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The local and observed photochemical reaction rates revisited†

Orlando M. Alfano, Horacio A. Irazoqui and Alberto E. Cassano*

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In a broad sense, photochemical reactions proceed through pathways involving several reaction steps. The initiation step is the absorption of energy both by the reactant or sensitizer molecules and in some cases, by the catalyst, leading to intermediate products that ultimately give rise to stable end products. Preferably, the reaction rate expression is derived from a proposed mechanism together with sound simplifying assumptions; otherwise, it may be adopted on an empirical basis. Under a kinetic control regime, the rate expression thus obtained depends on the local rate of photon absorption according to a power law whose exponent very often ranges from one half to unity. The kinetic expression should be valid at every point of the reactor volume. However, due to radiation attenuation in an absorbing and/or scattering medium, the value of the photon absorption rate is always a function of the spatial position. Therefore, the overall photochemical reaction rate will not be uniform throughout the entire reaction zone, and *the distinction between local and volume average photochemical reaction rates becomes mandatory*. Experimental values of reaction rates obtained from concentration measurements performed in well-mixed reaction cells are, necessarily, *average values*. Consequently, for validation purposes, experimental results from these cells must be compared with volume averages of the mechanistically or empirically derived local reaction rate expressions. In this work it is shown that unless the rate is first order with respect to the photon absorption rate or the attenuation in the absorbing and/or scattering medium is kept very low, when the averaging operation is not performed, significant errors may be expected.

1. Introduction

There is a group of reactions whose respective rates are functions of the position in the reaction zone, even under conditions of perfect mixing for stable species. With few exceptions, photochemical reactions belong to this category. This is due to the unavoidable non-uniformity of the radiation field caused by photon absorption or absorption and scattering (the latter taking place in heterogeneous media) occurring along the trajectories of light beams, together with the inherent impossibility of achieving good mixing of highly reactive, short-lived, unstable reaction intermediates. These phenomena contribute to the non-uniformity of the radiation distribution that is distinctive of photoreactors and, as a consequence, of some of the existing concentration fields.

With the exception of diffusion controlled overall rate processes, the rate of photochemical reactions depends on the value of the spectral rate of photon absorption per unit reaction volume. Since IUPAC has not defined this entity, let us call it the *Local Volumetric Rate of Photon Absorption*. For monochromatic radiation, on an amount basis, having units of Einstein s⁻¹ (or mol) m⁻⁴ (or m⁻³ nm⁻¹) and use the nomenclature LVRPA = $e_{\lambda}^a(\mathbf{x}, t)$, indicating that it is a function of position \mathbf{x} and time. Its reaction order, in the most typical of cases, with more or less complex mathematical expressions, results in linear and square root dependences.

Consequently, the unavoidable spatial non-uniformity of the photon concentration and that of most of the short-lived reaction intermediates, results in a non-uniform spatial distribution of the reaction rates of the stable species, even in well-mixed reactors from a strictly hydrodynamic point of view.

The conclusion is that yet, under conditions of good mixing all photochemical reaction rates are functions of position through their dependence on the e_{λ}^a , due to all radiation-absorbing reactants or absorption and scattering-causing heterogeneous dispersed catalysts (from now on the radiation “activated species”) present at every point in the reaction volume.

Let us look at the generalized case of a local reaction rate in a well-mixed reactor cell. Considering the established mixing conditions, in order to simplify notation, let us recall that, with the exception of the concentrations of stable species, temperature and pH, all the other variables are a function of position. Moreover, assuming isothermal operation and a chemical and mechanically stable catalyst, in actual terms the reaction rate and all the other concentration and radiation variables are a function of time.

$$R_i = R_i \left[C_i^{\text{Stable}}, \underbrace{C_j^{\text{Intermediate}}}_{\text{Function of position}}, \underbrace{e_{\lambda}^a}_{\text{Function of position}}, C_{\text{catalyst}}, T, \text{pH}, \text{etc.} \right] \quad (1)$$

The word “intermediate” is assigned to all unstable, short lived species. In this expression, two variables have an irreducible non-uniform distribution in the reaction space: In the majority of the cases, $C_j^{\text{Intermediate}}$ and always e_{λ}^a . The significance of the resulting problem may be better understood by comparison with thermal

INTEC, Universidad Nacional del Litoral and CONICET, (3000), Santa Fe, Argentina. E-mail: acassano@santafe-conicet.gov.ar; Fax: +54 (0)342-4511 087

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or catalytic thermal reactions. In these cases, due to the reaction rate dependence on temperature, kinetic studies are conveniently conducted under isothermal conditions. Hence, a unique temperature is well defined for the whole reactor and, under good stirring conditions, the reaction rate is truly independent of position, even when unstable intermediates take part in the reaction mechanism. The equivalent situation is difficult to obtain in photochemical reactions because the isoactinic condition can be approximated only when the concentration of the radiation attenuation species approaches zero, a condition where the reaction rate could be difficult to measure. Note that the experimentally observed reaction rates, based on the measurement of stable reactants or products concentrations, which are assumed to be uniformly distributed in space due to the prevailing good hydrodynamic mixing conditions, are volume averages of the unavoidably non-uniform reaction rates. Thus, before comparing experimentally observed reaction rates, which by their own nature are volume averages, with derived candidate kinetic expressions that *have, by definition, always local validity*, the latter must also be volume averaged.

Although often overlooked with significant consequences in highly absorbing media, the recognition of the problem is not new. Many years ago, it was raised by Noyes and Leighton¹ and Calvert and Pitts² with clear and simple arguments but, perhaps, the importance of the distinction between *local rates* and *overall, total, global or measured rates* was not stressed enough. The fact is that these differences are not generally taken into account when interpreting kinetic data, that could invalidate many kinetic measurements, particularly in numerous photocatalytic systems where attenuation of light is usually very strong. According to the words of Noyes and Leighton, in going from local rates to the observed rates an *integration step* is needed (which is precisely the previously mentioned averaging integral). The consequences of overlooking the need for this integration are analyzed in this contribution. It is fair to recognize that as one of the few exceptions, consistently, several contributions published by Li Puma and co-workers after 2004, have taken into account this aspect.³⁻⁵

2. Statement of the problem

Let us consider the case of a very simple experimental reactor. For example, a cylinder irradiated through one of its flat ends and operated batch-wise (Fig. 1). Assume that the whole reactor volume is well mixed, its temperature is uniform and, for simplicity, it is irradiated with a parallel beam of monochromatic light. Due to their very short lifetime, the local concentration of unstable reaction intermediates is assumed to be negligible compared to that of stable species, as well as their concentration variations over distances in which concentration differences of stable species begin to be detectable; *i.e.* the conditions for micro steady-state approximation apply.

To avoid unnecessary complications, consider that the reaction in progress follows a kinetic law, which depends on the concentrations of stable reactants and on the LVRPA as follows:

$$R_i = v_i k C_A^\alpha C_B^\beta [e_\lambda^a]^\gamma \quad (2)$$

Kinetic expressions of this form or, very often, more complex ones can be derived from detailed reaction mechanisms or could be proposed on an empirical basis. Even for steady irradiation,

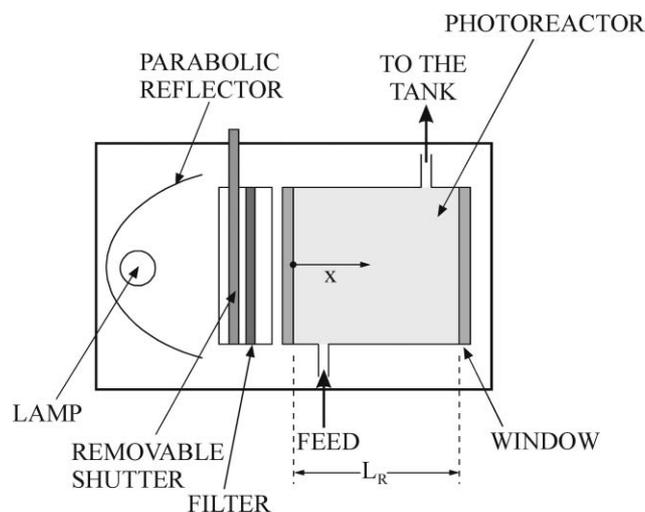


Fig. 1 Schematic description of the simple experimental reactor proposed to carry out this work.

the LVRPA is time-dependent whenever the absorption coefficient of the radiation absorbing species or the background fluid concentration also changes with time. Note that this is a *local*, position dependent kinetic expression, which is valid at any point inside the reactor. Due to its inherent non-uniformity, the LVRPA has a value that is different at each position inside the reactor volume as we move inwards from the irradiation window. As explained before, then, what we are actually measuring is an averaging integral:

$$\langle R_i \rangle_{V_R} = R_i = \frac{1}{V_R} \int_{V_R} \{v_i k C_A^\alpha C_B^\beta [e_\lambda^a]^\gamma\} dV \quad (3)$$

In eqn (3) $\langle \dots \rangle_{V_R}$ stands for the average value over the reactor volume of the property between the angular brackets. It must be *specially noted* that the reaction order with respect to the spectral LVRPA is a *part of the integrand* in eqn (3).

