

# Lecture 27

**Chemical Reaction Engineering** (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

# Web Lecture 27

## Class Lecture 23

- How Reaction Rate Varies with:
  1. Temperature
  2. Catalyst Particle Size
  3. External Flow Rate
- For
  - A. Reaction Rate Limited Reactors
  - B. Internal Diffusion Limited Reactions
  - C. External Rate Limited Reactions

And all 9 combinations of numbers and letters,  
Eq. 1A, 1B, 1C, 2A, 2B, 2C and 3A, 3B and 3C.



### **Svante August Arrhenius**

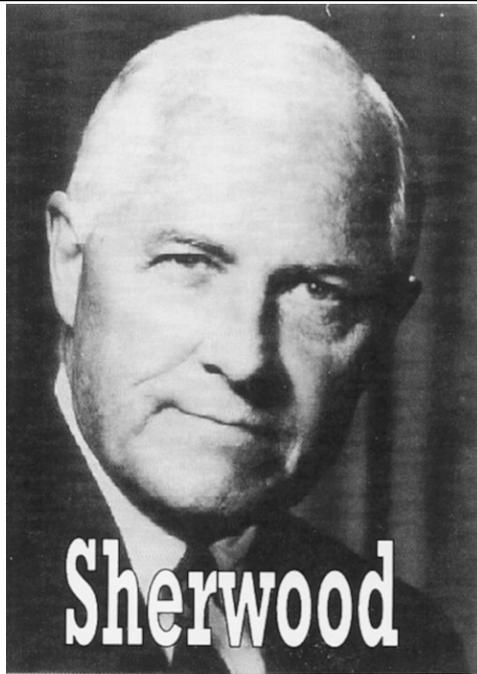
Born: February 19, 1859, Vik, Sweden

Died: October 2, 1927, Stockholm, Sweden

Arrhenius is said to have taught himself to read at the age of three and to have become interested in mathematics from watching his father add columns of figures. In 1876, he entered the University of Uppsala, studying mathematics, chemistry and physics. In 1881, he went to Stockholm to work under Professor E. Edlund where he began assisting on electromotive force measurements in spark discharges. This resulted in his thesis (1884) "Investigations on the galvanic conductivity of electrolytes." From his results the author concluded that electrolytes, when dissolved in water, become to varying degrees dissociated into electrically opposite positive and negative ions. The degree of dissociation depended above all on the nature of the substance and its concentration in the solution - being more developed the greater the dilution. Ions were supposed to be the carriers of the electric current, but also of the chemical activity. The relation between the actual number of ions and their number at great dilution (when all the molecules were dissociated) gave a quantity of special interest ("activity constant"). In late 1890's, when electrically charged subatomic particles were discovered, Arrhenius' ionic theory suddenly made sense. In 1903, he received the Nobel Prize in chemistry in recognition of services rendered to the advancement of chemistry by his electrolytic theory of dissociation. Arrhenius also studied the kinetic rate of inversion of cane sugar (saccharose), and through acids he discussed the temperature dependence of rate.

$$\ln k = \ln A - \frac{E_A}{RT}$$

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**Thomas Kilgore Sherwood**

Born: July 25, 1903; Columbus, Ohio  
 Died: January 14, 1976.

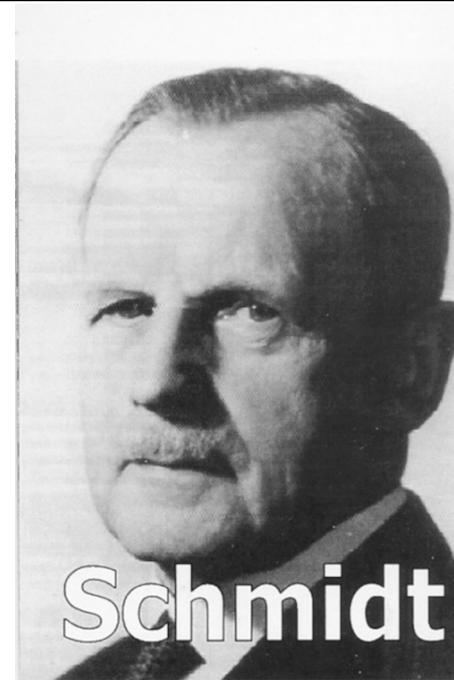
Sherwood was one of America's great chemical engineers. He came to M.I.T. in 1923 for graduate work in the Chemical Engineering Department and completed his doctoral thesis under Warren K. Lewis entitled "The Mechanism of the Drying of Solids" in 1929. From 1930 to 1969 he was professor at M.I.T. contributing decisively to the standards of excellence of this famous institution.

Sherwood's primary research area was mass transfer and its interaction with flow and with chemical reaction and industrial process operations in which those phenomena played an important part. His rapid rise to the position of world authority in the field of mass transfer was accelerated by the appearance of his book, "Absorption and Extraction", the first significant text in this area, published in 1937. Completely rewritten, with Pigford and Wilke in 1974 under the title "Mass Transfer", the book has had enormous influence. The worldwide use of the Sherwood Number is a memorial to that effort

In addition to three honorary doctorates many awards were bestowed on Sherwood, such as the U.S. Medal for Merit in 1948 and the Lewis Award in 1972.

$$Sh = \frac{h_{\text{mass}} L}{k_f}$$

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**Ernst Schmidt**

Born: February 11, 1892; Vögelsen, Germany  
 Died: 1975

German pioneer in thermodynamics. Studied civil & electrical engineering at Dresden and München. Joined Laboratory for Applied Physics at Technical University, München, in 1919.

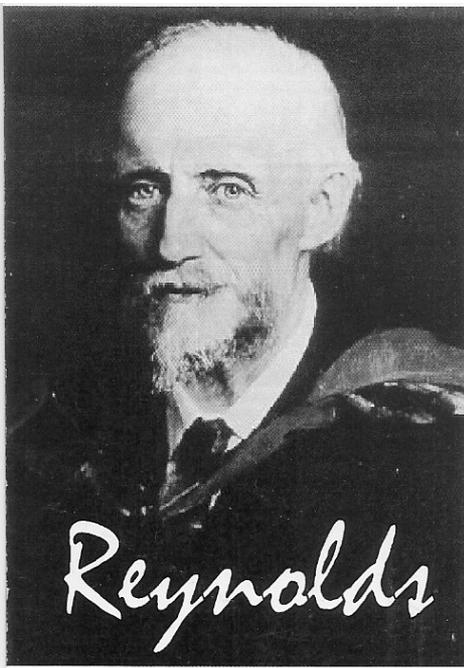
Early research was a careful measurement of the radiation properties of solids, from which he developed the use of aluminum foil as an effective radiation shield.

