

Notes on reaction-diffusion cases with effectiveness factors greater than one!

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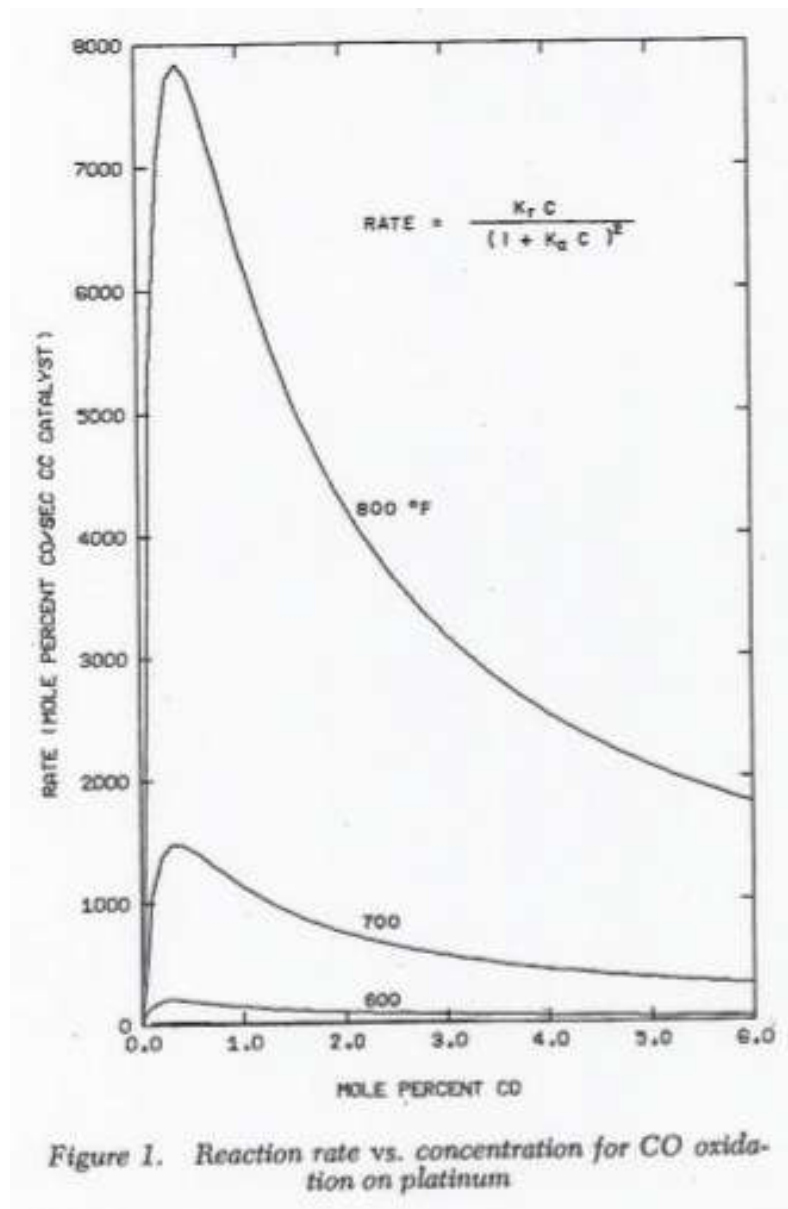
For isothermal n -th order reactions where $n \geq 0$, the catalyst effectiveness factor value is ≤ 1 . Effectiveness factor values > 1 can be obtained in some parameter ranges for isothermal catalysts with negative order reactions, and for non-isothermal catalysts with exothermic reactions.

