CHEMISTRY.—*Chemistry at high pressures and high temperatures.*[i] H. Tracy Hall, Brigham Young University, Provo, Utah. (Communicated by P. H. Abelson.)

It is now possible to do experimental work on a small scale at pressures of 3 million pounds per square inch up to temperatures of 5,000°C. This new pressure-temperature field was opened by the author's design of an apparatus known as the "belt" while at the General Electric Co. in January 1953. It was in this apparatus that the author succeeded in making diamonds late in 1954.   Fig. 1 shows this new pressure-temperature region in comparison to the region that was accessible prior to this development.

The significance of the opening of this hitherto unavailable experimental region will now be discussed. The physical and chemical changes that can be produced in a system are qualitatively related to the "intensity factor" (pressure, temperature, volts, etc.) of the energy that is put in to the system. Energy, of course, can be injected in to systems in various forms. One of the most important types of energies has been heat energy. One cubic centimeter kilo atmosphere is equivalent to 12.19° Kelvin.

It is now possible to expect to cause changes in condensed systems by application of pressure alone that are comparable to those formerly brought about by application of temperature alone.

In many respects pressure and temperature are diametric opposites, high pressure being equivalent to low temperature. As temperature is increased, solids transform to liquids, which in turn become gases. Systems then proceed to products of molecular dissociation, and finally, at sufficiently high temperatures, the atomic nuclei will be separated from the electrons by electronic dissociation.   On the other hand, increasing high pressures can cause gaseous systems to become liquids, which in turn transform to solids. This is followed by collapse of electronic shells and, at pressures of billions of atmospheres, nuclear fusion.

The general effect of high pressure in regard to reaction rates is one of reducing the rate. Therefore, in order to have a chemical reaction take place under high-pressure conditions in a reasonable length of time, it is almost always desirable to operate at high temperature.   A detailed consideration of the thermodynamics and reaction rates of systems has been given elsewhere.[ii]

The general problem of finding the region in a pressure-temperature field where a reaction will proceed at a measurable or useful rate is one of constructing a free-energy-equals-0 line from the thermodynamics of the system involved, coupled with the problem of determining a minimum-rate line as a function of pressure and temperature. The desired products will be made from the reactants in the region of overlap of these two curves above the free-energy-equals-0 line.

Pressures now available are great enough to influence strongly the external electronic configuration of the atoms.   Since chemistry depends on the characteristics of the external electrons, the ordinary chemical behavior of the
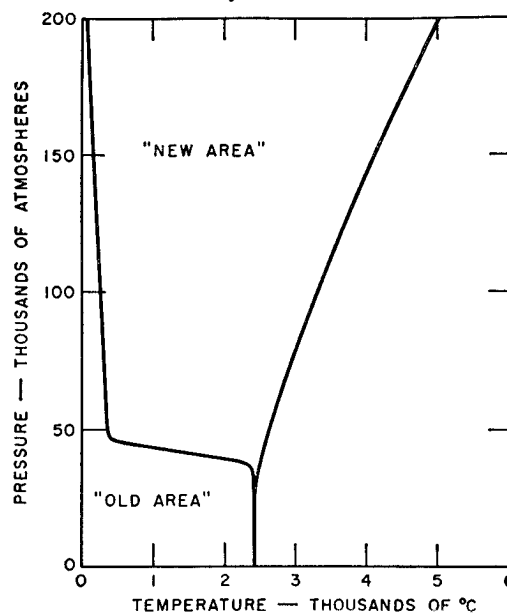

FIG. 1.—Comparison of the old pressure temperature region with the new region now available.

atoms can be drastically changed by the application of high pressure.   Indeed it is possible to force outermost electrons into vacant inner shells. This pressure effect on the external electrons is the most fascinating aspect of high-pressure research for the immediate future; for it should be possible under high-pressure conditions to, in effect, create a new periodic table, wherein the ordinary chemical properties

of the elements could be so changed that we would not recognize them.

Consider for a moment the periodic table shown in Fig. 2. In discussing the electronic structure of the various atoms, the terminology ordinarily applied to the free atom will be used. This will give qualitatively correct results.

