

INERT GASES —

Ideal Atoms for Research

by *Brian L. Smith*

— Argon, neon, helium, krypton, xenon, and radon sound like characters from the Old Testament of the Bible. They are actually members of the “inert gas” group of chemical elements, small amounts of which exist in every breath of air we take.

The inert gases were brought to light less than 70 years ago. Their discovery caused a considerable stir in scientific circles because their existence upset the ideas then current concerning the composition of the atmosphere, and the periodic classification of the elements. Once these difficulties had been settled, however, scientists soon lost interest in the inert gases. Only in recent years have they been recognized as valuable materials for research, and at Caltech, today, they are being studied in the divisions of chemistry, engineering, geology, and physics.

Argon was the first of the inert gases to be discovered. Shortly before the turn of the century, Lord Rayleigh, an English physicist, set out to redetermine the densities of the principal gases then known to scientists. The measurements were considered to be routine and Rayleigh did not anticipate that the in-

vestigation would lead to any startling results. Still less did he suspect that the work would lead to the discovery of a new element, for which he and his colleague, Sir William Ramsey, would be awarded Nobel Prizes.

The results of Rayleigh's experiments were consistent, except for nitrogen. Atmospheric nitrogen was found to be slightly more dense than nitrogen produced chemically. At this stage Rayleigh was joined in his researches by Ramsey, and the two men investigated the discrepancy. They found that the difference was due to the presence in atmospheric nitrogen of about one per cent of an unknown element, which they named argon (Greek—non-active) because of its apparent inertness. In 1895, Rayleigh and Ramsey announced their discovery to a meeting of the Royal Society in London.

Their news was greeted with a certain amount of scepticism. At that time it was commonly supposed that air consisted of nitrogen, oxygen, carbon dioxide, and water vapor. Scientists had forgotten the work carried out by the chemist, Henry Cavendish, more than a century earlier. Cavendish had experimented to see whether “phlogisticated” air (nitrogen) was homogeneous or a mixture of different gases. He had found a small bubble of gas—presumably mainly argon—for which he could not account, but had concluded his investigation with the comment, “. . . if there be any part of the phlogisticated air of our atmosphere which differs from the rest, we may safely conclude that it is not more than 1/120 part of the whole.”

Another upsetting factor which made scientists unprepared to accept the existence of argon was that it did not fit into the periodic table. The properties of argon were such that it did not correspond to any of the elements which scientists predicted would be

Inert Gases in the Atmosphere

Argon	1 part in 107
Neon	1 part in 55,000
Helium	1 part in 200,000
Krypton	1 part in 1,000,000
Xenon	1 part in 12,000,000
Radon	1 part in 10^{21}

brought to light because of the gaps left in the table.

The controversy was ended with the subsequent discovery of helium, neon, and the other inert gases. It was then realized that these gases formed an entirely new group in the periodic table—elements which were characterized by complete chemical inactivity.

Apart from radon, which is radioactive, and helium, which exhibits unusual properties at low temperatures, the inert gases had little obvious appeal as materials for research. In recent years, however, there has been a revival of interest in these substances because of the realization that they closely correspond to simple theoretical models, and are therefore useful in the development of molecular theory.

One of the most ambitious programs in which physicists and chemists are now engaged is the development of the molecular theory of the physical properties of matter. Their aim is to describe the macroscopic or “real-life” properties of gases, liquids, and solids, in terms of molecular behavior. In general, this is an impossible task because of the complicated mathematics involved; but for certain substances, of which the inert gases are outstanding examples, enough simplifying assumptions may be made for the development of such a theory to be possible.

For example, when calculating a macroscopic property, one should, in principle, consider the contributions made to the property by each of the molecules. It is, in other words, a “many-body” problem involving all n of the molecules, where n is probably about 10^{22} . This, of course, takes a long time to compute! Fortunately, the problem can be simplified somewhat for the inert gases.

The forces which act between inert gas molecules, and which bind them together in the liquid and solid states, are short-range and effective only over a distance of a few molecular diameters. They are also expressible in simple algebraic terms.

