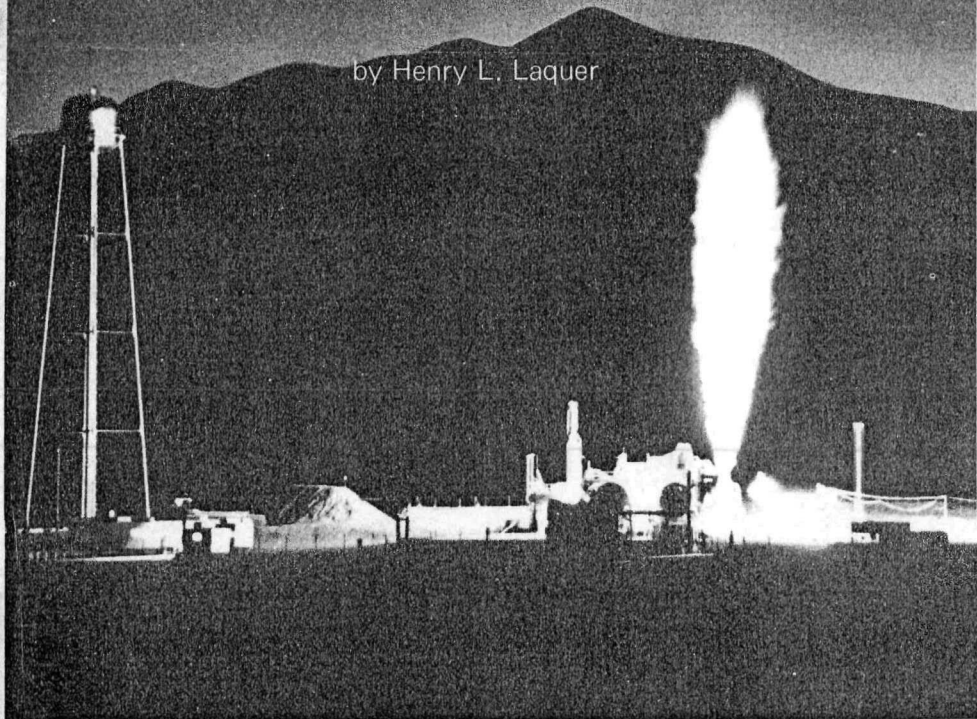


CRYOGENICS

the uncommon cold

by Henry L. Laquer



U. S. ATOMIC ENERGY COMMISSION—Office of Information Services



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Nuclear energy is playing a vital role in the life of every man, woman, and child in the United States today. In the years ahead it will affect increasingly all the peoples of the earth. It is essential that all Americans gain an understanding of this vital force if they are to discharge thoughtfully their responsibilities as citizens and if they are to realize fully the myriad benefits that nuclear energy offers them.

The United States Atomic Energy Commission provides this booklet to help you achieve such understanding.

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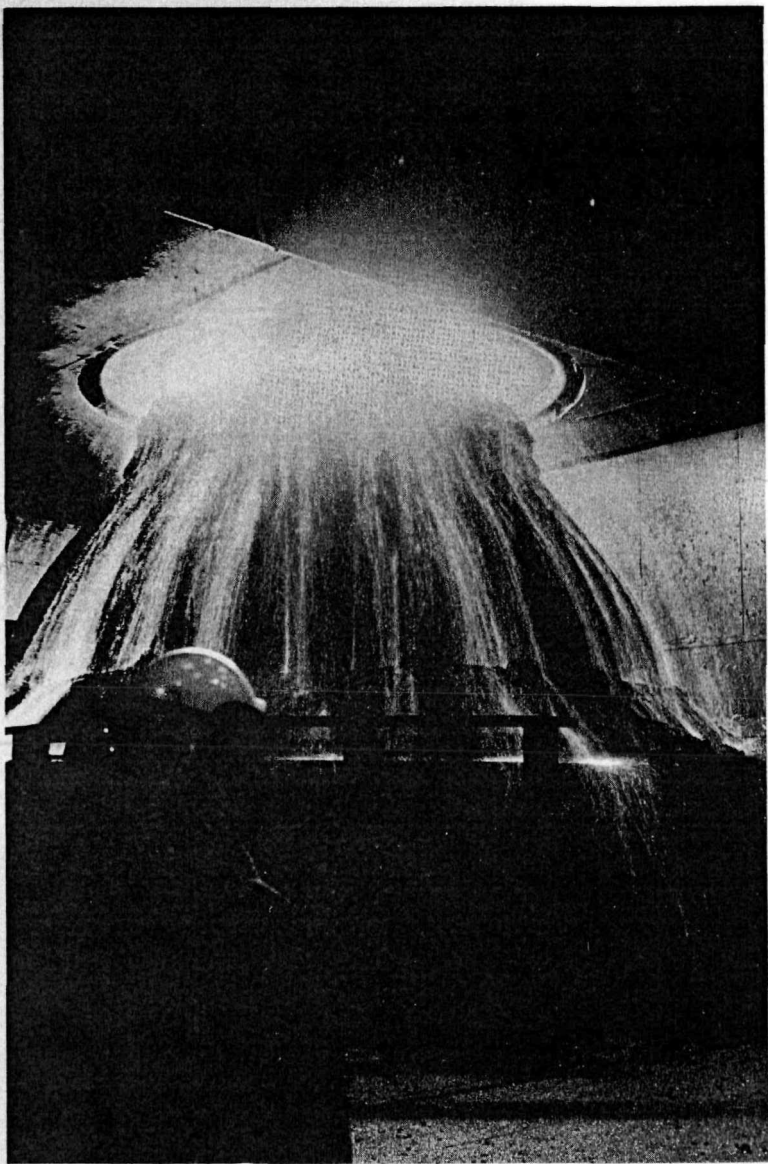
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Molten metal gushes, white-hot and fountain-like, out of this steel-making furnace when pure oxygen, produced under cryogenic conditions, is fed into the giant receptacle by a tube, or oxygen "lance". The steel industry is the largest user of liquid oxygen. (Also see Figure 21.)

CRYOGENICS

the uncommon cold

By HENRY L. LAQUER

HOW COLD IS COLD?

How cold is snow?

How cold is the water in the Arctic Ocean?

How cold is dry ice?

How cold is liquid helium?

How cold is outer space?

Can you answer these questions? Why does anyone want to know the answers? What is it possible to do at these low temperatures that can't be done otherwise?

The science of cryogenics—the study and use of very low temperatures—tries to answer some of these questions. Cryogenics may be concerned with practical engineering problems, such as producing tons of liquid oxygen for manufacturing high-quality steel or burning rocket fuel. It may be used to quick-freeze a surgical tissue specimen for a medical researcher or to freeze-dry a lightweight dinner for a mountaineer. Or it may help a physicist study some of the most basic properties of matter. To do so, cryogenic researchers work with temperatures down to within a millionth of a degree of the absolute zero—more than 459° below zero (on the Fahrenheit scale).

As a science, cryogenics has been pursued for at least 75 years. We now know that at ordinary temperatures the atoms and molecules in all matter are in constant motion

or agitation. This motion often hides the fundamental interactions between atoms, nuclei, and electrons. Lowering the temperature usually reduces the interference caused by this motion. Thus, low-temperature studies have contributed much to our understanding of the forces between atoms and molecules, of the mechanisms by which electric currents are carried in metals and in semiconductors, and of the nature of that well-known, yet still strangely mysterious force, magnetism.

Cryogenics also has been essential in the discovery of two completely unexpected phenomena, superfluidity and superconductivity. For 40 years almost every theoretical physicist of note has struggled to explain these "super" properties, yet it is only in the last 10 years that consistent answers have been formulated to the questions they pose. Even today most of the explanation for superfluidity and superconductivity can be given only in the abstract language of quantum mechanics, although both scientists and engineers make daily practical use of these amazing properties.

Just as cryogenics is the study of "uncommon cold" so these "super" properties are "uncommon" almost to the point of incredibility. At ordinary temperatures it would be unbelievable if a liquid ran uphill or flowed freely through virtually airtight barriers, yet this is just what superfluid helium does at the extremely low temperatures of cryogenics. It would be equally amazing if an electric current kept flowing—and flowing—through a home electric circuit long after all connections with the power source had been broken, yet this is what happens in a superconductor. These unusual movements are not tricks, not "perpetual motion", and not fantasies, but very natural and understandable—if surprising—phenomena associated with low temperatures.

Cryogenic Technology

The large-scale industrial technology of cryogenics is less than 25 years old. At present, it is mainly concerned with the liquefaction of the "permanent" gases, such as hydrogen, helium, and oxygen. When liquid, all these substances are denser (more concentrated)—and hence

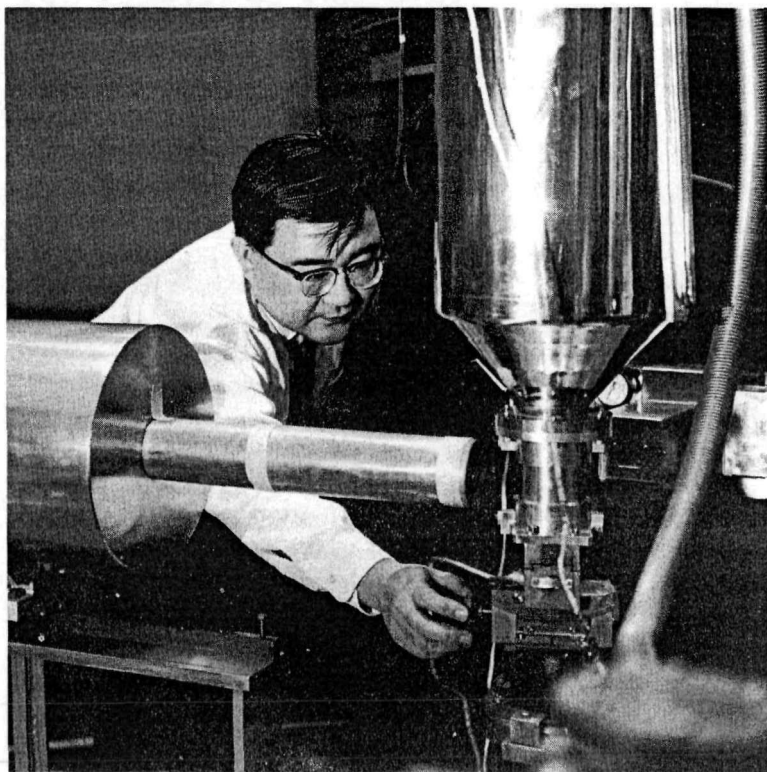


Figure 1 *A chemist adjusting equipment used with a large nuclear reactor to analyze crystal and magnetic structures of materials at extremely low temperatures. Sample of material is placed in the small holder below the large cylinder containing liquid helium. Tube, left, holds a detector to measure scattered neutrons.*

are handled more conveniently — than in the gaseous state. However, it took the demands of the Second World War and the space-exploration program, and the functioning of a vigorous economy to develop a national technology capable of producing liquid hydrogen and liquid oxygen in ton quantities. The commercial production of liquid helium began only in 1962.

Just as the study of nuclear physics has led to privately owned nuclear electric power plants, and the study of solid state physics led to transistor television sets, today's cryogenic research may lead to tomorrow's engineering marvels and even to new kinds of consumer goods. Cryogenic

techniques are now employed to produce ultra-high vacuums. Cryogenic computers and cryogenic high-field magnets for high-energy physics and controlled thermonuclear fusion research are also in use.

There may be other ways—ways we do not yet dream of—in which cryogenics can advance our technology or improve our lives. When radiation interacts with matter, significant changes are produced in the structure of matter, which may later be partially annealed (or healed), or altered in form by the constant motion of the atoms and molecules of which the matter is formed. We may gain an understanding of this process, as well as of the basic nature of matter itself, through the application of cryogenics.

This is because at the temperature of liquid helium we can “freeze in” the radiation effects by eliminating the healing effects of the atomic and molecular motion. This research already is of vital practical importance in select-

Figure 2 *Engineers lowering the world's largest high-field superconducting magnet into place for use with a bubble chamber for high-energy physics research. (Also see Figures 20, 31, and 32.)*

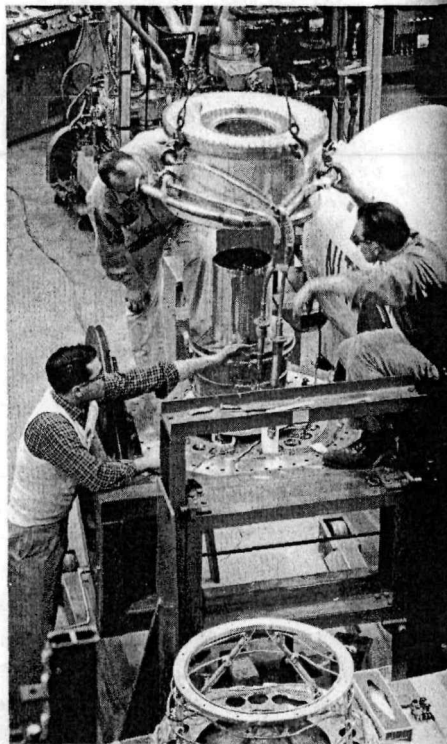




Figure 3 *Scientists checking a helium refrigerator developed for laboratory use to maintain temperatures as low as 0.04° above absolute zero. When in use the instrument is enclosed in a vacuum chamber.*

ing and processing materials for space exploration, since spacecraft operate in a cryogenic environment and are subjected to celestial radiation—and the resulting damage there is not even partially “healed”, as it might be at normal air temperature on earth. A related result of cryogenic research in space technology is the possible future use of superconducting magnets as shields for the protection of spacecraft from space radiation.

Still another important future use of supermagnets may be in magnetohydrodynamic (MHD) electric generators, which operate by passing a hot ionized gas, or plasma, rapidly through a magnetic field, thus converting the heat energy to electricity without the necessity of a boiler or turbogenerator.*

As we consider all these possibilities, we should keep in mind that the distinction between science and technology—basic research and engineering applications—is sometimes a little artificial and often hard to see. Today’s far-out science may be the foundation for tomorrow’s million-dollar industry in many fields, including cryogenics.

*See *Direct Conversion of Energy*, a companion booklet in this series, for an explanation of the MHD process.

