HIGH PRESSURE RESEARCH

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The evolution of high pressure research is briefly described. Professor Michels then surveys the various branches of science in which high pressure has become a new tool, primarily for varying the intermolecular distances. An indication of the economic value of this development to industry and a programme of research into the phenomena which depend on electronic clouds within molecules are given.

INTEREST in high pressure research and its practical applications has grown significantly during the past few decades. However, even as far back as the middle of the nineteenth century, ingenious and important work in this field was being conducted by the French schools of L. P. CAILLETET and E. H. AMAGAT. This was followed some years later by the investigations of G. TAMMANN in Germany, while in the United States P. W. BRIDGMAN—who still ranks as one of our ablest contemporaries—was already actively engaged in high pressure research at the beginning of this century. Many other famous names could be quoted and it is not through lack of appreciation that only these four coryphaei are singled out.

The elegance of these early experiments is notable and the pressures attained are impressive, bearing in mind the technological limitations of that period. As early as 1870, Amagat succeeded in producing pressures of 3000 atm.; Tammann attained 20,000 atm. and in 1922 Bridgman reported experiments up to 40,000 atm. In spite of the acknowledged importance of these efforts, their value was limited however because the fundamental and applied principles involved had not been elucidated.

By the second half of the nineteenth century it had been established that molecules exist as individual entities and the classical study of J. D. VAN DER WAALS revealed that the attractive force between them is inversely proportional to their distance apart. Moreover, it was known that this force differs in magnitude for different types of molecules. The molecules at the same time were ascribed volumes varying with each species. Van der Waals' equation states a functional relation for pressure, volume and temperature

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

and scientific curiosity was prompted to determine the extent to which this expression represents the behaviour of real substances.

About that time a thermodynamic theory was evolved by J. W. GIBBS, J. D. VAN DER WAALS, D. KORTEWEG and B. ROOSENBOOM and others relating to phase equilibria in two- and multi-component systems. This theory assumed that an equation of state of the same form as that for pure substances also holds for mixtures, provided it is modified by the introduction of constants a and b relating to the character of the constituents. It was then found that thermodynamics could predict a whole series of phenomena which would be affected by variation of pressure and temperature. This discovery again acted as an impetus to high pressure research.

A serious handicap remained however. New equipment was not readily available and practically every experimenter had to develop his own. Admiration is due to those pioneers who have achieved so much, frequently with tools which nowadays—notwithstanding their ingenuity—look very crude and bear the sign of the poor machine-shop facilities so common in university laboratories of fifty to eighty years ago.

In those early days industry showed little interest in the high pressure experiments. Steam engines

operating at 30 atm. were considered to be reaching the danger limit. It was not until F. HABER developed the synthesis of ammonia from hydrogen and nitrogen that practical application in the 300 atm. range became evident, and industrialists and engineers began to take an interest in this field. There was a growing appreciation of the advantages that would accrue to industry if it supported fundamental research in the thermodynamics of the process and efforts to measure the properties of the reacting gases, so as to find the most economic operating conditions. However, interest was still centred on the macroscopic properties, like compressibilities, and thermodynamic quantities as functions of pressure and temperature.

With the progress of engineering, improved methods for producing and measuring pressures were developed which provided the research worker with the means to extend his field of activity. High pressure research was, however, left to a few workers and small centres, and its pursuit on a large scale had to await two major advances. The more important of these was the formulation of an acceptable model of the structure of the atom. Thus, on the basis of the theories put forward by Lord RUTHERFORD and N. BOHR, it became possible to account for the mysterious forces of interaction between the original particles. From the concept that each atom consists of a positively charged heavy nucleus (having a diameter of 10^{-13} to 10^{-12} cm), surrounded by a cloud of much lighter negative electrons (moving at high speeds at distances of the order of 10^{-7} mm), it followed that the interaction is of an electrical nature. Moreover, it became apparent that studies of the physical properties of matter as a function of the average distance between the particles—certainly in the range of strong interaction, that is high densities—might provide important information about the behaviour of the particles during the time of interaction. This, however, necessitates the application of pressure.

Decrease of temperature also results in a density increase of course. If the temperature is lowered far enough, liquid densities, and even the solid state, can be attained at normal pressures. However, it must be understood that temperature variation alone simultaneously affects two quantities, the kinetic energy of the molecules and their distance apart. Since it is not satisfactory to work under conditions where two parameters are varied at the same time, high pressure research was indicated.

While the theoretical physicists prepared the ground for fundamental studies, the experimentalists started to evolve the equipment required to wring nature's secrets from her. These attempts were much hampered by the lack of a properly designed instrument for measuring pressure with an adequate degree of accuracy. It was not until 1922, when the theory of the pressure balance was properly understood and the reproducibility of pressure reading was pushed well above one part in 100,000, that precision research gained momentum.

