transfer processes in particles and drops are discussed through the Biot number, as well as in terms of overall effectiveness. Finally, fluid–fluid homogeneous reactions are discussed as examples of simultaneous diffusion processes and reactions inside the body of a reacting phase. In this context, the Hatta number is also introduced.

1. Summary of Basic Concepts

This section summarizes some basic concepts, concerning both reaction rates and transport phenomena, that will be used in the following material. A more detailed discussion of reaction rates is given elsewhere (see *Rate of Chemical Reactions: Their Measurement and Mathematical Expressions*), while fundamentals of transport phenomena can be found in the materials listed in the relevant bibliography.

1.1. Rates of Reaction and Production

When a chemical reaction takes place in a system, it is usually possible to characterize the change of the moles of each compound using a stoichiometric equation. This balanced reaction accounts for the rearrangement of atoms in various molecules, allowing for the numbers of each atomic species to be conserved. Let us consider, for example, a simple reaction like:



Such a reaction can be conveniently written in a different way:



that is, in the general form:

$$0 = \sum_{i=1}^{N_c} \nu_i A_i \quad (3)$$

In this relation the sum is taken over all compounds A_i and defines the stoichiometric coefficient, ν_i for each species. This is the number associated with each compound, which is assumed to be positive for products, negative for reactants, and zero for inert compounds. Given the following vector of species involved in the reaction in Eq. (2):

$$\mathbf{A} = [\text{CO} \quad \text{H}_2 \quad \text{CH}_3\text{OH}]^T \quad (4)$$

the associated stoichiometric vector is

$$\boldsymbol{\nu} = [-1 \quad -2 \quad +1]^T \quad (5)$$

This vector provides a link between the change in the moles of each species due to the chemical reaction, through the general relation:

$$n_i = n_i^0 + \nu_i \lambda \quad (6)$$

This expression, which is known as the *law of definite proportions*, defines the “extent of reaction,” λ , using the same dimensions as n_i . Considering a closed system (that is, one that does not exchange mass with the surroundings: see *Thermodynamic Systems and State Functions*) where the number of moles of each compound can only change as a result of a chemical reaction, n_i is the number of moles of species A_j at a given time, while n_i^0 is the number of its moles initially present in the system. In vector form, Eq. (6) becomes:

$$n = n^0 + \nu \lambda \quad (7)$$

The extent of reaction changes over time, and is a natural reaction co-ordinate. Consequently, we can define the rate of reaction as:

$$r' = \frac{d\lambda}{dt} \quad (8)$$

This equation defines the rate of reaction as an extensive property of the system, since λ itself has been defined as an extensive property. However, a more convenient definition involves an intensive property:

$$r = \frac{1}{X} \frac{d\lambda}{dt} \quad (9)$$

X is a measure of the extension of the system where the reaction proceeds. For instance, for a homogeneous reaction X is the volume of the system, V , leading to the traditional definition of the reaction rate in $\text{mol m}^{-3} \text{s}^{-1}$:

$$r = \frac{1}{V} \frac{d\lambda}{dt} \quad (10)$$

However, for multiphase systems the reactions take place only when reactants can contact one another, such as on the particle surface for fluid–solid reactions. In these situations, the interfacial surface area available for reaction, A , is a better measure of the extent of the reaction system, and the reaction rate assumes the dimensions of $\text{mol m}^{-2} \text{s}^{-1}$. Moreover, the interfacial area is often ill-defined, since it involves both the external particle surface and the internal pore surface. In this case, an alternative measure of the reaction system extension is the weight of the solid, W , leading to a reaction rate in $\text{mol kg}^{-1} \text{s}^{-1}$. Obviously, all these definitions can be interchanged readily using constant parameter values characteristic of the reaction system.