Under conditions of perfect mixing, the concentration of each of the stable species is independent of position, and eqn (3) becomes:

$$R_i = v_i k C_A^\alpha C_B^\beta \frac{1}{V_R} \int_{V_R} [e_\lambda^a]^\gamma dV = v_i k C_A^\alpha C_B^\beta \langle [e_\lambda^a]^\gamma \rangle_{V_R} \quad (4)$$

Once we have a kinetic model, the kinetic study is usually aimed at obtaining the values of $(k, \alpha, \beta, \gamma)$ from $R_i = \langle R_i \rangle_{V_R}$ measurements represented by eqn (3). The set of parameter values must be independent of the size and configuration of the experimental device, including the characteristics of the radiation source [*i.e.*, the lamp size and its output power; the reflector design if used, *etc.* (with the exception of the lamp output wavelength distribution)]. When these conditions are met, then *intrinsic parameter values* are obtained. However, the spectral distribution of the emitted radiation will be embedded in some of the parameters that describe the reaction rates. Hence, the wavelength restriction mentioned above, must be taken into account in any project involving reactor scale up.

In that which follows all mathematical details of the derivations leading to the equations included in the text will be presented in a series of Appendices at the end of this work. However, they are essential to justify the results described here. The fundamental

quantity in radiation transport theory is the local spectral Radiance as defined in Appendix I. The local spectral Radiance $L_{\underline{q},\lambda}$ can be obtained by solving the radiative transfer equation (RTE for short),^{6,7} with the boundary conditions appropriate to each problem.

The local values of e^a_{λ} can be calculated once $L_{\underline{q},\lambda}$ is known. First we must be able to compute the local spectral Fluence Rate for a divergent beam $E_{\lambda,o}$ defined for a surface of reception that could either reflect or scatter photons:

$$E_{\lambda,o} = \int_{4\pi} L_{\underline{q},\lambda} d\Omega \quad (5)$$

For a collimated beam of radiation (unidirectional irradiation), according to Appendix II the following equation applies:

$$L_{\underline{q},\lambda} = E_{\lambda,o} \quad (6)$$

i.e., the local Radiance coincides with the local Fluence rate. Even in one-dimensional reactors, the one-directional characteristics of the radiation propagation are lost when scattering by solid catalytic particles occurs.

In homogeneous systems without internal emission, the local spectral Radiance can be obtained from the application of the three-dimensional form of the well-known Lambert–Beer equation. In heterogeneous systems, the more complex RTE must be solved not only to account for light absorption, but for light scattering, as well.

Regarding kinetic modeling, the important difference between the chemically active radiation absorption species and several other compounds that may attenuate radiation in the reacting media to define the radiation field, is given in Appendix III.

If $E_{\lambda,o}$ is known, the spectral LVRPA due to all chemically active radiation-absorbing species (subscript $R_{\text{act.}}$), at a given point in the reaction volume, is given by:

$$e^a_{\lambda} = \alpha_{\lambda,R_{\text{act.}}} E_{\lambda,o} \quad (7)$$

This is the number of photons of a definite wavelength absorbed at a position x inside the reactor, at time t , by the *chemically active* radiation-absorbing species.

In the case that the reaction mechanism from which the rate expression of eqn (2) was derived, involves a single initiation step and that only one, the $i_{R_{\text{act.}}}$ chemically active energy-absorbing species exists, the following simplification applies:

$$\alpha_{\lambda,i_{R_{\text{act.}}}} = \kappa_{\lambda,i_{R_{\text{act.}}}} C_{i_{R_{\text{act.}}}} \quad (8)$$

$$e^a_{\lambda} = \alpha_{\lambda,i_{R_{\text{act.}}}} E_{\lambda,o} \quad (9)$$

Note that in calculating $E_{\lambda,o}$ the total linear spectral radiation absorption coefficient $\alpha_{\lambda,\text{Tot}}$ [eqn (A-III-2) in Appendix III] must be used because it is necessary to consider all radiation absorbing species affecting the radiation field. From eqn (8) and (9), eqn (2) becomes:

$$R_{i,\lambda} = v_i k C_A^\alpha C_B^\beta \left[\alpha_{\lambda,i_{R_{\text{act.}}}} E_{\lambda,o} \right]^\gamma \quad (10)$$

In the derivation of eqn (10) the existence of a monochromatic radiation field has been assumed. The subscript λ will be kept only for the spectral LVRPA, for the local spectral Radiance and the local spectral Fluence Rate. The rather simple kinetic model leading to eqn (10) was used for the sake of simplicity without

jeopardizing the validity of the conclusions we will arrive to in the following sections. This model allows a development of the subject proposed in the title, employing always analytical solutions which are much more useful for discussing the results. In order to simplify the notation the sub-subscript “Act.” will be dropped in the understanding that species i is the only *chemically active* radiation-absorbing species present.

Let us go back to the case of a batch photoreactor. From the differential mass balance, according to Appendix IV, the following result is obtained:

$$\frac{d}{dt} C_i = \langle R_i \rangle_{V_R} = R_i \quad (11)$$

Considering the simplifications explained in writing eqn (10), the mass balance under perfect mixing conditions results:

$$\frac{dC_i}{dt} = v_i k C_A^\alpha C_B^\beta \left\langle \left[e^a_{\lambda} \right]^\gamma \right\rangle_{V_R} \quad (12)$$

Note that the physical quantity averaged in eqn (12) is the spectral LVRPA corresponding to the radiation-absorbing chemically active species at a given point in the reaction volume, raised to the γ^{th} power.

To get around the problem of calculating the spectral LVRPA based on a model of the radiation field in the reaction cell as required by eqn (12), oftentimes an average value of e^a_{λ} , namely $\langle e^a_{\lambda} \rangle_{V_R} = e^a_{\lambda}$, is experimentally determined. Then, the expression of $R_i(t)$ is approximated with the substitution:

$$\left\langle \left[e^a_{\lambda} \right]^\gamma \right\rangle_{V_R} \approx \left[\langle e^a_{\lambda} \rangle_{V_R} \right]^\gamma = \left[e^a_{\lambda} \right]^\gamma \quad (13)$$

For the simple kinetic law chosen here as a test case, this substitution amounts to the following approximation:

$$R_i = v_i k C_A^\alpha C_B^\beta \frac{1}{V_R} \int_{V_R} \left[e^a_{\lambda} \right]^\gamma dV \approx v_i k C_A^\alpha C_B^\beta \left[\langle e^a_{\lambda} \rangle_{V_R} \right]^\gamma = v_i k C_A^\alpha C_B^\beta \left[e^a_{\lambda} \right]^\gamma \quad (14)$$

Obviously, in those cases when $\gamma = 1$ or e^a_{λ} is not a function of position (the latter condition holds in the case of isoactinic media), eqn (13) and eqn (14) become true equalities.

3. Errors introduced by the approximation

Assuming that the parameter set $\{k, \alpha, \beta, \gamma\}$ has been regressed from experimental data using the correct volume average reaction rate as expressed in eqn (12), or that the set $\{\alpha, \beta, \gamma\}$ has been derived from a proposed mechanism, we may have a first estimate of the error implied in the approximation of eqn (14). As shown in Appendix V:

$$\varepsilon = \frac{\left\{ \left\langle \left[e^a_{\lambda} \right] \right\rangle_{V_R} \right\}^\gamma - \left\langle \left[e^a_{\lambda} \right]^\gamma \right\rangle_{V_R}}{\left\langle \left[e^a_{\lambda} \right]^\gamma \right\rangle_{V_R}} \quad (15)$$

$$\left\langle \left[e^a_{\lambda} \right]^\gamma \right\rangle_{V_R} = \frac{\left[\alpha_{\lambda,i_{R_{\text{act.}}}} \right]^\gamma}{V_R} \int_{V_R} \left[E_{\lambda,o} \right]^\gamma dV \quad (16)$$

$$\left\{ \left[\left[e_{\lambda}^a \right]_{V_R} \right]^{\gamma} \right\} = \left\{ \frac{1}{V_R} \int_{V_R} [e_{\lambda}^a] dV \right\}^{\gamma} = \frac{[\alpha_{\lambda,iR}]^{\gamma}}{V_R^{\gamma}} \left\{ \int_{V_R} E_{\lambda,o} dV \right\}^{\gamma} \quad (17)$$

From eqn (15), it can be concluded that $\varepsilon = 0$ whenever $\gamma = 1$ and/or under isoactinic conditions, *i.e.*, when $E_{\lambda,o}$ is not a function of x , an operating condition very seldom achieved.

It is important to remark that ε , that is a function of time, is a *systematic error* that will not fade out by averaging repeated experimental measurements, as is the case with random, unbiased errors.

It will be interesting to show how the approximation of eqn (14) propagates to the values of the kinetic coefficients $\{k, \alpha, \beta, \gamma\}$. For this we assume that the instantaneous reaction rate $\langle R \rangle_{V_R} = R_i$, as well as the instantaneous concentrations C_A and C_B are known with high accuracy, *i.e.*, that the random errors involved in their experimental determination have been averaged to almost vanishing values by repeating their measurements a large number of times.

