

Mass and Heat Transfer in Solid Catalyst Bed

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Abstract

In heterogeneous catalysis much effort is put into the determination of the reaction kinetics. The primary of the kinetic research is either to be able to optimize the design of a reactor or to gain more insight on the fundamentals of a reaction. Since heterogeneous catalysis involves, by definition, at least two phases, exchange of heat and mass between the phases is required for the reaction to take place. Due to these transport phenomena, the observed rate at which the reaction takes place is not necessarily the same as its intrinsic rate, i.e. the unique rate for a given catalyst at given conditions. Thus, when investigating the reaction kinetics in a laboratory-scale catalytic reactor, one has to account for the factors that may generate a resistance to the reaction and that disguise the intrinsic kinetics. In solid catalyst beds heat and mass transfer presented by equations for the prediction of convective heat transfer, pressure drop, effective thermal conductivity and wall heat transfer whereas under the conditions of radiant heat transfer may be neglected. It having various applications in fluidized beds, packed beds, trickle beds, magnetically stabilized beds etc.

Keywords: Heterogeneous Catalysis, Mass Transfer, Heat Transfer, Catalyst Bed.

1.1 Introduction

Over the past 40 years, gas-liquid concurrent contacting in catalytic trickle bed reactors has achieved widespread acceptance in a number of industrial applications. Although the down flow configuration is ubiquitous in the petroleum and petrochemical industries. It is also effective for hosting other catalyst mediated reactions such as for the production of commodity and specialty chemicals, pharmaceuticals and herbicides for waste treatment & bio-scrubbing, in biochemical and electrochemical processing.

Gas-liquid reactions with heat and gas production are mainly analyzed with the model suggested by Thiele. In this model, the chemical reaction in the porous catalyst is considered together with mass and heat transfer, which is carried out by the molecular mechanism, i.e. liquid in pores has no forced convection. Such an approach, however, cannot be applied for some reactions during which considerable quantities of gas or heat are released. Indeed, in the case of the reaction with gas production, a gaseous compound remains in a soluble state in liquid until the total pressure in a pore (equal to the sum of pressure in the reactor and pressure corresponding to a soluble gaseous compound) exceeds the maximum possible pressure, which can be defined as the sum of the outside and capillary pressures. If this occurs, a gas bubble will appear inside the pore.

Since there are many conditions under which a catalytic reaction can operate, it is to be expected that these conditions may affect the mode of transport of gaseous molecules through the porous structure and, if the rate of transport is comparable with the rate of chemical reaction, influence the observed kinetics. It is therefore pertinent to consider the various modes of transport of gaseous molecules through the porous media. The rate at which molecules diffuse through porous media is very much less than that associated with the translational velocity of molecules. This is because molecules collide with the pore walls and with other molecules during their passage through the catalyst structure, resulting in a completely random molecular motion. However, it is sufficient to determine the net rate of molecular transport through an imaginary plane across which the concentration gradient is known. This net rate will depend on the magnitude of the pore radius as compared with the mean free path of the molecules and on whether or not there is a total pressure difference across the pore length. We shall distinguish there are three types of mass transport in pores such as Knudsen flow, Bulk flow & Forced flow.

1.2 Importance of Mass and Heat Transfer

1.2.1 Mass transfer in packed beds

When a gas flows through a packed bed of solid material, as it does in catalytic reactor, in addition to chemical reaction mass is transferred by molecular diffusion and bulk flow. It is possible to write down differential equations describing transport conditions within the bed by considering the conservation of mass within an elementary volume element of the containing vessel. Suppose some solid material is packed in a cylindrical tube of radius R and length L . Consider the mass entering and leaving volume as depicted in Fig. 1.

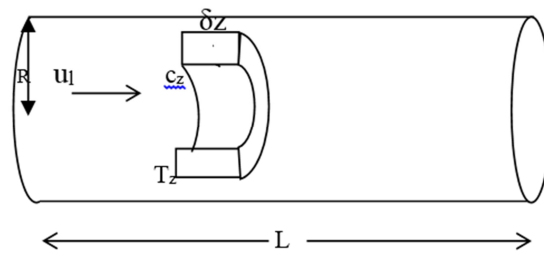


Fig 1. Conservation of mass and heat within an elementary cylindrical volume.