Isothermal porous catalysts

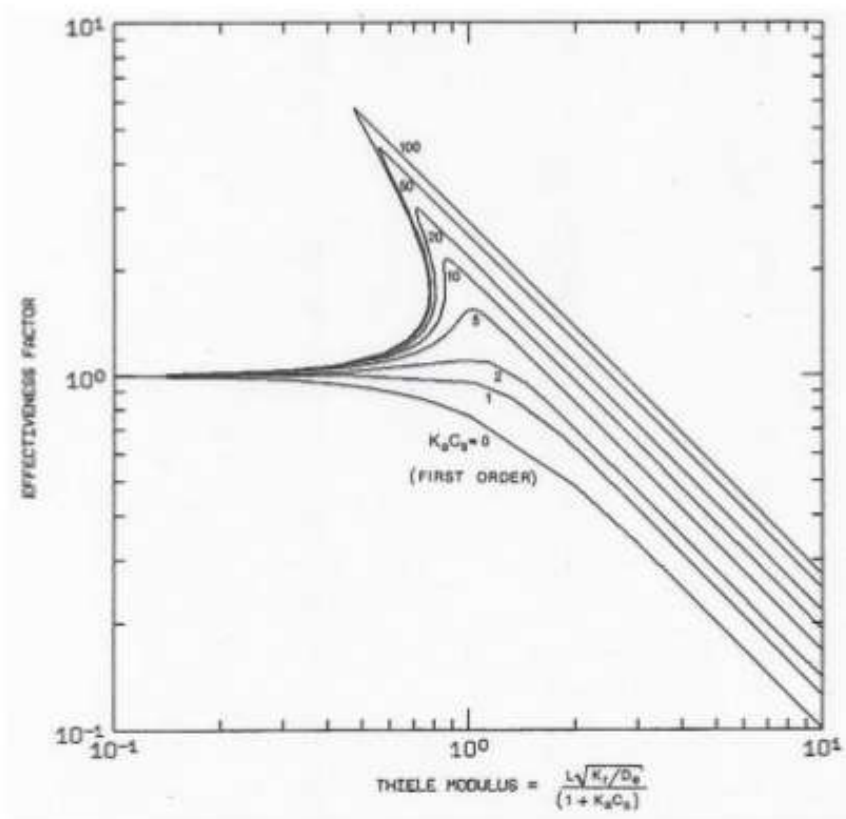
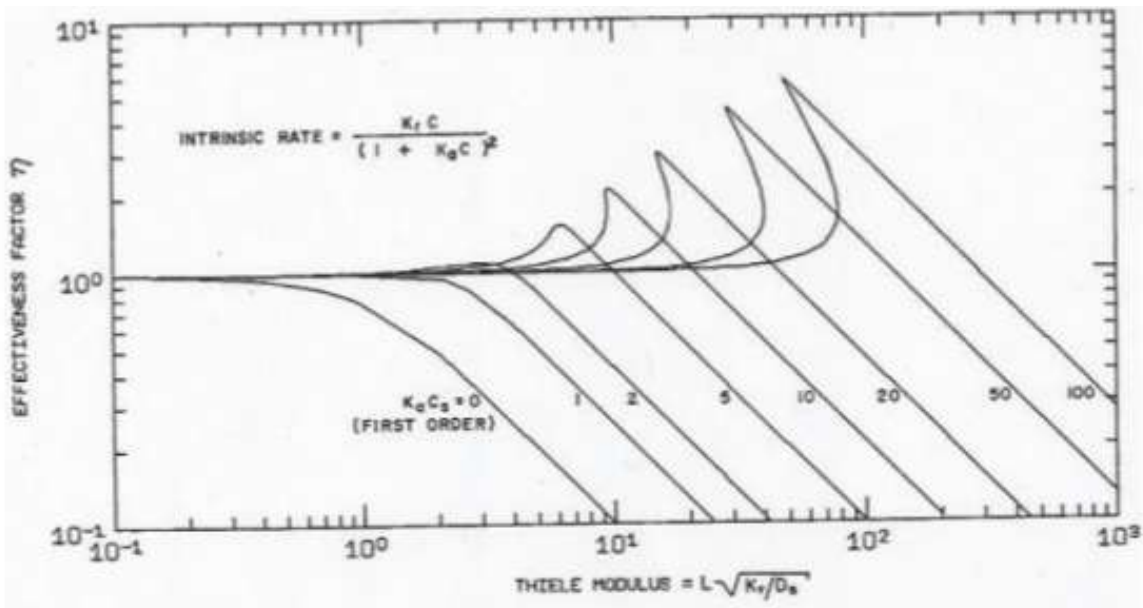
Reference for this section: J. Wei and E. R. Becker, "The optimum distribution of catalytic material in automotive catalysis," *ACS Adv. Chem. Ser.*, vol. 143, pp. 116-132, 1975.

