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Hydrostatic limits in liquids and solids to 100 kbar

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The hydrostatic properties of the materials methanol, isopropyl alcohol, water, sodium chloride, silver chloride, and the binary mixtures pentane-isopentane and methanol-ethanol have been determined in the diamond-anvil pressure cell up to 180 kbar by line-broadening and line-shift measurements of the sharp R_1 ruby fluorescence line. A liquid mixture 4 : 1 by volume of methanol : ethanol remains hydrostatic to almost 100 kbar at room temperature. This mixture exceeds the hydrostatic limit of the previous generally accepted fluid, 1 : 1 pentane : isopentane which has a hydrostatic limit of about 70 kbar. Silver chloride and water (ice VII) are better than sodium chloride as pressure-transmitting media, but do not even qualitatively approach hydrostatic conditions much above 70 kbar. The stress sensitivity level of the ruby limits the extent to which slight deviations from hydrostatic conditions can be determined in solid systems and suggests the qualitative nature of the method in characterization of quasihydrostatic states. The equilibrium freezing pressure of methanol at 24 °C was redetermined to be 35.8±0.8 kbar.

INTRODUCTION

The most meaningful studies of the physical properties of materials subjected to very high pressures require a hydrostatic (zero shear stress) environment. The use of an encapsulating fluid as a pressure-transmitting medium generally fulfills this requirement as long as the fluid does not solidify in the pressure range considered. Often solids such as AgCl or NaCl with relatively low shear strengths are used as pressure-transmitting media. These solid-medium pressure-transmitting environments are capable of producing quasistatic pressures to 100 kbar and above. However, the presence of stress and the unknown magnitude of stress in such systems has often cast serious doubt on the interpretation of the desired measurements.

Maintaining hydrostatic conditions in systems at high pressure involves the selection of an appropriate fluid. This is not a trivial task because most liquids at room temperature solidify below 20 kbar.[1-3] The use of room-temperature gases is not feasible nor practical because they present rather formidable handling problems for pressure-generating systems capable of 100 kbar. Bridgman and others have shown that many pure liquids and liquid mixtures slowly vitrify rather than crystallize as pressure is applied, and that some liquids remain hydrostatic to pressures well over 30 kbar.[4-6] In these cases, either a measurement of viscosity or a measurement of the initiation of shear is required to determine the limits of the hydrostatic pressure region. Bridgman measured the viscosity of many liquids to 30 kbar and showed relative increases of factors as high as 10^9 in some cases over this pressure range.[4] Of the liquids studied, pentane, isopentane, and methanol were shown to have the smallest increase in viscosity with pressure and to have relatively low absolute values at 30 kbar. All three of these substances have been shown to crystallize when pure, but all three also demonstrate a tendency to "super press" and vitrify.[2,3]

The use of a 1 : 1 mixture by volume of pentane : isopentane has become rather widespread in many high-pressure laboratories. Viscosity measurements by Barnett and Bosco demonstrated its usefulness to at least 60 kbar.[6] Methanol has not been used extensively due to its unsatisfactory electrical properties associated with its polar nature and the absorbed water contamination. The undesirable electrical properties are of no significance for some applications and according to Bridgman become less of a problem at high pressures.[4]

Quantitative measurements of pressure gradients within a specific apparatus using quasihydrostatic pressure-transmitting solids have been rather difficult to obtain and have been limited to rather specialized materials. Effects indicating the existence of pressure gradients are rather common, but generally these gradients are ignored and an average pressure is used.

To make meaningful pressure gradient measurements one requires a pressure sensor which is dimensionally small relative to the total sample and which also provides an observable signal continuously variable with pressure. The use of fixed point phase transitions, rather than a continuous pressure sensor, has been attempted but only qualitative results have been obtained. The advantage of an optical technique for isolating specific regions of the sample chamber was demonstrated by Lippincott and Duecker, who carried out a study of gradients in the diamond-anvil cell,[7] and studied the gradients only in the sample of the material used as the pressure sensor itself, namely nickel dimethylglyoxime, by a spectroscopic absorption method in the visible range of the spectrum. Their approach is similar to the method which we will presently describe, except that our technique employs the fluorescence of ruby as the pressure measurement. The use of ruby allows us to study many of the more interesting pressure-transmitting materials because ruby is chemically inert and the strength of ruby is much higher than the strength of most of the materials of interest. The high strength of ruby is significant because the weaker component of a mixture of two or more materials will dominate in establishing pressure gradients in the chamber.

