Coordination Chemistry Reviews 12 (1974) 185–220

HIGH PRESSURE IN COORDINATION CHEMISTRY

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(Received March 18th, 1973)

CONTENTS

A. INTRODUCTION

High pressures have long been used experimentally in physics and engineering laboratories, but with a few notable exceptions, most *chemical* work has been done at or near atmospheric pressure. *High pressure chemistry* is a prominent research field in its own right and a considerable volume of thorough work has been done by a fairly small number of specialists. However, the field is still very new, and large areas have been left relatively unexplored. In this review, it is hoped to show that the use of high pressure techniques is or could be of considerable benefit to many problems in the study of chemical reactions, equilibria, synthetic chemistry, spectroscopy and theoretical chemistry. In fact in many areas of chemistry, the information available from measurements as a function of pressure is as important, or more, than similar measurements made as a function of temperature. This is then a review in part of work completed or in progress, and in part of work that ought to be done.

The most important reason for the neglect is experimental: it is easy to heat a reaction or to freeze it, but significant changes in pressure tax the imagination, especially if we also wish to obtain useful measurements on the compressed sample. The recent emergence of high pressure chemistry owes much to the readier availability of suitable apparatus. Unfortunately the cost of apparatus for extremely high pressure work ($10^5 - 10^6$ atm) is still very high, and for a given experimental technique, the cost usually increases at least proportionally to the pressure attainable. However, a large number of chemically interesting effects are observed in the intermediate pressure range ($1 - 10^4$ atm) for which apparatus is usually inexpensive or can readily be made in the laboratory workshop.

Some of the earliest important high pressure studies were carried out by Amagat, who developed apparatus until pressures of about 10^3 atm were consistently obtainable[1]. The most important groundwork was done by P.W. Bridgman, a physicist, often called the father of high pressure chemistry, who gradually improved apparatus design until pressures approaching 10^5 atm could be regularly attained[2–4]. Much of Bridgman's work was also devoted to the gradual building up of tables of compressibility as a function of pressure for a large range of common liquids. Such data are very important in high pressure measurements in solutions or pure liquids, and many of Bridgman's original figures remain in regular use[3–6].

B. GENERAL EFFECTS OF PRESSURE

(i) Definition

Macroscopically, pressure is defined as force per unit area

$P = F/A$

but the simplest molecular basis for pressure is that used in the *Kinetic Theory of Gases:* the wall of a vessel containing a perfect gas, or a piston or any other body (assumed infinitely massive) lowered into it, is subjected to a force over its entire surface area due to the rate of exchange of momentum of the gas molecules colliding with it (elastically). The basis of elastic collisions is the mutual repulsion of the electron clouds of two impinging, non-bonding atoms or molecules suddenly brought together. In more condensed states of matter, such as liquids, solids or highly compressed gases, pressure is likewise provided by mutual repulsion of like charges per unit area and the individual atoms or molecules may or may not have significant momentum.

(ii) Units

The commonly used units of pressure have approximately equal magnitudes

1 atm = 1.01325×10^6 dyne. cm^{-2} (the defined *normal atmosphere*)
1 bar = 10^6 dyne. cm^{-2}
1 kg. cm^{-2} = 0.980665×10^6 dyne. cm^{-2} (the kilogram weight per cm^2)

The kilobar (kb) (10^3 bar) is also used. The S.I. unit of pressure is the newton per square meter

$$1\ \mathrm{N.m}^{-2} = 10\ \mathrm{dyne.\,cm}^{-2}$$

(iii) Moderate pressures ($< 10^5$ atm)

In general the boiling or condensation temperature of fluids increases with increasing pressure up to a critical point where gases and liquids are indistinguishable. By suitably varying temperature and pressure, we can actually go *around* the critical point, avoiding the liquid–gas phase transition entirely (Fig. 1). Melting/freezing temperatures, T_m, also normally increase with increasing pressure, i.e. ΔV, and hence dT_m/dP, is positive in the Clausius–Clapeyron equation $dT_m/dP = T\Delta V/\Delta H$, but no evidence has been found for analogous critical point behavior for the solid/liquid transition[7]. Within limited temperature and presure ranges, the liquid/solid temperatures also decrease with increasing pressure, in certain substances such as water, gallium, bismuth, antimony, germanium and potassium tetrasilicate ($K_2Si_4O_9$). Such negative values of dT_m/dP and ΔV accompany changes to more tightly packed structures in these substances. A maximum T_m^{max} has been suggested as a general feature of the melting curve of all materials at high pressure[8], and is now a known property of several substances[9–16], though it is certainly not general. The expected value of T_m^{max} in both elements, such as cesium, rubidium, barium and tellurium, and compounds, increases with mass number[14]. A current model for the behavior of liquids in the region beyond the pressure at T_m^{max} is a mixture of two components, one having short range order corresponding to a solid phase stable at a lower pressure and the other having short range order derived from a higher pressure solid[15].

A second important effect of pressure is an increase in the viscosities of most liquids. The increases depend greatly on the liquid's structure[17]: the viscosity of water doubles while that of the dimethylsiloxane octamer increases by a factor of about a million when the pressure is raised from 1 to about 10,000 atm. This is of obvious importance in liquid phase reactions.

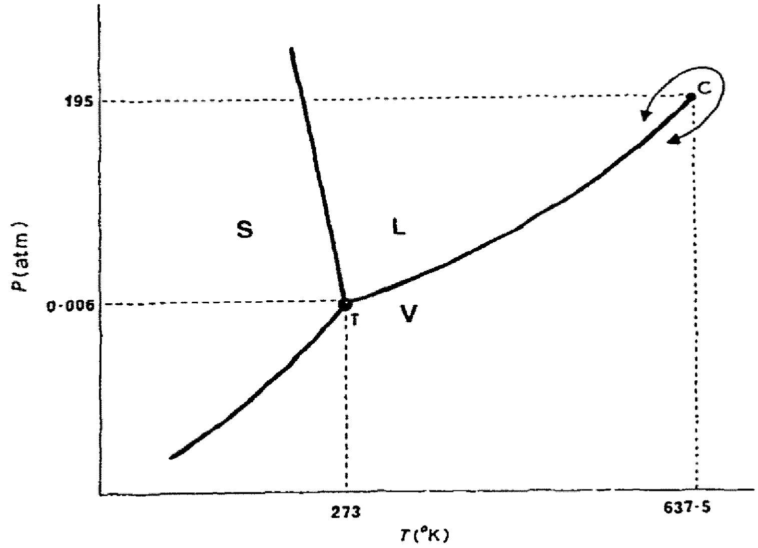


Fig. 1. (Fluid) Phase diagram of water (not to scale). T is the triple point and C the critical point.

A third interesting effect is the dramatic change in the properties of fluid water (and other substances such as weak electrolytes) with rising pressure. In the supercritical region (Fig. 1), compressed water adopts new solvent properties (as do other supercritical fluids), and acts as a powerful solvent for inorganic minerals and some metals[18].

A fourth interesting and important effect of pressure is solid to solid phase transitions, usually resulting from a change in crystal structure. For example, solid water probably has at least nine distinct phases[19–21] (Fig. 2), each stable in a specific temperature/pressure region, while in camphor no less then eleven different phases have been discovered[22]. Some non-metallic or semi-conducting substances undergo phase transitions to metallic states at moderate pressures, e.g. sulfur[23,24], selenium[24–26], tellurium[25,27], iodine[24], arsenic[24], red[28] and white[29] phosphorus[24,28–30]; a series of transition and rare earth metal chalcogenides[31]; the Group IV elements silicon[24,32] and germanium[24,32], the electronically analogous Group III – Group V intermetallics such as indium antimonide, and Group II – Group VI compounds such as cadmium telluride[32]. On the other hand, some metals undergo transitions to semi-conducting states, such as ytterbium, strontium and calcium[33]. Most such phase transitions revert spontaneously when the pressure is reversed, but some, such as "black phosphorus"[3,34] and diamond[35], are metastable at room temperature and pressure. Some, such as metallic hydrogen[36], once attained, are predicted to be metastable at room temperature and pressure.

In this pressure region, most substances are either solids or liquids, so that except at elevated temperatures[37], problems arising from the containment of gaseous materials often do not arise, which simplifies the design of much high pressure apparatus.

There is a small but significant decrease in interatomic distances in molecules in this pressure region, corresponding to a slight increase in bond strengths, greater ligand field splittings, and increasing importance of the covalent bond.

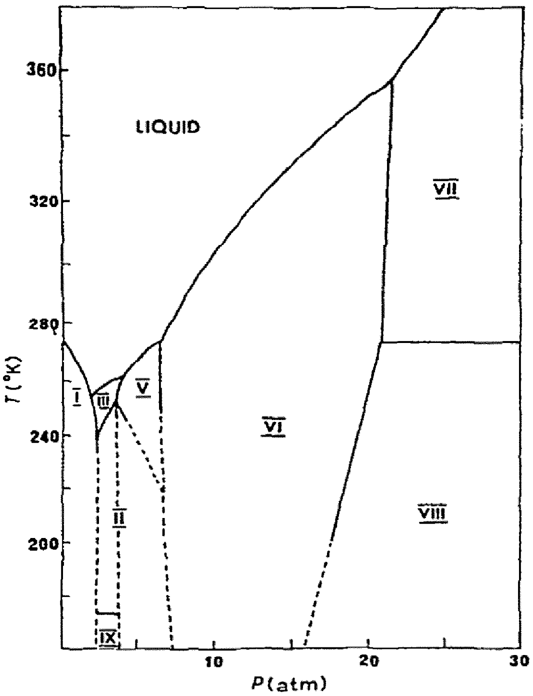


Fig. 2. (Solid) Phase diagram of water, showing some of the phases of ice.