The reaction rate is a property of the reaction, while the production rate, defined as the number of moles of a given species produced per unit time and volume (or surface area, or solid weight), is a property of each species:

$$R_i = \frac{1}{X} \frac{dn_i}{dt} \quad (11)$$

Reaction rate and production rate can be related to each other through the definition of the extent of reaction Eq. (6) as follows:

$$R_i = \frac{1}{X} \frac{dn_i}{dt} = \nu_i \frac{1}{X} \frac{d\lambda}{dt} = \nu_i r \quad (12)$$

This relation provides a mean of computing the reaction rate through measuring the change in the number of moles of a given species over time:

$$r = \frac{1}{\nu_i X} \frac{dn_i}{dt} \quad (13)$$

For a homogeneous system with constant volume $X = V$. Therefore, this relation becomes

$$r = \frac{1}{\nu_i} \frac{dC_i}{dt} \quad (14)$$

showing that the reaction rate is proportional to the time derivative of the molar concentration of each species ($C_i = n_i/V$) through its stoichiometric coefficient. For a reactant with stoichiometric coefficient equal to one, Eq. (14) can be further simplified to give

$$r = -\frac{dC_i}{dt} \quad (15)$$

while for a product with stoichiometric coefficient equal to one:

$$r = \frac{dC_i}{dt} \quad (16)$$

It is worthwhile stressing again that these relations provide the reaction rate when the change in moles or in molar concentration is caused only by chemical reactions. However, when dealing with multiphase systems, at least one of the species involved has to move before reacting towards the interfacial surface where the reactants meet one another; the reaction then proceeds. The rate of this transport phenomenon can influence the overall production rate.

Two limiting situations are often encountered in practice, namely *homogeneous* and *heterogeneous* reactions. In the first situation, reactions proceed only in one phase and

involve several reactants, at least one of which is originally present in a different phase. This means that this species must be transferred into the phase where reactions proceed before conversion of reactants can begin. This is the typical situation in gas–liquid reactions: the gas-phase reactant must diffuse from the gas phase into the liquid one where the reactions proceed before starting the conversion of the reactants. Heterogeneous reactions usually take place at the interface between two phases, most commonly at a catalytic surface (see *Mechanism of Elementary Reactions in Gaseous and Liquid Phase; Mechanism of Heterogeneous Reactions*). In this case, reactants have to be transported to the interface where the reactions proceed.

Reaction rate depends on the state variables of the system, such as temperature and composition. (Apart from in some peculiar cases, a dependence on pressure is usually implicit in the dependence on composition, which is expressed as molar concentration, mol m⁻³; for more details see *Rate of Chemical Reactions: Their Measurement and Mathematical Expressions*.) In the case of an irreversible reaction, it is usually assumed that dependence on temperature and concentration can be factorized as:

$$r = k(T)f(C) \quad (17)$$

When the dependence on concentration is represented by a power law, this is:

$$r = k(T)C_1^\alpha C_2^\beta C_3^\gamma \dots \quad (18)$$

The exponents $\alpha, \beta, \gamma \dots$ are termed the “order of reaction” with respect to each species, while their sum is called “total order of reaction.” The temperature dependence usually assumes an Arrhenius-like form, that is:

$$k(T) = k_o \exp\left(-\frac{E}{R_g T}\right) \quad (19)$$

R_g is the perfect gas constant; E is the “activation energy,” which can be computed from several measurements of reaction rate values at different temperature, as follows:

$$E = -R_g \frac{d \ln(r)}{d(1/T)} = -R_g \frac{d \ln(k)}{d(1/T)} \quad (20)$$

The aforementioned concepts can easily be generalized to a system where NR different reactions proceed through consecutive, simultaneous, and parallel steps. Each reaction can be written in a compact form similar to Eq. (3) as:

$$0 = \sum_{i=1}^{N_c} \nu_{ij} A_i \quad j = 1 \dots NR \quad (21)$$

where for each species A_i a stoichiometric coefficient, ν_{ij} , is defined with respect to each reaction j . Obviously, the stoichiometric vector Eq. (5) becomes a stoichiometric matrix and the link between the change of moles of each species due to the chemical reaction (Eq. (6)) is:

$$n_i = n_i^0 + \sum_{j=1}^{NR} \nu_{ij} \lambda_j \quad (22)$$

In this case, we define for each individual reaction its “extent of reaction,” λ_j . The extent of each reaction changes over time, and allows definition of the rate of each reaction as:

$$r_j = \frac{1}{X} \frac{d\lambda_j}{dt} \quad (23)$$

In this case X is also a measure of the extent of the system where the reactions take place.