In regard to the effect of high pressure on the elements, our first question arises with carbon, nitrogen, and oxygen, as we proceed with increasing atomic numbers through the periodic table. These elements contain unpaired "p" electrons. Can pressure force the "p" electrons with parallel spins into opposition, thereby decreasing the magnetic properties of these atoms? A like situation exists with respect to silicon, phosphorous, and sulphur. I think the answer is yes.

The second type of question arises with the element potassium, which has a vacant 3d shell. Should pressure force the 4s electron into this 3d orbital? This situation continues through nickel. All the elements underlined in Fig. 2 have empty "inner" orbitals and hence possess the possibility of forcing outer electrons at sufficiently high pressure into the empty orbitals, thereby changing the ordinary chemical properties of these materials. The underlined elements represent two-thirds of the periodic table. Again I think the answer is yes.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La⊗	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	85	Rn
87	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm								
⊗	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			

Fig. 2.--Periodic chart of the elements.   (Underlined elements have empty atomic orbitals)

The element cesium occupies a unique and outstanding position in the periodic table, in that there are 6s, 5d, and 4f orbitals, which are very close together energy-wise; and in that there is but one outermost electron, which normally occupies the 6s orbital. Application of pressure to cesium metal offers the possibility of forcing this electron into the 4f position, thereby making the cesium a nonconductor. Additional application of pressure offers the possibility of pushing the electron into the 5d orbital, where the material would again become an electrical conductor, the increasing energy sequence of these orbitals being 6s, 4f, and 5d. Increasing pressure, injecting increasing amounts of energy into the system, would likely cause an electron to follow this energy sequence.

Fig. 3 shows the change in electrical resistance of cesium metal with increasing pressure.[iii] At 53,200 atmospheres the electrical resistance increases very abruptly, as though the material were tending to become an electrical insulator. On increasing the pressure very slightly, the electrical resistance abruptly decreases. Actually, there is probably a distribution of electrons among the various available energy positions. Investigation of this phenomenon at low temperatures might well establish the merits of the foregoing conclusions.

A common statement to be found in textbooks discussing nuclear phenomena is that radioactivity is not influenced by temperature or pressure. Of course, this statement is true when ordinary pressures and temperatures are involved. At pressures of the order of 200,000 atmospheres and above, however, it should be
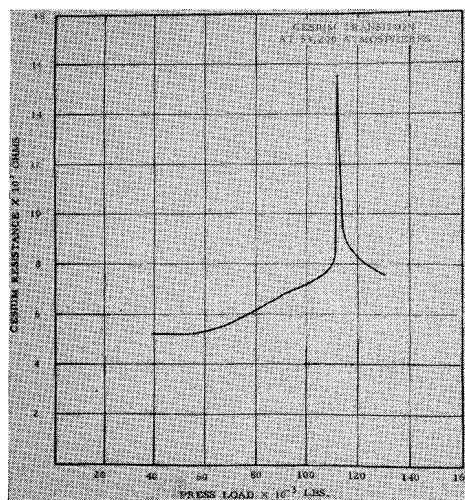

FIG. 3.—Cesium transition at 53,200 atmospheres.

possible to affect some of the innermost electrons within atoms. It might well be possible that K capture, the phenomenon in which an electron from the K shell falls into the nucleus, should be effected at very high pressure conditions. Dr. S. S. Kistler and his associates at the University of Utah are presently studying this phenomena.

In recent years man has plunged from a thorough study of the properties associated with the outermost part of atoms; i.e. the electrons, to a study of the innermost part, the nucleus. I have a hunch that there is an "in between world" waiting to be produced by application of extremely high pressures. In this world the normal electronic system would be displaced from its usual position to positions closer to the nucleus.

Let us now turn from these general electronic effects to some specific problems where high pressure might make a contribution. The field of geochemistry is ripe for exploitation with high-pressure, high-temperature techniques. This is true particularly in regard to the nature of the interior of the earth. Man's direct access to the earth's interior is, of course, very limited, the deepest excursions which he can personally make being limited to depths of about 1 mile (tunnels this deep are to be found in a South African gold mine). Oil wells have been drilled to depths of 4 miles, and, of course, instruments can be lowered to obtain information as to the nature of the earth at these depths.