(iv) High pressures (10^5 – 10^6 atm)

Only one state of matter is thermodynamically stable above about 10^5 atm at room temperature (helium solidifies at about 1.2×10^5 atm), and that is the solid state, and most apparatus design is then reduced to the problem of confining solids. With the decrease in interatomic distances, the importance of the covalent bond increases, as do the ligand field strengths in metal complexes[38]; most inorganic compounds become more like increasingly strongly bonded coordination complexes. High spin iron (II) in such minerals as olivine and garnet is made low spin at about 10^6 atm. This corresponds to a depth of about 2000 km. Four unpaired electrons are paired in such a process, leading to a reduction in metal–ligand bond lengths[39,40] of about 0.1Å. Even at lower pressures startling phenomena occur in iron (II) minerals: a UV charge transfer band in olivine grows in intensity with increasing pressure and its conductivity increases until the material becomes an opaque semi-conductor[41]; the increase in conductivity is about 10^5 when the pressure is raised to 3×10^5 atm. Thus for example the study of geochemistry below the outer part of the earth's crust is largely coordination chemistry at high pressures. Further decreases in interatomic distances are expected to break covalent bonds[42], so that at the pressures required for this phenomenon ($\sim 10^6$ atm), extremely fast reactions should be possible. The limits of available apparatus are fast approaching static pressures of this magnitude.

(v) Extremely high pressures (10^6 – 10^8 atm)

As pressure increases, eventually all outer electron repulsions are overcome and interatomic distances decrease to the combined radii of the next lowest electron shell. The outer electrons which had been localised on specific atomic centres, are now delocalised over the whole lattice, i.e. they are added to the "conductance band". Thus, all non-conducting and semi-conducting solids are eventually transformed by pressure into conducting (metallic) solids. In conductors, the interatomic distances likewise decrease and an increasing number of electrons is added to the conductance band. This process continues with increasing pressure as atomic electrons are stripped off layer by layer, to form ultimately an "idealized" metal consisting of nuclei embedded in a completely delocalised "free electron liquid", where the repulsion of like charges prevents further collapse of the structure.

(vi) The ultimate pressures

If pressure is sufficiently increased, ordinary matter collapses and aggregates to form essentially larger atoms: a compacted mass of protons, neutrons and electrons. The white dwarf stars, at a pressure of $10^{13}-10^{17}$ atm (density 10^4-10^8 g.cm^{-3}), can be regarded as extreme examples of giant "atoms". In this case, the orbiting electrons spend most of their time within the nucleus, and the electron orbits are so closely packed that the Pauli Exclusion Principle requires high electron velocity, which provides internal pressure, to prevent further collapse. If such material is compressed even further, electron energy would eventually become so high (about 0.5 MeV) that nuclear reaction between protons and electrons would form neutrons. Because of the high pressures, these neutrons would be packed rigidly in simple crystalline solids; such structures are postulated for neutron stars, which exist at pressures of $10^{20}-10^{24}$ atm (density $10^{11}-10^{15}$ g.cm^{-3})[43].

C. TYPES OF APPARATUS

The experimental problems of high pressure chemistry can be summarised under production, containment and measurement of the pressure.

(i) Production and containment of pressure

Most of the mechanisms for producing high pressures were originally described by Bridgman. For solid samples, the apparatus is relatively simple; the sample is placed between two or more pistons or "anvils" which are then pressed together[44], e.g. by a hydraulic press (Fig. 3). When two opposed anvils are used, the pressure gradient (usually undesirable) between the center and the edge of the sample may be reduced by surrounding the sample with a ring of another suitable material, such as pyrophyllite. A successful method of doing this is with a pyrophyllite gasket which is simultaneously compressed into the tapered section between the anvils[45]. This method has produced the highest static pressure so far obtained when external support was used. The importance of external support in pressure apparatus is discussed below. Insertion of a heating element between the anvils allows simultaneous temperature controls over a wide range[46]. Multiple anvil systems involving four ("tetrahedral" press), six ("cubic"), eight or more symmetrically opposed anvils permit larger sample volume and minimise pressure gradient problems[47]. A disadvantage is the stroke limitation imposed by the edges of the anvils pressing against each

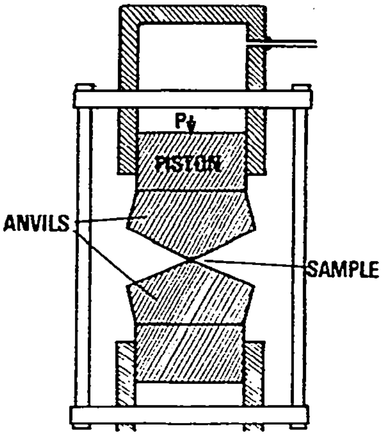


Fig. 3. High pressure squeezer (schematic), using opposed anvils.

other, and this can be overcome by the use of sliding anvils so that each anvil slides out of the path of the adjacent advancing anvil[48].

The problems, theory[49] and methods of apparatus design have been extensively discussed, and Bradley[50] has given details of both methods and suppliers of equipment in his recent monograph.

The simplest method for fluids consists of completely filling and sealing the sample container or "bomb" below the experimental temperature, and then heating it. The differential thermal expansion of the fluid and the container (usually a suitable type of steel) is too small to be of much use, but by adjusting the conditions to bring the liquid beyond its critical point (Fig. 2), the liquid is made to behave as a supercritical fluid, i.e. a gas, containing considerable internal pressure. The pressure to be attained can be adjusted by the temperature and the mass of liquid initially inserted. This method is frequently used when simulating geothermal or hydrothermal conditions (e.g. mineral synthesis). For example, gemstones are grown from seed crystals placed in the solution formed when the transition metal impurities and silica are dissolved in wet alkali carbonates and heated in a sealed bomb, and crystals of rare earth oxides, hydroxides, hydroxynitrates and hydroxycarbonates are grown from supercritical water up to 900°C and 1360 atm (ref. 51). The temperatures and pressures used normally range around $10^2 - 10^3$ °C and $10^2 - 10^3$ atm.

The usual method of compressing a fluid is to reduce its volume by the movement of a piston (usually solid, but occasionally an immiscible liquid or compressed gas) into a hollowed cylinder containing the fluid (Fig. 4). With solid pistons, the problem of leakage can be overcome with a soft disc (e.g. rubber or lead) at the front of the piston, or by a Bridgman "unsupported area" seal[3,5], a typical example of which is shown in Fig. 5: this consists of a metal "mushroom" with a "sandwich" of three washers A, B, C, of which B (e.g. neoprene) is softest, and seals at low pressures, while A and C (e.g. lead or copper) seal at high pressures. The piston is hollowed out so that its area of contact, a, with the packing sandwich is smaller than the area, a', of fluid supported. Since, at equilibrium, the forces on each side of the mushroom must have the same magnitude (f), the pressure in the

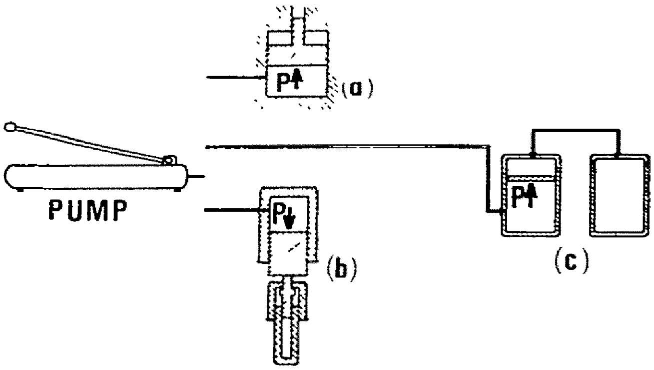


Fig. 4. Piston and cylinder pressure devices (schematic). Compressed fluid is pumped into cylinder to apply pressure to surface indicated by "P". (a) Pressure intensifier using large primary and small secondary piston areas. (b) Application of pressure with intensification, to fluid in a secondary cylinder with a locking nut for retaining the pressure after removal of the primary (larger) piston. (c) Phase separation of two potentially interacting fluids.

packing sandwich (f/a') is always greater than the pressure (f/a) in the fluid. Prevention of leakage unfortunately leads to significant frictional resistance to piston movement. Separate isolation cells for samples are sometimes desirable within a compression cylinder, and pools of mercury are often used to separate fluids which are not immiscible.

The experimental pressure may be intensified by allowing the primary pressure to act on a piston which in turn acts on a smaller piston (Fig. 4) in a secondary vessel. The intensification factor of the pressure is always less than the theoretical value expected from the inverse ratio of the piston areas, due to frictional losses. The upper pressure limit is determined by the ratio of internal to external radii of all cylinders (including connecting pipes) containing the pressure, so that a cylinder of given dimensions should undergo non-elastic deformation at a pressure determined by its Young's Modulus, and at another higher pressure, it should burst. However, this apparent limit can be exceeded, because what matters is the pressure difference between the inside and outside of the cylinder. Thus it is only necessary to compress the cylinder from the outside, e.g. by heat-shrinking another cylinder around it or work-hardening it beyond the elastic limit ("autofrettageing"), such that residual stresses compress the inner part of the cylinder as if another cylinder had been shrunk around it. The process can be repeated to produce a large cylinder, which effectively consists of a series of concentric cylinders, each compressing the one next inside, so that a much higher pressure can be contained in the sample cavity[52]. Such systems are usually adequate for the pressures normally desired in liquid samples, but a further limitation is that pistons, like cylinders, are expected to fail when the pressure is high enough. Straight pistons can be strengthened by external support, but the geometry of the apparatus makes this cumbersome and difficult[53]. Greater apparent piston strengths are obtained by using massive-supported pistons in "belt" or "girdle" high pressure systems, which are effectively tapered-piston, or anvil–cylinder combinations[54–58]. Removal of the cylinder now leaves us with the massive-supported Bridgman anvil system discussed above, which allowed the highest static pressure so far attained on small samples[45].

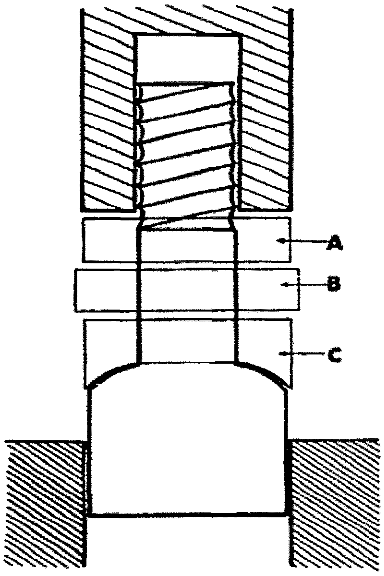


Fig. 5. Bridgman unsupported area seal (see text).

