RESULTS

The continuous water-gas shift reactor system was operated over a seven-month period from August 1984 to March 1985. Thirty-one experiments were performed in this study with a total operating time on stream in excess of 70 hours. In addition to these continuous reactor experiments, a limited number (7) of batch reactor tests were performed to produce vapor pressure data for the catalyst solutions at the operating conditions.

The continuous water-gas shift reactor system was operated in two distinct modes -- cold gas feed and preheated gas feed. Only limited testing with preheated gas was possible due to operating difficulties encountered when using the gas preheater. Details of the results with the gas preheater are included in the discussion of operation with preheated gas feeds. The cold gas feed experiments were performed in the continuous water-gas shift reactor system with or without feed gas compression (depending on the desired operating pressure). Table 2 summarizes the operating conditions of the various experiments; further detail regarding the experimental data is provided in Appendix A.

The actual data recovered from the experiments conducted in this study were in the form of gas compositions of the product gas. The product gas typically contained residual nitrogen from the startup phase of the experiment and traces of oxygen from air leakage during sample handling. The gas compositions were normalized based on the unreacted carbon monoxide and the carbon dioxide and hydrogen product gases only. When operated at steady-state the carbon dioxide and hydrogen partial pressures were nearly equal and were averaged to provide the basis for calculating conversion. The product gas during the early stages of the experiment contained large amounts of nitrogen as a residual from startup and often contained higher concentrations of carbon dioxide which has been attributed to formate formation. For these reasons, the early samples from the experiments are not used in the data analysis.

TABLE 2. Water-Gas Shift Experimental Parameters Studied

Temperature (°C)	Pressure Range (psi)	Flow Range (slpm)	Catalyst Type and Concentration (in weight %)
250	1000/1500	.26-1.28	sodium carbonate (6%)
	1000	.22-1.25	potassium carbonate (7.7%)
270	1500	1.3	sodium carbonate (6%)
280	1375	0.5	sodium carbonate (6%)
295	1380	.45-.73	sodium carbonate (6%)
300	1500-3000	.34-3.95	sodium carbonate (6%)
	3000	.57-2.6	sodium citrate (15.0%)
	3000	.67-3.7	cadmium hydroxide (8.1%)
	3000	2.4-2.9	ammonium hydroxide (3.8%)
	3000	.62-3.09	no catalyst
320	2500	.18-5.25	sodium carbonate (6%)
330	2500/3000	.46-3.19	sodium carbonate (6%)
337	2500	.53-2.18	sodium carbonate (6%)
350	3000	.21-2.21	sodium carbonate (6%)

Conversion is calculated on the basis of the relative amounts of carbon dioxide and carbon monoxide leaving the reactor when pure carbon monoxide was used as the gas feed to the reactor. The outlet flowrate is known for all the experiments. The inlet flow rate could be measured accurately only for the low pressure experiments which did not require a compressor. Pulsations in the gas flow due to the reciprocating compressor caused fluctuations in the rotameter readings so that inlet gas flow rate could only be determined indirectly when the compressor was in use.

In addition to the major focus of this experimental work which investigated the effects of the parameters of temperature, pressure and feed gas flow rate, a number of parameters of lesser importance were also considered. Effective contacting of gas and liquid phases in this reactor must be considered. Two contributing factors to the gas-liquid contact are the stirring rate in the reactor and the design of the dip tube. These two factors were studied to a limited degree. The catalyst concentration and identity are also potentially significant factors as they are in any chemical processing system. Our earlier batch reactor tests provided initial insights into the effects of these parameters (Elliott and Sealock 1983). As will be discussed later in the section on Phase Equilibrium Considerations, the catalyst concentration of our primary catalyst, (sodium carbonate) is limited by its reduced solubility at our operating conditions. Experiments to specifically study the catalyst concentration effect in the continuous reactor system were not undertaken due to resource limitations. Of the large number of aqueous base catalysts which we identified earlier (Elliott and Sealock 1983), we chose a few representatives to test in the continuous system.

Parameter Studies

In order to develop information about the water-gas shift reaction as catalyzed by aqueous base in a pressurized system, a potential operating range for parameters including temperature and pressure were identified. We initially proposed that the range of interest would be from 250 to 425°C and from 1000 to 4000 psig. We further proposed that during our first year of study we would develop the kinetics for the reaction in the temperature range from 270 to

370°C. Since our reactor operates as a two-phase system with a condensed liquid phase, the minimum operating pressure is a direct function of the liquid catalyst solution temperature. At METC's request we have emphasized the operation of the reactor system at low pressure. As a result, we have actually tested the reactor system at temperatures from 250 to 350°C and from pressures of 1000 to 3000 psig. Attempts to operate at yet lower conditions of 600 psig pressure and catalyst temperatures of 200°C are discussed in the section describing preheated gas feed experiments.

Unless otherwise noted, the data reported here were produced with aqueous sodium carbonate as the catalyst solution charged to the reactor. The solution consisted of 30.0 grams anhydrous sodium carbonate in 470.0 grams distilled water. The initial activity noticed on the lower temperature tests (250-300°C) was the generation of carbon dioxide. This gas production is attributed to the conversion of the carbonate to formate. The formate decomposition step in the water-gas shift is relatively slow at temperatures less than 300°C (Elliott, Hallen, and Sealock 1983) while the reaction of the base with carbon monoxide proceeds rapidly. Therefore, nearly an hour of operation is required before the catalyst solution comes to steady state and the product gas ratio of hydrogen to carbon dioxide approaches 1. This interpretation of the changes in the product gas composition is supported by analysis of the catalyst solution following the experiment. Using carbon-13 nuclear magnetic resonance with sodium acetate added as the internal standard, the used catalyst solution was determined to contain nearly 100% sodium formate for all experiments below 300°C.

The most dramatic parameter effect on reaction rate of the water-gas shift in our system is that due to changes in temperature. Figures 9 and 10 present data for experiments which compare the effect of gas flow rate on conversion at various temperatures. Figure 11 presents conversion versus temperature data at the lower temperatures studied. These three figures demonstrate both the increase in rate of reaction with increasing temperature as well as the decreasing extent of reaction with increasing flow rate, i.e. decreasing residence time.

