

SOME PROBLEMS IN HETEROGENEOUS PHOTOCHEMISTRY

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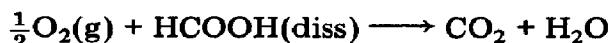
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Summary

Some photoreactions in gas-liquid, gas-liquid-solid and gas-solid systems are reviewed (in the last case the solid is a reactant). Attention is paid to the rate limitations due to transfer processes in these heterogeneous media. In gas-liquid systems the rate limitation due to the mass transfer of reactant A is governed by the well-known equation

$$\bar{n}_A = Ek_1aV_1(c_{A1} - c_{A1})$$

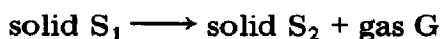
This is shown in several photoreactions. The preceding treatment can be extended to gas-liquid-solid systems (*e.g.* photocatalysis) provided that the resistance to mass transfer at the liquid-solid interface is included. The heterogeneous photocatalysis of the reaction



carried out in a semi-batch reactor is taken as an example.

The foregoing considerations are not restricted to photoreactions. However, the influence of interfaces on light propagation is specific to photoreactions. The resulting light scattering modifies that part of the light which is absorbed by the reacting medium. The theoretical treatment of such an effect is quite complicated, even in the case of photosensitized reactions. Examples of experimental studies are reviewed.

Only photodecompositions of the type



are considered for gas-solid systems, and the many problems encountered in the study of such reactions are indicated, taking as an example the photodecomposition of uranyl formate monohydrate. The importance of the occlusion of the gas G (*i.e.* CO₂) in the solid S₂ and of the slowness of its diffusion is shown. In fact, this diffusion controls the rate of the photochemical reduction of the uranyl ion. This suggests that the Lewis acid CO₂ inhibits the photochemical action which, in contrast, is enhanced by Lewis bases

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such as H_2O and NH_3 . Therefore consideration of diffusion as a rate-controlling step leads to a mechanistic feature which seems to be general and worthy of consideration.

1. Introduction

Classical photochemistry generally involves homogeneous systems in either the liquid or the gas phase. In both cases stirring of the reaction medium, if required, is sufficient to make it isotropic so that no diffusion-related problems arise and considerations involving light propagation and absorption are significantly simplified. However, an increasing number of heterogeneous photochemical systems, *e.g.* gas–solid photocatalytic systems, are encountered in both the laboratory and industry. These relatively well-known systems will not be considered in the following where we shall restrict ourselves to examining a few cases of photochemical reactions in gas–liquid, gas–liquid–solid and gas–solid systems (in the last case the solid is a reactant). This examination is confined to the influence of physical limitations on the rate of the overall process. In our final example we shall see that diffusion control inhibits the rate of the photochemical step.

2. Gas–liquid and gas–liquid–solid systems

Gas–liquid systems constitute one of the most important applications of photochemistry to industry, *e.g.* in chlorination, sulphochlorination, sulphoxidation, hydrosulphonation etc. The corresponding photoreactors are usually bubble reactors, in classical terminology. However, the physical limitations of these systems do not appear to have been studied as thoroughly as their technological importance warrants.

2.1. Interfacial mass transfer

As is the case for all heterogeneous systems, it is essential to know the parameters characterizing the interfaces, *i.e.* bubble diameter, interfacial area etc. Let us recall the double-film model which is generally used to account for the mass transfer of a reactant A (from the gas phase to the liquid phase in the example shown in Fig. 1) [1 - 3]. If there were no reaction in the liquid, the equations giving the molal flux of A (in moles per unit time per unit area of interface) would be

$$J_A = k_g(P_A - P_{A1}) = k_l(c_{A1} - c_{A2}) = k'_g(P_A - P_A^*)$$

where k_g , k_l and k'_g are the mass transfer coefficient on the gas side, the mass transfer coefficient on the liquid side and the overall mass transfer coefficient respectively. k'_g is introduced through the intermediary of a fictitious partial pressure P_A^* which is the pressure which would correspond to equilib-