Reaction rates and production rate can be related to one another, as in the case of a single reaction, as follows:

$$R_i = \sum_{j=1}^{NR} \nu_{ij} r_j \quad (24)$$

When several reactions proceed in a system, usually not all of them lead to the desired product. To investigate the success of a reaction network in producing the desired compound, it is useful to define the yield (Y) and selectivity (S) as follows:

$$Y = \frac{\text{rate of production of the desired product}}{\text{rate of conversion of the most important reactant}} \quad (25)$$

$$S = \frac{\text{rate of production of the desired product}}{\text{rate of production of the undesired product}} \quad (26)$$

The rate of conversion is equal to minus the rate of production as defined previously. Usually, both yield and selectivity should be maximized.

1.2. Mass-Transfer Rates

Mass transfer between phases is usually associated, in at least one phase, with *diffusion*. This is the movement, under the influence of a driving force (usually a concentration gradient or, more precisely, a gradient of chemical potential), of a species through a mixture. The presence of a concentration gradient tends to move a species in a direction capable of reducing the concentration gradient: that is, to make the concentration uniform. The rate of mass transfer is represented by the molar flux relative to the interface (assumed as a plane at rest): in other words, the number of moles of a species crossing the interface per unit surface area and time, J , in $\text{mol m}^{-2} \text{s}^{-1}$. The molar flux can be related to the concentration gradient through the following relation, which is known as the Fick first law of diffusion:

$$J_i = -D_{ij} \frac{dC_i}{dx} \quad (27)$$

where a mixture of components i and j is considered. D_{ij} is the diffusivity of component i in the mixture, while x is the coordinate perpendicular to the surface across which diffusion is occurring. However, mass transfer through interfaces is usually described using a mass-transfer coefficient, K , in m s^{-1} . The mass-transfer coefficient is defined as the rate of mass transfer per unit surface area and concentration difference, leading to the following relation for the molar flux:

$$J_i = K(C_{S,i} - C_i) \quad (28)$$

where $C_{S,i}$ is the concentration of species i at the interface. Assuming that the concentration gradient is confined in a thin stagnant layer close to the interface, the mass-transfer coefficient can be considered as the molecular diffusivity divided by the effective layer thickness, δ . This is the basic concept of the so-called film model, as illustrated in Figure 1 for the mass transfer of a species from the gas phase to the liquid one.

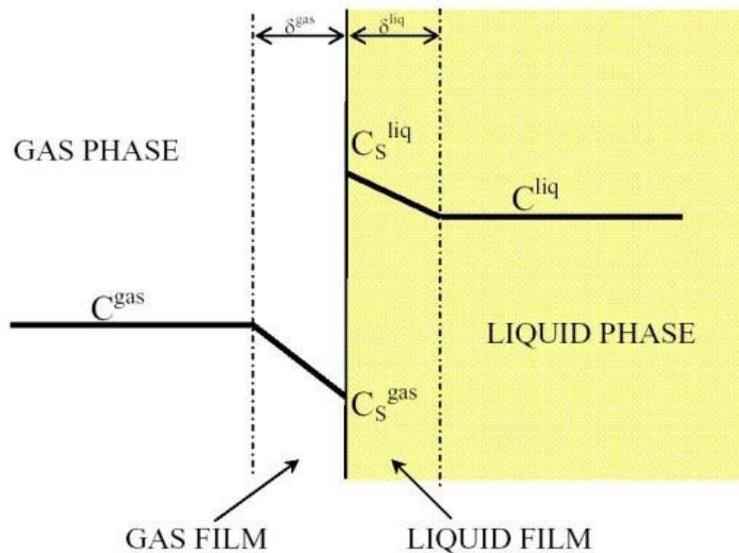


Figure 1. Schematization of the two-film model

With regard to $(C - C_S) / \ln(C / C_S) \ll 1$, the mass-transfer coefficient in the absence of chemical reactions does not depend on the bulk concentration of the diffusing species. Its value depends both on the local fluid dynamics (for instance, in the case of diffusion towards solid particles it depends on bulk fluid velocity and particle size), as well as on the physical parameters of the fluid, and it is usually measured experimentally. Empirical dimensionless relations are readily available in the technical literature, and allow the computation of mass-transfer coefficients in many different situations. These relations are usually expressed in terms of the Sherwood number, $Sh = K dp/D$, or Stanton number, $St = \epsilon K/u$: for example

