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SCHOOL OF ENGINEERING

High-Pressure Research in Chemical Engineering Department of Yale University

BY

BARNETT F. DODGE

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This paper reviews only the "high lights" of research in this field which has been conducted since 1925 in our chemical engineering laboratory under the author's direction. Work carried out prior to 1947 is given only passing mention and most of the paper is devoted to an outline of current work and some researches completed in the past 5 years.

HISTORY AND PRESENT STATUS OF HIGH-PRESSURE INVESTIGATIONS

THE research in this field which was initiated by the author in 1925, has been carried on continuously since that year, except for the war years 1940–1946, with the aid of graduate students working for the Doctor's degree under the direction either of the author or Prof. H. Bliss. The results of the work have been published in 18 papers which are listed at the end of this paper. An outline of the investigations up to the year 1947 is as follows:

1 Methanol and formaldehyde synthesis
  (a) Catalyst studies
  (b) Chemical equilibria
2 Vapor-phase hydration of ethylene
  Catalysts and equilibria
3 Reaction of CO with ethyl alcohol
4 Phase equilibria
  (a) System: N_2–C_6H_6
  (b) System: CO_2–C_6H_6
  (c) System: N_2–CH_3OH
  (d) Methane-isopentane
  (e) Hexane-toluene
5 P-V-T relations of N_2–CO_2 mixtures.

The maximum pressure used was 1000 atm, but most of these investigations were conducted at considerably lower pressures.

Research problems either completed since 1947, or currently under investigation or under consideration for initiation of work in the near future may be stated briefly as follows:

1 Carbon monoxide reactions
  (a) CO + dihydric alcohols
  (b) CO + cyclohexanol
  (c) CO + phenol, aniline, and some halogenated benzenes
2 P-V-T relations of gases
  (a) System: N_2–H_2
  (b) System: N_2–H_2–NH_3
3 Action of hydrogen on tensile properties of metals
  (a) Chemical action at elevated temperatures
  (b) Physical action at room temperature
4 Permeability of metals to hydrogen
5 The ammonia synthesis equilibrium at pressures above 1000 atm
6 Phase equilibrium in system: N_2–NH_3

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7 Catalytic oxidation of benzene
8 Equilibrium in hydration of C_2H_4 in presence of both vapor and liquid phases
9 Exploratory investigations of some reactions of butadiene
10 Kinetics of heterogeneous hydrogenation (system not yet chosen)
11 Chemical equilibrium in the water-gas reaction at high pressures
12 Reactions of carbon monoxide with ketones, diols, and some halogenated naphthenes
13 Problems under consideration but no work yet started
  (a) Polymerization of unsaturated hydrocarbons
  (b) Methanol-synthesis equilibrium
  (c) Effect of pressure on diffusivity and thermal conductivity of gases
  (d) Action of mercury on steels

THE HIGH-PRESSURE RESEARCH LABORATORY

Up to 1947 the research work was carried out in a very small, overcrowded, and ill-adapted space in the main chemical engineering laboratory. In 1947 the one-story, cinder-block building with 4000 sq ft of floor area shown in Fig. 1 was completed and is now used to house all the high-pressure work. Various interior
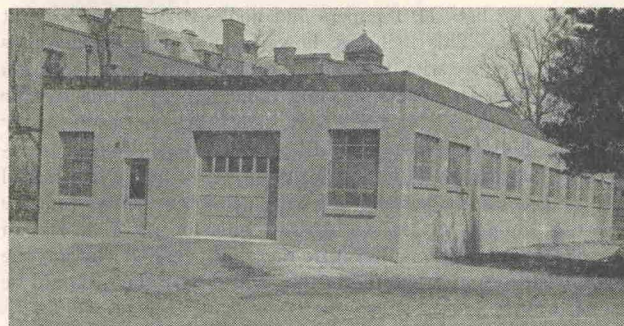

FIG. 1 EXTERIOR VIEW OF CHEMICAL ENGINEERING LABORATORY FOR RESEARCH AT HIGH PRESSURES

views of the laboratory are shown in Figs. 2 to 7 inclusive. Fig. 2 gives a general view of the main room showing on the right the seven steel-barricaded cells inside of which the experimental setups are mounted. Control valves are mounted so that they may be operated from the outside and most instruments such as pressure gages and thermometers are read from the outside. Fig. 3 shows a piston gage for measuring pressures to 4000 atm and some of the low-pressure equipment outside of a barricaded cell used for *pvt* measurements. Fig. 4 is a view of the pump and compressor room, and Fig. 5 shows an assembly of apparatus for investigating rate of absorption of gases in liquids in a packed tower at pressures up to about 500 psi. Figs. 6 and 7 show some of the apparatus inside the steel cells.

The main items of equipment in the laboratory for the production, measurement, and control of pressures up to 150,000 psi (10,000 atm) are listed in Table 1.

In addition there are many storage cylinders for gas at 2000, 3000, and 7500 psi, valves, fittings, and tubing for pressures up to 150,000 psi, relief valves, blowout-disk assemblies, and miscellaneous Bourdon-type pressure gages. The laboratory also has lathes, drill press, bench grinder and other shop equipment and
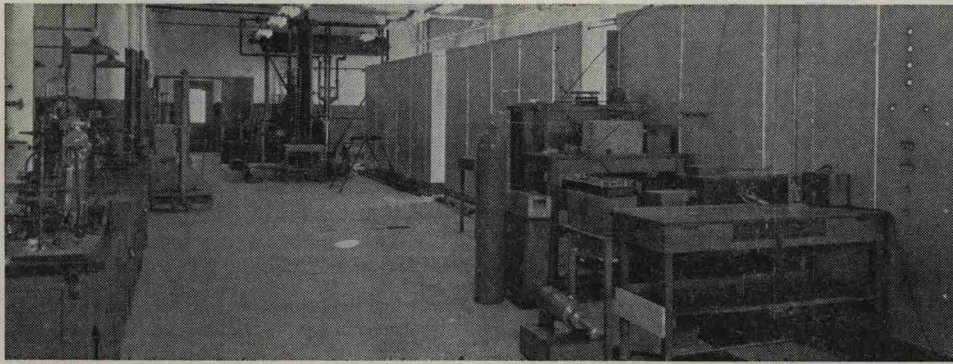
equipment for catalytic reactions, *pvt* measurement, temperature measurement, and control and gas analysis.

Review of Current Problems and Work Recently Completed

Action of Gases on Metals. Certain gases, notably hydrogen, nitrogen, oxygen, and carbon monoxide, have a deleterious effect on metals at elevated pressures and temperatures and a knowledge of these effects is important from the standpoint of safe design of equipment to handle gases under these conditions. We are particularly interested at the present time in hydrogen, and all the work to date in this laboratory has been with this gas.

This is by no means a new problem. It has been under study by many investigators over a period stretching from 1830 to the present time. A recent circular of the National Bureau of Standards (1)[2] lists 1191 papers and books written up to about October, 1949. This includes, however, not only publications which deal directly with the embrittlement of steel by hydrogen but many that are concerned only indirectly with this specific subject. For example, it also covers such things as the chemistry of the iron-hydrogen system, diffusion of hydrogen, solubility, removal of hydrogen, and various others. Three books which deal with the general subject and one with a chapter devoted to it are important enough to deserve separate mention (2, 3, 4, 5). In view of this voluminous literature one may wonder why anyone should wish to undertake further work and why there should be any need for it.