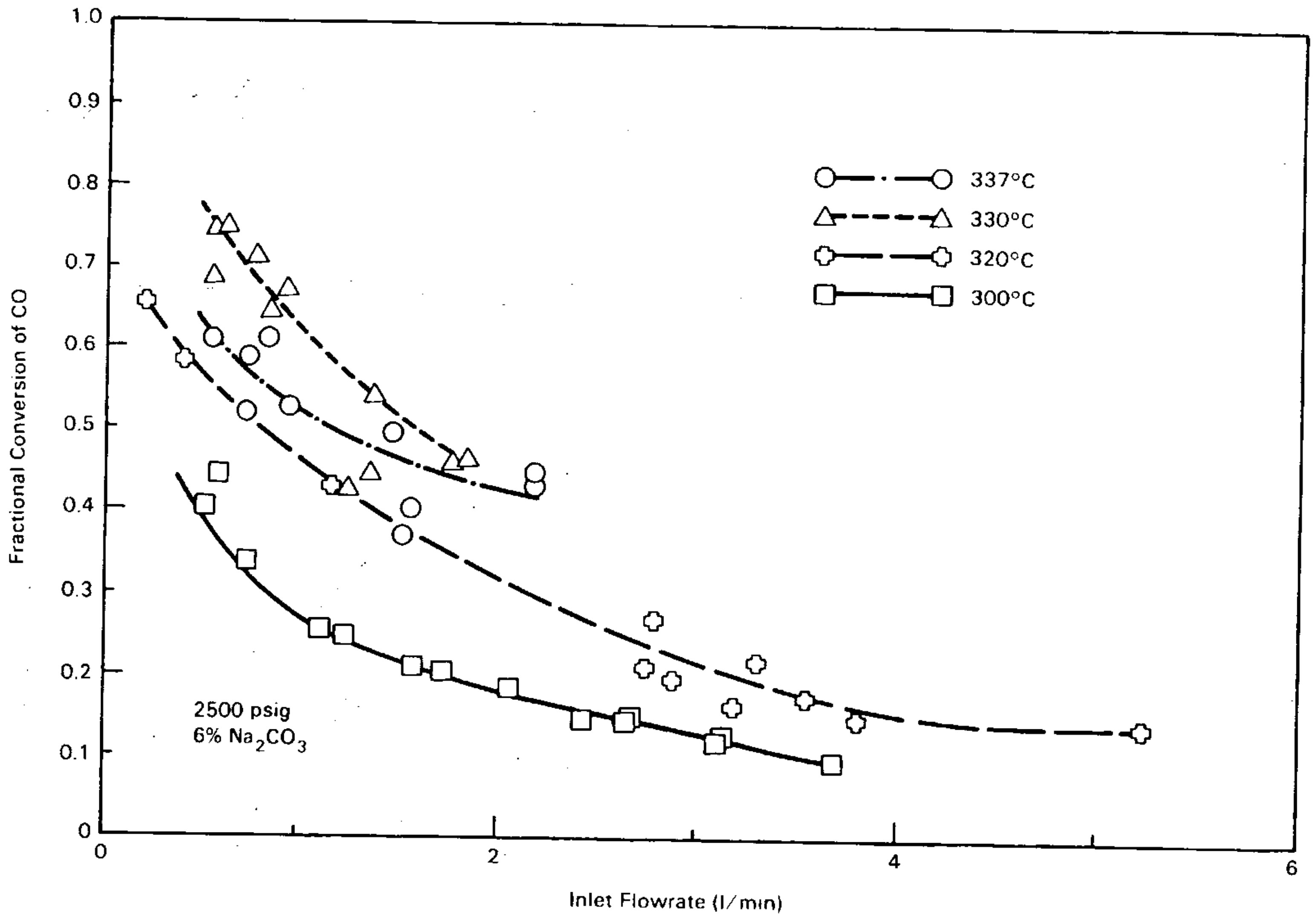

FIGURE 9. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 2500 psig

NOTE: Experiment at 337°C was performed at a lower agitation rate than the other experiments.