The experimentally known reaction rate R_i can be equated to its exact expression and to its approximate one, as long as we use different sets of time and composition independent parameters. It immediately follows:

$$\begin{aligned} \left[\frac{d}{dt} C_i \right]_{\text{exp}} &= v_i k C_A^{\alpha} C_B^{\beta} \frac{1}{V_R} \int_{V_R} [e_{\lambda}^a]^{\gamma} dV \\ &= v_i k' C_A^{\alpha'} C_B^{\beta'} \frac{1}{V_R^{\gamma'}} \left[\int_{V_R} [e_{\lambda}^a] dV \right]^{\gamma'} \end{aligned} \quad (18)$$

Where the “true” parameter set is $\{k, \alpha, \beta, \gamma\}$ and $\{k', \alpha', \beta', \gamma'\}$ is that affected by the systematic error ε . For the sake of simplicity, let us consider the particular, although very desirable case, that the parameter set $\{\alpha, \beta, \gamma\}$ was derived from a reaction pathway or mechanism and sound kinetic considerations. Then, it can be safely assumed that $\{\delta\alpha = 0, \delta\beta = 0, \delta\gamma = 0\}$ and the systematic inaccuracy introduced by the approximation of eqn (13), solely impacts on the value of the kinetic constant k . Then, as shown in Appendix VI:

$$\left(\frac{\delta k}{k} \right) = \frac{\varepsilon_{\lambda}}{[1 + \varepsilon_{\lambda}]} \quad (19)$$

Where we have substituted $k' = k - \delta k$. Eqn (19) relates the systematic error δk on the kinetic constant regressed from the experimental data, to the error ε_{λ} as defined in eqn (15).

4. Detailed analysis

Let us consider the same batch-wise operated reactor as that of Section 2, which is steadily irradiated on its flat, transparent wall of radiation entrance with a collimated beam of monochromatic radiation. As before, we will restrict this part of the analysis to a homogeneous, well mixed, non-scattering reaction medium. Due to the reactor axial symmetry and to the assumed good mixing, the radiation field will depend on the axial coordinate x (the “characteristic coordinate” for this system) and on the time t exclusively.

As pointed out before, in the case of parallel-ray radiation fields like the one considered here, the only contribution to the local spectral Fluence Rate $E_{\lambda,o}$ is that of the unidirectional local spectral Radiance $L_{\lambda,0,\lambda}$ associated to the axial direction of propagation of the bundle of parallel rays. Therefore, eqn (7) takes the particular form:

$$e_{\lambda}^a = \alpha_{\lambda,iR} L_{\lambda}(x,t) \quad (20)$$

Let $L_{\lambda}^0 = L_{\lambda}$ at $x = 0$ be the spectral radiance at the radiation entrance window at time t . At each point x along the reactor length, the spectral LVRPA is:

$$e_{\lambda}^a = \alpha_{\lambda,iR} L_{\lambda}^0 \exp[-\alpha_{\lambda,\text{Tot}} x] \quad (21)$$

where the instantaneous local spectral Radiance has been attenuated according to the Lambert–Beer equation.

Let us define $\vartheta_{\lambda} = \alpha_{\lambda,\text{Tot}} L_{\lambda}^0$ (the instantaneous total optical thickness). Then, as shown in Appendix VII the relative error results:

$$\varepsilon_{\lambda}(t) = \left\{ \frac{[1 - \exp[-\vartheta_{\lambda}(t)]]^{\gamma}}{[\vartheta_{\lambda}(t)]^{\gamma}} \times \frac{[\gamma \vartheta_{\lambda}(t)]}{[1 - \exp[-\gamma \vartheta_{\lambda}(t)]]} - 1 \right\} \quad (22)$$

The instantaneous error ε_{λ} as a function of $\vartheta(t)$ for $\gamma = 0.5$ is shown in Fig. 2(a). It should be stressed once more the fact that ε_{λ} is a *systematic error*.

Let us go back again to the particular case in the previous section where the parameters α, β and γ were derived from a reaction mechanism, and therefore eqn (19) holds. In this case, the relative systematic error on the reaction rate constant k is

$$\left(\frac{\delta k}{k} \right) = \frac{\varepsilon_{\lambda}}{[1 + \varepsilon_{\lambda}]} = \left\{ 1 - \frac{[\vartheta_{\lambda}]^{\gamma}}{[1 - \exp[-\vartheta_{\lambda}]]^{\gamma}} \times \frac{[1 - \exp[-\gamma \vartheta_{\lambda}]]}{[\gamma \vartheta_{\lambda}]} \right\} \quad (23)$$

The relative systematic error $(\delta k/k)$ vs. the optical thickness $\vartheta_{\lambda}(t)$ for $\gamma = 0.5$ is shown in Fig. 2(b).

5. The size of the reactor volume and the concept of fully irradiated photoreactor

It is important to note that the volume of the reaction cell to be used to obtain photochemical parameters with quantitative kinetic purposes can not be arbitrarily chosen. This restriction extends specifically to the reactor *volume employed to calculate the averaged reaction rate* [eqn (3)]. In all the experimental runs, the reactor volume and configuration must be chosen so that the radiation can reach every point in the reaction chamber with a non-vanishing local spectral Radiance; *i.e.*, the reactor must be *always fully irradiated in all and every point of its reaction space in order to calculate meaningful values of the averaging integral*. The importance of these considerations can be illustrated by considering a case where only a fixed region in V_R is reached by non-vanishing values of the spectral Radiance. In this case the average reaction rate calculated from the experimental results can be forced to approach zero by the simple expedient of considering larger reaction volumes to calculate the averaging integral, part of which have vanishing values of the local spectral Radiance, as can be concluded from eqn (3). *i.e.*, the choice of the value of V_R is not arbitrary, because if in some parts of the reaction space the reaction rate is equal to zero because no radiation is arriving to

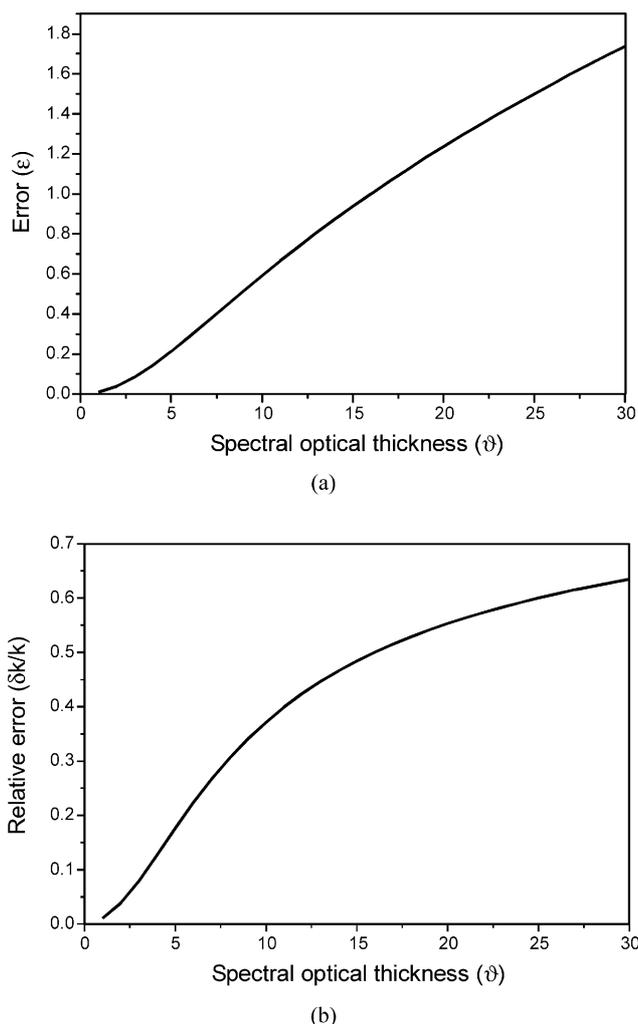


Fig. 2 (a) Instantaneous systematic error resulting from considering the local rate equal to the observed rate, as a function of the optical thickness for $\gamma = 0.5$. (b) Relative instantaneous systematic error in the kinetic constant resulting from considering the local rate equal to the observed rate, as a function of the optical thickness for $\gamma = 0.5$.

those points, and the value of $1/V_R$ does not take into account this situation, different results will be obtained for the averaged reaction rate, depending upon the ratio of the fully irradiated space with respect to the total volume employed in calculating the said average. In a hypothetical limit, it would be possible to calculate very low averaged—almost zero—reaction rates by making this ratio very small. This is a *spurious outcome* that will prevent the experimentalist to draw meaningful conclusions in support of the kinetic model under study. As shown in Appendix VIII the derived necessary condition can be stated as follows. Let us define: $\alpha_{\lambda, \text{Tot}} L_R [(x/L_R)] = (\vartheta_{\lambda, \text{Tot}})(x/L_R) = \vartheta_{\lambda, \text{Tot}} \zeta$. Then, inside the reaction cell $\vartheta_{\lambda, \text{Tot}} \zeta$ must be finite, *i.e.*:

$$0 < \zeta = (x/L_R) < 1 \quad (24)$$

With *this restriction*, we can ensure that a fraction of the radiation that entered the reaction cell will reach the exit window, no matter how small this fraction could be as far as it can be measured. Surprisingly enough, this limitation in the size of the reactor employed for kinetic studies, particularly in highly

absorbing media, has not been explicitly taken into account in the majority of the reported experiments. If this phenomenon occurs, we are in the presence of a *second systematic error*. Consequently, it is important to stress that there is an unavoidable link between the reactor size, its shape, the radiation absorption properties of the employed reactants, catalysts or other radiation absorbing species and the radiant power of the radiation source.

