Bestial limits. The Schulz-Flory equation prescribes rigid limits for the proportion of products that can be derived from the Fischer-Tropsch process. Two-carbon products (ethylene, ethanol) peak at 30 percent of the total; gasoline peaks at about 45 percent. Only a single, one-carbon, product (e.g. methane) can be produced at 100-percent yields.

Variations on a theme—the chemistry of carbon monoxide—are widening opportunities for producing fuels and chemicals from coal instead of petroleum.
In mid- to late 1983, the Tennessee Eastman Company, a division of Eastman Kodak, will start up yet another plant to make acetic anhydride, a chemical intermediate in the company's manufacture of synthetic fibers, base for photographic film, and the like. The plant, in Kingsport, Tennessee, is within 40 miles of the nearest coal fields. It is advertised as the first fully integrated plant in the United States to synthesize commercial chemicals from coal. Its only technological counterpart is South Africa's mammoth Sasol coal liquefaction complexes, which convert subbituminous coal to much of that country's fuel and basic chemicals. However, while Sasol pours out a farrago of chemicals that must be cleverly and expensively separated, the plant in Kingsport will produce essentially a single product. The Tennessee plant, in its chemical sophistication and presuming all goes well, will be a dramatic example of what is called carbon-one chemistry.

As its name implies, carbon-one chemistry begins with a molecule containing a single carbon atom, typically carbon monoxide. Hydrogen can be added to produce the multiplicity of hydrocarbons Sasol produces. If hydrocarbons are not to be the end products, adding methanol instead of hydrogen to the carbon monoxide will form acetic acid, another basic organic chemical. Alternatively, carbon monoxide can be combined with acetic acid to create still other organic acids. Carbon-one chemistry is building-block chemistry.

Because of its potential for improvement and almost endless flexibility, carbon-one chemistry is also forefront chemistry. Chemists and chemical engineers want to understand the precise paths, mechanisms, and molecular realignments of its chemical reactions. They are concerned with the workings of catalysts, agents that raise the rates of certain reactions and increase yields of some products at the expense of others. Why, for example, does a heterogeneous solid catalyst produce one set of products while essentially the same catalyst, homogeneous and in solution, delivers a completely different range of products?

Carbon-one chemistry is concerned further with creating or identifying new kinds of catalysts that will not only enable new carbon-one-based reactions to occur but will also yield products that are virtually pure. The Monsanto company, for example, has found a way to turn out 99-percent yields of acetic acid from methanol—a carbon-one derivative. And analogues of that success are being pursued in industrial and academic laboratories in most of the world's industrialized nations. Japan, for example, has organized a government-industry consortium built around the high promise of carbon-one chemistry.

To split or not to split

The seminal event in carbon-one chemistry is the encounter of a carbon monoxide molecule with catalytic metal atoms. The molecule may rupture, splitting the bond between its carbon and oxygen atoms. If it does, oxygen is usually lost, and the products of succeeding reactions are dominantly hydrocarbons. If the molecule stays intact, if the carbon-oxygen bond is kept, then the products will be oxygenated organic molecules: alcohols, esters, aldehydes, ketones, carboxylic acids—all building blocks of chemical manufacture.

Whether the result is divorce or stability depends both on the composition of the catalyst, and on whether it is a solid or dissolved with reactants. Ruthenium in solid form, as a metal, will split carbon monoxide, forming the simplest hydrocarbon—methane. But if the ruthenium is part of a soluble compound, it will leave the carbon monoxide intact; the product instead will be the simplest alcohol, methanol. Why a carbon monoxide molecule dissociates in one instance but not another remains an enigma.

That issue joins other mysteries surrounding the catalytic moment in carbon-one chemistry. For example, in many instances the molecular form of the active catalyst is not known. Nor is the exact role of material that supports it, though the role even of the support is now regarded as more than passive.