In this paper we address ourselves to two aspects of the experimental problems associated with hydrostatic and quasihydrostatic environments: (I) establishing the pressure limits of a given pressure-transmitting fluid below which the fluid can be considered truly hydrostatic, and (II) the quantitative measurement of pressure gradients and local shear stresses in quasihydrostatic media.

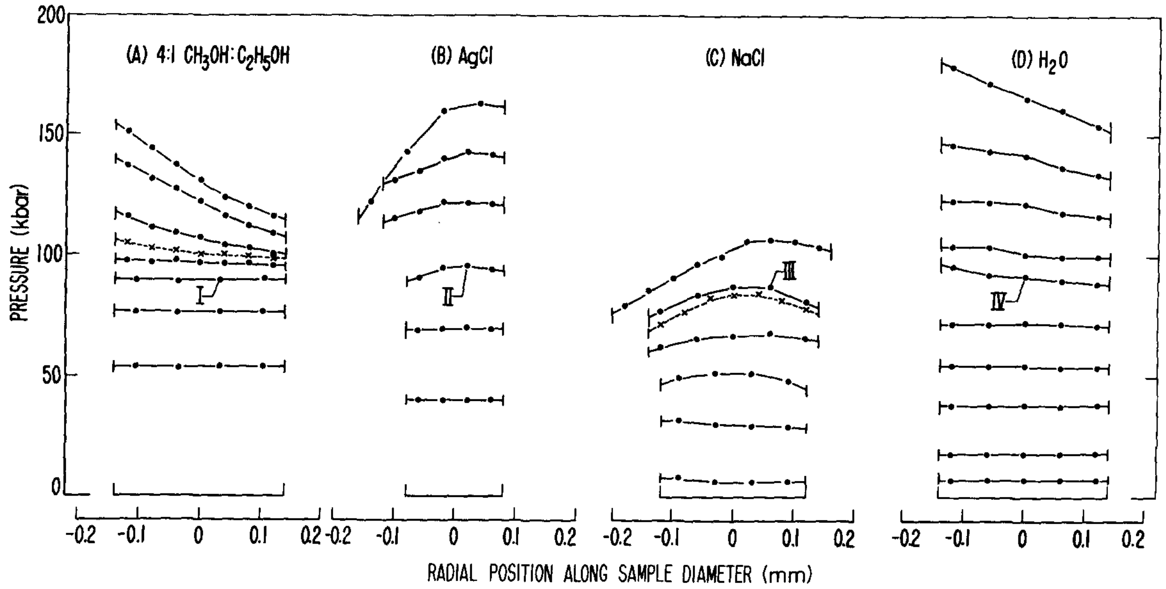

FIG. 1. Pressure distributions in several materials enclosed in the diamond-anvil cell with Inconel gaskets at varying applied loads.

TECHNIQUE

A recent development from our laboratory in pressure-measuring technique for the diamond-anvil pressure cell has provided a simple means of determining not only pressure, but also pressure gradients within the chamber.[8,9] The pressure measurement involves recording the sharp-line (R_1-line) luminescence spectrum of small crystals of ruby within the pressure chamber. The pressure causes a wavelength shift of the fluorescent R_1 line which was shown to be essentially linear with pressure to about 23 kbar.[8] The R_1-line emission is a pure electronic quantum transition within the chromium impurity atom, and the energy levels depend only on the local environment of the chromium ion. Since the fluorescence process is dependent on the environment of an impurity ion on an atomic basis, local uniaxial components of the stress will also influence the spectral frequency of the emitted light as well as the hydrostatic component. Thus, a spectral line broadening in excess of that expected from simple spacial pressure variations is evident in a nonhydrostatic environment. By optically isolating light emitted from localized areas of the sample, one can measure the local pressure over a small region relative to the sample. With the present apparatus using the diamond-anvil pressure cell, a circular area with a diameter as small as 40 μ can be isolated.

