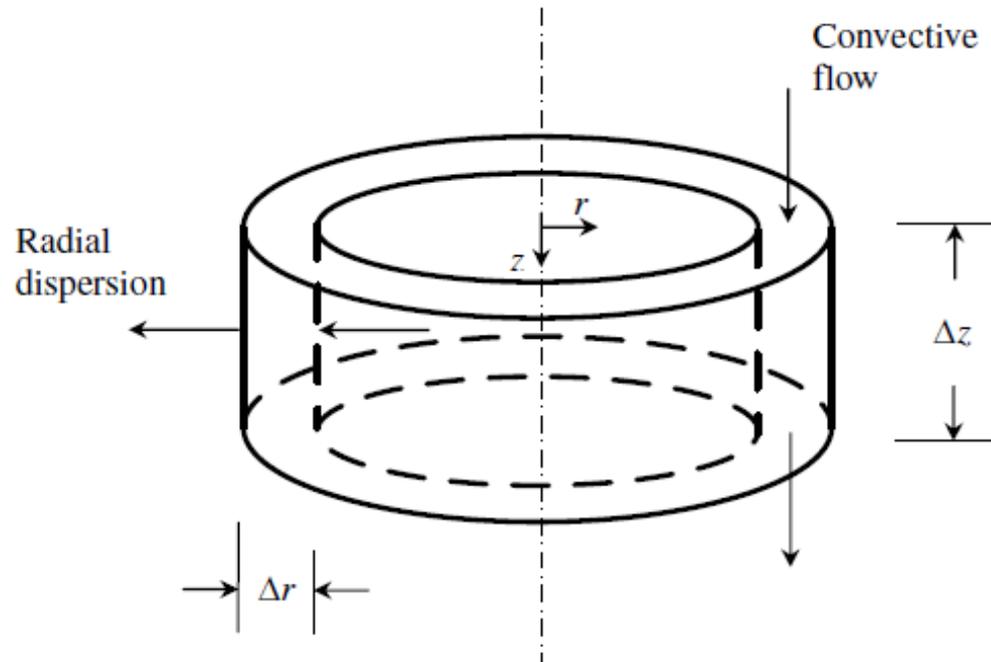


CHE 611

Advanced Chemical Reaction Engineering



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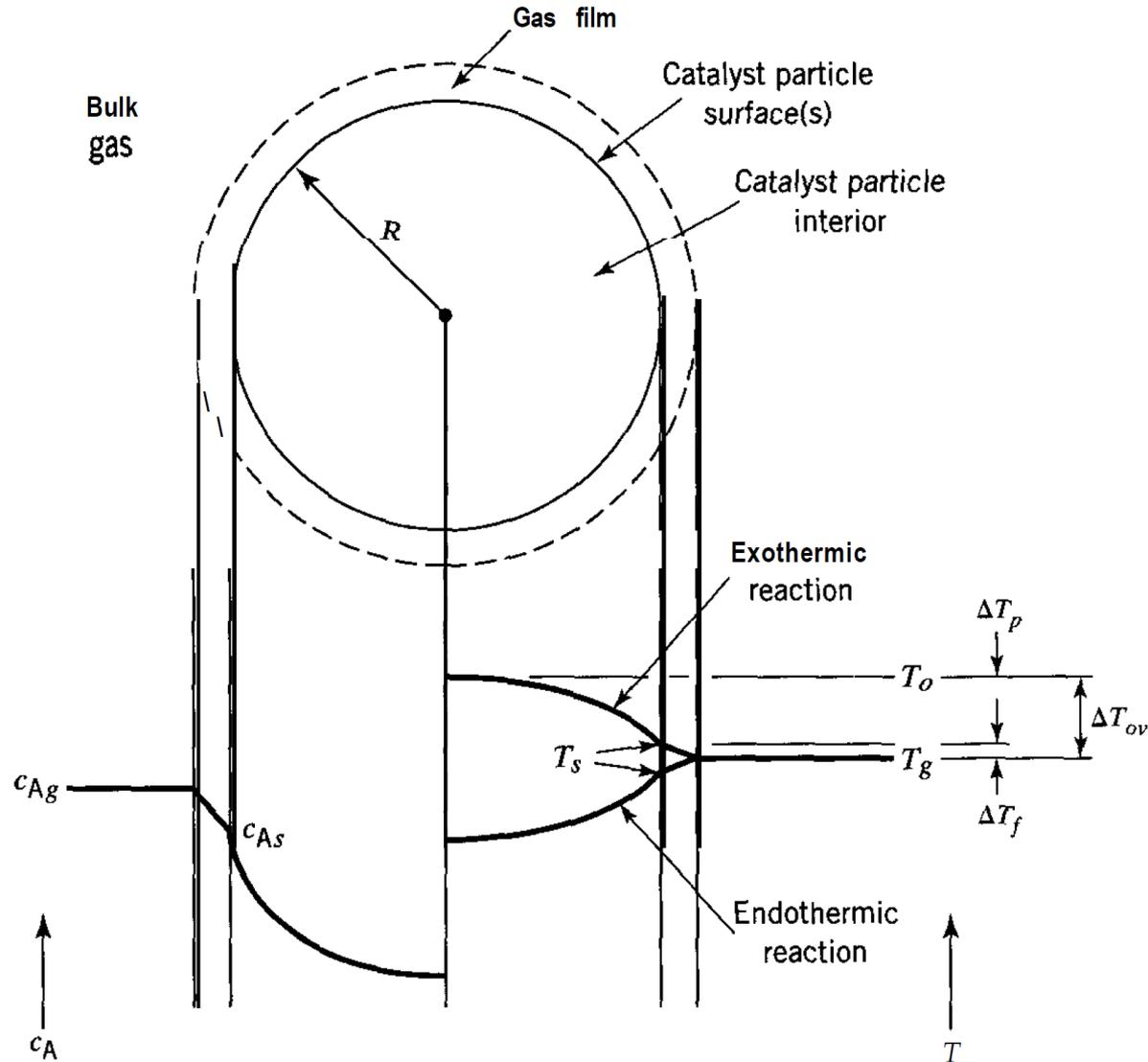
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Diffusion and reaction for porous catalysts

