RESEARCH

Gaseous C Is Polyatomic

Calculations from quantum theory show carbon in vapor phase is in polyatomic chains

GASEOUS CARBON at high temperatures is associated predominantly into polyatomic molecules; it is not exclusively in the form of monatomic carbon as has been assumed. This unexpected result stems from theoretical studies by Dr. Kenneth S. Pitzer and Dr. Enrico Clementi at the University of California.

Chemists have more or less assumed that gaseous carbon would be mostly monatomic with a few diatomic molecules, because the temperature would be high enough to rupture the carbon-carbon bonds. But no one really knew, and this lack of knowledge limited the use of carbon at high temperatures.

To fill this gap in knowledge, Dr. H. A. Chupka and Dr. M. G. Inghram at University of Chicago undertook experimental work and found, to their surprise, strong evidence for the existence of triatomic molecules and some indication of molecules with five carbon atoms in the vapor phase.

Quantum Mechanics. Obviously something had to be done to clear up this puzzling situation. Dr. Pitzer decided that the answer was a theoretical study using quantum mechanical methods. As Dr. Pitzer points out, quantum mechanics is now entering a third stage as a part of the working equipment of the chemist.

During the early days of the theory, much labor was expended in using it to compute spectra and other known data in order to verify the theory. When confidence in the theory had become firmly established, the second stage was reached. Proponents of the theory cried happily, "The day of the laboratory experimentalist is over! We can compute everything we need to know with quantum mechanical techniques."

But of course the laboratories throughout the world did not close their doors. For, says Dr. Pitzer, it soon became clear that in most cases the time and labor involved in computing results would far exceed the time and labor needed to get the same results experimentally.

Now, in the third stage, the chemist is coming to think of quantum mechanics as another tool to be used to supplement laboratory work in those cases where its use is appropriate.

The chemistry of carbon at high temperatures is such a case. With only one atomic species present, the complexities of computation are greatly reduced. Furthermore, Dr. Pitzer and Dr. Clementi were able to evaluate some of the more complex integrals empirically from spectral data on aromatic hydrocarbons.

Carbon Chains. It turns out that the simple and obvious assumption of monatomic carbon was wrong. Wrong, that is, under the conditions in which they were interested and under the conditions which the University of Chicago workers employed. If the gas phase is in contact with the solid phase in a closed system, it turns out that the increasing pressure is sufficient to prevent dissociation of the polycarbon molecules up to high temperature.

According to the calculations of Dr. Pitzer and Dr. Clementi, there will be relatively little monatomic carbon at 2500° C. or higher. Most of the molecules are in the form of chains, and those with an odd number of atoms are more abundant. They calculate that, at 2500° K., average chain length is 6.2 atoms. And, as though to demonstrate that the chemical laboratory is not obsolete, Dr. Pitzer has now undertaken experiments to test the calculations.

New DDT Behavior Noted

Variable results from use of DDT in ponds, lakes, and other mosquito breeding areas may be explained by a finding made in Orlando, Fla. Department of Agriculture chemists and entomologists have found that DDT at one part per hundred million in water does not remain in a uniform suspension but codistills with evaporating water and tends to concentrate at the surface and at the walls of containers.

This DDT behavior in water is a surprise, USDA says, because it has never been noted before despite the extensive use of DDT for many years. In similar tests, other insecticides—parathion, malathion, lindane, and dieldrin—did not show this action.

SiC Emits Electrons

Westinghouse finds silicon carbide can emit electrons with low power consumption

SILICON CARBIDE (see page 34) turns up also in news from Westinghouse. Research physicists W. J. Choyke and Lyle Patrick of Westinghouse's research laboratories have found that it can emit electrons directly and continuously from its surface, could thus act as the cathode in a vacuum tube.

One of the big disadvantages of vacuum tubes as they are built today, Westinghouse says, is that you need a lot of power to heat the cathode enough for it to emit electrons. But a silicon carbide semiconductor with a p-n junction needs very little power and yields electrons instantly and indefinitely when a small voltage is applied with reverse bias across the junction.