This elementary volume is a cylindrical shell of thickness δR and length δz and is concentric with the cylinder axis about which there is general symmetry. We assume that equimolar counter diffusion is occurring and write down, in turn, the mass which is entering the volume longitudinally and radially in a time δt .

Mass entering by longitudinal bulk flow

$$u_l 2\pi R \delta R c_z \quad (1)$$

Mass entering by radial diffusion:

$$-D_e 2\pi R \delta Z \left(\frac{\partial c}{\partial R}\right)_R \quad (2)$$

Mass entering by longitudinal diffusion:

$$-D_e 2\pi R \delta R \left(\frac{\partial c}{\partial Z}\right)_z \quad (3)$$

D_e is an effective diffusion coefficient, which, in general, will be different for the radial and longitudinal directions, but is, herein, assumed the same. Next, the mass leaving this elementary volume in time δt is accounted for.

Mass leaving by longitudinal bulk flow:

$$u_l 2\pi R \delta R c_{z+\delta z} = u_l 2\pi R \delta R \left\{ c_z + \left(\frac{\partial c}{\partial Z}\right)_z \delta z \right\} \quad (4)$$

Mass leaving by radial diffusion:

$$-D_e 2\pi (R + \delta R) \delta Z \left(\frac{\partial c}{\partial R}\right)_{R+\delta R} = -D_e 2\pi (R + \delta R) \delta Z \left\{ \left(\frac{\partial c}{\partial R}\right)_R + \left(\frac{\partial^2 c}{\partial R^2}\right)_R \delta R \right\} \quad (5)$$

Mass leaving by longitudinal diffusion:

$$-D_e 2\pi R \delta R \left(\frac{\partial c}{\partial Z}\right)_{z+\delta z} = -D_e 2\pi R \delta R \left\{ \left(\frac{\partial c}{\partial Z}\right)_z + \left(\frac{\partial^2 c}{\partial Z^2}\right)_z \delta z \right\} \quad (6)$$

Consider, for the moment, that no chemical reaction occurs within the bed, and that mass is transferred by equimolar counter diffusion only. The mass accumulating within the element in time δt is $(\partial c / \partial t) 2\pi R \delta R \delta Z$ and is equal to the algebraic sum of the quantities (1) to (6) inclusive entering and leaving the element. Neglecting second order differences, the conversion equation therefore

$$\frac{\partial c}{\partial t} = D_e \left\{ \frac{\partial^2 c}{\partial R^2} + \frac{1}{R} \frac{\partial c}{\partial R} + \frac{\partial^2 c}{\partial Z^2} \right\} - u_l \frac{\partial c}{\partial Z} \quad (7)$$

The diffusivity D_e is really an effective diffusivity, for it embraces both molecular diffusion and eddy diffusion by analogy with Boussinesq's concept of eddy viscosity [1]. The overall rate of diffusion per unit area is given by

$$N = -(D + \epsilon) \frac{\partial c}{\partial Z} \quad (8)$$

where D is the molecular diffusivity and ϵ the eddy diffusivity. Measurements and correlations of the effective diffusivity have been made [2, 3] for catalysts as a function of the particle diameter d_p and the tube diameter R . The results were expressed in terms of a dimensionless group (P_e), the Peclet number, which is given by $u_l d_p / D_e$. For Reynolds numbers between 30 and 700 it was found that (P_e) is a particular function f of the square of the ratio of particle diameter to tube diameter,

$$(P_e) = \frac{u_l d_p}{D_e} = f \left\{ \left(\frac{d_p}{2R}\right)^2 \right\} \quad (9)$$

Thus, for a given ratio of particle diameter to tube diameter, the function f gives the Peclet number and hence the effective diffusivity.

If, in addition to transport of matter by longitudinal and radial diffusion, chemical reaction occurs at a rate $r (=kc^n)$ per unit reactor volume, the conservation equation becomes

$$\frac{\partial c}{\partial t} = \frac{D_e}{u_l} \left(\frac{\partial^2 c}{\partial R^2} + \frac{1}{R} \frac{\partial c}{\partial R} + \frac{\partial^2 c}{\partial Z^2} \right) - \frac{\delta c}{\delta Z} - kc^n \quad (10)$$