6. The special cases when $\alpha_{\lambda, \text{Tot}} \rightarrow \infty$ and $\alpha_{\lambda, \text{Tot}} \rightarrow 0$

In addition to the observations made in Section 5, the cases when $\alpha_{\lambda, \text{Tot}}(t)$ is very large (*i.e.*, when $\alpha_{\lambda, \text{Tot}} \rightarrow \infty$) and when $\alpha_{\lambda, \text{Tot}} \rightarrow 0$ deserve a particular analysis. This is so because the limit and the integration operations do not commute, and the integrands cease to be “well behaved functions”, as those considered in previous derivations in the different Appendices. $\alpha_{\lambda, \text{Tot}} \rightarrow \infty$ physically means that the absorption of radiation abruptly occurs within a thin transverse layer very close to the radiation entrance point. As shown in Appendix IX:

$$\lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \left\langle [e_{\lambda}^a(x, t)]^{\gamma} \right\rangle_{L_R} = \infty \quad (25)$$

The physical interpretation of this result is that, for very large values of the linear Napierian absorption coefficient $\alpha_{\lambda, \text{Tot}}$, a *finite* amount of energy entering the reaction cell per unit time is absorbed in an *infinitely thin* slab, thus causing the rate of energy absorption *per unit volume* (*i.e.*, the spectral LVRPA) to be infinitely large.

It is straightforward to show that for $\gamma = 1$ and $\gamma < 1$:

$$\lim_{\alpha_{\lambda, \text{Tot}} \rightarrow 0} \left\langle [e_{\lambda}^a(x, t)]^{\gamma} \right\rangle \rightarrow 0 \quad (26)$$

7. Typical illustrative examples

We will consider now two different applications of Advanced Oxidation Technologies: a homogeneous case, where UVC radiation and hydrogen peroxide were used and a heterogeneous system, as is the case in photocatalysis employing titanium dioxide and UV radiation. In both cases the reactions can be applied to the decomposition of water pollutants. In Appendix X the general radiative transfer equation (the RTE) is presented and will be used in the applications described below.

7.1. Hydrogen peroxide reaction

We will consider a reactor such as the one represented by Fig. 1. It is irradiated on its flat, transparent wall with a collimated beam of monochromatic radiation. We will restrict this part of the analysis to a homogeneous, well mixed, non-scattering reaction medium. In particular, let us consider an aqueous solution of hydrogen peroxide in water contaminated with a chemical species transparent to radiation over the useful wavelength range. For this application, where the absorption coefficient of hydrogen peroxide is rather low we will think of a cylindrical reactor having a length equal to 10 cm fulfilling in excess the required condition established by eqn (24). We assume that radiation of 220 nm will be used since at this wavelength light absorption by hydrogen peroxide becomes more significant, with a molar spectral Napierian absorption

coefficient of $\kappa_\lambda|_{\text{HP}} = 2.576 \times 10^5 \text{ cm}^2 \text{ mol}^{-1} \text{ nm}^{-1}$ ($\alpha_\lambda|_{\text{HP}} = \kappa_\lambda|_{\text{HP}} C_{\text{HP}}$). The lamp spectral radiance at the reactor window is $L_\lambda^0 = 2.24 \times 10^{-10} \text{ Einstein cm}^2 \text{ s}^{-1} \text{ sr}^{-1} \text{ nm}^{-1}$, a value reported for this wavelength by Alfano *et al.*⁹ for a 360 W polychromatic mercury arc lamp. The hydrogen peroxide concentration will be changed from (0 to 4) $\times 10^{-6} \text{ mol cm}^{-3}$ and the reactor length is set equal to 10 cm. Therefore the range of $\vartheta_\lambda = \kappa_\lambda C_{\text{HP}} L_{\text{R}}$ in the present example is ($0 < \vartheta_\lambda < 10.304$).

The Radiative Energy Transfer Equation [eqn (A-X-1)] for a homogeneous medium and a collimated beam of radiation can be simplified into the following one-dimensional model:

$$\frac{dL_\lambda}{dx} + \alpha_\lambda L_\lambda = 0 \quad (27)$$

with the boundary condition:

$$L_\lambda(x=0) = L_\lambda^0 \quad (28)$$

The problem posed as eqn (27) and (28) can be easily solved. Then, as before, we will be able to calculate the systematic error ε_λ given by eqn (22).

For degrading organic compounds with UV radiation and hydrogen peroxide, reaction orders with respect to the LVRPA of 0.5 and 1 have been reported by Alfano *et al.*⁹ The instantaneous error $\varepsilon_\lambda(t)$ as a function of $\vartheta(t)$ for $0.5 < \gamma < 1.0$ is shown in Fig. 3(a). We are considering a case where the kinetic orders of the species intervening in the kinetic expression are known beforehand; therefore, in this case the relative systematic error on the reaction rate constant k can be calculated by eqn (23). The instantaneous values of $\left(\frac{\delta k}{k}\right)$ as a function of $\vartheta(t)$ for $0.5 < \gamma < 1.0$ are shown in Fig. 3(b).

It is important to notice that in other different homogeneous systems, larger values of κ_λ and C_i will be very commonly found; this point is certainly clear looking at this example where the radiation absorbing species concentration is very low, since in degradation reactions of pollutants employing HP and UVC radiation the oxidant concentration is always small. Thus, in systems having medium to larger values of the molar spectral Napierian absorption coefficient and, for example, working with pure substances, these errors will be significantly larger to the point of rendering unacceptable results.

7.2. Photocatalytic reaction in a slurry reactor

This is a typical heterogeneous system. In this case we must employ the complete RTE. For simplicity, we will use the same cylindrical reactor as the one described before with a slight modification: the window of radiation entrance is made of ground glass (Fig. 4). With this change, all entering radiation is diffuse and we assume azimuthal symmetry in the radiation field. Applying this assumption, the radiation field can be described with one-dimensional–one-directional models that greatly simplify the solution of the RTE. It has been shown¹⁰ that for the flat plate configuration, when there is absorption and scattering, eqn (A-X-1) takes the following form:

$$\mu \frac{\partial L_\lambda}{\partial x} + (\alpha_\lambda + \xi_\lambda) L_\lambda = \frac{\xi_\lambda}{2} \int_{\mu'=-1}^1 L_{\lambda,\mu'} B(\mu' \rightarrow \mu) d\mu' \quad (29)$$

The boundary conditions are:

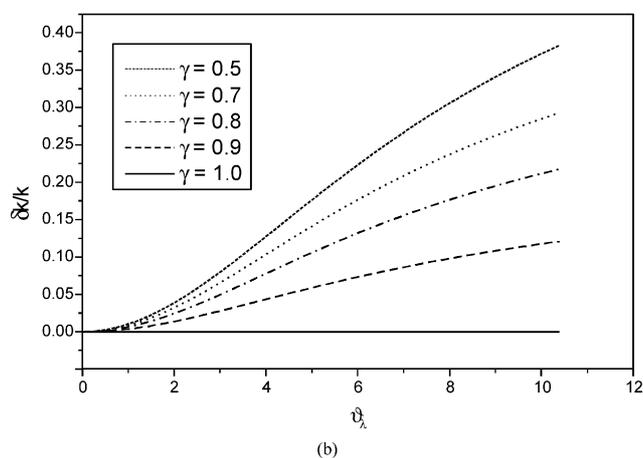
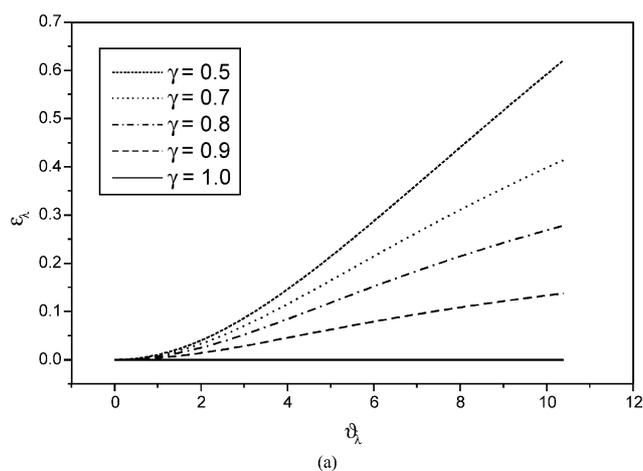


Fig. 3 (a) Instantaneous systematic error resulting from considering the local rate equal to the observed rate, as a function of the optical thickness, for a case using low concentrations of hydrogen peroxide in the homogeneous degradation of a pollutant, assuming that the kinetics can be represented by eqn (2). (b) Relative instantaneous systematic error resulting from considering the local rate equal to the observed rate, as a function of the optical thickness, for a case using low concentrations of hydrogen peroxide in the homogeneous degradation of a pollutant, assuming that the kinetics can be represented by eqn (2). C_{HP} from 0 to $(4 \times 10^{-6}) \text{ mol cm}^{-3}$; $L_{\text{R}} = 10 \text{ cm}$. (To simplify the analysis and obtain simple analytical expressions, no errors have been assigned to α , β , γ ; the approximation impacts only on the kinetic constant k).

