

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

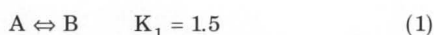
THE INFLUENCE OF CATALYSTS ON THERMODYNAMIC EQUILIBRIUM

JOHN L. FALCONER
University of Colorado
Boulder, CO 80309-0424

The influence of heterogeneous catalysts on how chemical equilibrium calculations are carried out is demonstrated by the following short problem, which will be viewed as a simplified representation of methanol synthesis.

Problem Statement

The inlet feed to a catalytic reactor is pure A. What is the *maximum* mole fraction of B that can be obtained in a catalytic reactor for the parallel, reversible reactions with the indicated equilibrium constants



Solution

A reasonable approach is to solve the two equilibrium equations simultaneously

$$K_1 = \frac{x_B}{x_A} \quad K_2 = \frac{x_C}{x_A}$$

to obtain the following mole fractions

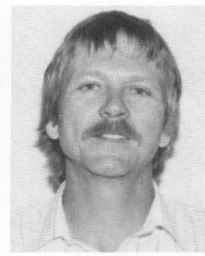
$$x_A = 0.08$$

$$x_B = 0.12$$

$$x_C = 0.80$$

But if the appropriate catalyst was chosen so as to accelerate Reaction (1) preferentially, then a much higher mole fraction of B could be obtained ($x_B = 0.60$). That is, the mole fraction as a function of time would follow a pathway such as that shown

John L. Falconer is professor of chemical engineering at the University of Colorado at Boulder, where he has been since 1975. He received his BS degree from the Johns Hopkins University and his PhD from Stanford University. He teaches courses in reactor design, thermodynamics, and catalysis. His research interests are in the areas of heterogeneous catalysis on supported metals and oxides, solid-catalyzed gas-solid reactions, photocatalysis, and catalytic membrane reactors.



in Figure 1, and the above mole fractions would only be obtained at long times. To simplify generation of Figure 1, the forward rate constant of Reaction (1) was assumed to be 100 times the forward rate constant of Reaction (2). In an actual catalytic system these rate constants can differ by many more orders of magnitude. If the reactor residence time was chosen in the broad region in Figure 1 where product B is favored, then a much higher concentration of B could be obtained than expected based on consideration of both equilibrium reactions simultaneously. Because of its larger rate constants, Reaction (1) reaches equilibrium so rapidly that it is not affected significantly by Reaction (2) until longer reaction times.

Discussion

Most undergraduate textbooks in kinetics and reactor design discuss heterogeneous catalysis because the majority of chemical processes use a catalyst to obtain desired products at high rates. Many of these textbooks, however, either do not mention the interaction between catalysts and thermodynamic equilibrium, or they give a false impression of how catalysts affect practical equilibrium obtained in a chemical reactor. For example, typical statements from reactor design textbooks about this topic are^[1-3]

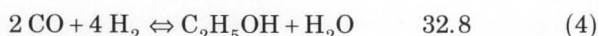
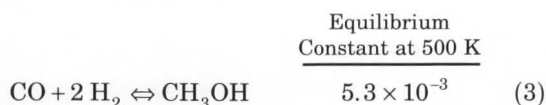
• The thermodynamic equilibrium is unaltered by the presence

of a catalyst.

- A catalyst changes only the rate of reaction; it does not effect the equilibrium.
- The position of equilibrium in a reversible reaction is not changed by the presence of a catalyst.
- Equilibrium conversion is not altered by catalysis.

These statements are all correct, but they may give the wrong impression because they only apply at times that may be long compared to the reactor residence time. They do not indicate that catalysts give us the option of deciding which reactions to consider in the equilibrium calculations.

Methanol synthesis from CO and H₂ clearly demonstrates this point. Consider the two reactions



At first glance, it would not appear worthwhile to build a methanol synthesis reactor; indeed, an ideal equilibrium calculation^[4] at 20 atm and 500 K for a 1:1 feed composition yields the following mole fractions:

$$x_{\text{CO}} = 0.50$$

$$x_{\text{H}_2} = 6 \times 10^{-3}$$

$$x_{\text{CH}_3\text{OH}} = 4 \times 10^{-5}$$

$$x_{\text{C}_2\text{H}_5\text{OH}} = 0.25$$

$$x_{\text{H}_2\text{O}} = 0.25$$

For this feed composition, the equilibrium calculation indicates that H₂ is almost completely consumed and the main products are ethanol and water. **Almost no** CH₃OH is predicted to form based on thermodynamic equilibrium for these two reactions. Of course, commercial plants exist that make methanol on a large scale from CO and H₂, and the undesired reactions are the formation of C₂H₅OH and hydrocarbons.

If only Reaction (3) is considered in the equilibrium calculation, however, then a reasonable yield of CH₃OH is predicted:

$$x_{\text{CO}} = 0.50$$

$$x_{\text{H}_2} = 0.36$$

$$x_{\text{CH}_3\text{OH}} = 0.14$$

In this case, only a fraction of the H₂ is consumed. Clearly this is the correct equilibrium calculation for the industrial process; **even though** C₂H₅OH **also forms**,^[5,6] we do not consider Reaction (4) in the equilibrium calculation because Reaction (3) is so