For a reaction in which there is a change in molar volume, the linear velocity will vary along the reaction path. In this case equation (10) should be written

$$\frac{\partial c}{\partial t} = \frac{De}{ul} \left(\frac{\partial^2(ulc)}{\partial R^2} + \frac{1}{R} \frac{\partial(ulc)}{\partial R} + \frac{\partial^2(ulc)}{\partial z^2} \right) - ul \frac{\delta(ulc)}{\delta z} - kc^n \quad (11)$$

The steady-state solution to this equation has been found for certain conditions [4]. In particular, Vignes and Trambouze [5] solved, by a numerical method, the equation for a second order reaction under isothermal conditions. Laminar flow conditions were assumed and for all points in the reaction volume the concentration of both reactants equated. A similar approach for isothermal catalytic reactions is possible. Baron, Manning and Johnstone [6] studied the isothermal catalytic oxidation of SO₂ by coating the wall of a reactor tube with a vanadium pentoxide catalyst. In this case they neglected longitudinal diffusion. Since no chemical reaction occurred within the volume of the tube, but only at the tube wall, for plug type flow the appropriate steady state equation is

$$\frac{\delta C}{\delta Z} = \frac{De}{u1} \left(\frac{\partial c^2}{\partial R^2} + \frac{1}{R} \frac{\partial c}{\partial R} \right) \quad (12)$$

with the boundary conditions

$$c=c_0 \text{ at } z=0 \text{ for all values of } R \quad (13)$$

$$\frac{\partial c}{\partial R}=0 \text{ at } R=0 \text{ for all values of } z \quad (14)$$

$$\frac{\partial c}{\partial R} = -\frac{kc}{De} \text{ at } R=d/2 \text{ for all values } 0 < z < L \quad (15)$$

where d and L are the tube diameter and length respectively. The boundary condition represented by equation (15) arises because, at the tube wall, chemical reaction is exactly balanced by diffusion. The solution may be accomplished analytically by using the laplace transform operator method. The result is an equation giving c in terms of an infinite series containing the two independent variables z and R.

In catalytic reactors conditions are very often non-isothermal, so the steady state solution of equation (12)

$$u1 \frac{\delta C}{\delta Z} = De \left(\frac{\partial c^2}{\partial R^2} + \frac{1}{R} \frac{\partial c}{\partial R} \right) - r \quad (16)$$

is required in conjunction with an equation for heat conservation. The solution of the simultaneous equations is accomplished by standard numerical methods and gives the concentration of reactant as a function of the two independent variables corresponding to radial position and length. If the reactor is a narrow tube, the change in concentration from axis to tube wall at any given position will be small, especially if the bulk flow rate is high. Under the circumstances equation (16) reduces and is therefore to be regarded as an equation for use whenever diffusion mass transfer in a direction perpendicular to flow is concomitant with a steady state chemical reaction. The complete solution of an equation such as (10) in conjunction with an analogous equation for heat transfer will give an indication of stability in packed beds.

1.2.2 Heat transfer in packed beds

Because the rate of a chemical reaction is an exponential function of temperature it is obvious that the conversion of reactant is very much influenced by heat transferred to or from the wall of the reactor and heat released during reaction. Furthermore, it is not always possible or even desirable, to operate chemical reactors under isothermal conditions. The highly exothermic nature of some reactions may enhance either the reaction rate, or the equilibrium yield, or both. For such reactions it is better for the heat of reaction to be absorbed by the reactants, as would be the case in a reactor operated adiabatically. Some reactions are so exothermic that the temperature increase over the first portion of the reactor length may be such that the catalyst activity is impaired. A compromise between adiabatic and isothermal operation is made in these circumstances.

By analogy with mass transfer effects in packed beds, a general equation for heat transfer may be deduced. Referring to Fig 1, an equation for the conservation of heat within an elementary cylindrical volume is deduced as follows:

Heat entering element by longitudinal flow:

$$\rho u c_p 2 \pi R \delta R (T - T_0)_Z \quad (17)$$

Heat entering by radial conduction:

$$-k_e 2 \pi R \delta z \left(\frac{\partial T}{\partial R} \right)_R \quad (18)$$

Heat entering by longitudinal conduction:

$$-k_e 2 \pi R \delta R \left(\frac{\partial T}{\partial z} \right)_z \quad (19)$$

Heat out of element by longitudinal flow:

$$\rho u c_p 2 \pi R \delta R (T - T_0)_{Z+\delta z} \quad (20)$$

Heat out by radial conduction:

$$-k_e 2 \pi (R + \delta R) \delta z \left(\frac{\partial T}{\partial R} \right)_{R+\delta R} \quad (21)$$