This discovery, although by no means comparable in importance with the elucidation of the atomic structure, was the second advance which led to the expansion of high pressure research. Gradually
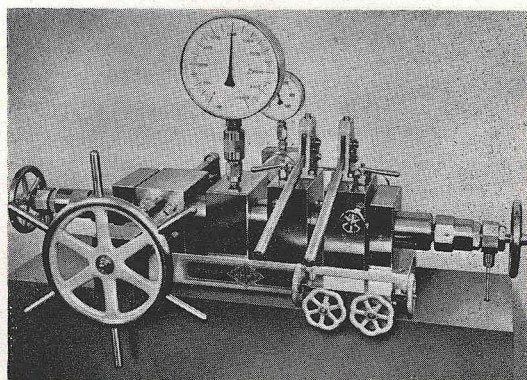

Figure 1. Pressure bench, with screwpress, for 5000 atmospheres

instruments were developed for a variety of experiments, and theoretical and experimental knowledge was accumulated. The number of institutions engaged in high pressure research grew slowly but steadily.

The next major impetus came from the industrial side. One far-seeing English company, realizing the potential merits of high pressure as a new tool, embarked on a research programme. It would be unjustified to consider this action purely as a gamble. An awareness that support for fundamental research is also a duty of honour for an organization which depends so largely on the results of science must be considered as a major motive. In due course the efforts paid off by the discovery of the first real high pressure process, when in 1935 polyethylene was first produced under pressures between 1500 and 3000 atm. As is well known, this material assumed tremendous importance during the 1939–45 war by making possible the construction of the fighter radar sets.

For high pressure development, the manufacture of polyethylene acted as a major incentive in stimulating research on the construction of

instruments and machinery, both for experimental and production purposes. Whereas twenty years ago a compressor for 3000 atm. was considered to be an impossibility, nowadays such equipment can be ordered almost as a matter of routine.

At this point it seems appropriate to state categorically that the time has passed when fundamental research could be qualified by the adjective ' academic ' in the old sense of the word. Aware that the theoretical knowledge gathered in university laboratories all over the world is providing too narrow a basis for their own requirements, many industries have taken an important share in fundamental research. Frequently the standard of their efforts is as high as, and in some fields even superior to, that prevailing in the universities. This challenge, it may be hoped, will not pass unnoticed by the authorities responsible for the scientific standing of academic research facilities.

It is not the intention here to enlarge upon aspects of so-called pioneering research: experiments to determine the effects on substances when subjected to extreme pressures. Neither is it proposed to examine the complicated engineering problems involved or to give details of ingenious instrumentation. Such work is important and has helped to raise knowledge to a level of which mankind can be proud but it falls outside the scope of this survey. This article is concerned with those planned and balanced researches where theory and experiment are closely linked, where theoretical speculation or working hypothesis demands experimental verification or criticism, where the experimental results again stimulate the theorist to increased effort, where the conditions in experimental accuracy in the different variables to be measured, and the ranges to be explored, are from the outset dictated by the goal to be achieved, and properly balanced against each other; in short, where the approach is based on strategic planning, but where the results expected may be less spectacular than those of the pioneers' attack. From the foregoing discussion it is obvious that pressure is primarily a tool for varying the intermolecular distances.

The ultimate aim of such researches is to determine how the properties of materials vary with change in density by compression, the average kinetic energy of the particles, and thus the temperature, remaining constant. Once measurements have been taken, there arises the problem of interpreting the gross effect in terms of the interaction between the individual particles—in other words, of arriving at a microscopic understanding from the macroscopic indications.

Such analysis is so complicated that progress must be slow. The fundamental reason is that in any phenomenon to be studied, two different but interrelated problems are encountered. The first, the quantum-mechanical problem, deals with each
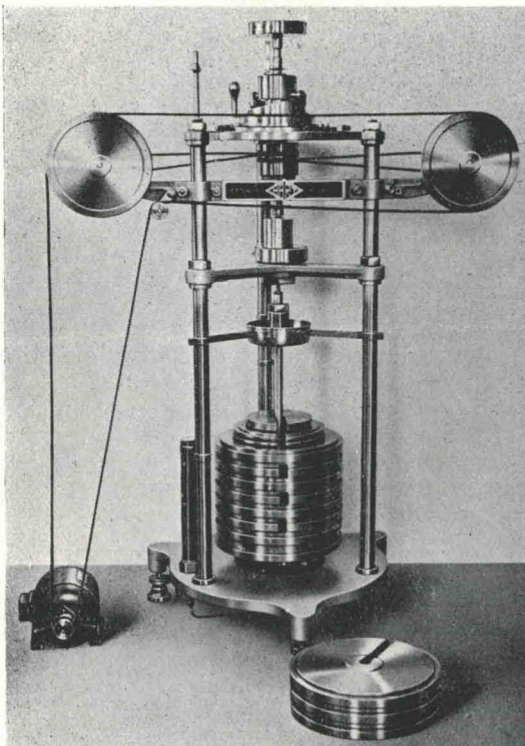

Figure 2. Pressure balance

simple molecule, its structure and its reaction to external forces. Secondly, there is the statistical-mechanical problem, the nature of which can be stated in the following terms.