The net force acting on any one molecule can therefore be accurately estimated by considering interactions with its nearer neighbors only. Molecules further away than a few molecular diameters will make no

contribution. The net force operating on the representative molecule can be expressed as a “two-body” force, acting between the molecule on one hand and its neighbors on the other.

The bulk property is then obtained by adding up these effects for all the molecules which are present, assuming that the net forces acting on them are the same as for the representative molecule.

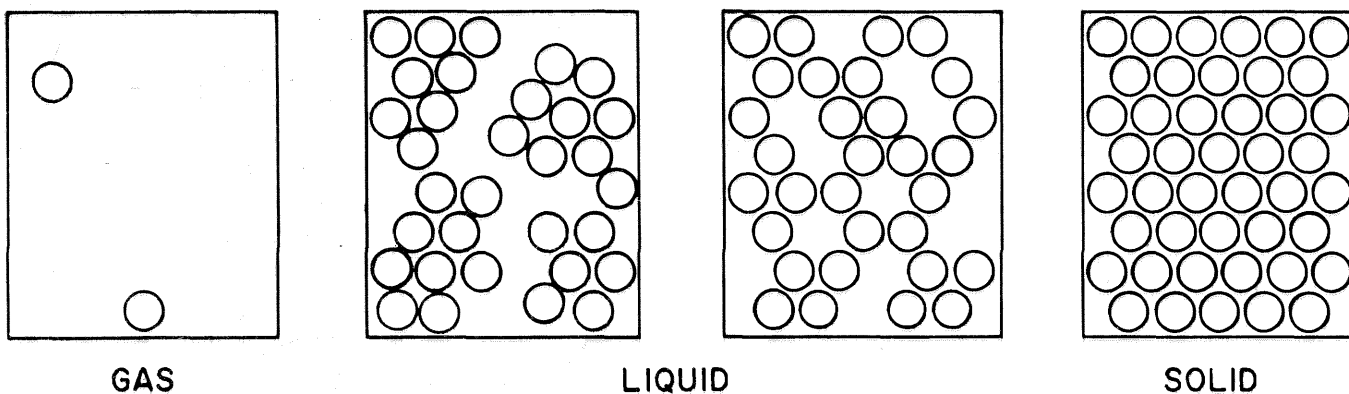
This type of calculation is relatively easy for the inert gases because the effect of “free” electrons does not have to be taken into consideration. The atoms are characterized by full and stable electron shells, and this is what gives them their inert properties. They are in fact like the miniature “ping-pong balls” often used in scientific theories—easy to handle mathematically because they are spherically symmetrical in their interactions.

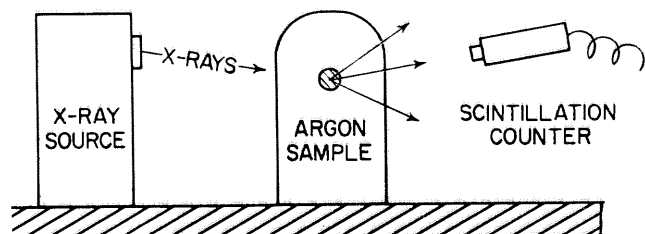
The inert gases, with the exception of helium, are readily liquefied and solidified by normal low temperature methods. They may therefore be studied as gases, liquids, or solids. At Caltech, for example, I am assisting C. J. Pings, associate professor of chemical engineering, in an investigation of the distribution of molecules in dense fluids, using argon.

This has been a puzzle for a long time. In a gas at low pressure, the molecules are distributed completely at random. In a solid, the molecules are usually fixed in some type of crystal lattice. The molecules in a dense gas or a liquid, however, have neither the complete “chaos” of a low pressure gas nor the “order” characteristic of a solid. The structure of these fluids is intermediary, and at present not known. A number of suggestions have been put forward as possible molecular distributions in a liquid, but more evidence is required before one of these “models” is established as correct.