New instruments and advances in organometallic chemistry are beginning to hint at some of the answers. These include methods for following the encounter of molecules with catalytic surfaces, with soluble metal clusters, and with molecular sieves called zeolites that can limit the diversity of molecular products of the reaction of carbon monoxide and hydrogen.

Beautiful and bestial

The doyen of carbon-one chemistry is the Fischer-Tropsch reaction: hydrocarbon production via a reaction of carbon monoxide with hydrogen. It is named for Franz
Fischer and Hans Tropsch, German chemists who described the reaction in 1926. As practiced at Sasol, the reaction entails passage of synthesis gas—a mixture of hydrogen and carbon monoxide—over iron catalysts. (In Germany during World War II, when Fischer-Tropsch chemistry was employed to make motor fuels, iron catalysts were used; the cobalt used by Fischer and Tropsch was too costly.)

If the starting point of the Fischer-Tropsch reaction is straightforward, the products are not. Indeed, they are discouragingly disparate. For example, with the typical iron catalysts that Sasol uses, the products may include methane. The products also include hydrocarbons in the gasoline range, containing five to eleven carbon atoms. These will often be diesel hydrocarbons, their carbon chains spanning the eleven- to twenty-five-carbon range. Finally, there will be heavy oils and waxes, carrying as few as thirty or as many as sixty or more carbon atoms in their molecular frames. Even some alcohol is made.

Bedeviling the Fischer-Tropsch reaction is what Werner Haag of the Mobil Research and Development Company calls the beautiful and bestial sides of an equation borrowed from classical polymer chemistry and proposed by Paul J. Flory of Stanford University and G. V. Schulz of the University of Maine. As fitted to carbon-one chemistry, the Schulz-Flory equation predicts the proportion of methane to gasoline to diesel to waxy hydrocarbons that will emerge once the starting conditions of the Fischer-Tropsch process are stated. The beautiful is the accuracy of the prediction; the bestial is its obduracy. Invariably, no matter how clever the chemist, the maximum proportion of gasoline hydrocarbons obtainable from conventional Fischer-Tropsch chemistry is about 45 percent. The smaller and larger hydrocarbons, invariably found on either side of that yield, require expensive separation. Indeed, the gargantuan Sasol facility in South Africa is a technological temple to the adamantine rule of the Schulz-Flory equation.

The challenge is to circumvent that rule. So far, efforts have taken several routes. One is to block the growth of hydrocarbon chains beyond, say, the gasoline range, or to break up oversized chains. Such sizing of hydrocarbons has been achieved using the kind of shape-selective molecular sieves,
or zeolites, developed by Mobil. A second way involves defining more sharply the mechanisms by which Fischer-Tropsch and other carbon-one reactions occur.

Most organic reactions occur in a series of linked steps called elementary reactions. The task in understanding complex reactions such as Fischer-Tropsch is to tease apart these simpler steps, to prove that they indeed occur, and—most difficult of all—to show that they occur exclusive of other possible reactions. Mechanistic work is frustrating. As one chemist put it, "You can’t definitively show—short of being a Maxwell’s Demon and crawling inside—what the reaction is."

There is no dispute with the original proposal by Fischer and Tropsch. It is accepted that the reaction involves the growth of molecular chains by sequential addition of specific monomers, or simple molecular beads, to a carbon chain grown from a seed. But the identity of the monomer is still disputed, as is that of the seed.

Ideas abound. The dominant mechanism (for now) is a reincarnation of one suggested initially by Fischer and resurrected and elaborated in the 1930s by British chemists S. R. Craxford and Eric Rideal. It is a reincarnation that Alexis T. Bell, of the University of California at Berkeley, calls the neocarbide, or nascent carbon, mechanism. As the process was originally described, the rupture of the carbon monoxide molecule on catalytic metal surface leaves a carbon atom bonded to a metal atom, producing a carbide. That carbide carbon reacts with hydrogen and the fragments interweave in a molecular do-si-do to produce the Fischer-Tropsch menage.