TEMPERATURE

Now to come back to our question, "How cold is *cold*?" This ought to be simple. We all have a subjective feeling about temperature—about heat and cold—and, given a common mercury thermometer, we can measure the temperature of the air, of water, or of snow. Somebody has put numbers on the glass for us. These numbers refer to a temperature scale that has been established by more or less general agreement, similar to other units of measurement used in science and commerce. All we have to do is put the thermometer into the substance we want to measure, wait until we can't see a further change, and then read the position of the top of the mercury column.

The thermometer scale allows us to translate our subjective feelings into scientifically usable quantities, quantities that have the same meaning from day to day or year to year, quantities that will be the same when measured with different thermometers (provided the thermometers are well made). Unfortunately, an ordinary mercury thermometer won't work in "dry ice"* since the mercury will freeze, and if we should immerse it in liquid air or liquid helium the thermometer glass probably would break. We will have to find other thermometers for our low-temperature measurements. Worse yet, we will have to use another scale, since the Fahrenheit† (°F) scale that is used to describe the weather, or more accurately to measure the temperature of the air, is a relic that survives only in the English-speaking countries. Most of the world, by international agreement, uses the Centigrade or Celsius‡ (°C) scale, both for everyday and for scientific temperature measurements. In low-temperature work, however, both these systems are cumbersome and we prefer to use the absolute or Kelvin§ (°K) scale of temperature. This

*Solid carbon dioxide, CO_2 .

†Named for Gabriel Fahrenheit, German-Dutch physicist, who invented the mercury thermometer as well as the Fahrenheit scale.

‡Named for Anders Celsius, Swedish astronomer, who devised it. Centigrade means "hundred steps".

§Named for William Thomson (Lord Kelvin), a Scots physicist, who conceived the scale, as well as the concept of absolute zero.

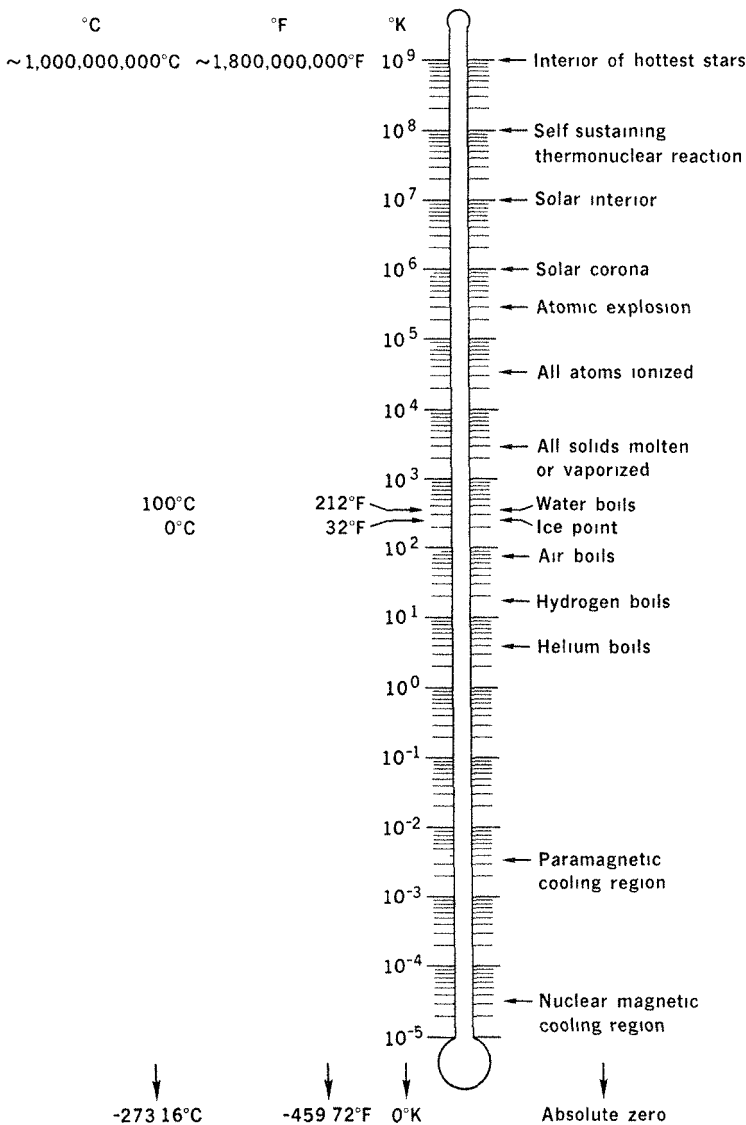


Figure 4 Temperature scales. The effort required to reach low temperatures is implied in the logarithmic presentation of the absolute temperature scale just to the left of the thermometer. This presentation also emphasizes that since heat always flows from a hotter to a colder region it will never be possible to reach the absolute zero of temperature in any laboratory apparatus.

scale is based on the rather difficult concept of an absolute zero of temperature.

Absolute Zero

The absolute zero represents that state of matter at which all motion has ceased. By motion is meant all spatial, mechanical, molecular, and vibrational motion, as well as some forms of electronic motion. Not included, however, is the quantum mechanical concept of "zero-point motion", which cannot be taken away without destroying the assembly or system of moving particles. (See Appendix.) By the nature of this definition the absolute zero can never be reached in any experiment, but it has been approached to within a millionth of a degree.

All these motions taking place within matter are called *thermal motions*. They are not visible as such on the surface of any material, but, as we shall see, the extent of this motion determines most temperature-dependent properties of matter.

Just as a straight line is determined by two and only two points, a temperature scale is defined by two fixed and reproducible temperatures. Originally, the Centigrade scale was defined by the melting point of ice (0°C) and the boiling point of water (100°C) at normal or standard atmospheric pressure (760 millimeters of mercury, or 760 torr*), and the absolute scale by the absolute zero (0°K) and the melting point of ice (273°K). Unfortunately, this amounted to having three fixed points, which led to inconsistencies. Because scientists wanted to have the size of the degrees exactly the same on both scales, it became necessary to change the number associated with one of the points by as much as a hundredth of a degree whenever accurate experiments on the interrelationships of the three points were undertaken.

At present, there is really only one fixed point (other than the absolute zero) established by international agreement, and that is the freezing point of water under its own vapor pressure, the "triple point of water". In 1948, it was permanently assigned the value of 273.16°K , or 273.16

*Named after Evangelista Torricelli, an Italian physicist who invented the first barometer

degrees Kelvin (above absolute zero). The normal freezing point of water subjected to the larger pressure of 1 atmosphere of air is slightly lower and becomes 273.15°K ($= 0^{\circ}\text{C} = 32^{\circ}\text{F}$), and the normal boiling point of water becomes 373.15°K ($= 100^{\circ}\text{C} = 212^{\circ}\text{F}$). Actual values in $^{\circ}\text{C}$ for these and a number of other secondary thermometric reference points (the so-called International Practical Temperature Scale), as well as the best methods for realizing them accurately in the laboratory, are published periodically by the International Committee on Weights and Measures.*

THERMOMETERS

Two, three, or five fixed points define one, two, or four segments of a temperature scale, but in order to measure arbitrary temperatures we need thermometers that give continuous coverage over the entire range. Fortunately, many physical properties of matter change sufficiently with temperature so that they can be used as the basis for thermometers. To do this, one assumes, at first, that the property changes smoothly and linearly with changes of temperature and therefore that the distance between the fixed points can be divided into a scale of equal parts with each degree occupying as much distance, or angle, or voltage, or whatever property, as the next degree.

Thus the mercury thermometer, which is based on the thermal expansion of liquid mercury relative to glass, usually has a linear scale. Other inexpensive thermometers for use at low temperatures, filled with colored alcohol or a liquid hydrocarbon, also have linear scales.

Length changes of many materials could be used if only one could find a comparison material that maintains an unchanging reference length. But this, in fact, is not easy to come by, and it is simpler to bond strips of two dissimilar metals over their entire length and then measure the sideways deflections of the bi-metal bar (because of the unequal

*There are also other temperature scales. For example, American space engineers use the Rankine scale ($^{\circ}\text{R}$), which is an absolute scale with the size of the degree equal to the Fahrenheit degree ($\frac{5}{9}$ of a Centigrade degree), so that $491.67^{\circ}\text{R} = 273.15^{\circ}\text{K} = 0^{\circ}\text{C} = 32^{\circ}\text{F}$.

expansion of its component pieces) as the temperature changes. In such a thermometer, equal angles represent equal temperature differences. Other thermometers use changes in electrical resistivity (resistance thermometers), or in thermoelectric power (thermocouples), or in vapor pressure.

One difficulty with having so many different means of measuring temperature is that the values at points other than the fixed or calibration points may not, and probably will not, agree exactly if measured with different types of thermometers. This problem becomes particularly serious at temperatures that are outside the region for which fixed points have been established. It turns out that *most* physical properties do not change uniformly with temperature.

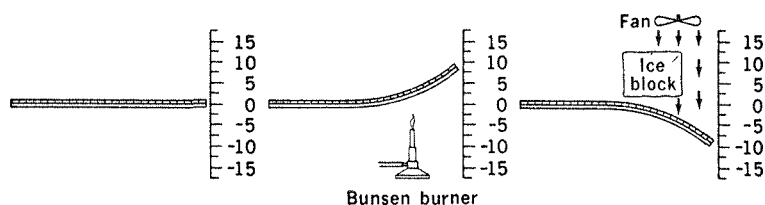


Figure 5 Action of a bimetal thermometer, showing deflection with temperature changes.

They do not follow a straight line very far; they are not linear, but if shown on a graph curve either up or down. Therefore, the assumption of equal scale increments breaks down sooner or later, and one has to decide which thermometer reads correctly and which one is in error.

The procedure for making this correction is closely related to the idea of a temperature scale with an absolute zero. The relation between the pressure (P), volume (V), and absolute temperature (T) of a given amount of gas is expressed by the well-known "Ideal Gas Law" equation:

$$P \cdot V = n \cdot R \cdot T$$

where n = the number of moles or molecules of gas, and
 R = the Gas Constant.

Thus when a fixed amount of gas is kept in a closed container, its pressure changes in direct proportion to the absolute temperature. An instrument making use of this law is called a constant volume gas thermometer. The exact temperature scale between fixed points is then defined by the "ideal gas" pressure.

Again, actual gases don't behave quite as indicated by the equation, but if their pressure is at a low enough level the necessary corrections are small. Nevertheless, to carry out precision gas thermometry is a tedious and exacting chore, and there are fewer than a dozen laboratories in the world that perform precision gas thermometer calibrations at low temperatures.

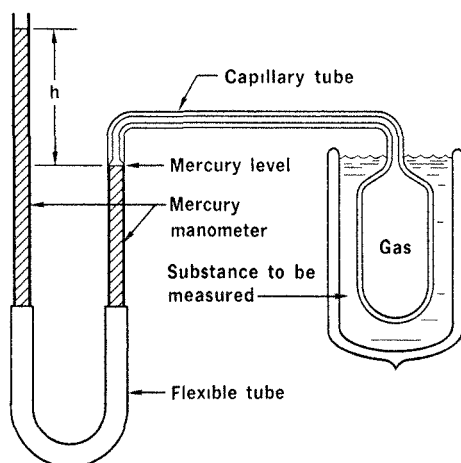


Figure 6 A constant-volume gas thermometer. The absolute temperature is proportional to h , the difference in height of the two mercury columns.

There are also some thermometers that can be used *only* at cryogenic temperatures because they depend on a physical property that varies *inversely* with the temperature, or as $1/T$, so that the response gets bigger as the temperature gets lower. These include the germanium-resistance and carbon-resistance thermometers and magnetic thermometers. The former measure electrical resistance and the latter magnetic susceptibility, that is, the response of the substance's individual elementary "mag-

nets" to a magnetic field, a response that will be described later.

Scientists studying low temperatures need more than anything else thermometers that give reproducible results.

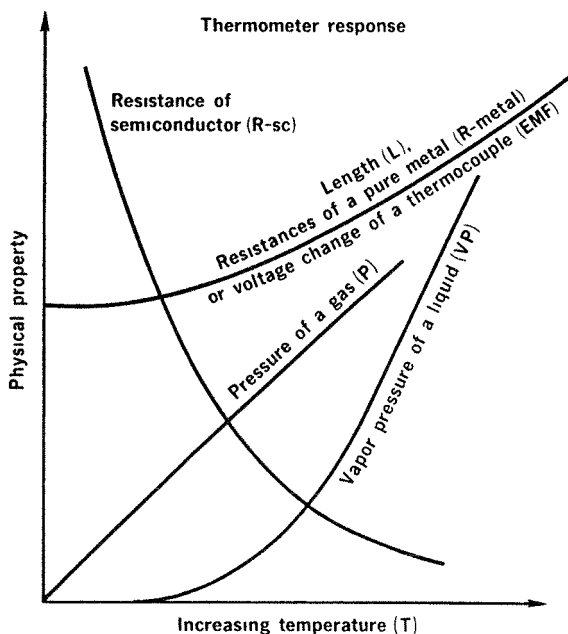


Figure 7 The relative response of various thermometers used in low-temperature work. The gas thermometer is the only instrument whose pressure indication remains linear over most of its range. The responses of the pure metal resistance thermometer, which changes resistance, and of the thermocouple, which generates a voltage proportional to the temperature difference, drop off to nothing between 10°K and 20°K but are almost linear above 70°K. A vapor pressure (V.P.) thermometer is never linear but usually has an exponential response.

STATES OF MATTER

We have already implied that temperature, whether hot or cold, always refers to something: air, water, the human body, or a specific substance. Temperature is a property of matter. We can raise the temperature of a substance only by adding energy to it, from the flame of a candle or an electric heating element, for instance, or from mechanical or electronic vibration. To lower any temperature requires the removal of energy. The amount of energy required to raise or lower the temperature of 1 gram of matter by 1 degree Centigrade is called the *specific heat* of that material.

If two different isolated substances at different temperatures are brought into contact, it is necessary to know the specific heat as well as the quantity of each material before one can predict the final equilibrium temperature of the new "assembly" of substances. The heat gain of the colder substance will be equal to the heat loss of the warmer substance.