From the density of a system and the number of molecules involved, it is possible to deduce the average distance between neighbouring molecules. The real distances, however, vary with time for each molecule and each submicroscopic volume cell. The distribution depends on the temperature and the forces which the molecules exert on each other. If these forces were known, together with the original position and velocity of each molecule, and if the concepts of classical mechanics are assumed to be valid, a ' supermind ' would be able to follow the development of the system with time. However these conditions cannot be satisfied, nor does the supermind exist that could handle such systems with, say, 10^{22} molecules per cubic centimetre.

Besides, science is not really interested in such a detailed picture of the state of the system; it does not want to know the position and velocity of each individual molecule at any given moment. In fact, modern physics has shown that with such a small particle both quantities can never be known with any degree of accuracy at a given moment. The question must thus be regarded as senseless.

To arrive at the required information, the actual motion of the system is replaced by a set of probabilities, and 'actual' behaviour is described by means of an averaging process. For the application of the specific probability laws the forces acting between the molecules must be known. These, however, are precisely the quantities it is desired to determine. Based on experimental data, to be discussed later, the laws are chosen so that they lead to the correct macroscopic properties.

To complicate the picture further still, the validity of the so-called additivity concept of the molecular forces has come to be questioned of late. Thus it appears that, in the case of three neighbouring molecules, the total action on molecule A does not equal the sum of the forces exerted by B and C independently.

Notwithstanding these difficulties important advances have been made. It now remains for the experimentalist to develop the equipment which will enable the necessary data to be measured. Most essential are those data which determine the relation between density, temperature and pressure—the equation of state. Instruments are needed which will record these three variables to an accuracy of 10^{-4} or each to 1 part in 30,000. The results obtained with such instruments will be of value in various fields. First, the data will facilitate further measurement of any property which depends on the density of matter. Thus in measurements of quantity X as a function of the average molecular distance at constant temperature, it is exceedingly difficult to determine density and the function X simultaneously. Equally, it is difficult to vary the temperature and keep the density constant. However, determination of X while pressure is kept constant, or its variation with pressure at constant temperature, is much easier to effect. When the functions $X=f(p,T)$ and $p=f(\rho,T)$ are known, $X=f(\rho,T)$ can be evaluated directly.

Direct use of the equation of state is made in the calculation of all thermodynamic functions. Internal energy, free energy, thermodynamic potential, Joule-Thomson coefficient, change in specific heat by compression (both c_p and c_v) can be derived by thermodynamic calculation from $f(p,\rho,T)=0$.

A justification of the statement that an accuracy of 10^{-4} is desirable can, for example, be found in the calculation of c_v at elevated pressure. The change of c_v by compression is given by

$$c_v = \int_\infty^v T\left(\frac{\delta^2 p}{\delta T^2}\right)_v dv$$

Now, even according to van der Waals' approximation, $(\delta^2 p/\delta T^2)_v=0$. Therefore, this is a function which with this approximation equals zero and yet must be known with a sufficient degree of accuracy to enable reliable results to be derived from experiments. Experience has shown that, for an accuracy in c_v of 1 per cent, $p=f(T)_v$ must be known within 1 part in 10,000.

The equation of state also provides information on the interaction between two molecules. The equation of state can be written in the form

$$\frac{pv}{RT} = 1 + B\rho + C\rho^2 + \cdots$$

where B refers to the interaction of two molecules only, C to three-body interaction mainly, and so on. At lower densities, where ρ^2 is small, multi-body interactions are so rare that their effect can be neglected (e.g. up to pressures of 50 atm.) Thus

$$\frac{pv}{RT} = 1 + B\rho$$

The value of B varies with temperature, and is dependent on molecular interaction.

It was stated earlier that at comparatively large distances the molecules attract each other with forces increasing rapidly as distances diminish until a point is reached where these forces decline, finally to reverse their sign and change into repulsive forces. The corresponding potential energy φ is given in *Figure 1*.