$$L_\lambda(x=0, \mu) = L_\lambda^0; \mu > 0 \text{ (Radiation propagating in the forward direction)} \quad (30)$$

$$L_\lambda(x=L_{\text{R}}, \mu) = 0; \mu < 0 \text{ (A non reflecting boundary on the opposite side)} \quad (31)$$

L_λ^0 is the spectral Radiance inside the surface of the reactor window, assumed to be independent of direction because of the diffuse radiation field at the reactor inlet wall. From an experimental point of view, independently of the azimuthal symmetry condition, the employed irradiating device must be such that the arriving Radiance at the reactor window must also be independent of the reactor radius, a condition that is implicit if one assumes that a collimated beam of radiation is employed. For the purpose of this work, the scattering phase function will be assumed to be

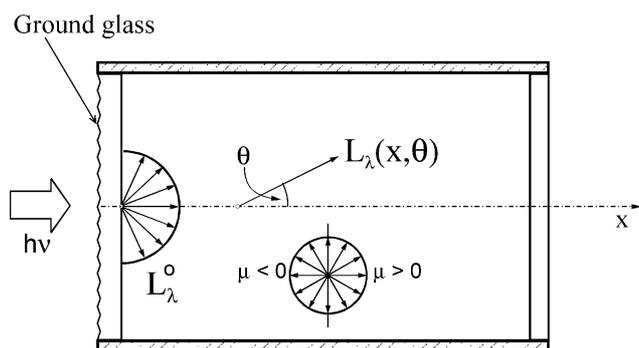


Fig. 4 Schematic representation of the geometry of a simple experimental reactor for slurry photocatalytic reactors, having the window of radiation entrance made of ground glass to simplify the rigorous analysis of the experimental data (the case includes absorption and scattering).

isotropic [$B_\lambda(x) = 1$]. Besides, in eqn (29), $\mu = \cos\theta$, with θ being the direction of propagation of a radiation beam inside the reactor, as is shown in Fig. 4. As for the end boundary condition, a non-reflecting surface has been assumed, considering that at the end of the reactor most (but not all) of the spectral Radiance has already been absorbed or scattered and the contribution to reflection can be neglected.

This problem can be solved numerically using the Discrete Ordinate Method.¹¹ With the values of the spatial and directional distribution of spectral Radiances $L_\lambda(x, \mu)$ obtained from eqn (29) to (31), the spectral Fluence Rate can be calculated according to eqn (5), which for this axially symmetric problem, can be simplified into the form¹²:

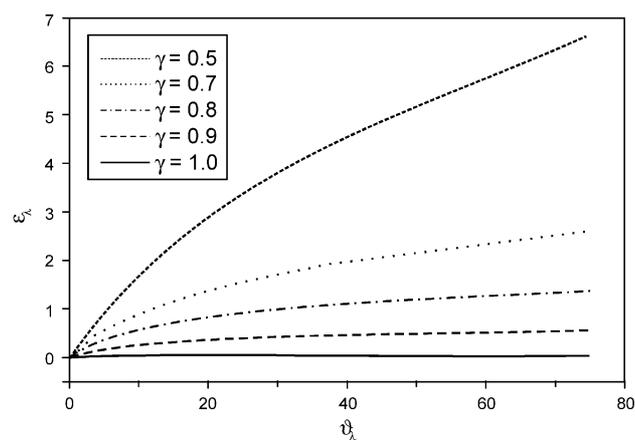
$$E_{\lambda,0} = 2\pi \int_{\mu=-1}^{\mu=1} L_\lambda d\mu \quad (32)$$

From eqn (5), (7) and (29) to (31), the spectral LVRPA for our axially symmetric, one-dimensional problem can be calculated.

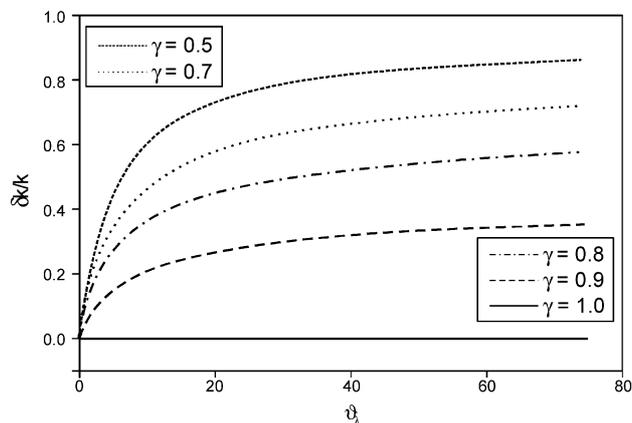
In our case we have considered a suspension of Degussa P 25 catalyst in water, irradiated with 313 nm monochromatic light. For this wavelength the mass spectral Napierian absorption and scattering coefficients are respectively $\kappa^*_\lambda = 18\,700 \text{ cm}^2 \text{ g}^{-1} \text{ nm}^{-1}$ and $\varphi^*_\lambda = 50\,400 \text{ cm}^2 \text{ g}^{-1} \text{ nm}^{-1}$. These values have been reported by Romero *et al.*¹² and are expressed per unit mass concentration of the catalyst. The intensity of the $\lambda = 313 \text{ nm}$ wavelength radiation at the entrance window is set equal to $L^0_\lambda = 6.37 \times 10^{-10} \text{ Einstein cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1} \text{ nm}^{-1}$, a value reported for this wavelength by Alfano *et al.*¹³ for a 360 W polychromatic mercury arc lamp. In order to calculate meaningful values of $e^\alpha_\lambda(x)$ and considering the high light absorption characteristics by titanium dioxide suspensions, a 2 cm long reactor was adopted ($L_R = 2 \text{ cm}$). The catalyst concentration was varied from 0.1 to $2 \times 10^{-3} \text{ g cm}^{-3}$, considering the usual range of typical photocatalyst loadings. The resulting span of $\vartheta_\lambda = \kappa^*_\lambda C_{mc} L_R$ is ($0 < \vartheta_\lambda < 74.8$).

With the obtained results, eqn (22) and (23) can be calculated for this system. Recall that as before the parameter set $\{\alpha, \beta, \gamma\}$ was derived from a reaction mechanism, and therefore all the weight of the systematic error is borne by the kinetic constant k , only.

Fig. 5(a) and (b) illustrates these results in a conclusive visual representation of results. For usual catalytic loadings (between 0.1 and $2 \times 10^{-3} \text{ g cm}^{-3}$) the systematic error is very important. One must add that kinetic law dependencies with respect to the spectral



(a)



(b)

Fig. 5 (a) Instantaneous systematic error resulting from considering the local rate equal to the observed rate, as a function of the optical thickness, for a case of a photocatalytic reaction in a slurry reactor employing titanium dioxide in a heterogeneous degradation of a pollutant, assuming that the kinetics can be represented by eqn (2). (b) Relative instantaneous systematic error resulting from considering the local rate equal to the observed rate, as a function of the optical thickness, for a case of a photocatalytic reaction in a slurry reactor employing titanium dioxide in a heterogeneous degradation of a pollutant, assuming that the kinetics can be represented by eqn (2). C_{mc} from 0 to $2 (\times 10^{-3}) \text{ g cm}^{-3}$, $L_R = 2 \text{ cm}$. (To simplify the analysis no errors have been assigned to α , β , γ ; the approximation impacts only on the kinetic constant k).

LVRPA of order 0.5 and 1 have been reported very often (See for example Alfano *et al.*,¹³ Ollis¹⁴).

From these figures it can be seen that when a high radiation absorption substance is present, the transformation of the local rates into the volume averaged results is unavoidable to abstain from making very large errors in the interpretation of experimental data. Employing titanium dioxide, isoactinic conditions are unreachable and the exponent 1 for the spectral LVRPA may be expected only at very low irradiation rates.^{13,14}

8. Conclusions

It has been shown that in photochemical reactions when the reaction order with respect to the Spectral Local Volumetric Rate of Photon Absorption (the spectral LVRPA) is different from one

or when absorption of radiation by the light absorbing species (a reactant or a catalyst) is not low, the kinetic models of local validity, cannot be extrapolated to the total reaction volume, without performing an averaging procedure.

Under the stated operating conditions, neglecting to perform the averaging integral procedure, will unfailingly lead to very large errors in the interpretation of experimental data.

For quantitative kinetic studies, the reactor size and configuration, as well as the Radiant Power Input to the reactor, can not be independent of the radiation absorption characteristics of the reactants, catalysts (if used) and other radiation attenuating species. A compromise between all these experimental conditions has to be found in order to lower systematic errors as much as possible. Otherwise, the experimentally measured volume averaged reaction rates will lose their usefulness for kinetic parameter regression purposes and from a reactor design perspective be totally useless.

When the value of the linear Napierian absorption coefficient is very large and the requirement that the reactor optical thickness remains finite is imposed, the value of the volume averaged spectral LVRPA approaches a limiting value equal to ∞ .

In laboratory experiments, when the reacting system must be operated with values of the spectral LVRPA that do not approach the isoactinic performance, it will be unavoidable to resort to the mathematical modeling of the radiation field inside the reactor, in order to calculate eqn (3). This conclusion is important, in order to secure the use of very simple laboratory reactor geometries to simplify the modeling task.