If we have for the warmer substance the mass m_1 , the specific heat c_1 , and the initial temperature T_1 , and for the colder substance the corresponding m_2 , c_2 , and T_2 , then the final temperature T_f can be obtained from the equation:

$$m_1 \cdot c_1 \cdot (T_1 - T_f) = m_2 \cdot c_2 \cdot (T_f - T_2)$$

Specific heats of different materials differ greatly, and even for the same material there are variations with temperature; in such a case, the above equation has to be more complicated, of course. The usual variation-with-temperature of the specific heat of most solids is shown in Figure 4. The specific heat is low at very low temperatures, rises sharply, and then levels off at about room temperature before starting to rise again. Eventually there is an abrupt break, or discontinuity, in the specific heat curves of all solids. Energy cannot be added indefinitely to a solid without changing its state, or phase, to a liquid; nor can it be added to a liquid indefinitely without turning it into a gas.

Sometimes there are also phase changes from one kind of solid structure to another one in which the atoms have

a different arrangement (such as graphite and diamond, which are different solid forms of carbon). Provided the pressure remains constant, a phase change always occurs at the same temperature. Once a solid starts to melt as heat is applied to it, heat is taken up in the melting process (the hidden or latent heat of melting), and the temperature remains constant until the entire solid has melted. The melting point of a pure substance therefore always represents a well-defined temperature and, as we have already

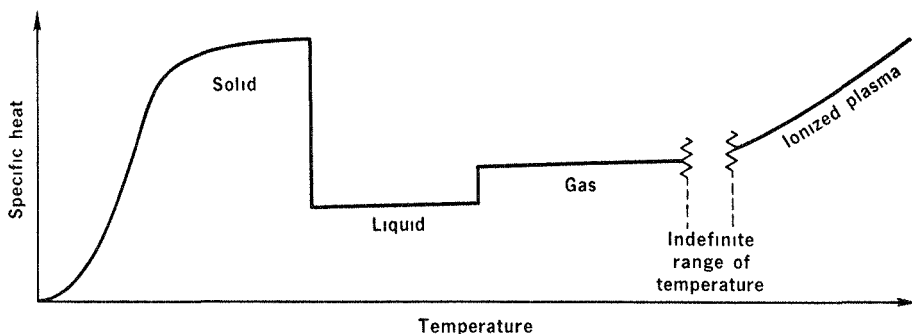


Figure 8 *Temperature variation of the specific heat of a typical substance. Note the abrupt breaks taking place at phase changes. Sketch does not indicate the magnitude of the latent heats taken up at the phase changes.*

seen, can be used to establish fixed points on the temperature scale. Clean snow melting in the sun at sea level is always at 0°C .

A similar process takes place on vaporization or boiling, and on the relatively rare phase change from solid directly to gas, which is called sublimation. Again a latent heat keeps temperature constant until the entire material has turned into vapor (provided the pressure remains constant). We already know that water boils at 100°C at sea-level barometric pressure, but not on a mountain where the atmospheric pressure is much lower. On Pike's Peak water boils at 83°C and atop Mount Everest it would boil at about 68°C . Solid carbon dioxide, "dry ice", sublimates and becomes vapor at -78.5°C , but if we can maintain it at a pressure of 5.2 atmospheres (5.2 times atmospheric pressure at sea level), it will melt and form a liquid at -56.6°C .

If we continue to add more energy to a gas or vapor, each atom or molecule will eventually start to break up into electrons and positive ions. This change to "the fourth state of matter", the ionized plasma, does not occur at a well-defined temperature but is spread over a temperature range. This is because there is no longer a simple, pure component of material, but a mixture of ions and electrons. The formation of a plasma is more similar to a chemical reaction than to a physical phase change. The study of ionized plasmas has given us a better understanding of the ion belts (the ionosphere) surrounding the earth and is basic to research on controlled thermonuclear fusion, since at the high temperatures required for fusion reactions, all matter is completely ionized.

Thermodynamic Studies

The measurement of specific heats and of latent heats is part of the study of thermodynamics and gives us clues to the nature of the forces between atoms and molecules, as well as about the arrangement and motion of the atoms in solids, liquids, or gases.

At very low temperatures, say within 5 or 10 degrees of the absolute zero, there is little atomic motion left and most specific heats appear to approach zero. However, there are quite a few substances whose specific heats rise again when the temperature drops to 1°K, or even lower. Such bumps or peaks in the specific heat curves* are often caused by the interactions between the tiny natural magnetic fields associated with the motion and the spin of the electrons surrounding some atoms† and, at still lower temperatures, by the still weaker "magnets" associated with some atomic nuclei.

These magnets can be thought of as permanently orbiting or spinning charged particles. Thus we speak of orbital magnetism and of electronic and nuclear spin magnetism, or "spin" for short. These elementary magnets can interact with their neighbors just as ordinary bar magnets interact

*The curves resulting from plotting specific heats against temperature on a graph.

†See *Microstructure of Matter*, a companion booklet in this series, for an explanation of electron spin.

with each other (except that with the elementary magnets the permissible energies do not vary continuously but in specific units or quanta). The interactions may be either a pairing with reversed polarity, so that there is a cancellation or neutralization of the magnetic fields, or the magnets may fall in line, reinforcing each other's polarity.

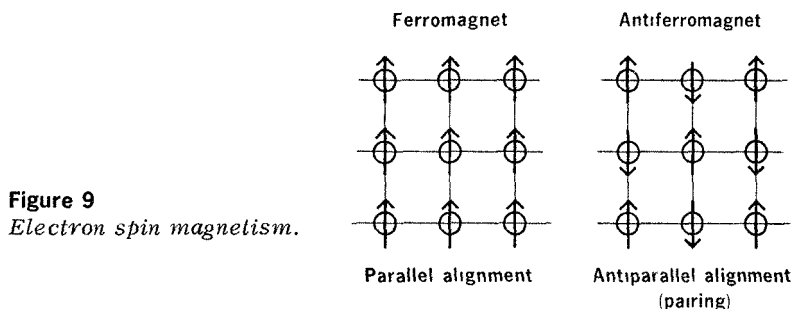


Figure 9
Electron spin magnetism.

Either arrangement represents a higher order than the random magnetic pattern that prevails at higher temperatures. The tiny magnets also respond to an externally applied magnetic field, and this forms the basis of the magnetic susceptibility thermometer mentioned previously.

Most of the magnets' pairing or ordering interactions are exceedingly weak, and since the energies corresponding to them are so much less than the energies corresponding to thermal motion at ordinary temperatures, they cannot become predominant to form stable assemblies until the very lowest temperatures are reached, when atomic and molecular motion is nearly nonexistent. The peak in the specific heat at or below 1°K corresponds to the gradual ordering as the temperature is lowered (or to disordering as the temperature is raised).

If the temperature can be lowered still further, a point is reached where the interaction is permanent and the magnets are rigidly locked together. Here, then, is another example of a phase change, from one kind of solid to another. If the magnets are all parallel and pointing in the same direction, we have a *ferromagnet* (such as steel and lodestone are at room temperature). If, on the other hand, the alternating magnets rigidly point in opposite directions there is complete cancellation of magnetic fields, and we have an *antiferromagnet*.

CREATION OF LOW TEMPERATURES

Just as raising the temperature of matter requires the addition of energy, lowering temperature requires the removal of energy. Unless there is a reservoir of cold available such as is provided by a large quantity of ice or snow, cooling usually is more difficult, and requires more complex machinery than heating. One reason is that heat will flow spontaneously from a hot object to a cold one, but never in the reverse direction. Energy can be removed by allowing a substance to do work—such as letting a gas expand, or by forcing a phase change to take place—such as letting a liquid evaporate.

This sort of cooling is a one-shot affair, and in either case, the substance will cool spontaneously and remain colder than it was as long as there is no influx of heat from its surroundings. Processes without heat influx from or outgo to the surroundings are called *adiabatic* processes, or, if they are done reversibly, *isentropic* processes, because then there is no change in entropy (to be explained later). On the other hand, an energy transfer that takes place at a fixed temperature while the substance is in firm contact with a heat reservoir (such as a large quantity of water) so that there can be no measurable change in temperature during the operation, is called an *isothermal* process. In contrast to one-shot cooling, modern continuous refrigeration involves the cyclic or repeated application of a cooling process and a working substance (a refrigerant) to cool some other substance or body. The four steps employed in a typical refrigeration cycle are shown in Figure 10 on page 18. They are:

1. The application of a constraint (compression phase), which will heat the working substance adiabatically.
2. The equilibration of the temperature of the working substance with a large heat reservoir at some fixed temperature without removal of the constraint.
3. The removal of the constraint (expansion phase) and the consequent automatic cooling of the working substance, again an adiabatic process.

4. The equilibration of the cooled working substance with a reservoir of the material to be cooled to the lower temperature.

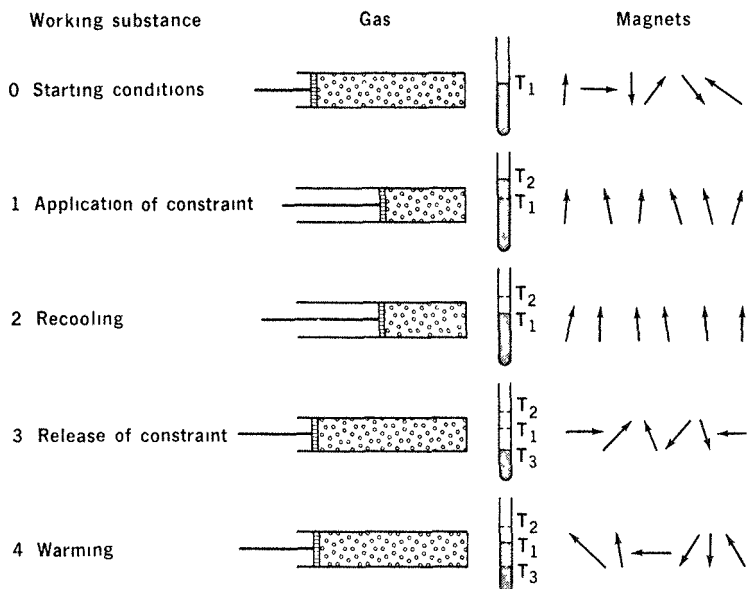


Figure 10 Steps required in all refrigeration cycles, left, and corresponding adiabatic demagnetization principles (see page 23).

In an ordinary household refrigerator, the refrigerating substance is one of the Freons, which are stable, nontoxic fluorocarbons. The Freon is compressed (step 1), and becomes liquid at room temperature in the so-called condenser (step 2). Reduction of the pressure lowers its temperature in the evaporator (step 3), which then cools the contents of the refrigerator (step 4). (See Figure 11.)

Cryogenic Refrigeration

Cooling anything to cryogenic temperatures is done with exactly the same series of steps, although the gases used as working substances in cryogenic refrigerators are the "permanent" gases, those which cannot be liquefied at room temperature by the application of pressure alone. Compression of the gas to 150 atmospheres (about 2000 pounds per square inch) applies a constraint and heats the gas (step 1).

Subsequently the temperature is lowered either to ambient (environmental) temperature using water cooling, or to a still lower value using a separate Freon refrigerator (step 2). Removal of the applied constraint by letting the gas expand while doing work, either by moving a piston or by overcoming the internal forces pulling individual atoms or molecules together, represents step 3 and leads to cooling.

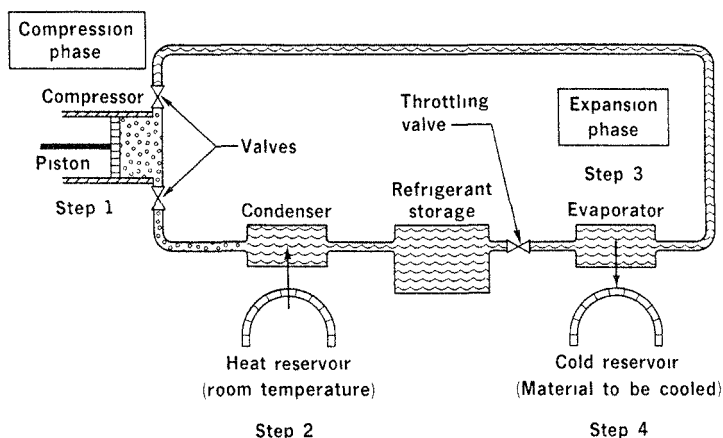


Figure 11 *Operation of a household refrigerator.*

This cooling or heating noted when gases do only internal work is known as the Joule-Thomson* effect. It arises from the fact that adjacent gas molecules, particularly when compressed, do not act like rigid billiard balls and merely exclude each other from a certain region of space. Instead they may have a very slight amount of attraction for each other, and also the ability to deform elastically, which in turn leads to repulsion. The attractive force is the same force that at low enough temperatures makes all gases condense to form liquids. When a gas expands, energy is required from some source to overcome this force; if the expansion is adiabatic, the gas cools. The elastic repulsion on the other hand means that it takes extra work to compress the gas and this energy appears as heating during adiabatic expansion. These opposing effects thus lead to

*Named for the British scientists, James P. Joule and William Thomson (Lord Kelvin), on whose work it is based.

with the object being cooled. Actually, in order to be most efficient, to make the initial cool-down possible, and to avoid building many stages of equipment operating at intermediate temperatures, all cryogenic refrigerators use countercurrent heat exchangers. These have two pipes or flow passages that are in good thermal contact over their entire length, and in which the gas flows in opposite directions so that the temperature difference between the two gas streams is always as small as possible. One gas stream cools the other as the second warms the first. This is the most efficient way to equalize the temperature between the compressed gas coming down from step 2 to

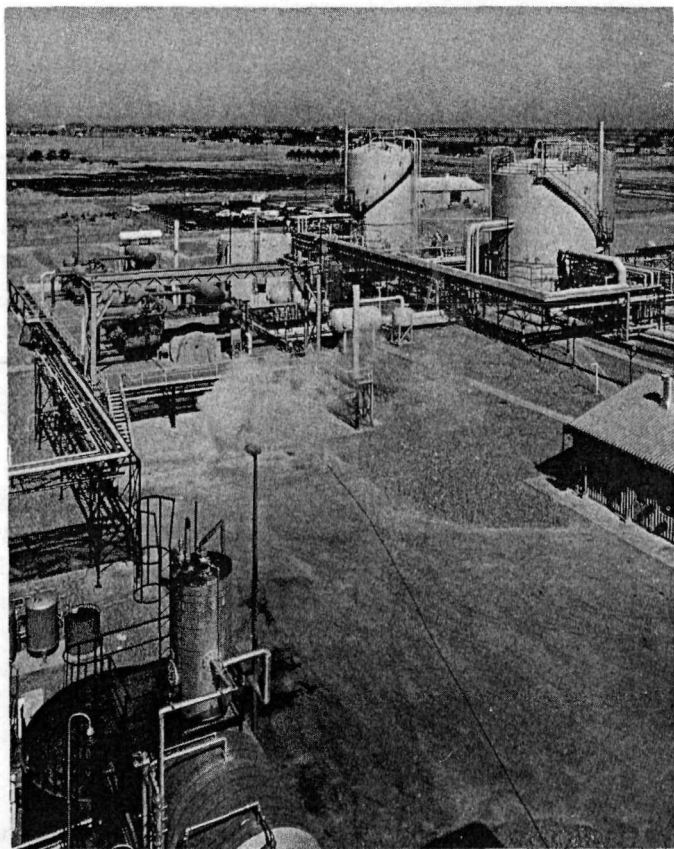


Figure 13 *This hydrogen liquefaction plant near Sacramento, California, produces 60 tons of liquid hydrogen a day for use in rocket testing.*

step 3 and the expanded, still-cold gas going up from step 4 and back to the beginning of the cycle. In a way we may look upon these heat exchangers as extensions of the equilibration steps, 2 and 4.