Became director (1925) of Engineering Laboratory at the Technical University, Danzig. Published graphical difference method for unsteady heat conduction. First to measure velocity & temperature fields in a free convection boundary layer and heat transfer coefficients in droplet condensation.

Noted analogy between heat and mass transfer and the dimensionless quantity involved (Schmidt Number). Became director of the Institute for Propulsion of the newly founded Aeronautical Research Establishment at Braunschweig in 1937. Occupied chair for thermodynamics at the Technical University of München in 1952, which had been held by Nusselt. Continued his scientific activity after his retirement (1961) until his death. Received the Ludwig Prandtl Ring, The Max Jacob Award and The Grashof Commemorative Medal.

$$Sc = \frac{v}{D_{AB}} = \frac{\text{momentum}}{\text{mass diffusivity}}$$

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### Osbourne Reynolds

Born: Aug. 23, 1842; Belfast, Ireland  
 Died: Feb. 21, 1912, Somerset, England

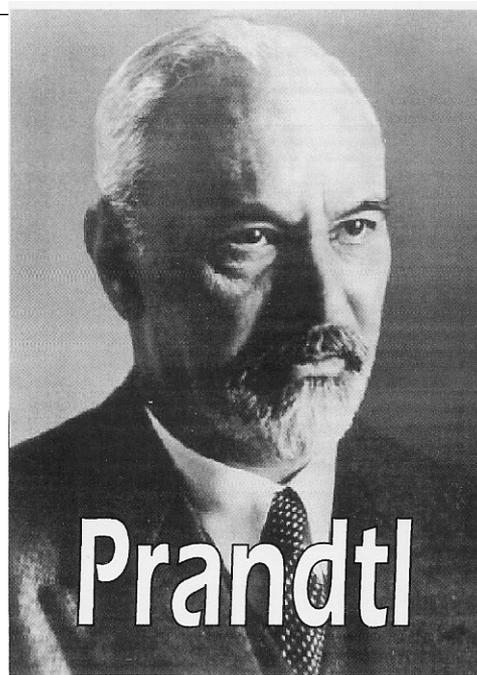
English engineer and physicist, best known for his work in the field of hydraulics and hydrodynamics. Gained early workshop experience and graduated from Queens' College Cambridge in 1867. Became the first professor of engineering in the Owens College, Manchester in 1868. Elected a fellow of the Royal Society in 1877 and a Royal Medallist in 1888.

Reynolds' studies of condensation and the transfer of heat between solids and fluids brought radical revision in boiler and condenser design, while his work on turbine pumps laid the foundation of their rapid development. A fundamentalist among engineers, he formulated the theory of lubrication (1886), and in his classical paper on the law of resistance in parallel channels (1883) investigated the transition from smooth, or laminar, to turbulent flow, later (1889) developed the mathematical framework which became standard in turbulence work.

Name perpetuated in the *Reynolds Number*, a criterion for dynamic similarity and hence for correct modeling in fluid flow experiments. Among his other work was the explanation of the radiometer and an early absolute determination of the mechanical equivalent of heat. Retired 1905.

$$Re = \frac{vL}{\nu} = \frac{\text{inertial forces}}{\text{viscous forces}}$$

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### Ludwig Prandtl

Born: February 4, 1875; Freising, Bavaria  
 Died: August 15, 1953; Göttinger, Germany

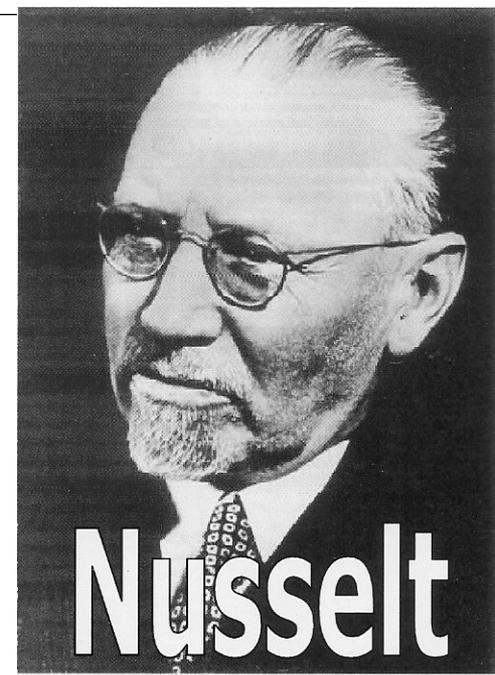
German physicist famous for his work in aeronautics. He qualified at München in 1900 with a thesis on elastic stability, and was professor of applied mechanics at Göttingen from 1904 until his death. In 1925 he became director of The Kaiser Wilhelm Institute for Fluid Mechanics.

His discovery (1904) of the "Boundary Layer" which adjoins the surface of a body moving in a fluid leading to an understanding of skin friction drag and of the way in which streamlining reduces the drag of airplane wings and other moving bodies. His work on wing theory, published in 1918-1919, which followed that of F.W. Lanchester (1902-1907) but was carried out independently, elucidated the flow over plane wings of finite span.

Prandtl made decisive advances in boundary layer and wing theories, and his work became the basic material of aeronautics. He also made important contributions to the theories of supersonic flow and of turbulence, besides contributing much to the development of wind tunnels and other aerodynamic equipment. In addition, he devised the soap-film analogy for the torsion of noncircular sections and wrote on the theory of plasticity and of meteorology.

$$Pr = \frac{\nu}{\alpha} = \frac{\text{momentum}}{\text{thermal diffusivity}}$$

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### Wilhelm Nusselt

Born: November 25, 1882; Nürnberg, Germany  
 Died: September 1, 1957; München, Germany

Studied machinery at the Technical Universities of Berlin-Charlottenburg and München. Graduated in 1904 and conducted advanced studies in mathematics and physics. Became an assistant to Knoblauch at the Laboratory for Technical Physics in München and completed his doctoral thesis on the conductivity of insulating materials in 1907, using the "Nusselt Sphere" for his experiments.

