Part 4
Reactor and Reaction Engineering

CHAPTER 14

Fundamentals of Radiation Transport in Absorbing Scattering Media

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14.1 Introduction

The modeling of conventional reactors based on first principles usually requires the solution of the momentum, thermal energy and multicomponent mass conservation equations. In the case of photocatalytic reactors, the equation of radiative transfer must be considered. This equation can be solved independently of the thermal energy equation since thermal effects are usually negligible for photocatalytic processes. Therefore, the main interest of this chapter will be focused on the evaluation of the radiation absorption and its effect on the kinetics of the photocatalytic reaction.

The evaluation of the photon absorption rate is schematically exemplified in Figure 14.1.[1] Firstly, expressions of the reaction rates for each one of the

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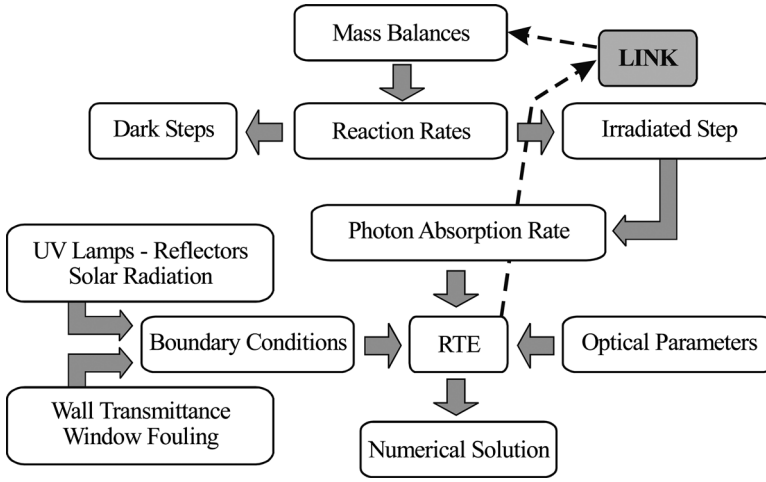

Figure 14.1 Evaluation of the photon absorption rate. (Reprinted with permission from ref. 1. Copyright 2008 De Gruyter.)

reacting species are required for the mass balances. As it is known, one of the reaction steps is initiated by radiation absorption (irradiated step). Then, the formulation of the local volumetric rate of photon absorption (LVRPA) or the local surface rate of photon absorption (LSRPA) is needed to evaluate the rate of the irradiated step (Section 14.2). In turn, to calculate the LVRPA or LSRPA, the radiative transfer equation (RTE) and the constitutive equations for radiation absorption, emission and scattering are required (Section 14.3). Boundary conditions to solve the RTE can be considered taking into account different possibilities: emission models developed for tubular lamps (with voluminal or superficial emission), photocatalytic reactions initiated by solar radiation (direct and diffuse components) and actinometric reactions employed to assess the radiation flux incident on the reactor window (Section 14.4). Specific numerical methods should subsequently be applied to solve the RTE in the reaction space for absorbing and scattering media (Section 14.5).

14.2 Definitions

A simplified characterization of the photon distribution in directions and wavelengths, in a volume V in space bounded by a surface A with an outwardly directed normal vector $\mathbf{n}$, is presented in Figure 14.2. In Figure 14.2(a); the streams of photons are represented by arrows with any directions and two different, representative wavelengths (white and black dots) inside the elementary volume. The wavelength λ_1 is represented by white dots and the wavelength λ_2 by black dots. Instead, in Figure 14.2(b), photons with any direction and with a single wavelength λ_1 (white dots) are illustrated. Lastly, Figure 14.2(c) shows photons with a single direction and a single wavelength λ_1.

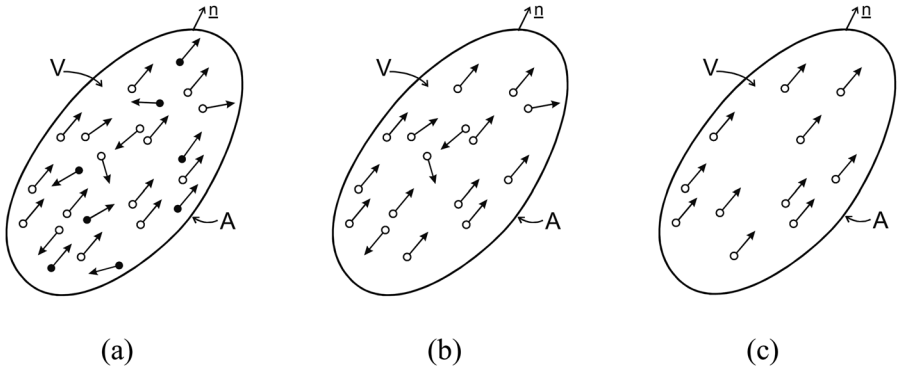

Figure 14.2 Characterization of the photon distribution in directions and wavelengths. (Reprinted with permission from ref. 1. Copyright 2008 De Gruyter.)