These conclusions are important not only for the exact determination of the reaction kinetic constants, but also for the correct evaluation of the reaction order corresponding to the Spectral Local Volumetric Rate of Photon Absorption (spectral LVRPA), *i.e.*, to obtain γ from experimental observations. Similar considerations apply if polychromatic radiation is used.

Notation

a_V = surface area per unit suspension volume, m^{-1}
 B = phase function for scattering distribution, dimensionless
 C_i = molar concentration of the i component, $mol\ m^{-3}$
 $e_{\lambda}^a(\mathbf{x}, t)$ = Local Volumetric Rate of Photon Absorption, Einstein $s^{-1}\ m^{-3}\ nm^{-1}$
 $E_{\lambda,0}$ = spectral Fluence Rate, Einstein $s^{-1}\ m^{-2}\ nm^{-1}$
 HP = hydrogen peroxide
 $j_{\lambda}^e(\mathbf{x}, t)$ = internal radiation emission, Einstein $s^{-1}\ m^{-3}\ sr^{-1}\ nm^{-1}$
 k = kinetic constant, units depend on the reaction orders in eqn (2).
 L = length, m
 $L_{\lambda,\underline{\Omega}}$ = local spectral radiance, Einstein $s^{-1}\ m^{-2}\ sr^{-1}\ nm^{-1}$
 LVRPA = Local Volumetric Rate of Photon Absorption
 N_i = molar flux of the i component, $mol\ m^{-2}\ s^{-1}$
 Q = radiant energy, Einstein
 R = reaction rate, $mol\ m^{-3}\ s^{-1}$
 RTE = Radiative Transfer Equation
 s = spatial coordinate along a given direction of radiation propagation, m
 S = surface area, m^2
 S_g = catalyst specific surface area, $m^2\ g^{-1}$
 t = time, s

T = temperature, K
 V = volume, m^3
 \mathbf{x} = position vector, m
 x, y, z = rectangular Cartesian coordinates, m

Greek letters

α_{λ} = linear spectral Napierian absorption coefficient, $m^{-1}\ nm^{-1}$
 α = reaction order
 β = reaction order
 γ = reaction order with respect to the LVRPA
 ε = systematic error defined in eqn (15)
 κ = molar Napierian absorption coefficient, $m^2\ mol^{-1}$
 κ_{λ}^* = mass spectral Napierian absorption coefficient, $m^2\ kg^{-1}\ nm^{-1}$
 θ = spherical coordinate, rad
 ϕ = spherical coordinate, rad
 $\mu = \cos\theta$
 λ = wavelength, nm
 ν_i = stoichiometric coefficient of component i
 ξ_{λ} = linear spectral Napierian scattering coefficient, $m^{-1}\ nm^{-1}$
 $\zeta = x/L_R$, dimensionless
 ρ = density, $g\ m^{-3}$
 φ_{λ}^* = mass spectral Napierian scattering coefficient, $m^2\ kg^{-1}\ nm^{-1}$
 ϑ = optical thickness, dimensionless
 Ω = solid angle, sr
 \underline{g} = unit vector in the direction of photon propagation

Subscripts

Cat = catalyst property
 cm = catalyst mass property
 Het = heterogeneous property
 HP = hydrogen peroxide property
 i, j = denote different species
 0 = single direction of a collimated beam of radiation
 R_{act} = chemically active radiation-absorbing species
 R = reactor property
 Tot = total property
 λ = denotes wavelength of monochromatic radiation

Superscripts

0 = at the radiation entrance window
 ' = parameter affected by a systematic error

Special symbol

$\langle \rangle$ = denotes an average value in a defined reaction space

Appendix I: Definition of the monochromatic local Radiance^{6,7}

The monochromatic local radiance is defined as

$$L_{Q,\lambda}(\mathbf{x}, t) = \lim_{(\Delta S, \Delta \Omega, \Delta t, \Delta \lambda) \rightarrow 0} \frac{\Delta Q_{\lambda}}{\Delta S \cos \theta \Delta \Omega \Delta t \Delta \lambda} \quad (\text{A-I-1})$$

\mathbf{x} is the spatial coordinate, Q_{λ} is the Radiant energy, ΔS is the elementary surface area, $\underline{\Omega}$ defines the direction of propagation and θ is the angle between the incoming ray and the surface

ΔS . sr is a measure of the solid angle for a divergent beam of radiation. L depends on position and time, and also on the photon wavelength λ and on the direction of propagation of the radiation beam. Regarding its λ dependence, the local spectral Radiance is a photon number distribution function over the entire wavelength range. According to this, the product $L_{\underline{\Omega},\lambda}(\underline{\mathbf{x}},t)d\lambda$ is the probability or fraction of photons with wavelength between λ and $\lambda + d\lambda$, at position $\underline{\mathbf{x}}$ and time t , propagating in the direction $\underline{\Omega}$.

Appendix II: Radiance for a collimated beam of radiation

In a field of collimated, parallel rays there is a single direction of irradiation. Let $\underline{\Omega}_0$ be this direction. In this very particular case, the direction-dependent local spectral Radiance $L_{\underline{\Omega},\lambda}(\underline{\mathbf{x}},t)$, assumes the following special form:

$$L_{\underline{\Omega},\lambda}(\underline{\mathbf{x}},t) = L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t)\delta(\underline{\Omega} - \underline{\Omega}_0) \quad (\text{A-II-1})$$

Where $\delta(\underline{\Omega} - \underline{\Omega}_0)$ is the Dirac delta “function”, which is zero when $\underline{\Omega} \neq \underline{\Omega}_0$ and unbounded when $\underline{\Omega} = \underline{\Omega}_0$. Besides, $\delta(\underline{\Omega} - \underline{\Omega}_0)$ integrates to unity when the integration is performed over the entire range of directions $\underline{\Omega}$, *i.e.*

$$\int_{\Omega} \delta(\underline{\Omega} - \underline{\Omega}_0) d\Omega = 1 \quad (\text{A-II-2})$$

Substituting eqn (A-II-1) and (A-II-2) into eqn (5), gives

$$\begin{aligned} E_{\lambda,0}(\underline{\mathbf{x}},t) &= \int_{\Omega} L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t)\delta(\underline{\Omega} - \underline{\Omega}_0) d\Omega \\ &= L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t) \int_{\Omega} \delta(\underline{\Omega} - \underline{\Omega}_0) d\Omega = L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t) \end{aligned} \quad (\text{A-II-3})$$

Eqn (A-II-3) reflects the fact that, in the case of the highly stylized parallel-ray radiation field, the only contribution to the local spectral Fluence Rate $E_{\lambda,0}(\underline{\mathbf{x}},t)$, is that of the local spectral Radiance $L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t)$, associated to the direction of propagation of the bundle of parallel rays $\underline{\Omega}_0$. Despite of having different physical meanings, in this particular case the value of $E_{\lambda,0}(\underline{\mathbf{x}},t)$ coincides with that of $L_{\underline{\Omega}_0,\lambda}(\underline{\mathbf{x}},t)$.

Appendix III: The “chemically active species” local linear Napierian spectral absorption coefficient and the “total” linear Napierian spectral absorption coefficient

The difference between the chemically active radiation absorption species (either a reactant or a catalyst) and several other compounds that may attenuate radiation in the reacting media to define the existing radiation field must be distinguished. It is important noting that the “chemically active species” local linear Napierian spectral absorption coefficient $\alpha_{\lambda,R_{\text{act}}}(\underline{\mathbf{x}},t)$ links the local radiation field to the concentration field of a *particular group of energy-absorbing species* (whether they are reactants or catalysts). If $\kappa_{\lambda,i}$ is the spectral molar Napierian absorption coefficient of a particular energy-absorbing species “ i ”, the chemically active species spectral local linear Napierian absorption coefficient is given, using the Beer’s approximation, by:

$$\alpha_{\lambda,R_{\text{act}}}(\underline{\mathbf{x}},t) = \sum_i \alpha_{\lambda,i,R_{\text{act}}}(\underline{\mathbf{x}},t) = \sum_i \kappa_{\lambda,i,R_{\text{act}}} C_{i,R_{\text{act}}}(\underline{\mathbf{x}},t) \quad (\text{A-III-1})$$

Where the summation index $i_{R_{\text{act}}}$, covers all the radiation-absorbing reactants or catalysts. Note that for a catalyst, the term spectral “molar” Napierian absorption coefficient must be substituted by a spectral “mass” Napierian absorption coefficient $\kappa_{\lambda,mc}^*$ in units of $\text{m}^2 \text{nm}^{-1} \text{kg}^{-1}$ and the employed concentration will be C_{mc} in terms of kg m^{-3} . Instead, the “total” linear Napierian spectral absorption coefficient $\alpha_{\lambda,\text{Tot}}(\underline{\mathbf{x}},t)$ links the local radiation field to the concentration field of *all energy-absorbing species*, whether they are chemically active or not (the latter, for example, could be an inert, inner filtering species). The expression of $\alpha_{\lambda,\text{Tot}}(\underline{\mathbf{x}},t)$ is:

$$\alpha_{\lambda,\text{Tot}}(\underline{\mathbf{x}},t) = \sum_i \alpha_{\lambda,i}(\underline{\mathbf{x}},t) = \left[\sum_i \kappa_{\lambda,i} C_i(\underline{\mathbf{x}},t) \right] + \kappa_{\lambda,mc}^* C_{mc}(\underline{\mathbf{x}},t) \quad (\text{A-III-2})$$

where the summation index i covers all radiation-absorbing species excluding the catalyst that employs mass concentration properties.