The Concept of Entropy

The operation of a refrigerator always requires the expenditure of more energy than one would calculate from the specific heat and temperature change of the working substance alone, and this would be true even if the refrigerator had a mechanical efficiency of 100%. This inequality of energies does not imply a breakdown of the law of conservation of energy (which states that energy cannot be created or destroyed), but rather describes the fact that heat energies of matter at different temperatures are not strictly comparable. What *is* comparable is the ratio of energy to the temperature. This is called the *entropy*.

Entropy thus measures the amount of thermal energy stuck, or "wrapped up", in a substance and not available to do mechanical work. As we have already mentioned, the entropy cannot change in an isolated (adiabatic) system that is "static" or in which reversible processes take place. However, most adiabatic processes cannot be performed in an exactly reversible manner; hence some entropy is lost and the processes therefore are not quite isentropic. The heat exchangers help to make the refrigerators more nearly reversible, but there always remains a fundamental limitation to the efficiency of any refrigeration machine or any thermal engine, that is, one that converts mechanical work into heating or cooling and operates between two different temperatures. Just as a steam power plant becomes *more* efficient the higher the operating temperature, a refrigerator becomes *less* efficient the lower its working temperature.

If the main purpose of a refrigerator is to produce low-temperature liquefied gases, it is called a *liquefier*. All that is needed is to provide some means of equilibrating the temperature of the gas with a reservoir at a temperature sufficiently low to change the gas into a liquid. Quite often the gas to be liquefied is itself the working substance of the refrigerator.

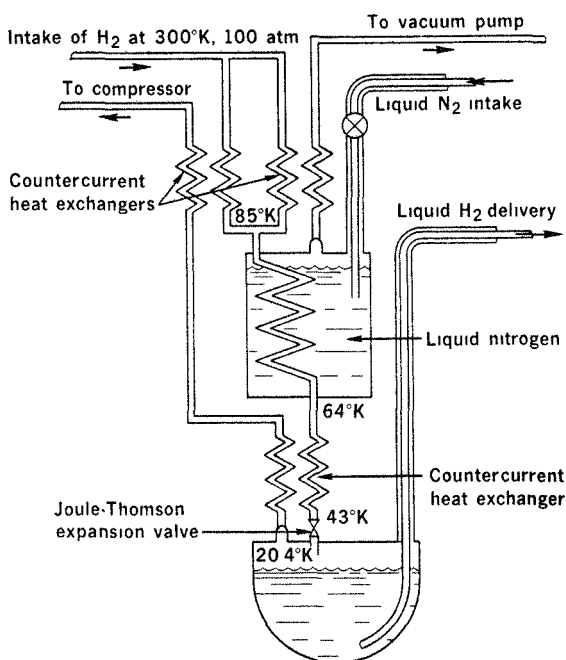


Figure 14 *Hydrogen liquefier. Intermediate cooling is by liquid nitrogen produced in a separate liquefier. "Pumping" on the liquid nitrogen lowers its temperature to 64°K. Liquid hydrogen is produced by Joule-Thomson expansion from 43°K.*

There are several advantages in using cryogenic liquids to cool down other materials. First, the liquids can be transported relatively cheaply, whereas a refrigerator is usually a fixed installation. Also, liquefier plants to serve a large section of the country can be made larger and more efficient than individual refrigerators. A final advantage of a liquid is that by pumping away some of the liquid, one can use the latent heat of vaporization to simultaneously lower the temperature and vapor pressure of the remaining liquid, and thus obtain stable temperatures lower than the normal boiling temperature. Thus, although helium boils at 4°K, it can easily be cooled by pumping down to 1°K.

A rather special kind of one-shot refrigerator or cooler is the adiabatic demagnetization apparatus whose working principle was shown in Figure 10 on page 18. It is used in a number of laboratories to produce temperatures in the

millidegree (0.001°K) region, starting from 1°K . In such an apparatus, the working substance consists of the elementary spin magnets of some atoms present in alums or similar salts, and the constraint consists of a magnetic field, yet the four steps in the cooling process are identical with the ones listed previously. The constraint (step 1) is applied by the magnetic field, which partially aligns the spins. Equilibration (step 2) is with a helium bath at 1°K . Removal of the constraint (step 3) is called the demagnetization, and the salt then cools whatever experimental equipment is connected to it (step 4), as the directions of the spins become random once more.

In order to reach *microdegree* (0.000001°K) temperatures it is necessary to start in the millidegree region and to do an adiabatic demagnetization on the still weaker nuclear spins. Such an experiment was done at Oxford University.* Scientists there attained a temperature of about a microdegree in a part of their sample. However, since the sample was not really isolated from the millidegree "heat" reservoir, it returned to its starting temperature in about 30 to 90 seconds.

The lowest temperature that now can be maintained for times of a few minutes to several hours is 1 or 2 millidegrees. This is now done routinely in some laboratories.

*Performed by Nicholas Kurti, Sir Francis Simon and their associates in 1956.

PRESERVATION OF LOW TEMPERATURES

It is seldom sufficient just to create the low temperatures or the cryogenic liquids. It is also necessary to maintain these temperatures. Energy flows from any temperature to a lower temperature region by the three usual processes of heat transfer: *conduction*, *convection*, and *radiation*. Different methods are used to cut back or reduce the energy or heat that is transferred by each of these processes.

Conduction of heat takes place in all materials — solids, liquids, or gases. If we want to reduce conduction in solids, we select materials that are poor conductors of heat, such as glass or alloys (like brass or stainless steel) rather than good conductors like copper or aluminum. We should also make the connecting link between regions with different temperatures as long as possible and as thin as possible, since the total heat conduction (K) is equal to the conductivity of the link (k) times the ratio of its cross-sectional area (A) to length (L) times the temperature difference ($T_2 - T_1$):

$$K = k \cdot (A/L) \cdot (T_2 - T_1)$$

Of course, there are limits to how far we can go. To reduce gas conduction, we try to remove all gas by enclosing the low-temperature region in a double-walled container with an evacuated space between the two walls. This requires a very high vacuum; sometimes it is easier to maintain a vacuum for a long time by adsorbing any gas that leaks in onto materials with large surface areas, such as charcoal, rather than by continuous pumping.

Convection, which involves the actual motion or circulation of matter, is of course eliminated when the gas is removed; where this can't be done, baffles can be used to cut down convection heat transfer, both in gases and in liquids.

Heat transfer by radiation is a somewhat more difficult process to visualize than conduction and convection. First of all, it should be pointed out that it is mostly invisible, long wavelength, or infrared radiation that is of concern here. Every body radiates energy in an amount propor-

tional to its surface area, its emissivity, and to the fourth power of its absolute temperature. The emissivity of a charcoal black surface is close to 1.00 (or 100%) and that of a shiny polished surface may be only 0.01 or 0.02 (1 or 2%) depending on the quality of the surface.

Heat Radiation In Space

A cold body facing a warm surface will simultaneously radiate energy and absorb energy from the radiation field of the warm surface. The question of temperature in outer space, incidentally, is best discussed in terms of heat radiation, since beyond the earth's atmosphere, matter is so dilute that there can be no conduction of heat. Also, the very dilute ionized plasmas present in much of space are transparent and do not radiate very much in the infrared region of the energy spectrum. Hence there is left only the radiation from the individual stars and galaxies, and in spite of the fact that each star may have a surface temperature between 1000 and 1,000,000°K, the average radiation received at any point in space from the firmament corresponds to a temperature of only 4°K. On the other hand, the temperature of a satellite in "near space" will be governed by the amount of radiation it receives from the earth, which radiates at about 280°K, from the bright side of the moon at 350°K, from the dark side of the moon at 150°K, and from the sun's surface at 6000°K.

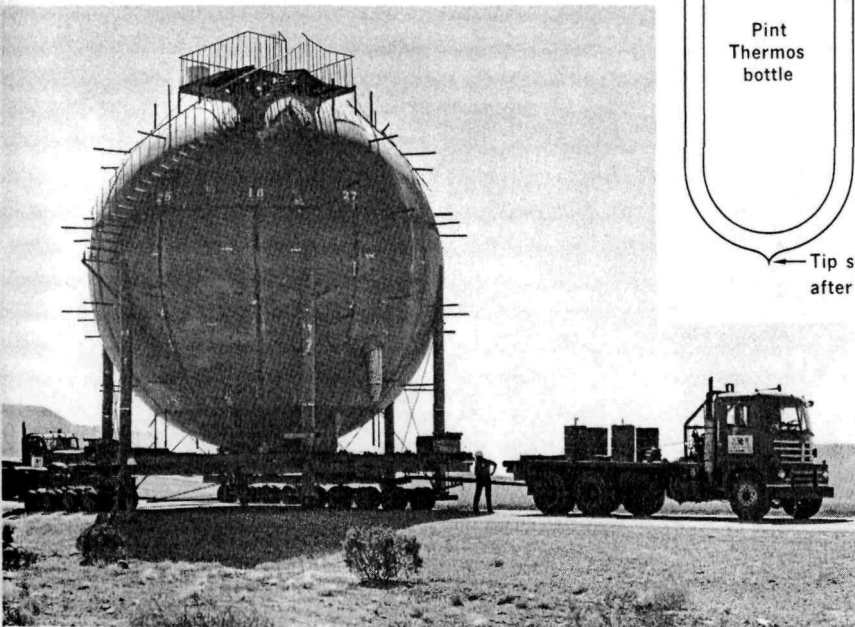
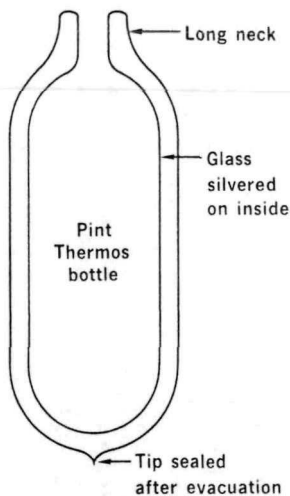
The first way to reduce radiant heat transfer, either in cryogenic equipment or in a satellite, is to polish or plate all surfaces (hot and cold) to make them shiny and highly reflective. A second improvement can be obtained by installing many "thermally floating" radiation shields. These are highly reflecting, lightweight metal or aluminized plastic foils having low heat capacity, thermally isolated from each other or from any heat reservoir; these foils can quickly change their temperature as dictated by the balance between the radiation falling on them and being emitted from them. The third step is to reduce the warm temperature "seen" by the cold body. This amounts to interposing at an intermediate temperature a container or surface that may be cooled by a cheaper, more readily available cryogenic liquid.

The best-known insulating container is the vacuum or Thermos bottle. Its scientific equivalent is called a Dewar (pronounced doo'er) vessel after its Scots inventor, Sir James Dewar (see page 54). The design principles are identical. Radiant heat transfer is reduced by polished or silvered surfaces. Gas convection is removed by evacuation, and conduction is reduced by using structures with long necks and thin cross sections. A properly designed Dewar loses less than 1% and often less than 0.1% of its contents per day. This loss or boil-off is a direct measure of the energy getting through the insulation, since

$$\text{Heat flux} = \left(\begin{array}{c} \text{Amount of gas} \\ \text{vaporized} \end{array} \right) \times \left(\begin{array}{c} \text{Latent heat} \\ \text{of vaporization} \end{array} \right)$$

Figure 15 shows a simple glass Thermos bottle compared with a welded 500,000-gallon steel container being assembled in the Nevada desert. The larger the container becomes the less important are conduction heat losses (or

Figure 15 Dewar flasks. *The construction of a pint Thermos bottle has some similarity to that of this 500,000-gallon liquid-hydrogen storage Dewar being moved to a fixed installation at a rocket-testing site in the Nevada desert.*



heat leaks) and the main effort is spent on reducing radiation. The double-wall jacket of the large container is filled with a volcanic powder (perlite) that in some ways serves as a multiple radiation shield. Other containers use "super-insulation" (Figure 16), which consists of many hundreds of layers of aluminum foil loosely spaced by glass or paper fibers.

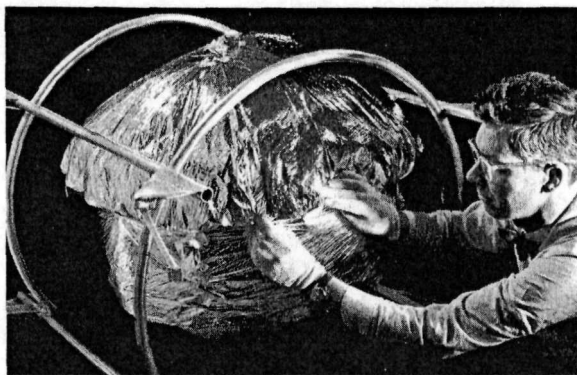


Figure 16 "Superinsulation" for long-term storage of cryogenic liquids in space. A worker wraps an experimental container with the aluminized plastic foil.



Figure 17 Liquid hydrogen transport truck. This 13,400-gallon Dewar, largest mobile unit in the United States, meets all regulations for safe highway transport of liquid hydrogen. It is vacuum-insulated but to conserve space and weight only a few inches of "superinsulation" are used in the vacuum space.

PROPERTIES AND USES OF CRYOGENIC LIQUIDS

Table I lists some important properties for the most common cryogenic liquids: oxygen, nitrogen, hydrogen, and helium. The *critical point* column shows the temperature above which it is impossible to liquefy the gas no matter what pressure one applies.

