

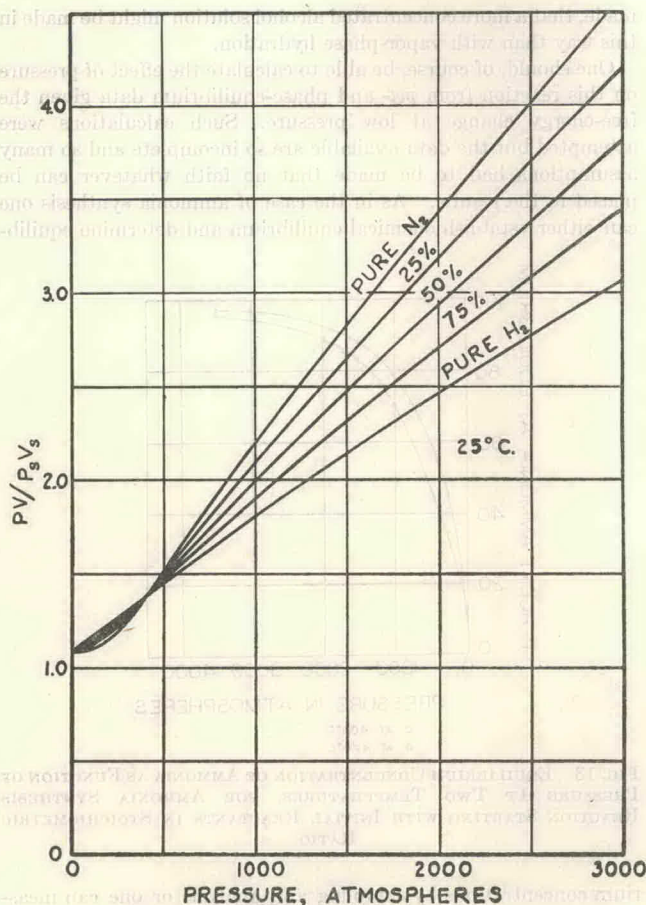


FIG. 12 AMAGAT COMPRESSIBILITY FACTORS FOR NITROGEN-HYDROGEN MIXTURES

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

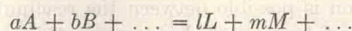
thermal data is well known and treated in most texts on thermodynamics applied to chemistry and chemical engineering. The relation between the constant at any pressure and that at zero pressure is given by the equation

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

where  $K_p$  = equilibrium constant defined by the function

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

for the generalized reaction



$K_{p0}$  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

$\sum \nu = l + m + \dots - a - b \dots$

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

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



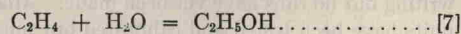
would not be at all feasible at low pressures. The production of ammonia, methanol, urea, synthetic fuels, higher alcohols, and polyethylene are only a few of the many examples that could be cited. Several pressure reactions have been studied recently in this laboratory and some are now in progress.

In a university laboratory the investigation of a chemical reaction 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 reactions 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 conditions 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 investigated more minutely.

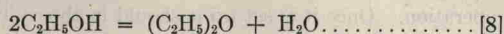
**Ammonia-Synthesis Equilibrium.** An investigation of the ammonia-synthesis equilibrium by the direct method (in contrast to the indirect one as previously discussed) was completed a few years ago but the results have not heretofore been published. Although this is a reaction of great industrial importance 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 complete. This may be compared to the maximum conversion of 27 per cent which is obtained at 450 C and 200 atm, a condition commonly used in present industrial processes.

Before publishing this work in detail we are waiting for a confirmation 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



which requires elevated pressures for appreciable yields. Along with this reaction the following one occurring simultaneously also must be considered



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 investigation 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-

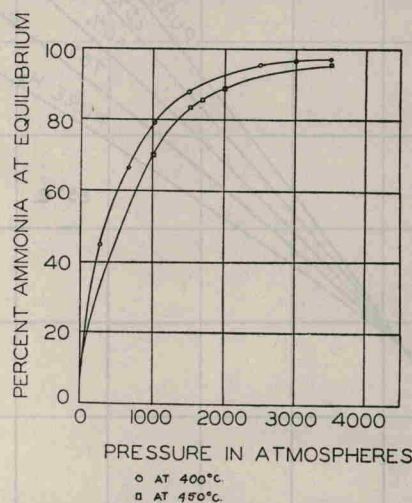


FIG. 13 EQUILIBRIUM CONCENTRATION OF AMMONIA AS FUNCTION OF PRESSURE AT TWO TEMPERATURES, FOR AMMONIA SYNTHESIS REACTION STARTING WITH INITIAL REACTANTS IN STOICHIOMETRIC RATIO

rium concentrations by sampling and analysis or one can measure *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 presented themselves. These were (a) the development of an accurate and reliable analytical method for determining ethanol and ethyl ether in the presence of each other in dilute aqueous solutions, and (b) the development of a suitable liner for the autoclave (Aminco shaking autoclave) to withstand the corrosive action of dilute mineral acids, particularly sulphuric acid, at temperatures of 300–350 C. The solution to (a) has been developed and thoroughly tested but it required much time and effort. 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 stainless 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 consisting 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-