From 1907 to 1909 he worked as an assistant of Mollier in Dresden, qualifying himself for a professorship with a work on heat and momentum transfer in tubes. In 1915, published his pioneer paper: "The Basic Laws of Heat Transfer" in which he first proposed the dimensionless groups now known as the principal parameters in the similarity theory of heat transfer.

Other works include film condensation of steam on vertical surfaces, combustion of pulverized coal and the analogy between heat and mass transfer in evaporation, the well known solutions for laminar heat transfer in the entrance region of tubes, and for heat exchange in cross-flow and the basic theory of regenerators.

Professor at the Technical Universities of Karlsruhe from 1920 to 1925 and at München from 1925 until retirement in 1952. He was awarded the Gauss-Medal and the Grashof Commemorative Medal.

$$Nu = \frac{hL}{k_f} \equiv \frac{\text{dimensionless temperature}}{\text{gradient at surface of solid}}$$

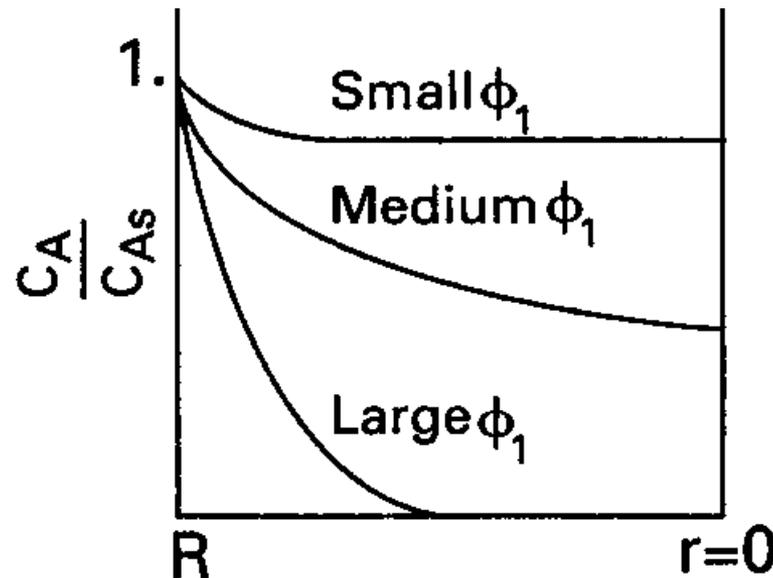
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## Internal Diffusion

How will we know these trends discussed in the last slide:

1. Solve the diffusion and reaction equation for catalyst particle for concentration gradient

$$C_A = \frac{C_{A0}}{\lambda} \left| \frac{\text{Sinh}(\Theta_1 \lambda)}{\text{Sinh} \Theta_1} \right|$$



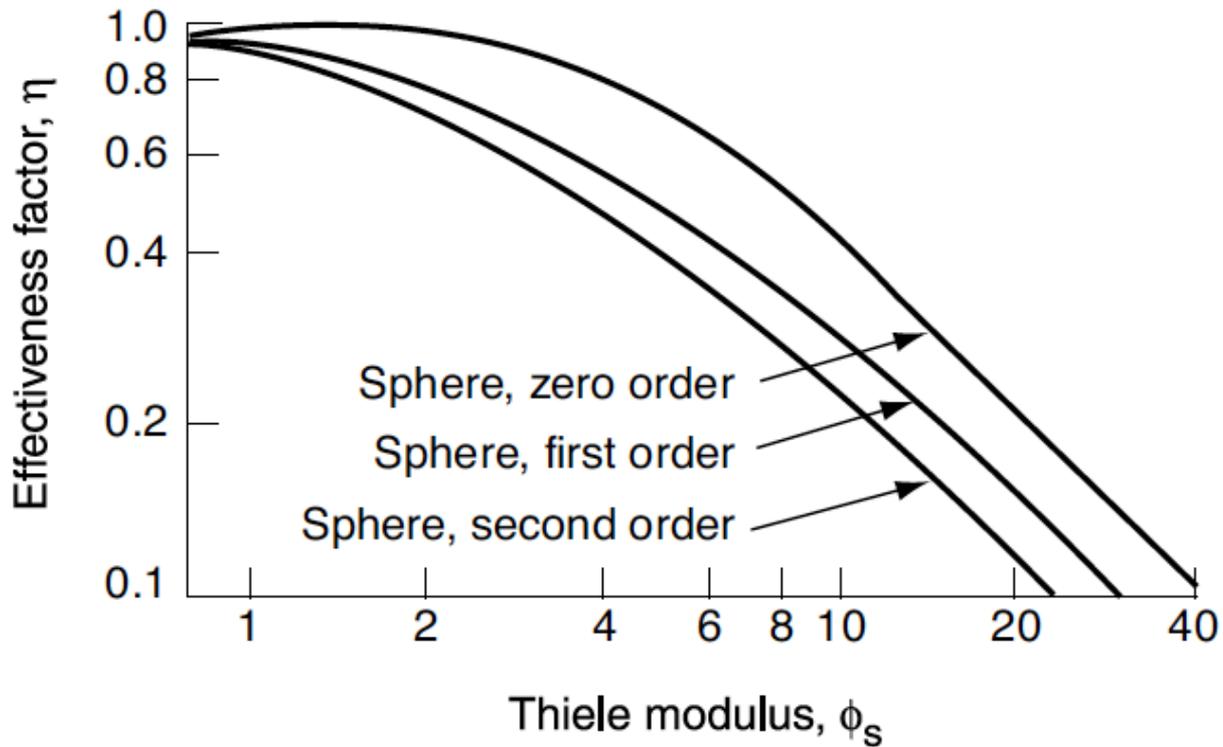
2. Find the true rate of reaction as a function of the external and internal surface reactions.

