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This Week's Citation Classic

Weisz P B & Hicks J S. The behavior of porous catalyst particles in view of internal mass and heat diffusion effects. *Chem. Eng. Sci.* **17**:265-75, 1962. [Mobil Oil Company, Inc., Research Department, Paulsboro, NJ 08066]

The effectiveness of porous catalyst depends on the interplay between the rates of molecular transport (diffusion) and the intrinsic activity (chemical kinetics). This interaction has been analyzed in many past investigations. This paper examines the additional phenomena that can occur when the chemical reactions release or absorb heat. Unusual reaction behavior can then result. [The *SCI*® indicates that this paper has been cited over 175 times since 1962.]

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"This problem of how the intra-particle diffusion of molecules would modify the overall reaction behavior of porous catalyst particles had been studied over nearly a quarter of a century In essentially all cases, the temperature throughout the particles was assumed constant However, the majority of chemical reactions are accompanied by a heat effect: they either release or absorb heat This can lead to appreciably increasing (or decreasing) temperature toward the particle center Since chemical reaction rates vary rapidly (exponentially) with temperature, this effect could radically change the behavior of the catalyst particles from that which we would otherwise expect Depending on the physical (thermal) properties used in the two catalysts, they could behave very differently under otherwise identical conditions, even if their chemical, i.e., catalytic, properties were also identical.

"What might happen for example, in the case of an exothermic (heat generating) reaction, if the thermal conduction of heat outwards from the particle interior was slow enough to cause a positive increment in internal temperature? Would this not further increase the internal reaction rate (and heat release), thereby amplifying the temperature rise further, and so forth? just where would this condition go? We felt that there was a set of physical circumstances that might lead to some rather curious results.

"A rigorous mathematical analysis was difficult because of the nonlinear character of the relationships (differential equations).

"In a "blackboard" discussion with my long-term colleague, C. D. Prater, of an oversimplified model, a one-dimensional catalyst material, we noted that there existed a relatively simple mathematical relationship between two parameters the temperature and the reactant concentration at any one point We later found that C. Damkohler had already pointed this out in 1943 [1] But Prater managed to prove that this relationship was valid for all systems It was an intriguing additional piece in the search for a solution, but the basic system of equations remained nonlinear

"My colleague, John S Hicks, had been specializing in applying the growing computer resources to numerical analysis of complex engineering questions, and we pooled interest It became a symbiosis of physics, chemistry, and computing, first the formulation of the physical questions m terms adapted to numerical solution, and then finding a suitable computing technique which could handle the format used in the expression of the physical and chemical concepts We cycled several times around this sequence, and finally obtained what seemed to be useful and valid data But then, as we explored other ranges of our parameters, strange things happened: we obtained-dl multiple solutions indicating up to three states ot activity behavior for a catalyst at otherwise identical operating conditions. I remember the months of agony that followed Was this multiplicity a consequence of a peculiarity in the computing technique? Or, was it really a meaningful characteristic of the physical/chemical parameters which we had "presented" in this inquiry? Slowly but steadily we eliminated the technique as a cause for the unusual results. Thus, agony gave way to new excitement and curiosity Among other things, we wanted to test where in the real world we might encounter the combination of parameters that could lead to multiple solutions, and thereby instabilities in true behavior As engineers, we were happy to find that most materials (catalyst systems) and most operating conditions would not be so ill-behaved Yet, as scientists, we were excited to find that circumstances could be compounded where unusual effects might occur.

"Why has the resulting paper been used so often? We think perhaps because: (1) the calculations predicted some intriguing physical phenomena that might be observable in the laboratory, and might even have dramatic, practical consequences in engineering practice; for example, catalyst particles may possess activities much *greater* than expected from the applicable reaction conditions, instabilities, and the possible existence of multiple states of behavior; (2) our emphasis was not really on the mathematical and theoretical side, but on defining which real circumstances and catalyst materials could and which could not produce unusual effects; and (3) we were able to present a generalized solution without approximations.

"Beyond all, we think that the curiosities conand the time was ripe!"

1. **Damkohler G.** Ubertemperatur in kontaktkornern. (Excess temperature in catalyst grains.) Z. *Phys. Chem.* A193:16-28, 1943.