Heat out by longitudinal conduction:

$$-k_e 2\pi R \delta R \left(\frac{\partial T}{\partial z} \right)_{z+\delta z} \quad (22)$$

Heat out by chemical reaction:

$$-2\pi R \delta R \delta z r \Delta H \quad (23)$$

ρ is the gas density, c_p the specific heat at constant pressure and k_e the effective thermal conductivity of the bed assumed the same in both longitudinal and radial directions. T_0 is any arbitrary temperature to which the heat content of the system may be referred. The heat accumulating within the element is calculated by defining a mean specific heat $(c_p)_m$ and a mean density ρ_m . The heat capacity of the system is then given by

$$(c_p)_m \rho_m = c_p \rho \Psi_b + (c_p)_s \rho_s (1 - \Psi), \quad (24)$$

where Ψ_b is the void space per unit reactor volume. The subscript s refers to the solid. The resulting equation for the conservation of heat is then

$$(c_p)_m \rho_m \frac{\partial T}{\partial t} = k_e \left(\frac{\partial^2 T}{\partial R^2} + \frac{1}{R} \frac{\partial T}{\partial R} + \frac{\partial^2 T}{\partial z^2} \right) - \rho u_i c_p \frac{\partial T}{\partial z} - r \Delta H \quad (25)$$

Because this is more than one mechanism by which heat may be transferred within the packed bed, k_e is a property of the system which depends on variables such as temperature, gas flow rate, particle diameter and porosity, and the thermal conductivity of gas and solid. In fact, k_e will, in general, depend on radial position, and an additional term $(\partial k_e / \partial R) (\partial T / \partial R)$ must then be added to the right hand side of equation (25).

For most design problems the steady state solution of equation (25) is required,

$$\rho u_i c_p \frac{\partial T}{\partial z} = k_e \left(\frac{\partial^2 T}{\partial R^2} + \frac{1}{R} \frac{\partial T}{\partial R} \right) - r \Delta H \quad (26)$$

This latter equation represents an approximation, since the temperature of the gas and the solid are assumed identical at every point in the reactor volume. If gas and solid temperatures differ, the procedure is to write an energy balance equation for the gas and for the solid and then solve the two resulting simultaneous partial differential equations numerically. Considerable simplification results if the gas is sufficiently well mixed for the gas temperature T_g to be constant over any given cross-section. Then only the conservation equation for the solid need be considered, but this will involve an additional term due to a quantity of heat $k_g 2\pi R \delta R \delta z (T - T_g)$ transferred from the gas.

Wilhelm and co-workers [7] have discussed the solution for a case in which longitudinal heat transfer is neglected and the heat liberated by chemical reaction is considered to be a linear function of temperature. The conservation equation which Wilhelm obtained is

$$\kappa_e \left(\frac{\partial^2 T}{\partial R^2} + \frac{1}{R} \frac{\partial T}{\partial R} \right) - k_g (T - T_g) + (\alpha + \beta T) = 0 \quad (27)$$

the last bracketed term representing the heat liberated by reaction. The kinetic coefficients α and β may be found from separate experiments designed specifically to examine the reaction rate. The effective thermal conductivity κ_e , and the heat transfer coefficient k_g (based on the reactor volume), can be found from experiments in which the reactor tube is packed with inert material having similar thermal properties to the catalyst. Equation (27) may be reduced to a Bessel equation of order zero and may thus be solved analytically for a particular set of boundary conditions.

When it is safe to ignore the variation in temperature across the tube radius, a fairly simple approach to the problem of heat transfer is possible. An equation for the conservation of energy may be written by considering an elementary section, thickness δz , of the tube of cross sectional area A_c . the surface area of the wall per unit length will be $2 A_c / A_w$, therefore the amount of heat exchanged with surroundings is:

$$k_w A_w (T_m - T_w) \delta z \quad (28)$$

where T_m is the mean temperature over the cross section, T_w is the wall temperature and k_w a heat transfer coefficient.