The conceptual idea presented in Figure 14.2 is useful to define the spectral (or monochromatic) radiation intensity.[1]

14.2.1 Radiation Intensity

This fundamental quantity of the radiation field can be defined as the amount of radiative energy per unit wavelength interval, per unit solid angle, per unit normal area, and per unit time.[1–5] Notably, for a given wavelength, the spectral radiation intensity is a function of position (**x**), direction (**Ω**), and time (t). Thus:

$$I_\lambda(\mathbf{x},\mathbf{\Omega},t) = \frac{\mathrm{d}E_\lambda}{\mathrm{d}A\cos\theta\,\mathrm{d}\Omega\,\mathrm{d}\lambda\,\mathrm{d}t} \tag{14.1}$$

For example, in the analysis and design of photocatalytic reactors, typical units for the spectral radiation intensity are Einstein per second, per steradian, per square meter, and per nm.

14.2.2 Incident Radiation

In the general case, radiation may be arriving at one point inside a photocatalytic reactor from all directions in space. Consequently, an important radiation property that takes this into account is the spectral incident radiation G_λ, defined by:

$$G_\lambda(\mathbf{x},t) = \int_\Omega I_\lambda(\mathbf{x},\mathbf{\Omega},t)\mathrm{d}\Omega = \int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2} I_\lambda(\mathbf{x},\theta,\varphi,t)\sin\theta\mathrm{d}\theta\mathrm{d}\varphi \tag{14.2}$$

In eqn (14.2) an integral for all possible directions over the spherical space has been performed. In addition, for polychromatic radiation, an integral

(or a summation) over the useful wavelength range of interest must be performed. Accordingly, the polychromatic incident radiation G is given by:

$$G_\lambda(\mathbf{x},t) = \int_{\lambda_1}^{\lambda_2}\int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2} I_\lambda(\mathbf{x},\theta,\varphi,t)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\lambda \tag{14.3}$$

14.2.3 Local Volumetric Rate of Photon Absorption (LVRPA)

In an elementary volume of radiation absorption, photons are absorbed according to the expression:[6]

$$e^{\mathrm{a}}_\lambda(\mathbf{x},t) = \kappa_\lambda(\mathbf{x},t)G_\lambda(\mathbf{x},t) \tag{14.4}$$

where e^{a}_λ is the spectral local volumetric rate of photon absorption. For polychromatic radiation, an integral over the useful wavelengths must be performed:

$$\begin{aligned} e^{\mathrm{a}}_\lambda(\mathbf{x},t) &= \int_{\lambda_1}^{\lambda_2}\kappa_\lambda(\mathbf{x},t)G_\lambda(\mathbf{x},t)\mathrm{d}\lambda \\ &= \int_{\lambda_1}^{\lambda_2}\int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2}\kappa_\lambda(\mathbf{x},t)I_\lambda(\mathbf{x},\theta,\varphi,t)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\lambda \end{aligned} \tag{14.5}$$

14.2.4 Net Radiation Flux

Another important radiation property is the spectral net radiation flux $q_\lambda(\mathbf{x},t)$. It is defined as the net flow of monochromatic radiative energy across a surface normal to a given direction $\mathbf{n}$, per unit time, per unit area and per unit wavelength, due to radiation coming from all directions in the space:[2]

$$q_\lambda(\mathbf{x},t) = \mathbf{n}\cdot\mathbf{q}_\lambda(\mathbf{x},t) = \int_\Omega I_\lambda(\mathbf{x},\boldsymbol{\Omega},t)\boldsymbol{\Omega}\cdot\mathbf{n}\,\mathrm{d}\Omega \tag{14.6}$$

where $\mathbf{q}_\lambda(\mathbf{x},t)$ is the spectral radiation flux vector.

14.2.5 Local Surface Rate of Photon Absorption (LSRPA)

The local surface rate of photon absorption may be evaluated from a local radiative energy balance in terms of the spectral net radiation flux $q_\lambda(\mathbf{x},t)$ defined in the previous section. Thus, at each point of the photocatalytic film, the LSRPA can be calculated according to the following expression:[7,8]

$$e^{\mathrm{a,S}}_\lambda(\mathbf{x},t) = \int_0^{\delta_\mathrm{f}}\kappa_\lambda(\mathbf{x},t)G_\lambda(\mathbf{x},t)\mathrm{d}\delta = q_{\lambda,\mathrm{in}}(\mathbf{x},t) - q_{\lambda,\mathrm{tr}}(\mathbf{x},t) - q_{\lambda,\mathrm{rf}}(\mathbf{x},t) \tag{14.7}$$

where δ_f is the thickness of the catalyst film, $q_{\lambda,\mathrm{in}}(\mathbf{x},t)$ the spectral radiative flux that reaches the catalytic surface, $q_{\lambda,\mathrm{tr}}(\mathbf{x},t)$ the spectral radiative flux that is transmitted through the catalytic film, and $q_{\lambda,\mathrm{rf}}(\mathbf{x},t)$ the spectral radiative flux that is reflected by the catalyst surface.