Solid catalysts are usually porous structures in order to have high surface area (m^2) per unit gram. Due to the porous nature, the inner surface is many times greater than the outer particle surface. Now as the reactants have to reach the inner surface through small pores, there may be significant resistance to mass and heat diffusion (transfer). Due to the reason, concentration and temperature profiles may be developed across the particle, i.e., within the particle.

For temperature distribution, if a reaction is exothermic, higher temperatures are possible at the center of the particle than at the outer surface and vice versa for an endothermic reaction.

Diffusion and reaction for porous catalysts [10]



Diffusion and reaction for porous catalysts : Effectiveness factor

The rate (kinetics) of a chemical reaction are dependent on the concentration of the reactant, say A , and temperature at any point of the catalyst. Now as concentration and temperature may vary from point to point so does the rate of the reaction. Therefore, it is required to account for these variations (diffusional resistances) to define the rate which represents the particle as whole. It may be interpreted that the effectiveness of the catalyst towards the rate of reaction varies within the catalyst particle and this effectiveness has to be considered in the final rate law. A factor known as effectiveness factor is required and that effectiveness factor is defined as the ratio of the observed or overall rate of reaction to the intrinsic rate of reaction at the outer surface of the particle where there are no diffusional limitations.

Diffusion and reaction for porous catalysts: Effectiveness factor

$$\eta = \frac{(-r_A)_{obs}}{(-r_A)_{int}}$$

$(-r_A)_{int}$ is the rate of the reaction at the conditions at the outside surface, i.e., c_{AS} and T_s .

$(-r_A)_{obs}$ is the rate of the reaction actually observed.