We were led to undertake work in this field for a number of reasons which seemed valid. In general, there is a great deal of conflicting information and it is exceedingly difficult to predict what the result of exposure to hydrogen would be under a given set of specific conditions. Also, the effect of pressure as a variable has been studied to only a small extent and there is almost no information for the effect of pressures above 200 atm. Many new alloys have appeared since some of the studies were made and just to extend the work to include these new metals is a worth-while objective in itself. Finally, much remains to be done to elucidate the mechanism of the action and, until this is more clearly understood, most of the facts that have been collected from all the painstaking research of many years will remain as unrelated observations incapable of being generalized. For an excellent review of the broad subject of the action of gases on metals and for further justification of the need of additional work, the paper by Schuyten (6) is recommended.

Although somewhat of an oversimplification it has been found useful to divide the problem into the four following aspects:

1 The chemical reaction between hydrogen and the various elements that are present in small amounts in metals, especially carbon.

Fig. 3 Apparatus for Measurement of Pressure and of Gas Compressibility

Fig. 4 Compressor and Pump Room

2 A purely physical action involving a penetration of the gas into the crystal lattice with consequent disruptive effects.

3 The rate of diffusion or permeation of gases through metals.

4 The solubility or occlusion of hydrogen by metals.

Let us consider each of these very briefly.

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[2] Numbers in parentheses refer to the Bibliography at the end of the paper

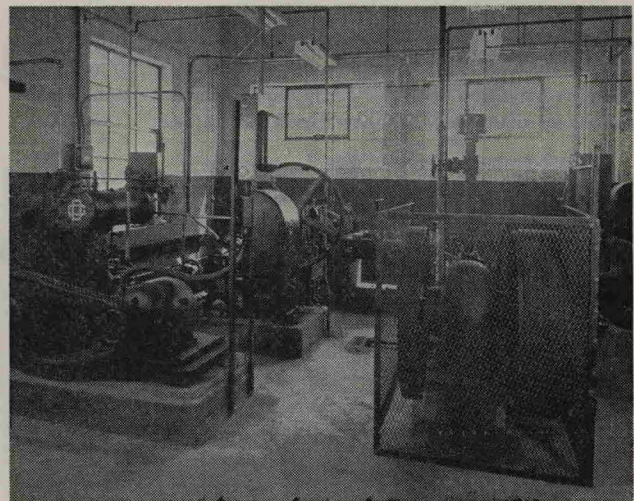TABLE 1 PRINCIPAL EQUIPMENT IN HIGH-PRESSURE
LABORATORY

Single-stage, double-acting, Gardner-Denver horizontal compressor, size
9 × 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; dis-
placement = 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 intensi-
fiers; 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 $3/32$, $3/16$, $9/8$, and
$17/32$ in. diam with oil-injector pump for 1000 atm and small intensifier to in-
ject 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 equip-
ment for resistance measurement

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

Struthers-Wells $3/4$-gal autoclave with rotating stirrer for maximum pres-
sure of 10,000 psi

Aminco $4^3/8$-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 × $8^1/2$ ft × 8 ft high of $1/4$-in.
steel plate

FIG. 6 APPARATUS INSIDE ONE OF PRESSURE CELLS, FOR INVESTI-
GATION OF PHASE EQUILIBRIA AT HIGH PRESSURES
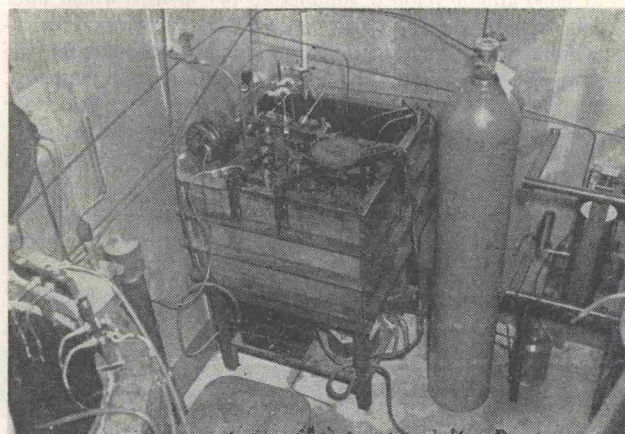
FIG. 7 APPARATUS INSIDE OF A PRESSURE CELL, FOR INVESTIGATION
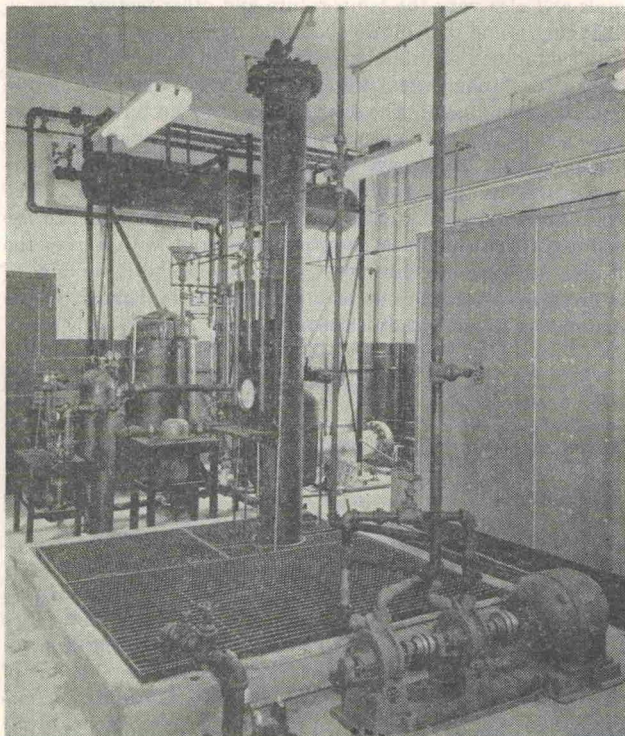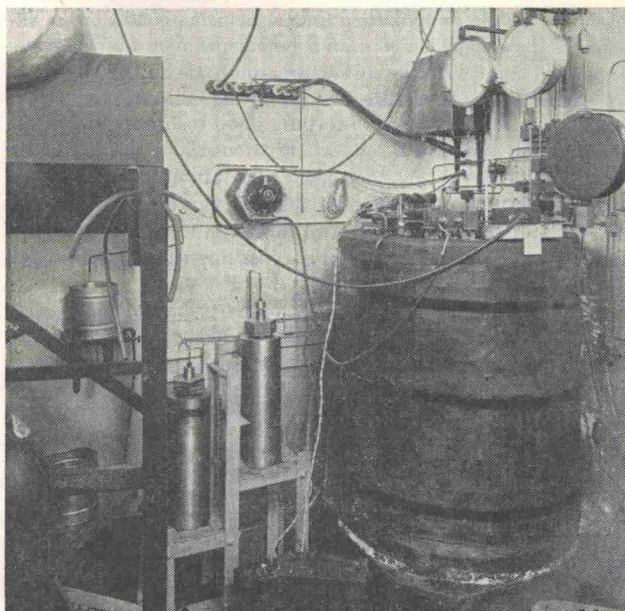OF COMPRESSIBILITY OF GASES AT HIGH PRESSURES

FIG. 5 APPARATUS ASSEMBLY FOR INVESTIGATION OF RATE OF AB-
SORPTION 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 fis-
suring. Even if no methane were formed the removal of the car-
bon itself would alter the structure and presumably change the
tensile properties. This action takes place at elevated tempera-
tures, i.e., at 300 C or higher and, since chemical reaction rates
are, in general, greatly accelerated by temperature, it is to be ex-

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 tempera-
tures. 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 em-
ployed the word "attack" as a general term for the action of
hydrogen on metals at elevated temperatures. The term "decar-
burization" 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, zir-
conium, 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.[3]

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, wiredrawing, 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

³ 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)

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

whereas the permeability P is usually defined by

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

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 Δx. 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

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

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-

porting this conclusion is the fact that the rate of permeation of a diatomic gas is generally proportional to the square root of the pressure. This would be expected if the diffusion were due solely to atoms, in view of the equilibrium relation

$$K = \frac{p_H}{\sqrt{p_{H2}}} \quad \dots \dots \dots \dots \dots \dots \quad [4]$$

where K is the equilibrium constant of the dissociation reaction and p_H and p_{H2} are partial pressures of atomic and molecular hydrogen, respectively.