Escape of electrons from the silicon carbide is accompanied by emission of visible light—a form of electroluminescence which occurs when enough voltage is applied to break down the junction's electrical resistance. This light is concentrated in small, blue spots at the junction. The spots are small—about 130 microns across—but give currents up to one microampere, which is an electron density comparable to that from the cathode of a typical vacuum tube, Westinghouse points out.

Although the Westinghouse research is in an early stage, the company can already foresee many uses for this phenomenon. It could be a help in miniaturizing cathode ray tubes, for example. Or you could build vacuum tubes with many components in them and still not be faced with a major problem in heat dissipation. And since the electrons come from almost a point source, you could focus the electron beam readily.

Other semiconductors also exhibit this property, the company adds. But none have reached this high an electron density. Silicon itself and cesium on germanium, for example, give densities which correspond to about one micromicroampere.

Westinghouse points out that this electron emission might help to bring the vacuum tube back to popularity.

should be possible to grow silicon carbide crystals from solution in alloy melts. Dr. Frank A. Halden, working at SRI under a contract with the Electronic Warfare and Parts Branch of the Bureau of Ships, took up the idea and reduced it to practice.

He has found a suitable solvent and has designed equipment which works well enough to show that Dr. Shockley's idea is sound. But a lot of further work is needed to improve the art before the process approaches commercialization. BuShips, recognizing this, has renewed the research contract for another year.

▸ Crystal Pulling Furnace. As a solvent Dr. Halden uses molten silicon or a metal-silicon alloy at temperatures around 1500° to 1600° C. (Silicon melts at 1420° C.) The crystal growing furnace is a modification of the Czochralski furnace used for producing transistor-grade silicon. A graphite resistance heater—a thin cylindrical shell about 4 inches in diameter and 6 inches long—is connected to a 30-kw. power supply through a temperature controller.

The molten silicon is contained in a graphite crucible some $2^1/_2$ inches in diameter and 3 inches high. This is mounted within the heating element so that it can be rotated from below by an electric motor at 4 to 5 r.p.m. The whole heating zone is surrounded by molybdenum radiation shields and a double walled shell through which cooling water flows. View ports and holes for temperature measurement with an optical pyrometer pierce this outer shell.

During a run, carbon from the crucible wall diffuses into the molten silicon so the solution is always saturated with silicon carbide. Since the silicon-carbon bond is stronger than the average of the silicon-silicon and the carbon-carbon bonds, silicon carbide will crystallize from this solution with a minimum of contamination.

In growing the silicon carbide crystal, a seed crystal is rotated in the opposite direction to the crucible and slowly withdrawn from the solution. The seed is mounted on the end of a $^1/_4$-inch rod which is supported with its motor on a platform above the crucible. This entire assembly can be moved vertically by means of a screw mechanism at variable speeds down to 0.1 micron per second. Crystals grow either on the seed or on the walls of the graphite crucible, depending on the thermal configuration.