We have used two methods to determine the onset of pressure gradients within a fluid subjected to increasing pressure. The first method (I) uses finely powdered ruby fragments (10% by volume) immersed in the fluid within the sample chamber. The pressure is measured at several localized areas across the diameter of the diamond window of the pressure chamber. This technique is time consuming but yields quantitative measurements of pressure gradients at different locations in the chamber. At pressures below the glass transition (the pressure where the viscosity has increased until the shear stresses are not relieved within the experimental measuring time) no measurable pressure differences are observed across the sample region within our experimental error of ±0.5 kbar.[9] The second method (II) uses several small ruby crystals or just one large crystal fragment in the sample chamber. The spectral linewidth of the R_1 line emitted from an extended region of the sample chamber is measured. At pressures below the glass transition, the linewidth decreases slightly with increasing pressure but increases dramatically as pressure exceeds the glass transition.

Technique (II) yields only a qualitative measure of the pressure gradient but is much more rapid and establishes the glass transition pressure with as great a precision as the more time-consuming method (I). Technique (II) takes advantage of the shear stress within the ruby as well as the spatial pressure gradients within the fluid environment. In this regard, care must be exercised to prevent the buildup of uniaxial loads on the ruby from the diamond anvils which may simultaneously come into contact with the crystal.

RESULTS

In Fig. 1, we show a comparison of a few materials with respect to pressure variation across the sample region using method (I). Charts (A), (B), (C), and (D) were determined from measurements made on gasketed systems with the sample intimately mixed with finely powdered ruby which had been passed through a No. 325 mesh sieve. The methanol : ethanol mixture (4 : 1 by volume) was studied because of its potential importance as a truly hydrostatic medium. NaCl and AgCl were studied because of their wide usage as pressure-transmitting media in solid-media high-pressure systems, and H_2O was studied because of the general geological interest in this fundamental material. In the charts in Fig. 1, the abscissa is in mm, dimensions with the origin representing the center of the circular shape of the sample as seen through the microscope by the observer. The direction is along a diameter, with the positive and

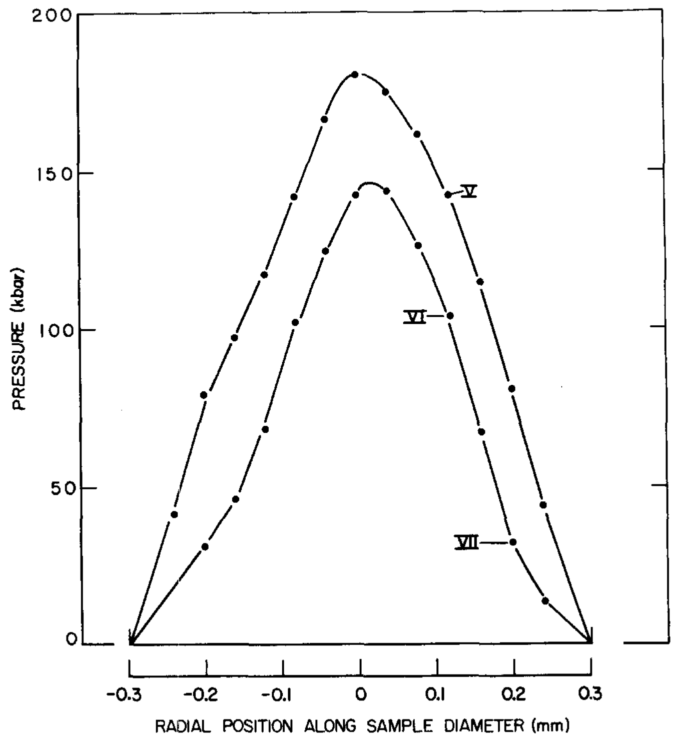

FIG. 2. Pressure distributions in an ungasketed sample of powdered NaCl in the diamond-anvil cell at two different applied loads.