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions, } C_{As}, T_s} \quad (15-28)$$

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1) \quad (15-32)$$

$$\eta \approx \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}} \quad (15-33)$$

$$\begin{aligned} -r_A &= \left( \frac{\text{Actual reaction rate}}{\text{Reaction rate at } C_{As}} \right) \times (\text{Reaction rate at } C_{As}) \\ &= \eta (-r_{As}) \\ &= \eta (k_1 C_{As}) \end{aligned} \quad (15-34)$$



Zero order  $\phi_{s0} = R\sqrt{k_0'' S_a \rho_c / D_e C_{A0}} = R\sqrt{k_0 / D_e C_{A0}}$

First order  $\phi_{s1} = R\sqrt{k_1'' S_a \rho_c / D_e} = R\sqrt{k_1 / D_e}$

Second order  $\phi_{s2} = R\sqrt{k_2'' S_a \rho_c C_{A0} / D_e} = R\sqrt{k_2 C_{A0} / D_e}$

# Internal Diffusion

$$\eta \approx \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}} \quad (15-33)$$

$$-r_A = \left( \frac{\text{Actual reaction rate}}{\text{Reaction rate at } C_{As}} \right) \times (\text{Reaction rate at } C_{As})$$

$$= \eta (-r_{As})$$

$$= \eta (k_1 C_{As})$$

$$= \eta \approx \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}}$$

(15-34)

$$D \sim T^{1.75}$$

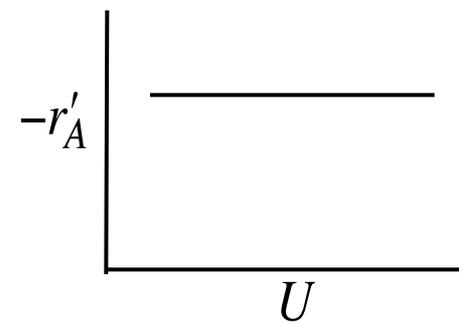
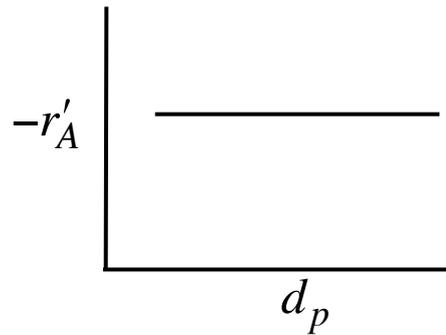
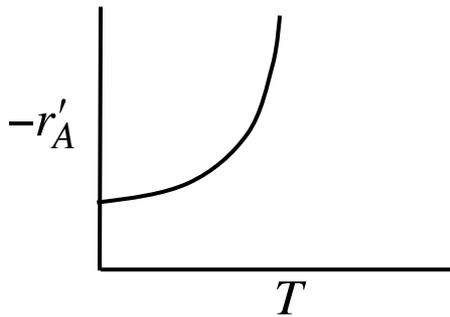
$$k_r \sim e^{-E/RT}$$

$$-r'_A = \frac{3}{R} \sqrt{\frac{D_e}{k_r}} k_r = \frac{3}{R} \sqrt{D_e k_r}$$

$$-r'_A \approx D^{0.875} e^{-E/2RT}$$

# Surface Reaction

$$-r_A = k_r C_A = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$



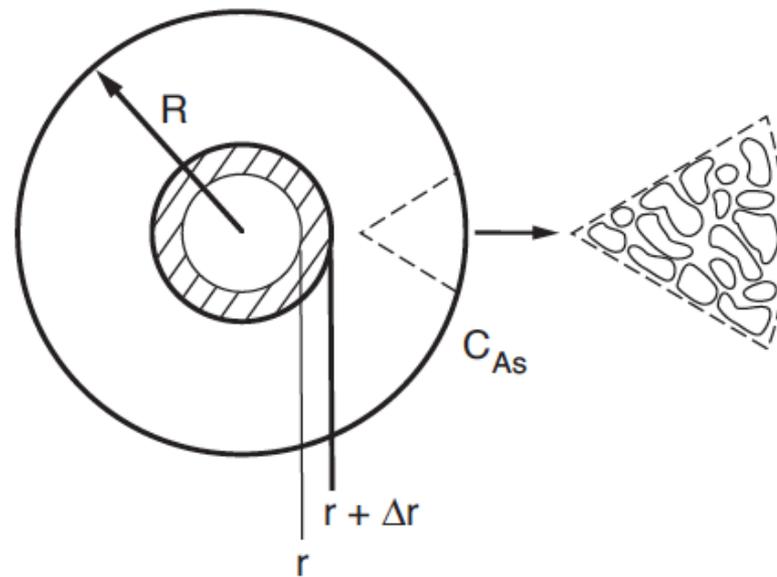


Figure 15-3 Shell balance on a catalyst pellet.

$$\begin{aligned}
 & \text{(In at } r) \quad - \quad \text{(Out at } r + \Delta r) \quad + \quad \text{(Generation within } \Delta r) = 0 \\
 & (W_{Ar} \times 4\pi r^2|_r) - (W_{Ar} \times 4\pi r^2|_{r+\Delta r}) + (r'_A \rho_c \times 4\pi r_m^2 \Delta r) = 0 \quad (15-5)
 \end{aligned}$$

$$\frac{d(W_{Ar} r^2)}{dr} - r'_A \rho_c r^2 = 0$$

$$W_{Ar} = -D_e \frac{dC_A}{dr} \quad \text{and} \quad -r_A = -k_n C_A^n$$

$$\frac{d[-D_e(dC_A/dr)r^2]}{dr} - r^2 \rho_c r'_A = 0$$

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \left( \frac{dC_A}{dr} \right) - \frac{k_n}{D_e} C_A^n = 0$$

*The boundary conditions are:*

1. The concentration remains finite at the center of the pellet:

$$C_A \text{ is finite} \quad \text{at } r = 0$$

2. At the external surface of the catalyst pellet, the concentration is  $C_{As}$ :

$$C_A = C_{As} \quad \text{at } r = R$$

### 15.2.3 Writing the Diffusion with Catalytic Reaction Equation in Dimensionless Form

$$\psi = \frac{C_A}{C_{As}}$$

$$\lambda = \frac{r}{R}$$

$$\frac{dC_A}{dr} = \left( \frac{dC_A}{d\lambda} \right) \frac{d\lambda}{dr} = \frac{d\psi}{d\lambda} \left( \frac{dC_A}{d\psi} \right) \frac{d\lambda}{dr}$$

$$\frac{dC_A}{d\psi} = C_{As} \quad \text{and} \quad \frac{d\lambda}{dr} = \frac{1}{R}$$

