

pound can be induced to turn itself into the lower one by introducing platinum as a catalyst. This kind of reaction is what is involved when people talk of having platformate in their gasoline.

There is a byproduct to this reaction, four hydrogen molecules. These are combined with nitrogen to make ammonia for fertilizer. This is the source of most of the hydrogen in the world, Whitesides says. "One of the things that people sometimes don't understand is the connection between petroleum and food production."

In the reforming reaction, two basic things occur. A new carbon-carbon bond is formed and hydrogen is lost. "This really makes gasoline work in a high compression engine," Whitesides says.

The chemists started out to investigate the "central step" in the reforming reaction, how the platinum reacts to break the CH bond, how it inserts itself into that bond and pulls it apart. "Despite the vast economic importance of this reaction, no one really knows how it goes." One reason for that is that it takes place on the surface of the heterogeneous catalyst (the platinum) where "it is almost impossible to get at." Whitesides and other chemists decided to try to study the reaction in a "tractable model," some system that would let them study the carbon-hydrogen bond breaking in a more accessible circumstance rather than on pieces of platinum scattered on alumina — although he adds that that is a widely followed study also.

The first step is to make the platinum soluble, so that the problem is no longer one of a reaction taking place on an inaccessible surface. This is done by attaching it to some other substances. One can then combine the platinum in solution with the other compounds of interest and, says Whitesides, drawing on the end of a bond, "hang out here the kinds of groups that we want to study in a homogeneous way." These are the same kinds of groups as are in the petroleum derivatives, and the physical chemists find that they can begin to learn what they want to study about the way platinum breaks that carbon-hydrogen bond.

The first step was a bit of an embarrassment. They found out that they didn't know anything about the reaction. But Whitesides says this one step backward may ultimately lead to two steps forward. They may learn what they want to know about the reforming reaction, and the method of modeling may apply to other heterogeneously catalytic reactions. This is no small topic. Whitesides estimates that these reactions contribute to industrial processes that yield 10 or 15 percent of the gross national product. "They are most crucially involved in energy processes," he says. He believes that an important part of chemistry in the immediate future will be to understand the catalysts now used and, if possible, find out how to make new ones. □

## Photography: Going against the grain

Researchers have borrowed the dyes from color-film technology to improve black-and-white film. The result is the first black-and-white film with silverless negatives.

Silver is used in conventional black-and-white film to create the image of the object being photographed. The new film — developed by researchers in the Ilford division of Ciba-Geigy Co. in Paramus, N.J. — uses silver only as an image receiver. In what is termed "coupling development," the silver reacts with the developer chemicals to form a product that in turn reacts with a precursor dye to produce an active chromogenic dye. A bath of bleach fix removes the recyclable metallic element, leaving an image made up of only the insoluble dyes.

"Using dyes to form a negative image, the new film reverses many of the principles which have guided photographers for more than 100 years," says Ilford spokesman Norman C. Lipton. While overexpo-

sure of conventional black-and-white film results in rougher, grainier prints, for example, overexposure of the new film produces smoother pictures with finer grain. Moreover, the film has a speed of 400 ASA but a grain quality comparable to that of other black-and-white film at about 50 ASA (ASA is a measure of a film's sensitivity to light; the higher the number, the more sensitive it is to light and the greater its ability to take pictures with less light). "It has always been the goal [in photography research] to make higher-speed film with smaller grain," says a technical manager at Ilford. And, says Lipton, even with tenfold enlargements, the grain stays small. "Technically, the film heralds a new era in black-and-white photography," he says.

The new film — on display this week in Cologne at Photokina, the "World's Fair of photography" — received a favorable rating from professional photographer Bob Schwalberg in the September POPULAR PHOTOGRAPHY. Ilford spokesmen warn, however, that for individual photographers, silver recovery will be insignificant. In addition, the use of dyes is likely to make the new film more expensive than the conventional silver films. □

## Cycling toward a hydrogen economy

You won't find Carlos E. Bamberger's thermochemical research in the present hydrogen fuel supply picture: Tapping hydrogen from declining reserves of natural gas is still the best economic bet. "But when water becomes the only source of hydrogen, the rules of the game will change," says the Oak Ridge National Laboratory researcher, and generating hydrogen by using heat to split water in a chemical cycle may take the lead.