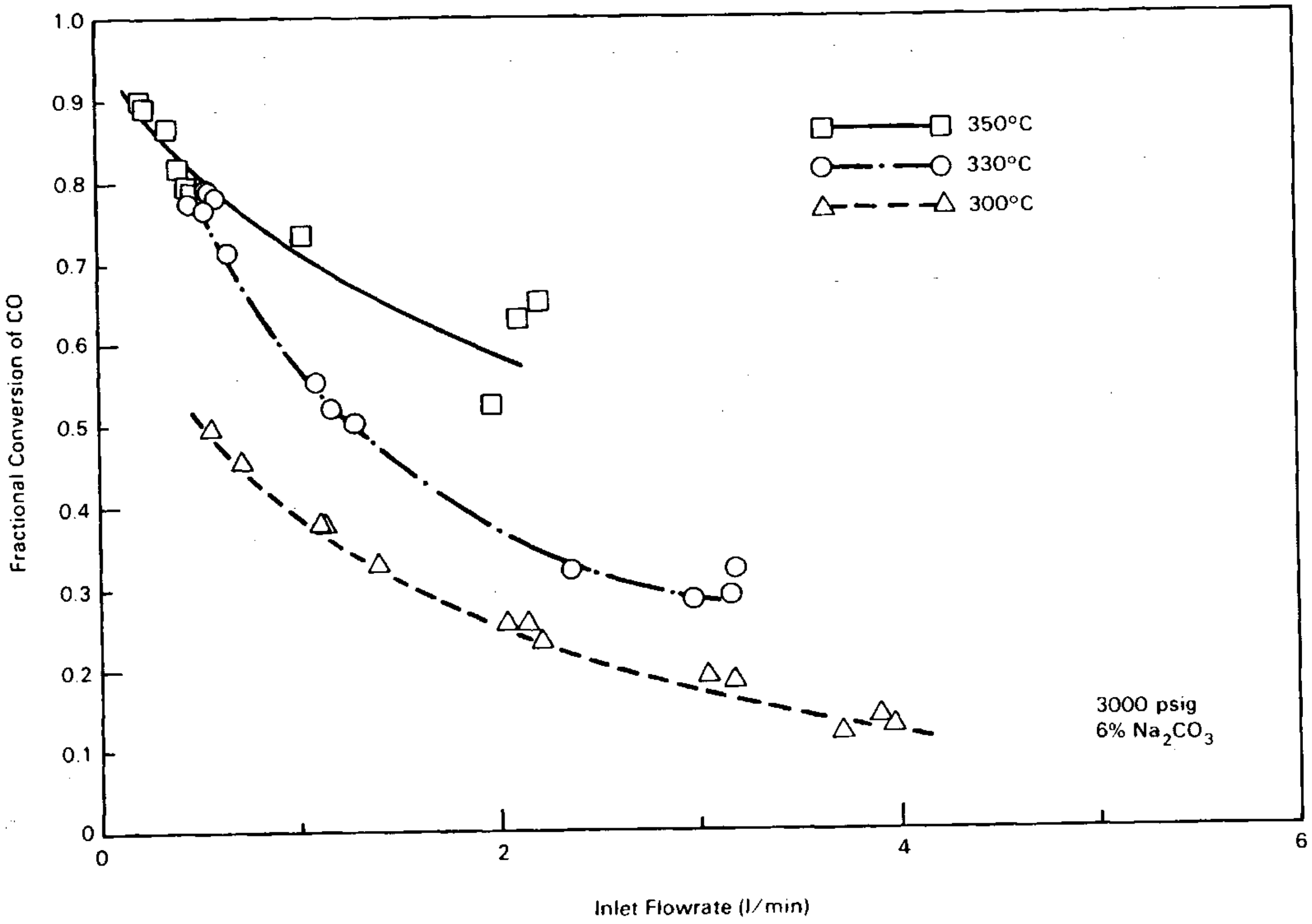

FIGURE 10. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 3000 psig

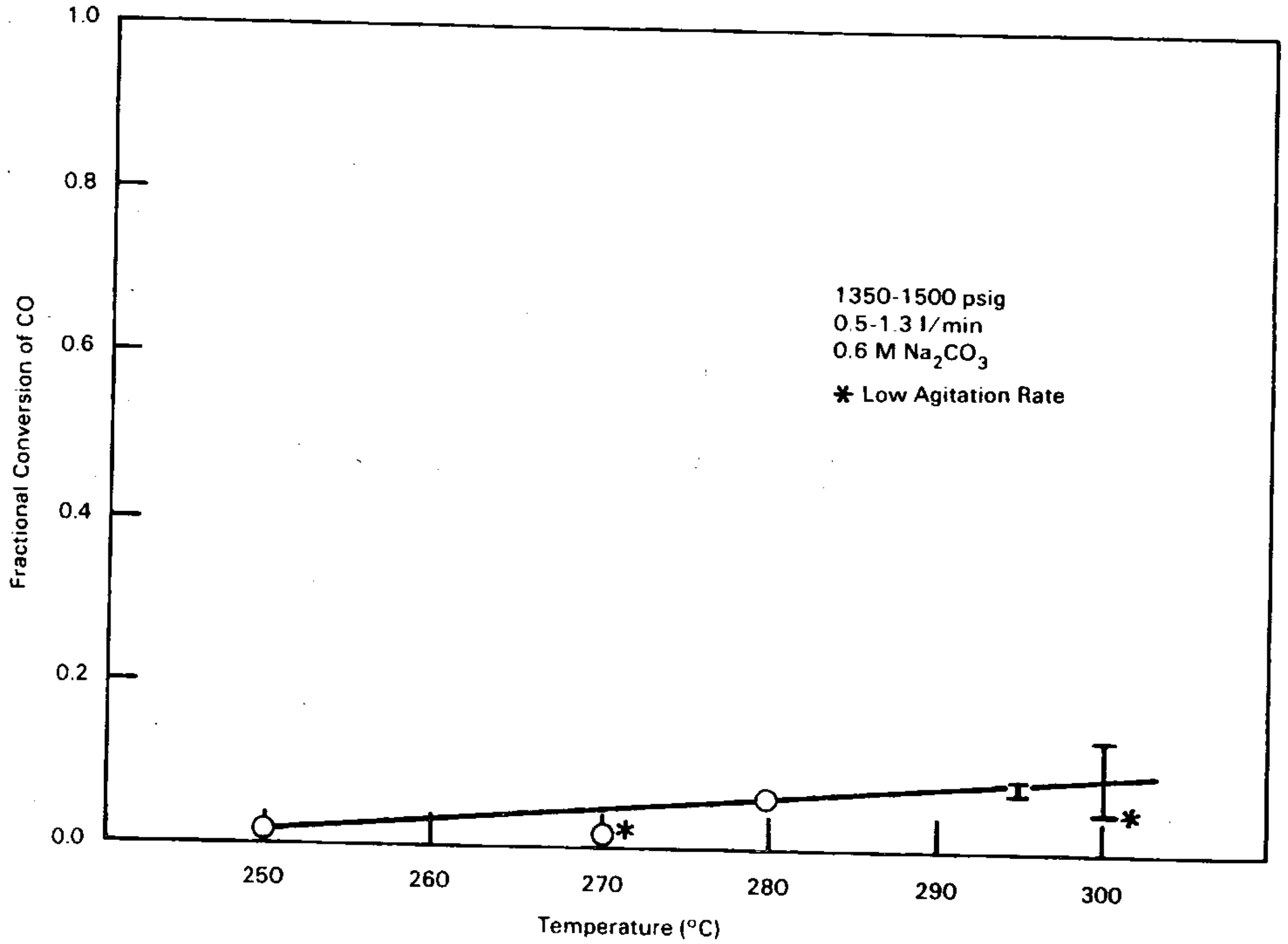

FIGURE 11. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 1500 psig

The effect of operating pressure on the reaction is demonstrated in Figure 12. This figure cross-compares the data from Figures 9, 10, and 11 by drawing out the data for operation at 300°C. Similar comparisons can be made for operational data at 250 and 330°C. Although there are only two points for these temperatures, the same trends are apparent as those found at 300°C.

Gas Contacting Studies

Since the pressurized aqueous catalytic system involves a gas feedstock and a liquid phase catalyst, intimate mixing of the two phases is an expected requirement for optimum operation. In our stirred-tank reactor system the liquid-gas contact is obtained through stirring and injection of the gas into the liquid phase with a dip tube. Both techniques underwent limited study.

The stirring rate was varied in order to determine its effect on reaction rate. As shown in Figure 13, the effect of varying the stirring rate was minimal at 250°C and 1000 psig. However, if the rate limiting step does not involve reaction across the gas/liquid interface then no effect on the reaction rate would be noticed with changes in agitation. When considering the proposed mechanism of the reaction, the rate limiting step may not be the reaction of the carbon monoxide with the aqueous base to produce formate but the decomposition of the formate itself. Previous studies indicate that the decomposition of sodium formate below 300°C is slow (Elliott, Hallen and Sealock 1983). It is apparent as the temperature is increased to 270°C or 300°C (as noted in Figure 11) that the slower stirring causes only a marginal decrease in the rate of the water-gas shift. At 337°C the effect of slower stirring rate was apparently large enough to result in a lesser rate of conversion than was noted at 330°C (see Figure 9).

The effect of the dip tube upon the observed reaction rate was also studied. Experiments were run under conditions which were very nearly the same except for the diameter and length of the dip tube. In the first experiment, the dip tube used was the standard 4 inch x 0.25 inch o.d. tube. In the second experiment, this tube was replaced with a 4 foot x 0.0625 inch o.d. tube, coiled