We use x-rays to investigate the structure of liquid argon. A narrow beam of monochromatic x-rays impinges on a sample of argon, contained in a cylindrical beryllium tube and maintained at a constant temperature and pressure. The x-rays are scattered both by the argon sample and the beryllium tube. Some of the x-rays are absorbed and others deflected

Distribution of Molecules in a Gas, Liquid, and Solid





In Caltech's chemical engineering laboratories, an x-ray diffractometer is used to investigate the structure of liquid argon.

at various angles. Of those that are absorbed, a certain percentage are re-emitted, but with a longer wavelength. The emergent beam forms a diffraction pattern which is detected and recorded either by means of photographic film or an electronic counter.

In the present work, we use a scintillation counter to measure the intensity of the diffracted beam. The counter is able to rotate about the axis of the specimen. It can, therefore, be used to measure the intensity of the x-rays which are scattered at different angles.

From these measurements, a quantity known as the "radial distribution function" is calculated. This is a mathematical function which represents the average configuration of molecules at the particular temperature and pressure at which the experiment was performed. Hence, the radial distribution function, although a most useful concept from a theoretical point of view, does not give the positions of individual molecules. Thus, x-ray diffraction cannot be used directly to confirm or refute a model for the liquid state.

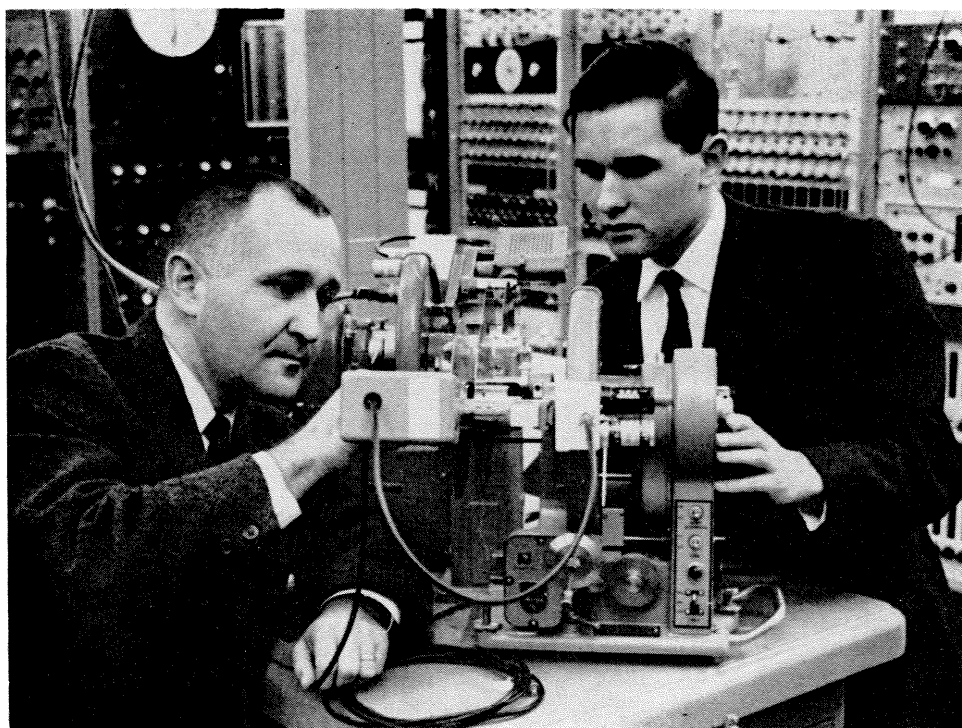
However, properties such as the pressure and en-

ergy content can be estimated from the radial distribution function. These data can then be compared with the results of theoretical computations based on the various models which have been suggested. The comparison should indicate which of these is correct.

The radial distribution function for molecules in liquid argon has been determined before. However, the results of earlier work are not sufficiently accurate or extensive for a definite conclusion to be reached with regard to its molecular structure. The recent development of high precision counters and techniques for handling diffraction data now allows radial distribution functions to be determined with a greater accuracy than was previously possible. Whereas in crystallographic work intensity measurement is only of secondary importance, with x-ray diffraction in liquids accurate determination of intensity is essential.