η is effectiveness factor

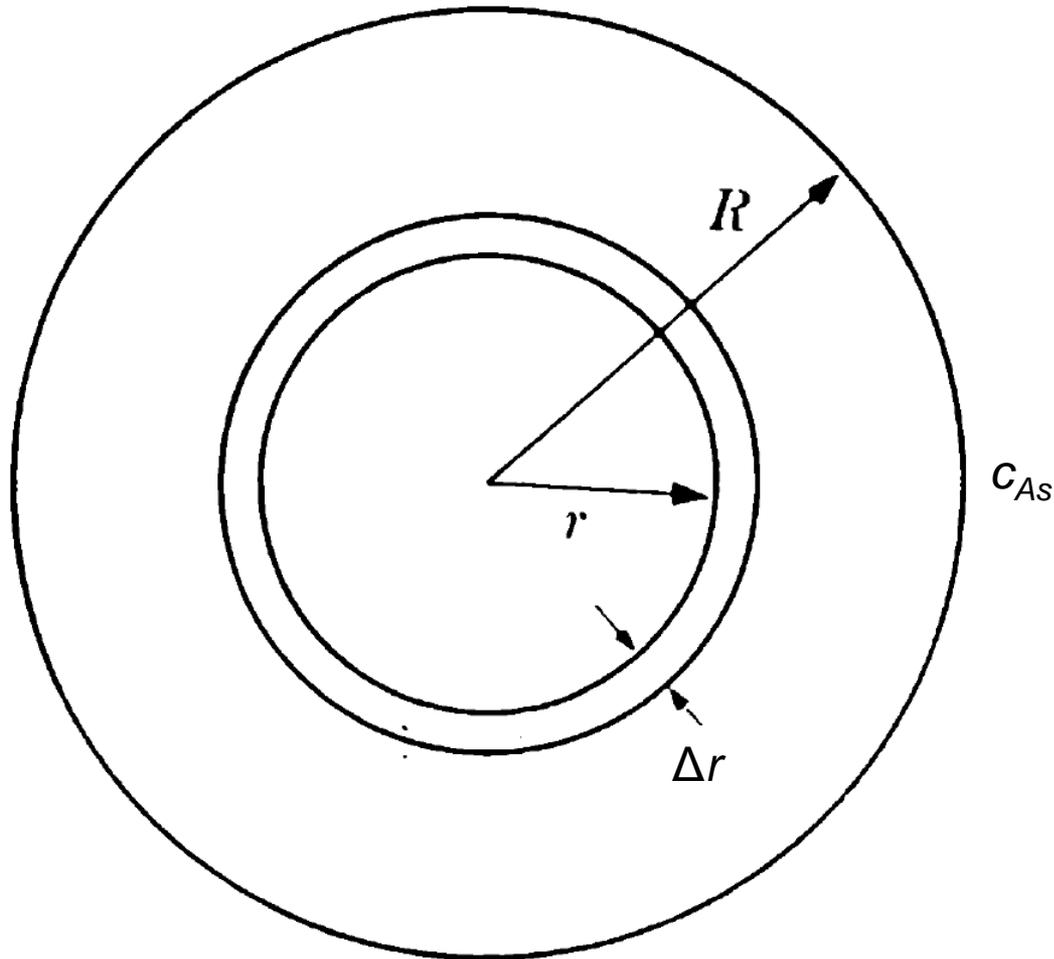
Diffusion and reaction for porous catalysts

Satterfield [11] defines the effectiveness factor

“the ratio of the actual reaction rate to that which would occur if all of the surface throughout the inside of the catalyst particle were exposed to reactant of the same concentration and temperature as that existing at the outside surface of the particle”.

Diffusion and reaction for porous catalysts

Consider, now, a spherical catalyst particle of radius R as shown in the figure below:



Diffusion and reaction for porous catalysts

Considering a thin spherical shell within the catalyst particle and apply mass balance across the thin shell for the following assumptions:

- 1) Porous particle is spherical;
- 2) Porous particle is isothermal
- 3) Reaction is $A \rightarrow \text{Products}$ (irreversible)
- 4) Kinetics are represented by $(-r_A) = k \cdot c_A^n$
- 5) Steady-state conditions
- 6) Reactants are transported through diffusion and there is no turbulence. The diffusion is described by Fick's law with mass diffusivity defined as effective diffusivity.

Diffusion and reaction for porous catalysts

Applying boundary conditions:

$$\text{BC-I:} \quad c_A = c_{As} \text{ at } r = R$$

$$\text{BC-II:} \quad \frac{dc_A}{dr} = 0 \text{ at } r = 0$$

And defining Thiele modulus, ϕ , as

$$\phi = R \sqrt{\frac{k \cdot c_{As}^{n-1}}{D_{eff}}}$$

and for $n = 1$, it may shown that

$$\frac{c_A}{c_{As}} = \frac{\sinh\left(\phi \cdot \frac{r}{R}\right)}{\left(\frac{r}{R}\right) \cdot \sinh \phi} \quad (\text{This is for sphere and first order reaction, when } n = 1)$$

The above equation describes the concentration profile in the spherical particle. 9

Diffusion and reaction for porous catalysts

The rate of reaction throughout one spherical porous particle is:

$$Rate = 4\phi\pi \cdot R \cdot D_{eff} \cdot c_{As} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \text{mol/s}$$