A further method of obtaining high pressures in either solids or liquids is by shock wave techniques[59]. A shock wave, produced by an explosion near the sample, or by a flat plate fired at it, brings the sample to elevated temperatures and pressures, and experiments are performed during the passage of the shock wave. The actual temperatures and pressures obtained depend on the composition of the sample itself, Much higher pressures (several million atmospheres) are possible by this method in solids than in liquids. Disadvantages of the technique are the very short time (usually not more than 10^{-5} sec and often much less) during which high pressures and temperatures are obtained, inability to raise temperature and pressure independently, the fact that the sample and at least part of the apparatus must be expendable. Apart from the particle velocity vs. shock velocity, electrical conductivities are probably the easiest properties to measure in shock experiments, but spectroscopic and X-ray diffraction data can be obtained with strong incident beams[60].

(ii) Measurement of the pressure

Many methods have been used for pressure (and temperature) measurement and calibration[3,5,6,60–63], and difficulties arise mainly under extreme conditions, such as $\gtrsim 10^5$ atm[64–66]. For lower pressures, especially in fluids, pressure measurement and calibration is straightforward and the instrumentation is usually readily available commercially and will not be discussed here. Frequently it is convenient or necessary to use internal calibrants for which the pressure dependence is known for some easily measured property, and instances of this will be discussed below. For example, the pressure dependence of the unit cell dimension of sodium chloride gives a good indication in cases where the apparatus permits X-ray diffraction measurements[65,67].

D. EXPERIMENTAL TECHNIQUES

The first problem in carrying out any experiment at high pressure is to decide which part of the experiment or apparatus should be under pressure. The sample to be studied must be under pressure, but as little as possible (or none) of the rest of the apparatus should also be compressed in order to simplify the experiment. Within this constraint, the problems of apparatus design are invariably surmountable.

(i) Magnetic susceptibility

Many of the common methods for determining magnetic susceptibility are amenable to high pressure measurements, and just a few examples will be mentioned here. For the Gouy and Foner[68] methods, the sample alone can be sealed in a non-magnetic (diamagnetic) high pressure bomb which is hung between the poles of the magnet in a Gouy balance, or attached to the end of the vibrating sample holder between the magnet poles in the Foner magnetometer. Such a high pressure bomb is simplest in the case of liquid samples (or solutions or suspensions) and one type has already been used with the Gouy method: the sample tube is a small piston—cylinder bomb with a Bridgman mushroom seal, the piston being clamped in a fixed position via a retaining nut after pressure has been applied with an external press[40,69,70]. The only limitations are that the bomb should be as light as possible (especially for the Gouy method), and relatively weakly magnetic. The temperature may be varied simultaneously within the limit permitted by the liquid sample[71].

Another common method for magnetic susceptibility determinations, the induction method[72], may be adapted to high pressure measurements in the same way with the primary and secondary coils wound around the high pressure bomb, in which case this bomb again should be diamagnetic, or the coils embedded with the sample inside the bomb. The latter method permits higher pressures (~ 10^5 atm), but the necessarily smaller sample size reduces accuracy and the technique is principally applied to the pressure dependence of the critical points of lattice ferro-and antiferromagnets[73,74]. Paramagnetic susceptibility in solution may be determined by NMR[75], and this could be adapted to high pressure in the same way that the NMR technique itself has been adapted to high pressure measurements.

(ii) Electronic spectra

Absorption spectra can be observed in the standard high pressure devices discussed in Section C, modified to include transparent "windows" of appropriate strength. Various materials, such as glass, quartz, sapphire, and sodium chloride are used as windows. The design is simple for relatively low pressures on liquid or solution samples[76], and in 1937 Poulter reported pressures in excess of 40,000 atm in a cylinder with glass windows[77]. The actual pressure must have been considerably less, since Poulter used very high friction seals, with no corrections, but a slightly modified Poulter apparatus was taken to 21,000 atm as determined by direct measurement with a manganin gauge[78]. The same apparatus was also used by the author to 20,000 atm using a new manganin gauge with all appropriate corrections made. Under such pressure, ordinary glass can be bent to a spherical curvature having a radius of 4 inches, and compensating lenses are desirable. Several other cells for liquids at pressures to about 10^4 atm have been described recently[79–81]. Commercial cells are now available, which normally employ quartz or sapphire windows, and machine oil pistons. In many applications, these require an isolation cell, such as the cell (Fig. 6)[82] designed for the Aminco Super Pressure No. 41–11552. Here mercury is used to separate the piston liquid from the sample, and is more satisfactory than a polythene plug in this application. A larger cylindrical isolation cell has been designed for a longer cylindrical cavity with the light path perpendicular to the cylinder axis, and a polythene plug to transmit the pressure[83]. The pressure is the same inside and outside these cells, so that the windows require no great strength. In the absence of any change in composition or nature of solution species due to pressure, the Beer–Lambert Law is still expected to hold after correction for increase in concentration due to compressibility. The same apparatus can be used to study the pressure effect of fluorescence quenching[84].

Piston and cylinder cells have also been designed for much higher pressures ($\sim 2 \times 10^5$ atm) in solids, and sodium chloride can serve both for the windows and as the pressure transmitting material[85–87]. Difficulties with this method, such as the relatively poor transmission of light by the NaCl windows and the unknown reactivity of NaCl with samples at high pressures, are overcome by an opposed anvil cell[88], using carefully prepared transparent diamond anvils[89]. However, the diamond cell does have a significant pressure gradient between the center and the edge of the sample.

(iii) Infrared spectra

High pressure infrared (and Raman) spectra have essentially the same requirements as UV – visible spectra: bombs or squeezers with suitable optics (e.g. NaCl, etc); and commercial apparatus is available[50]. Suitable cells have been described for both liquid[90] and solid samples[88,91].

(iv) The Mössbauer Effect

The Mössbauer Effect is only observable in solids, and high pressure measurements may be carried out with the sample compressed in a simple squeezer in which either the anvils, or any gaskets used, are relatively transparent to γ-rays, i.e. the γ-ray path should be of low atomic weight, such as beryllium, boron or lithium hydride. Several experimental systems are available[62,92–95]. Since only the relative velocities of the γ-ray source and the sample are important in Mössbauer work, either the source or the sample may be compressed and the other is moved, but for chemical applications it is generally preferable to compress the sample.

(v) Magnetic resonance

Various kinds of apparatus for magnetic resonance experiments have been discussed in detail, but so far only a very limited amount of experimental work has been done[96]. The usual requirement is a diamagnetic high pressure bomb in the sample cavity, since the magnetic field is normally supplied from outside the high pressure apparatus. For example,

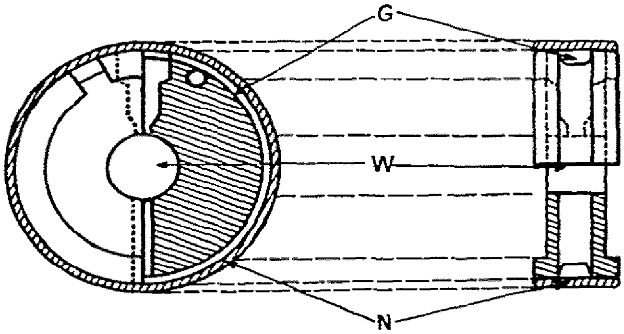


Fig. 6. Disc-shaped spectrophotometer isolation cell for Aminco cell. Excess sample solution extends below the window (W) area to a pool of mercury which extends upwards for $\frac{1}{3}$ to $\frac{2}{3}$ of the circumference of the disc in a groove (G) cut around the disc. The mercury is held in the groove by a nylon ring (N), fitted tightly around the disc, and open at the top to admit the compressing fluid, which acts on the mercury, which in turn acts on the sample from beneath. The light path is along the axis of the disc.

fiberglass NMR sample tubes have been used, though much higher pressures are attainable in copper–beryllium or stainless steel bombs[97]. Depending on whether low or high pressures are desired, the RF coil may be outside or inside the bomb, though in the latter case, some accuracy is lost due to inability to spin the sample. In a specialized application involving the detection of the ^{57}Fe resonance in powdered metallic iron, the magnetic field was supplied by the ferromagnetic iron itself, no external magnet being necessary[98].

ESR apparatus is similar in principle, except that the electromagnetic radiation must be introduced into the cavity from the transmission line via capacitive coupling in a typical apparatus[99] designed to operate around 9 kmc and to 10^4 atm. For higher frequencies (~ 24 kmc), the coupling may be through a sapphire window, so that optical experiments may be carried out simultaneously[100].

The ESR technique is sufficiently sensitive to detect ligand field perturbation (especially asymmetric perturbations) when many transition metal complexes are compressed[101,102], and uniaxial stresses on single crystals would give even more information. Some magnetic resonance work has been done on crystals under uniaxial stress[101,103], but an improved method of applying uniaxial stress to such crystals, which promises to have much wider applications, is the recently developed UMER technique[104]. In this technique, the crystal is vibrated ultrasonically, and perturbations in ligand field due to uniaxial stress (i.e. uniaxial pressures) may be observed by ESR.

(vi) Nuclear quadrupole resonance

The problems associated with NQR in the presence of a magnetic field are similar to those of NMR except that, like the Mössbauer effect, NQR can only occur in solids, and liquid samples need not be considered. Zero field NQR is even simpler, the greater problem being the detection of the resonance rather than the application of pressure[105–108].

(vii) X-ray crystallography

Most high pressure X-ray work has been done on powders, though there is no reason in principle why extensive single crystal work could not be done, at least in the lower pressure region. Normally, only solid samples are of interest, and the experimental problems are similar to those encountered in many types of optical and Mössbauer apparatus; either the pressure-generating anvils should be transparent to X-rays (e.g. beryllium or diamond) or the beam must pass between them, in which case any gasketing used must transmit X-rays. A significant advance[109] in this technique is the use of polychromatic X-rays at constant Bragg angle (θ); the crystal d-spacings are found from the diffracted wavelengths observed at constant θ with a semi-conductor detector[110] coupled to a multichannel analyzer.