Table I—PROPERTIES OF LIQUIDS

	Critical temperature (°K)	Boiling point (°K)	Melting point (°K)	Density at B.P. (g/cm ³)	Heat of vaporization (joule/liter)
Water, H ₂ O	647.	373.2	273.2	1.0	2257000
Oxygen, O ₂	154.8	90.2	54.4	1.14	243000
Nitrogen, N ₂	126.1	77.4	63.2	0.80	161300
Hydrogen (99.7% para), p-H ₂	32.9	20.3	13.8	0.071	31600
Helium (four), ⁴ He	5.2	4.2	—	0.125	2720
Helium (three), ³ He	3.32	3.19	—	0.0586	480

Oxygen is usually obtained by liquefying air and then separating it from the liquid nitrogen in a low-temperature fractionating column, taking advantage of the fact that the boiling points of oxygen and nitrogen are quite different. Next to fluorine, oxygen is the strongest oxidizing agent known and almost all of it is used for oxidation purposes, both in chemical rockets and in the manufacture of steel. Daily production of liquid oxygen amounts to many thousands of tons in this country. Medical oxygen, although used in the form of a gas, is also frequently shipped and stored as liquid for economic reasons.

Liquid nitrogen, being a by-product of the liquid oxygen manufacturing process, has become increasingly plentiful and much more readily available in recent years.* It is chemically inert and has always been used to provide a safe, nonreactive, cryogenic environment both for research and for some commercial purposes, such as shrink fitting and tempering of steel parts. Because of its cheapness

*Tanks of "nitrogen" fertilizer used in farming are misnamed. The fertilizer is always based on ammonia, NH₃, or a derivative of it, and not on free N₂.

(about 50 cents a gallon), it is beginning to replace dry ice and refrigeration machinery in the shipment of perishable foods (Figure 18).

Liquid hydrogen is a dangerous, chemically reactive substance. It will react explosively with oxygen (even that present in the air) to form H_2O . This reaction is one of the most energetic chemical reactions known, and for this

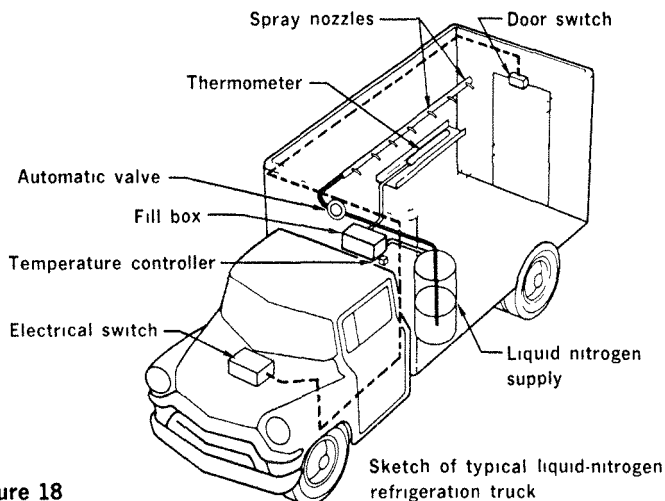


Figure 18

reason hydrogen and oxygen are used in chemical rockets (Figure 19). An entirely different property of hydrogen is made use of in the nuclear rocket being developed under Project Rover, a joint research effort of the National Aeronautics and Space Administration (NASA) and the Atomic Energy Commission (AEC).*

The effectiveness of any rocket engine is measured in terms of the *specific impulse*, I_s , which is the ratio of the thrust to the rate of fuel consumption when a hot gas expands in a rocket nozzle:

$$I_s = (\text{a constant}) \times \sqrt{T/MW}$$

where T = temperature of the gas, and
 MW = molecular weight.

*See *Nuclear Propulsion for Space*, another booklet in this series, for details of this project.

Hydrogen has the lowest molecular weight and hence will produce the greatest specific impulse when heated in a nuclear rocket reactor. Naturally then, it would seem best

Table II—COMPARISON OF VARIOUS METHODS OF
ROCKET PROPULSION

Source of Power	Specific Impulse (seconds)
Liquid oxygen + Kerosene (chemical)	300
Liquid oxygen + Liquid hydrogen (chemical)	390
Liquid fluorine + Liquid hydrogen (chemical)	410
Liquid hydrogen + Reactor at 1500°K (nuclear)	720
Liquid hydrogen + Reactor at 3000°K (nuclear)	1020

to make the temperature of the reactor as high as possible in order to raise the specific impulse; but, unfortunately, the strength of most materials decreases with increasing temperature, well before they start to melt.

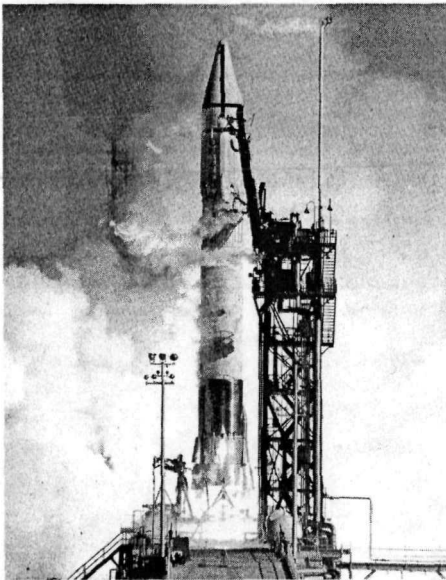


Figure 19 *This mighty Atlas-Centaur rocket, being launched at Cape Kennedy, Florida, uses 30,000 pounds of liquid hydrogen, in combination with liquid oxygen, in producing enough thrust to send a 2300-pound spacecraft to the moon. Note the vapors caused by the condensation of atmospheric moisture on the cryogenic liquid supply lines.*

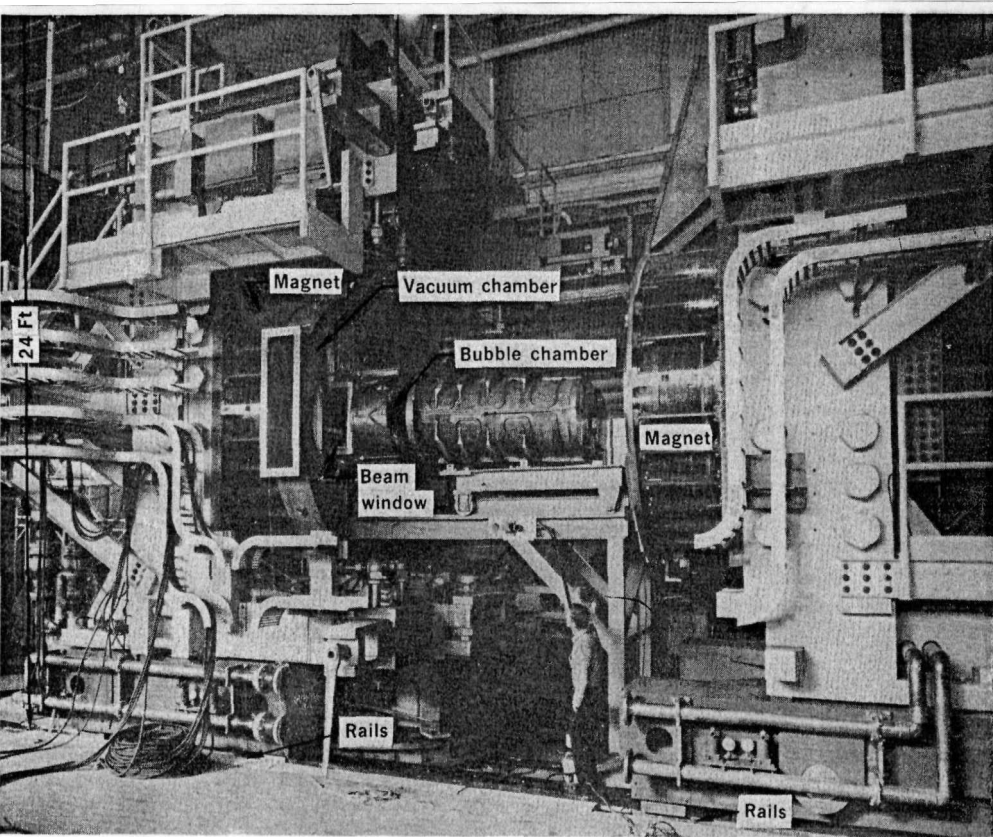


Figure 20 This 80-inch bubble chamber at Brookhaven National Laboratory uses 1500 liters of liquid hydrogen to help scientists visualize reactions of high-energy particles. The chamber is made "ready" by suddenly reducing pressure on the liquid, using a large lightweight piston (not shown). Fast-moving particles from an accelerator, entering the chamber through the beam window, cause the formation of fine gas bubbles along their paths. These are recorded photographically. The photo shows the bubble-chamber complex partially disassembled; the vacuum chamber and magnet can be closed by sliding the two halves together on rails.

There are other uses of liquid hydrogen based on the fact that the hydrogen nucleus, or proton, is the simplest nucleus and therefore the easiest with which to develop and test nuclear theories. The liquid hydrogen bubble chamber used for studies of high-energy particles, for example, enables scientists to study the interactions between high-energy particles and protons. These interactions are simpler than the interactions of the particles with heavier, more complex nuclei (Figure 20).

Ortho and Para Hydrogen

Molecular hydrogen, H_2 , exists in two different forms, depending on whether the nuclear spins of the two atoms are in the same direction (*ortho* hydrogen), or in the opposite directions (*para* hydrogen). There is a difference in energy between the two forms. Hence they act as if they were different chemical species and we can think of the processes by which changes from ortho to para hydrogen occur as we would of a chemical reaction. For instance, just as in a chemical reaction, the equilibrium ratio of the number of ortho to para hydrogen molecules in a mixture depends on and varies with the temperature. At room temperature the equilibrium concentration is 75% ortho hydrogen, whereas at 20°K the equilibrium composition has changed to 99.8% para hydrogen.

Liquefaction of room-temperature hydrogen gas leads to an unstable mixture that slowly converts to para hydrogen, giving off enough heat in the process to boil away 70% of the liquid produced. This used to make the storage of liquid hydrogen very difficult. The ortho-para hydrogen system, incidentally, was the first-known example of a gross effect that can be attributed to one of the usually hard-to-observe nuclear properties, like spin. Today most liquid hydrogen is passed over a catalyst to bring about ortho-para conversion during liquefaction; the best catalysts for this purpose are finely divided particles of a magnetic substance, such as chromic oxide or iron oxide, which provide a large surface on which the hydrogen molecules can rest or be adsorbed. The presence of the iron or chromium oxide magnets makes it easier for the hydrogen atoms' spins to realign themselves, adjusting to assure the proper equilibrium ratio of the ortho to para, so that the heat, or energy, of conversion can be absorbed in the liquefier. The resulting almost-pure liquid para hydrogen can be stored without large evaporation losses.

Liquid helium has the lowest boiling point of the common cryogenic liquids. It is chemically inert. Helium gas is obtained from some natural gas wells, and some liquid helium is produced commercially and shipped and sold (for about \$25 a gallon) in Dewar vessels holding 5 to 100 gal-

lons. It is an extremely valuable substance for much laboratory and space research, but as yet it has no commercial or manufacturing uses. As shown in the table, it has no melting temperature. Helium will remain liquid down to the lowest temperatures unless a pressure of 25 atmospheres is applied to it to make it become solid. The strange superfluid properties of liquid helium will be discussed later.

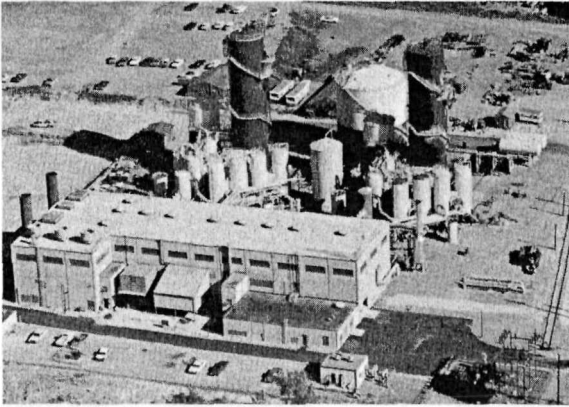


Figure 21 *This air separation plant at Gary, Indiana, is the world's largest, producing 4800 tons of oxygen and nitrogen by low-temperature distillation. From such plants oxygen often is piped directly to steel mills through high-pressure gas lines. (See Figure 1.)*

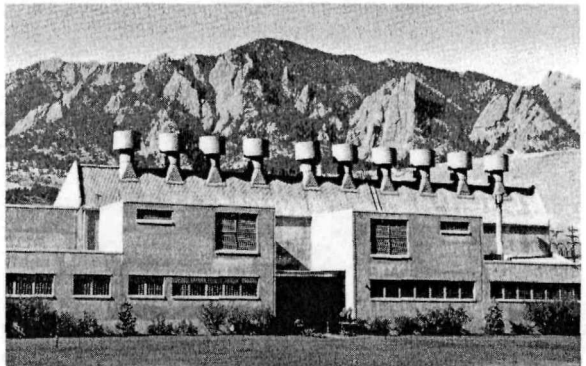


Figure 22 *In this building at the National Bureau of Standards, Boulder, Colorado, a hydrogen liquefier, operated for the Atomic Energy Commission for several years beginning in 1952, furnished a major portion of the nation's liquid hydrogen.*

PROPERTIES OF MATTER AT LOW TEMPERATURES

Mechanical Properties

It is not particularly difficult to design low-temperature apparatus, but there are some changes in the physical properties of all materials that must be taken into account in doing so. One of the most striking changes in the mechanical properties of many substances is that of embrittlement. A favorite demonstration of this effect is to dip a flower or a piece of rubber hose into liquid nitrogen and then to shatter the quick-frozen specimen into bits by dropping it on the floor. Ordinary steel also embrittles and may fail catastrophically at just slightly reduced temperatures, such as might be encountered in the Arctic or the North Atlantic Ocean (Figure 23).