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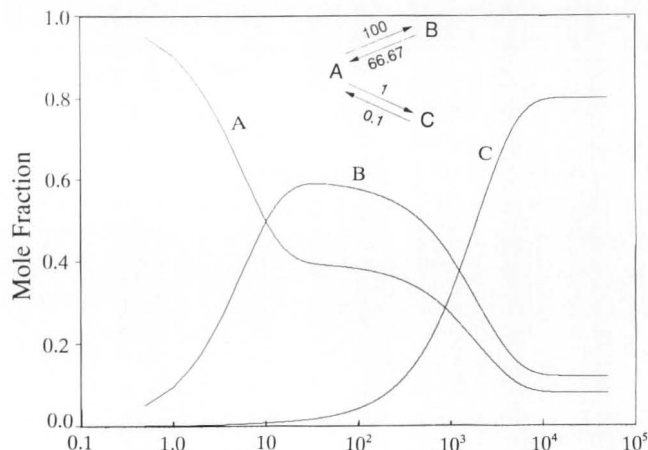


Figure 1. Mole fractions of A,B,C versus reaction time for the parallel, reversible decomposition of A to form B and C. Rate constants in inverse minutes are indicated for first-order reactions.

much faster. If we did, we would conclude that the measured methanol conversion is significantly higher than the equilibrium conversion. The formation of CH₃OH from CO and H₂ follows the same type pathway as shown for component B in Figure 1, except that the equilibrium constants differ by almost four orders of magnitude for Reactions (3) and (4) instead of one order of magnitude for Reactions (1) and (2).

The interaction between catalysis and thermodynamics was discussed by Hamilton and Greenwald,^[7] but their ideas are not addressed in most of the reactor kinetics or thermodynamics textbooks; only a few textbooks on heterogeneous catalysis discuss the influence of thermodynamic equilibrium.^[8] Hamilton and Greenwald distinguished between true equilibrium (infinite time) and practical equilibrium. Indeed, if the methanol synthesis reaction is run for extremely long contact times, then almost no CH₃OH remains.^[6] Hamilton and Greenwald emphasized that the catalyst constrains possible reaction pathways so that the uncatalyzed reaction is essentially forbidden. Thus, the minimum Gibbs free energy is not obtained; instead the minimum along a highly constrained path is obtained.

As pointed out by Satterfield,^[8] a selective catalyst directs one reaction essentially to completion while having little or no effect on other reactions. Thus, the most stable products are not formed. What the reaction to synthesize methanol from synthesis gas shows is that in calculating equilibrium conversion, we must consider the two reactions separately because the rates of reaction differ significantly. That is, the Gibbs free energy is not minimized for the system; instead, each equilibrium calculation is done independently of the other. For our example, this

means that the maximum mole fraction for CH_3OH is 0.14, not 4×10^{-5} .

Thus, catalysts can modify practical thermodynamic equilibrium by dictating that equilibrium for each reaction be considered separately. Catalysts do not change *equilibrium constants*, but the properly chosen catalyst allows us to ignore many of the reactions in equilibrium calculations because their rates are low. As pointed out by Hamilton and Greenwald^[7]

Of all the compounds that might theoretically form, it is well known that it is necessary to have thermodynamic information on only CO , H_2 , and CH_3OH to calculate equilibrium concentrations and yields in such a selectively catalyzed system.

We ignore an entire class of reactions when we calculate the equilibrium yield for methanol without also considering the equilibrium for paraffins formation, even though $\Delta G > 0$ for methanol formation, and $\Delta G < 0$ for methane and higher paraffin formation. All the higher alcohols and all the paraffins are more thermodynamically favored than methanol,^[9] but they are formed in very low concentrations over the typical $\text{ZnO/Cr}_2\text{O}_3$ catalyst.

In summary, catalysts affect practical equilibrium

conversions because conversions much higher than those calculated from equilibrium can be obtained in catalytic reactors.

ACKNOWLEDGMENTS

I wish to thank Prof. William B. Krantz for very fruitful discussions about this topic and Prof. Scott H. Fogler for some useful suggestions. Thanks also to Eric M. Cordi for generating Figure 1.

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ChE book review

INTRODUCTION TO MACROMOLECULAR SCIENCE

by Peter Munk

John Wiley and Sons, Inc., New York; 522 pages,
\$44.95 (1989)

Reviewed by
Matthew Tirrell
University of Minnesota

As a research field, polymer science has flourished within chemical engineering more than in any other traditional academic discipline and, while I have not surveyed this quantitatively, I feel confident in asserting that many more courses on aspects of polymer science and technology are taught in chemical engineering than in any other kind of department. That fact alone makes the appearance of a new textbook on polymer science a noteworthy event for chemical engineering. On top of that, there is the fact that polymer science has become so broad a topic that there are many ways to approach its presentation and concomitant, there is a general dissatisfaction with the books available for instruction during the last five years. It was precisely this feeling that led Professor Munk to write this book, as he explains in the Preface; for this, I salute him, since complaining is certainly easier and more immedi-

ately gratifying than bookwriting.

The book is intended for a first course in polymer science but is at a level that would be appropriate for introducing the subject to either seniors or graduate students. It comprises five chapters, the first four of them quite large and broad in themselves: Structure of Macromolecules, Techniques for Synthesis of Polymers, Macromolecules in Solution, and Bulk Polymers. These are solid, information-rich chapters. The fifth chapter, Technology of Polymeric Materials, is but ten pages long and is not really up to the job announced by its title.

The flow of topics, beginning with a detailed discussion of the ways that macromolecules can be put together, followed by a second detailed chapter on synthetic methods is, in my view, exactly appropriate for an introductory book. Connections made between uncharged, synthetic polymers, which are the main subject of the book, and important related topics, such as polyelectrolytes, micelles, proteins, and polynucleotides, are very well done and useful. Particular care has gone into placing polymer science in a proper context, which is both educational for the reader and likely to stimulate student interest by helping them see connections.

The third chapter on polymers in solution is also filled with important and useful information on the basic physical chemistry of mixture of polymers with solvents. I begin to find divergence between the