The importance of dissociation into atoms is also indicated by the exponential effect of temperature which is the effect that would be expected if the rate controlling the permeation were an activated adsorption on the surface resulting in some dissociation. Another bit of evidence is the fact that nascent hydrogen will diffuse in a metal against a high pressure of hydrogen.

The equation that is usually accepted as expressing the effect of pressure and temperature is as follows

$$J = \frac{K}{L}(p_1^{1/2} - p_2^{1/2})e^{-E/RT} \quad \dots \dots \dots \dots \quad [5]$$

where

J = rate of permeation per unit of area
K = constant depending on metal and probably on several factors related to state of metal
L = thickness of metal membrane through which gas is permeating
p_1 = pressure on high-pressure side of membrane
p_2 = pressure on low-pressure side
E = an activation energy
R = gas constant
T = absolute temperature

Although this law of pressure and temperature dependence is supposedly general, the limits within which it applies are not well known and the effect of variables on K is not at all established.

The relation between rate of permeability and practical effects on the properties of the metals is not clear but we are hoping that further work along this line may lead to some useful correlations. Even if it doesn't, the data on the permeability will have some value in indicating which metals are best for applications where no leakage of gas through a metal wall can be tolerated. It also will have application to the selection of liners for steel vessels.

4 The retention or occlusion of gases by metals may be of importance in some applications but as yet we have not had an opportunity to study the considerable literature on the subject. It is mentioned here only to call attention to a part of the general subject of interaction between gases and metals which may bear study and which may have an important relation to the other three aspects that we have considered.

In passing, it may be worth mentioning that the retention of gases by metals once they have penetrated beyond the surface is generally believed to involve not only solid solution, i.e., a penetration of the crystal lattice by atoms of the gas, but also an accumulation of gas at grain boundaries and in imperfections or rifts within the crystals.

Experiments on Hydrogen Attack. Our work in this field will now be reviewed briefly. The question of hydrogen attack by decarburization or other chemical reaction could be approached from a fundamental angle. The two basic factors in dealing with any chemical reaction are (a) chemical equilibrium and (b) rate of reaction. One could investigate the equilibrium and kinetics of the reduction of various metal carbides by hydrogen but the situation in an actual metal is probably far more complex and it, seems doubtful if such information would be useful in predicting the practical effect of hydrogen on the tensile properties of a given metal under a given set of conditions. For this reason we have chosen a practical and not particularly fundamental approach to the problem. Briefly it is this: Hollow pieces of metal in the form of a tensile test specimen are subjected to internal hydrogen pressure while being held in a furnace for some time at a constant temperature. A control sample is subjected to the same temperature but without the hydrogen pressure. At the end of a certain period of time the samples are removed from the furnaces and tested in a standard tensile testing machine to determine the ultimate tensile strength, the elongation and the reduction in area. For comparison, the same tests were made on untreated samples from the same lot of material. Sections of exposed and unexposed specimens also are examined microscopically by the standard metallographic procedures. A drawing of the test specimen used is shown in Fig. 8, and Fig. 9 gives a schematic representation of the assembly for exposing the specimens.

To date tests have been made on 26 different metals under test conditions which may be summarized as follows:

Temperatures of 300 to 500 C
Pressures of 1000 and 2000 atm
Time of exposure varied from 4 to 10 weeks

In a paper of this broad scope it is not possible to present the results in any detail but a few general conclusions of the work so far accomplished may be interesting and will be enumerated. Before doing this, however, it is desirable to explain the basis for them. If the specimen exposed to hydrogen had, within reasonable limits of reproducibility, the same tensile properties as the unexposed control sample, it was concluded not to have been attacked. If these properties have been lowered in value but the microscope reveals no fissuring or if heating in the absence of hydrogen restores to a considerable extent the original properties, the sample is concluded to have been embrittled but not attacked. Finally, if the tensile properties have deteriorated and fissuring is clearly revealed by the microscopic examination, it is concluded that the metal has been attacked:

1 Plain-carbon steels, even those of low carbon content, were severely attacked at 400 C in a relatively short time. This, of course, was to be expected from the literature. At 300 C the attack was inappreciable.

2 Some alloy steels were attacked severely, others were embrittled, and others not appreciably affected. Not enough results are available to establish any definite pattern but contrary to expectations some Cr-Mo steels with as much as 5 per cent Cr were definitely attacked at 2000 atm even though they were low in carbon (about 0.10 per cent). There was some evidence, but not conclusive, of attack on a Cr-Mo steel containing 10 per cent Cr.

3 High-nickel alloys such as K-Monel, Inconel, and Hastelloy B were either attacked or embrittled.

4 Some embrittled samples had their original properties restored by heating to somewhat higher temperatures in the absence of hydrogen.

5 Results on high-chromium alloys such as chromax, nichrome, and nichrome V are somewhat inconclusive in that specimens of nichrome and chromax were unaffected but nichrome V was attacked severely.

6 Tentatively it appears that 2000 atm was a considerably more severe condition than 1000 atm. Some metals that were not affected appreciably at 1000 atm were attacked severely or embrittled at 2000 atm.

7 No effect was observed on any stainless steels either of the 300 or the 400 series (only one of the latter was tested).
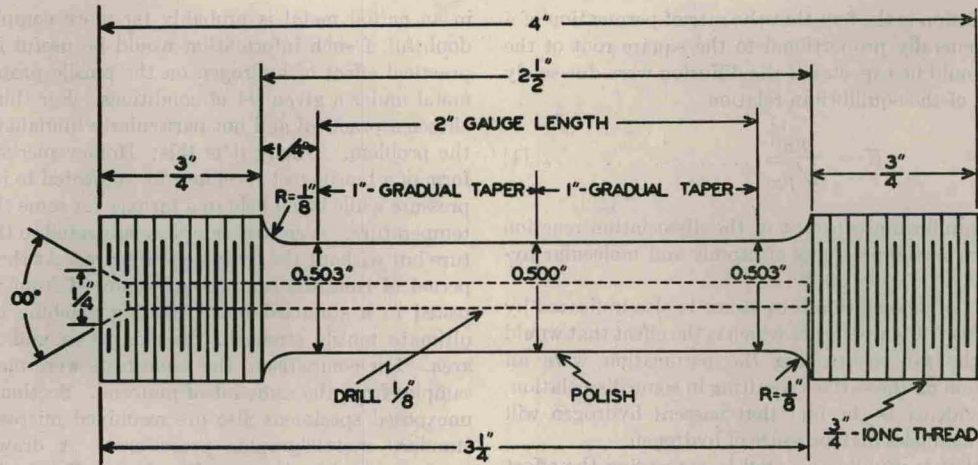
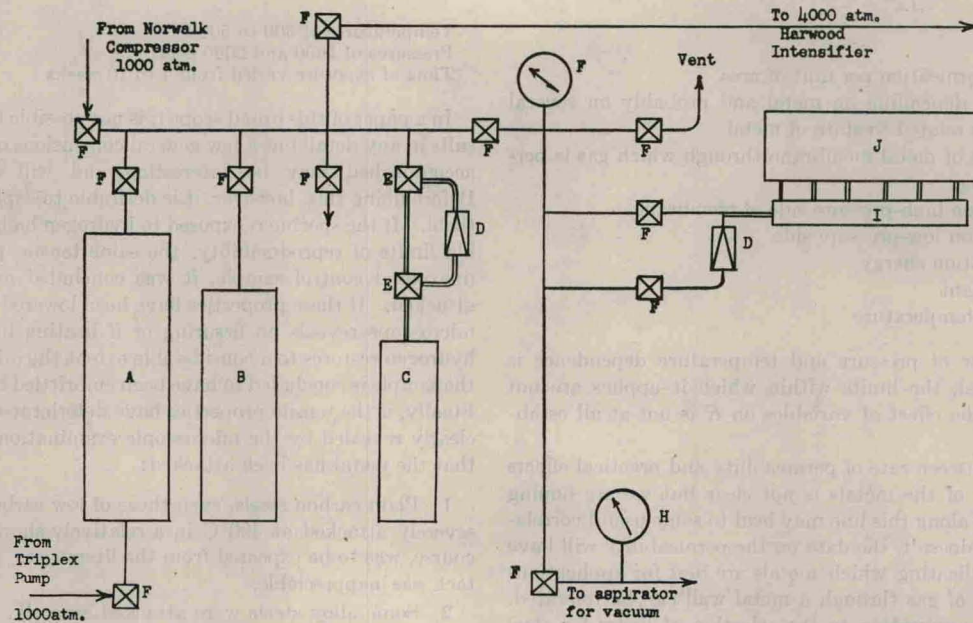FIG. 8　TENSILE TEST SPECIMEN FOR EXPOSURE TO HYDROGEN