X-ray diffraction patterns may be used to calibrate high pressure apparatus using standard samples of known cell constants, known and relatively high compressibility, an absence of phase transitions in the region of interest, and for which at least several intense diffraction lines are readily observed. These criteria are satisfied by sodium chloride[111], as well as a number of other salts[66].

E. EQUILIBRIA UNDER PRESSURE

(i) Pressure dependence of equilibria

The effect of pressure on simple chemical equilibria may be understood in terms of the mathematical description[112] of Le Chatelier's Principle[113]. Thus, the decomposition under pressure of the double salt $\mathrm{Co\,Cu(CH_3 \cdot COO)_4 \cdot 8H_2O}$ into its component single salts and water was observed as predicted in 1887, since this salt has a greater volume than its component parts[114]. For the equilibrium (1) in solution

$$a\,\mathrm{A} + b\,\mathrm{B} + \ldots \rightleftharpoons x\,\mathrm{X} + y\,\mathrm{Y} + \ldots \tag{1}$$

the equilibrium constant K is written in terms of the relative concentrations (strictly the activities) of the component substances·

$$K = \{[\mathrm{A}]^a\,[\mathrm{B}]^b \ldots\ldots\}/\,\{[\mathrm{X}]^x\,[\mathrm{Y}]^y \ldots\ldots\}$$

The molar volume change due to complete transition from the left to the right side of eqn. (1) is

$$\Delta V = -2.303\,RT \left(\frac{\partial \log K}{\partial P}\right)_T \tag{2}$$

(Strictly this should be denoted ΔV^0, where the volume change is the algebraic sum of the individual molar volumes.) Equation (2) expresses both the extent and the direction of the pressure effect. In real situations, ΔV may vary with pressure, due to solvent effects, the various compressibilities of the different components, and other complicating factors not taken into account by eqn. (1).

(ii) Effect of pressure on a planar–tetrahedral geometric equilibrium

Certain four-coordinated nickel(II) complexes such as the bis (N-R-substituted amino-

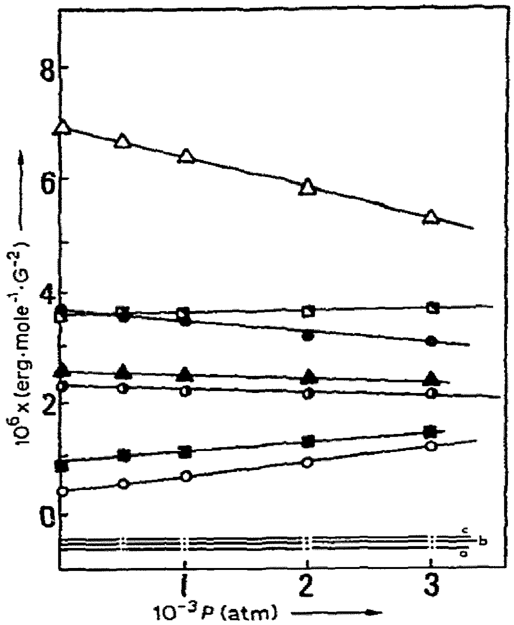
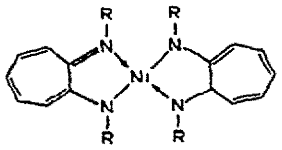


Fig. 7. Pressure dependence of magnetic susceptibility. (△) Tris (*N*,*N*-di-*n*-butyldithiocarbamato) iron (III) in $CHCl_3$; (□) bis(*N*-phenylsalicylaldimino) nickel (II) in $CHCl_3$; (●) bis(*N*,*N'*-diethylamino-troponeimineato) *nickel (II)* in $CHCl_3$; (▲) tris(*N*-ethylxanthato) iron (III) in $CHCl_3$; (⊙) tris(*N*-methylxanthato) iron (III) in $CHCl_3$; (■) bis(*N*-*n*-heptylsalicylaldimino) nickel (II) in CH_2Cl_2; (○) bis(*N*-*n*-propylsalicylaldimino) nickel (II) in $CHCl_3$; a, b, c – common solvents, $CHCl_3$, CH_2Cl_2 and $(CH_2OH)_2$ respectively.

troponeiminate) nickel (II), I, have either a planar or pseudo-tetrahedral environment about



I

the nickel atom in the solid state, and exhibit an equilibrium between the planar and tetrahedral species in solution[115]. In the planar form the compound is diamagnetic d^8, ${}^1A_1$, while in the tetrahedral form the complex is paramagnetic d^8, ${}^3T_1$. The relative volumes of the two species and hence the pressure dependence of the equilibrium cannot be predicted a priori.

The effect of pressure is to decrease the magnetic susceptibility (Fig. 7) and increase the proportion of planar low spin species at the expense of the high spin tetrahedral one[69]. The appropriate equilibrium constant, between the high (H) and low (L) spin species, is given by

$$K = \frac{[H]}{[L]} = \frac{\mu_{obs}^2 - \mu_L^2}{\mu_H^2 - \mu_{obs}^2} \tag{3}$$

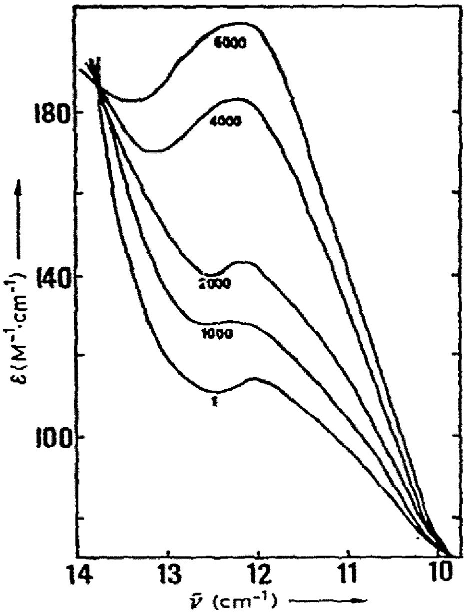


Fig. 8. Pressure dependence of the spectrum of nickel (II) *N*,*N'*-di-2-naphthylaminotroponeiminate in CH_2Cl_2 in the range 1–6000 atm.

where μ_H and μ_L are the magnetic moments of the pure high spin and of the pure low spin species at the temperature and pressure of the experiment, and μ_{obs} is the observed moment. The partial molar volumes of the two species differ by an amount ΔV given by eqn. (2)

For these compounds, the tetrahedral form is larger in solution by about 8 cm^3. mole^{-1} than the planar form, as evidenced by the decrease in magnetism (Fig. 7) and the increase in intensity at 12,000 cm^{-1} (Fig. 8) with increasing pressure. This ΔV value may be attributed in part to the volume increase in unpairing two electrons in the planar species to form the tetrahedral complex[69]. Such a promotion, involving spin uncoupling, has been shown to be accompanied by volume increase[40,70]. Solvation plays a part in determining the partial molar volume of the complexes, and the pressure[69] and temperature-dependent studies[115] indicate that the planar species is more strongly solvated. Thus, solvation increases the numerical value of ΔV somewhat, and this effect is greater in chloroform than in dichloromethane. The solvent molecules are not coordinated to the complexes, even when pyridine is used as solvent and the solution is compressed. The value of ΔV decreases initially with increasing pressure, then levels off (above about 500 atm) to a constant, as would be expected from the greater initial compressibility of the looser solvation shell around the tetrahedral molecules compared with the more strongly held solvation shell around the planar species.

A necessary conclusion from the above observations is that a wide range of nickel complexes, known to be tetrahedral (and paramagnetic) at atmospheric pressure, can be made planar by the application of pressure.

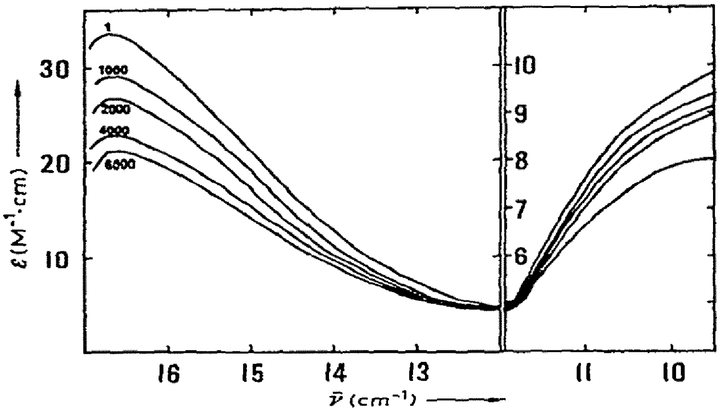
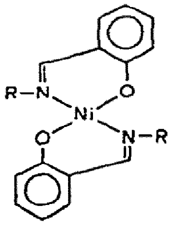


Fig. 9. Pressure dependence of the spectrum of bis(*N*-phenylsalicylaldimino)-nickel(II) in CH_2Cl_2 in the range 1–6000 atm. The bands near 16,000 cm^{-1} and below 10,000 cm^{-1} arise from monomeric and associated forms of the complex respectively.

(iii) Effect of pressure on associative equilibria

Nickel (II) complexes of *N*-substituted salicylaldimines (II) undergo equilibria between monomeric (planar, diamagnetic) and dimeric (pseudooctahedral, paramagnetic) forms which are found to be concentration-, temperature-[116–188] and pressure-dependent[69], and the magnetic (Fig. 7) and optical measurements (Fig. 9) indicate that the equilibrium is shifted towards the side of the associated complex (from eqn. (2), $\Delta V \sim 7$ cm^3.mole^{-1} for a range



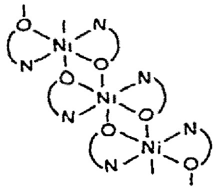
II

of complexes with R = *n*-alkyl in such solvents as $CHCl_3$ and CH_2Cl_2). Depending on the assumed structure[116,117,119], the formation of a dimeric salicylaldimine involves the formation of two or three new metal–ligand bonds. The promotion of an electron to form an octahedral bond will decrease the magnitude of ΔV, while the greater solvation (again $CHCl_3$ solvates more strongly than CH_2Cl_2) of the dimeric molecules than of monomers (deduced from the initially larger ΔV which gradually levels off – see discussion of this effect in Section E(*i*)) increases ΔV, but the predominant contribution arises from the new bond formation[69].