As often happens in science, the ideas came before the tools with which to verify them. The tools are now available, and they support the fundamental tenet of the carbide hypothesis: that rupture of the carbon monoxide molecule is a prerequisite to Fischer-Tropsch processes and that a uniquely reactive carbon atom so produced is the reaction’s seed. The major embellishments, which constitute the neocarbide mechanism, require the more exact definition of the nature of the carbide carbon, its location solely on the catalytic surface, the measurement of its brief lifetime, the tracing of its various fates, the limning of its remarkable reactivity, and the identification of the likely molecular fragments, the monomers, reacting with it.

Chain growth
The appearance of the carbide carbon is the overture. The main theme is the creation of hydrocarbons of varying lengths by chain growth. It is a process of many still-veiled steps and many transient intermediate products. Bell, his Berkeley colleague Gabor Somorjai, and other groups at other institutions in several countries have looked at the reaction in the effort to identify its intermediates. Somorjai, for example, does a Fischer-Tropsch reaction in a high-pressure cell, freezes the reaction by dropping to an ultravacuum within one or two seconds, and then looks for intermediates. His results are suggestive, but they leave questions.

"It is not clear," Somorjai says, "which species are the reactive intermediates and which are a sort of dead layer on the surface and do not contribute to the reaction."

Only some 10 to 15 percent of the surface is actually catalyzing the reaction, so the problem becomes not only of identifying the actual intermediates but also of coupling them to an active site. That for now is beyond the state of the art.

Bell uses a different approach, called reactive scavenging of the surface intermediates. At some sacrifice of the sensitivity Somorjai’s stopped-action methods achieve, Bell scans the live reaction. With olefins as his scavengers, he has caught a proposed intermediate in the Fischer-Tropsch reaction: methylene, a highly reactive (one carbon, two hydrogens) molecular fragment. Other experiments, notably those of Kensi Tamaru of the University of Tokyo and the late Rowland Pettit of the University of Texas, support methylene as an intermediate in the production of Fischer-Tropsch hydrocarbons.

To sum up, the starting point—the seed for the Fischer-Tropsch reaction—is the highly reactive carbide carbon placed on the catalytic surface by the rupture of a carbon monoxide molecule. This seed can then react with hydrogen to form methane, a complete molecule; or reactive molecular fragments including methyl and methylene groups can form. Chain growth starts, Bell says, when a methylene group is interposed between the metal surface and the carbon of a methyl group attached to it. Then the product is a two-carbon fragment which, if still attached to the surface, can keep growing by the continuing addition of methylene groups. The monomers in the growth of Fischer-Tropsch molecular chains—the pearls in the necklace—are the methylene groups. Growth stops if the chain gains or loses a hydrogen atom.

Finally, Somorjai points out as "an important catalytic fact" the narrow temperature window in which these reactions can occur. If the temperature is too low, dissociation of the carbon and oxygen cannot occur. If it is too high, graphite (a nonreactive species of carbon) forms immediately—and everything stops dead. Additionally, the putative intermediates are stable only in a narrow temperature range, the range where the chemistry produces carbon-one and other valuable compounds.

Sieves

While Bell sees "a growing consensus in the catalytic community" that this carbon-based mechanism will prevail as an explanation, there is no consensus that new catalysts will follow shortly. It is considered possible, however, that the Schulz-Flory distribution may be pushed in a more sophisticated way than Sasol has yet done. The key lies in the filtering action of zeolites. These are natural or synthetic molecular sieves. Typically, they are composed of silica and alumina.