FIG. 9　DIAGRAM OF APPARATUS FOR EXPOSING TENSILE SPECIMENS TO GAS AT ELEVATED PRESSURE
AND TEMPERATURE

A, 1/4 cu ft, 1000 atm storage
B, 1/8 cu ft. 1000 atm storage
C, 200 cc, 4000 atm storage
D, Check valves
E, Harwood 3-way 100,000 psi valves
F, Aminco 60,000 psi valves

H, Vacuum gage
I, Manifold
J, Furnace
——— Aminco 1/4 × 1/16 in. 60,000 psi tubing
═══ Harwood 5/16 × 1/16 in. 100,000 psi tubing

Experiments on Embrittlement at Room Temperature. In addition to the tests at elevated temperature, other tests were made at room temperature on specimens consisting of strips 1/2 in. × 4 in. × 16 gage, designed to yield information on the second aspect of the general problem. The strips were exposed to the gas in a vessel shown diagrammatically in Fig. 10. This is so constructed that the outer vessel of alloy steel which withstands the pressure is not exposed to hydrogen under pressure. The specimens rest on a shelf inside the inner stainless-steel vessel, above the level of the oil which is used to compress the gas from 1000 atm to higher pressures. Since the head of the vessel will be indirectly in contact with high-pressure hydrogen though its solubility in the oil, it was constructed of beryllium copper which was believed to be

unaffected by hydrogen and could be heat-treated to give a yield strength of the order of 150,000 psi. The outer vessel and the intensifier could only be exposed to high-pressure hydrogen by virtue of diffusion of dissolved hydrogen through the oil. This is a very slow process and could never proceed very far in short-time tests because the process is interrupted frequently by venting the dissolved hydrogen to the atmosphere.

The exposed specimens were given a bending test in a simple, homemade, hand-operated bending device designed to give 180-deg bending. Several specimens of a given metal were exposed together and then tested to obtain an average number of bends before breakage. This figure then could be compared with a similar average obtained with unexposed specimens.
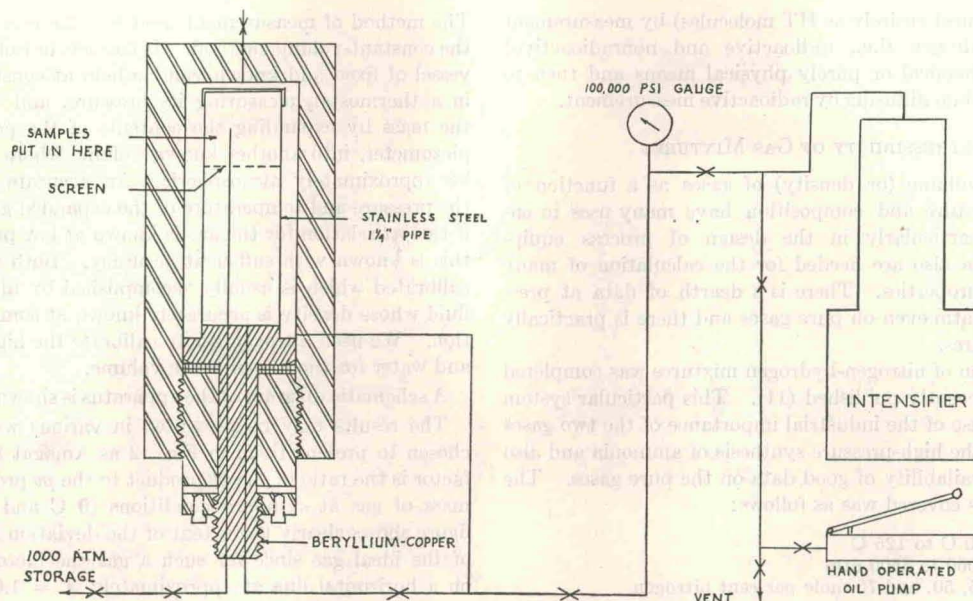
FIG. 10   DIAGRAM OF APPARATUS FOR TESTS OF HYDROGEN EMBRITTLEMENT AT ROOM TEMPERATURE

Only a very few tests have been made with this apparatus so that no results can be reported at this time. All we can say is that it works in the sense that relatively short exposures (a matter of hours) cause a very considerable effect on some samples when pressures of the order of 4000 atm are used.

Experiments on Permeability. The work on permeability is still in the stage of apparatus design and test. We have learned a few things about how not to build it but we have still to develop and prove a suitable design.

It is recognized that it may be exceedingly difficult to obtain reproducible results in these experiments because of the many variables which may affect the rate and because some of them will be difficult to control. For example, there are numerous variables connected with the previous history of the specimen such as its heat-treatment and the amount of cold-working it received which may be important. The nature of the surface may be significant. It is known that there is an "aging" effect which manifests itself in a decreasing rate of permeation with time. There may be flaws in the specimen which will give spurious results. What this means is that we cannot expect results of high precision but this is probably not too important since only gross differences are likely to be of interest and have practical application. It is planned to investigate a number of variables among which are the following:

(a) Nature of the gas; various pure gases and also gas mixtures.

(b) Pressure.

(c) Temperature.

(d) Composition of the metal.

(e) Previous history of the metal; cold-working, heat-treatment, etc.

(f) Condition of the surface.

(g) Strained versus unstrained metal.

The apparatus as now envisaged will consist of a tubular specimen surrounded by a jacket which can be evacuated and the whole assembly placed in an electric-tube furnace for temperature control. The rate of permeation will be measured by the rate of rise of pressure in the evacuated jacket.

Some thought has been given to the use of tritium, the radio-active isotope of hydrogen, as a tracer in these experiments.[4] It might be used simply as a sensitive means of determining how much hydrogen has permeated through a metallic membrane. A very sensitive means of measurement would have some advantages since the amount of gas permeating in any short interval of time is very small indeed and the problem of determining rate of permeation is a difficult one especially at the lower temperatures. We also had in mind the use of tritium to shed some light on the mechanism of permeation. Suppose one used tubular specimens and placed hydrogen containing tritium under pressure inside the tube. The amount of hydrogen retained in the specimen and its radial distribution conceivably might be measured by cutting off successive layers of the tube, dissolving each cut in acid and measuring the radioactivity. The radioactivity measurements would be a means of distinguishing the hydrogen that originated from the acid from that which permeated the metal.