Appendix IV: Mathematical demonstration of the need of the volume averaging integral

The differential molar balance for each of the stable species at every point in the batch reactor is:

$$\overbrace{\frac{\partial C_i(\underline{\mathbf{x}},t)}{\partial t} + \nabla \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t)}^{\text{LOCAL VALUES}} = \underbrace{R_i(\underline{\mathbf{x}},t)}_{\text{Homogeneous reaction rate}} \quad (\text{A-IV-1})$$

Time rate of change All molar fluxes

By volume averaging eqn (A-IV-1), as we already did with eqn (3):

$$\left\langle \frac{\partial C_i(\underline{\mathbf{x}},t)}{\partial t} + \nabla \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t) \right\rangle_{V_R} = \left\langle \frac{\partial C_i(\underline{\mathbf{x}},t)}{\partial t} \right\rangle_{V_R} + \langle \nabla \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t) \rangle_{V_R} = \langle R_i(\underline{\mathbf{x}},t) \rangle_{V_R} \quad (\text{A-IV-2})$$

From the divergence theorem we have:

$$\langle \nabla \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t) \rangle_{V_R} = \frac{1}{V_R} \int_{V_R} \nabla \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t) dV = \frac{1}{V_R} \int_{S_R} \underline{\mathbf{n}} \cdot \underline{\mathbf{N}}_i(\underline{\mathbf{x}},t) dS \quad (\text{A-IV-3})$$

In a batch reactor, there are no inlet or outlet streams and the reactor walls are non-permeable. Therefore the term in eqn (A-IV-3) is equal to zero. Eqn (A-IV-2) becomes:

$$\left\langle \frac{\partial C_i(\underline{\mathbf{x}},t)}{\partial t} \right\rangle_{V_R} = \frac{d}{dt} \langle C_i(\underline{\mathbf{x}},t) \rangle_{V_R} = \langle R_i(\underline{\mathbf{x}},t) \rangle_{V_R} = R_i(t) \quad (\text{A-IV-4})$$

Because of the assumed perfect mixing of stable species, we have:

$$C_i(\underline{\mathbf{x}},t) = C_i(t) \quad (\text{A-IV-5})$$

and eqn (A-IV-4) assumes the following form:

$$\frac{d}{dt} C_i(t) = \underbrace{\langle R_i(\underline{\mathbf{x}},t) \rangle_{V_R}}_{\text{ALL EXPERIMENTAL MEASUREMENTS}} = R_i(t) \quad (\text{A-IV-6})$$

Note that for a superficial reaction rate $[R_{\text{Het},j} \text{ (mol cm}^{-2} \text{ s}^{-1})]$ which, in real terms, is a boundary condition, the following transformation will be needed:

$$\frac{d}{dt}C_j(t) = \langle R_{\text{Het},j}(\underline{\mathbf{x}},t) \times a_V \rangle_{V_R} = R_j(t), \text{ with } a_V = S_{\text{g,Cat.}} \rho_{\text{Cat.}} \quad (\text{A-IV-7})$$

Appendix V: Error produced by ignoring the spatial distribution of the LVRPA

A first estimation of the error implied by the approximation can be estimated as follows:

$$\begin{aligned} \varepsilon(t) &= \frac{\left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]_{V_R}^{\gamma} \right\rangle - \left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} \right\rangle_{V_R}}{\left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} \right\rangle_{V_R}} \\ &= \frac{\left\{ \int_{V_R} \int_{4\pi} L_{\Omega,\lambda}(\underline{\mathbf{x}},t) d\Omega dV \right\}^{\gamma} - V_R^{\gamma-1} \int_{V_R} \int_{4\pi} L_{\Omega,\lambda}(\underline{\mathbf{x}},t) d\Omega dV}{V_R^{\gamma-1} \int_{V_R} \int_{4\pi} L_{\Omega,\lambda}(\underline{\mathbf{x}},t) d\Omega dV} \quad (\text{A-V-1}) \end{aligned}$$

Where, under perfect mixing conditions of stable species: $\alpha_{\lambda,\text{Tot}}(\underline{\mathbf{x}},t) = \alpha_{\lambda,\text{Tot}}(t)$ and $\alpha_{\lambda,\text{R}}(\underline{\mathbf{x}},t) = \alpha_{\lambda,\text{R}}(t)$. Then,

$$\left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} \right\rangle_{V_R} = \frac{[\alpha_{\lambda,\text{R}}(t)]^{\gamma}}{V_R} \int_{V_R} \int_{4\pi} L_{\Omega,\lambda}(\underline{\mathbf{x}},t) d\Omega dV \quad (\text{A-V-2})$$

Conversely, in the second case we get:

$$\begin{aligned} \left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]_{V_R}^{\gamma} \right\rangle &= \left\{ \frac{1}{V_R} \int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right\}^{\gamma} \\ &= \frac{[\alpha_{\lambda,\text{R}}(t)]^{\gamma}}{V_R^{\gamma}} \left\{ \int_{V_R} \int_{4\pi} L_{\Omega,\lambda}(\underline{\mathbf{x}},t) d\Omega dV \right\}^{\gamma} \quad (\text{A-V-3}) \end{aligned}$$

Resorting to the Schwartz' inequality⁸ it is also possible to demonstrate that when $0 < \gamma < 1$ the left hand side of eqn (13) is always smaller than the right hand side.

Appendix VI: Relative error when the spatial distribution of the LVRPA is neglected

Rearranging eqn (18), we get:

$$\frac{k}{k'} C_A^{\alpha-\alpha'}(t) C_B^{\beta-\beta'}(t) = \frac{1}{V_R^{\gamma-1}} \frac{\left[\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right]^{\gamma}}{\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} dV} \quad (\text{A-VI-1})$$

If we call $\delta\gamma = \gamma - \gamma'$, $\delta\alpha = \alpha - \alpha'$ and $\delta\beta = \beta - \beta'$ the systematic errors introduced in the kinetic parameters by eqn (18), substitution in eqn (A-VI-1) gives:

$$\frac{k}{k'} C_A^{\delta\alpha}(t) C_B^{\delta\beta}(t) = \frac{1}{V_R^{\gamma-1-\delta\gamma}} \frac{\left[\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right]^{\gamma-\delta\gamma}}{\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} dV} \quad (\text{A-VI-2})$$

By rearranging eqn (A-VI-2), the following equivalent expression is obtained:

$$\frac{k}{k'} C_A^{\delta\alpha}(t) C_B^{\delta\beta}(t) \frac{1}{V_R^{\delta\gamma}} \left[\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right]^{\delta\gamma} = \frac{V_R}{V_R^{\gamma}} \frac{\left[\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right]^{\gamma}}{\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} dV} \quad (\text{A-VI-3})$$

Where, from eqn (A-V-1), we have the expression:

$$\frac{V_R}{V_R^{\gamma}} \frac{\left[\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right] dV \right]^{\gamma}}{\int_{V_R} \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]^{\gamma} dV} = 1 + \varepsilon(t) \quad (\text{A-VI-4})$$

Which involves only "true" parameters. Upon substitution in eqn (A-VI-3), we get:

$$\frac{k}{k'} C_A^{\delta\alpha}(t) C_B^{\delta\beta}(t) \left[e_{\lambda}^a(t) \right]^{\delta\gamma} = [1 + \varepsilon_{\lambda}(t)] \quad (\text{A-VI-5})$$

Now, for the sake of simplicity, let us consider the particular, although very desirable case, that the parameter set $\{\alpha, \beta, \gamma\}$ was derived from a reaction pathway or mechanism and sound kinetic considerations. Then, it can be safely assumed that $\{\delta\alpha = 0, \delta\beta = 0, \delta\gamma = 0\}$ and the systematic inaccuracy introduced by the approximation of eqn (13), solely impacts on the value of the kinetic constant k. Then:

$$\frac{k}{k'} = [1 + \varepsilon_{\lambda}(t)] \quad (\text{A-VI-6})$$

Appendix VII: Relative error as a function of the characteristic radiation path

Recalling that here $E_{\lambda,o}(\underline{\mathbf{x}},t) = L_{\Omega,\lambda}(\underline{\mathbf{x}},t)$, eqn (21) into eqn (16) and (17) gives:

$$\begin{aligned} \left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]_{L_R}^{\gamma} \right\rangle &= \frac{[\alpha_{\lambda,\text{R}}(t) L_{\lambda}^0(t)]^{\gamma}}{L_R} \int_0^{L_R} \exp[-\gamma\alpha_{\lambda,\text{Tot}}(t)x] dx \\ &= \frac{[\alpha_{\lambda,\text{R}}(t)]^{\gamma} [L_{\lambda}^0(t)]^{\gamma}}{\gamma\alpha_{\lambda,\text{Tot}}(t) L_R} \left\{ 1 - \exp[-\gamma\beta_{\lambda,\text{Tot}}(t) L_R] \right\} \quad (\text{A-VII-1}) \end{aligned}$$

