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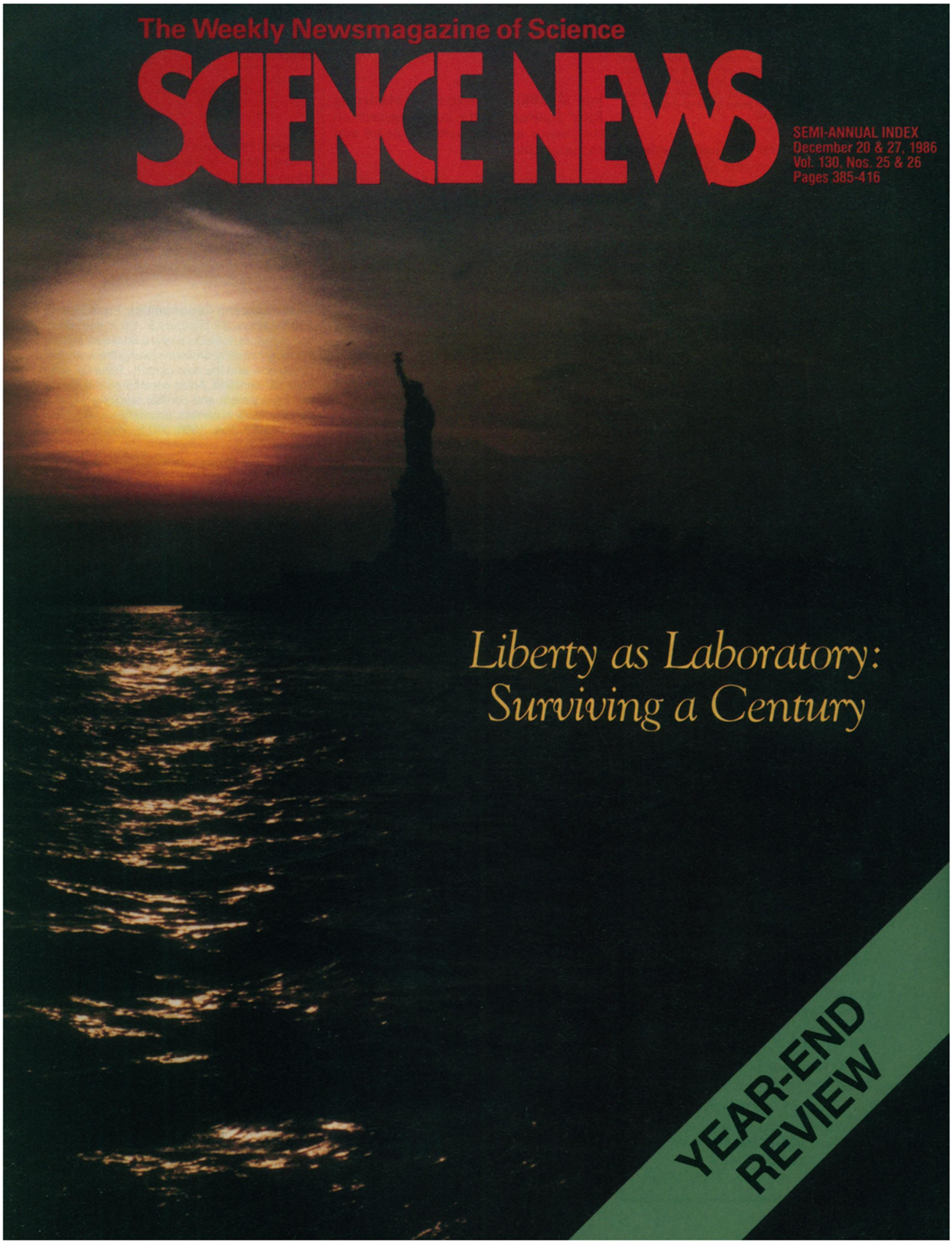


Liberty as Laboratory: Surviving a Century

YEAR-END REVIEW

The Pressure Extrapolation

Modern automotive catalytic converters contain rhodium which promotes chemical reactions to remove pollutants from a car's exhaust. Scientists at the General Motors Research Laboratories have recently made discoveries about one such chemical reaction, the reaction between nitric oxide and carbon monoxide, pointing the way toward new or improved catalysts.