In studying the effect of pressure on permeability, one usually increases the pressure on one side of the metal wall and maintains a low pressure on the other side. This results in an increase both in the total pressure and in the pressure gradient. For some purposes it would be desirable to increase the total pressure at constant pressure difference. It would be difficult in this case to measure the rate of permeation by the usual techniques but the use of a radioactive tracer offers a possible method.

When the pressure is not the same on the two sides of the diffusion membrane it will be strained. It might be of interest to measure also the permeability under a condition of no strain. This might be done by using an inert, i.e., nondiffusing gas, such as helium or argon, to equalize the total pressures while still maintaining a partial-pressure difference of hydrogen. In such a case the use of tritium to "tag" the hydrogen molecules in order to measure those which penetrate the wall of the metal, would be most useful.

One difficulty that arises in the use of tritium to trace hydrogen is the fact that these two isotopes are quite different in atomic weight and may have appreciably different rates of diffusion. However, it should not be too difficult to measure the relative permeation rates of hydrogen and tritium (actually the latter

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[4] This was first suggested by Dr. S. W. Wan, formerly Research Associate in Chemical Engineering at Yale.

will be present almost entirely as HT molecules) by measurement of the total hydrogen (i.e., radioactive and nonradioactive) permeating by chemical or purely physical means and then to determine the tritium diffusing by radioactive measurement.

COMPRESSIBILITY OF GAS MIXTURES

Data on the volume (or density) of gases as a function of pressure, temperature and composition have many uses in engineering and particularly in the design of process equipment. Such data also are needed for the calculation of many thermodynamic properties. There is a dearth of data at pressures above 1000 atm even on pure gases and there is practically nothing on mixtures.

An investigation of nitrogen-hydrogen mixtures was completed and the results recently published (11). This particular system was chosen because of the industrial importance of the two gases and their use in the high-pressure synthesis of ammonia and also because of the availability of good data on the pure gases. The range of variables covered was as follows:

Temperature: 30 C to 125 C
Pressure: 1000 to 3500 atm
Composition: 25, 50, and 75 mole per cent nitrogen

The method of measurement used was the one commonly called the constant-volume method. It consists in isolating the gas in a vessel of fixed and known volume held at constant temperature in a thermostat, measuring its pressure, and then determining the mass by expanding the contents of the pressure vessel, or piezometer, into another known volume where the pressure will be approximately atmospheric. An accurate measurement of the pressure and temperature of the expanded gas gives the mass if the pvt relation for the gas is known at low pressure. Usually this is known with sufficient accuracy. Both volumes must be calibrated which is usually accomplished by filling them with a fluid whose density is accurately known at some specified condition. We used nitrogen gas to calibrate the high-pressure vessel and water for the low-pressure volume.

A schematic diagram of the apparatus is shown in Fig. 11.

The results may be presented in various ways but we have chosen to present them in Fig. 12 as Amagat factors A. This factor is the ratio of the pv product to the pv product of the same mass of gas at standard conditions (0 C and 760 mm). The figure shows clearly the extent of the deviation from the concept of the ideal gas since for such a gas the factors would all fall on a horizontal line at approximately $A = 1.072$. At the top
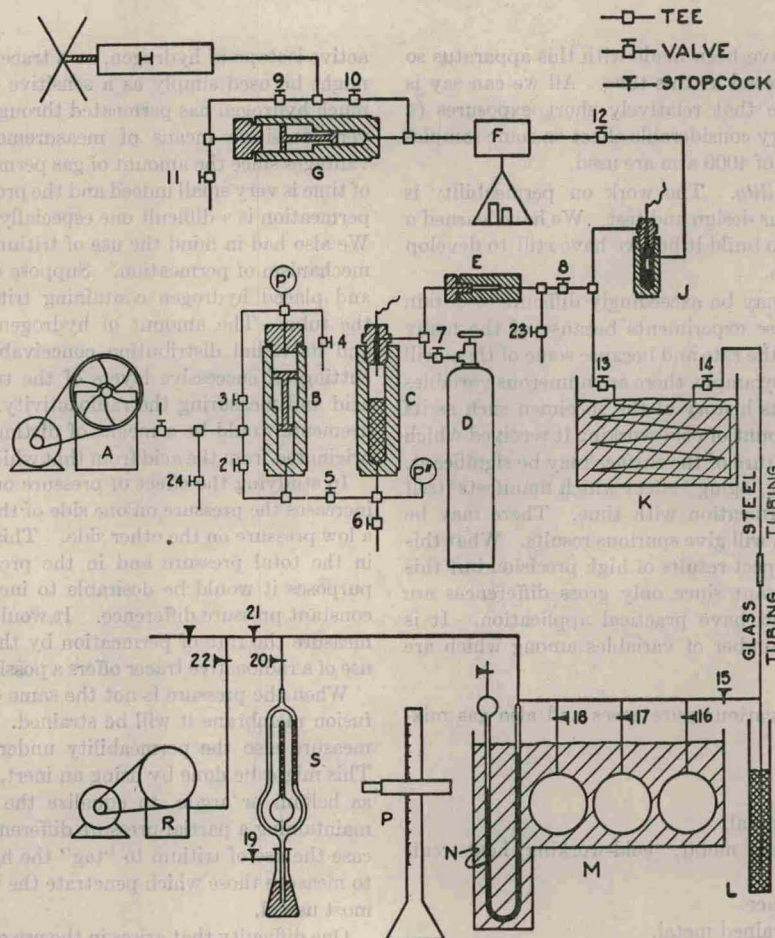
FIG. 11 DIAGRAM OF APPARATUS FOR COMPRESSIBILITY MEASUREMENT

A	Triplex hydraulic pump	J	Mercury U-tube
B	Aminco intensifier	K	Constant-temperature oil bath
C	Gas-compression chamber	L	Safety tube
D	Gas-storage cylinder	M	Constant-temperature water bath
E	Drier	N	Mercury manometer
F	Dead-weight piston gage	P	Cathetometer
G	Small intensifier for piston gage	R	Vacuum pump
H	Cailletet pump	S	McLeod gage

FIG. 12 AMAGAT COMPRESSIBILITY FACTORS FOR NITROGEN-HYDROGEN MIXTURES
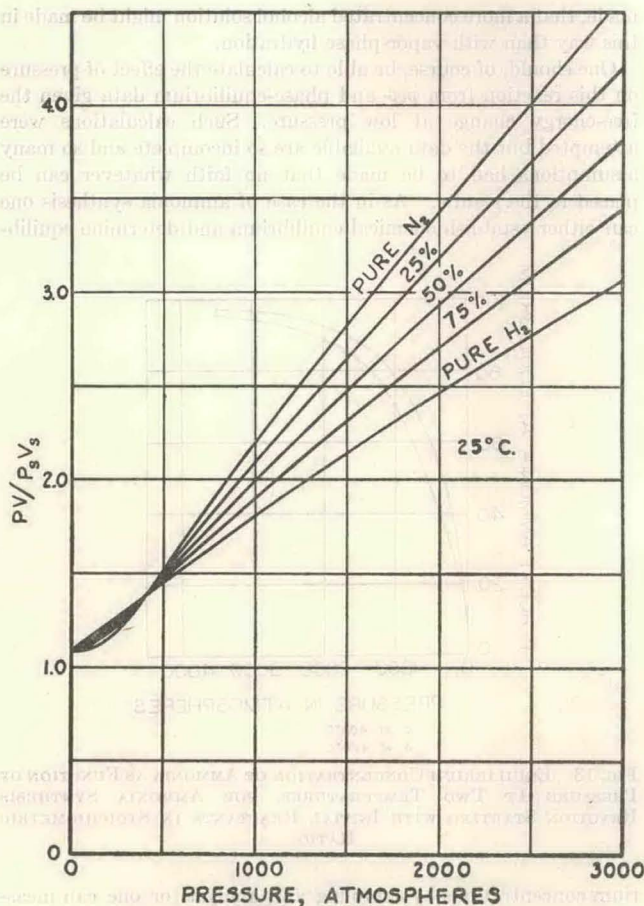
pressure of 3000 atm it may be noted that the specific volume of nitrogen is over 4.5 times what it would be if the gas were ideal. Another interesting fact is that at these high pressures all the gas mixtures obey the ideal solution law (volumes are additive at constant pressure and temperature) within about the experimental error of the measurement (0.2 per cent).

