

TABLE 1 PRINCIPAL EQUIPMENT IN HIGH-PRESSURE LABORATORY

Single-stage, double-acting, Gardner-Denver horizontal compressor, size 9 X 12; maximum pressure 125 psig; displacement at 225 rpm = 166 cfm

Two-stage, duplex, vertical, Gardner-Denver compressor; maximum pressure 500 psig; displacement 75 cfm at 720 rpm

Three-stage, vertical, Rix compressor; 4500 psig; displacement = 5.3 cfm at 400 rpm

Five-stage, horizontal, duplex tandem, Norwalk compressor; maximum pressure 1000 atm; displacement = 15.0 cfm at 250 rpm

Dunning and Boschert, triplex hydraulic pump; 1000 atm pressure; displacement = 0.47 gpm at 80 rpm

Harwood intensifier; maximum pressure = 60,000 psi; ratio of cylinder areas = 64; displacement of high-pressure cylinder per stroke = 160 cc

Harwood intensifier; maximum pressure = 150,000 psi; ratio of cylinder areas = 175; displacement of high-pressure cylinder per stroke = 43 cc

Gerotor rotary oil pump for operating low-pressure cylinders of intensifiers; 1.5 gpm at 800 psi; maximum pressure = 1500 psi

Two Black hawk, hand-operated, oil pumps for 10,000 psi

Two dead-weight piston pressure gages with pistons of  $\frac{3}{32}$ ,  $\frac{3}{16}$ ,  $\frac{1}{8}$ , and  $\frac{17}{32}$  in. diam with oil-injector pump for 1000 atm and small intensifier to inject oil at 4000 atm; maximum pressure = 4000 atm

Foxboro Bourdon-type pressure gage with stainless-steel helical element for maximum pressure of 60,000 psi

Manganin resistance pressure cell for 150,000 psi with auxiliary equipment for resistance measurement

Several Bourdon-spring pressure gages with maximum scale reading to 100,000 psi

Struthers-Wells  $\frac{3}{4}$ -gal autoclave with rotating stirrer for maximum pressure of 10,000 psi

Aminco  $4\frac{3}{8}$ -in. series shaking mechanism with autoclave for 15,000 psi

Aminco micro series shaking mechanism with reaction vessels for 13,000 psi at 100 F

Three storage vessels for gas at 1000 atm; one of 0.26 cu ft volume, one of 0.17 cu ft volume, one of 0.89 cu ft volume

Three gas holders for atmospheric-pressure storage; one of 50 cu ft and two of 100 cu ft capacity

Seven steel pressure cells (barricades) 7 ft X  $8\frac{1}{2}$  ft X 8 ft high of  $\frac{1}{4}$ -in. steel plate

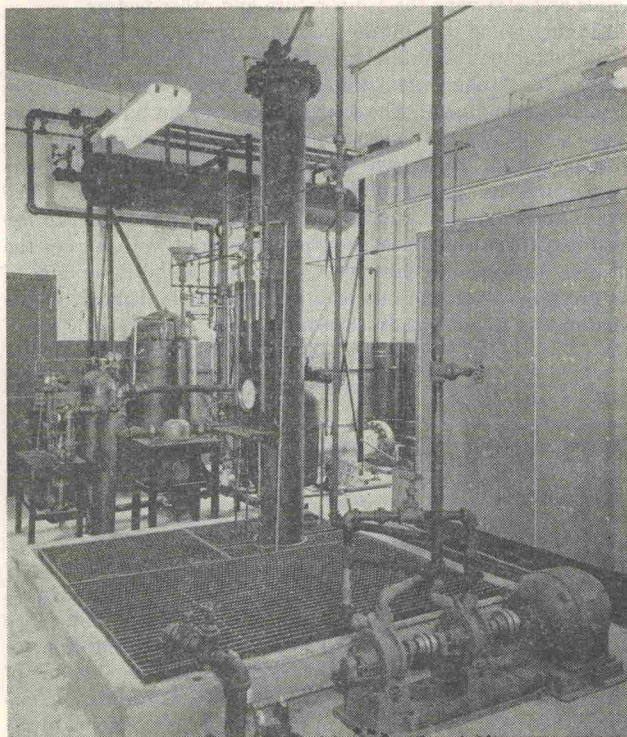


FIG. 5 APPARATUS ASSEMBLY FOR INVESTIGATION OF RATE OF ABSORPTION OF GASES BY LIQUIDS AT ELEVATED PRESSURE IN PACKED TOWERS

1 The main chemical reaction in the case of steels is believed to be the reaction with carbon to form methane and much, if not all, of the damage to the metal is caused by the trapped methane which is unable to diffuse out of the metal with the result that very high localized gas pressures are developed which cause fissuring. Even if no methane were formed the removal of the carbon itself would alter the structure and presumably change the tensile properties. This action takes place at elevated temperatures, i.e., at 300 C or higher and, since chemical reaction rates are, in general, greatly accelerated by temperature, it is to be ex-