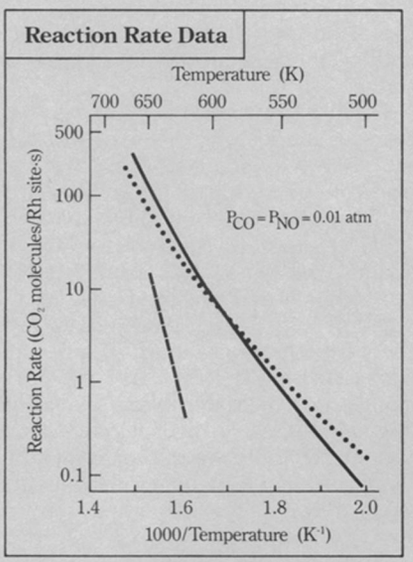


Figure 1: Rate comparisons for the NO-CO reaction. Measured data over single crystal Rh(111) (solid line) and over supported Rh (dashed line); model predictions (dotted line).

MOST FUNDAMENTAL catalytic studies using surface science techniques require an ultrahigh vacuum environment (10^{-13} atm). They are best suited for studying well characterized materials, such as metal single crystals. Catalytic reactions of practical interest, however, involve polycrystalline materials, in the form of small metal particles dispersed on supports. And they take place at atmospheric pressures rather than in an ultrahigh vacuum.

Now Dr. Galen B. Fisher and Dr. Se H. Oh have demonstrated how the wealth of chemical information obtained from ultrahigh vacuum (UHV) studies of ideal, single-crystal catalysts can be applied to the understanding of real-world systems that have different catalyst environments and that operate at much higher pressures.

These researchers concentrated their studies on the many chemical reactions that occur in modern automotive catalytic converters. One such reaction is the reduction of nitric oxide (NO) by carbon monoxide (CO) over a rhodium (Rh) catalyst to yield carbon dioxide (CO_2) and nitrogen (N_2) (Figure 2).

Dr. Fisher used various surface science spectroscopies in ultrahigh vacuum to study all of the elementary reactions over a rhodium single crystal [Rh(111)] that might be involved in this specific reaction. Over several years he measured the rates and determined the activation energies of each of these reactions. For most of these reactions, this was the first time these parameters had been measured. Based upon these results, Dr. Fisher hypothesized that the elementary reactions shown in Figure 2(a-f) were the significant steps involved in the NO-CO reaction and that nitrogen recombination and desorption (Figure 2f) was the rate-controlling step on Rh(111).

Dr. Fisher and Dr. Oh also initiated kinetic studies of this reaction at realistic reactant partial pressures and temperatures using two different catalysts—one was a rhodium single crystal [Rh(111)], and the other consisted of rhodium particles supported on alumina [Rh/Al_2O_3]. The rhodium concentrations on the support were similar to those used in an automotive catalytic converter. The studies with the single crystal at realistic, high pressures were done in collaboration with Dr. D. Wayne Goodman of Sandia National Laboratories.

At the same time, Dr. Oh devised a mathematical model for this reaction. The model consists