negative direction arbitrary. The gasket diameter dimension is indicated by the heavy vertical demarcation lines on each side of the origin for each chart. Note that for (A) and (D), the gasket dimension is essentially constant while for (B) and (C) it increases slightly as the pressure is increased. Increase in gasket dimensions indicates that the gasket wall has weakened and some outward flow has resulted, which is not an uncommon occurrence, particularly at extreme pressures. In cases where gasket movement initiates it will continue as pressure is increased until ultimately the pressure seal has been broken.

Pressure values are based on a recent calibration of the ruby R_1-line shift up to approximately 200 kbar using the lattice constant of NaCl as the pressure standard coupled with Decker's equation of state.[10,11]

Figure 1(a) indicates no measurable pressure gradient in the sample of 4 : 1 methanol : ethanol until the pressure on the system exceeds approximately 95 kbar. At this pressure there appears to be a slight measurable pressure difference across the sample which becomes more pronounced at higher pressures. At extreme pressures, differences as great as 40 kbar are supported by the glass, indicating that very high coefficients of internal friction come into play. The dashed curve near 100 kbar is a series of measurements taken at the same load as those immediately above it following a 16-h time elapse, and illustrates the relaxation experienced by the system with time. From other experiments, we have determined that a major portion of the relaxation occurs within the first few hours following a major load change. Relaxation effects can be neglected over the period of time involved (approximately 30 min) in making a series of measurements across the sample at a given load. This can be demonstrated by the fact that the pressure distribution in the hydrostatic region in (A) is essentially uniform within the experimental error (±0.5 kbar).

The measurements of pressure gradients taken for AgCl to over 160 kbar are shown in Fig. 1(B). Although effectively no gradient is indicated below 65 kbar, line-broadening data, which will be discussed later, demonstrate definitely the nonhydrostatic character of this material even though the average pressures are uniform. It is interesting to note that in the 150-kbar range, pressure gradients are extreme, i.e., differences greater than 40 kbar exist. Data for NaCl, Fig. 1(C), indicate a similar behavior to that of AgCl, except that gradients are built up at a much lower pressure and become quite prominent above 40 kbar. However, it should be pointed out that in these cases the gasket dimension has increased, as indicated by the increase in distance between the two small vertical lines which delineate the gasket boundaries. The enlargement of the gasket undoubtedly plays a significant role in establishing the magnitude of these pressure gradients. It appears that for both AgCl and NaCl, a slight maximum in pressure at the approximate center of the sample is generated prior to observable gasket movement. However, this pressure maximum could also be the result of gasket movement so small as to be unobservable by our method. In any case, the magnitude of the pressure gradients appears to be directly related to the extent of gasket flow for a given material, e.g., AgCl, as well as the magnitude of the load on the anvils. For these reasons, we are restricting our comparison of the relative merits of these materials as pressure-transmitting media to conditions prior to the onset of gasket flow. Nevertheless, the observed pressure distributions in systems which have undergone gasket enlargement are certainly a qualitative measure of the hydrostatic character of the material. The dashed curve near 80 kbar again reflects a relaxation time of over 16 h duration. Data on H_2O shown in Fig. 1(D) indicate an unexpected low-pressure gradient to very high pressures (above 100 kbar) and appear to be at least as good as and perhaps better than AgCl. The relative stress state of these two materials will be discussed ruther in connection with line-broadening studies.

From pressure gradient measurements shown in Fig. 1 and also from line-broadening data discussed later, H_2O appears to have less shear strength than either AgCl or NaCl. One might expect the pressure distribution to maximize at the center of the sample region as is approximately demonstrated by AgCl and NaCl. This is obviously not the case as is shown by both methanol : ethanol and H_2O. We attribute these effects to the noncylindrical properties and the onset of flow of the gasket. Note that the sample often distorts into noncircular forms and the measurements are taken across an arbitrary diameter.