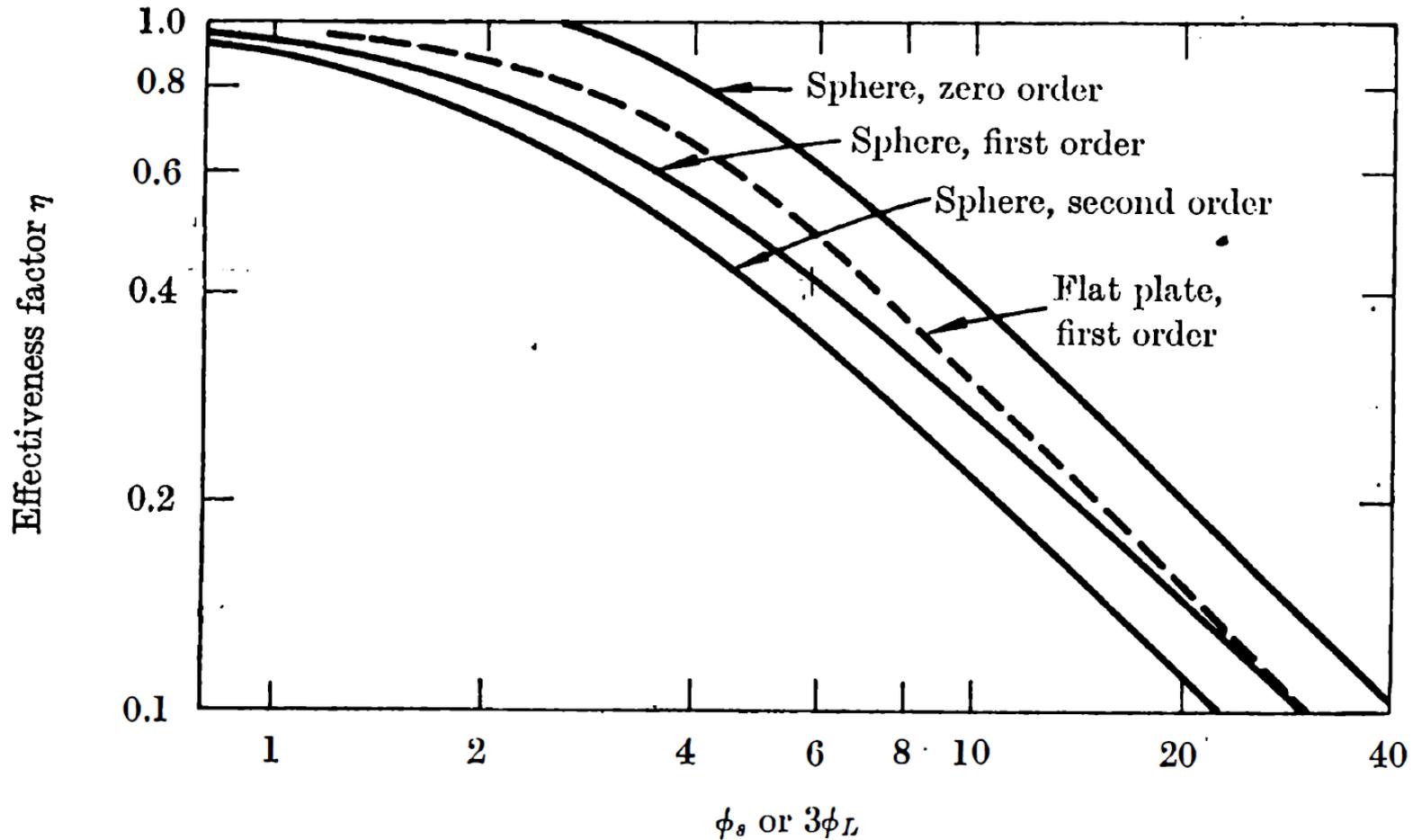
If all the internal surface is at the concentration outside the surface, i.e., c_{As} , then:

$$Rate = \frac{4}{3} \pi \cdot R^3 \cdot k \cdot c_{As} \text{mol/s}$$

By the definition of effectiveness factor, η

$$\eta = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right)$$

Diffusion and reaction for porous catalysts [11]



Effectiveness factor with power-law kinetics.