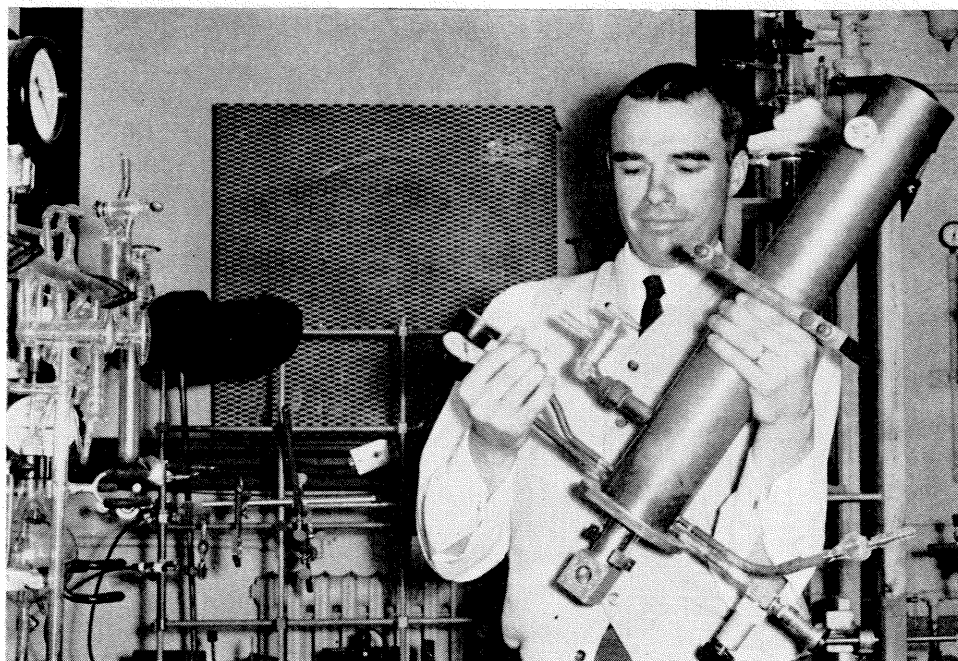
One pertinent question which has arisen from the work is—how monochromatic do x-rays have to be in order for them to correspond to the single wavelength relations used in diffraction theory? To a certain extent the practical answer is a compromise. The x-rays must obviously have a finite band width in order for the determination to be experimentally possible. What is not evident, however, is how wide a wavelength band can be tolerated without the diffraction pattern becoming smeared. This problem is being examined as an auxiliary investigation.

Another project which is in progress in the chemical engineering department is a study of the optical properties of the inert gases. In this study, Dr. Pings and I are measuring the refractive index of fluid argon over a wide range of temperature and pressure to provide experimental data for comparison with theoretically predicted values. The method should be



C. J. Pings, associate professor of chemical engineering, and Brian L. Smith, research fellow, estimate the molecular distribution of liquid argon with the x-ray diffractometer, then compare the results with theoretically predicted values.

An absorption cell containing xenon is used in the study of molecular spectra by G. Wilse Robinson, professor of chemistry.



familiar to anyone who has taken a freshman laboratory course in physics. Inside a cryostat, the argon sample is condensed in the form of a prism. The refractive index is measured by means of an optical spectrometer.

Refractive index measurements are useful because they can be used to calculate the "polarizability" of a molecule, which is the distortion produced in the molecule due to the presence of its neighbors. The polarizability is directly related to the radial distribution function. Hence, refractive index measurements can give useful information regarding the molecular distribution in a liquid and provide a valuable check on x-ray diffraction data.

Robert M. Mazo, assistant professor of physical chemistry, is currently engaged in theoretical work on the liquefied inert gases, examining recent theories and checking their logical consistency by means of a series of calculations.