The shape of these curves can be determined from the experimental data of B as a function of temperature. The value of σ may be interpreted as a measure of the diameter of the molecules. For the simple molecules its value lies between 2×10^{-8} and 5×10^{-8} cm. J. E. LENNARD JONES has shown that, within experimental error, φ can be represented by the relation

$$\varphi = \frac{A}{r^{12}} - \frac{B}{r^6}$$

It should be noted that a number of simplifying assumptions have been made here, for instance that the molecules are spherically symmetrical. For simple molecules this approximates to the actual conditions. Non-spherical molecules rotate with an enormous speed between 10^{13} to 10^{14} times a second, so that on the average they present a field
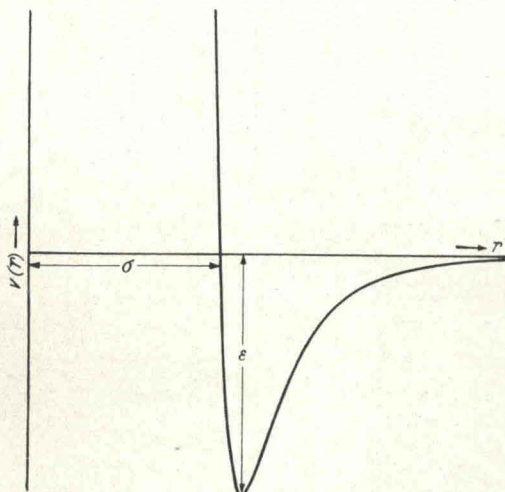
Figure 3. Intermolecular potential field $\varphi(r)$

towards other molecules whose average in time is not far from spherical. It is obvious that more precise considerations will reveal deviation from this simple assumption.

Finally there is another interesting conclusion to be derived from the data of the equation of state, which is directly related to the character of molecular interaction. It has been shown that, if the total energy of a gaseous system includes the energy of the nuclei of the molecules and the electrons revolving round these nuclei, then on compression at constant temperature the following relation will hold:

$$3\Delta(pv) = \Delta U + \Delta K$$

where U indicates the change in total energy and ΔK the change in kinetic energy. Now $\Delta(pv)$ is determined from the experimental data; U can be evaluated from the same data by using the thermo-dynamic equation

$$\Delta U = \int_{\infty}^{v} \left[T\left(\frac{\delta p}{\delta T}\right)_v - p \right] dv$$

giving a value for ΔK, the magnitude of which varies for the gases measured, between 3000 and 15,000 calories per gram molecule for a compression from 1 to 3000 atm.

However, as the compression is effected at constant temperature, the kinetic energy of the molecules does not change, and the enormous increase in kinetic energy can be only accounted for by a higher speed of the electrons. This indicates that molecular interaction is accompanied by an intramolecular change and is in agreement with the old law that action always calls for a reaction. The

obvious interpretation is that the molecular forces represent the combined action of all the charged particles of one molecule on those of the second, leading at the same time to a displacement of these particles relative to each other during the interaction.

The change of the electronic kinetic energy, to which reference has already been made, is found to be much more closely related to pressure than to density, a fact which may be explained by consideration of the nature of the pressure which a compressed gas exerts on the walls of the container. The pressure is the cumulative effect of the molecules impinging on this wall. But the kinetic energy with which they hit the wall is that energy which, during a collision, allows the molecules to penetrate each other's repulsive field and, by doing so, to disturb the electron orbits of the colliding particles.

This indicates the scope for a whole field of research: to obtain experimental data and to build a theoretical picture into which these results fit logically. This programme embraces all phenomena which depend on the electronic clouds within molecules; for example, optical phenomena such as absorption and emission spectra, including molecular spectra, refractive index; polarizability, both of gases and solids; for the solid state, more particularly magnetic properties, electrical conductivity, Hall effect and semi-conductivity.

The effect of pressure on chemical reactions constitutes another important field. As the chemical bond is closely related to the electronic structure, it is obvious that distortion of the electronic cloud must affect chemical reactivity, particularly since the greatest disturbance, resulting from compression, can be expected on the outer electrons which are primarily responsible for the chemical bond.

The so-called transport phenomena—diffusion, thermal diffusion, heat conductivity and viscosity—must also depend on the molecular interaction, as some experiments which were conducted at elevated densities have shown. The interpretation here is, however, still more complicated, as the statistical treatment is much more involved than under static conditions.

The new tool of high pressure is gradually attracting more and more interest. Its widespread application is undoubtedly assured once equipment is readily available not only to produce, contain and measure high pressures, but also to measure different physical properties under the extreme conditions of high pressure and high accuracy. However, our arsenal of novel instruments is growing and justifies the hope that more fundamental information will be obtained in the near future.