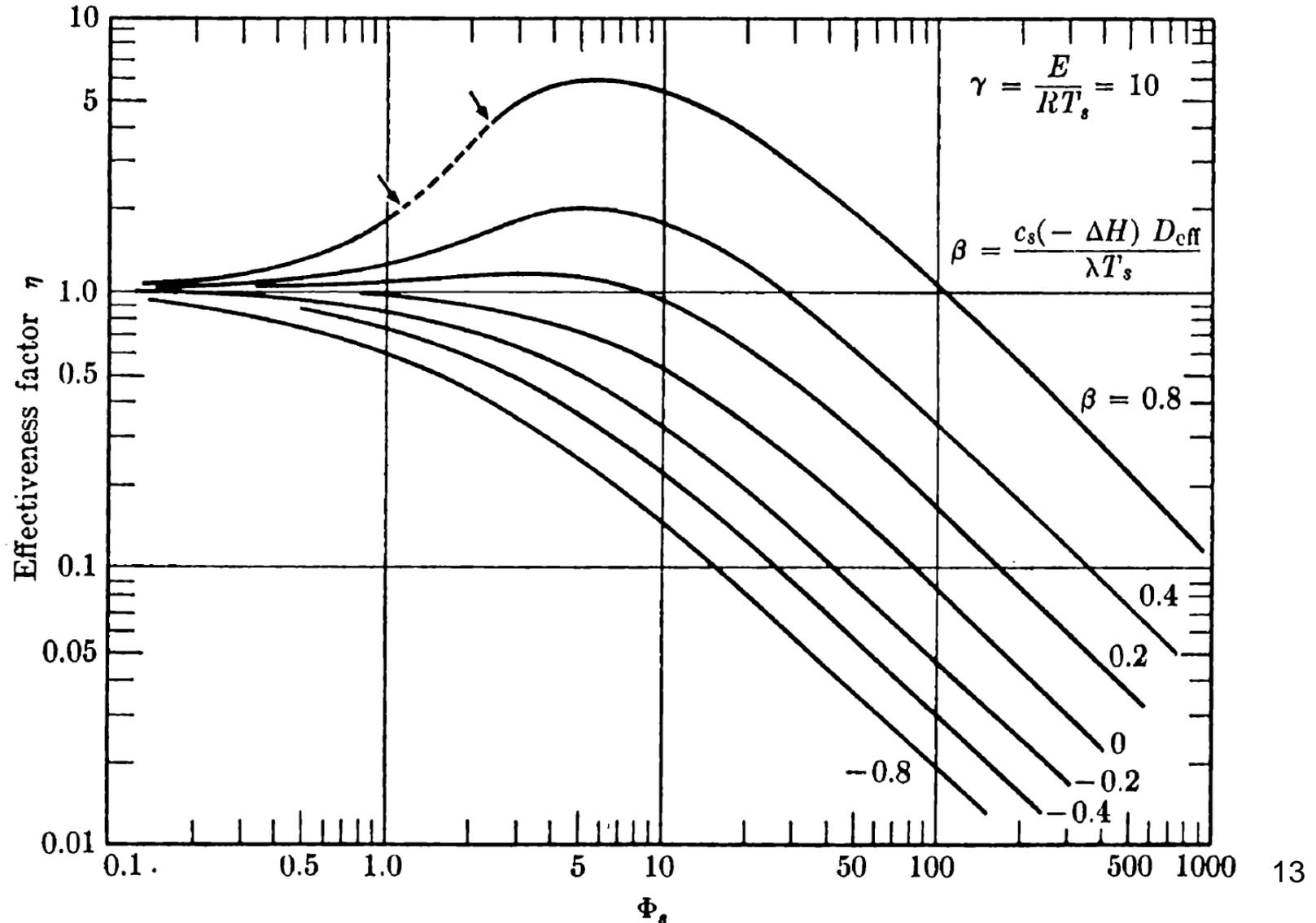
Diffusion and reaction for porous catalysts

A modified Thiele modulus can be defined which is based on observed values

$$\Phi = \frac{R^2}{D_{eff}} \left(-\frac{1}{V_c} \frac{dn}{dt} \right) \frac{1}{c_{As}}$$

This modified Thiele modulus is related for various values of heat generation function, β , and dimensionless Arrhenius number to include the effect of temperature while determining the effectiveness factor. One such relationship (graph) is shown in the figure on the next slide.

Diffusion and reaction for porous catalysts [11]



Diffusion and reaction for porous catalysts: Effective diffusivity

The effectiveness diffusivity can be calculated by the following equation

$$\frac{1}{D_{eff}} = \frac{1}{D_{Kn,eff}} + \frac{1}{D_{A,eff}}$$

Where,

D_{eff} effective mass diffusivity, m²/s

$D_{A,eff}$ ordinary or bulk effective mass diffusivity, m²/s

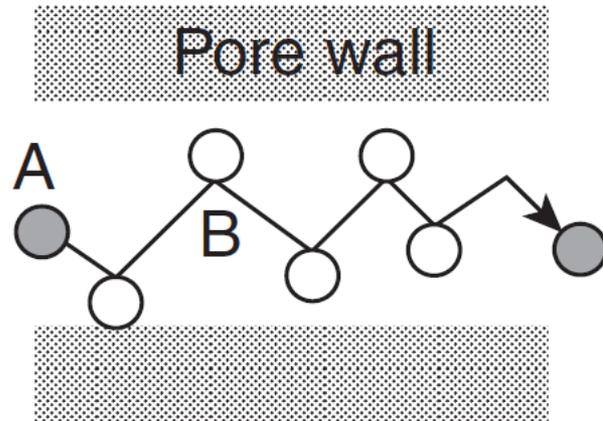
$D_{Kn,eff}$ effective Knudsen mass diffusivity, m²/s