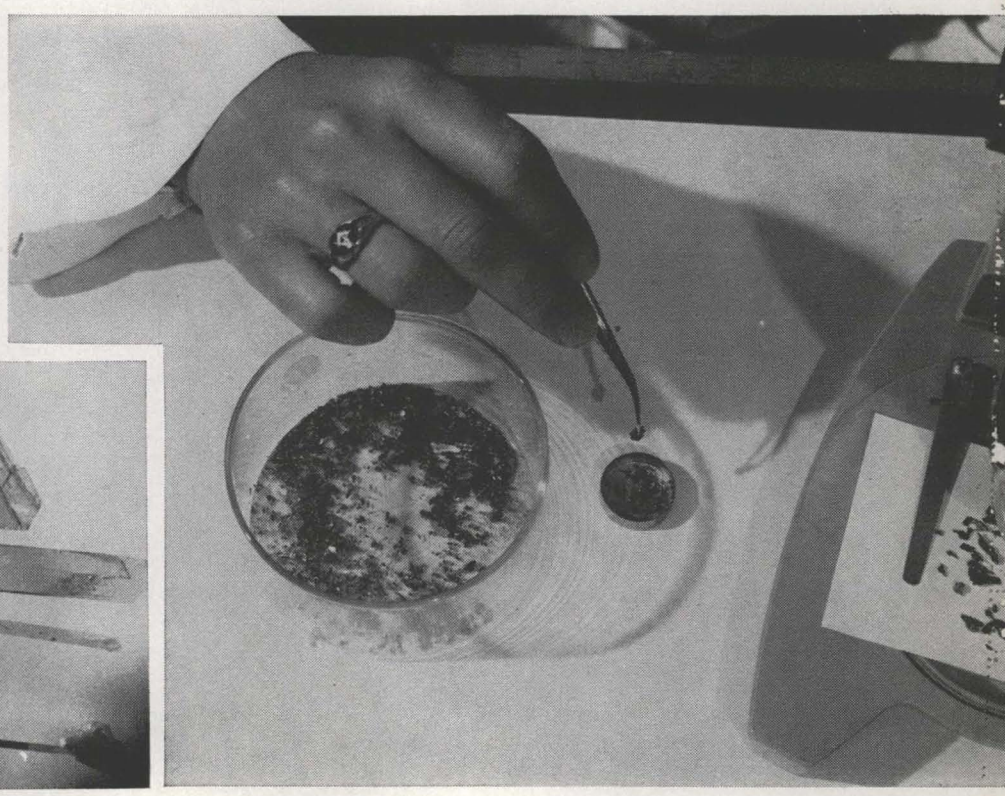
▸ Typical Run. In a typical run, the operator heats the furnace to the melting point of silicon under a vacuum of 10^{-4} mm. to remove any gas. He then starts purified helium flowing through the furnace and increases heat until the desired operating temperature is reached.

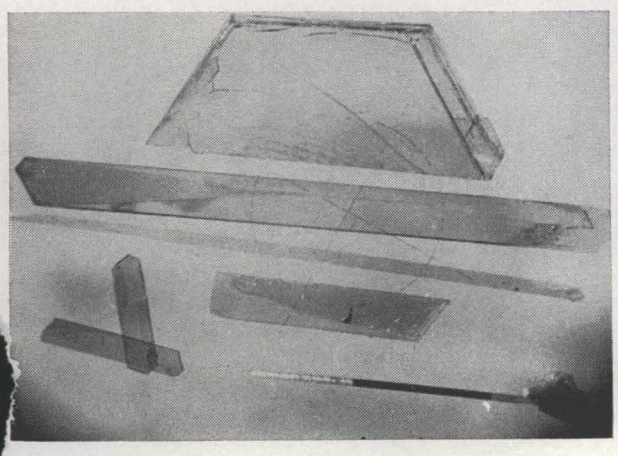
By raising the crucible to the thermal gradient region of the furnace and lowering the seed crystal on the end of its rod into the melt he starts crystallization. The pulling mechanism then withdraws the seed and its attached crystal at a rate which is adjusted visually to equal the rate of crystal growth.

Dr. Halden has shown that Dr. Shockley's idea works. He has indeed grown single crystals of high purity. But the crystals thus far are small—4 or 5 mm. long—and the purity has not yet been measured accurately enough to determine whether it is high enough for semiconductor applications.

One of the troubles so far has been with temperature control. Until recently, the temperature has been controlled manually, and line fluctuations during runs as long as 48 hours have resulted in rather wide temperature swings. A new control system will hold temperature constant within 0.4° C.

Dr. Halden feels that now it is a matter of juggling variables such as temperature, temperature gradient, and crucible design to find the optimum conditions for growing crystals large enough to be commercially useful.





MANY CRYSTALS. Crystals from the furnace are classified under a microscope. A typical platelet is thin, up to 7 mm. long, and is pale yellow. Dr. Halden has had some difficulty in keeping a constant temperature during the runs—which last up to 48 hours. He has improved the control system to hold temperature within 0.4° C., is now studying variables such as temperature, temperature gradient, and crucible design to get larger crystals