14.3 The Radiative Transport Equation (RTE)

Let us consider an elemental volume V in space having an absorbing, emitting and scattering medium, such as that represented previously in Figure 14.2(a). We are interested in those photons with a flight path lying within the solid angle of propagation $d\Omega$ which transport radiant energy of wavelength λ. Let these photons be called the $\mathbf{\Omega},\lambda$ photons. The photon transport equation can be represented by the following balance:

$$\begin{bmatrix}\text{Time rate of change of } \Omega,\lambda \text{ photons in the volume } V\end{bmatrix} + \begin{bmatrix}\text{Net flux of } \Omega,\lambda \text{ photons within the volume } V \text{ across the surface } A\end{bmatrix} = \begin{bmatrix}\text{Net gain of } \Omega,\lambda \text{ photons owing to emission, absorption, in- and out-scattering in the volume } V\end{bmatrix} \tag{14.8}$$

On the right-hand side of eqn (14.8) the following terms of radiation can be considered (Figure 14.3): (i) emission ($W^{\text{em}}_{\mathbf{\Omega},\lambda}$), (ii) absorption ($W^{\text{ab}}_{\mathbf{\Omega},\lambda}$), (iii) out-scattering ($W^{\text{ou-s}}_{\mathbf{\Omega},\lambda}$) and (iv) in-scattering ($W^{\text{in-s}}_{\mathbf{\Omega},\lambda}$). Thus:

$$\frac{1}{c}\frac{\partial I_{\mathbf{\Omega},\lambda}}{\partial t} + \nabla\cdot\left(I_{\mathbf{\Omega},\lambda}\mathbf{\Omega}\right) = W^{\text{em}}_{\mathbf{\Omega},\lambda} - W^{\text{ab}}_{\mathbf{\Omega},\lambda} - W^{\text{ou-s}}_{\mathbf{\Omega},\lambda} + W^{\text{in-s}}_{\mathbf{\Omega},\lambda} \tag{14.9}$$

Constitutive equations are needed for each one of the source and sink terms defined on the right-hand side of eqn (14.9).

The first term represents the emission of radiation by the matter, which is related to Planck's black-body radiation intensity by:

$$W^{\text{em}}_{\mathbf{\Omega},\lambda} = \kappa_\lambda(\mathbf{x},t)\, I_{\lambda,\text{b}}[T(\mathbf{x},t)] \tag{14.10}$$

where $I_{\lambda,\text{b}}$ is the black-body radiation intensity at temperature T.

For the second term, linear isotropic constitutive equations are generally used to characterize the absorption of radiation. Thus, the radiation absorption is represented by the constitutive equation:

$$W^{\text{ab}}_{\mathbf{\Omega},\lambda} = \kappa_\lambda(\mathbf{x},t)\, I_{\mathbf{\Omega},\lambda}(\mathbf{x},t) \tag{14.11}$$

In eqn (14.11) κ_λ is the spectral volumetric absorption coefficient, also called the linear absorption coefficient, which represents the fraction of the incident radiation that is absorbed by the matter per unit length along the path of the beam. Notice that the volumetric absorption coefficient has a unit of length^{-1}.

For the third term, linear constitutive equations are also used to represent the scattering of radiation. Accordingly, the radiation scattering term is given by the following constitutive equation:

$$W^{\text{ou-s}}_{\mathbf{\Omega},\lambda} = \sigma_\lambda(\mathbf{x},t)\, I_{\mathbf{\Omega},\lambda}(\mathbf{x},t) \tag{14.12}$$