Some very interesting thoughts on the nature of the core of the earth have recently been advanced by Dr. W. H. Ramsey.[iv] In contrast to the usual view that the core is iron nickel with a silicate flux floating on top, Ramsey proposed that the core is composed of olivine which has been converted at the tremendous pressure of 1.4 million atmospheres to a metallic substance of density near 10. To support this theory Ramsey has studied the relationships existing among the planets in the solar system and has pointed out that the two smallest planets, Mars and Mercury, are not large enough to develop a pressure of 1.4 million atmospheres estimated necessary to support a core. Metallic and nonmetallic forms of elements are known in the laboratory. Gray tin is nonmetallic with a density of 5.75g per cc. Application of pressure to gray tin will form a metallic white variety with a density of 7.28g per cc. Arsenic has a yellow low-pressure modification of density 2.0 and a high-pressure metallic modification of density 5.73. Phosphorus has a low-pressure yellow form of density 1.82 and a high-pressure black form of density 2.70. E. Wigner and H. B. Huntington[v] have calculated that hydrogen could be transformed into a metallic form by application of pressures over 250,000 atmospheres.

Other geological problems can be answered by laboratory mineral synthesis at high pressure and high temperature. The field of mineral synthesis in addition to its geological implications, can, of course, have industrial significance, as witness the recent synthesis of diamond and of cubic boron nitride. In the synthesis of minerals, it is desirable to use a catalyst or mineralizer. At high pressure and high temperature, all the oxides and silicates seem to have reasonable solubility in water. Therefore, water is probably the most important of the mineralizers. However, there is a long list of materials that can be used, which includes various salts, particularly those containing nitrogen, fluorine, carbon dioxide, and hydrogen. In the high-pressure equipment that I have used, it is possible to make the containing vessel or capsule of tantalum, nickel or other metal that readily passes hydrogen when the container is hot. It is, therefore, possible to allow for the continuous escape of hydrogen from a reaction, with the attendant decrease in volume.

Since high-pressure reactions are driven in the direction of decreasing volume, it is possible to almost always devise a scheme for synthesizing a desired product at high pressure and high temperature. For example, consider the following reaction for the synthesis of aluminum oxide:

$$\underbrace{2AlCl_3 + 2Fe + 3H_2O}_{V\,=\,305cm^3} \rightarrow \underbrace{Al_2O_3 + 2FeCl_3 + 3H_2\uparrow}_{V\,=\,131cm^3}$$
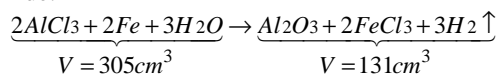
Since high pressure tends to reduce "open" structures to closer packed structures and strives to arrange atoms in positions of maximum three-dimensional symmetry, any system not in cubic or hexagonal close packing is a worthy object of study at high pressure and high temperature, for here the possibility exists of producing a higher density system.

The synthesis of hard materials might be considered at this point. Hardness is a property resulting from high bond density and from high three-dimensional symmetry. A measure of high bond density is the so-called cohesive energy density. A measure of cohesive energy density is the heat of vaporization of a material per cubic centimeter. When such information is not available, a relative measure of bond density can be obtained by dividing the boiling point of a substance by its molar volume. Graphite and diamond have the highest cohesive energy densities of any known materials. Graphite, however, is soft, whereas the diamond is the hardest of all known substances. The reason for this is that graphite does not fulfill the second requirements of high 3-dimensional bond symmetry. Carbides, nitrides, borides, oxides, and sulphides of elements in the neighborhood of

carbon and silicon, together with some of the heavy metals of the periodic table, have high cohesive energy densities. Some of these materials produced under ordinary conditions do not have high bond symmetry. Since high pressure tends to force bonds into positions of highest 3-dimensional symmetry, the application of high pressure and high temperature to some of these materials can result in the production of hitherto unknown materials of very high hardness. The recent synthesis of "borazon" by Dr. R. H. Wentorf, Jr., of the General Electric Research Laboratory is an example of this situation.