and

$$\begin{aligned} \left\{ \left\langle \left[e_{\lambda}^a(\underline{\mathbf{x}},t) \right]_{L_R}^{\gamma} \right\rangle \right\} &= \frac{[\alpha_{\lambda,\text{R}}(t)]^{\gamma} [L_{\lambda}^0(t)]^{\gamma}}{L_R^{\gamma}} \left\{ \int_0^{L_R} \exp[-\alpha_{\lambda,\text{Tot}}(t)x] dx \right\}^{\gamma} \\ &= \frac{[\alpha_{\lambda,\text{R}}(t)]^{\gamma} [L_{\lambda}^0(t)]^{\gamma}}{[\kappa_{\lambda,\text{Tot}}(t)]^{\gamma} L_R^{\gamma}} \left\{ 1 - \exp[-\alpha_{\lambda,\text{Tot}}(t) L_R] \right\}^{\gamma} \quad (\text{A-VII-2}) \end{aligned}$$

respectively. Then, defining $\vartheta_{\lambda}(t) = \alpha_{\lambda,\text{Tot}}(t) L_R$ (the total optical thickness), we get:

$$\varepsilon_{\lambda}(t) = \left\{ \frac{[1 - \exp[-\vartheta_{\lambda}(t)]]^{\gamma}}{[\vartheta_{\lambda}(t)]^{\gamma}} \times \frac{[\gamma\vartheta_{\lambda}(t)]}{[1 - \exp[-\gamma\vartheta_{\lambda}(t)]]} - 1 \right\} \quad (\text{A-VII-3})$$

In eqn (A-VII-1) and (A-VII-2) it is important to note the different meaning between L_{λ}^0 (the inlet spectral Radiance) and L_R (the reactor length)

Appendix VIII: The fully irradiated reactor

Let us recall the variable $\vartheta(t) = \alpha_{\lambda, \text{Tot}}(t)L_R$; *i.e.*, the instantaneous spectral optical thickness, which depends on the molar spectral Napierian absorption coefficient and concentration of the absorbing species, whether they are reactive or not, as well as on the characteristic reactor length. Let us look at the particular analysis that must be conducted when $\alpha_{\lambda, \text{Tot}}(t)$ is very large (*i.e.*, when $\alpha_{\lambda, \text{Tot}}(t) \rightarrow \infty$). It is important noting that the limit for $\alpha_{\lambda, \text{Tot}}(t) \rightarrow \infty$ physically means that the absorption of radiation abruptly occurs within a thin transverse layer very close to the radiation entrance point, a situation that can be encountered, for example, in the case of highly concentrated suspensions of titanium dioxide. As said before, caution should be exercised when choosing the characteristic length L_R , which in turn is a design parameter, in situations close to this limit of very large absorption coefficients. Because the amount of energy absorbed is finite, the **average** spectral rate of absorbed radiant power density $\left[\langle e_{\lambda}^a(\underline{x}, t) \rangle_{V_R} = e_{\lambda}^a(t) \right]$ can be made arbitrarily small by choosing L_R sufficiently large. This situation lacks of physical meaning, since most of the cell will be inaccessible to useful radiation. We can get round this problem by requiring, for example, for the unidirectional, collimated beam, that the exponent in the employed equation to calculate $\langle e_{\lambda}^a(x, t) \rangle_{L_R}$ namely, $\alpha_{\lambda, \text{Tot}}(t)L_R[x/L_R] = (\vartheta_{\lambda, \text{Tot}}(t))(x/L_R) = \vartheta_{\lambda, \text{Tot}}(t)\zeta$ be finite inside the entire reaction cell:

$$0 < \zeta = (x/L_R) < 1 \quad (\text{A-VIII-1})$$

Appendix IX: Very large and very small values of the linear absorption coefficient.

Taking the limit for $\alpha_{\lambda, \text{Tot}}(t) \rightarrow \infty$, and including the restriction stated in eqn (A-VIII-1) we may write:

$$\begin{aligned} \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \left\langle [e_{\lambda}^a(\underline{x}, t)]^{\gamma} \right\rangle_{L_R} &= \\ \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \frac{[\vartheta_{\lambda, iR}^0(t)L_{\lambda}^0(t)]^{\gamma}}{(L_R)^{\gamma}} \int_0^1 \exp[-\gamma\vartheta_{\lambda, \text{Tot}}(t)\zeta] d\zeta &= \\ \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \frac{[\vartheta_{\lambda, iR}^0(t)L_{\lambda}^0(t)]^{\gamma}}{\gamma\vartheta_{\lambda, \text{Tot}}(t)(L_R)^{\gamma}} \{1 - \exp[-\gamma\vartheta_{\lambda, \text{Tot}}(t)]\} & \end{aligned} \quad (\text{A-IX-1})$$

In eqn (A-IX-1), the limit for $\alpha_{\lambda, \text{Tot}}(t) \rightarrow \infty$ subjected to the constraint that $\vartheta_{\lambda, \text{Tot}}$ be finite, implies that $L_R \rightarrow 0$. Therefore, **independently of the value of $\gamma > 0$:**

$$\lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \left\langle [e_{\lambda}^a(\underline{x}, t)]^{\gamma} \right\rangle_{L_R} = \infty \quad (\text{A-IX-2})$$

The same arguments as the ones above, lead us to the conclusion for the approximation that:

$$\begin{aligned} \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \left\langle [e_{\lambda}^a(\underline{x}, t)] \right\rangle_{L_R} &= \\ \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \frac{[\vartheta_{\lambda, iR}^0(t)L_{\lambda}^0(t)]^{\gamma}}{(L_R)^{\gamma}} \int_0^1 \exp[-\vartheta_{\lambda, \text{Tot}}(t)\zeta] d\zeta &= \\ \lim_{\substack{\alpha_{\lambda, \text{Tot}} \rightarrow \infty \\ (\vartheta_{\lambda, \text{Tot}} = \text{finite})}} \frac{[\vartheta_{\lambda, iR}^0(t)L_{\lambda}^0(t)]^{\gamma}}{[\vartheta_{\lambda, \text{Tot}}(t)(L_R)^{\gamma}} \{1 - \exp[-\vartheta_{\lambda, \text{Tot}}(t)]\} &= \infty \end{aligned} \quad (\text{A-IX-3})$$

with the same physical interpretation as indicated in the main text. Consequently, the appropriate average used to determining intrinsic kinetics will be useful if, in addition to satisfy the just discussed constrains (Section 5), also represent as close as possible the radiation field inside the reaction cell.

Appendix X: The general Radiative Transfer Equation (RTE)^{6,7}

The equations used in the applications will be derived from the general equation for photon transport in a three-dimensional space regardless if the medium is homogeneous or heterogeneous:

$$\begin{aligned} \frac{dL_{\underline{\Omega}, \lambda}(s, t)}{ds} + \underbrace{\alpha_{\lambda}(s, t) L_{\underline{\Omega}, \lambda}(s, t)}_{\text{Absorption}} + \underbrace{\xi_{\lambda}(s, t) L_{\underline{\Omega}, \lambda}(s, t)}_{\text{Out-scattering}} &= \\ \underbrace{\frac{\xi_{\lambda}(s, t)}{4\pi} \int_{\underline{\Omega}' = 4\pi} B_{\lambda}(\underline{\Omega}' \rightarrow \underline{\Omega}) L_{\underline{\Omega}', \lambda}(s, t) d\Omega'}_{\text{In-scattering}} & \end{aligned} \quad (\text{A-X-1})$$

In this equation, $\alpha_{\lambda}(s, t)$ and $\xi_{\lambda}(s, t)$ are the Linear Spectral Napierian Absorption and Scattering coefficients, respectively (units of $\text{m}^{-1} \text{nm}^{-1}$ or $\text{cm}^{-1} \text{nm}^{-1}$). In the presence of a solid catalyst, $\alpha_{\lambda}(s, t)$ and $\xi_{\lambda}(s, t)$ must be calculated in terms of the properties of the catalyst: $\alpha_{\lambda} = \kappa_{\lambda}^* C_{\text{cm}}$ and $\xi_{\lambda} = \phi_{\lambda}^* C_{\text{cm}}$. Here κ_{λ}^* is the mass spectral Napierian absorption coefficient [$\text{m}^2 \text{kg}^{-1} \text{nm}^{-1}$], ϕ_{λ}^* the mass spectral Napierian scattering coefficient [$\text{m}^2 \text{kg}^{-1} \text{nm}^{-1}$], C_{cm} the catalyst mass concentration [kg m^{-3}] (or, with the corresponding changes in the linear coefficients, g cm^{-3}), and B_{λ} the Phase Function for scattering distribution. In eqn (A-X-1) internal radiation emission has been neglected [$j_{\lambda}^e(\underline{x}, t) = 0$] assuming that the work is carried out at not too high temperatures and no internal forms of induced emission exist. Scattering has been assumed elastic, multiple and independent and s is a directional coordinate in a three-dimensional space. Note that Radiance must be consider to depend on five coordinates and one parameter: (x, y, z) for the spatial position of the directional coordinate s , (θ, ϕ) for characterizing the propagating direction $\underline{\Omega}$, and λ to give information concerning the energy transported by the involved photons.

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