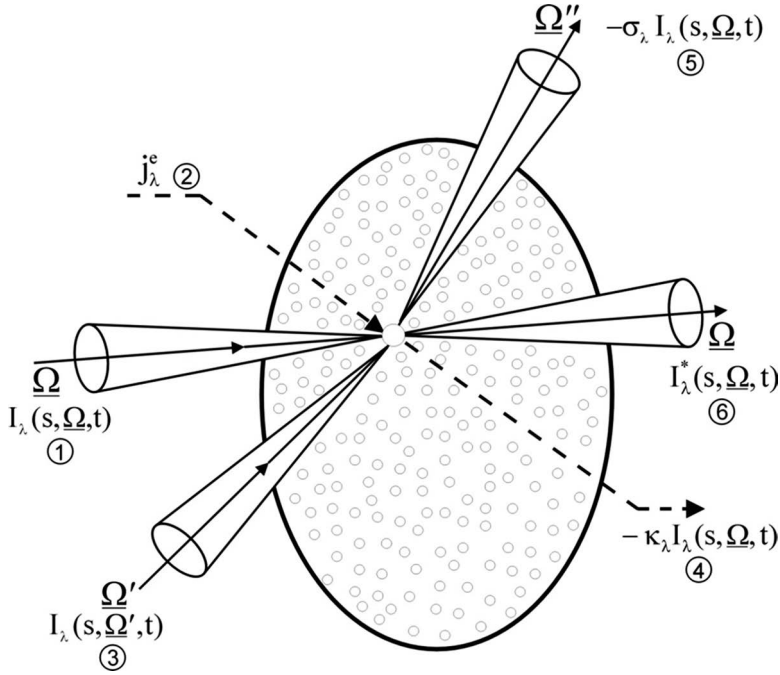

Figure 14.3 Schematic representation of the absorption, emission and scattering phenomena in radiation transport for the wavelength λ. (1) Incident intensity along s with direction $\mathbf{\Omega}$, (2) emission of radiation in the direction $\mathbf{\Omega}$, (3) intensity in a representative, arbitrary direction $\mathbf{\Omega}'$ to be scattered in the direction $\mathbf{\Omega}$, (4) absorbed intensity in the direction $\mathbf{\Omega}$, (5) scattered intensity in a representative, arbitrary direction $\mathbf{\Omega}''$ out of the direction $\mathbf{\Omega}$, and (6) emerging intensity along s in the direction $\mathbf{\Omega}$, after losses by absorption and out-scattering and gains by emission and in-scattering. (Adapted with permission from ref. 6. Copyright 1995 American Chemical Society.)

Here σ_λ is the spectral volumetric scattering coefficient, or the linear scattering coefficient. It represents the fraction of the incident radiation that is scattered by the matter in all directions, per unit length along the path of the beam. The coefficient σ_λ has also a unit of length^{-1}.

Notably, eqn (14.12) does not provide any information with regard to the directional distribution of scattered radiation. Consequently, a new function must be introduced to describe this aspect: the phase function $p_\lambda(\mathbf{\Omega}' \rightarrow \mathbf{\Omega})$. It is a normalized function, defined as:

$$\frac{1}{4\pi}\int_{4\pi} p_\lambda\left(\mathbf{\Omega}' \rightarrow \mathbf{\Omega}\right)\mathrm{d}\Omega = 1 \qquad (14.13)$$

Eqn (14.13) is valid for coherent scattering, *i.e.* when the wavelength of the scattered radiation is equal to that corresponding to the incident radiation.

Finally, the fourth term takes into account that part of the scattered radiation is incorporated to the ($\mathbf{\Omega}$,λ) photons according to the directional

distribution provided by the phase function. Therefore, the in-scattering term is used to compute the contribution for all directions in space:

$$W_{\mathbf{\Omega},\lambda}^{\text{in-s}} = \frac{1}{4\pi}\int_{4\pi} \sigma_\lambda(\mathbf{x},t)\, p_\lambda\left(\mathbf{\Omega}' \to \mathbf{\Omega}\right) I_{\mathbf{\Omega}',\lambda}(\mathbf{x},t)\mathrm{d}\Omega' \tag{14.14}$$

A methodology to evaluate the optical properties of aqueous titanium dioxide suspensions using spectrophotometric measurements can be found elsewhere.[9]

At this point, two important assumptions are introduced in eqn (14.9). Firstly, the first term on the left-hand side can be neglected because the factor $1/c$ is very low. Consequently, at a given time, the radiation field reaches the steady state almost instantaneously:

$$\frac{1}{c}\frac{\partial I_{\mathbf{\Omega},\lambda}}{\partial t} \cong 0.$$

Secondly, the radiation emission is generally important at high temperatures. Therefore, this term is usually neglected at the low working temperatures of the photocatalytic processes ($W_{\Omega,\lambda}^{\text{em}} \cong 0$).

Finally, taking into account the two previous assumptions and the eqn (14.10)–(14.14), the final expression of the RTE is given by:

$$\frac{\mathrm{d}I_{\mathbf{\Omega},\lambda}(s,t)}{\mathrm{d}s} = \left[\kappa_\lambda(s,t) + \sigma_\lambda(s,t)\right] I_{\mathbf{\Omega},\lambda}(s,t) + \frac{\sigma_\lambda(s,t)}{4\pi}\int_{4\pi} p_\lambda\left(\mathbf{\Omega}' \to \mathbf{\Omega}\right) I_{\mathbf{\Omega}',\lambda}(s,t)\mathrm{d}\Omega' \tag{14.15}$$

where s is a directional coordinate along the ray path.

Two useful definitions are frequently utilized in the modeling of photocatalytic reactors: the spectral extinction coefficient (β_λ) and the spectral albedo (ω_λ). The extinction coefficient is the sum of the absorption coefficient and the scattering coefficient:

$$\beta_\lambda(\mathbf{x},t) = \kappa_\lambda(\mathbf{x},t) + \sigma_\lambda(\mathbf{x},t) \tag{14.16}$$

The spectral albedo is defined as the ratio of the scattering coefficient to the extinction coefficient. Thus:

$$\omega_\lambda(\mathbf{x},t) = \frac{\sigma_\lambda(\mathbf{x},t)}{\beta_\lambda(\mathbf{x},t)} \tag{14.17}$$

14.4 Boundary Conditions for the RTE

To evaluate the volumetric (or surface) rate of photon absorption is necessary to compute the radiation intensity (or the net radiation flux) that arrives at the reacting system. These boundary conditions in photocatalytic reactors

can be provided by incidence or emission models.[10] In this section, the following boundary conditions will be considered: tubular lamp emission models, reactors activated with solar radiation and actinometric reactions used to evaluate the radiation flux incident on the reactor window.