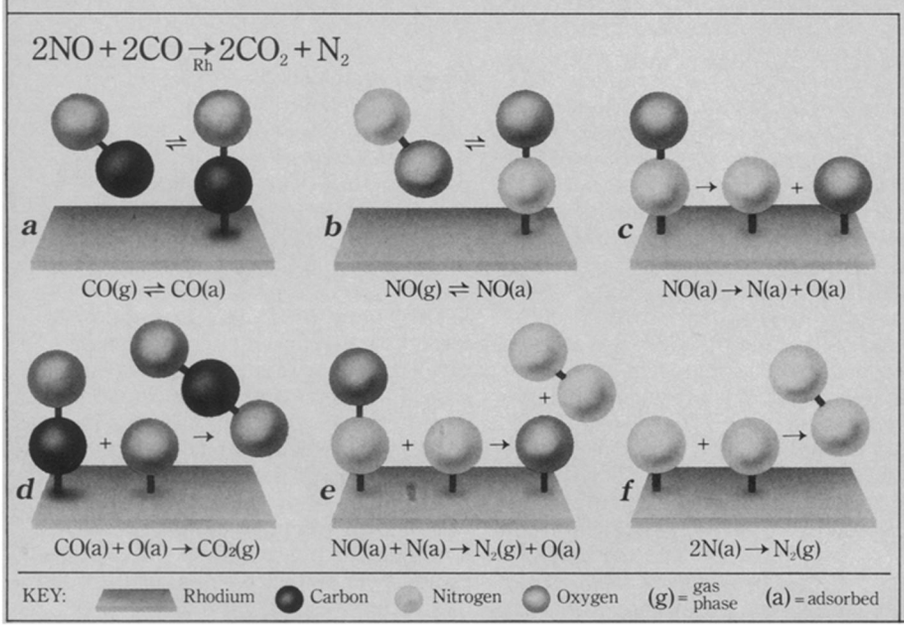


Figure 2: Schematic representation of the elementary intermediate steps for the NO-CO reaction.

of steady-state conservation equations for the surface species, based on the reaction mechanism and the rate expressions for the individual reaction steps determined in Dr. Fisher's UHV studies. Overall reaction rates could then be computed from the surface concentrations satisfying the conservation equations. The reaction rates predicted by this model, which depend only on reactant partial pressures, are shown in Figure 1 (dotted line).

The kinetics of the NO-CO reaction measured over a rhodium single crystal using realistic reactant partial pressures are shown in Figure 1 (solid line). The agreement with the model predictions indicates that Drs. Fisher and Oh had correctly identified all of the intermediate reaction steps and confirms that, in this case, nitrogen recombination and desorption (Figure 2f) is the rate-controlling step on Rh(111). The fact that the agreement is so good also indicates that the rates of the elementary reactions measured under UHV conditions are still valid at realistic reactant partial pressures—a pressure extrapolation of more than ten orders of magnitude.

THE KINETICS of the NO-CO reaction measured over the supported rhodium catalyst (Figure 1, dashed line), however, were much slower than predicted by the model. In addition, infrared studies have shown that NO is the predominant surface species on the catalyst, suggesting that in this case NO dissociation (Figure 2c) is the rate-controlling step. In fact, if the rate constant for NO dissociation measured under UHV conditions and used in the model is reduced by a factor of 2000, the kinetics of the NO-CO reaction measured over the supported rhodium catalyst are correctly predicted.

The difference between the kinetics of the NO-CO reaction measured over a rhodium single crystal and the kinetics measured over supported rhodium shows that this reaction depends on the environment of the rhodium in the catalyst. The reaction model strongly suggests that the NO dissociation reaction is the reaction step most sensitive to the rhodium environment.

"While our reaction model cannot tell us why NO dissociation is slower on supported rhodium," observes Dr. Oh, "it can help identify the kinds of studies necessary to clarify the origins of such sensitivity." Comparative kinetic studies can also provide useful insights for developing improved NO reduction catalysts. "Our studies have already told us," adds Dr. Fisher, "that one possible path to improving automobile catalysts is to make modifications that increase the NO dissociation rate."