So far, people tend to be most sanguine about the unique zeolites developed by Mobil. They limit, by the size of their internal pores, the size of the hydrocarbons passing through. The unique aspect of Mobil’s synthetic zeolites (called ZSM-5, for Zeolite-Sonony-Mobil) is their extremely high proportion of silica to alumina. Rather than the five-to-one or ten-to-one proportions usual to most zeolites, those of the ZSM series range between twenty to one and 100,000 to one. The unique chemistry done by these zeolites is in their transformation of methanol, a one-carbon alcohol, to a hydrocarbon mixture dominated by gasoline hydrocarbons. New Zealand intends to build a plant using this methanol-to-gasoline via-zeolite process to produce about 35 percent of its gasoline needs. (The methanol there will come from the methane in its Maui natural-gas fields.)

Hard upon the discovery that Mobil’s zeolites would transform methanol to gasoline hydrocarbons came the finding that they also narrow the range of Fischer-Tropsch hydrocarbons, producing a product group richer in gasoline than Schulz-Flory would allow. This zeolitic modulation is particularly impressive in its flexibility. Whether the Fischer-Tropsch catalyst and the ZSM-5 material are kept separate or the two are mixed physically, the results appear to be similar. Says Haag, "I get the same product distribution whether I mix the two compounds very intimately or put the zeolite behind the iron catalyst."

A pilot plant in Paulsboro, New Jersey, built by Mobil with Department of Energy funding, is testing the two-stage variant:
passing the carbon monoxide and hydrogen reactants over a catalyst and passing the resulting hydrocarbons through zeolites. In a related development, the Dow Chemical Company has reported a Fischer-Tropsch reaction in which, by combining a molybdenum catalyst with ZSM-5, the products are mainly small hydrocarbons—two to five carbons; propane is an example—that are essential to chemical manufacturing.

Traffic control

The structure of a new zeolite is now largely fortuitous, and the obvious goal is to predesign zeolites for specific uses. Mobil Research and Development’s ZSM-5, for example, is composed of ten-membered rings, ten pairs of silicon and oxygen atoms. “We would like to have fourteen-membered rings, eleven-membered rings, nine-membered rings,” Haag says.

“The cutting edge in zeolite research,” according to James Cusumano of Catalytica Associates, an international research and consulting firm specializing in catalysis and located in Santa Clara, California, “is in learning to make zeolites with varying pores and geometries to see the way pores intersect and interact. We also need to learn the effects of acidity on zeolite catalysis.”

One tactic is the use of organic templates “as seeds for the synthesis of zeolites,” Cusumano says, since in solution such seeds may “impart a geometry” to the zeolites growing on them. If such methods can indeed be used to control and not simply to vary pore size and geometry, then zeolites’ potential contributions to carbon-one chemistry expand enormously.

Clusters and surfaces

Whether it is mediated by a heterogeneous catalyst, one bound to a surface and currently the most common kind, or a homogeneous one dissolved in a fluid, the most interesting event in carbon-one chemistry is that of conception: the moment when the catalyst interposes itself and drives a reaction toward a particular point. Much of the work—and much of the frustration—of carbon-one chemistry pivots on that moment. Molecular metal clusters offer one way to look at that event; they are prisms for examining catalytic conception.

There is no rigid definition of clusters. They are molecular arrangements that have metal-to-metal bonds, an ordered architecture, and side groups, or ligands, that

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are often carbonyls—molecular fragments in which carbon atoms are doubly bonded to oxygen atoms.

Clusters are a relatively new addition to organometallic chemistry, prompted by the pioneering work of the late Paolo Chini of the University of Milan and by the arrival of relatively quick and inexpensive X-ray crystallographic techniques for looking at cluster structure. The smallest cluster has two metal atoms, and the largest so far—assembled by Lawrence Dahl and his colleagues at the University of Wisconsin—has 38 platinum atoms and 44 carbonyl groups.

There are many similarities between clusters and the surfaces of bulk metals that catalyze reactions, as Earl Muetterties of the University of California at Berkeley points out. They differ, however, in their electronic structure and hence they differ in their chemistry.