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \left( \frac{dC_A}{dr} \right) - \frac{k_n}{D_e} C_A^n = 0$$

$$\frac{dC_A}{dr} = \frac{d\psi}{d\lambda} \frac{C_{As}}{R}$$

$$W_{Ar} = -D_e \frac{dC_A}{dr} = -\frac{D_e C_{As}}{R} \left( \frac{d\psi}{d\lambda} \right)$$

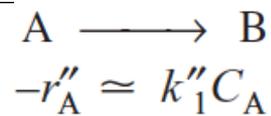
$$\frac{d^2 C_A}{dr^2} = \frac{d}{dr} \left( \frac{dC_A}{dr} \right) = \frac{d}{d\lambda} \left( \frac{d\psi}{d\lambda} \frac{C_{As}}{R} \right) \frac{d\lambda}{dr} = \frac{d^2 \psi}{d\lambda^2} \left( \frac{C_{As}}{R^2} \right)$$

$$\frac{d^2 \psi}{d\lambda^2} + \frac{2}{\lambda} \left( \frac{d\psi}{d\lambda} \right) - \phi_n^2 \psi^n = 0$$

$$\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda} \left( \frac{d\psi}{d\lambda} \right) - \phi_n^2 \psi^n = 0$$

$$\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e}$$

$$\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R C_{As}^n}{D_e [(C_{As} - 0)/R]} = \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}}$$



For a first-order reaction, Equation (15-19) becomes

$$\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda} \frac{d\psi}{d\lambda} - \phi_1^2 \psi = 0$$

The Thiele modulus for this first order reaction is

$$\phi_1 = R \sqrt{\frac{k_1'' \rho_c S_a}{D_e}} = R \sqrt{\frac{k_1}{D_e}}$$

$$\text{B.C. 1: } \psi = 1 \quad \text{at } \lambda = 1$$

$$\text{B.C. 2: } \psi \text{ is finite} \quad \text{at } \lambda = 0$$

$$\frac{d^2y}{d\lambda^2} - \phi_1^2 y = 0 \quad (15-25)$$

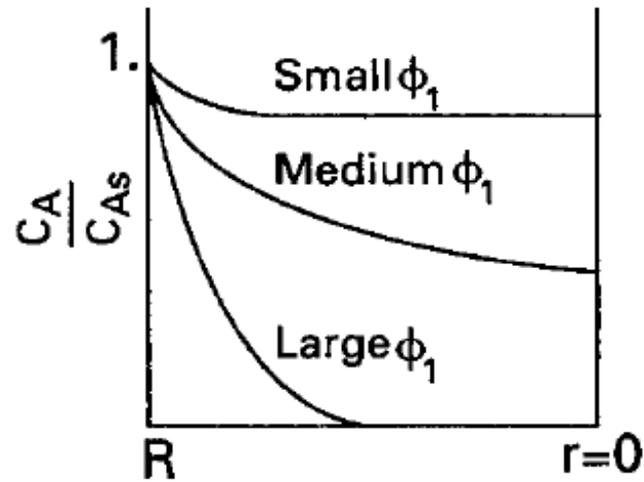
This differential equation has the following solution (Appendix A.3):

$$y = A_1 \cosh \phi_1 \lambda + B_1 \sinh \phi_1 \lambda$$

In terms of  $\psi$ ,

$$\psi = \frac{A_1}{\lambda} \cosh \phi_1 \lambda + \frac{B_1}{\lambda} \sinh \phi_1 \lambda \quad (15-26)$$

$$\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda} \left( \frac{\sinh \phi_1 \lambda}{\sinh \phi_1} \right)$$



**Figure 15-4** Concentration profile in a spherical catalyst pellet.

$$\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda} \left( \frac{\sinh \phi_1 \lambda}{\sinh \phi_1} \right)$$

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s}$$

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r'_A}{-r'_{As}} = \frac{-r''_A}{-r''_{As}}$$

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r_A \times \text{Volume of catalyst particle}}{-r_{As} \times \text{Volume of catalyst particle}} = \frac{M_A}{M_{As}}$$

$$M_{As} = \frac{\text{Rate at external surface}}{\text{Volume}} \times \text{Volume of catalyst}$$

$$= -r_{As} \times \left( \frac{4}{3} \pi R^3 \right) = k C_{As} \left( \frac{4}{3} \pi R^3 \right)$$

$$M_A = 4\pi R D_e C_{As} \left. \frac{d\psi}{d\lambda} \right|_{\lambda=1}$$

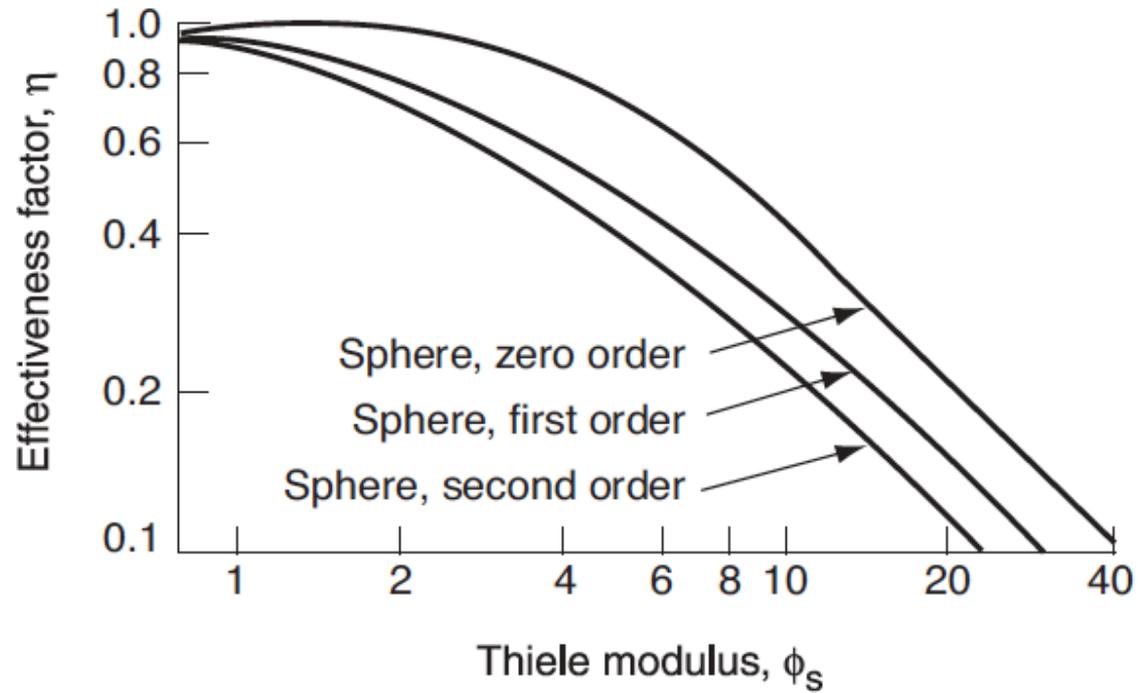
$$M_A = 4\pi R D_e C_{As} (\phi_1 \coth \phi_1 - 1)$$