Knudsen diffusivity

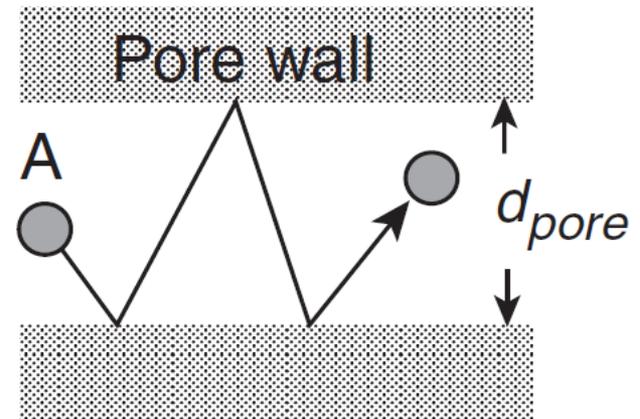
“If the gas density is low, or if the pores are quite small, or both, the molecules collide with the pore wall much more frequently than with each other, This is known as Knudsen flow or Knudsen diffusion. The molecules hitting the wall are momentarily adsorbed and then given off in random directions (diffusively reflected). The gas flux is reduced by the wall resistance. Knudsen diffusion is not observed in liquids.” [11]

Knudsen diffusivity [12]

Pure molecular
diffusion



Pure knudsen
diffusion



Knudsen diffusivity

Based on kinetic theory of gases, Knudsen diffusivity can be obtained as

$$D_{Kn} = 9700 \cdot r_p \cdot \sqrt{\frac{T}{M}}, \text{ cm}^2/\text{s}$$

Where,

T absolute temperature, K

M molecular weight

r_p pore radius, cm

Knudsen diffusivity

The pore radius defined above is for a round straight pore, the actual pore geometry is complex and the therefore including the effect of pore geometry, the following relationship can be written for the effective Knudsen diffusivity [11]:

$$D_{Kn,eff} = 19400 \frac{\theta^2}{\tau_m \cdot S_g \cdot \rho_p} \sqrt{\frac{T}{M}}, \text{ cm}^2/\text{s}$$

Where,

θ particle voidage

ρ_p density of particle, g/cm³

τ_m tortuosity factor when D_{Kn} is calculated based on mean pore radius

S_g surface area of the article, cm²/g

Diffusion and reaction for porous catalysts: Effective diffusivity

The effectiveness bulk diffusivity can be calculated by the following equation

$$D_{A,eff} = \frac{D_A \cdot \theta}{\tau_m}$$

D_A ordinary diffusion , cm²/s

θ particle voidage

τ_m tortuosity factor when D_A is calculated based on mean pore radius

Bulk diffusion coefficient for gases at low pressure

Based on the Chapman-Enskog theory, the following equation using ideal gas law for the determination of total concentration “ c ” may be written [8]

$$\begin{aligned} \mathcal{D}_{AB} &= \frac{3}{16} \sqrt{\frac{2(RT)^3}{\pi} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{\tilde{N} p \sigma_{AB}^2 \Omega_{\mathcal{D},AB}} \\ &= 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{p \sigma_{AB}^2 \Omega_{\mathcal{D},AB}} \end{aligned}$$

Here, D_{AB} is in cm^2/s , σ_{AB} is \AA , and p in atm.

The mass diffusivity D_{AB} for binary mixtures of nonpolar gases is predictable within about 5% by kinetic theory.

Bulk diffusion coefficient for gases at low pressure

The parameters σ_{AB} and ε_{AB} could, in principle, be determined directly from accurate measurement of D_{AB} over a wide range of temperatures. Suitable data are not yet available for many gas pairs, one may have to resort to using some other measurable property, such as the viscosity of a binary mixture of A and B . In the event that there are no such data, then we can estimate them from the following combining rules for non-polar gas pairs.

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \qquad \sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$$

Use of these combining rules enables us to predict values of D_{AB} within about 6% by use of viscosity data on the pure species A and B , or within about 10% if the Lennard-Jones parameters for A and B are estimated from boiling point data as discussed in Chapter 1 of Bird et al. 2002 [8].

Bulk diffusion coefficient for gases at low pressure

✚ The Lennard-Jones parameters can be obtained from the Appendix of the book [8] and in cases when not known can be estimated as described in first chapter of the book [8]. To avoid interpolation, a graphical relationship for collision integral is given on the next slide.

✚ A mathematical relationship by Neufeld is recommended for computational (spreadsheet) work [9].