In order to compare pressure gradient properties in the gasketed and nongasketed diamond-anvil systems, we have made pressure gradient measurements on NaCl. Figure 2 illustrates the pressure distribution in an intimate mixture of NaCl and ruby in an ungasketed system, i.e., with the mixture (approximately 10% by volume of

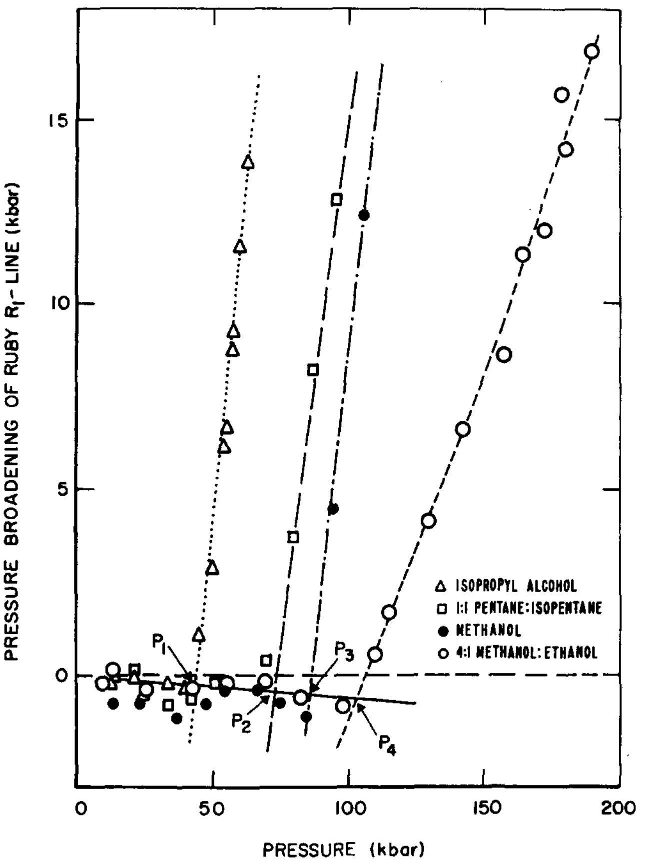

FIG. 3. Pressure broadening of the sharp ruby R_1 fluorescence line for various pressure-transmitting liquids relative to the 1-atm linewidth.

ruby) squeezed between two anvils with the mixture itself acting as its own seal. The general feature of this distribution is similar to that reported earlier using nickel dimethylglyoxime as the pressure sensor.[7]

It is important to note that the coordinate scale factors are identical for both Figs. 1 and 2. Thus, a comparison between the two figures illustrates clearly that even for a small area within the sample, pressure gradients in the ungasketed system exceed greatly the gradients in gasketed systems. Even in the peak areas of the ungasketed sample where there appear to be small pressure gradients, line-broadening studies discussed later demonstrate the existence of very large localized shear stress.

In order to obtain a better characterization of the stress state of the material, it is possible to measure line broadening and obtain an indication of the local stress state of the sample independent of the gross pressure gradients. The line broadening observed in a truly hydrostatic environment is independent of ruby particle size and gasket dimensions. If nonhydrostatic stress states exist, then the linewidth is dependent on ruby particle size, the magnitude of the gradient, and the local stress state.

Line-broadening data using technique (II) are illustrated in Fig. 3 for four liquids: (i) isopropyl alcohol, (ii) 1 : 1 mixture by volume of pentane : isopentane, (iii) a 4 : 1 mixture by volume of methanol : ethanol, and (iv) methanol. The broadening shown represents the change in half-maximum linewidth from the measured half-width at 1 atm and 25 °C, in equivalent pressure units, and is shown as a function of line shift also in equivalent pressure units. Note that the linewidth actually decreases with increasing hydrostatic pressure. The initiation of broadening is rather abrupt, and the increase of broadening with increased pressure is very large above the initiation point for all four fluids studied. The points P_1, P_2, P_3, and P_4 are interpreted as an approximate measurement of the glass transition pressure at room temperature for each fluid, and are determined by extrapolation of lines drawn by inspection through points above and below the abrupt increase. The estimated reproducibility in the determination of these glass-transition pressures in our limited experiments is approximately 3 kbar. When studying pure methanol the sample may crystallize, in which case the glass transition is not measurable. The data shown in Figs. 3 and 4 for methanol were on a sample in which no crystallization occurred. The scatter in the points along the line at pressures below the transition are indicative of the measurement sensitivity. The slight negative slope of the line below the transition must be attributed to a fundamental decrease in the true width of the spectral line which at room temperature is significantly temperature broadened. This small decrease in linewidth with pressure is probably related to a small increase in the Debye temperature for ruby at these pressures.

