

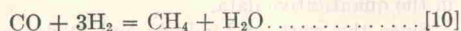
stic oxide appeared to be the best. It is doubtful in our minds if any solid catalyst will be as good as the mineral acids. We are not interested in the catalyst per se but must have a reasonably active one to approach equilibrium.

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



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



and



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 chloro-butene-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
 $\text{CO} + 1,4 \text{ butane diol} \rightarrow \text{adipic acid}$ 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 + $\text{CO} + \text{H}_2\text{O} \rightarrow \text{benzoic acid} + \text{HCl}$
- dichlorobenzene + $\text{CO} + \text{H}_2\text{O} \rightarrow \text{terephthalic acid} + \text{HCl}$
- 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
CO ₂ -benzene.....	10-60	1-95
N ₂ -benzene.....	30-125	60-300
N ₂ -benzene.....	50-150	100-1000
N ₂ -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 N₂-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, N₂-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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