$$M_A = 4\pi R D_e C_{As} (\phi_1 \coth \phi_1 - 1)$$

$$\eta = \frac{M_A}{M_{As}} = \frac{M_A}{(-r_{As}) \left( \frac{4}{3} \pi R^3 \right)} = \frac{4\pi R D_e C_{As}}{k_1 C_{As} \frac{4}{3} \pi R^3} (\phi_1 \coth \phi_1 - 1)$$

$$= 3 \frac{1}{\underbrace{k_1 R^2 / D_e}_{\phi_1^2}} (\phi_1 \coth \phi_1 - 1)$$

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1)$$

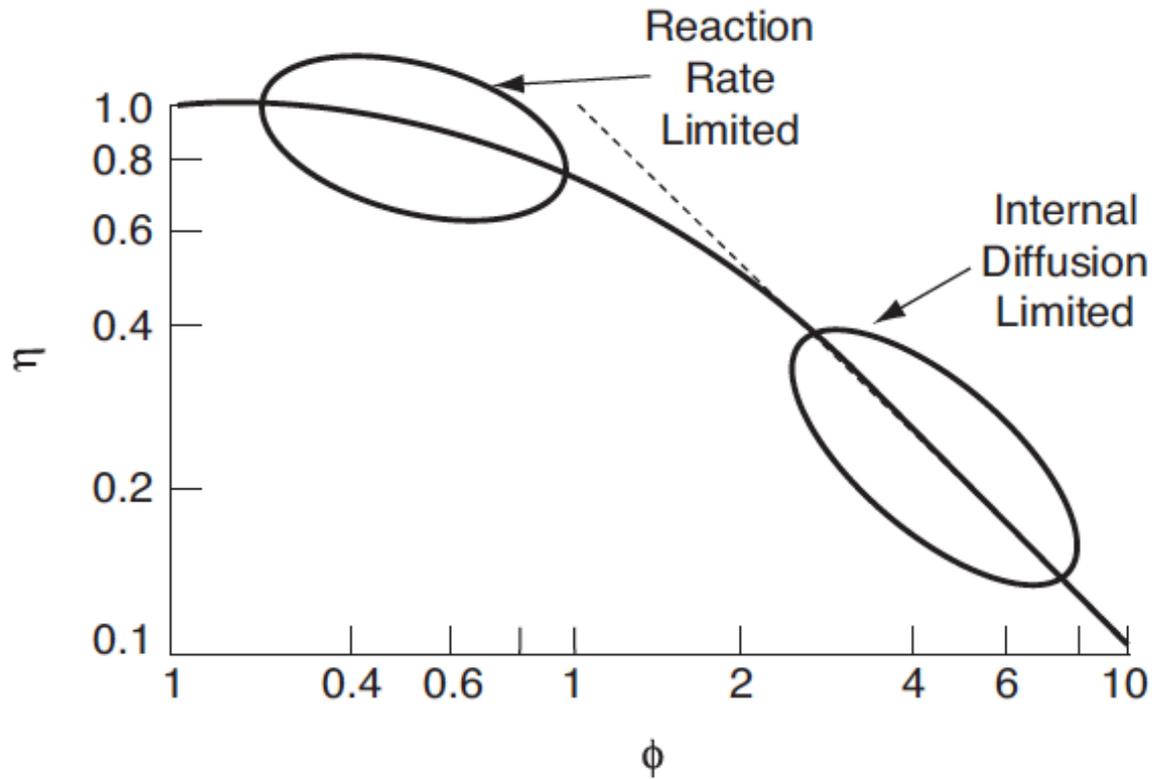


Zero order  $\phi_{s0} = R\sqrt{k_0'' S_a \rho_c / D_e C_{A0}} = R\sqrt{k_0 / D_e C_{A0}}$

First order  $\phi_{s1} = R\sqrt{k_1'' S_a \rho_c / D_e} = R\sqrt{k_1 / D_e}$

Second order  $\phi_{s2} = R\sqrt{k_2'' S_a \rho_c C_{A0} / D_e} = R\sqrt{k_2 C_{A0} / D_e}$

(a)



Sphere  $\phi_1 = (R/3)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{3}\sqrt{k_1 / D_e}$

Cylinder  $\phi_1 = (R/2)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{2}\sqrt{k_1 / D_e}$

Slab  $\phi_1 = L\sqrt{k_1'' S_a \rho_c / D_e} = L\sqrt{k_1 / D_e}$

(b)