G. Wilse Robinson, professor of physical chemistry, is interested in the condensed inert gases, but from an entirely different standpoint. Liquid argon, krypton, and xenon are good solvents for many substances. They are also transparent to radiation ranging from the ultraviolet to the infra-red, and including the visible region. Hence, by dissolving a small amount of a substance such as mercury in, say, liquid xenon, the absorption spectrum may be studied. The effect of the environment of xenon molecules on the spectra can be estimated either theoretically by calculating the interaction, or experimentally by varying the density and noting the differences in the spectra produced by the changing intermolecular distances.

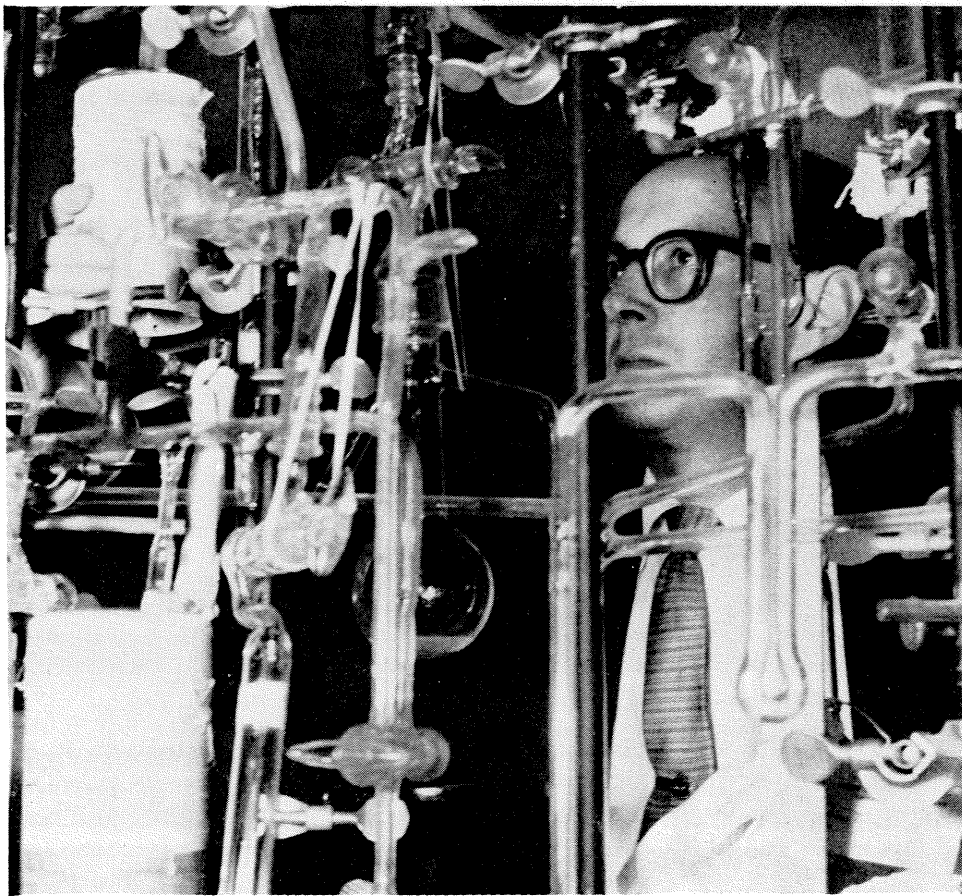
The results of one of these experiments has thrown some light on the problem of molecular distribution in a liquid. Dr. Robinson noted that one of two components of the spectrum, observed for mercury atoms

dissolved in liquid xenon, corresponded almost exactly in position with the spectral line recorded for mercury in solid xenon. Similar results have been observed for a number of other simple solvents. This indicates that there is a tendency for "clusters" to form in these liquids, with intermolecular distances and local density very similar to that found in the solid. The second component in the liquid phase spectrum is tentatively identified as arising from mercury atoms adjacent to vacancies in the liquid structure.