A planar ⇌ tetrahedral equilibrium can exist side by side with the associative equilibria[120–122] in complexes of type II, but the concentration of tetrahedral species is small in *n*-alkylsalicylaldimines, and the data described in Section E(*i*) indicate that pressure will decrease the concentration even further. Thus for nickel (II)*N*-*n*-alkylsalicylaldimine complexes, the monomer $\rightleftharpoons$ associated equilibrium is the only one of importance. On the other, hand, for *N-sec*-alkylsalicylaldimines, the concentration of tetrahedral species is greater and the planar $\rightleftharpoons$ tetrahedral equilibrium occurs to a significant extent, though the monomer $\rightleftharpoons$ $\rightleftharpoons$ associated equilibrium still predominates, and the nett effect is a smaller ΔV than in the other associative equilibria[69].

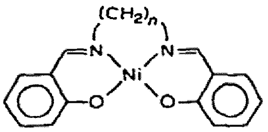
Theoretical calculations indicate that planar triplet nickel(II) species might exist in complexes such as II in non-coordinating solvents[123,124], but the high pressure results are not in keeping with the presence of any appreciable quantity of such species. However, in coordinating solvents such as pyridine, strong association with the solvent leads to an equilibrium of the diamagnetic planar complex with a paramagnetic octahedral dipyridine adduct. The formation of pyridine adducts of nickel (II) complexes involves the formation of two metal–ligand bonds per Ni atom, and the pressure dependence of the adduction, as measured by the magnetic susceptibility or by the optical spectrum, is greater than that for a monomer $\rightleftharpoons$ dimer association in a non-coordinating solvent[69,125].

In the solid state (using a solid solution in paraffin wax and an aqueous suspension) pressures up to 3000 atm produced rather little association in *n*-alkyl complexes of type II. Complex II with R = CH_3 on heating, irreversibly forms a paramagnetic polymer which has the probable structure III, (ref. 119) and this reaction should be accompanied by a volume decrease. However, compression of the solid complex to 45,000 atm left the sample unchanged when returned to normal pressure[69].

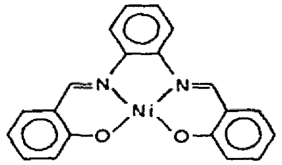


III

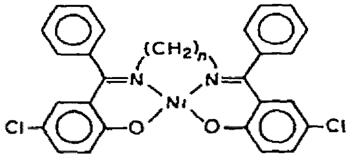
Measurements on the nickel complexes of tetradentate salicylaldimines such as IV (n = 2) and V suggests that as in complex II, there is a pressure-dependent increase in susceptibility in non-coordinating solvents, but this could not be stated with certainty, owing to the low solubility of the complexes[69]. The related complexes VI[126] clearly show the monomer $\rightleftharpoons$ associated equilibrium[127] for the complexes with n = 5 – 12, all of which are



IV



V



VI

TABLE 1

COMPARISON OF PRESSURE EFFECTS ON MAGNETISM OF EQUILIBRIA INVOLVING NICKEL COMPLEXES

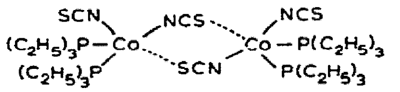
(Tet = tetrahedral, Pl = planar, M = monomer, D = dimer, T = trimer, dm = diamagnetic, pm = paramagnetic, N = number of Ni atoms made pm, ΔV = volume change).

Reaction	No. of new bonds	ΔV	N	P effect on magnetism (NΔV)
(1) $\underset{\text{pm}}{\text{Tet M}} \rightarrow \underset{\text{pm}}{\text{PlM}}$	0	V_1	−1	$-V_1$
(2) $\underset{\text{dm}}{\text{PlM}} + 2\text{Py} \rightarrow \underset{\text{pm}}{\text{M(Py)}_2}$	2	$2V_2$	1	V_2
(3) $\underset{\text{dm}}{\text{PlM}} \rightarrow \underset{\text{pm}}{\tfrac{1}{2}\text{D}}$	$1.5^a(1)$	$1.5V_2{}^a(V_2)$	1	$1.5V_2{}^a(V_2)$
(4) $\underset{\text{dm}}{\tfrac{1}{3}\text{PlM}} + \underset{\text{pm}}{\tfrac{1}{3}\text{D}} \rightarrow \underset{\text{pm}}{\tfrac{1}{3}\text{Tr}}$	$1^a(\tfrac{2}{3})$	$V_2{}^a$	$\tfrac{1}{3}$	$V_2{}^a\tfrac{1}{9}(2V_2)$
(5) $\underset{\text{pm}}{\text{Tet M}} \rightarrow \underset{\text{pm}}{\tfrac{1}{2}\text{D}}$	1.5	$V_1 + 1.5V_2$	0	0
(6) $\underset{\text{pm}}{\tfrac{1}{2}\text{D}} \rightarrow \underset{\text{pm}}{\tfrac{1}{4}\text{Tr}} + \underset{\text{dm}}{\tfrac{1}{4}\text{PlM}}$	0	0	$-\tfrac{1}{4}$	0

[a] Values depend on solution structure: 3 bonds are assumed to hold an "M" molecule to another Ni species; if only 2 bonds are involved the quantities in parenthesis apply.

highly soluble in organic solvents such as $CHCl_3$, and benzene; the analogs of type IV are only a little less soluble and show a similar pressure dependence[127], despite a report that these complexes are insoluble polymers in which each ligand acts as two bidentates on different metal atoms linked by the alkyl chain[128].

The effect of pressure on the various association, and tetrahedral planar, equilibria in nickel(II) can be compared quantitatively, as shown in Table 1. The effect of pressure on analogous magnetic equilibria involving other transition metals is readily deduced. Thus in a monomer ⇌ dimer equilibrium in cobalt(II) compounds VII[129], the dimer is low spin

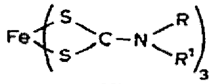


VII

while the monomer is high spin, and the susceptibility decreases markedly with increasing pressure[130].

(iv) Effect of pressure on "electronic" equilibria and possible geological implications

In iron(III) dithiocarbamates VIII, the high spin ($^6A_1$) and low spin ($^2T_2$) states are



VIII

nearly equienergetic, so that the relative populations of these states are both temperature- and pressure-dependent[40,70,131]. The low spin state is favored by increasing pressure, so that magnetic moments decrease with pressure. Here ΔV is 6 cm^3. $mole^{-1}$, which corresponds to a change in the average Fe–S bond length[40] of 0.1 Å, consequent upon the pairing of two electrons.

This kind of experiment gives a direct measurement of the volume change (or bond length change) associated with the pairing of two unpaired electrons in a simple molecule in a situation where the change in other factors is kept to a minimum. The geometry of the high spin and low spin species is essentially the same, so that solvation effects cancel and may be ignored. Similarly Mössbauer[132] and magnetic[130] data that indicate high spin → → low spin transitions are induced by pressure in $FeLX_2$, where L is a phenanthroline or dipyridyl ligand and X = NCS or NCSe. Single crystal X-ray studies have confirmed the 0.1 Å average bond length contraction on pairing of two electrons in these complexes[133,134]. Recently spin pairing has also been induced by pressure on iron(II) doped into samples of MnS_2, $MnSe_2$ and $MnTe_2$, studied by the Mössbauer effect[135].

The equilibrium is of considerable biological significance since several ferrihemoprotein complexes are near the high spin – low spin crossover[136], and the biological activity of these molecules is probably closely tied to their ready ability to change their spin state. As proteins are stable[137] up to 3000 atm, but denature under relatively low temperature variation, high pressure methods are much preferred for such molecules. Some measurements of this type have already been carried out: the Soret band, a strong sharp absorption occurring in all hemoproteins near 400 nm, is known to be at lower energy in low spin derivatives[138], and a shift in this direction has been observed in some hemoproteins with increasing pressure.

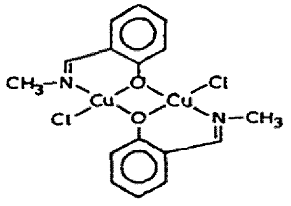
It can be shown that ligand field strength Δ should increase as a function of decreasing metal–ligand bond length r, approximately as r^{-5} in complexes of near octahedral symmetry[139,140]. This has been demonstrated directly by using steric strains to increase the metal–ligand bond lengths in iron(II) complexes, which caused either shifts in absorption bands dependent on Δ, or a change in spin state from low to high spin[141,142]. Again, increasing pressures produce shifts to higher energy in absorption bands dependent on the ligand field splitting in metal complexes (e.g. $E(^3A_2 \rightarrow {}^3T_2) = \Delta$ in Ni^{II}, d^8)[38,143]. Thus all high spin complexes in which spin pairing is theoretically possible, should at some pressure show crossover behavior like the ferric dithiocarbamates and other such complexes. For example, in CoF_6^{3-}, the high spin to low spin crossover is expected to occur[144] near $2.2 - 2.5 \times 10^5$ atm. At higher pressures, further increase in Δ should produce low spin behavior in all complexes where spin pairing is possible. It has already been shown that iron(II) can be spin paired in gillespite, $BaFeSi_4O_{10}$, at moderate pressures[145,146].

It is a necessary conclusion from the above observations that octahedral iron(II), iron(III) and cobalt(III) minerals become spin paired deep in the earth's mantle (below the transition zone between the upper mantle and lower mantle) where the pressure is high enough to produce spin pairing. In addition to the effect this will have on the magnetic properties of the lower mantle, the concentration of metal–ligand bonds could cause an enrichment of low spin ions or ions which can become low spin at depth[146]. The increase in crystal field stabilization energy with increasing pressure may also play a part in enriching these ions with particularly high crystal field stabilization energy; supporting evidence for this is provided by minerals believed to come from the lower mantle (carbonaceous chondrites) which show a strong enrichment in iron, cobalt and nickel complexes compared with rocks from the upper mantle[147]. Thus, the effect of pressure is of considerable importance in determining the composition and geological history of the earth. It is also of importance to the thermal history: the redistribution of heat by radiation in the mantle and towards the corre-mantle boundary will be critically dependent on the absorption spectra of the complexes present, and these in turn are strongly affected by pressure (especially if spin pairing is induced)[147].