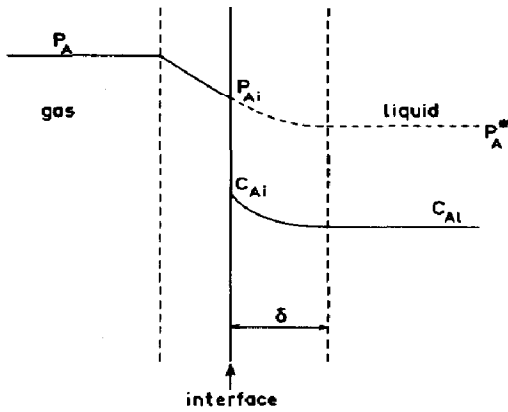


Fig. 1. Double-film model for interfacial transfer.

rium with the bulk liquid phase concentration c_{A1} . For example, if Henry's law holds

$$P_A^* = K_A c_{A1}$$

In order to take into account the reaction occurring in the liquid, the above equations are modified by introducing the enhancement factor E :

$$J_A = k_g(P_A - P_{Ai}) = Ek_1(c_{Ai} - c_{A1}) = k'_g(P_A - P_A^*)$$

The steady state consumption of reactant A (in moles per unit time) is equal to the rate of diffusion through the liquid film:

$$\bar{n}_{Ad} = J_A a V_1 = Ek_1 a V_1 (c_{Ai} - c_{A1})$$

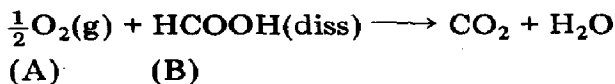
where a is the interfacial area referred to the liquid volume V_1 . In this expression c_{Ai} is determined by the equilibrium established at the interface and c_{A1} , which is usually different from c_{A1} , depends on the reaction regime which is governed by E . In turn, E can be evaluated from the dimensionless Hatta number Ha which includes both kinetic and mass transfer parameters. For instance, in the simplest case of an irreversible reaction of order one with respect to A and with constant k_c

$$Ha = \frac{(k_c \mathcal{D})^{1/2}}{k_1}$$

If Ha is large, E is also large, the regime is fast and c_A can be taken as zero in the bulk of the liquid; thus the reaction is almost totally restricted to a film of thickness δ . If Ha is small, E is close to unity, the reaction regime is slow and c_{A1} can be taken as constant throughout the liquid bulk. The term $k_1 a$ depends, among other factors, on the flow rate [4], i.e. the gas flow rate \bar{V}_g in a bubble reactor in which the liquid is at rest. $k_1 a$ is an increasing function of \bar{V}_g [4] so that \bar{n}_{Ad} tends towards the limiting value \bar{n}_{Ac} imposed by the chemical reaction at sufficiently large values of \bar{V}_g . This qualitatively justifies the findings of Brkic *et al.* [5] in their study of the dye-sensitized

photo-oxidation of olefins by gaseous oxygen; in one of their photoreactors the oxygen interfacial transfer always controlled the rate, which was a steadily increasing function of \bar{V}_g , whereas a plateau was reached in the other photoreactor.

A worked example from our laboratory is the photo-oxidation of dissolved formic acid by oxygen catalysed by iron ions:



This reaction was carried out in the semi-batch reactor, shown schematically in Fig. 2, for which the following equations hold:

$$\bar{n}_{A \text{ in}} - \bar{n}_{A \text{ out}} = J_A a V_1 = E k_1 a V_1 (c_{A i} - c_{A 1}) \quad (1)$$

$$E k_1 a V_1 (c_{A i} - c_{A 1}) + \nu_A r_V V_1 = V_1 \frac{dc_{A 1}}{dt} \quad (\nu_A = -\frac{1}{2}) \quad (2)$$

$$\nu_B r_V = \frac{dc_{B 1}}{dt} \quad (\nu_B = -1) \quad (3)$$

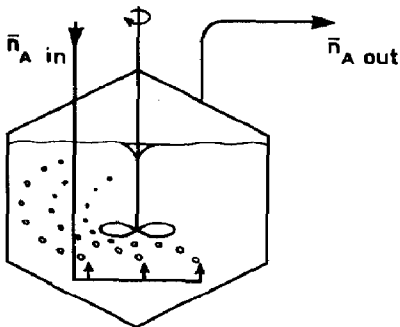


Fig. 2. Schematic diagram of the semi-batch stirred-tank reactor.