Bamberger first sang the praises of thermochemistry last year when he and colleagues reported hydrogen production from a cerium oxide-sodium hydrogen phosphate cycle (SN: 8/4/79, p. 85). At that time, however, the energy balance, or energy input versus energy output, of the process had not been evaluated. Now, researchers from Los Alamos Scientific Laboratory (LASL) in New Mexico, sharing with Oak Ridge the lead in the search for appropriate thermochemical cycles, have calculated energy conversion efficiencies of various processes. "Estimated overall efficiencies for thermochemical water-splitting are 40 percent to over 50 percent depending on the temperature at which heat is delivered to the process," reports LASL researcher Kenneth E. Cox.

In contrast to one-step water-splitting processes that require impractical temperatures in excess of 3,000°C (5,400°F), most multi-step thermochemical cycles require temperatures around 800°C to 900°C (1,500°F to 1,650°F). The different steps of the process form "a closed loop in which the starting chemicals are regenerated and passed through the process

The LASL Bismuth Sulfate Cycle (Hybrid)			
1.	$2\text{H}_2\text{O} + \text{SO}_2 \xrightarrow{\text{aqueous}} \text{H}_2\text{SO}_4 + \text{H}_2$	Room Temp.	
2.	$\text{H}_2\text{SO}_4 + \text{Bi}_2\text{O}_3 \xrightarrow{\text{electrolysis}} \text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 + \text{H}_2\text{O}$	Room Temp.	
3.	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 \xrightarrow{\text{electrolysis}} \text{Bi}_2\text{O}_3 \cdot \text{SO}_3 + \text{SO}_2$	800°C	
4.	$\text{SO}_2 \xrightarrow{\text{electrolysis}} \text{SO}_2 + 1/2\text{O}_2$	800+°C	
The LASL Cadmium Cycle			
1.	$\text{Cd} + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{electrolysis}} \text{CdCO}_3 + \text{H}_2$	Room Temp.	
2.	$\text{CdCO}_3 \xrightarrow{\text{electrolysis}} \text{CdO} + \text{CO}_2$	300°C	
3.	$\text{CdO} \xrightarrow{\text{electrolysis}} \text{Cd} + 1/2\text{O}_2$	1500+°C	
The Sulfur-Iodine Cycle (General Atomic Company)			
1.	$2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \xrightarrow{\text{aqueous}} \text{H}_2\text{SO}_4 + 2\text{HI}$	Room Temp.	
2.	$2\text{HI} \xrightarrow{\text{electrolysis}} \text{H}_2 + \text{I}_2$	300°C	
3.	$\text{H}_2\text{SO}_4 \xrightarrow{\text{electrolysis}} \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$	800°C	
The Hybrid Sulfur Cycle (Westinghouse Electric Corporation)			
1.	$2\text{H}_2 + \text{SO}_2 \xrightarrow{\text{aqueous}} \text{H}_2\text{SO}_4 + \text{H}_2$	Room Temp.	
2.	$\text{H}_2\text{SO}_4 \xrightarrow{\text{electrolysis}} \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$	800°C	

Hydrogen-producing thermochemical cycles that have been verified experimentally and are now under development.

over and over without loss," Cox reports.

Although more than two hundred thermochemical cycles have been proposed, "only a few of these cycles have been shown to be technically feasible and worthy of further study," Cox says. LASL researchers believe the bismuth sulfate process to be one such cycle. Cox and co-workers developed this cycle "to overcome some of the problems that occur in other thermochemical cycles that involve sulfuric acid as a major ingredient." While most sulfuric acid cycles need high concentrations of the acid for efficient operation, the LASL cycle operates with lower concentrations, avoiding problems of corrosion. Still, the bismuth sulfate cycle is not without flaws: One major problem is the separation of a solid bismuth compound from water. Says Cox, "The 'best' thermochemical cycle probably has not yet been discovered." □