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The authors considered a simplified rate equation for CO oxidation over Pt-group metal catalysts in the presence of excess O_2 :



For a slab-geometry (1D) porous catalytic layer, such as the "washcoat" in a monolith catalyst in an automobile catalytic converter, integration of the steady-state diffusion-reaction equation gives the following effectiveness factors:



Here are reactant concentration profiles for one value of $K_a C_s$ (adsorption equilibrium constant for reactant times reactant concentration at external surface of porous catalytic layer):

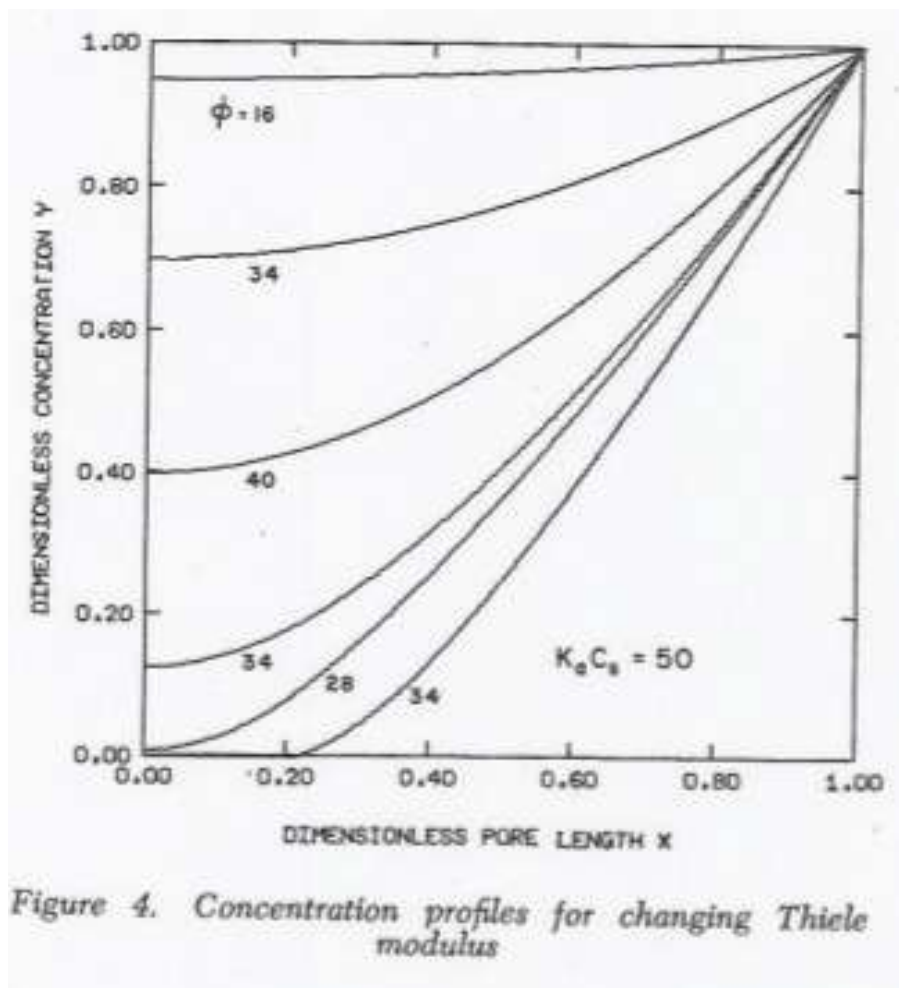


Figure 4. Concentration profiles for changing Thiele modulus

Note that, for a value of Thiele modulus, $\phi = 34$, there are three curves. At these conditions, there are "multiple steady states" possible, or "rate multiplicity." Which curve for $\phi = 34$ is established depends on the history of the system. For example, if the concentration at the external surface is being increased from a low value to a higher value, the lowest curve can be reached. The lowest concentration curve represents a high reaction rate state (large concentration gradient at external surface on right side) and a high effectiveness factor. If the concentration is increased further and then lowered to the previous value, the highest concentration curve will be established. The highest curve represents lower reaction rate state (smaller concentration gradient) and an effectiveness factor closer to one.

Thus, there is "hysteresis" observed in the overall reaction rate as the concentration is varied. The middle curve probably can't be reached by normal variation of parameters and is probably an unsteady state. Locate the position of these states on the effectiveness factor plots on the previous page.