We were able to measure simultaneously the rate r_V of formic acid consumption and the concentration $c_{A 1}$ of dissolved oxygen (Fig. 3). It is found that $dc_{A 1}/dt = 0$ (*i.e.* the steady state is reached for oxygen) and that the Hatta number is very low so that $E \approx 1$. Equation (2) then reduces to

$$k_1 a = \frac{r_V}{2(c_{A i} - c_{A 1})} \quad (4)$$

k_1 can be evaluated using one of the many empirical correlations available in the literature, *e.g.* that of Akita and Yoshida [6], and is found to be roughly equal to 0.54 m h^{-1} . Hence the interfacial area a can be calculated for various values of \bar{V}_g and compared with the values obtained using the conventional sulphite oxidation method [7] which is a non-photochemical homogeneous catalytic process in a fast regime. As can be seen in Fig. 4,

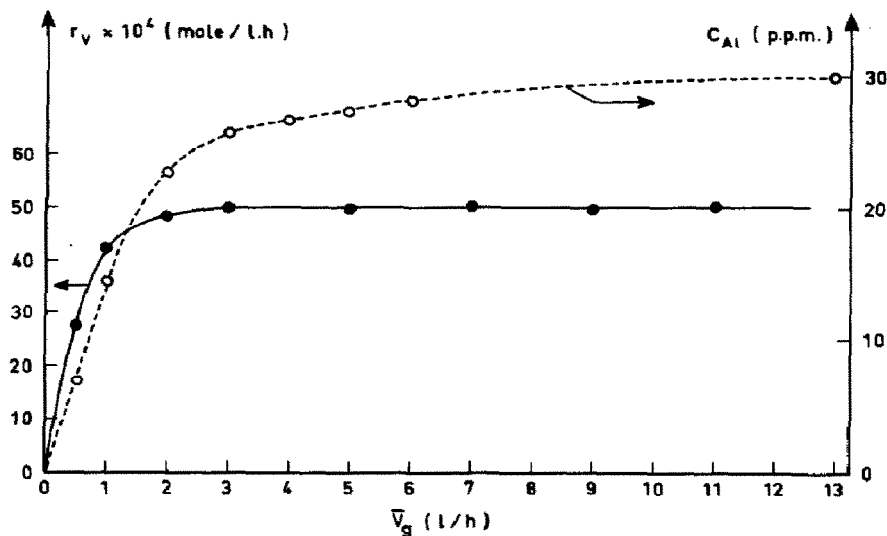


Fig. 3. Photocatalysis of the reaction $\frac{1}{2}\text{O}_2 + \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ by iron ions: the concentration of dissolved oxygen (○) and the reaction rate (●) are shown as functions of the volume flow rate of oxygen.

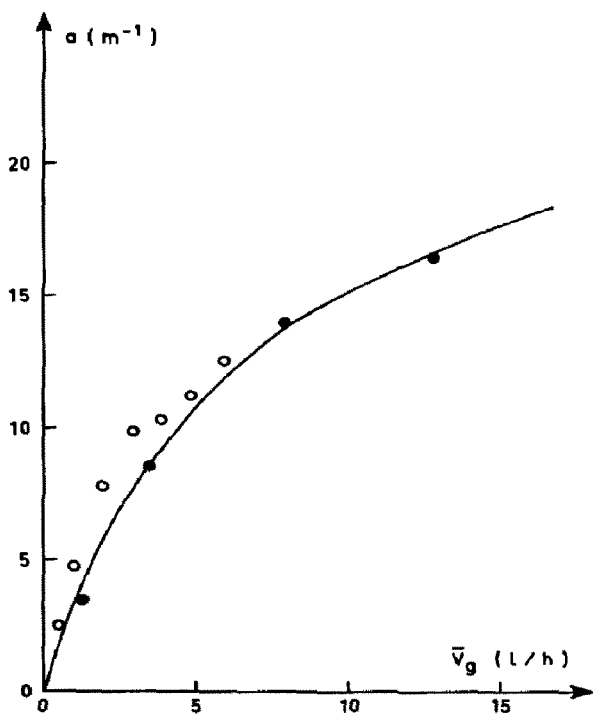


Fig. 4. Comparison of the interfacial areas obtained using the conventional sulphite oxidation method (●) and by calculation from the data in Fig. 3 (○).

these two different and independent methods of interfacial area determination agree remarkably well if all the underlying approximations are taken into account.