If  $\phi_1 > 2$

then  $\eta \approx \frac{3}{\phi_1^2} [\phi_1 - 1]$

If  $\phi_1 > 20$

then  $\eta \approx \frac{3}{\phi_1}$

$$\eta \approx \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}}$$

## Articular Cartilage Defect

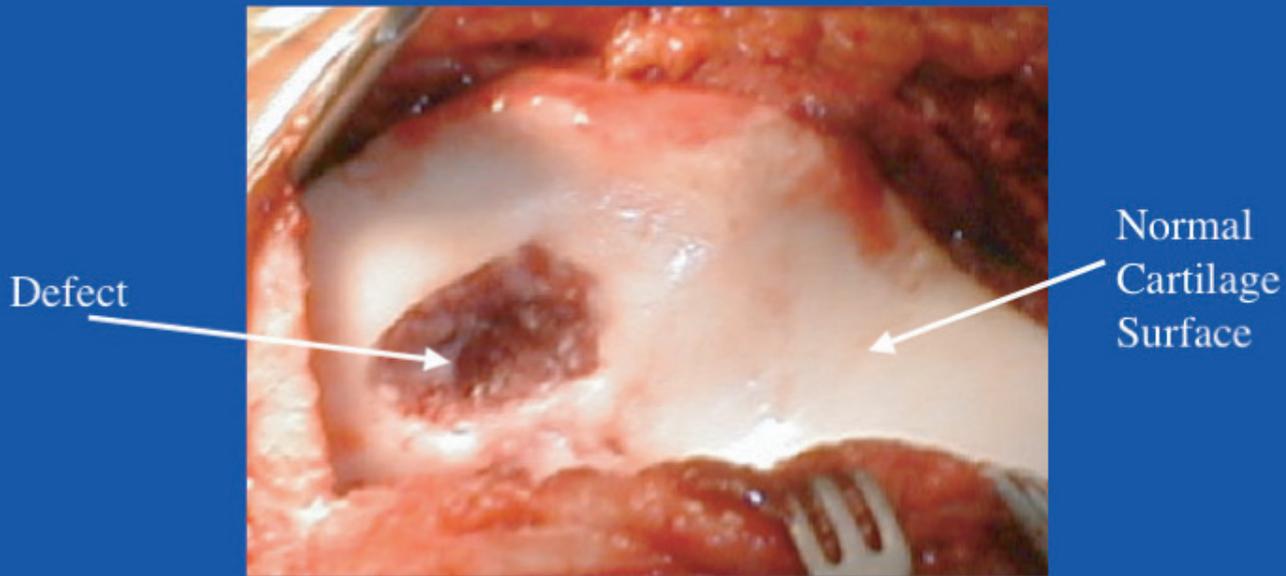
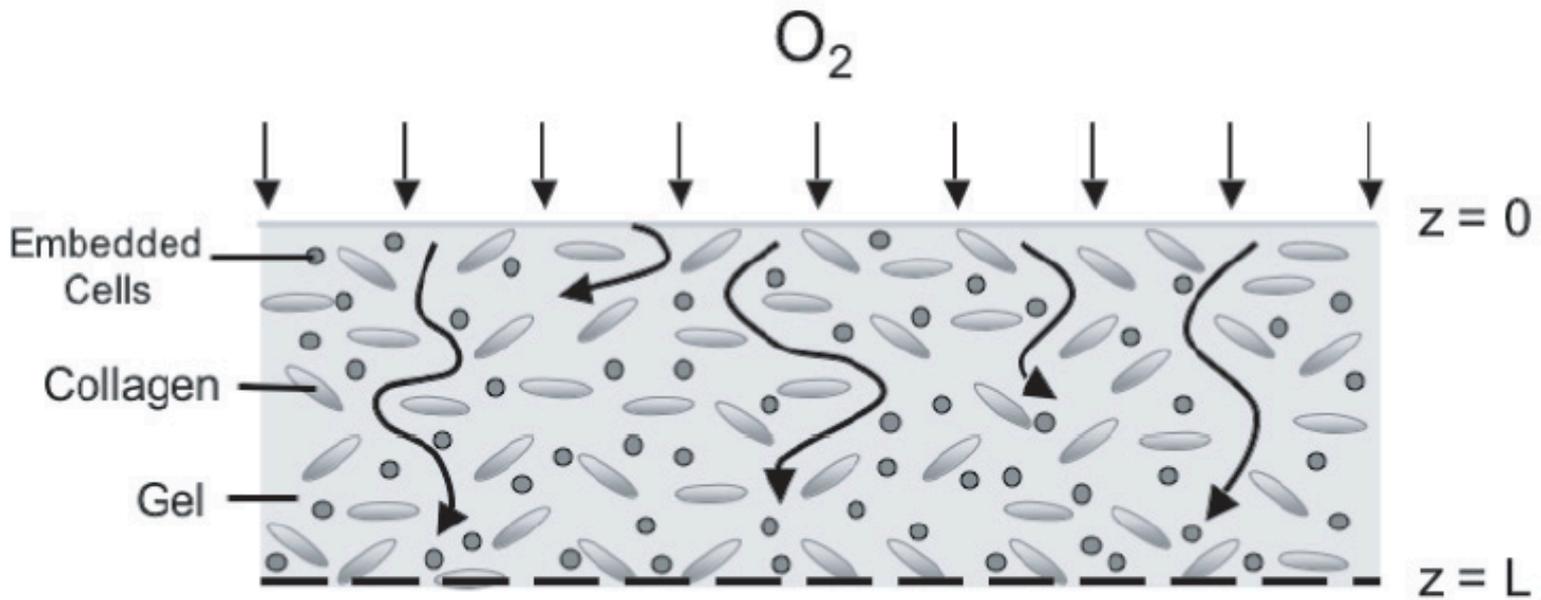
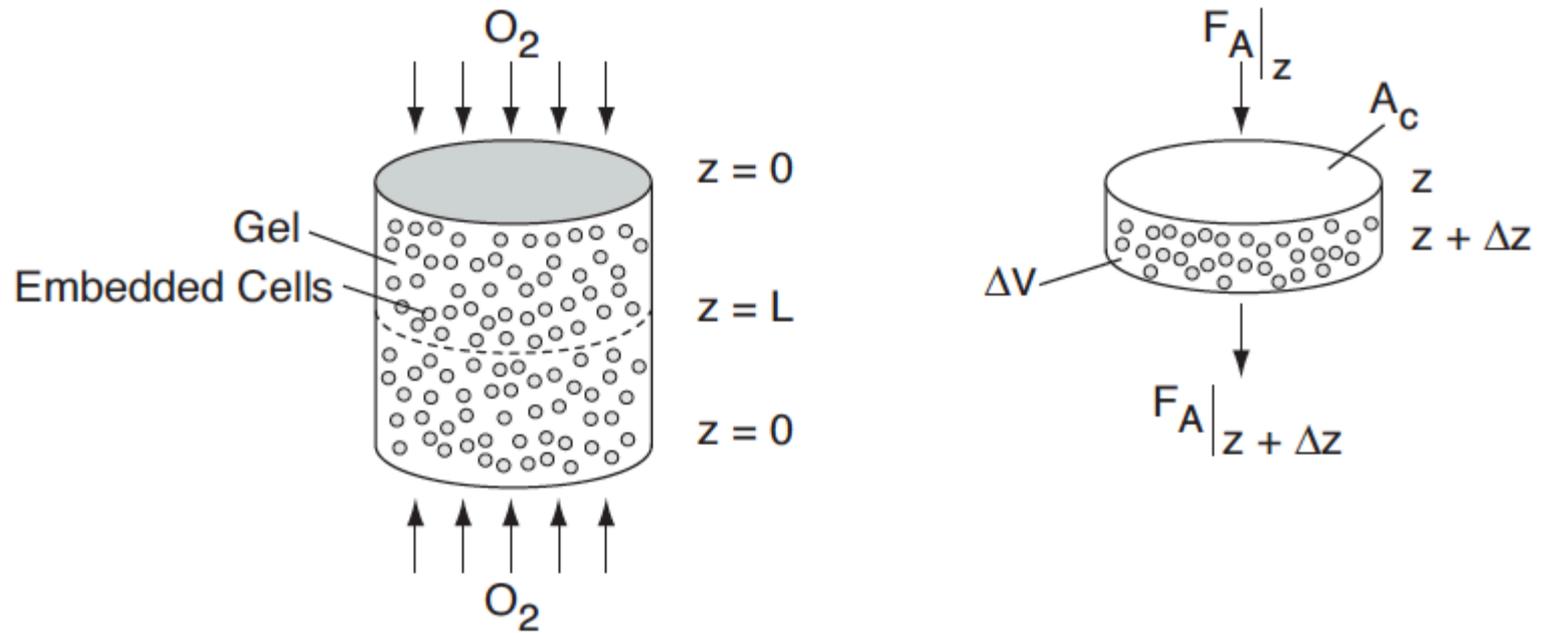