The authors go on in the paper to consider the temperature dependence of the parameters K_r and K_a and also the temperature dependence of external mass transfer resistance. Below is a plot of steady-state reactant conversion vs. temperature:

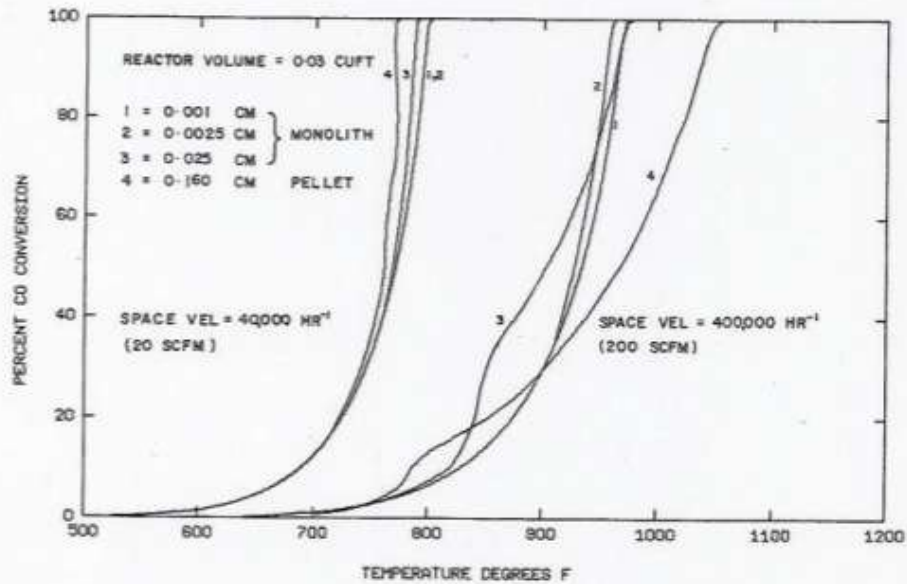


Figure 9. Effect of catalyst layer thickness on CO conversion for platinum kinetics

Inlet CO concentration, 4 mole %

At the higher space velocity and some temperatures, the thicker monolith catalyst layer and the pellet give higher conversion than the thinner monolith catalyst layers. The authors conclude:

In a negative first order reaction such as CO oxidation over platinum, a thick catalytic layer is often superior to a thin layer, especially when the space velocity of the gas is large and the inlet concentration of CO is high. However, these advantages are not very great when we measure results in terms of CO conversion efficiencies; it seldom amounts to more than a 28°C (50°F) shift in the temperature needed for 50% conversion. However, the effects of lead poisoning could increase this shift greatly, especially when lead deposition is concentrated in a zone of about 0.002 cm. Lead poisoning could also cause complete destruction of the egg shell catalyst but only a slight deterioration in the thick layer catalyst. It may be advantageous to have a sacrifice layer of alumina on the surface to adsorb lead and thereby protect the platinum in the interior.

The optimum distribution of catalytic material on the support depends on the kinetic order of the reaction catalyzed. When platinum is used for CO and hydrocarbon oxidation in automotive catalysis, the reverse of the normal wisdom is in order—platinum should be distributed toward the interior of the support layer to form a new type of egg yolk catalyst.

This is an old paper and the authors mention lead as a catalyst poison. Lead was removed from gasoline for this reason and because of health concerns. The remarks apply, however, to phosphorus from lubricating oil, which also serves as a catalyst poison.

Nonisothermal catalysts and exothermic reactions

Reference for this section: G. F. Froment and K. B. Bischoff, Chemical Reactor Analysis and Design, Wiley, 1990.

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The material and energy balance equations for reaction within a slab-geometry porous catalyst are:

$$\frac{d}{dz} \left[D_{eA} \frac{dC_s}{dz} \right] = r_A(C_s, T_s) \rho_s$$

$$- \frac{d}{dz} \left[\lambda_e \frac{dT_s}{dz} \right] = (-\Delta H) r_A(C_s, T_s) \rho_s$$

The spatial coordinate z is zero at the external surface and L at the layer centerplane for a layer of thickness $2L$ exposed to fluid on both sides, or L at a sealed, non-permeable face. The subscript s denotes properties of the solid and the fluid concentration of A inside the porous solid layer. The rate r_A for reactant A in these equations is positive-valued. The heat of reaction value is negative for an exothermic reaction, thus, for an exothermic reaction, the second derivative of temperature with respect to z has a negative value. At $z = 0$, the first derivatives are zero (zero-flux boundary condition). At the external surface, $z = L$, denoted by superscript s , the boundary conditions are that the concentration is C_s^s and the temperature is T_s^s .