Nonmagnetic stainless steel, on the other hand, withstands low-temperature environments quite well and is

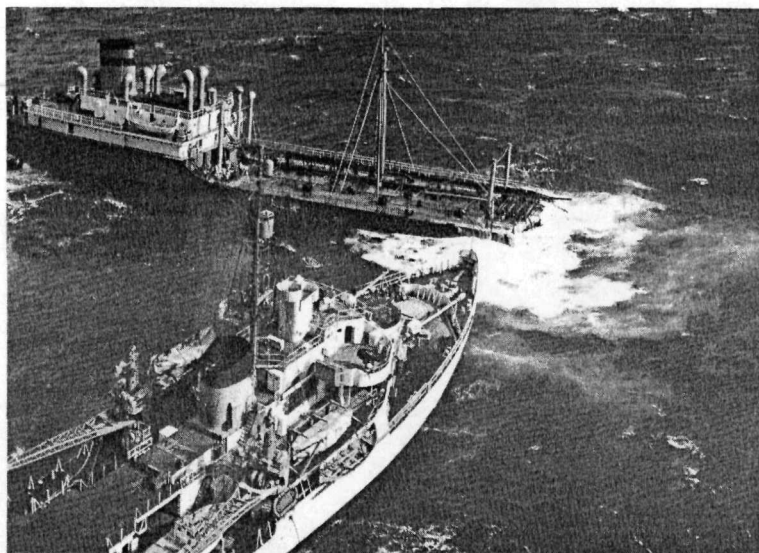


Figure 23 *The Coast Guard Cutter Eastwind (bottom) rescuing crew members from a broken merchant tanker during a winter gale in the North Atlantic. Ordinary iron and steel become brittle at low temperatures, especially under stress, and many welded ships broke up during World War II on this account.*

used in construction of much low-temperature equipment. Aluminum, copper, brass, and a number of other alloys are also suitable. As a matter of fact, the strength of most of these increases somewhat on cooling. The fact that most materials also shrink on cooling (0.1% for glasses, 0.2 to 0.4% for metals and 1 or 2% for most plastics, in a temperature change from 300°K to 4°K) must also be taken into account. This contraction is a direct consequence of the fact that the thermal motion of the molecules and atoms is reduced at low temperatures.

Electrical Properties

Temperature and thermal motion also affect the electrical properties of all materials. Solids, in fact, can be classed into three groups according to their electrical conductivity: metals, semiconductors, and insulators.

Metals

In all metals an electric current is carried by the negatively charged conduction electrons; that is, the metals are conductors of electricity. Under the influence of an externally applied voltage, these electrons will move freely through the solid, avoiding, for the most part, the positively charged metal ions that are located in a regular, repetitive three-dimensional pattern called a crystal structure or crystal lattice.*

The moving electrons do not pile up in any one place, since this would lead to an imbalance of electric charge between one point and another. If the electrons were completely free (as they are in an electronic vacuum tube) they would be accelerated by the applied voltage and reach very high velocities. In fact, however, they quickly attain a limiting velocity in metals, just as water does when it is forced through a pipe by a pressure difference. In the case of water, the flow velocity is limited by viscous friction between the liquid and the walls of the pipe. For the electrons, we have a somewhat similar interaction with the

*The particular arrangement of the metal ions determines the crystal lattice and is the most distinctive characteristic of all solids (except glasses). No two solids have the same crystal lattice and lattice dimensions.

fixed atoms of the crystal lattice, but only when these atoms are displaced from their equilibrium position. The process is a little bit like trying to throw a "superball" in a dense forest in which the trees are planted in an orderly pattern. There are passages between trees that are completely free of obstructions and the ball can travel freely; but if a tree has been planted out of line, or if the wind suddenly pushes a tree into the path of the ball, the ball will be deflected and bounce off in a new direction. Similarly, the electrons are scattered or deflected by any out-of-line or dislocated atom or by a foreign or impurity atom that doesn't belong in the lattice, as well as by the thermal motion, or "swaying", of the atoms about their equilibrium positions.

Thus the resistivity of metals, which is the reciprocal of the conductivity, is made up of three components, reflecting the pattern, the purity, and the thermal motion of the atoms. The thermal resistivity drops almost linearly as the temperature is lowered. For pure metals, the impurity and dislocation resistivities do not vary much with temperature and comprise only a small fraction (0.1 to 10%) of the total room-temperature resistivity. However, between 10 and 20°K the situation is reversed: The impurities and dislocations control resistivity.

If a metal, such as copper or silver, is sufficiently pure, its low-temperature resistivity can be less than 0.1% of its room-temperature resistivity. We must keep in mind that the electrons continually pick up energy from the applied voltage (which in turn may come from a generator or battery) and exchange some of that energy with the lattice in each electron-scattering event, so that we have a steady loss of energy that shows up as heat, raising the temperature of the conductor. In the case of metallic alloys, the impurity, or lattice-disturbance scattering, is so predominant that the drop in resistivity with decreasing temperature is much smaller than in pure metals. Some alloys, such as manganin (a combination of copper, manganese, and nickel), have so small a temperature variation in their resistivity that they are used as resistance standards for precision measurements.

Nonmetals

Nonmetals may be either semiconductors or insulators. In these materials there are no free conduction electrons. Insulators have no charge carriers at all. Semiconductors have a relatively small number of positively or negatively charged charge carriers (depending on their trace impurity composition). Also some of their electrons are sufficiently loosely bound to the atoms so that a slight increase in temperature breaks the bonds and makes more and more charge carriers available. Accordingly, semiconductors in general behave differently from metals in that their resistivity decreases (and conductivity increases) as the temperature is increased. All materials that have these strong changes in resistivity with temperature may be used as thermometers. The platinum resistance thermometer, made of a pure metal, can be used over a wide range of temperatures, and the carbon resistance thermometer, a semiconductor, is most useful for temperature measurements at the very lowest temperatures.

High Field Electromagnets

A recent application of the low resistivity of pure metals at low temperatures has been in the construction of strong, or high-field, electromagnets. Magnetic fields are measured in gauss (pronounced gowss).^{*} The earth's field has a strength of about 0.5 gauss, and the field between the ends of a good horseshoe magnet is about 1000 gauss, or 1 kilogauss. Iron concentrates magnetic field intensity, but only up to 20 kilogauss, at which point the iron "saturates". To produce stronger fields, pure electromagnets with many turns of high-current conductors are required.

Conventional water-cooled laboratory magnets in the 60-to-100-kilogauss range require several thousand kilowatts of electrical power to achieve their strength. Specially designed pure copper, sodium, or aluminum electromagnets, however, can be operated in liquid hydrogen, or near that temperature, so that their electrical power requirements are less than 1% of what they would be at room temperature

^{*}Named for Johann Karl Friedrich Gauss, a great German mathematician and pioneer in terrestrial magnetism.

(Figure 24). Even if one considers the power required to produce the refrigeration to keep them at cryogenic temperatures, there may still be a net power saving with some of these devices. However, it may well be that supercon-

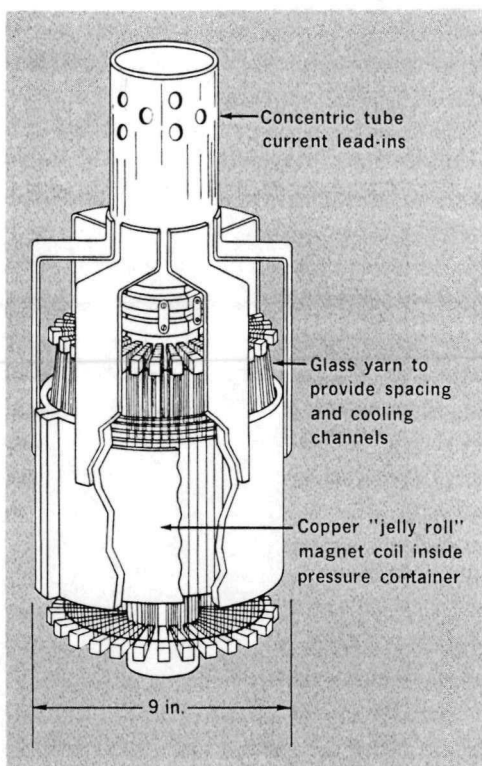
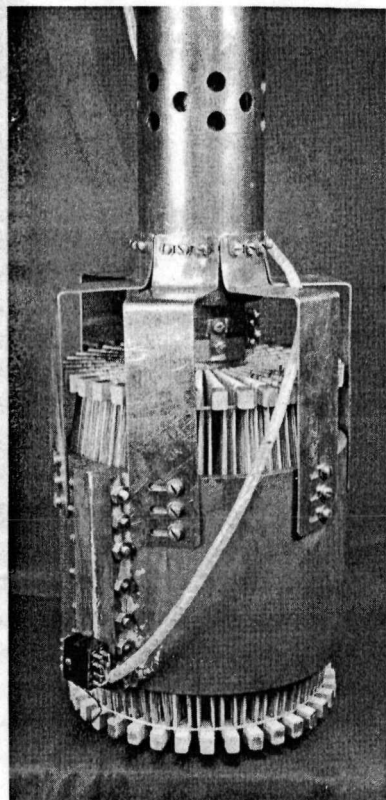


Figure 24 An 80-kilogauss electromagnet, cooled by circulating 50 gallons of liquid hydrogen per minute, was developed and is used by Los Alamos Scientific Laboratory for high magnetic field research. This "jelly-roll" copper magnet coil, in constant use since 1958, requires only 25 kilowatts of power to produce an 80-kilogauss field in a 2-inch working space. The entire apparatus is operated inside a Dewar.

ducting magnets (which will be discussed later) will soon make these "ordinary" cryogenic magnets obsolete. One important reason for the interest in economical magnetic fields is that they offer the only known way of containing ionized plasmas, such as would be required to achieve controlled thermonuclear, or fusion, reactions, a possible new source of cheap, abundant power.*

*For more about this process, see *Controlled Nuclear Fusion*, a companion booklet in this series.

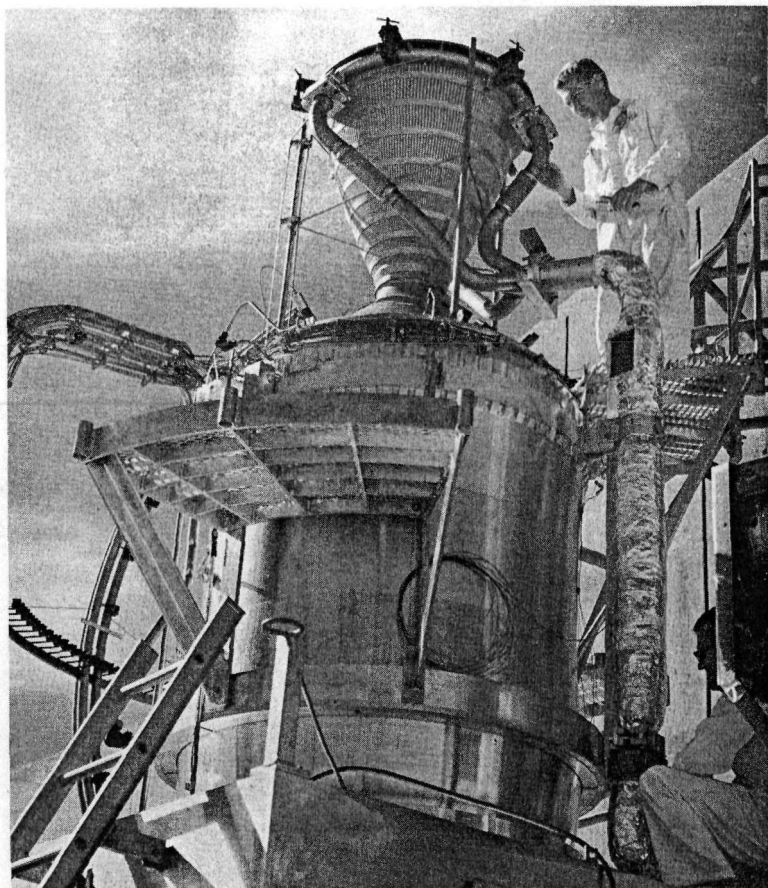


Figure 25 Workmen put finishing touches on the insulated pipes that will carry liquid hydrogen to the nozzle of the Kiwi reactor before the hydrogen is heated for firing tests. (See cover.)

QUANTUM FLUIDS

By far the most striking phenomenon that has been observed at low temperatures is *superfluidity*. This property is found both in liquid helium, which changes below 2.2°K from an ordinary liquid into one that has *no viscosity whatsoever*, and in a number of normally resistive metals and alloys, which at various temperatures below 20°K become *superconducting* and exhibit *no electrical resistivity whatsoever*! These superfluids are also called *quantum fluids*, because only quantum mechanical arguments* can be used to explain their behavior—behavior that is so special that these conditions have also been called a “fifth state of matter”. Both types of superfluidity were discovered at the University of Leiden, The Netherlands; superconductivity was discovered about 50 years ago by the Dutch physicist H. Kamerlingh Onnes; and the helium abnormality about 15 years later by W. H. Keesom.

In every respect the onset of superfluidity is a phase change. In spite of the fact that the fluid in one case consists of helium atoms and in the other case of electrons, there are so many similarities in the two processes that they can be considered at the same time. In both cases we have a new phase called a condensed phase, in analogy to the condensation of vapor into liquid. In each, there are telltale bumps on the curves when the specific heats of materials are plotted against temperature, indicating changes in the energy of the system. In both cases, the fluid in the condensed phase behaves as if it were one single giant molecule, no matter how many millions of atoms or electrons are present in the assembly. And in both cases there can be large-scale motion of helium atoms or superconducting electrons without the usual friction or resistance to flow observed in normal fluids, and therefore without the usual energy dissipation.

The reasons for the condensation process are different in the two cases and, as mentioned earlier, pose a difficult problem that has occupied theoreticians for many years. It has taken involved quantum mechanical reasoning and

*See Appendix.

calculations to justify the mechanisms or interactions thought to be responsible for the condensations. Counting or statistical methods are used and the results depend on the number of elementary particles involved, their spins and arrangements within the atom. For helium, a statistical method invented independently by the Indian scientist S. N. Bose and the famed Albert Einstein is used. For superconductors, a young American, Leon Cooper, suggested the pairing of electrons of opposite spin and angular momentum, and this approach has provided the basis for our present understanding. From these models the theorists then try to calculate the permissible and available energy levels of the system. For low energies we have many closely spaced energy levels, as indicated schematically in Figure 26, but as the energy increases a relatively large gap in the spac-

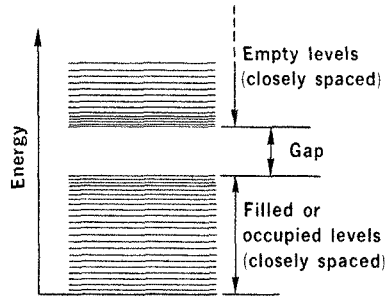


Figure 26
Energy levels with gap.

ing appears. It turns out that all the particles exactly fill all the levels below the gap, and that the thermal energy available per atom below a critical transition temperature is not sufficient to give any particle enough energy to bridge the gap. Thus the particles move about without interacting or exchanging energy with their surroundings, and we have frictionless or resistanceless flow. In effect, the motion of the particles throughout the macroscopically* large body of the superfluid is as unobstructed as the motion of electrons around a microscopically small nucleus.