Another investigation in this field is now in progress which involves *pvt* measurement on the ternary system: Nitrogen-hydrogen-ammonia over the temperature range 300–500 C and at pressures up to 3000 atm. One of the main objectives of this study is the prediction of the ammonia-synthesis equilibrium at pressures above 1000 atm. The qualitative effect of pressure on chemical equilibrium is well known from Le Chatelier's principle. The quantitative effect can be obtained from either of the following approaches: (a) Direct experimental measurement of the concentrations of the three gases under equilibrium conditions; or (b) calculation of the equilibrium constant at zero pressure from the free-energy change of the reaction followed by calculation of the effect of pressure on this constant with the aid of *pvt* data on the ternary system. There are advantages and disadvantages in both methods. Method (a) requires that the reaction be carried out and equilibrium established at all the pressures and temperatures for which the equilibrium conversion is desired. Among other things this involves establishment of equilibrium by use of an active catalyst and accurate sampling and analysis of the equilibrium mixture—two things that are not easy to accomplish. Method (b) is attractive in that it does not require that chemical equilibrium be established at all. The calculation of the zero-pressure equilibrium constant by means of
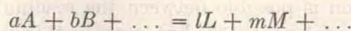
thermal data is well known and treated in most texts on thermodynamics applied to chemistry and chemical engineering. The relation between the constant at any pressure and that at zero pressure is given by the equation

$$\ln \frac{K_p}{K_{p0}} = -\Sigma \nu \left[\frac{1}{RT} \int_0^p \left(\bar{V}_i - \frac{RT}{p} \right) dp \right] \dots [6]$$

where Kp = equilibrium constant defined by the function

$$\frac{(x_L)^l (x_M)^m \cdots}{(x_A)^a (x_B)^b \cdots} p^{\Sigma \nu}$$

for the generalized reaction

$aA + bB + \ldots = lL + mM + \ldots$
K_{p0} is its value at $p = 0$
x_A, x_B, etc., are mole fractions of components A, B, etc.
p is total pressure
a, b, etc., are the stoichiometric numbers
$\Sigma \nu = l + m + \ldots - a - b \ldots$

$\bar{V}_i$ is partial volume, $\left(\dfrac{\partial V}{\partial n_i} \right)_{p, T, n}$

where i refers to any component and n = number of moles.

The integral in Equation [6] can be evaluated with the aid of *pvt* data on the mixture. With the values of K_p obtained in this way, one is in a position to calculate the equilibrium conversion at any pressure and temperature and initial gas composition covered by the *pvt* data. For further details on such calculations a number of sources may be consulted (12, 13, 14).

The experimental method being used in this investigation is the same in principle as the one previously used but the presence of ammonia and the higher temperature range necessitated certain changes in detail which may be outlined as follows:

1 The long tubular constant-volume piezometer used in the measurements on the binary system was replaced by a thin-walled cylindrical vessel so disposed inside a heavy-walled vessel that the gas pressures inside and out would be approximately equalized. This was done to minimize hydrogen permeation through the metal wall which, it was feared, might be serious at these conditions. The differential pressure across the wall of the piezometer is indicated by an electric strain gage fastened to a diaphragm separating the two compartments and roughly controlled manually within about 200 atm.

2 A fused salt bath instead of an oil bath is used for temperature control.

3 Parts of the assembly outside of the thermostat are located in an air bath maintained at 140 C to prevent any condensation of liquid ammonia.

The apparatus assembly is practically complete at the present writing but no runs have yet been made. Most of the individual units have been tested and calibrated but unexpected difficulties keep cropping up to delay the operation of the entire setup as a functioning unit. It is of interest to note that an apparatus assembly of this character takes an inexperienced investigator, such as a graduate student, from 2 to 3 years to set up and put into operation. Once it is set up it should in theory be used for the study of a number of systems but, unfortunately, in university research this is seldom possible.

CHEMICAL REACTIONS AT HIGH PRESSURE

Pressure is an important variable in carrying out many reactions. It has an important effect both on the equilibrium and hence the maximum possible degree of conversion and on the reaction rate. Many important products of industry are now made by chemical reactions operating at high pressure which

would not be at all feasible at low pressures.   The production of ammonia, methanol, urea, synthetic fuels, higher alcohols, and polyethylene are only a few of the many examples that could be cited.   Several pressure reactions have been studied recently in this laboratory and some are now in progress.

In a university laboratory the investigation of a chemical re-action should be from as fundamental a standpoint as possible. Ideally, this means that one should study the equilibrium in the reaction and its kinetics.   When these two factors have been investigated fully one presumably has a complete knowledge of the course of the reaction under all important conditions.   In actual practice the problem is seldom as simple as that.   In a simple reaction such as the synthesis of ammonia (simple in the sense that only one reaction is possible between the reactants) one can take this fundamental approach, but even in this case the kinetics are complex and still not well understood.   This is probably true of all catalytic reactions in which the reaction occurs on the surface of a solid.   In the case of most organic re-actions the situation is further complicated by the many possible reactions that can occur with a given set of reactants.   It is not very fruitful to study reaction rate or equilibrium until one knows just what reactions he is dealing with and under what con-ditions they will proceed to a measurable extent.   For this reason much of the initial work in this field has to be of an exploratory character.   It is not concerned with precise physicochemical measurements to "pin-point" an effect but rather with rough, order-of-magnitude studies designed to sketch the broad outlines of the problem and locate those areas which later may be in-vestigated more minutely.

Ammonia-Synthesis Equilibrium.   An investigation of the ammonia-synthesis equilibrium by the direct method (in con-trast to the indirect one as previously discussed) was completed a few years ago but the results have not heretofore been published. Although this is a reaction of great industrial importance and is now conducted at pressures as high as 1000 atm, it is doubtful if higher pressures are of more than academic interest.   The equilibrium was investigated at 400 C and 450 C over the pressure range 1000–3500 atm.   The results obtained are shown in Fig. 13 in the form of mole per cent ammonia in the equilibrium mixture when starting with pure gases in stoichiometric ratio or when starting with ammonia.   It is of interest to note that at 3500 atm the conversion to ammonia is nearly 100 per cent com-plete.   This may be compared to the maximum conversion of 27 per cent which is obtained at 450 C and 200 atm, a condition com-monly used in present industrial processes.

Before publishing this work in detail we are waiting for a con-firmation of the results by the indirect method utilizing *pvt* data.