The ratio of the temperature change across the layer to the temperature at the external surface (superscript s) can be considered as the dimensionless heat of reaction:

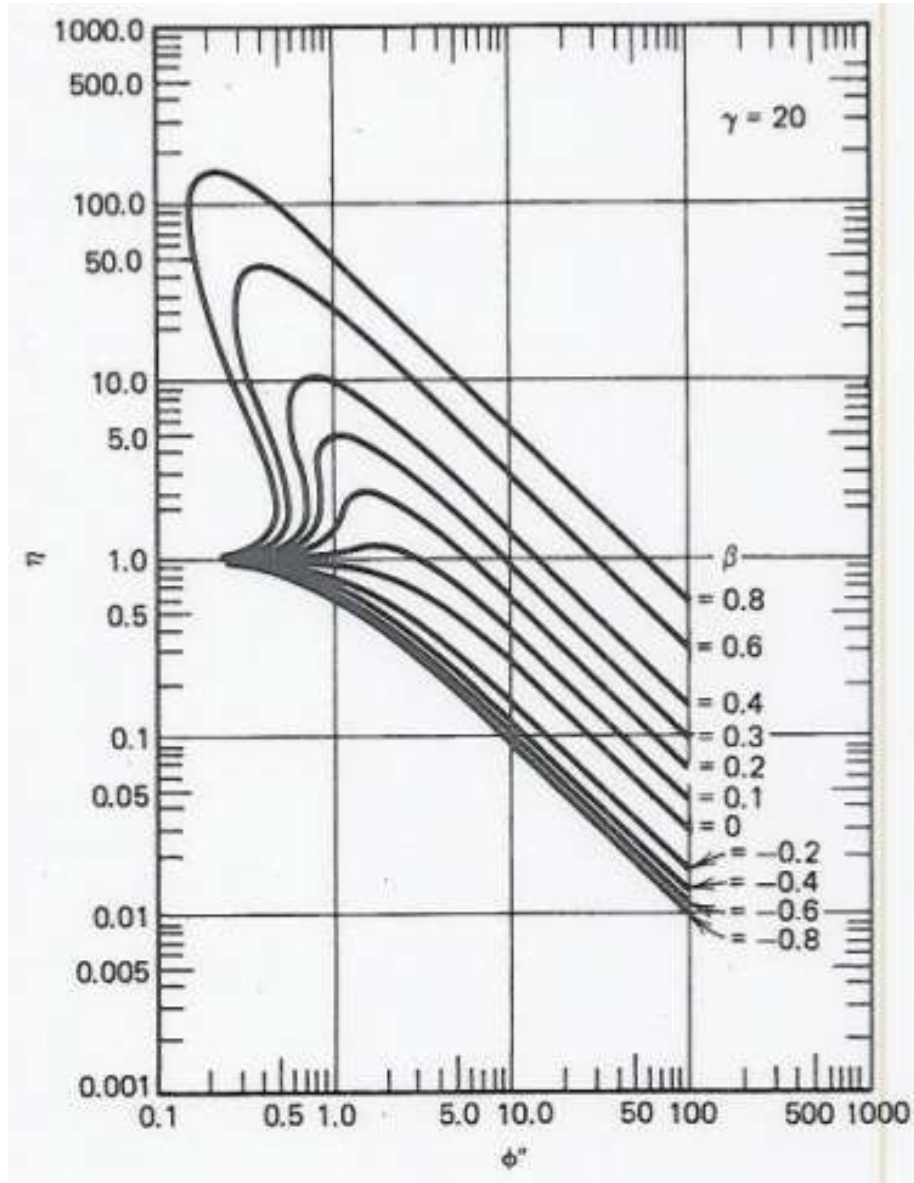
$$\frac{(\Delta T_s)_{max}}{T_s^s} = \frac{(-\Delta H) D_{eA} C_s^s}{\lambda_e T_s^s}$$

$$= \beta$$

Another important parameter is the dimensionless activation energy:

$$\gamma = \frac{E}{RT_s^s}$$

A plot of effectiveness factor shows the possibility of effectiveness factors greater than one for some parameter ranges:



The high branch of these curves can be approximated by the following formula:

$$\eta \cong \frac{1}{\phi_s} \exp\left(\frac{\beta\gamma}{5}\right)$$

The authors present some values for industrial catalysts:

PARAMETERS OF SOME EXOTHERMIC CATALYTIC REACTIONS*					
Reaction	β	γ	$\gamma\beta$	Lw'	ϕ
NH ₃ synthesis	0.000061	29.4	0.0018	0.00026	1.2
Synthesis of higher alcohols from CO and H ₂	0.00085	28.4	0.024	0.00020	—
Oxidation of CH ₃ OH to CH ₂ O	0.0109	16.0	0.175	0.0015	1.1
Synthesis of vinyl chloride from acetylene and HCl	0.25	6.5	1.65	0.1	0.27
Hydrogenation of ethylene	0.066	23–27	2.7–1	0.11	0.2–2.8
Oxidation of H ₂	0.10	6.75–7.52	0.21–2.3	0.036	0.8–2.0
Oxidation of ethylene to ethylenoxide	0.13	13.4	1.76	0.065	0.08
Dissociation of N ₂ O	0.64	22.0	1.0–2.0	—	1–5
Hydrogenation of benzene	0.12	14–16	1.7–2.0	0.006	0.05–1.9
Oxidation of SO ₂	0.012	14.8	0.175	0.0415	0.9

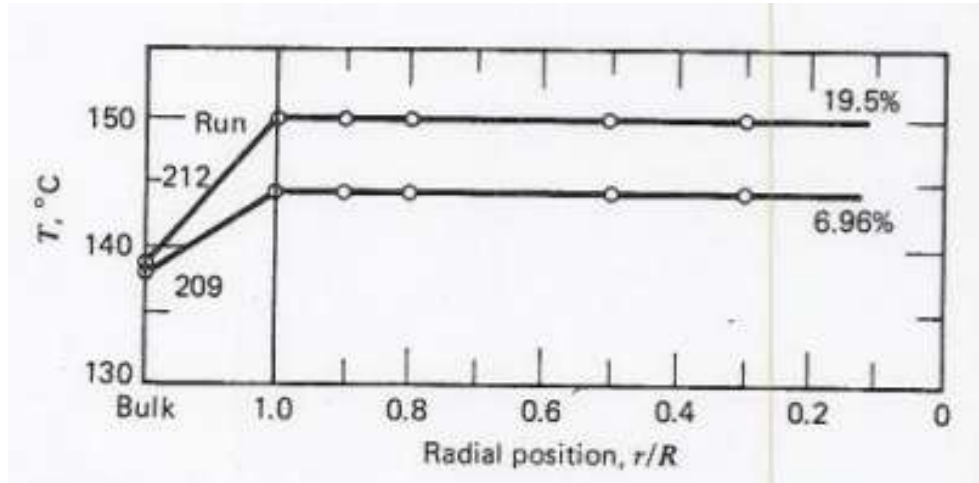
The authors conclude that internal temperature gradients will rarely occur in industrial practice.

However, external temperature gradients are more likely. The authors show the development of the equations, starting with the modified boundary conditions at the face of the layer exposed to flowing fluid, where k_g is the external mass transfer coefficient and h_f is the external heat transfer coefficient.

$$D \epsilon_A \frac{dC_s}{dz} = k_g(C - C_s)$$

$$\lambda \epsilon \frac{dT_s}{dz} = h_f(T - T_s)$$

Kehoe and Butt (AIChEJ, 1972) made a catalyst layer instrumented with internal thermocouples and studied benzene hydrogenation. They measured a significant temperature difference between the bulk gas and the surface of the layer, but negligible gradients within the layer.



Questions for you the student:

Can you explain why it is more likely to get internal concentration gradients than external concentration gradients? That is, as the reaction rate constant is increased, significant internal concentration gradients will form before significant external concentration gradients. Hint: think about the relative magnitude of the rate of diffusion through a stagnant fluid within a porous solid relative to the rate of diffusion and convection in a flowing fluid.

Can you explain why it is more likely to get external temperature gradients than internal temperature gradients? That is, as the reaction rate constant is increased, significant external temperature gradients will form before significant internal temperature gradients. If this is true, is it true for both endothermic reactions and exothermic reactions? Hint: think about the relative magnitude of the rate of conduction through a porous solid (which may have a high thermal conductivity relative to the fluid, hint, hint) filled with fluid relative to the rate of conduction and convection in a flowing fluid.

Make sure you can qualitatively sketch concentration and temperature profiles for both endothermic and exothermic reactions.