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High-Pressure Research in Chemical Engineering Department of Yale University

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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
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 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.

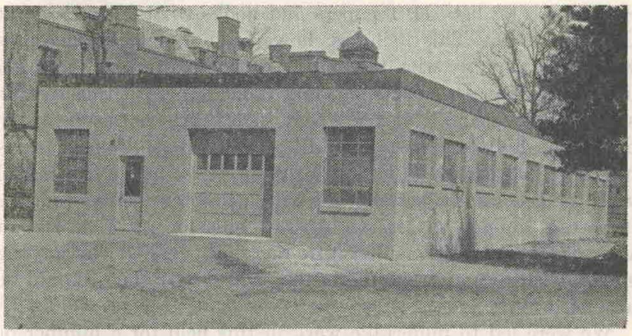

Fig. 1 Exterior View of Chemical Engineering Laboratory for Research at High Pressures

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

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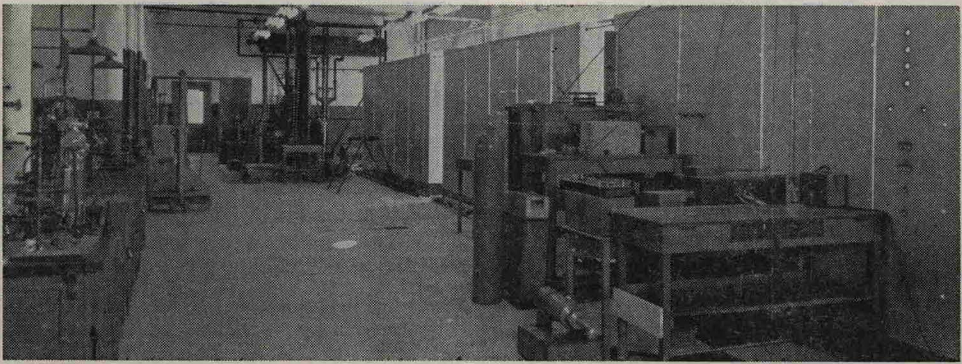

Fig. 2 General View of Interior of Laboratory, Showing Steel-Walled Cells at Right for Protection of Personnel

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.

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

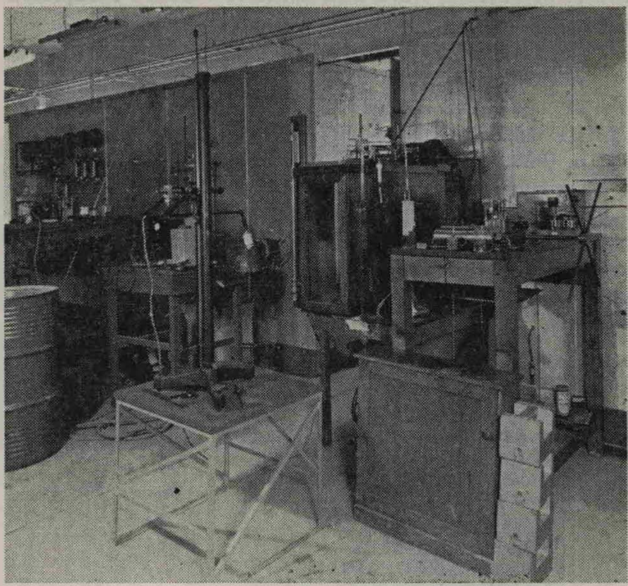

Fig. 3 Apparatus for Measurement of Pressure and of Gas Compressibility

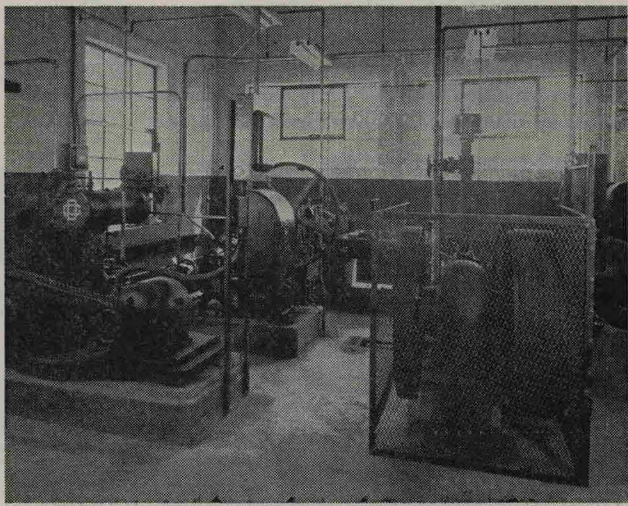

Fig. 4 Compressor and Pump Room

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.