Another technique employed by Dr. Robinson to obtain molecular spectra consists of freezing one of the inert gases in such a way that molecules of the substance under study are trapped in the crystal lattice. Diatomic carbon frozen in a solid xenon lattice is particularly interesting because it is an experimental example of a quantum mechanical harmonic oscillator in a small box.

The inert gases are also of interest to the chemical biologist. For example, xenon is found to be an almost perfect anesthetic agent—in spite of its chemical inertness. This has been a puzzle for some time, but is understandable in the light of a recent theory of anesthesia. Originally proposed by Linus Pauling, professor of chemistry at Caltech, the theory is now being investigated by John F. Catchpool, research fellow in chemistry. Dr. Pauling suggests that anesthetics cause unconsciousness by reacting with the water in the brain to form microcrystalline hydrates. The effect of these crystals is to reduce the electrical conductivity and, hence, the activity of the brain. The only known chemical property of xenon is that of forming a crystalline hydrate—a fact which is most significant in the light of Pauling's theory of anesthesia, as it could account for the effectiveness of xenon as an anesthetic agent.

G. J. Wasserburg, associate professor of geology, is



G. J. Wasserburg, associate professor of geology, uses isotopes of argon and xenon to determine the age at which a mineral crystallized.

interested in the inert gases as they occur in nature. For example, the A^{40} isotope of argon is produced by the radioactive decay of the potassium isotope K^{40} , and may be used to determine the age at which a mineral crystallized. This method has been used to date meteorites. The amounts of A^{40} and K^{40} measured in some stony meteorites showed that these objects have existed for about 4.4 billion years. Helium, argon, and xenon have cast some light on the nature and origin of natural gas accumulations.

Even in an engineering field such as jet propulsion, the inert gases are proving to be useful materials for research. R. G. Jahn, assistant professor of jet propulsion at Caltech, uses a 21-foot-long tube of argon to study the ionization of gases by shock waves. The wave is made to travel through the tube at speeds ranging from seven to ten times the velocity of sound. The passage of the wave raises the temperature for an instant to 5000°C —high enough to initiate measurable ionization in the argon. The rate at which the argon approaches its equilibrium ionization level is measured by its absorption and reflection of a probing microwave beam.

Studies of this nature are valuable because conditions in the shock tube are similar to those found in jet propulsion devices. The knowledge gained by performing experiments with simple substances such as argon may lead to a better understanding of the basic mechanisms which occur in these devices and thus result in improved designs.

Argon, krypton, and xenon have normal physical properties. Helium, however, falls into a category of its own. Helium gas condenses at about 4°Kelvin to form a colorless liquid. If this is cooled, at about 2°Kelvin it undergoes a "second order" phase change to form another type of helium, known as liquid helium II.

Further cooling will not produce solid helium, however. Helium has a high "zero-point vibrational energy," which is sufficient to prevent the light helium molecules from forming a crystal lattice. Even if it were possible to lower the temperature to 0°Kelvin , a pressure of 25 atmospheres would be required to overcome the vibrational energy sufficiently for solid helium to be formed.

Liquid helium II demonstrates many unusual properties. It is sometimes referred to as a "quantum" fluid because much of its behavior is understandable only in the light of quantum theory.

To explain the properties of helium II, physicists have proposed what is known as the "two-fluid" theory. On the basis of this theory, liquid helium is supposed to consist of two fluids, one a "normal" fluid and the other a "superfluid." These both occupy the same space, but nevertheless operate independently of one another.

The normal fluid is responsible for the properties of liquid helium II which are usually associated with liquids—for example, viscosity and heat content. The superfluid, on the other hand, has no viscosity or

even entropy. It does, of course, still possess its zero-point energy. As the temperature of liquid helium drops toward absolute zero, the relative amount of the superfluid increases and that of the normal fluid decreases. At 0° Kelvin, only superfluid would remain and helium would then be a "perfect" fluid.