The broadening at each pressure above the transition is a qualitative measure of the nonhydrostatic stress within the glass at that location. As the pressure is increased the stresses increase proportionally, giving an approximate linear curve. The slope of the lines above the transition depends on such things as the dimensions of the pressure gasket, the size of the ruby crystals, and the mechanical properties of the glass and the gasket material.

In recording the data for Fig. 3, pressure was in-

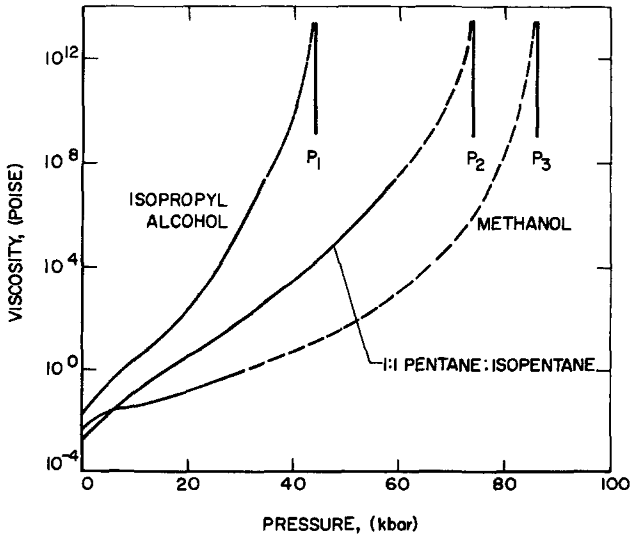

FIG. 4. Extrapolations of viscosity data to measured glass-transition pressures for isopropyl alcohol (P_1), 1 : 1 pentane : isopentane (P_2), and methanol (P_3).

creased at intervals of from 10 to 20 min. Relaxations of a few percent were observed if periods of hours were allowed to elapse. The use of 4 : 1 by volume of methanol : ethanol mixture was dictated by the desire to inhibit crystallization of pure methanol in our early experiments. An isopentane : pentane 1 : 1 by volume mixture was studied to demonstrate the greater hydrostatic pressure range of the methanol-ethanol mixture, and also because the former mixture was considered to be the only one to provide hydrostatic conditions to 65—70 kbar. Isopropyl alcohol was selected in order to correlate our data with previously reported viscosity measurements near the glass transition.[6]

A correlation of the approximate glass-transition values as measured herein with available viscosity data is shown in Fig. 4. The solid lines represent viscosity data reported by Bridgman[4] and by Barnett and Bosco.[6] The pressures P_1(43 kbar), P_2 (74 kbar), and P_3 (86 kbar), taken from Fig. 3, are shown as vertical asymptotes on Fig. 4 which the viscosity curves must approach. The broken lines on Fig. 4 are hand-drawn asymptotic extrapolations. The consistency for isopropyl alcohol and for the pentane-isopentane mixture is very good and gives support to the methanol correlation. Since viscosity depends strongly upon temperature, as well as pressure, a relatively small increase in temperature influences the pressures P_1, P_2, and P_3. This was demonstrated in two different experiments in which the temperature of the cell was raised to values between 50 and 125 °C after pressure well above the glass-transition pressure for the liquid had been established. In each case, the strains were dramatically reduced only after a sufficiently high temperature was reached. No quantitative data were taken.