Metal surfaces have electrons that are available at a low energy cost. "As a result," Muetterties says, "a metal, or really a metal surface, is a relatively good electron donor. In contrast to this, if you take a cluster, even a relatively large cluster, you have a much, much smaller number of atoms—core metal atoms—and the electrons are more tightly bound. The typical cluster is not a very good electron donor." The upshot is that while metal surfaces tend to be quite reactive, the typical carbonyl cluster is not; few clusters have shown high levels of catalytic activity.

Nonetheless, intense work is being done to find clusters that are catalytically active. Researchers hope that cluster catalysts will offer one of two unique chemistries, or possibly both. One sort of chemistry postulates reactions catalyzed by different metals contained within the same cluster: say, hydrogenation in one part of the cluster and the addition of carbon monoxide, or carbonylation, in another, thus collapsing two or more distinct reactions into one. The second postulated chemistry for cluster catalysts involves identical cluster atoms acting in concert to enable a reaction to take place that otherwise is not likely to.

Muetterties is skeptical about the double-reaction possibility. "There’s a presumption," he says, "that chemistry would be different at those different metal sites. I don’t think that’s very likely for the metal clusters made so far, but it certainly is for new cluster classes."

The second possibility, the combined effects of neighboring cluster atoms, may produce novel chemistry. "I know from solid-state physics that I change the electronic, and therefore the chemical, properties . . . if I alloy a metal with other metals . . .," Cusumano explains. Researchers are attracted to the area by some recent spectacular successes with heterogeneous metal alloys, notably catalysts invented by John Sinfelt of Exxon, that can re-form naptha into gasoline.

While this demonstrates a provocative route, it does not necessarily promise homogeneous, soluble catalytic clusters. While reactive clusters can be and indeed have been made, they frequently suffer one of several fates: Either they break apart once dissolved, or a molecule of the solvent fills the empty coordination space, or the required ligands are inappropriate.

Clusters may be precursors of catalysis, however. They may supply the metal atoms upon which reactions occur. The reason most clusters are not catalysts as such, Cusumano explains, is that the cluster, once dissolved, falls apart, equilibrates, and forms other clusters. He calls the solution of those problems the future of cluster catalysis—to make clusters, stabilize them, and keep them in solution. "What good is it if I make this complicated cluster, as sophisticated as it may be, if I put it into solution and it falls apart?" However, he adds, "looking at organometallic clusters..."
A taxonomy of reactions

The multiplicity of reactions possible with a single-carbon molecule falls into three divisions. The divisions are a bit deceptive, for in most cases not only the starting materials but also the add-ons are derived from synthesis gas. For example, while the single-product Tennessee Eastman process (see "Take a Carbon Atom and...") requires many steps to go from synthesis gas to acetic anhydride, the net reaction is reducible to the reaction of four carbon monoxide molecules with four hydrogen molecules to form a molecule of acetic anhydride and water. The point is that as the art of catalysis enlarges, direct synthesis from carbon monoxide and hydrogen becomes both more probable and more possible.

First among the possibilities along this line are reactions deriving directly from synthesis gas. The Fischer-Tropsch reaction of carbon monoxide with hydrogen is the classic. Its products include gasoline and diesel fuels, as well as alcohols. With different catalysts, heterogeneous or homogeneous, a spectrum of oxygen-containing materials can also be obtained, including ethylene glycol, acetic acid, ethanol, and dimethyl ether. An example is a Union Carbide process for making ethylene glycol. Roy Pruett (now at Exxon) and the late R. E. Walker devised the process, using carbon monoxide and hydrogen as reactants; the catalyst is a soluble rhodium carboxyl compound; the yield is about 78 percent.

Secondary possibilities are indirect reactions, in which methanol derived from synthesis gas is further reacted with the same gas. The Tennessee Eastman process falls into this category.