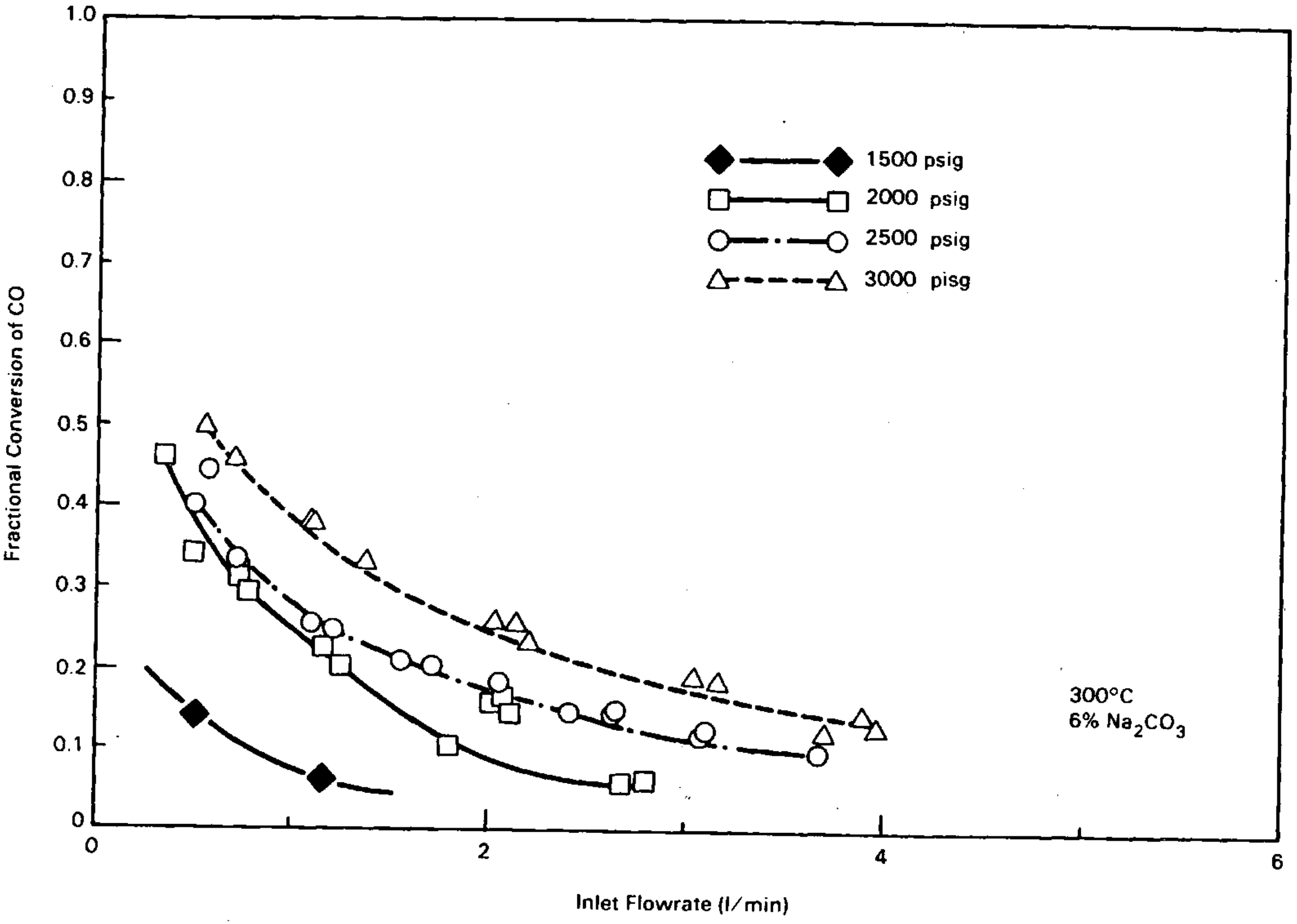

FIGURE 12. Effect of System Pressure on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 300°C

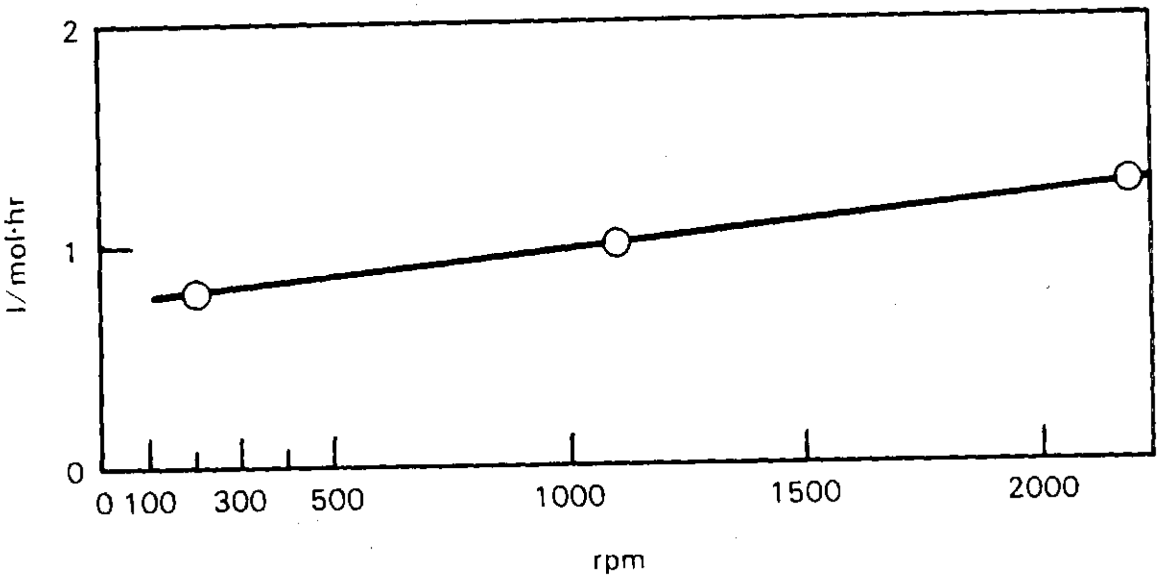

FIGURE 13. Effect of Agitation Rate on the Catalyst Turnover

to fit inside the reactor vessel. A 7.7% (by weight) solution of potassium carbonate was used as the catalyst in both experiments. One would expect that this change in the dip tube might have two potential rate-increasing effects; raising the gas temperature by increasing the heat transfer from the catalyst solution to the incoming gas, and increasing the mass transfer by decreasing the gas bubble size (which in turn creates a greater amount of contact area per unit volume of gas). While it was not possible to measure these changes directly, the net effect upon the observed reaction rate shown in Table 3 is so small that it is statistically insignificant.

TABLE 3. Effect of Dip Tube Size on Reaction Rate (7.7 wt. % potassium carbonate @ 250°C, 1000 psig total pressure)

length	4 inch	48 inch
diameter	0.25 inch	0.0625 inch
surface area	3.14 inch^2	9.42 inch^2
avg. rate	0.000315 mol/liter hr	0.000309 mol/liter·hr
avg. CO pressure	418 psig	397 psig

In light of the relatively small effect of both dip tube diameter and agitation rate on the reaction rate, it appears that mass transfer is not the primary rate-limiting mechanism. While this conclusion is quite reasonable for the small continuous stirred tank reactor used in these experiments, mass transfer limitations are nonetheless a major consideration for scale-up of the system (Bjurstrom 1985). The additional heating of the feed gas prior to its introduction to the reactor (which is an expected result of increased gas velocity and contact area inside the narrower, longer dip tube) appears to have no discernable effect upon the reaction rate. The effect of preheating the feed gas will be further discussed later in this report.