The heat produced by reaction in the element is:

$$-\Delta H_r A_c \delta z \quad (29)$$

where r is the reaction rate and ΔH the enthalpy of reaction. The energy balance is therefore

$$\sum m_i c_p \delta T = k_w A_w (T_m - T_w) \delta z - \Delta H_r A_c \delta z \quad (30)$$

where the summation on the left of the equation represents the net increase in enthalpy of all the components of the reaction mixture. Finally, a rate equation such as

$$F \delta x = r A_c \delta z \quad (31)$$

must be written. These simultaneous equations can be solved by standard numerical procedures. If the reactor is adiabatic, then no heat is exchanged with the surrounding and the energy conservation equation is

$$-\Delta H_r A_c \delta z = F \Delta H \delta x = \sum m_i c_p \delta T \quad (32)$$

In this case the solution is simpler, since a relation between temperature and conversion is first found, and then equation (32) subsequently integrated.

1.3 Applications

Knowledge of the particle to liquid heat and mass transfer coefficients in trickle beds is important. Particularly in contexts where exothermic reactions impede liquid replenishment over dried spots in the catalyst bed, or when the transport, especially in liquid limited reactions, is curbed by excessive liquid-solid interfacial resistance. Although particle liquid-heat and mass transfer coefficients in trickle beds are linked to each other, the known Chilton-Colburn analogy or similar failed to yield. A single Nu/Sh correlation to quantify both heat and mass transfer phenomena at the pellet scale. In this work, a single correlation embedding the heat and mass transfer information into a Peclet number was derived and validated over 1259 particle-liquid heat and mass transfer coefficients in trickle beds. Depending on whether a heat or mass Peclet number was used, the proposed correlation predicted Nu and Sh numbers with average absolute relative error of 18 and 22%, respectively. In particular, when equal heat and mass Peclet numbers occur, under physically and geometrically similar conditions, the correlation predicts true analogy between heat and mass transfer at the pellet level [8].

A theoretical analysis of thermal processes in liquid-gas exothermic reactions in a porous catalyst shows the existence of the alternating motion of liquid in the pore. According to this model, if the released heat in the pore exceeds a certain critical value, the alternating motion of the liquid driven by the formation of the bubble takes place in the pore. Specifically, because of the heating of the liquid in the pore, the partial pressure of vapor saturated in liquid increases until the total pressure of the saturated gas and vapor becomes greater than the maximum possible pressure in the pore (equal to the sum of capillary pressure and pressure in the reactor) and the bubble thereby comes into being. The growing bubble pushes the liquid out of the pore. Since the reagent(s) is no longer in the pore, the reaction ceases and the generated heat dissipates. The liquid penetrates into the pore due to capillary force and the process of bubble formation occurs once again. A detailed analysis of this non-stability is undertaken. This paper seeks to show how this theory can explain some dependencies of the reaction rate observed in practice, mass and heat transfer in the fixed and suspended catalyst as well as some practical recommendations for catalyst development and process intensification. Analogy between oscillation behaviour and the boiling process is considered [9].

The theoretical analysis of liquid and gas behaviour in catalyst pores in chemical reactions producing a gas phase shows the existence of pulsating, oscillating movements of liquid in pores. The necessary conditions for the occurrence of such oscillations are defined. Influences of oscillation behaviour on the chemical rate as well as its possible influence with regard to increasing mass transfer are discussed. Analysis and illustration of this kind of reactions are carried out using the results of hydrogen peroxide decomposition on CuCr catalyst [Chem. Eng. Sci. 51 (1996) 2721] [10].

This article discusses the effects of extra- and intraparticle mass and heat transfer in transient experiments over heterogeneous catalysts. To this purpose, the time-dependent transport in a catalyst particle when introducing a reactant in an inert gas phase has been analyzed. The analysis has led to one criterion assuring the absence of both extra- and intraparticle mass transfer limitations during steady-state experiments. Furthermore, criteria for the absence of mass and heat transport limitations during transient experiments have been developed by extending the criteria for the absence of mass and heat transport limitations during steady-state experiments. As will be shown, transient kinetics are not affected by heat transfer as long as the steady-state criteria for the absence of mass and heat transport limitations are fulfilled [11].

1.4 Conclusion

Mass and Heat transfer in packed beds have been considered. The differential equations describing transport conditions within the bed by considering the conservation of mass and heat within an elementary volume element of the containing vessel are recommended. Nu/Sh correlation for particle liquid heat and mass transfer coefficients based on Peclet similarity, Oscillations in pores of a catalyst particle and Analysis of heat processes and their influence on chemical conversion, mass and heat transfer also recommended.

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