Hydration of Ethylene.   Another reaction now under study in this laboratory is the ethylene-hydration reaction

$$C_2H_4 + H_2O = C_2H_5OH \dots \dots \dots \dots [7]$$
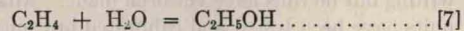
which requires elevated pressures for appreciable yields.   Along with this reaction the following one occurring simultaneously also must be considered

$$2C_2H_5OH = (C_2H_5)_2O + H_2O \dots \dots \dots \dots [8]$$
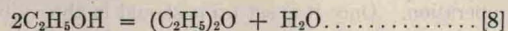
Investigations of catalysts for Reaction [7] carried out in the vapor phase and of the equilibrium, completed some years ago in this laboratory, were among the first in this field.   The results were published in two papers (15, 16).   The present investiga-tion is concerned with the heterogeneous system, i.e., both liquid and vapor phases present.   We are particularly interested in the two-phase system because the available data on it are very meager and it appears, from approximate calculations we have

made, that a more concentrated alcohol solution might be made in this way than with vapor-phase hydration.

One should, of course, be able to calculate the effect of pressure on this reaction from *pvt*- and phase-equilibrium data given the free-energy change at low pressure.   Such calculations were attempted but the data available are so incomplete and so many assumptions had to be made that no faith whatever can be placed in the results.   As in the case of ammonia synthesis one can either establish chemical equilibrium and determine equilib-
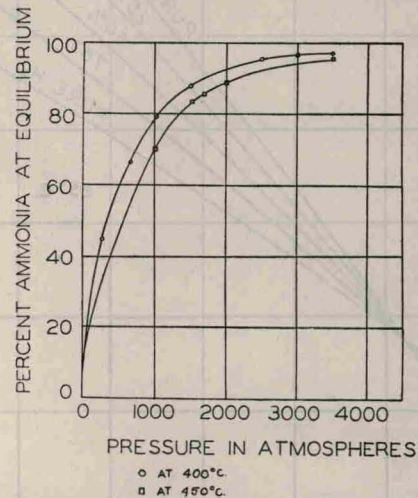
FIG. 13   EQUILIBRIUM CONCENTRATION OF AMMONIA AS FUNCTION OF PRESSURE AT TWO TEMPERATURES, FOR AMMONIA SYNTHESIS REACTION STARTING WITH INITIAL REACTANTS IN STOICHIOMETRIC RATIO

rium concentrations by sampling and analysis or one can meas-ure *pvt*- and phase-equilibrium compositions and calculate the chemical equilibrium.   In this case we chose the direct method.

During the planning of the attack two major problems pre-sented themselves.   These were (a) the development of an ac-curate and reliable analytical method for determining ethanol and ethyl ether in the presence of each other in dilute aqueous solu-tions, and (b) the development of a suitable liner for the auto-clave (Aminco shaking autoclave) to withstand the corrosive ac-tion of dilute mineral acids, particularly sulphuric acid, at temperatures of 300–350 C.   The solution to (a) has been de-veloped and thoroughly tested but it required much time and ef-fort.   Problem (b) enters because some of the best catalysts for this reaction are dilute mineral acids.   Glass could be used as a liner for the high-pressure autoclave but because of the need for a thermocouple well and for gas and liquid-phase sampling tubes, the design of a suitable glass liner appeared out of the question and besides, its fragility is against it.   We decided to try and design a metal liner.   Very little information is available either in the literature or from manufacturers of metals on corrosion resistance to sulphuric acid at temperatures this high.   Several metals seemed a possibility, particularly one or two of the stain-less steels, titanium, tantalum, and some of the Hastelloys.   After considerable study of the matter, Hastelloy B was chosen and a liner was designed and fabricated with the aid of the Haynes-Stellite Company.   It has not yet been tested.

The question of a suitable catalyst is a very important one for this reaction.   In addition to dilute solutions of various mineral acids we intend to try a sulphonic acid and a solid catalyst con-sisting of tungstic oxide supported on silica.   During the war the Germans did considerable work on ethylene hydration in the presence of a liquid phase, some of which has been published in the FIAT reports.   Various solid catalysts were tried but tung-

stic oxide appeared to be the best. It is doubtful in our minds if any solid catalyst will be as good as the mineral acids. We are not interested in the catalyst per se but must have a reasonably active one to approach equilibrium.

Water-Gas Reaction at High Pressure. Another reaction on which work has just been started is the water-gas reaction

$$CO + H_2O = CO_2 + H_2 \dots \dots \dots [9]$$

This is a very important industrial reaction usually carried out at about atmospheric pressure but there has been some recent industrial interest in the use of higher pressures. Since there is no change in number of moles in the reaction one is apt to conclude at first thought that pressure has no effect on the equilibrium. This would be true for ideal gases but for actual gases there is an effect though it may not be great. Although the reaction has been extensively studied at atmospheric pressure there appears to be only one published paper dealing with the effect of pressure on the equilibrium. Sartori and Newitt (17) found that the equilibrium constant, K_p, decreased about 20 per cent as the pressure increased from 1 to 100 atm. Our present plans call for investigating the reaction in the temperature range 380 to 450 C and the pressure range from 100 to 2000 atm with some variation also in initial reactant composition.

Other reactions such as

$$CO + 3H_2 = CH_4 + H_2O \dots \dots \dots [10]$$

and

$$CO_2 + C = 2CO \dots \dots \dots [11]$$
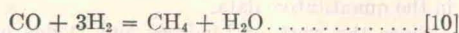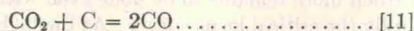
are also possible in this system, and one of the useful pieces of information that may come out of the investigation is something about the conditions which tend to favor or suppress these side reactions.

Reactions of Butadiene. We have started an investigation of certain reactions of butadiene that might be favored by pressure. This is very much of an exploratory research as so little is known about any such reactions that one cannot take the fundamental approach of studying equilibrium or reaction kinetics. Here we are simply trying to find out under what combination of conditions—temperature, pressure, concentration, catalyst, and so on—the proposed reaction will proceed to a measureable extent and what the side reactions will be. Butadiene was chosen because it is a reactive organic chemical which, almost a laboratory curiosity only 10 to 15 years ago, suddenly became available in very large quantities as a result of the synthetic-rubber program.

The reactions under consideration may be listed as follows:

1 With sulphur dioxide to yield cyclic sulphones.
2 With HCN to give nitriles and also possibly pyridine.
3 Diels-Alder reaction with ethylene to form cyclohexene.
4 Dimerization to 4-vinyl cyclohexene or to cyclo-octadiene.
5 With formaldehyde to produce a variety of possible compounds including alcohols, adipaldehyde, cyclic formals, and a dioxane.
6 The oxo reaction—hydrogen, carbon monoxide, and an olefin reacting to yield an aldehyde.
7 Hydration to tetrahydrofuran, possibly in two steps with 1, 4 butane diol as the intermediate.
8 With hypochlorous acid to give the isomeric chlorobutene-ols which could probably be converted to tetrahydrofuran.
9 Reaction with cyanogen and nitriles to give various products such as 2-cyanopyridine and 2-ethyl pyridine.
10 With sulphur or hydrogen sulphide to make thiophene.
11 With ammonia to produce pyrrole or acetonitrile and higher nitriles.

12 Reaction with steam to yield furan and hydrogen.

Most of the products of these reactions are either substances of industrial importance or of potential importance if they could be produced in good yields. Not all of the reactions would need to be carried out at elevated pressures or be favored by pressure but pressure certainly would be an important factor in some of them.