Catalyst Studies

Our proposed mechanism for the water-gas shift reaction in a pressurized aqueous system allows for a broad range of active catalytic materials, including essentially any carbonate, formate or hydroxide generating compound. Sodium carbonate is perceived to be among the least expensive of these and has been the focus of this investigation. Other compounds included in this study are sodium citrate, cadmium hydroxide, ammonium hydroxide and potassium carbonate. Figure 14 shows comparative results for these and the baseline uncatalyzed case at 300°C and 3000 psig. The potassium carbonate is not included in Figure 14 as it was tested at 250°C and 1000 psig. The potassium results suggest a doubling of the rate of reaction compared to the sodium carbonate (3.6-4.0 % conversion @ 0.28-0.22 l/min vs. 1.8% @ 0.26 l/min) at these conditions of low conversion. The comparisons are based on an equimolar charge of catalyst to the reactor. Since the volume of catalyst solution was maintained at a nearly constant level for all the catalysts studied, the concentration of the catalyst solution on a weight basis varied while the molarity remained nearly constant.

The catalytic compounds were not recovered in the same form as they were put into the reactor. As was pointed out earlier, the equilibrium in the carbonate-hydroxide-formate cycle strongly favors the formate at temperatures of 300°C and below in the presence of alkali metals. As a result the sodium and potassium carbonates are typically converted to formate during the initial stages of the experiment. In contrast, the cadmium hydroxide generates a gray precipitate similar to that found earlier in batch experiments with cadmium carbonate and formate (Elliott, Hallen and Sealock 1983). The precipitate appears to be a mixture of cadmium metal and cadmium carbonate (mixture properties included a density of 6.29 g/ml and infrared absorbancies typical of $CdCO_3$).

In the case of the sodium citrate, it apparently decomposed under the operating conditions and was not recoverable. The catalyst solution following the experiment contained primarily formate but substantial amounts of acetate and lactate were also present. The condensate recovered from the secondary condenser contained formic, acetic, and lactic acids in addition to an unidentified ketone or aldehyde which was the primary organic component. Although the effectiveness of the ammonia-based catalyst is demonstrated by the data in Figure 14, utilization of ammonium hydroxide as a catalyst poses an additional

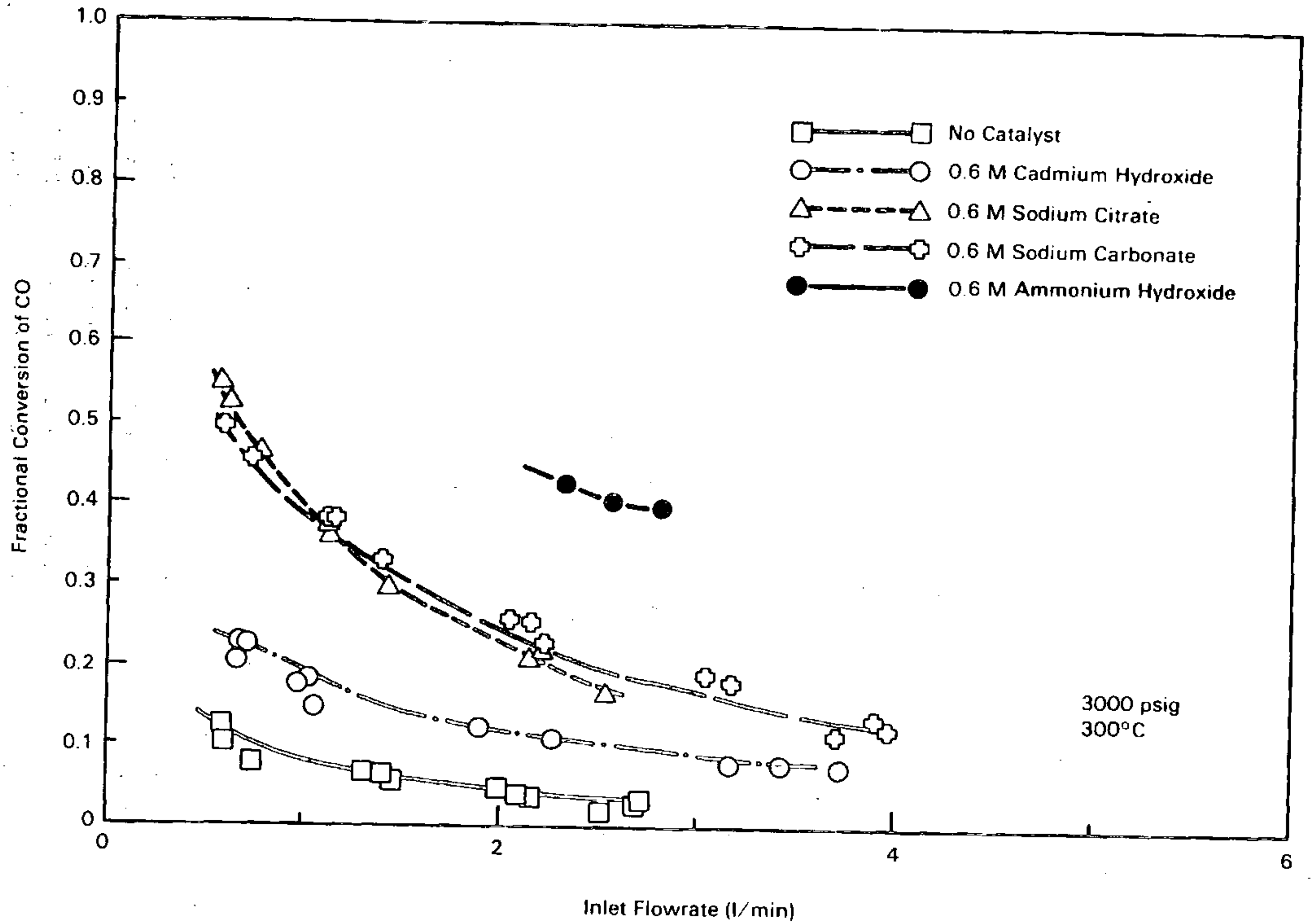

FIGURE 14. Effect of Catalyst on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction

problem due to its high volatility. The carryover of the ammonia into the secondary condenser (condensate at pH 9) indicates that a catalyst recycle stream will probably be required.

Use of Preheated Feed Gas

One means of circumventing the temperature-pressure limitations inherent in the pressurized aqueous system is to operate with a preheated feed gas where it is quenched by the aqueous catalytic bath. This approach to operation is more similar to the likely commercial application of our process than is the use of a cold feed gas. By preheating the feed gas to temperatures of 400 to 500°C the water-gas shift reaction rate should be greatly increased at the gas-liquid interface. However, the duration of this thermally enhanced reaction rate is limited due to the heat transfer between the two phases. The preheated feed gas operating mode is actually a competition between the rate of reaction and the rate of heat transfer.