Properties of He II

We have already mentioned that ordinary helium, designated as He I, changes into a superfluid, designated as He II,

*Visible to the naked eye, as contrasted with *microscopic*.

at about 2.2°K . He II has many other strange properties in addition to being able to move rapidly (because of its lack of viscosity) through pinpoint holes and through channels too narrow for even helium gas to penetrate easily. He II conducts heat a thousand times better than copper. It will not stay in a beaker that has been raised above a bath of the liquid but will gradually creep in a film over the rim and drip back into the bath (Figure 27). It can be made to squirt forcefully out of a tube by the application of heat, and it will propagate a type of heat or temperature wave motion called "second sound", in contrast to normal liquids, which only support the pressure wave motion that comprises ordinary, or first, sound.

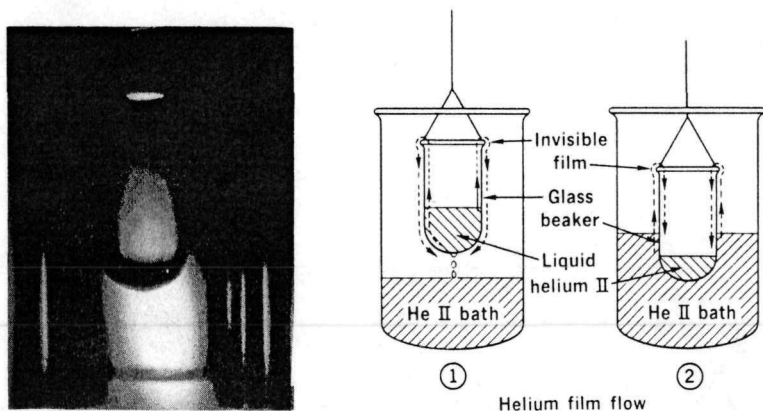
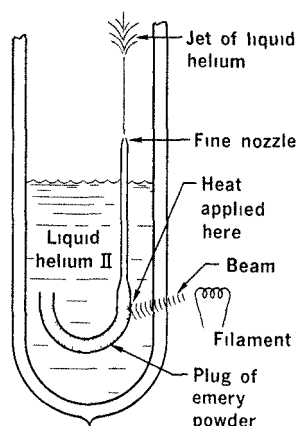


Figure 27 *Superfluidity. When a beaker partially filled with helium II is raised above the level of a larger bath of helium II, the contents of the beaker will creep over the lip in a thin film and drip into the larger vessel, eventually emptying the beaker (diagram 1 and photo). Similarly, if an empty beaker is partly submerged in a helium II bath, the superfluid liquid will flow into it until the level inside is the same as that on the outside (diagram 2). Since helium II has no viscosity, once the film starts creeping there is nothing to stop it, and the whole mass of liquid in the beaker acts almost like a large piece of Jello flopping over the edge of the dish.*

Bose-Einstein statistics are applicable only when the basic unit, the helium nucleus in this case, contains an even number of particles. In the most common isotope, ^4He , we have 2 protons and 2 neutrons, but there also exists a rare isotope, ^3He , whose nucleus contains 2 protons and only

1 neutron. This is an odd number of particles, so Bose-Einstein statistics are not applicable. Although ^3He is present only to the extent of one part per million in natural (gas well) helium, it is today readily available in pure form from the Atomic Energy Commission, because it is obtained as a by-product in the radioactive decay of the hydrogen isotope, tritium.

Figure 28 A "fountain" effect in helium II. When radiant energy is absorbed by the emery powder plug in the apparatus shown, superfluid rushes in so rapidly that liquid is expelled from the nozzle with considerable force. Fountains up to 30 centimeters high have been observed.



Properties of ^3He

The properties of ^3He are being studied and used in many laboratories. For one thing, ^3He has been added in varying amounts to ^4He to see how the superfluid transition temperature is changed in the mixture. But the most important question is whether ^3He by itself, in spite of its different statistics, undergoes some sort of condensation. So far no evidence has been found that ^3He displays superfluidity. However, in the summer of 1964, a well-known Russian scientist reported a bump or peak in the specific heat curve at about 5 millidegrees (0.005°K). On the other hand, an equally well-known professor at the University of Illinois has looked for such an anomaly in the same temperature region and has seen nothing. So the discussions go on, with the experimental scientists trying to reach lower and lower temperatures and the theoretical scientists arguing whether and at what temperature a condensation should take place in pure ^3He . All these investigations are inspired by a more

or less intuitive feeling that normal liquids or fluids should not exist at the absolute zero!

As previously mentioned, superconductivity is found in many metals and alloys. As a matter of fact, one fundamental question being asked at the present time, and quite analogous to the liquid ^3He condensation problem, is whether superconductivity will be found in *all* pure nonmagnetic metals, provided they are pure enough and provided the temperature is low enough. Careful chemical purification has

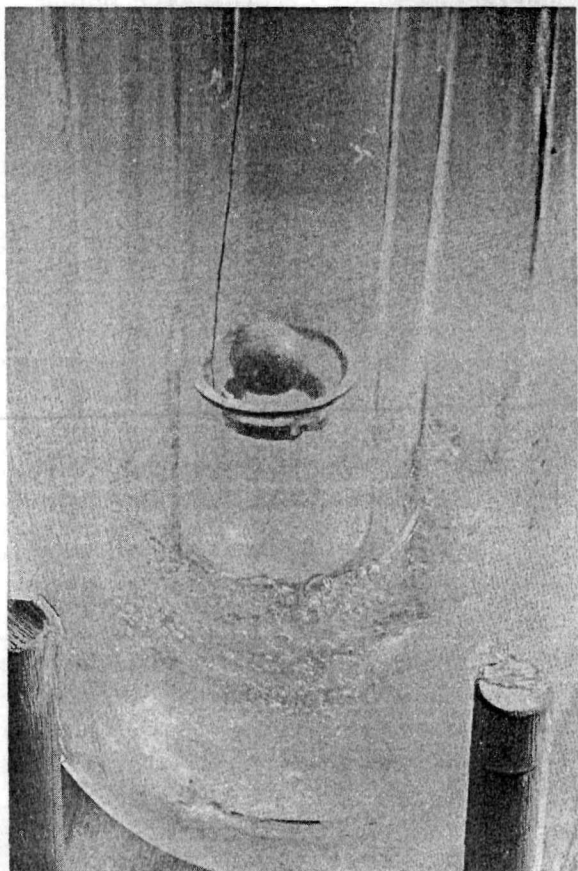


Figure 29 *Superconductivity. This hollow lead ball is supported, floating in space, by the magnetic fields of two superconducting lead rings with induced persistent electric currents moving around them in opposite directions. The experiment is conducted in a vessel cooled to 4.2°K by a liquid helium bath.*

produced a number of "new" superconductors in recent years, and for this reason the suggestion has been made that all metals probably do become either superconducting or ferromagnetic (or antiferromagnetic) at very low temperatures.

We have already seen that superconducting electrons have interacted (by some process or possibly by different processes) to form pairs of lower energy than two normal electrons would have, and that these pairs are able to move through a metal lattice, conducting an electric current without interacting with the lattice. The minimum energy to destroy superconductivity, that is, to break such a pair of superconducting electrons into two normal (resistive) electrons, is simply not available from the lattice in a single scattering collision at the low temperatures we are dealing with. However, when the temperature of the lattice reaches a certain value, the so-called critical temperature, T_c , the energy for destroying superconductivity is available, and superconductivity does not occur above that temperature.

Table III lists the critical temperatures for a number of materials. It is interesting to note that the pure metals with the highest critical temperatures are the ones like niobium, lead, and tin that are relatively poor conductors of electricity at room temperature. These metals try spontaneously to exclude all magnetic fields from their interior

Table III—PROPERTIES OF SOME SUPERCONDUCTORS

	Formula	T_c (°K)	$H_c(0)$ (gauss)	$H_{c2}(0)$ (kilogauss)
Cadmium	Cd	0.56	30	—
Aluminum	Al	1.19	99	—
Indium	In	3.41	283	—
Tin	Sn	3.72	306	—
Mercury	Hg	4.15	410	—
Lead	Pb	7.18	803	—
Niobium	Nb	9.46	1945	—
Lead-Bismuth	Pb-Bi	8.8	—	15
Niobium-25% Zirconium	Nb-Zr	10.8	—	65
Niobium-33% Titanium	Nb-Ti	9.3	—	120
Vanadium-Gallium	V ₃ Ga	14.5	—	300?
Niobium-Tin	Nb ₃ Sn	18.2	—	200?

regions once they become superconducting, but there is a limit, depending on temperature, on how large a magnetic field they can stand. We can draw a diagram (Figure 30) showing fields and temperatures at which a material can remain superconducting. The maximum field, extrapolated to the absolute zero is called the critical field H_c at 0°K , or $H_c(0)$, which is also given in Table III. We see that $H_c(0)$ amounts to only a few hundred gauss for the pure metals.

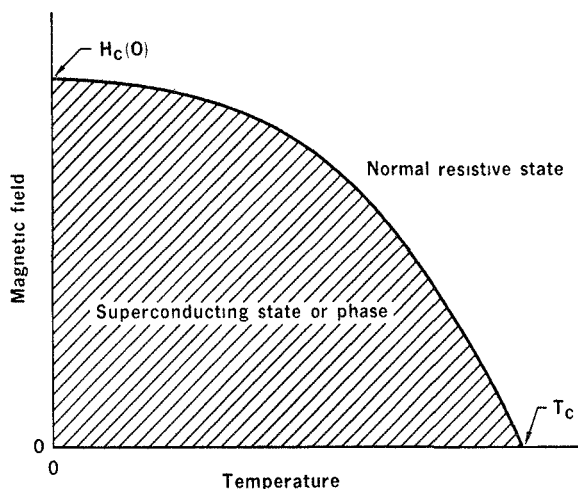


Figure 30 *Diagram of superconductor. Superconductivity is destroyed both by excessive temperatures and by excessive magnetic fields; the area below the parabolic curve indicates combinations of fields and temperatures under which superconductivity exists in a given material.*

Some of the superconducting alloys also listed in the table have been shown in the last 5 years to be able to withstand considerably higher magnetic fields before losing their superconductivity. They are able to do this by not “fighting” the magnetic field, which would require a lot of energy, but by letting it penetrate almost completely. Since their behavior is so different from the “classical” superconductors, they are called type II superconductors. In type II, the phase change from the superconducting to the normal state is not abrupt but gradual, and the material goes through a so-called mixed state. At any given temperature below T_c , the mixed state usually starts at a few hundred

gauss (where the magnetic field first starts to penetrate) and extends to an upper critical field, designated H_{c2} , which represents the upper limit of superconductivity. As the table shows, the values for H_{c2} at 0°K can be very high, some so much in excess of 100,000 gauss that they haven't yet been determined accurately.

Superconducting Magnets

Some of these alloys are being used at present to build high-field superconducting electromagnets that require no electrical power whatsoever to maintain the magnetic field

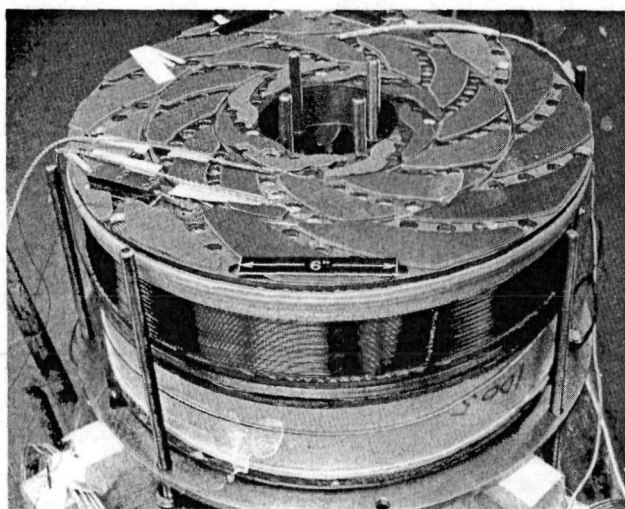


Figure 31 *This superconducting magnet built at the Argonne National Laboratory is used to bend the tracks of the nuclear particles passing through a bubble chamber. An equally strong conventional magnet would require 50 megawatts of electrical power and tremendous cooling towers.*

once it is established. All that is required is that the temperature be maintained well below T_c , usually in boiling helium, and that the field be built up gradually. Once this is done, the magnet coil can be short-circuited within the low-temperature region and the field will persist indefinitely.

Superconducting magnets of 50 or 60 kilogauss strength are available today for research purposes from commercial

suppliers, and a few 90 to 100 kilogauss coils have been built recently (Figure 31). It is difficult to foresee what the availability of "permanent" 100-kilogauss magnets might

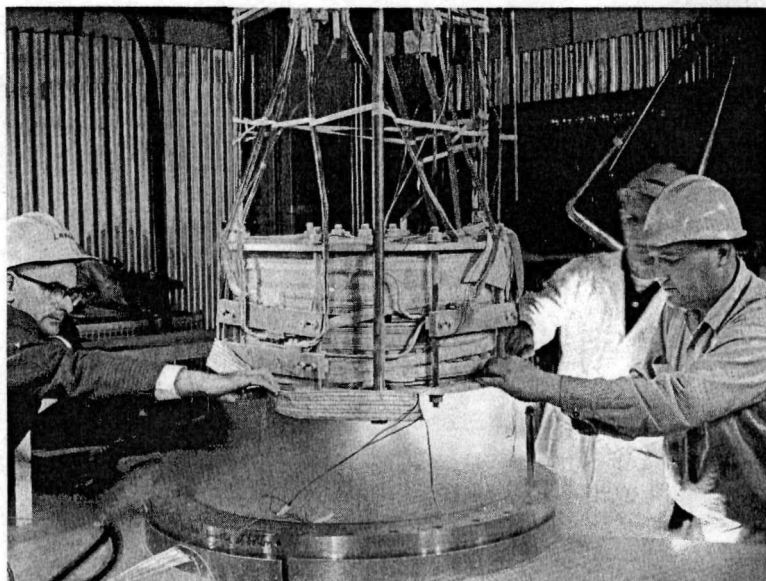


Figure 32 *One of the world's largest high-field superconducting magnets is being lifted from a liquid helium tank after tests at Argonne National Laboratory where it was built. This small magnet can sustain a 67-kilogauss field, stronger than that of almost any big conventional magnet, but uses almost no electricity.*

mean in the future to the field of electrical engineering, inasmuch as iron—vital in present electromagnets, electric generators, and transformers—"saturates" at about 20 kilogauss, and that it is now difficult to produce magnetic fields of this strength extending more than 1 or 2 inches in free space. It is apparent that developments with superconductive and cryogenic electrical engineering are only limited by the imagination of designers of the machinery of the future.