$$StSc^{2/3} = 0.81 \left(\frac{ud_p}{\nu} \right)^{-0.5} \quad (29)$$

where $Sc = \nu/D$ is the Schmidt number, d_p the particle diameter, ε the volumetric fraction of the fluid phase, u the superficial fluid velocity, and ν the kinematic viscosity. This relation, which is valid for mass transfer to particles surface as far as $5 < u d_p / \nu < 50$, clearly shows K 's weak dependence on temperature.

When dealing with heterogeneous reactions, and when the solid is impervious (that is, non-porous), one needs only to consider diffusion in the fluid phase, and a single film close to the solid surface is involved. Reactants diffuse from the fluid towards the solid surface where the reaction proceeds, while products have to diffuse back from the surface to the fluid bulk.

When dealing with homogeneous reactions, however, two fluid phases are involved, and one must consider a film layer on both sides of the interface. It is clear from its definition that we must use a different mass-transfer coefficient for each side of the interface. Assuming steady-state conditions for the two films, we may deduce a relation between the two mass-transfer coefficients (see also Figure 1):

$$J_i = K^{liq} (C_{S,i}^{liq} - C_i^{liq}) = K^{gas} (C_i^{gas} - C_{S,i}^{gas}) \quad (30)$$

It is assumed that, in almost all practical situations, the species are in equilibrium at the interface. Consequently, the interface concentrations are related each other by a thermodynamic equilibrium relation (see *Equilibrium in Multiphase Reacting Systems*):

$$C_{S,i}^\alpha = H_i C_{S,i}^\beta \quad (31)$$

Here α and β refer to the two phases, and the proportionality constant H_i can depend on species concentrations, temperature, and pressure. When species concentration dependence is disregarded, the relation above is known as the Henry law for supercritical gas-liquid equilibrium, the Raoult law for subcritical vapor-liquid equilibrium, and the Nernst law for liquid-liquid equilibrium. In this case, the interface concentration can be eliminated easily from Eq. (30), giving an expression for the molar flux as a function of the bulk concentrations alone:

$$J_i = \left(\frac{1}{K^{liq}} + \frac{H_i}{K^{gas}} \right)^{-1} (H_i C_i^{gas} - C_i^{liq}) \quad (32)$$

In the gas phase there is a simple proportionality between partial pressure and concentration: consequently, both can be used in the relations above as long as the correct values for the coefficients H and K are used.

1.3. Microkinetics and Macrokinetics

In heterogeneous systems, the two steps (mass transfer and chemical reaction) usually proceed in series. As a consequence, if the rate of diffusion from the bulk of the fluid phases towards the interface (a physical phenomenon) is much higher than the rate of the chemical reaction (a chemical phenomenon) the production rate is entirely controlled by the chemical kinetics, and the reaction rate computed through Eq. (13) provides a measure of the true chemical kinetics: in other words, of the chemical phenomena alone. This rate is usually called *microkinetic*. On the other hand, physical phenomena also influence the production rate when the diffusion velocity is not much higher than the chemical reaction rate, and Eq. (13) does not provide a measure of the rate of the chemical phenomena alone. This rate is usually called *macrokinetic*, and accounts for both chemical and physical phenomena.

In the following, for the sake of simplicity, we will focus only on isothermal conditions. However, it is important to stress that the presence of thermal gradients (due, for instance, to exothermic or endothermic reactions) can change system behavior significantly. The reader interested in these peculiar conditions is referred to materials listed in the Bibliography.