The use of the gas preheater described in the experimental section allowed us to perform experiments with feed gas heated to 350-450°C. The hot gas was injected into the catalyst pool which was maintained at 200°C and 700 psig. The limited number of experiments performed with this system were plagued by plugging in the gas feed lines due to carbon deposition which occurred in the preheater, where wall temperatures of 600°C and pressures of 700 psig were present. The carbon formation was attributed to the reverse Boudouard reaction:

$$2\ CO \rightarrow C + CO_2 \tag{2}$$

Attempts to minimize this reaction included tests of different heat transfer packing materials to minimize catalytic effects and the use of dilute carbon monoxide containing streams. A combination of the use of alumina packing and a simulated fuel gas feedstock in conjunction with the injection of water upstream of the preheater allowed us to make three experiments with the preheated gas feedstock. It was determined that significant changes in the feed gas composition were occurring in the preheater prior to the water-gas shift reactor. Therefore, gas sampling between the preheater and the reactor was undertaken to assure that the effect of the water-gas shift reactor could be isolated and determined. Typical gas analyses for the three streams are given in Table 4:

TABLE 4. Typical Gas Analyses (corrected mole percent)

	feed gas	preheated gas	shifted gas
CO	12.6	7.3	6.6
CO_2	6.9	12.1	12.5
H_2	26.4	27.4	28.3
N_2	54.1	53.2	52.5

370°C gas feed to shift reactor at 200°C, 700 psig

Assuming that the amount of nitrogen leaving the shift reactor was the same as the amount entering the reactor, a mass balance around the shift reactor can be calculated. The calculation indicates that there is a 7.7% conversion of carbon monoxide by the water-gas shift reactor with a gas inlet temperature of 370°C and a gas outlet flow of 7.9 l/min. This conversion and flow are equivalent to 9.4 l/mol·hr (catalyst turnover), about the level of activity achieved at catalyst solution conditions of 295°C and 1500 psig with a cold gas feed at 0.5 l/min.

These results with the preheated gas feed should be considered with a diminished level of confidence relative to other results in this study. In order to overcome the preheater coking problem it was necessary to use a dilute stream of carbon monoxide. This gas was fed at higher than usual flow rates to obtain the required amount of heat transfer. The resulting changes in gas composition are of nearly the same order of magnitude as the uncertainty in the chromatography analysis of gas composition. Considering the potential for error in the calculations it is still useful to report that the catalyst turnover numbers ranged from 4.4 to 13.2 l/mol·hr with gas feed temperatures ranging from 353 to 430°C. Tests with higher feed gas temperatures were indicated, but were not feasible within the limitations of the existing equipment and restrictions of the project research schedule.

Phase Equilibrium Considerations

Even at moderate process temperatures, the use of an aqueous reactor system necessitates the use of relatively high pressures in order to maintain a liquid phase. The pressure-temperature diagram shown in Figure 15 clearly illustrates this need. The curve shown defines a phase boundary above which water will exist as a vapor rather than a liquid. Aqueous solutions of inorganic salts exhibit similar behavior, although the absolute magnitude of their vapor pressures is generally lower by an amount proportional to the salt concentration in the solution.

Developing an insight into the effect of sodium carbonate and other potential catalysts upon the phase behavior of their solutions is important to the understanding of the catalyst system under study. For most non-electrolytes (assuming negligible vapor pressures), this depression of vapor pressure may be estimated at low solute concentrations by the use of Raoult's law. The accuracy of Raoult's law suffers at high solute concentration and in solutions of highly polar salts such as those used as catalysts in this work. The effect of these materials on the solution vapor pressure is generally greater than would be predicted by the use of Raoult's law. More sophisticated approaches to modeling the pressure volume temperature behavior of electrolyte solutions exist (Chen et al. 1980), but the complexity of ionic solutions limits their applicability to well-characterized systems. Unfortunately, only limited published data exists for aqueous solutions of electrolytes, particularly at temperatures much above 100°C (Souririajan and Kennedy 1962). The lack of experimental data or applicable theoretical correlations made experimentation necessary.

The emphasis placed upon reaction kinetics in the original project plan did not justify the collection of extensive thermodynamic data; however, approximate data was needed for general design work and as a basis for future process evaluation. Low cost, limited precision experiments were indicated. A simple heated autoclave equipped with a pressure transducer constituted the experimental system. The autoclave was similar in most ways to the one used for the water-gas shift experiments, with the exception that it was operated in