The preceding model can be extended to gas-liquid-solid systems, *e.g.* for heterogeneous catalysis by a solid of reactions taking place in the dissolved state. This is the case for the catalysis of the photo-oxidation of dissolved formic acid by TiO_2 [8]. Again, r_v and c_{A1} are measured as functions of \bar{V}_g (Fig. 5) and the values of $\ln(k_1a)$ deduced from eqn. (4) are plotted as functions of $\ln \bar{V}_g$ (Fig. 6). The points fit well on a straight line with a slope of 0.80, which is in agreement with accepted literature data [4].

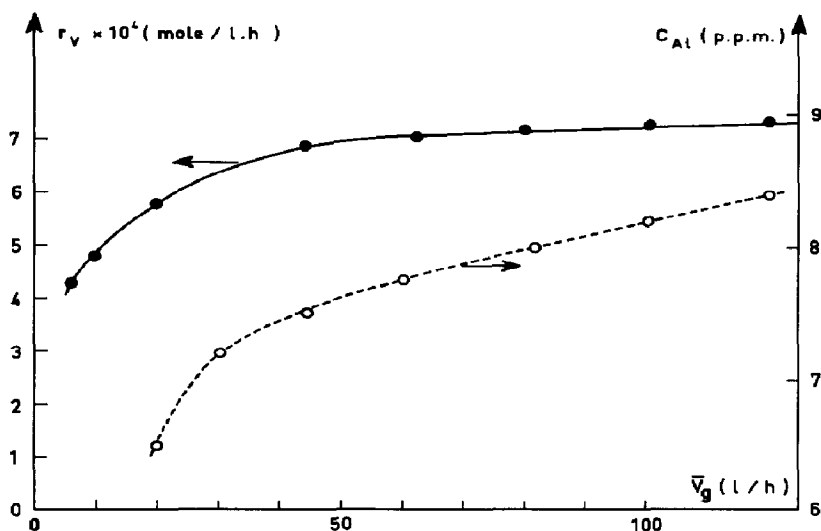


Fig. 5. Photocatalysis of the reaction $\frac{1}{2}\text{O}_2 + \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ by TiO_2 : the concentration of dissolved oxygen (\circ) and the reaction rate (\bullet) are shown as functions of the volume flow rate of oxygen.

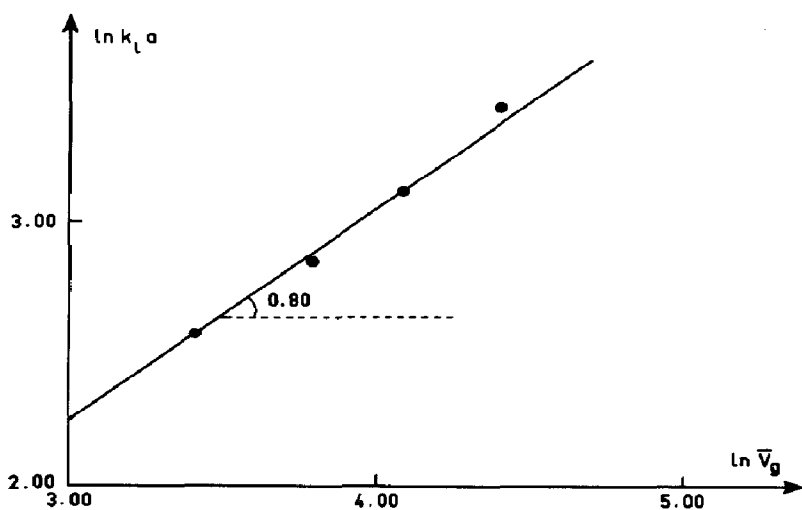


Fig. 6. $\ln(k_1a)$ as a function of $\ln \bar{V}_g$ for the oxidation of formic acid photocatalysed by TiO_2 .

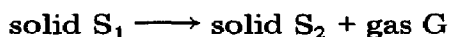
2.2. Light scattering

Interfacial mass transfer is now relatively well understood and is not unique to photoreactions. What is specific to these reactions is the effect of interfaces on the propagation of light. The resulting scattering can modify the light absorbed by the reaction medium. The quantitative treatment of this effect is very complicated even in the case of photosensitized reactions (*i.e.* when the concentration of the light-absorbing species remains constant) [9, 10]. An experimental study of uranyl-ion-sensitized oxalic acid photolysis in media with various scattering properties has been performed [11]. The work of Otake *et al.* [12] who measured the light intensity profile in a laterally illuminated gas-liquid dispersion should also be noted. They showed that the effective absorption coefficient measured in the presence of nitrogen bubbles was a function of the interfacial area a and that it resulted in a variation of the rate of reduction of potassium ferrioxalate.