1.4. A Simple Example of Microkinetics versus Macrokinetics: First-Order Heterogeneous Reactions

When the overall transformation requires several steps in series, the rate of all the steps must be the same in steady-state conditions: that is

$$r_{overall} = r_1 = r_2 = \dots = r_N \quad (33)$$

These rates depend on the concentration values at the interface, which are usually unknown. When all the rates are first-order with respect to the species concentration, it is possible to deduce a simple expression for the overall reaction rate; when nonlinear dependencies are involved in the rate expressions, the overall rate becomes much more complicated. As an example, let us consider a simple irreversible reaction among a species A_1 in the fluid phase and a solid compound A_2 :



The two steps in series (diffusion of species A_1 from the bulk of the fluid phase to the solid surface and reaction between A_1^{gas} and A_2^{sol}) can be shown as in Figure 2, where C is the concentration of species A_1 in the bulk of the fluid phase and C_s its concentration on the solid surface.

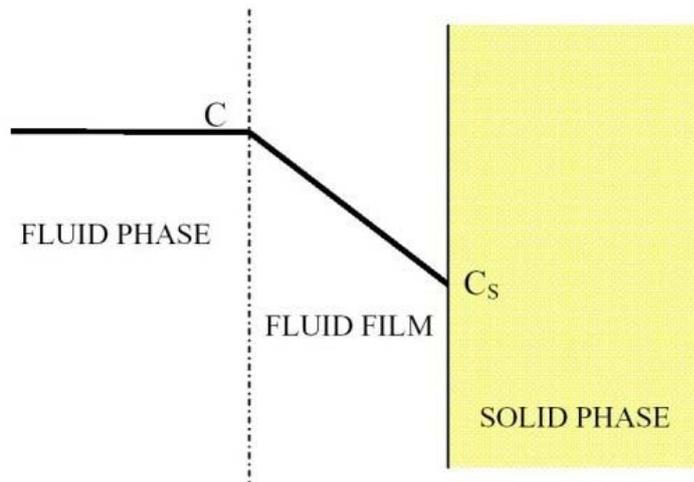


Figure 2. Sketch of a simple gas–solid reaction: *macrokinetic* conditions

The rate of mass transfer of species A_1 from the bulk to the surface can be computed as (units $\text{mol m}^{-2} \text{s}^{-1}$):

$$r_{\text{physical}} = J = K(C - C_s) \quad (35)$$

while that of the first-order chemical reaction, also in this case in $\text{mol m}^{-2} \text{s}^{-1}$, is:

$$r_{\text{chemical}} = r = kC_s \quad (36)$$

At steady state, the two rates must be the same, thus leading to the following relation for the production rate of species A_1 :

$$R = -r_{\text{chemical}} = -r_{\text{physical}} = -kC_s = -K(C - C_s) \quad (37)$$

The surface concentration can then be expressed as:

$$C_s = \frac{K}{K + k} C \quad (38)$$

In addition, the overall rate becomes:

$$R = -kC_s = -\frac{1}{1/K + 1/k} C = -k_{\text{eff}} C \quad (39)$$

Eq. (39) shows that when all the rates in series are linear with respect to a single reactant concentration the expression of the overall rate is also linear, and involves an effective rate constant. In this case, the two resistances ($1/K$ and $1/k$) can simply be

added, and Eq. (39) is a *macrokinetic* rate equation accounting for both physical and chemical rates. However, when the mass-transfer rate is much higher than the chemical reaction rate (that is, $K \gg k$) the previous relation can be simplified to give:

$$R \approx -kC \quad (40)$$

This means that the surface concentration in this case is almost equal to the bulk concentration (see Eq. (38): this is to be expected since mass transfer is much faster than a chemical reaction, thus allowing for prompt replacement of the species A_1 consumed by reaction at the solid surface. This condition, which is a *microkinetic* one, is shown in Figure 3.