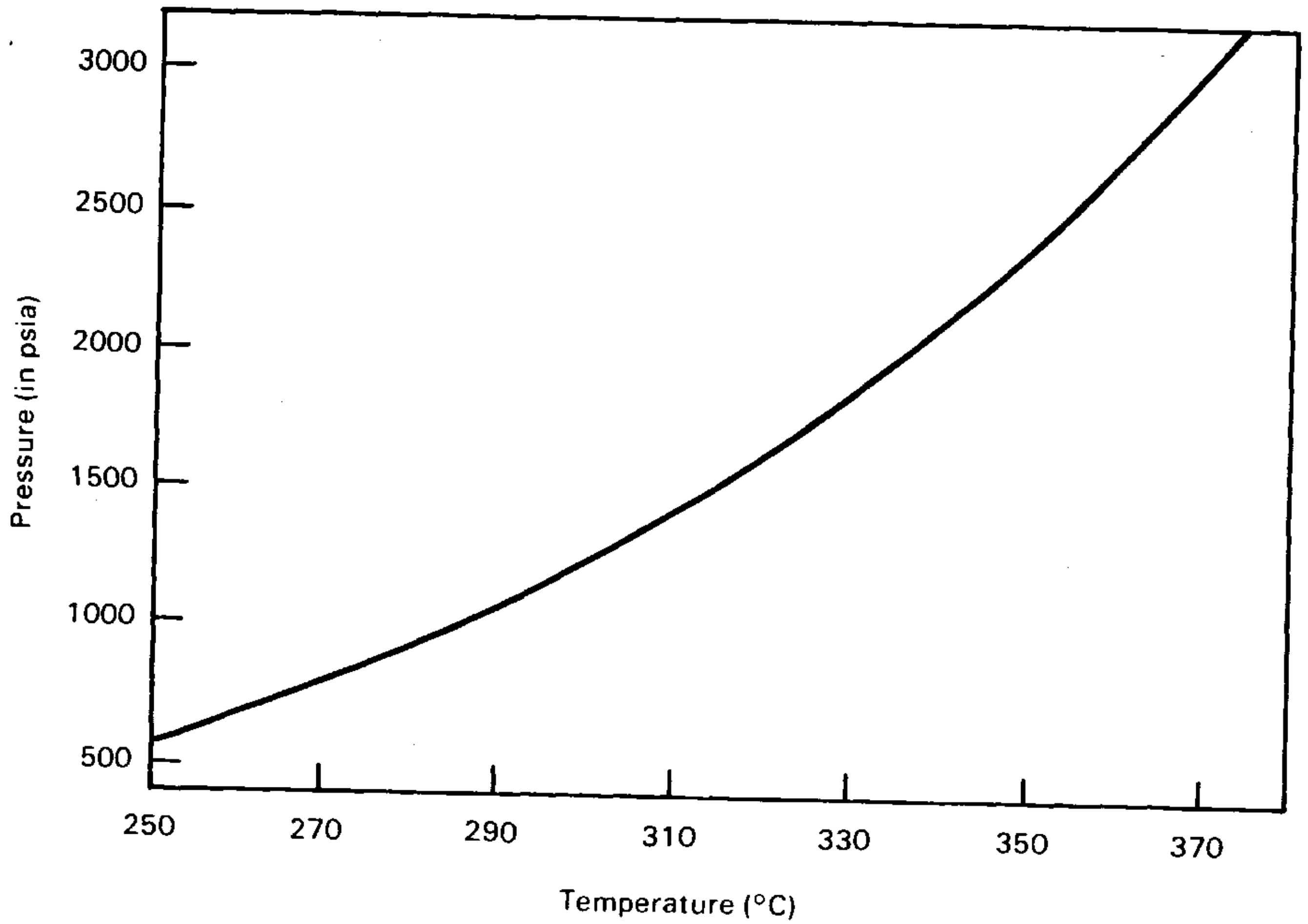

FIGURE 15. Pressure-Temperature Phase Diagram for Pure Water Adapted from the Steam Tables

a batch mode. In each experiment, the autoclave was filled with catalyst solution, sealed, and heated slowly to temperature. Pressure readings were taken every 10 degrees from 250 to 400°C. The experiment was repeated several times, with a range of solutes and solute concentrations. Some of the results are presented graphically in Figures 16 and 17.

The data is of limited accuracy and precision. Nonetheless, a few conclusions can be drawn from the experiments. For all solutes tested, vapor pressure depressions in excess of those predicted by Raoult's law were observed. Also, with sodium carbonate, the effect upon vapor pressure seemed to decrease with increasing temperature, possibly indicating a limit to solubility at high temperature. Finally, there are indications that the sodium formate solutions rapidly decomposed at temperatures above 300°C, liberating hydrogen gas. This last observation coincides with the proposed mechanism for the water-gas shift reaction under basic aqueous conditions.

All of the catalysts used in the vapor pressure studies dissociate into ions in aqueous solution. Because of this dissociation, one would expect that their effect upon solution vapor pressure would be underestimated by Raoult's law, which states that the vapor pressure of a solution of a non-volatile, non-electrolyte solid is lowered by an amount proportional to the decrease in solvent concentration. More precisely,

$$P(\text{solvent}) = y_{(a)} \; P_{(tot)} = x_{(a)}P_{(a)} \tag{3}$$

where P(solvent) equals the vapor pressure of the solvent over the solution, $y_{(a)}$ and $x_{(a)}$ represent the mole fraction of the solvent in the vapor phase and liquid phase, respectively; $P_{(a)}$ is the vapor pressure of the pure solvent. For practical purposes, one assumes that the solute exerts no vapor pressure so that $y_{(a)}$ is equal to unity.

Using Raoult's law, a 6 weight percent (1.07 mole percent solute, or 98.93 mole percent water) sodium carbonate solution should have a vapor pressure of 1229 psia at 300°C, while the observed value was 1205. This greater than predicted effect on vapor pressure is thought to be due to electrostatic forces

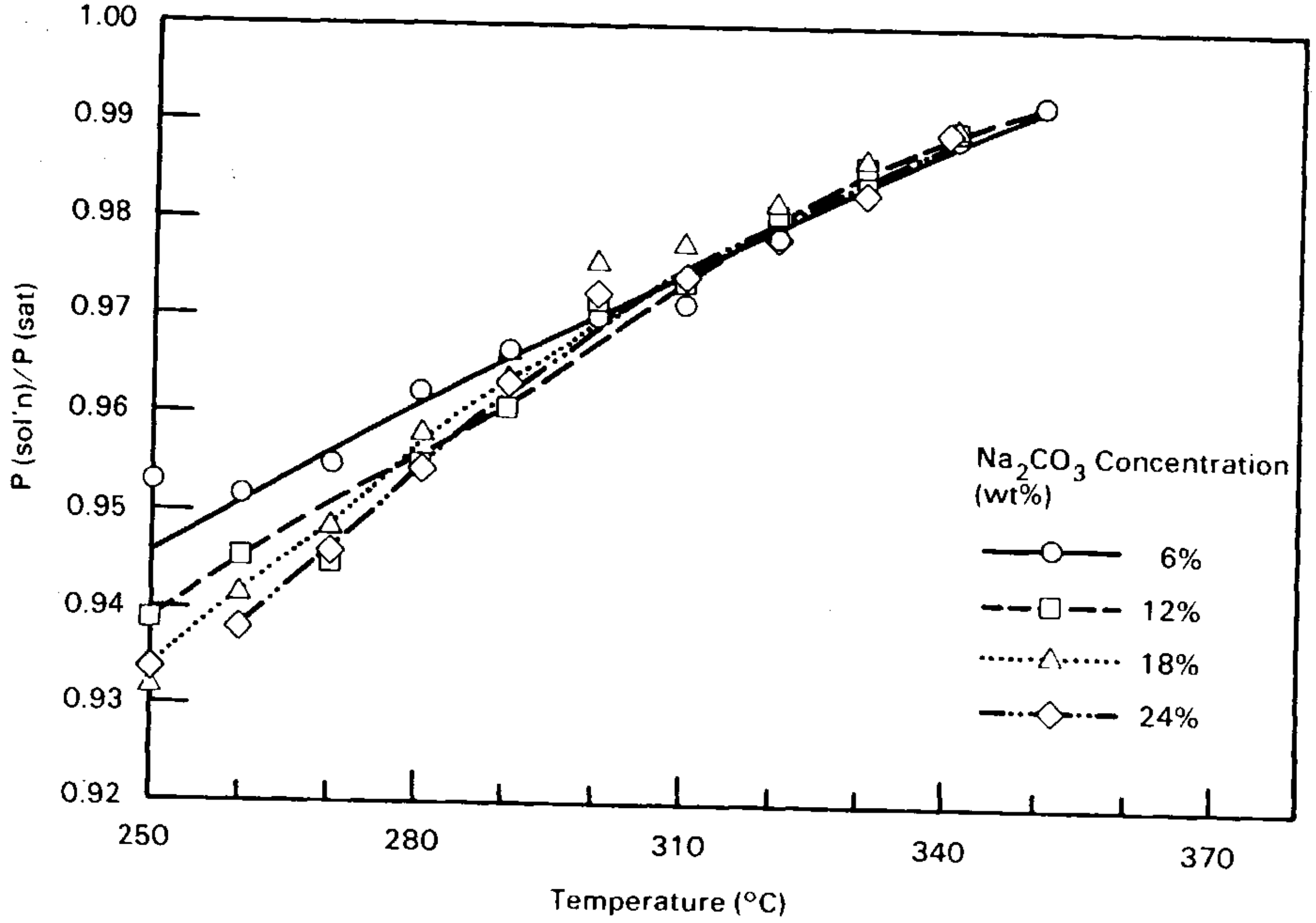

FIGURE 16. Effect of Initial Sodium Carbonate Concentration on the Vapor Pressure of Heated Solutions