14.4.1 Extended Source with Superficial Emission (ESSE)

In the case of tubular lamps with superficial emission, the discharged arc between electrodes induces the radiation emission produced by a specific substance that covers the inner surface of the lamp. As a result, the actual emission is produced by the lamp surface (Figure 14.4(a)), *e.g.* black light lamps, actinic lamps, *etc.*

Considering the main assumptions made in previous contributions,[6,11,12] the spectral radiation intensity incident on the reactor wall is given by:

$$I_{\lambda}^{0}(\theta,\varphi) = \frac{\gamma_{\mathrm{R},\lambda} P_{\lambda}}{2\pi^{2} R_{\mathrm{L}} L_{\mathrm{L}}} \tag{14.18}$$

where R_{L} is the lamp radius, L_{L} the lamp length, P_{λ} the emission power of the lamp and $\gamma_{\mathrm{R},\lambda}$ the reactor wall transmission coefficient.

To complete the information needed to compute the LVRPA, the limits of integration for solving eqn (14.5) may be obtained by means of trigonometric relationships. They can be calculated from the expressions [Figure 14.4(b)]:

$$\theta_{1}(\varphi) = \tan^{-1}\left\{\frac{r\cos\varphi - \left[r^{2}\left(\cos^{2}\varphi - 1\right) + R_{\mathrm{L}}^{2}\right]^{1/2}}{L_{\mathrm{L}} - z}\right\} \tag{14.19}$$

$$\theta_{2}(\varphi) = \tan^{-1}\left\{\frac{r\cos\varphi - \left[r^{2}\left(\cos^{2}\varphi - 1\right) + R_{\mathrm{L}}^{2}\right]^{1/2}}{-z}\right\} \tag{14.20}$$

$$-\varphi_{1} = \varphi_{2} = \cos^{-1}\left[\frac{\left(r^{2} - R_{\mathrm{L}}^{2}\right)^{1/2}}{r}\right] \tag{14.21}$$

14.4.2 Extended Source with Voluminal Emission (ESVE)

When tubular lamps with voluminal emission are considered, the photons are emitted directly from the arc inside the tube. Therefore, the emission is produced by the whole volume of the tubular lamp; for instance, the mercury arc low-, medium- and high-pressure lamps.

Taking into account again the main assumptions proposed on the emission of tubular lamps,[6,11] the spectral radiation intensity incident on the reactor boundary may be written as (Figure 14.5):

$$I_{\lambda}^{0}(\theta,\varphi) = \frac{\gamma_{\mathrm{R},\lambda} P_{\lambda}}{2\pi^{2} R_{\mathrm{L}}^{2} L_{\mathrm{L}}} \frac{\left[r^{2}\left(\cos^{2}\varphi - 1\right) + R_{\mathrm{L}}^{2}\right]^{1/2}}{\sin\theta} \tag{14.22}$$

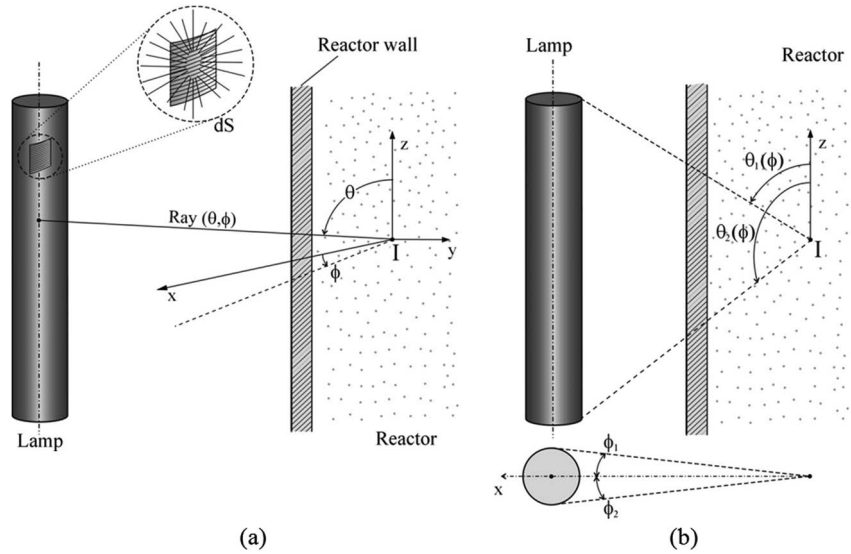

Figure 14.4 (a) Extended source with superficial emission model; (b) limits of integration for the tubular lamp. (Adapted with permission from ref. 6. Copyright 1995 American Chemical Society.)