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

$$T^* = kT / \varepsilon_{AB}$$

$$A = 1.06036$$

$$B = 0.15610$$

$$C = 0.19300$$

$$D = 0.47635$$

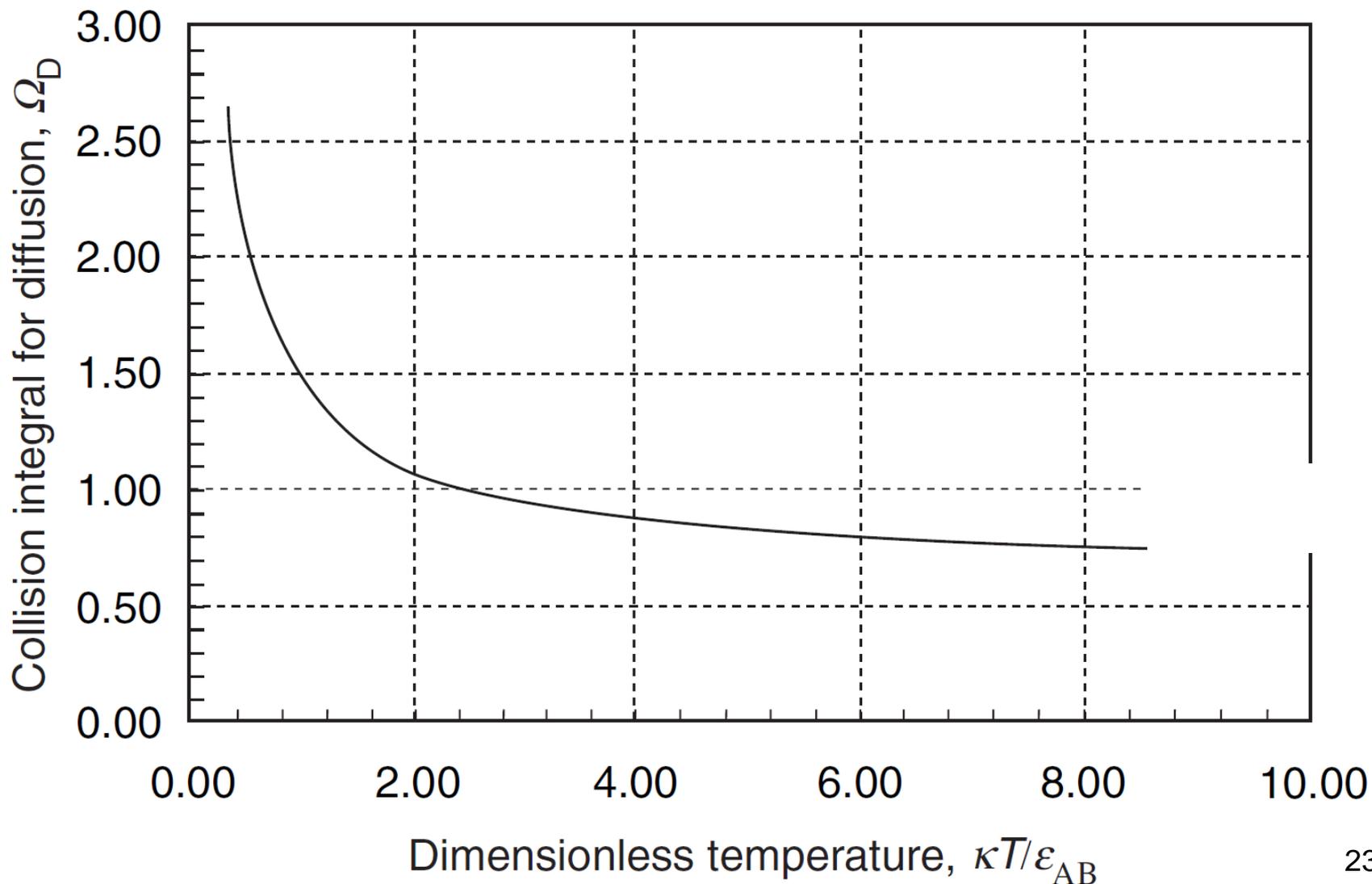
$$E = 1.03587$$

$$F = 1.52996$$

$$G = 1.76474$$

$$H = 3.89411$$

Bulk diffusion coefficient for gases at low pressure [12]



Bulk diffusion coefficient for gases at high density

The behavior of gases at high pressures (dense gases) and of liquids is not well understood and difficult to interpret to a mathematical evaluation. The following approach can be used for estimating the mass diffusivity of gases at high pressures. The method is very good for gases at low pressures. At high pressures, due to the lack of large number of experimental data, a comparison is difficult to make.