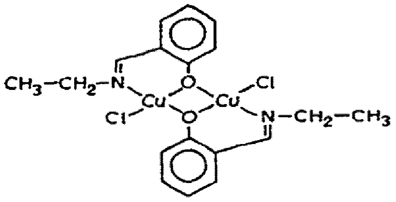
(v) Effect of pressure on some antiferromagnetic and some ferromagnetic substances

Magnetic exchange interactions, both lattice-wide (intermolecular) and discrete (intramolecular), occur in a wide variety of transition and rare earth metal compounds[148–151]. Whether the mechanism is direct orbital overlap or superexchange (via intermediate atoms), the application of pressure is useful in ferromagnetic, ferrimagnetic and antiferromagnetic ordering because it permits variation of the interatomic distances. The effect of pressure on the Curie or Neel temperatures of lattice ferro- or antiferromagnetic complexes depends on whether or not the reduced volume enhances the orbital overlaps required for the interactions. In general the overlap, and hence the strength of antiferromagnetic interactions, should increase with increasing pressure, and this has been observed for a number of lattice antiferromagnets[74]. The situation is more complex in the case of the compounds EuX, which are ferromagnetic for $X = O$ or S, and antiferromagnetic for X = Se or Te, all of which have the same (NaCl) structure. The effect of pressure should follow the effect of the decreasing cubic cell constant: decreasing antiferromagnetism or increasing ferromagnetism as pressure rises. The expected increase in ferromagnetism is observed in EuO (ref. 152) and EuS (ref. 153), but in EuSe and EuTe, contrary to expectations, the antiferromagnetic interactions apparently increase or remain unchanged[74,154], though the experimental results are controversial[74,155,156]. In any case, the results indicate that the interatomic distances do not alone determine the magnetic ordering in the europium compounds. Metallic iron itself undergoes a ferromagnetic to paramagnetic transition (accompanied by a resistance change) near 125,000 atm, due to a structural change from the normal body-centered cubic lattice to hexagonal close packed[45,156].

The simplest situation involving magnetic exchange exists where only pairs of isolated paramagnetic atoms take part in antiferromagnetic interactions, so that the interpretation of results should be simplified. Unfortunately, in intramolecular antiferromagnets, the sharp magnetic transition temperature is replaced by a broad maximum, which increases the experimental difficulty. Very little pressure effect was observed in solid dimeric copper(II) acetate, chloroacetate or succinate, the polymeric oxalate, and no effect was evident at all in chloroform solutions of other dimeric copper(II) alkanoates[157], indicating that the singlet (spin-paired) and triplet (spin-free) forms of these molecules have about the same volume. The orbital overlap responsible for the magnetic exchange in these complexes has been described in terms of a weak δ-bond[158,159], or superexchange interactions between isolated coppers[160], both of which are compatible with the high pressure data, and in terms of a strong σ-bond or a strong δ-bond overlap between the metal atoms[161,162], which does not agree well with the lack of significant volume dependence[157]. The pressure dependence of the electronic spectra of the complexes is also compatible with descriptions based on weak δ-bonding or a mixture of weak δ-bonding[159] and superexchange interactions[163]: band I (650 nm) increases in intensity with rising pressure, in agreement with its assignment as ${}^2B_1 \rightarrow {}^2E$, allowed by low symmetry ligand field elements, while the intensity of band II (370 nm) decreases, as expected, since this band is believed to be vibronically allowed[163]. Solid complexes of the type chlorobis(*N*-methylsalicylaldimino)dicopper(II), IX, showed no significant change in magnetism with increasing pressure, indicating that singlet and



IX



X

triplet species in these molecules again have about the same volume. This observation is confirmed by single-crystal X-ray structural determinations on chlorobis(*N*-ethylsalicylaldimino)dicopper(II), X and IX, in which the ratios of singlet and triplet species at room temperature differ significantly, but in which all the analogous bond lengths are the same within experimental error, i.e. no volume difference arises due to pairing or unpairing of electrons.

(vi) Effect of pressure on nitro–nitrito equilibrium

In the complexes $NiL_2(NO_2)_2$, where $L = RR'N-CH_2-CH_2-NR''R'''$ an equilibrium exists between nitro and nitrito forms of the complexes, for certain combinations of alkyl groups R, R′, R″, R‴[165]. There is no difference in magnetism of the two species, but the spectra differ so that the equilibrium can be studied spectroscopically, and preliminary data show this equilibrium to be strongly pressure-dependent, the nitro species being favored by pressure[166] (Fig. 10). The equilibrium here is a little more complicated than those described above in that it involves formation and recombination of ions, but it is clear from comparison with solid state spectra that in solvents such as chloroform, only the neutral species contribute significantly to the spectra. Thus, only the neutral species need be considered in the equilibrium. In this case, the equilibrium species can differ little in molar volume, and solvation effects must be responsible for the bulk of the pressure dependence of the equilibrium. As expected with solvation (see Section E(*ii*), (*iii*)), the pressure dependence decreases from an initial high to a constant lower value. The organic part of the molecules remains unchanged in the equilibrium, so that the different degrees of solvation of the two species must represent the degrees of solvation of the NO_2 and ONO forms of the anionic ligand. The results indicate that NO_2 is more efficient in filling the available space near the metal than the ONO, which presumably leaves some "holes"

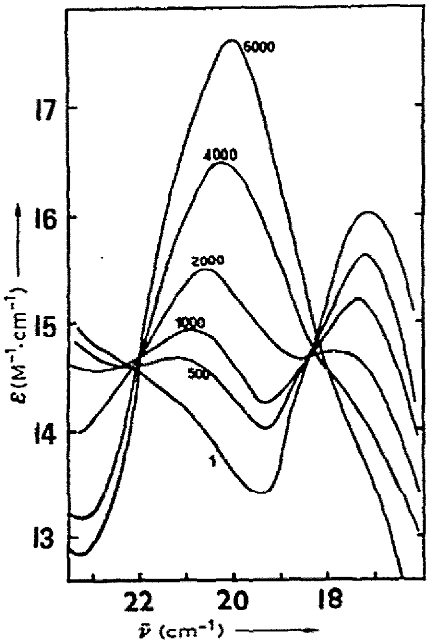


Fig. 10. Pressure dependence of $NiL_2(NO_2)_2$ in the range 1–6000 atm where L = N,N′-diethylenediamine. The band near 20,000 cm^{-1} is due to the nitro form of the complex.

inaccessible to the solvent. The NO_2 form is more strongly solvated at low pressures than the ONO form, and the difference between the two illustrates how strongly even aprotic solvents such as chloroform and dichloromethane can be held to metal complexes.

(vii) Pressure dependence of ionic equilibria

In the equilibria discussed above, the solvent either played no part other than to transmit the pressure, or its role was limited to solvation of the solute complex but without coordinating to it. An exception was planar nickel(II) in pyridine, in which the solvent does coordinate in a simple specific way, without otherwise causing much alteration in the remainder of the complex. In general, there may be specific solvent interaction with one of the interacting species, making a specificant contribution to ΔV, and sometimes the solvent must be considered as one of the reagents, or the solvent itself undergoes pressure-dependent changes. Thus the dimerization of nitrogen dioxide in carbon tetrachloride to form nitrogen tetroxide is much more enhanced by pressure than would be expected from the molecular sizes, due to solvent interactions with the tetroxide[167]. In alcohols, frequently used as solvents, the proportion of hydrogen-bonded polymers increases with rising pressure, and ΔV is about 4 $cm^3.mole^{-1}$ for formation of the hydrogen bond[168,169]. The molar volume of water is greater than its equivalent in hydroxyl and hydrogen ions, as evidenced by a ΔV of 19.5 $cm^3.mole^{-1}$ in neutralization reactions[170]. Thus increasing pressure greatly increases the ionization of fluid water[171], a fact of considerable importance in geochemistry and marine biology, and when compressed to the density of molten sodium hydroxide, water has about the same electrical properties as the sodium hydroxide. The formation of any solute ions in water is accompanied by drastic volume reduction, so that the dissociation of weak electrolytes such as phosphoric acid is greatly enhanced by pressure, and all weak electrolytes becomes strong electrolytes when compressed in aqueous solution.

The contraction (electrostriction) of a classical uniform dielectric around spherical molecules when these are given a single charge should be about 10 $cm^3.mole^{-1}$, or about 20 $cm^3.mole^{-1}$ for the two ions of a 1 : 1 electrolyte[169,172], in good agreement with experimental data fitted to eqn. (2). Although the higher initial magnitude of the contraction is expected to decrease with increasing pressure[173], it levels off to values large enough to produce dramatic changes in electrolyte strength with relatively small pressure changes. For example, the degree of ionization of ammonia increases[174] from about 4% at 1 atm to 65% at 12,000 atm. In general, any increase in the concentration of ionic species is enhanced by pressure in water and other highly polar solvents. Thus in equilibrium mixtures of tetrahedral (blue) and octahedral (pink) cobalt(II) species such as

$$\underset{\text{pink}}{Co(H_2O)_6{}^{2+}} + n\,Cl^- \rightleftharpoons \underset{\text{blue}}{[CoCl_n(N_2O)_{4-n}]^{2-n}} + (2+n)\,H_2O$$

the equilibrium is shifted to the left by pressure[77,175]. Similarly, the breakup of the dimeric copper alkanoates discussed above is enhanced by increasing pressure

$$[Cu(RCO)_2\,.\,H_2O]_2\,(S) \rightleftharpoons 2\,Cu(RCOO)_2\,(S) \rightleftharpoons 2\,Cu^{2+}\,(S) + 4\,RCOO^-\,(S)$$

where S is a solvent species such as water or ethanol which may be present in high concentration or dispersed in another solvent such as chloroform. Once the equilibrium is shifted to the right by pressure, hydrolysis of the complexes is also enhanced, so that the equilibrium is no longer completely reversible. When no change in the concentration of the ionic species is involved, the nett solvent effect may be unimportant, and in the equilibrium

$$I_2 + I^- \rightleftharpoons I_3{}^-$$

the formation of a new bond alone accounts well[77,173] for the observed ΔV of -5.4 $cm^3.mole^{-1}$. One example of dissociation of ion pairs under pressure has also been studied.

$$(Mg^{2+}\,SO_4^{2-})\text{ ion pairs} \rightleftharpoons Mg^{2+} + SO_4^{2-} \qquad (4)$$

As expected, this dissociation is favored by pressure like the dissociation of neutral molecules, though with a smaller than average ΔV(7 $cm^3.mole^{-1}$)[176]. The reflection of sonic waves in sea water was thought to arise[177] from the relaxation of equilibrium (4). The effect of pressure waves on equilibrium (4) results in high ultrasonic absorptions, though there are a number of complicating factors in sea water[178].