Figure E15-1.1 Damaged cartilage. (Figure courtesy of Newsweek, September 3, 2001.)



Diffusion of  $O_2$  around collagen



**Figure E15-1.2** Schematic of cartilage cell system.

A mole balance on oxygen, A,

$$F_A|_z - F_A|_{z+\Delta z} + r_A A_c \Delta z = 0$$

Dividing by  $\Delta z$  and taking the limit as  $\Delta z \rightarrow 0$  gives

$$\frac{1}{A_c} \frac{dF_A}{dz} + r_A = 0$$

$$F_A = A_c \left[ -D_{AB} \frac{dC_A}{dz} + UC_A \right]$$

$$D_{AB} \frac{d^2 C_A}{dz^2} + r_A = 0$$

$$D_{AB} \frac{d^2 C_A}{dz^2} - k = 0$$

$$\lambda = \frac{z}{L}, \quad \psi = \frac{C_A}{C_{A0}}$$

$$\frac{d^2 \psi}{d\lambda^2} - \frac{kL^2}{D_{AB} C_{A0}} = 0$$

$$\phi_0 = \frac{kA_c L}{A_c D_{AB} \frac{(C_{A0} - 0)}{L}} = \phi_0 = \frac{k}{2D_{AB} C_{A0}} L^2 = \frac{\text{Reaction Rate}}{\text{Diffusion Rate}}$$

$$\frac{d^2\psi}{d\lambda^2} - 2\phi_0 = 0$$

$$\text{At } \lambda = 0 \quad \psi = 1 \quad C_A = C_{A0}$$

$$\text{At } \lambda = 1 \quad \frac{d\psi}{d\lambda} = 0 \quad \text{Symmetry condition}$$

$$\frac{d\psi}{d\lambda} = 2\phi_0\lambda + K_1$$

$$\frac{d\psi}{d\lambda} = 2\phi_0(\lambda - 1)$$

$$\psi = \phi_0\lambda^2 - 2\phi_0\lambda + K_2$$

$$\psi = \phi_0\lambda(\lambda - 2) + 1$$

*Note:* The dimensionless concentration profile given by Equation (E15-1.13) is only valid for values of the Thiele modulus less than or equal to 1. This restriction can be easily seen if we set  $\phi_0 = 10$  and then calculate  $\psi$  at  $\lambda = 0.1$  to find  $\psi = -0.9$ , which is a negative concentration!! This condition is explored further in Problem P15-10<sub>B</sub>.

### Parameter Evaluation

Evaluating the zero-order rate constant,  $k$ , yields

$$k = \frac{10^{10} \text{ cells}}{\text{dm}^3} \cdot \frac{10^{-13} \text{ mole O}_2}{\text{cell} \cdot \text{h}} = 10^{-3} \text{ mole /dm}^3 \cdot \text{h}$$

and then the ratio

$$\frac{k}{2C_{A0}D_{AB}} = \frac{10^{-3} \text{ mol/dm}^3 \cdot \text{h}}{2 \times 0.2 \times 10^{-3} \text{ mol/dm}^3 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}}} = 70 \text{ cm}^{-2} \quad (\text{E15-1.14})$$

The Thiele modulus is

$$\boxed{\phi_0 = 70 \text{ cm}^{-2} L^2} \quad (\text{E15-1.15})$$

- (a) Consider the gel to be completely effective such that the concentration of oxygen is reduced to zero by the time it reaches the center of the gel. That is, if  $\psi = 0$  at  $\lambda = 1$ , we solve Equation (E15-1.13) to find that  $\phi_0 = 1$

$$\boxed{\psi = \phi_0 \lambda (\lambda - 2) + 1}$$

$$\phi_0 = 1 = \frac{70}{\text{cm}^2} L^2 \quad (\text{E15-1.16})$$

Solving for the gel half thickness  $L$  yields

$$L = 0.12 \text{ cm}$$