One supermagnet system built at the Atomic Energy Commission's Argonne National Laboratory near Chicago, for instance, was composed of three smaller supermagnets, nested inside each other, so potent that together they can

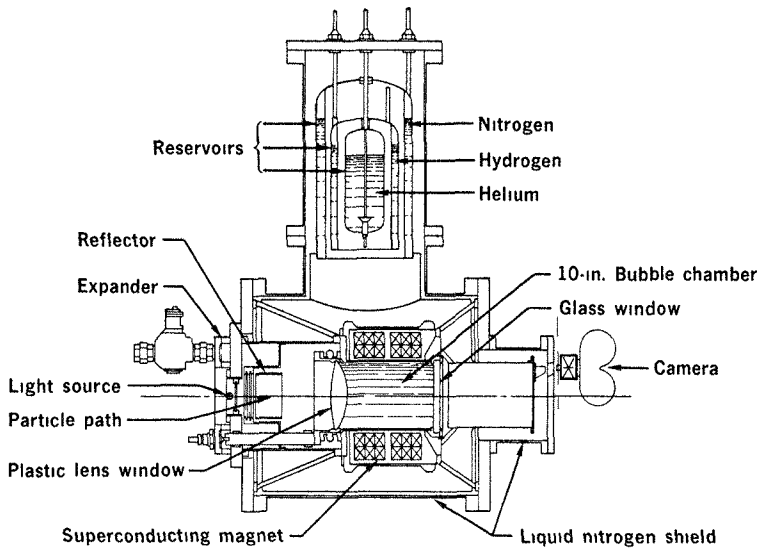


Figure 33 *How a 10-inch superconducting magnet is used with a liquid helium bubble chamber in high-energy physics experiments. Central reservoir at top contains liquid helium, shielded by liquid nitrogen and liquid hydrogen. When the expander moves the plastic lens window, the pressure is reduced in the chamber and bubbles form on the tracks of charged particles moving from a nearby accelerator. The magnet deflects the particles' paths and the camera photographs them.*

hold a magnetic field of 67 kilogauss, or 134,000 times as strong as the magnetic field of the earth. These magnets can be "charged" by a small power source, then operated for months without additional power, provided they are kept chilled to liquid helium temperatures. The system uses high-strength super-conducting cable that also was developed at Argonne, as were special winding and cable-making machines to construct the cable. The entire magnet system weighs only 800 pounds, but it is equal to conventional magnets that weigh several tons and use enough electricity to power a small city. In one of the earliest uses of magnets of this sort (shown in Figure 31) for high-energy physics research, a team of physicists from Argonne National Laboratory and the University of Michigan discovered a new nuclear particle, heavier and with a longer lifetime than any other ever found up to that time.

CRYOGENICS AS A TOOL

Almost everybody has seen astronauts' launchings on television, and so cryogenically fueled rockets are familiar indeed. Similarly, the problems of cryogenic storage of liquid hydrogen and oxygen for use in satellite fuel cells have been widely publicized. There are also many other areas of science and engineering that are making increasing use of cryogenic techniques.

Solid state physics uses cryogenics in many ways. One is in the study of radiation damage. Nuclear radiation can knock atoms out of their normal lattice positions. At room temperature this damage anneals, or heals itself, fairly readily, but at low temperatures the damage remains in its initial form and can be observed.

Many masers, lasers, and infrared radiation sensors are operated at low temperatures because their efficiencies are adversely affected by thermal vibration. Much of the research on the Mössbauer effect, to measure the extremely minute recoil energies of single gamma-ray emissions, is also done at low temperatures.

Low-temperature distillation is used in several countries to separate the heavy hydrogen isotope deuterium in order to produce heavy water for nuclear reactors. "Cryopumping" provides a means of reducing the pressure in large space-simulation vacuum chambers, by letting all the gases condense or freeze out on surfaces cooled by liquid hydrogen or helium. This permits the low pressures to approach the vacuum of space—a much higher vacuum than can be obtained by the best modern high-vacuum pumps.

In the last few years cryogenic techniques have been developed for use in medicine, biology, and food processing. Success in this work depends on controlling details of the process by which the moisture present in all biological materials changes into ice. Fast freezing generally produces many small crystals with less destruction of the cell structure than in gradual freezing. Hence some freeze-dried foods are quick-frozen by a liquid nitrogen spray prior to a vacuum dehydration (sublimation) process, in order to better preserve the food texture. Similar techniques are used to freeze-dry vaccines and other biological

materials. Whole blood and bull spermatozoa are stored and shipped at liquid-nitrogen temperatures, often in the presence of glycerol or sugar solutions that prevent ice crystals from forming altogether. There are also low-temperature tissue and organ storage banks, to provide replacements needed for surgery. But the problem of storing complete higher animals in suspended animation at low temperatures has been solved so far only in science fiction tales.

Cryosurgery uses vacuum insulated, liquid nitrogen cooled tips or *cannulae* to kill, and sometimes remove, selected nerve cells, regions of the brain, ulcers, or tumors.

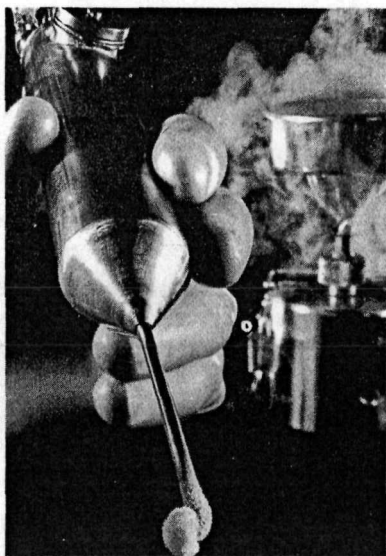


Figure 34 *A cannula, its tip frosted, used for cryosurgery. The Dewar, containing the liquid nitrogen coolant that flows through the instrument, is in the background.*

Careful control of tip temperature and of application time allows removal of diseased tissue with little damage to nearby healthy organs. The freezing process not only stops immediate bleeding, but also cauterizes small blood vessels and thus greatly reduces postoperative bleeding (Figure 34).

Cryogenics, in short, is far from being a mysterious art that emerged because of modern demands. It is now one of the most basic and familiar branches of physics, with a modern technology that promises many benefits in years to come.

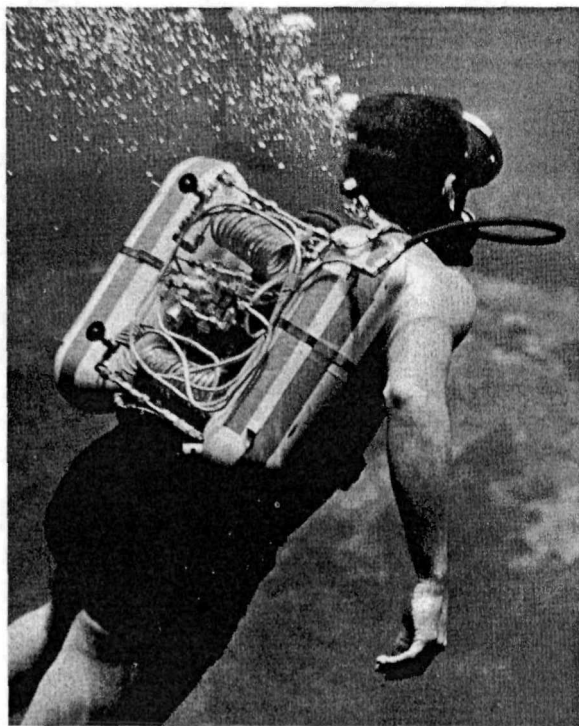


Figure 35 *Cryogenic scuba diving gear. Liquid air at a temperature below -317.8°F is pumped into divers' tanks. In use it is warmed in coils and released as a breathable mixture at a slow, even rate. Use of liquid air permits diver to carry a 6-to-8-hour air supply.*

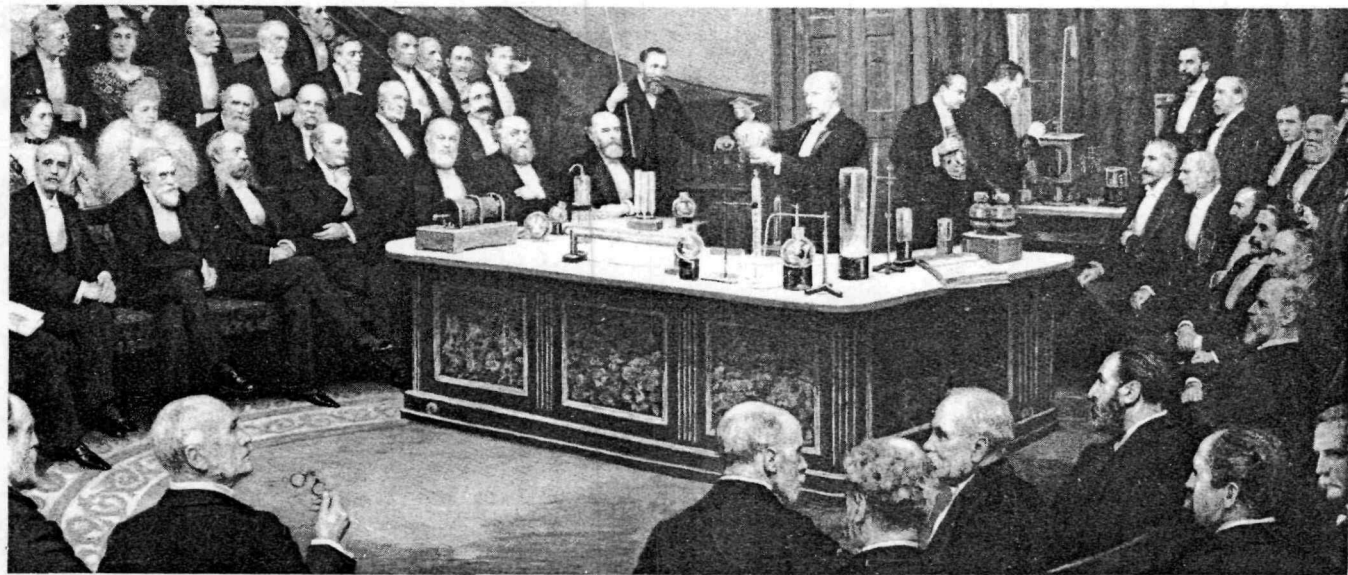


Figure 36 Sir James Dewar, a pioneer in low-temperature research, gave a series of scientific demonstrations at the Royal Institution for more than 60 years. These demonstrations culminated in his liquid hydrogen experiments, one of which is illustrated in this painting. On the left in the front row is Sir William Crookes; fourth from left is Lord Rayleigh. On the right side of the painting in the front row, Sir Francis Galton is second from the table at the back. Commendatore Marconi (man without a beard) is behind Galton, second from the edge of the painting. Dewar's own recent researches were usually reflected in these exhibitions. In 1893, he demonstrated his vacuum vessel, the Dewar flask, which he used for storing liquid gases at low temperatures. In 1898-1899, he built a large machine with which methods for liquefying and solidifying hydrogen were perfected.

APPENDIX

Quantum Mechanics

Quantum mechanics is the highly mathematical formulation and study of the properties and behavior of elementary particles (electrons, neutrons, protons) and of their interactions, as in atoms or molecules. Any particle exhibits both individual corpuscular, or particle-like properties, and "assembly", or wave, properties. The stable, "permissible" energy states of an assembly are calculated (at least in principle) by a so-called "wave equation". One property of these equations is that solutions exist only for certain discrete energies, that is, the permissible energies of a system cannot vary continuously, but only in definite steps. Hence the energy levels of any system are said to be *quantized*. Also, there is a minimum energy or zero-point energy for any assembly of elementary particles, and we can associate some zero-point motion with this energy.

Much of the work of theoretical physicists is concerned with setting up plausible models for interactions between elementary particles, trying to solve the corresponding wave equations, and then comparing the calculated energies with experimentally observed effects.

The original quantum theory was based mostly on spectroscopic observations, but new information obtained in low-temperature research, particularly on superconductors and superfluids, guides and stimulates the theorists, just as their theories suggest new avenues for experimental investigation.

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THE COVER



The uncommon nature of cryogenic materials is strikingly illustrated in the cover photo—a night view at Jackass Flats, Nevada, where a test of a Kiwi nuclear reactor, designed to heat rocket propellant, is under way. The reactor is attached to an upside-down rocket nozzle so that the hydrogen propellant will emerge upward and not push the reactor and other test equipment off the ground. Hydrogen is a desirable rocket propellant because of its low molecular weight, but to be handled easily it must be in liquid form—at a temperature of 423° below zero Fahrenheit—when it enters the reactor. Flowing at a rate of 5000 gallons per minute, the liquid hydrogen is heated by the reactor to a temperature of 4000° Fahrenheit to provide sufficient thrust for rocket propulsion. As the hot hydrogen gas emerges, it is ignited to dispose of it safely. The spectacular flame, shooting high into the desert air, can be seen for miles.

THE AUTHOR

HENRY L. LAQUER has been a staff member in the Cryogenics Group at the Los Alamos Scientific Laboratory since 1947. He has worked on solid state physics research, the generation of high magnetic fields, and superconductivity. He has published numerous scientific reports on these subjects, and holds several patents on superconducting devices.

This booklet is based in part on a 1965 summer science seminar for high school students, in which he participated.

Dr. Laquer received his secondary education in Europe, an A.B. from Temple University, and a Ph.D. in Physical Chemistry from Princeton University.



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