Similar studies have been carried out on aqueous solutions containing equimolar amounts of FeX_3 and HX, where X = Cl, ClO_4 and NO_3. As expected, pressure favors the breaking up of FeX^{2+} complexes, but the pressure effect on $FeNO_3^{2+}$ is less than on $FeCl^{2+}$, suggesting that the former may be an ion pair rather than a complex[179].

(viii) Reversible effects on electronic spectra

The pressure effects on the spectra associated with some of the above equilibria have already been discussed. Other reversible pressure effects such as on ligand field spectra have also been mentioned. The crystal field splitting, Δ, in a regular octahedral (or tetrahedral) array of charges depends on $<r^4>/R^5$ where $<r^4>$ is a function of electron positions and R the metal-ligand distance. Thus, taking $<r^4>$ as constant, Δ should increase with increasing pressure, i.e. increasing R^{-5}. By inspection of the Tanabe–Sugano diagrams, a blue shift is predicted for all spin-allowed d–d transitions. This has been observed in a range of octahedral transition metal complexes, though the shift is invariably greater than predicted[38,143,144] from estimation of R^{-5}.

Also important here is the increase in covalency associated with a decrease in R. The increase in metal-d-orbital overlap with the ligand orbitals is expected to increase transition probabilities and to decrease the Racah parameter B with increasing pressure. Experimental spectra[38,143,144] show the expected increase in intensity and in general the reduction of B. There are some apparent exceptions, but a number of other factors affect the experimental values; if any lower symmetry elements are present, then assuming no change in geometry with pressure, the distortion splitting must increase just as Δ does. Changes in geometry are quite possible and could significantly affect the spectra and drastically alter the estimated B. Spin–orbit coupling will alter with pressure in a manner determined by the combined effect of the increase expected from compression of the free ion and the decrease due to increasing covalency. Just as experimental measurement is usually the only method of obtaining B for complexes at normal pressures, so also is the dependence of B on R in real complexes outside the scope of current quantitative calculations. The variation of the Coulomb and exchange integrals and hence of the electron positions with R would be required, which is not simple, even in the absence of ligand effects.

Drickamer and Zahner have also examined rare earth spectra where the crystal field gives rise to splittings in the f shell[38]. The results are qualitatively similar to those obtained for transition metal complexes.

Many charge transfer spectra have been found to be red-shifted and broadened by pressure, due to increasing delocalisation of the charge transfer process[38]. Extrapolation of this effect would predict decay of the spectra into an absorption edge which is characteristic of a lattice (cooperative) effect (as in a semi-conductor) rather than of a discrete molecular site. The conversion of olivine and related minerals to semi-conductors due to this phenomenon at high pressures has already been mentioned[41].

The effects of pressure on spectra and fluorescence of a wide range of aromatic molecules have also been investigated[180].

F. REACTIONS UNDER PRESSURE

(i) Reactions and syntheses

The classical Haber syntheses of ammonia, and the hydrogenation of unsaturation carbon compounds with pressurised hydrogen, are typical examples of chemical reactions enhanced by fairly low pressures.

Certain chromium(II) and chromium(III) complexes, when reduced electrochemically in anhydrous solvents (such as pyridine) saturated with carbon monoxide at pressures of 50–300 atm, produce good yields of chromium carbonyl $Cr(CO)_6$. Typical complexes that may be used for this reaction are tris(acetylacetonato)chromium(III), $Cr(acac)_3$, dichloro(tripyridine)chromium(III), $CrCl_3(py)_3$, and dichloro(dipyridine)chromium(II), $CrCl_2(py)_2$. Similar carbonylation reactions occur with vanadium, manganese, iron, cobalt and nickel over a wide range of pressures[181].

Trihydrides MH_3 are formed on reaction with hydrogen at atmospheric pressure and moderate temperatures by all the rare earth metals except ytterbium and europium which form only the dihydrides[182], a manifestation of the stability of the filled and half-filled 4*f* subshells. However, relatively small increases in pressure (~ 22 atm) in excess hydrogen yields $YbH_{2.55}$, though no higher hydrides of europium could be formed[183]. $YbH_{2.55}$ is paramagnetic, having a moment intermediate between that of Yb^{III} complexes and the diamagnetic Yb^{II}, and X-ray diffraction shows it to be a new compound[184]. The properties and thermodynamics of formation of the rare earth and other hydrides more closely resemble those of intermetallic alloys than metal–nonmetal compounds (see Section G(*iii*))[185]. Other apparently nonstoichiometric compounds may be formed under pressure: $UO_{2.37}$ is typical. This substance is formed by heating UO_2 and U_3O_8 together at 30,000–40,000 atm. X-ray diffraction shows it to be a new compound, and single-crystal studies[186] may show it to be U_8O_{19}.

Stable, crystalline lead compounds PbS_2, $PbSe_2$, PbSSe, previously unknown, can be prepared by heating appropriate mixtures of Pb, S, Se or PbS, PbSe, S, Se at 20,000–70,000 atm in BN capsules[187]. The reaction of PbS and S to form "α-PbS_2" was found to occur with explosive force, destroying part of the apparatus. Substitution of nickel reaction vessels for BN led to formation of Ni_3PbS_2. There are many other examples of violent transitions under pressure. Bridgman[2] reported that black phosphorus forms from yellow phosphorus in the region beyond 12,000 atm and 200°C, but not immediately: the reaction proceeds very slowly at first but at a gradually accelerating rate until suddenly, the reaction completes explosively. The oxidation of MnO_2 to MnO_4^{2-} by KNO_3 or $KClO_4$ proceeds explosively above 19,000 atm at comparatively low temperatures (80–90°C)[188].

A new rhenium carbide, with a structure of the γ′-MoC type (space group $D_{6h}^4 = P6_3/mmc$), is formed[189] above 60,000 atm and 800°C.

It has been shown that high pressures and temperatures will sometimes allow the formation of unknown rare earth compounds[190]. In particular, high pressures aid the synthesis of rare earth dimanganese compounds[191] and rare earth tritin[192], having $MnZn_2$ (Laves) and $AuCu_3$ (face-centered cubic) structures respectively. Known and previously unknown stable and metastable compounds could be made with various rare earth metals. Size differences due to the lanthanide contraction probably cause instability of the crystal structure in some of the compounds, especially the tritin compounds of the heavier rare earths. High pressures change the relative sizes of the atoms, permitting the formation of the compounds, which, once formed, are metastable at room temperature and pressure.

Chromium(IV) dioxide is best prepared at high pressures and temperatures, from Cr_2O_3 and HgO (~ 15,000 atm, 700°C)[193], at higher pressures[194], directly from Cr_2O_3, or by the hydrothermal decomposition of CrO_3 (400–525°C, 500–3,000 atm)[195].

Some organic reactions are similarly made possible or enhanced, so that high pressure could also become a major tool in organic chemistry[196].

(ii) Kinetics under pressure

Measurements at various pressures are useful in determining reaction mechanisms, and the transition state theory is probably the best approach to an analysis of the role of pressure in chemical kinetics[169]. To adequate approximation, pressure dependence of the rate constant k is given by

$$-\frac{RT\,\partial \ln k}{\partial p} = -\Delta V^{\dagger}$$

where $\Delta V^{\dagger}$ is the excess of the partial molar volume of the transition state over the partial molar volumes of the initial species, all at the composition of the mixture. It is convenient to split $\Delta V^{\dagger}$ into two terms $\Delta_1 V^{\dagger}$ and $\Delta_2 V^{\dagger}$, where $\Delta_1 V^{\dagger}$ is the volume change of the reacting molecules when they form the transition state, while $\Delta_2 V^{\dagger}$ is the accompanying change in volume of the surrounding liquid, arising principally from changes in electrostriction[197]. Thus the theoretical considerations here are very like the treatment of equilibria above, the equilibrium being between the reactants and the transition state and the rate of reaction is governed by the proportion of transition species in the reaction mixture.

It is frequently possible to discriminate between various postulated mechanisms for a reaction on the basis of $\Delta_1 V^{\dagger}$ determinations since the volume requirements can usually easily be imagined. In simple dissociation reactions, the breaking bond stretches somewhat to form the transition state, and this stretch, though variable, appears to average around a third of the original bond length[169,197]. Thus in the absence of other complicating effects, simple dissociation reactions are retarded by rising pressure. Reactions involving the formation of new bonds constitute the reverse situation, and there is a contraction as the reactant molecules approach each other from an initial separation by the sum of their van der Waals distances to the closer approach in the bonded transition state. The $\Delta_1 V^{\dagger}$ in this case is normally somewhat larger in absolute magnitude than for the corresponding dissociation reactions[169,197]. Thus in reactions involving the simultaneous bond breaking and formation, the two $\Delta V^{\dagger}$ values compete, but the bond formation predominates, so that in the absence of other complications, the nett effect is an acceleration of the rate.