I think there are some excellent prospects in the field of metallurgy for experimental work at high pressure and high temperature. It is well known that the calculated yield strengths of many metals are 100 to 10,000 times greater than those measured. Yield strength is a structure-sensitive property; that is, the strength is dependent on the existence of vacant sites, dislocations, small- and large-angle boundaries, etc. The elimination of vacant sites, etc., would result in an improvement of the yield strength of metals. This elimination would also result in a volume decrease in the material; and since the application of high pressure tends to drive things in the direction of decreasing volume, such application might prove beneficial. There are undoubtedly activation barriers opposing the removal of the above. These barriers could be reduced by use of high temperature and catalysts (fluxes); and hence the necessary eliminations could be carried out at a reasonable rate.

Most metallic materials are polycrystalline. This is another factor causing lower than calculated yield strengths. Of course, single crystals would have a smaller volume than polycrystals, since the density of the grain boundaries is about ten percent less than that of the grains. There is also a certain amount of free energy associated with the grain boundaries. Application of high pressure would favor the elimination of grain boundaries and the growth of single crystals from polycrystals. The heat treatment of metals in an indispensable process carried out in our modern industrial economy. The formation of desirable properties in metals by heat treatment is, in general, brought about by heating a material, for example, steel, to a rather high temperature, at which temperature certain transformations take place. The material is then quenched (rapidly cooled) to a lower temperature. This quenching produces certain desirable structures in the material.

Temperature, then (for fixed composition), has been the only variable the metallurgist has had at his command. Certainly, pressure could be introduced as a variable, and as an example, the following sequence might be followed in producing certain desired properties in a metal: (1) The metal is heated at 1 atmosphere pressure to a certain temperature; (2) high pressure is now applied to the metal; (3) the temperature is lowered; and (4) the pressure is lowered. This sequence of events could conceivably "lock-in" properties that could be obtained in no other way.

High pressure could offer a new crystallization technique. Normally, metals are produced from the melt by cooling. Metals could be crystallized from a melt by leaving the temperature constant and increasing the pressure. In multi-component systems, this might produce some unusual results.

At the present time, the volume of material that can be subjected to high pressure and high temperature is rather small, practical size being not greater than a few cubic centimeters. For commercial application, this requires that the material made at high pressure be quite valuable. Two categories of material come to mind that fit this classification: They are diamonds, or other materials of comparable hardness, and drugs, or other biological materials. It is quite possible that some directed, tricky substitutions in complicated molecules of biological importance could be brought about by application of pressure that could be achieved in no other way.

The melting points of substances are profoundly affected by pressures of the order of 200,000 atmospheres. Note the 600° lowering of the melting point recently reported.[vi] Of course germanium is an exception to the general rule that melting point increases with increasing pressure. The melting point of some refractory materials has been increased by well over 1,000°C. by application of extremely high pressures. This fact makes it possible to work at higher temperatures at high pressure than would be possible at one atmosphere. As a matter of fact, it is quite possible to work with a "liquid" refractory under high pressure conditions. A liquid can flow only if it contains holes into which the molecules can move. At 200,000 atmospheres, the number of holes in a molten refractory can be severely reduced, and the material will be extremely viscous.

Work on the melting points of substances at high pressure has considerable significance, in that it should throw some light on the old

question as to the possible existence of a critical point between a gas and a liquid.

High pressure increases the electrical conductivity of most metals by approximately 20 percent at 100,000 atmospheres. However, the conductivity of some metals in increased by as much as 400 percent. This phenomenon is, of course, falls in line with the fact that, in general, high pressure behaves like low temperature. This raises the question: Is superconductivity possible at sufficiently high pressure?

Certainly, many applications of high pressure at low and high temperatures are to be found in atomic and molecular theory, geology, chemistry, physics and other scientific disciplines.

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[ii] Hall, H. Tracy. Proceedings of a symposium, High temperature—a tool for the future: 161-166, 214-215. 1956. Published and distributed by Stanford Research Institute, Menlo Park, Calif.

[iii] This phenomenon was first observed by P. W. Bridgman. Proc. Amer. Acad. Arts and Sci. **81**: 165-251. 1952

[iv] Nature **168**: 667, 1951

[v] Journ. Chem. Phys. **3**: 764-770. 1935.

[vi] Hall, H. T. Journ. Phys. Chem. **59**: 1144. 1955.