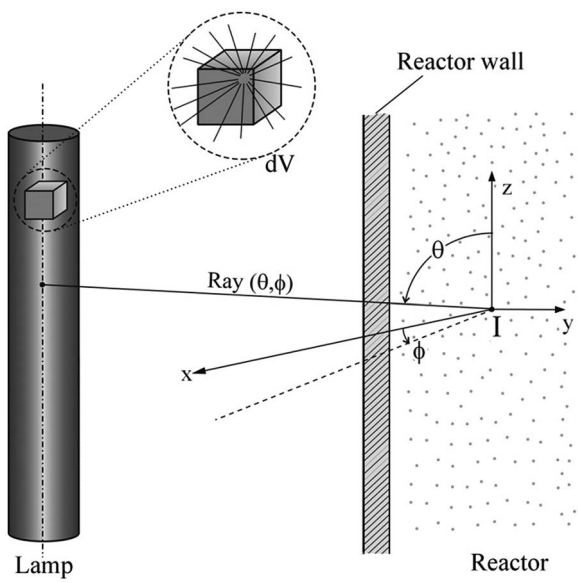

Figure 14.5 Extended source with voluminal emission model. (Adapted with permission from ref. 6. Copyright 1995 American Chemical Society.)

The limits of integration to compute the photon absorption rate are those given previously by eqn (14.19)–(14.21).

In some cases, photocatalytic reactors are irradiated by tubular lamps with the aid of a cylindrical reflector of different cross sections; for example, elliptical, parabolic or circular cross sections. The existence of a reflector causes a much more complicated problem to evaluate the photon absorption rate inside the reactor. The set of equations required to obtain the limiting angles for integrating the RTE may be developed working with the concept of lamp images instead of the lamp itself. The general methodology previously proposed[13] can be applied for tubular lamps and any form of the cylindrical reflector cross section.

14.4.3 Solar Radiation

To evaluate the LVRPA (eqn (14.5)) or the LSRPA (eqn (14.7)) in solar photocatalytic reactors it is necessary to evaluate the radiation intensity or the net radiation flux that arrives at the reactor window. These values are the boundary conditions for solving the RTE under solar irradiation.[14] To do this, the solar radiation flux at ground level, on horizontal and/or inclined planes, must be computed.

When solar radiation is used to drive a chemical reaction, an additional problem arises: even for the same geographic location, the solar radiation flux varies with the hour of day, the day of the year and the atmospheric conditions. Accordingly, a radiation flux that changes with position and time must be taken into account in the analysis and design of solar photocatalytic reactors.

Two types of approaches are usually employed in the literature: (i) simple, parameterized computational codes and (ii) sophisticated rigorous (or RTE) codes. The Simple Solar Spectral Model (SPCTRAL2)[15] and the Simple Model for the Atmospheric Radiative Transfer of Sunshine (SMARTS2)[16] are representative examples of the first group; the MODTRAN[17] and TUV[18] codes are typical examples of the second group.

This section presents a summary of the parameterized computational codes. Basically, these models consider that the direct beam radiation on a surface normal to the sun direction, under cloudless sky atmospheres and wavelength λ, is given by:

$$q_{B,\lambda} = H_{o,\lambda} D\, T_{r,\lambda} T_{a,\lambda} T_{w,\lambda} T_{o,\lambda} T_{u,\lambda} \tag{14.23}$$

In this equation $H_{o,\lambda}$ is the extraterrestrial solar radiation at the mean sun–earth distance, D is the correction factor for the sun–earth distance, and $T_{i,\lambda}$ are transmittance functions of the atmosphere at the wavelength λ. The sub-index i refers Rayleigh (or molecular) scattering (r), aerosol extinction (a), water vapor absorption (w), ozone absorption (o), and uniformly mixed gases (u).

On the other hand, the diffuse radiation on a horizontal surface at ground level, for cloudless sky conditions and wavelength λ, can be divided into three principal components: Rayleigh scattering ($q_{r,\lambda}$), aerosol scattering ($q_{a,\lambda}$) and multiple reflection between the ground and the air ($q_{g,\lambda}$). Thus:

$$q_{D,\lambda} = q_{r,\lambda} + q_{a,\lambda} + q_{g,\lambda} \tag{14.24}$$

Different expressions have been proposed to calculate the individual transmittances and the diffuse components introduced in the previous equations.[15,16]

Finally, the global solar radiation on a horizontal surface at ground level for cloudless sky atmospheres and wavelength $\lambda(q_{G,\lambda})$ is then simply the sum:[16,19]

$$q_{G,\lambda} = q_{B,\lambda} \cos\theta_Z + q_{D,\lambda} \tag{14.25}$$

where θ_Z is the solar zenith angle.

In contrast, the global solar radiation on an inclined surface is represented by:

$$q_{T,\lambda} = q_{B,\lambda} \cos\theta_i + R_d q_{D,\lambda} + \rho_{g,\lambda} R_r q_{G,\lambda} \tag{14.26}$$

where θ_i is the angle of incidence of the sun rays on the tilted surface and $\rho_{g,\lambda}$ the local reflectance of the ground close to the tilted surface. The mathematical expressions needed to evaluate θ_i, $\rho_{g,\lambda}$, and the conversion factors R_d and R_r, defined in the previous equation, can be obtained from the quoted ref. 16.