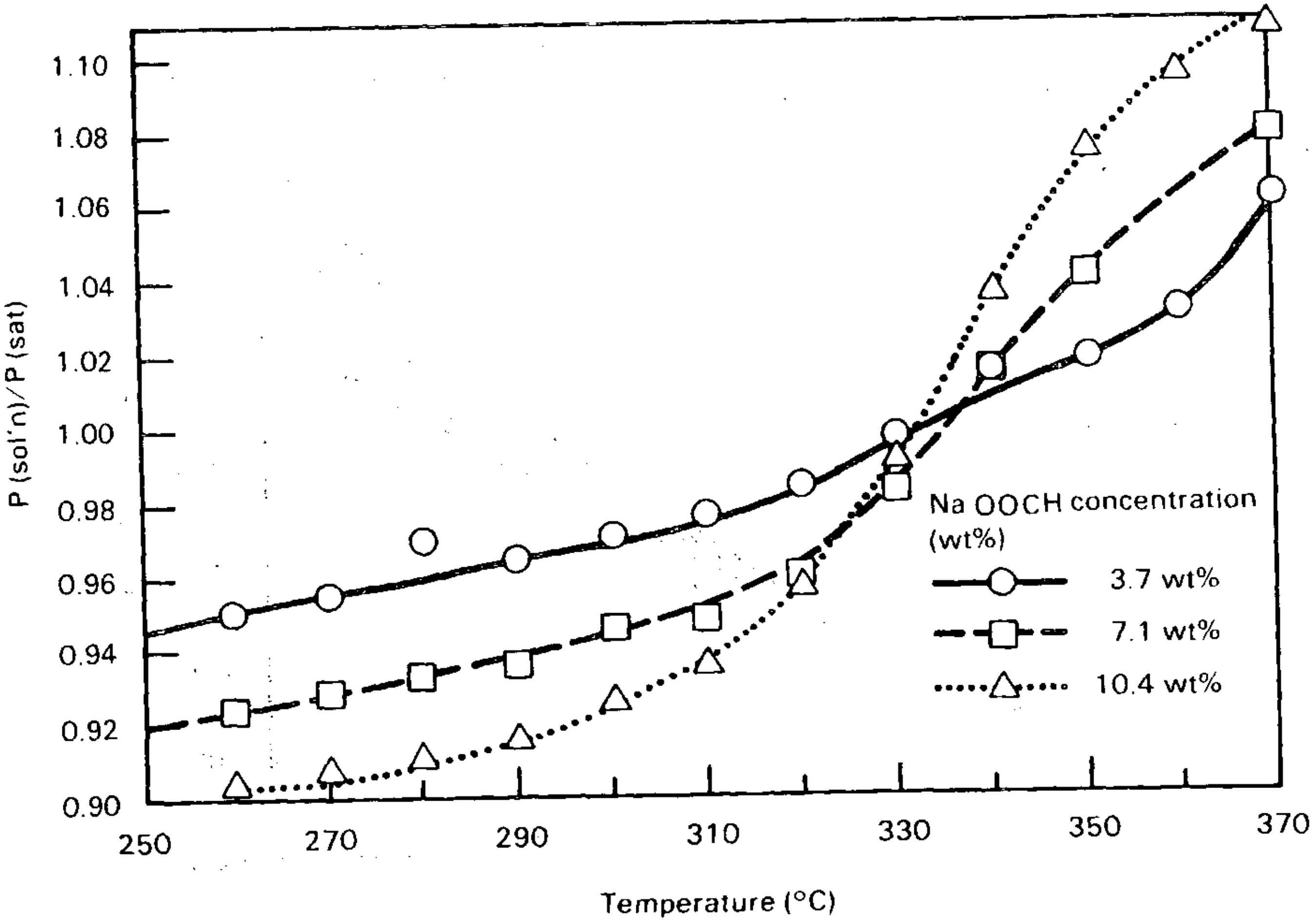

FIGURE 17. Effect of Initial Sodium Formate Concentration on the Vapor Pressure of Heated Solutions

between solvated ions. In practical terms, the vapor pressure reduction was of little benefit because even a 24 weight percent carbonate solution has a molar concentration of only 4.28%, and because the solubility of sodium carbonate is apparently limited to less than 24 weight percent at high temperatures. Thus, only a relatively small decrease in vapor pressure could be obtained at high temperatures, regardless of the initial sodium carbonate concentration.

Unlike many salts, the solubility of sodium carbonate in water decreases with increasing temperature. Taking into account Le Chatelier's principal, one could predict this behavior based upon the observation that a substantial amount of heat is liberated in the process of making up a solution of carbonate. Data taken at temperatures between 40 and 100°C confirms this (Perry and Chilton 1973). Nonetheless, the solubility of sodium carbonate in boiling water is still quite high (approximately 31% by weight, or 7.1 mole percent), certainly much higher than 3-6 weight percent.

At higher temperatures (and correspondingly higher pressures), the evidence suggests that the maximum solubility of sodium carbonate becomes quite limited. Convergence of curves of vapor pressure vs. temperature for several initial concentrations of sodium carbonate (see Figure 16) may be due to the precipitation of sodium carbonate from solution. Deposits of solid sodium carbonate found in the autoclave liner also seem to confirm this. While solubility data was not obtained for the system, it is believed that the solubility of sodium carbonate at 300-350°C is less than 6% by weight, based upon the convergence of the curves in Figure 16. This solubility limit may place an upper bound upon catalyst concentration within the water-gas shift reactor system, although the effect on solubility of converting the carbonate to formate is not yet known. Another possible explanation for the convergence of the curves is the decomposition of carbonate at high temperatures to form CO_2. No evidence of this decomposition was found.

The vapor pressure-temperature curves in Figure 17 also converge at elevated temperatures. Experimental evidence indicates that this convergence is not caused by solubility effects like those discussed above, but by decomposition of the formate ion at temperatures above 310°C. The detection of liberal amounts of hydrogen gas above the solution subsequent to heating offers substantial support to the conclusion that the formate is decomposing. Less direct evidence is provided by the observation that the curves diverge again at 340°C. Above this temperature, the pressure increases with increasing formate concentration, indicating that the amount of gas produced increased in proportion to the formate concentration. This independent observation of hydrogen production would seem to support the proposed reaction mechanism for the aqueous water-gas shift reaction (Elliott, Hallen and Sealock 1983).