The bimolecular reaction

$$OH^- + [Co(NH_3)_5Br]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{2+} + Br^-$$

is retarded by pressure in water[198] ($\Delta V^{\dagger} = 8.3$ cm^3.mole^{-1}). In the absence of solvent effects, a seven-coordinate transition state could explain the results, while a simultaneous bond breaking and formation mechanism would normally have required an acceleration of the reaction. However, these two mechanisms cannot be distinguished here because the reaction may involve the release of some bound solvent molecules, i.e. a $\Delta_2 V^{\dagger}$ contribution. The $\Delta_2 V^{\dagger}$ contribution can be removed from the ionic equilibrium by careful choice of reactions and isotopic labeling. Thus a positive $\Delta V^{\dagger}$ (1.2 cm^3.mole^{-1}) for the reaction

$$[Co(NH_3)_5(H_2{}^{18}O)]^{3+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + H_2{}^{18}O \qquad (5)$$

indicates a large transition state and therefore a dissociative mechanism[199], in keeping with the view that a dissociative (I_d) mechanism is involved[200,201]. In fact, the dissociative Eigen mechanism and rate-determining I_d step has widely been assumed for M^{2+} and M^{3+} complexes, although the greater charge on the trivalent metal should favor associative over dissociative activation[202]. The preference for the dissociative Eigen mechanism by divalent metals such as Ni^{II} and Cu^{II}, is evidenced by the large positive $\Delta V^{\dagger}$ values observed in substitution reactions with uncharged ligands[203], but for cationic complexes it appears that an associative transition state is normal, with Co^{III} being the exception. The $H_2{}^{18}O$ exchange of $[M(NH_3)_5H_2{}^{18}O]^{3+}$ with solvent water (eqn. (5)) is accelerated[204] by pressure when M = Cr, Rh, as is the reaction[205]

$$[Cr(H_2O)_6]^{3+} + H_2{}^{18}O \rightarrow [Cr(H_2O)_5(H_2{}^{18}O)]^{3+} + H_2O$$

in keeping with an associative mechanism, of the Langford–Gray associative interchange (I_a) type[200,206]. It is interesting to note that the $\Delta_2 V^{\dagger}$ contribution can sometimes be significant, even in some of these reactions involving no change in the number of ionic species: the acceleration of the reactions is even greater than expected, especially for hexaaquo complexes[199,201,204]. This is interpreted in terms of a large well-structured solvation shell around the $[M(H_2O)_6]^{3+}$ ion, which collapses into a poorly structured shell around the $[M(H_2O)_7]^{3+}$ transition state, and fills the vacancy left when the attacking H_2O moves from the solvation shell to the metal. The contribution to $\Delta V^{\dagger}$ is larger with aquo ligands than amines because the acidic aquo protons form more extensive hydrogen-bonded solvation shells, and it is larger in Cr^{III} than Rh^{III} because the larger Rh ion has the smaller electrostatic potential. Estimates of the sizes of the solvated ions, from the rate of elution from ion exchange resins, support these conclusions[204].

G. OTHER PRESSURE EFFECTS

(i) Reversible reduction of iron(III)

A number of iron(III) compounds have been examined by Mössbauer spectroscopy under pressure (up to 2 × 10^5 atm), and from the appearance of new peaks with quadrupole splittings and isomer shifts in the region normally taken as characteristic of iron(II)[140,207], a fairly general pressure-dependent reduction of iron(III) compounds to iron(II) has been suggested[208–212]. Although the peaks are broad and poorly resolved, the new peaks grow with rising pressure, and when the pressure is released, the reduction is partially reversed in most cases (but not completely, suggesting chemical alteration of part of the sample). Clearly these observations are of considerable importance to high pressure inorganic chemistry, and in the chemistry of the earth's interior.

Gardiner et al.[213], on reinvestigating some of the postulated reductions using infrared spectroscopy (up to 5 × 10^4 atm) observed no irreversible changes. They point out that reductions are normally inhibited by pressure, and that large shearing stresses can irreversibly transform iron(III) ferricyanide to iron(III) ferrocyanide[214], and shear stress set up during compression of the sample may be responsible for some of the apparent reversible reductions[215]. However, the Mössbauer data indicate that only a small amount of the postulated reduction would be expected at 5 × 10^4 atm, so that the absence of irreversible change in the stretching vibrations does not invalidate the reduction mechanism. There is also some supporting evidence for the reduction from electronic spectra[210,212].

(ii) Phase changes and metastable states

In recent years, the search for new phases of inorganic compounds has been particularly successful[30,65,189,192,216–222], largely because most substances undergo a number of phase transitions in the experimentally accessible pressure range and the availability of simple high pressure X-ray diffraction apparatus has made the detection of new polymorphs particularly easy. In general, the rate of transformation from one solid phase to another increases with increasing pressure, a fact which also aids the detection of new phases. Thus many high pressure phases can be detected during the very short duration of a shock wave passing through a sample. Phase changes may be characterized by abrupt changes of any physical properties, such as those measured by the techniques described in Section D, but the observation of a new X-ray diffraction pattern is the most reliable method.

The predominant phases at depths between 200 and 900 km in the earth's mantle are generally believed to be denser high-pressure polymorphs, or disproportionation products, of common silicate minerals[223]. Thus, pressure-induced phase transitions are of great geological interest (as, of course, are pressure-induced reactions[224]). Although it is difficult to simulate the temperatures and pressures corresponding to depths greater than 800 km, possible polymorphic transitions may be investigated by the use of model compounds which undergo transitions at lower pressures. A good example is the isomorphic replacement of silicon in silicates by germanium[225], to permit structural investigation of the high pressure form. A possible mechanism for deep-focus earthquakes is a phase transition (the pyroxene–garnet transformation, which should occur at depths of the order of 350 km) in large blocks of eclogite (a basaltic silicate) sinking through the mantle after being formed in the earth's crust[226].

Other potential or existing metastable phases of great interest are metallic hydrogen, diamond, borazon and potential new superconducting compounds.

(iii) Metallic hydrogen

The main difference between metallic hydrogen and other metastable forms of the elements, such as diamond, is that it has not been isolated. However, the requirements for the formation of a metal, viz. the presence of a small number of electrons in the outermost electron shell, are satisfied by hydrogen. Thus it should be possible to assemble metallic hydrogen in the same way as metallic sodium or lithium, the "free electron gas" being formed from the single outer *s* electron of some of the atoms, and holding together the resulting lattice of positive ions. Calculations show that metallic hydrogen should have a density of 0.68 g.cm^{-3} (metallic deuterium should have twice that density), and be thermodynamically stable with respect to atomic hydrogen, and metastable (with a barrier of about 0.2 eV/electron) with respect to molecular hydrogen[36,227]. The metallic structure is the simplest of all possible structures, and it follows that the formation of metallic hydrogen requires only a pressure high enough (estimated to be near 10^6 atm at room temperature) to produce the required closeness of approach of hydrogen atoms; although the required pressure is not yet available in the laboratory, rapid technological advances may alter this situation[36,228].

In its physical properties, molecular hydrogen behaves as would be expected for the lightest member of the halogen series (. . . Cl_2, F_2, H_2), though chemically hydrogen shows relatively few halogen-like properties. Instead its behavior conforms to that expected for the lightest of the alkali metals (. . . Na, Li, H), its commonest salts being the mineral acids and common organics being its "organometallic compounds", which, as expected, are much more stable than organolithium compounds.

Metallic hydrogen would be the highest melting of the alkali metals (1800°C) and would probably have the highest critical superconducting temperature of any substance; it may be a superconductor up to 100°K or more, and this fact alone would make it extremely valuable[227]. Moreover, it should be a relatively hard and strong metal, and with its low density it would probably have the highest strength-to-density ratio of any metal. At its boiling point, and at all temperatures below, where it has a significant vapor pressure, hydrogen would evaporate irreversibly into diatomic gaseous form, but with relatively little release in energy (estimated at about 35 kcal/mole). Chemically it would be stable to attack by water, mineral acids and saturated organics, but would be attacked by mercury to form gaseous hydrogen, and would burn in air.

Though metallic hydrogen is not known on the earth's surface, it inevitably exists elsewhere. The static pressure beneath the atmosphere of the planet Jupiter is sufficient to convert hydrogen to the metallic form, and the integrated mass of that planet suggests that it consists largely of hydrogen, with an inner core of helium[229]. It is therefore probable that the bulk of the planet consists of metallic hydrogen, and possible that this is superconducting, given the low temperature of the planet (100–200°K)[227]. Persistent currents in the superconducting state may be significant in determining the planet's magnetic field, and perhaps also its radiowave emissions. The helium core may also be metallic.

(iv) Diamond and borazon

Although diamond is only metastable with respect to graphite under normal conditions it will remain unchanged indefinitely once formed. The transformation of graphite into diamond is similarly sluggish if the temperature and pressure are just within the stability region of the diamond phase, and considerable excess pressure is required, while high temperatures are desirable to accelerate the reaction further. The early syntheses used molten transition metals such as nickel, manganese and copper as solvents for graphite and catalysts[35,230]. At the high temperatures and pressures of shock waves, the reaction is much more rapid[231], and small particles of black diamond form in a shock front corresponding to about 3×10^5 atm for about a microsecond[232]. Very high static pressures also produce the transition without catalysts[58], with the simultaneous high temperatures required becoming less as higher pressures become available[228]. A wide range of organic compounds, including raw peanut, also react to form diamond[233] at about 150,000 atm and 2000°C, which demonstrates the ease with which diamond can form under natural conditions.

Hexagonal boron nitride, BN, undergoes a similar transition, with a density change of 2.25–3.45 $g.cm^{-3}$, to form a new phase, borazon, which has a cubic structure[234]. Borazon is able to scratch diamond, and has about the same hardness. The possibility of forming other such metastable or stable phases is a considerable incentive for high pressure research.

(v) Superconductivity

New phases produced by high pressure of some elements (such as Si, Ge, Bi, Sb, P, Te, Se, As, Ba, Ce, Cs), are superconducting while the normal phases are not. The critical temperature T_c, below which superconductors show superconducting properties, is usually 10°K or less, and normally decreases as a function of pressure, except in some transition metals[235]. High pressure (20,000–200,000 atm) may produce new phases, metastable at atmospheric pressure, having higher T_c than the normal, low pressure, phase. In each of InSb alloy[236], Sn, Ga (ref. 237), Bi, and La (ref. 238), the high pressure phase has a higher T_c (1–5°K) than the normal phase.

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