14.4.4 Chemical Actinometry

Chemical actinometry is an old and valuable method developed in the chemistry field to calculate the amount of photons absorbed in a reactor using a well-known reacting system.[20,21] In the analysis and design of photocatalytic reactors, actinometry can be a helpful tool to compute the boundary condition needed to solve the RTE. However, its usefulness is limited for scaling-up purpose, since in this case a larger reactor has not yet been built to carry out the actinometric experiments.[22]

Until now, several chemical reactions have been proposed to evaluate the radiation flux that arrives to the reactor window. Despite this, potassium ferrioxalate is one of the most widely used actinometers in aqueous systems. Under restricted temperatures and concentrations, the overall chemical reaction of this actinometer is represented by:

$$2Fe^{3+} + C_2O_4^{-2} \rightarrow 2Fe^{2+} + 2CO_2 \tag{14.27}$$

The Fe^{2+} concentration generated by this reaction is measured by means of spectrophotometric measurements at 510 nm of the complex formed with 1,10-phenanthroline.

A simple experimental system can be used to illustrate the evaluation of the boundary condition in a laboratory reactor operated in a recirculation batch mode.[23] The experimental setup consists of the reactor, the emitting system (lamp and reflector), the pump to recirculate the actinometer, and the storage tank. In this case, the external side of the reactor window was made of ground glass. For this homogeneous system, the following one-dimensional (x), one-directional ($\mu = \cos\theta$) monochromatic RTE with diffuse boundary condition has been proposed:

$$\mu \frac{\mathrm{d}I_{\mu,\lambda}(x,t)}{\mathrm{d}x} + \kappa_{\lambda,\mathrm{T}}(x,t) I_{\mu,\lambda}(x,t) = 0 \text{ with } \mathrm{I}_{\mu,\lambda}(0,t) = I_{\lambda}^{0} \neq f(\mu) \tag{14.28}$$

Integrating (eqn (14.28)) in the well-mixed photoreactor, the spectral radiation intensity is obtained:

$$I_{\mu,\lambda}(x,t) = I_{\lambda}^{0} \exp\left[-\frac{\kappa_{\lambda,\mathrm{T}}(t)}{\mu} x \right] \tag{14.29}$$

Inserting eqn (14.29) into the eqn (14.5), the following expression of the LVRPA is found for the proposed reacting system:

$$e_{\lambda}^{\mathrm{a}}(x,t) = 2\pi\kappa_{\lambda,\mathrm{Fe}^{3+}}(t) \int_{0}^{1} I_{\mu',\lambda}(x,t)\mathrm{d}\mu' = 2\pi\kappa_{\lambda,\mathrm{Fe}^{3+}}(t) I_{\lambda}^{0} E_{2}\left[\kappa_{\lambda,\mathrm{T}}(t) x\right] \tag{14.30}$$

where $E_2(z)$ is the second-order exponential integral function.[5]

Considering a first-order reaction rate of the actinometer with respect to the LVRPA and calling Φ_{λ} the monochromatic overall quantum yield, the mass balance for the ferrous ion is given by:

$$\left.\frac{\mathrm{d}C_{\mathrm{Fe}^{2+}}(t)}{\mathrm{d}t}\right|_{\mathrm{Tk}} = \frac{V_{\mathrm{R}}}{V_{\mathrm{T}}} \left\langle R_{\lambda,\mathrm{Fe}^{2+}}(x,t) \right\rangle_{L_{\mathrm{R}}} = \frac{V_{\mathrm{R}}}{V_{\mathrm{T}}} \Phi_{\lambda} \left\langle e_{\lambda}^{\mathrm{a}}(x,t) \right\rangle_{L_{\mathrm{R}}} \tag{14.31}$$

The reactor length-average of the LVRPA (from eqn (14.30)) is:

$$\left\langle e_{\lambda}^{\mathrm{a}}(x,t) \right\rangle_{L_{\mathrm{R}}} = \frac{1}{L_{\mathrm{R}}} \int_{0}^{L_{\mathrm{R}}} e_{\lambda}^{\mathrm{a}}(x,t)\mathrm{d}x = \frac{\pi I_{\lambda}^{0}}{L_{\mathrm{R}}} \frac{\kappa_{\lambda,\mathrm{Fe}^{3+}}(t)}{\kappa_{\lambda,\mathrm{T}}(t)} \tag{14.32}$$

In this equation it has been applied that $E_3(0) = 1/2$ and $\lim_{z \to \infty} E_3(z) \to 0$, because the product $\kappa_{\lambda,\mathrm{T}} L_{\mathrm{R}}$ is very large. Computing the initial reaction rate from the experimental work, the final expression of the boundary condition is obtained by means of eqn (14.31) and (14.32):

$$I_{\lambda}^{0} = \frac{V_{\mathrm{T}}}{\pi A_{\mathrm{R}} \Phi_{\lambda}} \lim_{t \to t_0} \left(\frac{C_{\mathrm{Fe}^{2+}}(t) - C_{\mathrm{Fe}^{2+}}^{0}}{t - t_0} \right) \tag{14.33}$$

14.5 Solution Methods of the RTE

Special numerical methods must be used to solve the RTE in heterogeneous media. Most of these numerical techniques were originally developed in the area of neutron transport theory.[24] Revisions on rigorous and/or approximate methods of solution can be found elsewhere.[2,25,26] Two rigorous methods have been proposed for solving the RTE: (i) Case's normal-mode expansion technique and (ii) the integral method; both procedures have been mainly developed for one-dimensional, plane-parallel configurations. Conversely, several approximate methods have been proposed; among them, we can mention the two-flux method, the exponential kernel approximation, the spherical harmonics method, and the six-flux method. However, the most common numerical techniques of solving the RTE are the discrete ordinate (DO) method, the Monte Carlo (MC) method and the finite volume (FV) method. This section presents a summary of DO and MC techniques.