The advantage of using a methanol-ethanol mixture instead of pure methanol can be seen by comparing line-broadening data for the two fluids. Note that pure methanol deviates from hydrostatic conditions at a significantly lower pressure than the methanol-ethanol mixture, which indicates the onset of vitrification at a lower pressure than the mixture. The respective glass-transition pressures are P_3 (86 kbar) and P_4 (104 kbar).

One must remember, however, that even in liquids, time-dependent shear stresses do exist and the rate of change in pressure for a given system must be carefully considered. In large-volume systems such as a piston-cylinder apparatus, the rate of pressure increase may become critical when the viscosity of these hydrostatic fluids exceeds roughly 10^{10} P. Under these circumstances it is likely that plastic deformation will occur in low-shear-strength solid specimens as a result of low-magnitude stresses which are insensitive to the ruby monitor.

The rate of pressure application on a given system depends on the geometry of that system and the viscosity of the pressure-transmitting fluid in the pressure range considered. Therefore one can, in principle, calculate the time-dependent shear stresses for the system if the viscosity and system geometry are known. An estimate of the viscosity for the desired pressure range can be made from the extrapolations shown in Fig. 4. With an appropriate margin for error, it is possible then to establish a rate of pressure increase for a given system which may help to avoid the problem of plastic deformation of the specimen.

Based on the conclusions of Barnett and Bosco,[6] time-dependent shear stresses in a sample surrounded by a highly viscous liquid (greater than 10^8 P) will be negligible if pressure changes are made on a time scale of a few seconds or longer. This suggests that in most static generating pressure systems, the 1 : 4 ethanol : methanol mixture will provide a stress-free environment for even low-shear-strength samples to approximately 90 kbar, provided reasonable pressurization rates are used.

In the course of these experiments, the equilibrium freezing pressure of methanol was determined at room temperature to be 35.8 ± 0.8 kbar based on a calibration presently in preparation for publication.[11] This value was obtained after partial crystallization and observing an equilibrium situation between solid and liquid. This value is greater than the 30 kbar reported by Bridgman,[12] but is contrary to the suggestion put forth by Davies[13] that the methanol freezing pressure is in excess of 38 kbar. This suggestion was made because the reported data on the pressure shift of the visible absorption band in nickel dimethylglyoxime indicated significant curvature above 20 kbar. Our value of 35.8 kbar produces somewhat less curvature than that reported in Davies's results, particularly above 15 kbar.

From a practical standpoint, the significance of this study on liquids is the establishment of the fact that a liquid mixture exists that is hydrostatic to pressures near 100 kbar at room temperature and to even higher pressures at higher temperatures. This mixture exceeds the previously accepted attainable hydrostatic limit of about 70 kbar obtained by using a 1 : 1 by volume mixture of pentane-isopentane.

It is important to note that the above technique [method (II)] for measuring local stresses has potential in a fundamental study of glasses and glass formation induced by pressure, i.e., particularly with respect to the variation of the glass-transition point as a function of both pressure and temperature.

Linewidth measurements of the ruby R_1 line are relatively simple in an hydrostatic environment. In solids, however, where the pressure environment is not hydrostatic, such measurements become somewhat less meaningful. For example, the results are not too consistent because of the many variables involved such as ruby size and distribution, gasket material and diameter, sample material, properties, and size.

Linewidth data obtained with powdered ruby in NaCl, AgCl, and H_2O were not defined well enough to be described graphically because of the many variables mentioned above. Nevertheless, the results appear to be in agreement with the distribution data shown in Fig. 1, namely, that the increase in linewidth, and hence the pressure gradients and localized stresses initiated at lower pressures, are greater in NaCl than in either H_2O or AgCl. The supporting data which are typical are shown in Table I.

TABLE I. Line-broadening data on the ruby fluorescence R_1 line for several materials in the diamond-anvil pressure cell.