Diffusion coefficient for gas mixtures [8]

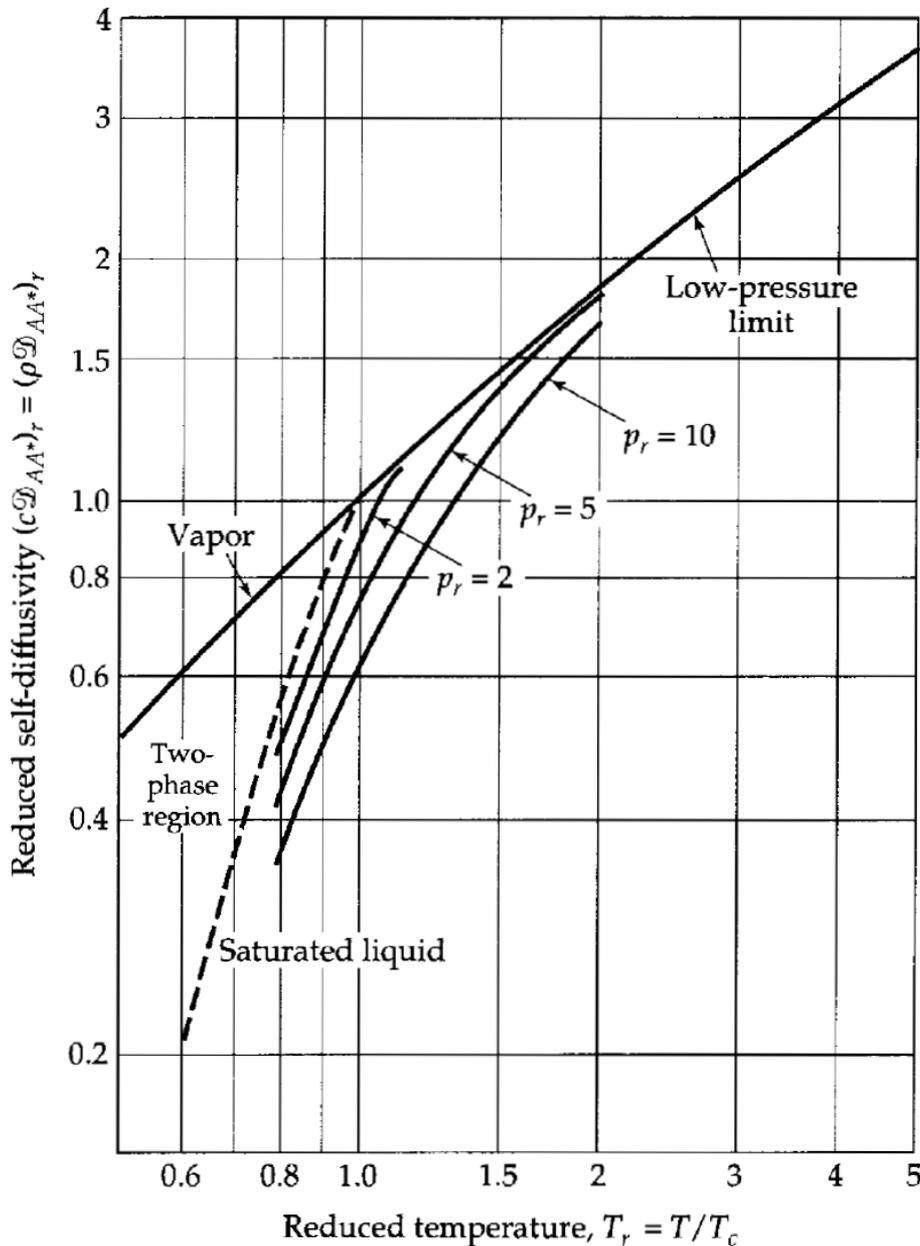


Fig. 17.2-1. A corresponding-states plot for the reduced self-diffusivity. Here $(cD_{AA^*})_r = (\rho D_{AA^*})_r$ for Ar, Kr, Xe, and CH_4 is plotted as a function of reduced temperature for several values of the reduced pressure. This chart is based on diffusivity data of J. J. van Loef and E. G. D. Cohen, *Physica A*, **156**, 522–533 (1989), the compressibility function of B. I. Lee and M. G. Kesler, *AIChE Journal*, **21**, 510–527 (1975), and Eq. 17.3-11 for the low-pressure limit.

Diffusion coefficient for gas mixtures [8]

$$cD_{AB} = (cD_{AB})_r (cD_{AB})_c$$

The value of $(cD_{AB})_r$ can be obtained from the graph above by knowing reduced temperature and reduced pressure.

$$T_r = \frac{T}{\sqrt{T_{cA} T_{cB}}}$$

$$p_r = \frac{p}{\sqrt{p_{cA} p_{cB}}}$$

$$(cD_{AB})_c = 2.96 \times 10^{-6} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \frac{(p_{cA} p_{cB})^{1/3}}{(T_{cA} T_{cB})^{1/12}}$$

Where, D_{AB} is in cm^2/s , T in K, and p_c in atm.

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