The DO method is one of the most broadly applied numerical techniques that provides a wide range of applications in the numerical solution of the RTE; for example, one- or multi-dimensional systems with rectangular or curvilinear geometries.[4,24] The DO method transforms the integro-differential eqn (14.15) into a system of algebraic equations that can be solved by computation. For the simple problem of one-dimensional slab geometry with azimuthal symmetry, the spectral radiation intensity $I_{\mu,\lambda}(x)$ is obtained from the following discretized equations in plane geometry:

$$I_{i+1/2,\mathrm{m},\lambda} = \frac{1-(1-\gamma)\beta_\lambda\left(\Delta x_i/\mu_\mathrm{m}\right)}{1+\gamma\beta_\lambda\left(\Delta x_i/\mu_\mathrm{m}\right)} I_{i-1/2,\mathrm{m},\lambda} + \frac{S_{i,\mathrm{m},\lambda}}{\gamma\beta_\lambda + \left(\mu_\mathrm{m}/\Delta x_i\right)} \quad (\mu > 0) \qquad (14.34)$$

$$I_{i-1/2,\mathrm{m},\lambda} = \frac{1+(1-\gamma)\beta_\lambda\left(\Delta x_i/\mu_\mathrm{m}\right)}{1-\gamma\beta_\lambda\left(\Delta x_i/\mu_\mathrm{m}\right)} I_{i+1/2,\mathrm{m},\lambda} + \frac{\mathrm{S}_{i,\mathrm{m},\lambda}}{\gamma\beta_\lambda - \left(\mu_\mathrm{m}/\Delta x_i\right)} \quad (\mu < 0) \qquad (14.35)$$

In these equations γ is a weighting factor of the numerical method; in addition, the source term $S_{i,\mathrm{m},\lambda}$ can be calculated by the Gaussian quadrature:

$$\mathrm{S}_{i,\mathrm{m},\lambda} = \frac{\sigma_\lambda}{2}\sum_{n=1}^{N} \omega_n p_{n\mathrm{m}} I_{i,n,\lambda} \qquad (14.36)$$

where ω_n is the Gaussian quadrature weighting factor and $p_{n\mathrm{m}}$ the phase function discretized into n angles. An iterative strategy should be used to update the source term and solve eqn (14.34)–(14.36).

The MC method may be employed for simulating the radiation absorbed by the photocatalyst inside suspended, fluidized or packed bed reactors.[27–30] This technique is based on the generation of random numbers, between zero and one, to determine the trajectories and fates of a large number of photons coming from the emitting system (lamp or lamp/reflector) or from the sun.

For example, an MC simulation was employed to evaluate the surface rate of photon absorption in a fixed-bed photocatalytic reactor to degrade a model pollutant in aqueous solution.[7] The reactor bed was made with quartz wool coated with a thin film of TiO_2. Briefly, the following events were considered in the Monte Carlo simulation:

(i) Photons are emitted by the lamp; the emission position on the lamp, the direction of propagation and wavelength are stochastically defined.
(ii) Photons follow a linear trajectory in the medium between the lamp and the reactor window. Absorption and scattering are considered negligible in the air phase.
(iii) Photons that reach the reactor window can be reflected or refracted. Specular reflection is considered for reflected photons and Snell law to calculate the propagating direction of refracted photons. The Fresnel equation was used to compute the reflectivity.
(iv) Each quartz fiber was assumed uniformly distributed with its axis parallel to the reactor window and its angle randomly assigned.
(v) The mean free path of photons was estimated considering the reactor volume and the total projected area of fibers.
(vi) The advance of the photon inside the reactor was estimated by a randomly generated number.
(vii) The effective transmittance of the TiO_2 film can be evaluated by means of the spectral volumetric absorption coefficient and the film average thickness.

Finally, a computer program was developed to compute the trajectories and fates of all photons. The surface rate of photon absorption as a function of position inside the reactor was evaluated by the expression:

$$e^{a,s}(x,y,z) = \frac{N_{p,abs}(x,y,z) P_L V_R}{N_{p,T} \Delta x \Delta y \Delta z A_R} \tag{14.37}$$

where $N_{p,abs}(x,y,z)$ is the number of photons absorbed in the element volume at position (x,y,z), $N_{p,T}$ the total number of photons, P_L the total emission power of lamps, $\Delta x \Delta y \Delta z$ the element volume, V_R the total reactor volume and A_R the total photocatalytic reactor surface.

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