The experimental work has been started with a study of the reaction with hypochlorous acid (No. 8) the latter being produced in situ by bubbling CO_2 through a suspension containing calcium hypochlorite and butadiene and sometimes chloroform as a solvent. Most of the runs were made under pressure in a rocking autoclave with a glass liner. The product has been found to consist of a mixture of the 1, 2 and the 1, 4 monochlorohydrins and the dichlorohydrin. The relative amount varied with the conditions but the dichloro and the 1, 2 mono isomer predominated. Low temperatures, around 4–5 C, gave the best yields. The work is being continued to find the best conditions for good yields of the chlorohydrins, after which some of the other reactions will be studied.

Reactions of Carbon Monoxide. A number of interesting and important possible reactions may be mentioned such as the following:

1 with dihydric alcohols to give dibasic acids
   $CO + 1,4$ butane diol $\rightarrow$ adipic acid is just one example
2 with cyclohexanol to give the corresponding carboxylic acid
3 with phenol to give benzoic acid or salicylaldehyde
4 with anilin to form benzamide
5 with chlorobenzene (also the bromo- and iodo-benzenes) and water to yield acids
   Typical reactions are
   chlorobenzene $+ CO + H_2O \rightarrow$ benzoic acid $+ HCl$
   dichlorobenzene $+ CO + H_2O \rightarrow$ terephthalic acid $+ HCl$
6 with tetrahydrofuran and water to give adipic acid
7 with acetone to yield methacrylic acid
8 with cyclohexyl chloride and water to form cyclohexane carboxylic acid

Reactions 1 through 5 have been tried in this laboratory and the others are about to be tried. Catalysts used are nickel carbonyl, boron trifluoride, and benzoyl peroxide. Pressures vary from 1000 psi to 5000 psi and in the future work it is proposed to work at pressures up to 15,000 psi and possibly higher. Some work was done on reaction 7 using boron trifluoride as the catalyst and no methacrylic acid obtained, but in the proposed work use will be made of nickel carbonyl whose remarkable catalytic properties came to light only after the war. The possibility of obtaining the desired product hinges on the postulate that the acetone is an equilibrium mixture of the keto and enol forms. Work on reaction 1 using the butane diol and on reaction 6 was started in this laboratory but the experiments had to be stopped before any results of value were obtained.

Reaction 2 took place with yields up to 65 per cent.

Reaction 3 gave the aldehyde rather than the acid.

Reaction 4 took place but with very small yield.

Several of the reactions of series 5 gave appreciable yields. For example, paradichlorobenzene yielded 33 per cent of mixed p-chlorobenzoic and terephthalic acids.

Partial Oxidation of Aromatic Hydrocarbons. The possibility of partial vapor-phase oxidation of benzene to phenol by oxygen gas and of many related reactions has intrigued researchers for many years. In spite of all the work that has been done very little has been accomplished toward achieving the partial oxidation. In some cases investigators claimed high yields of phenol but the conversions per pass were very low. Most of the work had been performed at low pressures and the motivating factor behind our work was the thought that elevated pressures might favor the survival of the intermediate products of oxidation. It was felt that increased pressure would increase reaction rates

and thereby make possible the use of lower temperatures. At lower temperatures the relative rates of the partial and the complete oxidation reactions might be so altered that appreciably higher yields of intermediates would be obtained.

The experimental data obtained were rather meager. So much time was devoted to overcoming troubles with the apparatus that little time was available to the student to vary many of the conditions. Runs were made under a limited set of conditions at a maximum pressure of about 200 atm. About the only conclusion we are justified in drawing is the very general one that conversions to phenol were very low under all conditions tried. Although a number of the important conditions such as pressure, temperature, ratio of air to benzene, and contact time were varied, the results are not conclusive enough to give the effect of any one of them. Further work on benzene at higher pressures and on other aromatic hydrocarbons as well as on naphthenic hydrocarbon appears desirable.

PHASE EQUILIBRIA AT HIGH PRESSURES

This is a very wide and largely uncultivated field of investigation. Some years ago we completed an investigation of the pressure-temperature-composition (ptx) relations in the liquid-vapor systems: nitrogen-benzene, carbon dioxide-benzene, and nitrogen-methanol. The conditions under which these binary systems were studied are given in Table 2.

TABLE 2 CONDITIONS FOR STUDY OF BINARY SYSTEMS

System	Temperature deg C	Pressure, atm
CO₂-benzene	10-60	1-95
N₂-benzene	30-125	60-300
N₂-benzene	50-150	100-1000
N₂-methanol	50	200-500

The first two sets of results have been published (18, 19) but those on nitrogen-benzene at the higher pressures and on nitrogen-methanol are still unpublished (20). The most recent work, just published (21), is that on the system nitrogen-ammonia at pressures up to 3000 atm which was concerned primarily with the critical phenomena and the immiscibility phenomena that occur when the system is composed of two substances whose critical temperatures differ widely. In this case we have nitrogen with a critical temperature of —146 C and ammonia with a critical temperature of +132 C. We chose this particular system for three main reasons:

1 The composition was easily determined by chemical analysis.

2 Data were already available up to 1000 atm and this was a logical extension to a higher pressure.

3 Recent work of Russian investigators on this and a few other systems revealed some interesting and unusual phenomena. One of these is the existence of a gas-gas equilibrium or immiscibility in phases ordinarily regarded as both gaseous, at pressures higher than those at which the usual gas-liquid equilibria are observed. The other is the so-called "barotropic phenomenon" which consists in the fact that the initially more dense of the two phases becomes the less dense phase as the pressure is increased. This is something like saying that in the case of a liquid and gas phase in equilibrium the liquid changes to the gas and the gas to a liquid as pressure is increased.

Neither of these phenomena is very new; the gas-gas immiscibility was predicted by Van der Waals (22) nearly 60 years ago and discussed in some detail from a theoretical viewpoint by Onnes and Keesom (23). No experimental observation was reported, however, until the appearance of the paper by Krichevsky and Bolshakov in 1941 (24). The barotropic phenomenon was first discovered in 1906 by Onnes (25) while working with mix-

tures of hydrogen and helium at liquid-hydrogen temperatures. He observed visually that when two phases were in co-existence at a pressure a little below 49 atm and then the pressure increased, the helium-rich lighter phase became the heavier phase. In other words a "gas" phase sank as a bubble through the "liquid" phase. By alternate lowering and raising of the pressure he could cause the bubble to rise or sink at will.

A search of the literature revealed only 12 systems whose phase equilibria have been investigated at pressures above 1000 atm and the highest pressure used was 9650 atm. A complete list of these literature references is given in the paper by Lindroos and Dodge (21). It may be noted that two other systems besides the N_2-NH₃ one, namely, ammonia-methane and nitrogen-sulphur oxide, were found by Russian investigators to exhibit limited miscibility in a region that would normally be regarded as a homogenous gas-phase region.

A discussion of this so-called "gas-gas" equilibrium in the light of the various types of critical locus curves of binary systems is given by Lindroos and Dodge (21) and their paper should be consulted for further details on this phenomenon and on the experimental methods used.

The results, presented in tabular form, and also as px, tx, and pt curves for the system, are in qualitative agreement with those of the Russian investigators but there is considerable disagreement in the quantitative data.

Since the work of Lindroos and Dodge on the one system, N_2-NH₃, no further work has been done at this laboratory. Much more remains to be done even with this system to explore fully the critical locus curve. At the highest pressure reached by the Russians (9650 atm) the system is still heterogeneous and one wonders whether at still higher pressures another critical point will be reached and the system become homogeneous once more. It would be of interest to replace the ammonia by many other substances whose critical temperatures are far removed from that of nitrogen and likewise to replace the nitrogen by other gases of low critical temperature such as oxygen, carbon monoxide, argon, neon, helium, and hydrogen. Unfortunately for progress in this field, it involves difficult techniques so that results are very slow to accumulate and as far as we can see at present are purely of scientific interest with no practical bearing whatever.

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