THE MEN BEHIND THE WORK

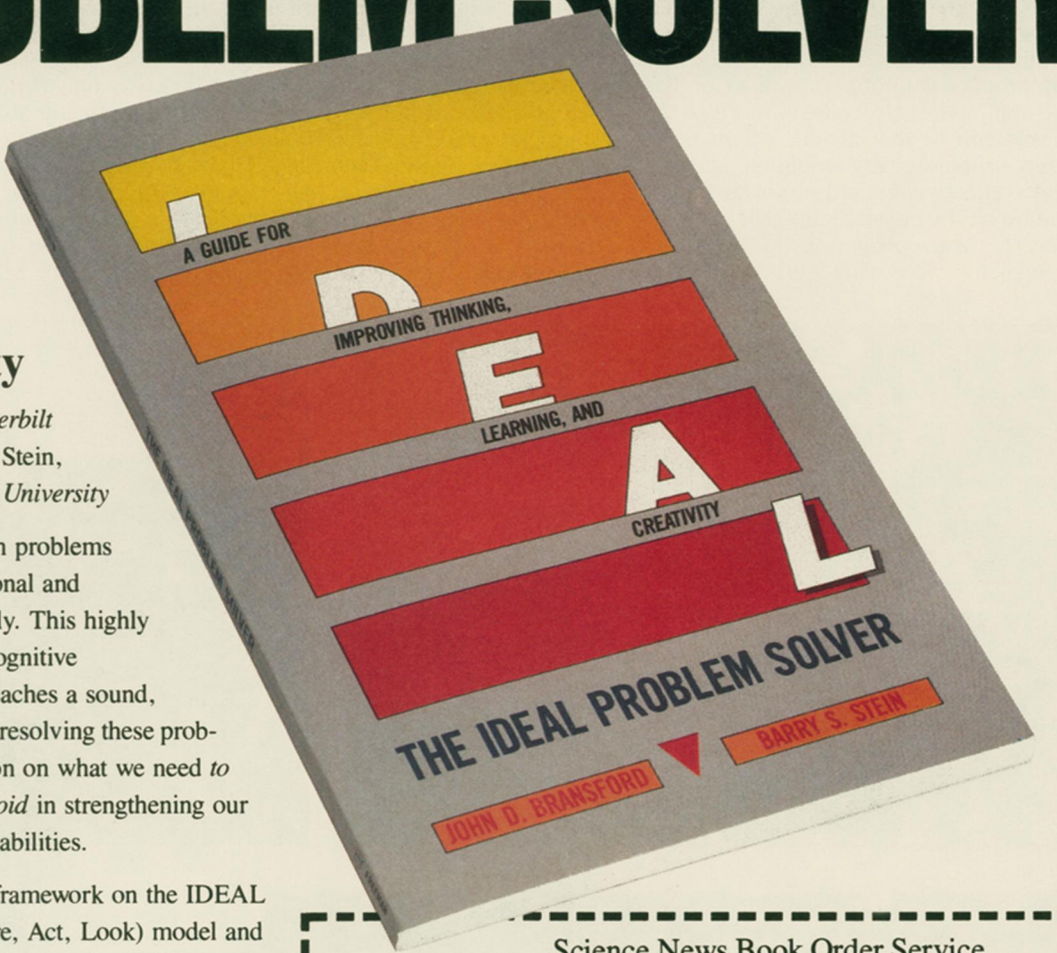
Dr. Galen B. Fisher (left) and Dr. Se H. Oh are both Group Leaders in the Physical Chemistry Department at the General Motors Research Laboratories.

Dr. Fisher holds the title of Senior Staff Research Scientist, and heads the Surface Chemistry and Corrosion Science Group. He attended Pomona College as an undergraduate and received his graduate degrees from Stanford University in Applied Physics. Before coming to General Motors in 1978, he did post-doctoral studies at Brown University and worked at the National Bureau of Standards. Since then, his research has been involved with surface science studies of various catalytic reactions.

Dr. Oh is a Senior Staff Research Engineer, heading the Catalytic Kinetics Group. He received his undergraduate degree from Seoul National University and holds a doctorate in Chemical Engineering from the University of Illinois. Dr. Oh did post-doctoral work at the University of Toronto prior to joining GM in 1976. Since then, he has been involved in measuring and modeling the kinetics of catalytic reactions.

A positive, practical "I can do it" approach to solving problems

THE IDEAL PROBLEM SOLVER



A GUIDE TO
Improving Thinking, Learning, and Creativity

John D. Bransford, *Vanderbilt University,* and Barry S. Stein, *Tennessee Technological University*

We all face and deal with problems and predicaments—personal and professional—almost daily. This highly readable book, by two cognitive psychologists, actually teaches a sound, methodical approach for resolving these problems by focusing attention on what we need *to do* as well as what *to avoid* in strengthening our natural problem-solving abilities.

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W. H. Freeman & Co., 1985,
150 pages, paperback, $9.95

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