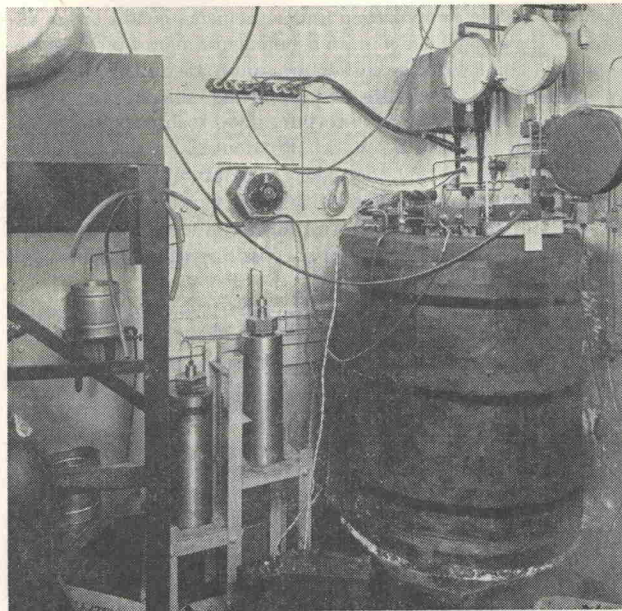


FIG. 6 APPARATUS INSIDE ONE OF PRESSURE CELLS, FOR INVESTIGATION OF PHASE EQUILIBRIA AT HIGH PRESSURES

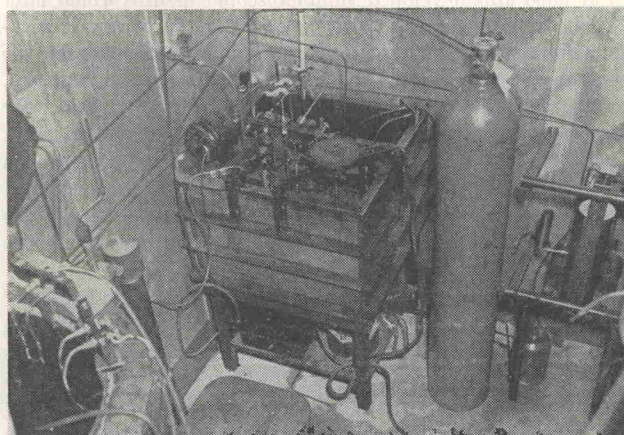


FIG. 7 APPARATUS INSIDE OF A PRESSURE CELL, FOR INVESTIGATION OF COMPRESSIBILITY OF GASES AT HIGH PRESSURES

pected that the action would be negligible at room temperature.

The pressure is a less important variable than the temperature and its main effect is probably to speed up the attack or to cause it to take place at an appreciable rate at somewhat lower temperatures. According to Schuyten (6) there is a leveling off in attack with pressure at about 10,000 psi but it should be noted that this is based on very little evidence since almost no work has been done at pressures above 10,000 psi. To distinguish this chemical action from the purely physical action to be discussed next we have employed the word "attack" as a general term for the action of hydrogen on metals at elevated temperatures. The term "decarbonization" also is used extensively in the literature, but this implies that the only reaction is that with carbon. Severe attack occurs in some alloys with low carbon content and it is possible that other reactions such as hydride formation or reduction of oxide inclusions may be important. In general, though, it is known that steels of high carbon content are more susceptible to attack than those of low carbon content.

Certain alloying elements used in steel such as chromium, molybdenum, vanadium, tungsten, and possibly titanium, zirconium, and a few others, form carbides that are relatively stable

(i.e., nonreducible by hydrogen under the usual conditions of exposure) and steels which contain a sufficient amount of these elements to combine with the carbon are said to be quite resistant to hydrogen attack. Elements such as nickel, silicon, and copper form no carbides and confer no immunity to hydrogen attack. The effect of manganese is somewhat in doubt.

It should be noted that the theory that immunity to hydrogen attack is only a question of stability of the carbides has been disputed by some investigators. As a matter of fact, little is known about any of the carbides except possibly those of iron and chromium.

2 This purely physical action that can occur at approximately room temperature is what we choose to describe by the word "embrittlement." It occurs at low pressures when hydrogen is liberated at the surface of the metal in the so-called "nascent" form (presumably atomic hydrogen) as, for instance, by electrolysis or by chemical reaction or when the metal is exposed to the gas through which a high potential electrical discharge is passed. Ordinary molecular hydrogen is apparently without appreciable effect at pressures below 1000 atm (except possibly over very long periods of time). A few isolated and not very systematic observations of Bridgman (7) and of Poulter and Uffelman (8) comprise the entire literature for the action when the hydrogen pressure is greater than 1000 atm.<sup>3</sup>

Bridgman found that a Cr-V steel vessel used to contain hydrogen at 9000 atm developed submicroscopic fissures which later developed into cracks visible to the eye. The same vessels withstood liquids at 25,000 atm with no damage. Even when the vessel was separated from the hydrogen by kerosene, it ruptured, presumably because of solution of hydrogen in the liquid. He found somewhat the same result with air but to a lesser degree.