In some cases crude models based on one-dimensional propagation of light and the Beer-Lambert law adequately describe the experimental data [8]. These models are valid when a reflector surrounding the reactor reflects most of the light back into the reaction medium. Then, if radiant energy losses at the interfaces are neglected, all incident, reflected or scattered light which can be absorbed is effectively absorbed owing to the increase in the optical pathlength.

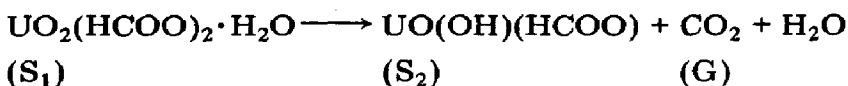
3. Gas-solid systems

When the irradiated phase is a solid the photoreaction itself creates heterogeneity. Transfer processes become dominant, as is shown by the example of silver halides in photography (transfer of electrons, holes and silver ions [13]). We shall limit ourselves to photodecompositions of the type



which are under investigation at present with respect to non-conventional photo-imaging systems (lead halides [14], iron oxalates [15], cobalt oxalates [16], copper and nickel oxalates [17] etc.). However, the study of such reactions presents many difficulties. Firstly, the solid photoproduct S_2 generally absorbs the actinic light, and therefore reduces the extent of the reaction, even for long exposure times. Therefore its characterization by conventional analytical methods is not easy. In particular, since S_2 is formed at a low temperature, it usually exhibits poor crystallinity or is amorphous and does not produce an X-ray diffraction pattern suitable for analysis. Secondly, the gas G has to diffuse through a layer of S_2 which is usually slightly porous if the starting material has a low porosity. The situation is then quite different from that of thermal decomposition, which usually occurs at higher temperatures where the open porosity of the solid product S_2 is larger.

These characteristics have been quantitatively measured for the photolysis of uranyl formate monohydrate [18] which has overall stoichiometry



This photolysis is an internal redox process, as can be seen from the conventional oxidation number: the oxidation number of uranium changes from 6+ to 4+ through the intermediary of 5+, whereas the oxidation number of carbon changes from 2+ in the initial salt to 4+ in CO₂. We shall limit ourselves to consideration of the evolution of CO₂. In a typical irradiation lasting for 10 h, the ratio of CO₂ evolved to the uranium(IV) produced is about 2:100. Thus it must be assumed that most of the CO₂ produced remains in the solid mixture. In fact, bands characteristic of gaseous CO₂ are found in the IR spectra of the solid. It is possible to extract part of this occluded CO₂ by pumping at higher temperatures (60 °C) after irradiation. This extraction obeys a kinetic law from which a value of about 10⁻⁸ cm² s⁻¹ can be derived for the diffusion coefficient \mathcal{D} of CO₂.

The importance of diffusion processes in the photolysis of solids has been discussed by Morantz *et al.* [19] in their study of the photolysis of lead bromide. They obtained the following relationship for the thickness l of the photoproduct layer:

$$l = Kt^{1/2} \tag{5}$$

Equation (5) can be checked fairly easily [20] for the photolysis of uranyl formate. Moreover, the rate of photo-oxidation in the presence of CO₂ ($P = 1$ atm) is slower than that in vacuum (Fig. 7) [21]. This poses the problem of the role of CO₂ in photolysis. It has been established that there are no reactions between CO₂ and the initial solid S₁, between CO₂ and the final solid S₂ or between CO₂ and the pre-irradiated solid S₁, *i.e.* a solid which already contains uranium(V). Therefore the only possible explanation for the control of the rate by CO₂ diffusion is that CO₂ exerts an inhibiting influence on the photochemical step.

This observation would not be unexpected if we were dealing with the formation of a complex in solution. However, in this case the reaction takes place in the solid state and CO₂ probably does not form a complex with the other components. This is why it can be assumed that its influence should be ascribed to its electron-acceptor character. Electron donors should enhance the rate of photolysis, as has been observed for H₂O and NH₃ [22]. This *a priori* surprising observation has been reported in other cases; for instance, the quantum efficiency of the photodecomposition of lead iodide is enhanced in the presence of moisture [23].