Another, quite spectacular, example is the reaction developed and recently reported by John F. Knifton of the Texaco Chemical Company. His process, using homogeneous ruthenium and rhodium catalysts, enables the synthesis of a series of carboxylic acids in which the carbon chain is lengthened stepwise. For example, the reaction of acetic acid, with synthesis gas produces a sequence of straight-chain carboxylic acids with at least three carbon atoms each. Since acetic acid is itself obtainable from synthesis gas, it would be possible to make a series of carboxylic acids directly from synthesis gas or other single-carbon-atom combinations.

Finally, there are reactions in which a third molecule enters into reactions with either synthesis gas or methanol obtained from synthesis gas. If that third molecule is an alcohol, then the possible products of the reaction are carboxylic acids and higher alcohols; if ammonia, then nitriles and amines may appear; if aromatics, then isocyanates, urethane, and styrone; if olefins, then alcohols, ketones, and aldehydes. An example of the use of olefins is the reaction of propene, an olefin, with synthesis gas to make n-butyraldehyde in yields larger than 90 percent. Thirteen plants are now being built in nine countries to exploit a rhodium-catalyzed version of this reaction, created by Pruett. This version requires lower pressures than comparable reactions and yields little by-product.

for catalytic reactions is something that has only begun in the past few years."

Molecular carbide chemistry

Clusters are undeniably critical to the emergence of what is being called molecular carbide chemistry. That emergence supports the belief that cluster metals, acting in concert, offer unique chemistry. It also supports the basic tenets of the neocarbide mechanism for Fischer-Tropsch chemistry.

For example, using gentle oxidation, John S. Bradley and his associates at the Exxon Research and Engineering Company have removed one of the faces of an iron carbonyl cluster, thereby exposing a carbide carbon atom within the cluster. They reacted that uncaged carbon with carbon monoxide and methanol to form a metal-bound ester group; after hydrogenation, this ester group gave methyl acetate.

The reaction is reversible, and according to Bradley’s colleague Roy L. Pruett it constitutes “remarkable chemistry.” The reaction confirms the belief that carbon-to-carbon bonds could form between a carbide carbon and other organic molecules. “In a way,” Pruett explains, “it may be viewed as a simulation [with a cluster] of the iron surface of a Fischer-Tropsch catalyst.” The work also supports the idea that clusters may offer a unique catalytic pathway, as Bradley and his colleagues have reported, “by virtue of the unique environment provided by adjacent metal atoms.”

Even more direct support for the neocarbide mechanism came from work by Muetterties and a postdoctoral student, Mamoru Tachikawa. Using a four-iron carboxyl cluster containing a carbide carbon, the two showed that hydrogen would indeed add to the carbon, as argued via the neocarbide mechanism. Muetterties notes that this work demonstrates “the feasibility of particular steps—in this case, the Fischer-Tropsch reaction—of reactions catalyzed by a metal surface. We showed that a carbide carbon atom can react with hydrogen to form a carbon-to-hydrogen bond.”

More than carbon monoxide

In all this, in terms of its availability, another carbon-one molecule, carbon dioxide, is even more interesting than carbon monoxide. “It is,” says Gabor Somorjai, “the only carbon energy source that is abundant and readily available. The only problem is that carbon dioxide requires energy, about as much as is needed to split water, to dissociate into carbon monoxide and oxygen.” Nonetheless, there are glimmerings that for some reactions carbon dioxide may perform better than carbon monoxide. For example, methane can be formed from carbon dioxide at lower temperatures and pressures and with greater selectivity than it can from carbon monoxide.

Finally, to speculate a bit further, the central molecule of the future in chemical manufacture may be methanol, whether derived from carbon monoxide, carbon dioxide, or the methane of natural gas. As Pruett points out, “the processes for making methanol are selective and already commercial.” Moreover, the multiplicity of reactions leading to other oxygenated compounds begins with methanol or flow through it; as the advances in understanding the chemistry of one-carbon compounds continue, they will enlarge the already substantial industry that depends on methanol.

“I think that this is the opportunity in catalysis: finding new and very, very selective reactions of methanol,” Muetterties says. As he sees it, that may be “the raw material of the future.”