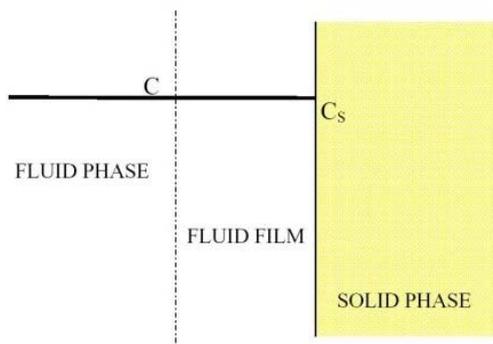


Figure 3. Sketch of a simple gas–solid reaction: *microkinetic* conditions. Moreover, since in this case $k_{eff} \approx k$, the measured temperature dependence of k_{eff} follows the usual Arrhenius law. However, when the chemical reaction rate is much faster than the mass-transfer rate (that is, $k \gg K$), Eq. (39) gives:

$$R \approx -KC = -K(C - 0) \quad (41)$$

which shows that in this case the surface concentration of A_1 is close to zero (see also Eq. (38), since the reactant is suddenly consumed as it reaches the solid surface. It should be noted that in this case $k_{eff} \approx K$ and the measured values of k_{eff} are almost unaffected by temperature.

2. Fluid–Solid Interphase Diffusion and Reactions

This section discusses the situation involving heterogeneous reactions among reactants present in different phases, as in the previous example. In particular, fluid–solid reactions will be considered where at least one reactant has to diffuse from the fluid phase towards the surface of a nonporous solid, which can convert the fluid reactant to different products:



Here the first reactant (A_1) diffuses from the bulk of the fluid phase, and only reacts

with the second reactant (A_2) on the solid surface.

In order to show the influence of mass-transfer limitations on the overall reaction rate, let us consider isothermal steady-state conditions where the physical mass-transfer rate of the reacting compound must equal its conversion rate:

$$Ja = -R(C_s) = r(C_s) \quad (43)$$

In the relation above, we have considered the conversion rate in $\text{mol m}^{-3} \text{s}^{-1}$; consequently, we have multiplied the molar flux, J , by the interfacial surface area per unit volume, a , in $\text{m}^2 \text{m}^{-3}$. Moreover, since this equation refers only to the diffusing species A_1 the subscript 1 has been disregarded.

As indicated in Eq. (43), the production rate depends on the surface concentration of the diffusing species, C_s . If we further assume that a simple power law of order n applies for the *microkinetics* of the surface reaction, this relation can be recast in the following form:

$$Ja = Ka(C - C_s) = -R = r = kC_s^n \quad (44)$$

It is clear that the maximum reaction rate can be obtained in the absence of any mass-transfer limitation. In this case, the surface concentration of the reactant, C_s , approaches its bulk value, C , and the *macrokinetic* rate equation equals the *microkinetic* one. However, the presence of relevant mass-transfer limitations reduces the surface concentration with respect to the bulk one, and a reduction in the surface reaction rate results. In this case, the *macrokinetic* rate equation differs from the *microkinetic* one.

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Biographical Sketch

Renato Rota was born on June 8 1961 and is married with two sons. He took his degree in Chemical Engineering in 1986 at the Politecnico of Milano, Italy. From 1986 to 1988 he worked at the chemical engineering company Snamprogetti S.p.A. He obtained a position for a three-year “*Corso di Perfezionamento*” (i.e., a Ph.D.) at the Scuola Normale Superiore di Pisa, Italy, in 1988. He was a visiting student at the Purdue University, IN, USA, in 1988/1989. From 1990 to 1998 he worked at the Politecnico di Milano as a researcher, doing research and teaching in several courses (e.g., Applied Physical Chemistry; Thermodynamics; Applied Chemical Kinetics; and Fundamentals of Technology). Since 1998 he has been a professor of Chemical Engineering, Thermodynamics, and Safety and Reliability in the Process Industries at the Politecnico di Milano. In 1986 he won the National Award *ENIChem–Piano giovani*, reserved for degree theses. and in 1996 the VIII National Award *Federchimica–per un futuro intelligente*, reserved for chemical researchers and professors. His scientific work is summarized in about 150 publications.