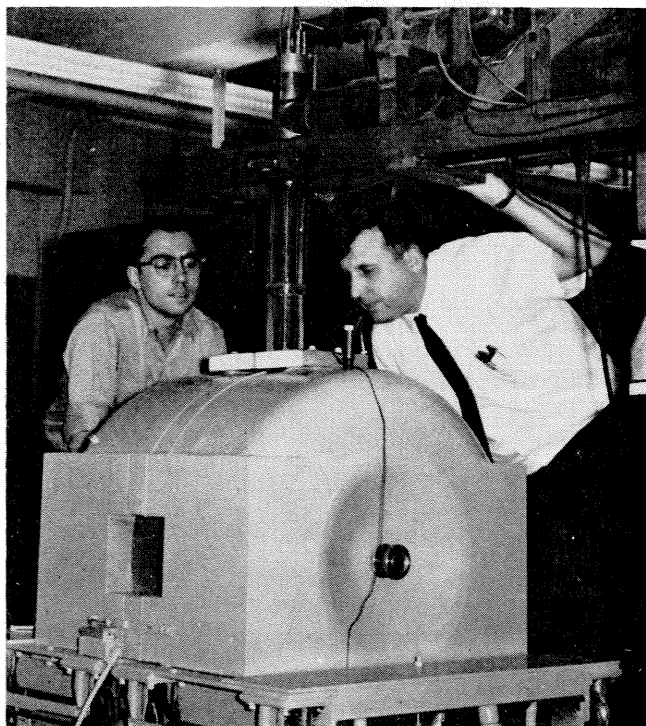
At Caltech, John Pellam, professor of physics, has carried out experiments designed to test the two-fluid theory. One of these involves a concept known as the "second-sound" method of heat propagation. In a normal substance heat transfer by conduction is "smeared out" as it travels through the material. According to the second-sound theory, however, a heat pulse will travel through superfluid helium without losing its thermal profile and will advance according to a wave type of propagation.

There are, of course, definite properties associated with waves. Before the second-sound theory was accepted, these characteristics had to be demonstrated for second-sound thermal waves. Dr. Pellam, in conjunction with John Mercereau, assistant professor of physics, devised an experiment in which a diffraction pattern was produced by a number of thermal sources placed equal distances apart. Several orders of thermal intensity maxima were observed at angles to the thermal grating similar to those observed when x-rays are diffracted by a crystal. This wave-like behavior presented striking evidence in favor of the second-sound theory.

Arising from the superfluidity of helium II, a novel device known as the "superfluid wind tunnel" has



Kenneth Harwell, graduate assistant in aeronautics, and R. G. Jahn, associate professor of jet propulsion, use a 21-foot-long tube of argon to study the ionization of gases by shock waves. Conditions in the shock tube at high pressures are similar to those found in jet propulsion devices.



In Caltech's low temperature laboratory, Harris Notary, graduate student, and Donald B. Lawson, cryogenic engineer, use liquid helium and an electromagnet to produce temperatures close to absolute zero.

been invented by Dr. Pellam to test the basic principles of hydrodynamics. According to theory, bodies of arbitrary shape exposed to the flow of a perfect fluid will not experience "lift" or net force, but only a torque. By utilizing the so-called "thermomechanical effect," the superfluid in helium II is made to flow past the model of a wing assembly while the normal fluid remains stationary. The results of this experiment confirm the theoretical predictions. Within certain limits of superfluid velocity no "lift" is observed on the wing assembly.

An experiment performed by Dr. Pellam some years ago is particularly interesting because it provides a link with the historical past. A thermal "Rayleigh disc" was used to measure the torque produced by second-sound waves in liquid helium II. This device works on the same principle as the disc which was invented by Lord Rayleigh before the turn of the century, and which was employed by him for refined acoustical measurements.

It is appropriate that Rayleigh's name is still heard in the laboratory in connection with the inert gases, because he is the man who started the ball rolling with the discovery of argon. Seventy years ago the inert gases were unknown; now, at Caltech and elsewhere, they are firmly established as valuable materials for research.