We tentatively propose an interpretation based upon a conventional collective model of adsorption on a semiconductor [24]. When the adsorbate A is negatively charged, as for CO₂ (Fig. 8(a)), band bending in the space charge region repels the electrons to the semiconductor bulk. Hence the light encounters fewer electrons in the vicinity of the surface and the photochem-

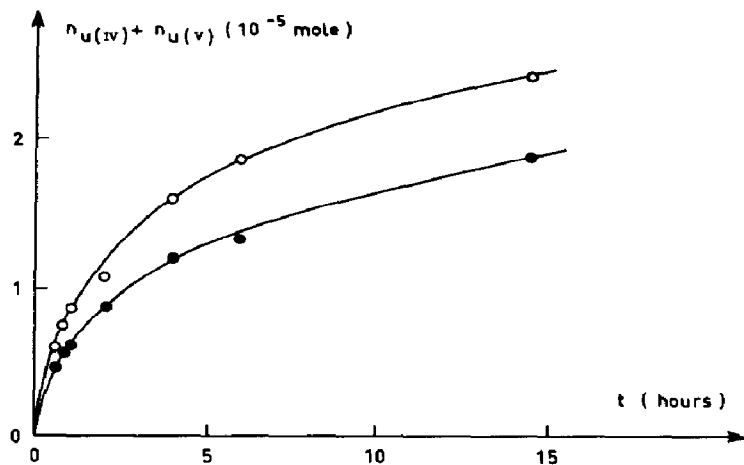


Fig. 7. Influence of the CO_2 pressure on the rate of photolysis of uranyl formate monohydrate: \circ , in vacuum; \bullet , under a CO_2 pressure of 1 atm.

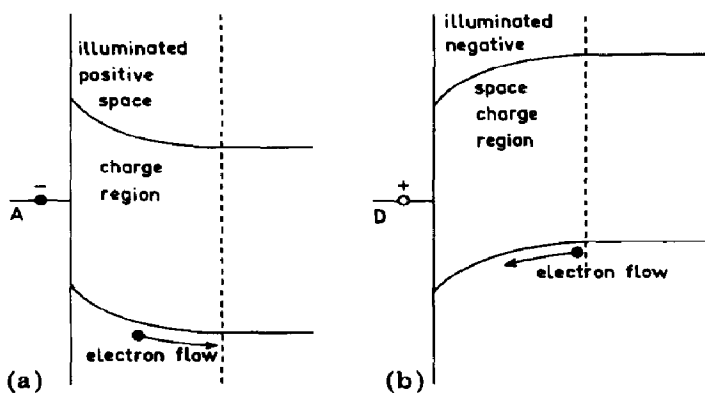


Fig. 8. (a) Depletion and (b) accumulation layers due to ionosorption at the surface of a semiconductor.

ical effect is inhibited. The opposite situation occurs when the adsorbate D is positively charged (Fig. 8(b)). Of course, confirmation of this interpretation requires further experimental evidence.

4. Conclusion

The influence of transfer phenomena in heterogeneous photochemistry, as for any heterogeneous reaction, cannot be overemphasized. In fact they can control the rate, even that of the photochemical step. Therefore they require careful investigation.

Acknowledgment

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Appendix A: Nomenclature

- a* interfacial area per unit volume of liquid phase, length⁻¹
c concentration, moles per unit volume
E enhancement factor
J molal flux, moles per unit time per unit area
k mass transfer coefficient, moles per unit time per unit area for k_g and k'_g , and length per unit time for k_l

l	photoproduct thickness
n	number of moles
\bar{n}	molal flow rate, moles per unit time
P	pressure
r	reaction rate, moles per unit time
t	time
V	volume
\bar{V}	volume flow rate, volume per unit time
\mathcal{D}	coefficient of diffusion, area per unit time
δ	film thickness
ν	algebraic stoichiometric coefficient

Subscripts

A	pertaining to component A
c	pertaining to the chemical reaction
d	pertaining to diffusion
g	pertaining to the gas phase
i	at the interface
in	at the reactor inlet
l	pertaining to the liquid phase
out	at the reactor outlet
V	per unit volume

Superscripts

*	at equilibrium
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