Poulter and Uffelman observed rapid penetration of hydrogen through steel at 6000 atm though there was no similar effect at 4000 atm. However, when the hydrogen was generated by the action of acid on zinc, a rapid penetration of hydrogen took place at 4000 atm.

In an interesting paper on "Mechanism of Cavitation Erosion," Poulter (9) points out the fundamental similarity of the following apparently unrelated phenomena: Corrosion, caustic embrittlement, steam erosion, cavitation erosion, gun-barrel erosion, wire-drawing, creep of metals, fatigue, and the penetration of gases and liquids into metals. In this paper he gives a few observations on the effect of high-pressure hydrogen but the exact conditions of exposure are not described clearly. For example, he refers to cracks in a cylinder wall forming in only a few minutes at 30,000 psi but it is not certain whether the exposure was to ordinary molecular hydrogen or to hydrogen generated in situ from zinc and acid.

Various investigators have studied the properties of hydrogen and hydrogen-containing gases at pressures of 3000 atm and even 5000 atm without making any observations on damage to their equipment.

From a study of this very meager amount of information it did not seem to us likely that we would encounter any serious trouble if we compressed hydrogen in an ordinary alloy-steel vessel to

<sup>3</sup> Since this statement was written, a brief note (*Chemical Engineering News*, vol. 30, 1952, p. 2942) has come to our attention in which mention is made of failure in laboratories of the du Pont Company of small equipment using hydrogen at room temperature and pressures above 2000 atm. Mention also is made, but no details given, of bursting tests on pressure vessels using both oil and hydrogen to develop the pressure. Vessels that withstood oil pressures of 7000 atm failed in very short periods of time when pressured by hydrogen at only 2000 atm. The best solution to this problem was found to be the use of stainless-type 316 steel liners in the vessels and the use of grooves and leakage holes in the walls of the latter to prevent build-up of pressure between the liner and the vessel.

3000 atm but we were wrong. An intensifier which had been used repeatedly to pump oil at 4000 atm and several times to compress nitrogen to the same pressure, failed within a matter of minutes when used to compress hydrogen at not over 3000 atm. The failure consisted in the development of very fine cracks barely visible to the naked eye but easily seen when special techniques were used to develop them. They were sufficiently large to render the intensifier completely useless even with oil only. This sad experience brought home to us very forcibly the need for more work on the effect of high-pressure hydrogen.

3 The rate at which hydrogen and other gases permeate metals has been studied by a great number of investigators but there are so many variables influencing it that the picture is far from complete and many of the results are conflicting and hard to explain. Consider the effect of pressure. It has been fairly well established that the rate is proportional to  $\sqrt{p}$  indicating that it is only atomic hydrogen which actually penetrates the metal and permeates through it. With many steels the rate becomes constant at about 100 atm and no further increase occurs as the pressure is increased. This is surprising and apparently no satisfactory explanation of it has been found. In the case of nickel the leveling off occurs at a pressure of only 20 atm (10). Further work is indicated. For example, it would be of interest to increase the pressure to 1000 atm and beyond and to study different metals and also vary the temperature and other factors.

Although some writers use the terms "permeation" and "diffusion" more or less interchangeably in describing the penetration of gases through metal walls, it is better to make a distinction on the following basis: The over-all process from bulk gas phase on one side of the wall to gas phase on the other is best described as permeation. This consists of interactions at the metal surfaces as well as the actual transport through the metal. The term diffusion strictly applies just to the latter process. In the usual experiment one measures the permeation rather than the diffusion because one deals only with the over-all driving force of gas pressure. A coefficient of diffusivity  $D$ , is defined by the equation (for linear, steady-state diffusion)

$$J = -D \frac{c_1 - c_2}{\Delta x} \dots \dots \dots [1]$$

whereas the permeability  $P$  is usually defined by

$$J = \frac{-P}{\Delta x} \dots \dots \dots [2]$$

where  $J$  is the diffusion current per unit of area and  $(c_1 - c_2)/(\Delta x)$  is the concentration gradient in the metal wall of thickness  $\Delta x$ . It is clear that  $P$  will depend on the gas pressure difference on the two sides of the wall. One could define a permeation coefficient by basing it on a pressure gradient. The usual values of  $P$  have been obtained with a 1-atm pressure difference. If one assumes that the concentration in the metal is proportional to the square root of the pressure, the permeability might be defined by

$$J = -P \frac{\sqrt{p_1} - \sqrt{p_2}}{\Delta x} \dots \dots \dots [3]$$

That the penetration of a gas into a metal is not simply along crystal boundaries but directly through the lattice is quite well established by the work on single crystals which has shown that the rate of diffusion through the latter is just as rapid as through polycrystalline material.

It also has been fairly well established that the diffusion of a gas occurs only when it is in the form of atoms dissociated from the molecule. Molecular hydrogen does not diffuse nor do any of the monatomic gases. One of the chief bits of evidence sup-