Substance	Data points[b]	Line broadening (kbar)[c]	Pressure (kbar)
MeOH : EtOH[a]	I	d	90
AgCl	II	7	95
NaCl	III	11	87
H_2O	IV	6	92
NaCl	V	62	142
NaCl	VI	60	104
NaCl	VII	27	32

[a] MeOH : EtOH is a 4 : 1 by volume mixture of methyl alcohol and ethyl alcohol, respectively.

[b] Data points I—IV are identified in Fig. 1, while V—VII appear in Fig. 2.

[c] Line-broadening data represent the difference in full width at half-maximum (FWHM) between the 1-atm-room-temperature value and the value at pressure in equivalent kbar units.

[d] The pressure broadening is negative, indicating hydrostatic environment surrounding the ruby crystals.

GASKETED VERSUS UNGASKETED DIAMOND-ANVIL TECHNIQUE

The diamond-anvil pressure cell has been used extensively with a metal gasket to study liquids and somewhat less in studies of samples embedded in liquids. The cell has been used more extensively without a metal gasket to study solid materials in which the solid acts as its own gasket. This ungasketed technique has been used to much higher pressures than the gasketed technique, but the pressure gradients are very severe. We have studied pressure gradients within the sample using both of these techniques in order to evaluate the relative merits in obtaining low-shear-stress conditions. These data are also used to compare the gradients in some of the commonly used pressure-transmitting media of quasihydrostatic techniques with the vitrified liquids above the glass point.

The pressure profiles for measurements in NaCl in a gasketed and ungasketed sample are shown in Figs. 1(C) and 2, respectively. The pressure distribution curves for the ungasketed sample (Fig. 2) are similar to those reported by Lippincott and Duecker who used nickel dimethylglyoxime as the pressure sensor.[7] The localized nonhydrostatic stresses in equivalent kbar units as determined from line broadening are shown in Table I for two points along one of the curves. Note that the pressure differences in the region of the peak in the curve are small and one might conclude, as some have done, that by sampling this small-peak region, pressure gradient effects can be minimized. However, linewidth data over this same peak region indicate localized extreme nonhydrostatic stresses which can be as large as 62 kbar as sample V in Table I demonstrates. Hence, the assumption that low pressure gradients at the peak region of the distribution curve produce a low localized stress state is not valid.

Comparison of the line-broadening data in Table I and line shift in Figs. 1 and 2 demonstrates dramatically that NaCl in gasketed systems exhibits significantly lower localized nonhydrostatic stresses and also less pressure differences than the same material in ungasketed systems. Hence it is concluded that, in general, in any high-pressure experiment using the diamond cell, it is desirable to use a gasketed system to produce really quantitative results. At present this may not always be possible, particularly when pressures above 200 kbar are required. However, it should be noted that in our calibration work[11] we have attained a maximum pressure of approximately 195 kbar with localized nonhydrostatic stresses of about 15 kbar in a gasketed system. Owing to an elastic bending of the Waspaloy cell body, the calibration was not continued to higher pressures.

CONCLUSIONS

In summary the following conclusions can be listed: (i) A liquid mixture 4 : 1 by volume of methanol : ethanol remains truly hydrostatic to almost 100 kbar at room temperature. This mixture far exceeds the hydrostatic limit of the previous generally accepted fluid, 1 : 1 pentane : isopentane, which has a hydrostatic limit of about 70 kbar. (ii) Liquids exhibit gradient effects only when the glass-transition pressure is reached or exceeded. (iii) Solids in gasketed systems have dramatically lower localized stress states than solids in ungasketed systems. In any quantitative high-pressure experiment with the diamond-anvil pressure cell, it is therefore desirable to use a gasketed system. (iv) AgCl and H_2O are better than NaCl as pressure-transmitting media, but do not even qualitatively approach hydrostatic conditions much above 50 kbar. (v) The solids NaCl, AgCl, and solid H_2O are dominated by local shear effects. (vi) Stress and gradient phenomena are not simply related as often thought. (vii) Uniform average pressures do not necessarily imply zero local stress. (viii) The freezing pressure of methanol at 24 °C is redetermined to be 35.8 ± 0.8 kbar.

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