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Effect of Carbon Dioxide on the
Kinetics of the
Fischer-Tropsch Synthesis on Iron Catalysts

by

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Abstract

A recently proposed kinetic expression applicable to feed ratios H_2/CO of about 0.8 or less correlates the synthesis rate by an equation containing an inhibition term for CO_2 and assumes that water vapor concentrations are too low to offer significant inhibition (Deckwer et al., 1986). Experimental studies here with synthesis gas of H_2/CO ratios of 0.67 to 0.72 to which CO_2 was added show, in contrast, that CO_2 is relatively inert and that the data are well correlated by an equation developed by Huff (1982) which contains an inhibition term for H_2O , but not for CO_2 . We suggest that the inhibition attributed to CO_2 was instead actually caused by H_2O formed by the reverse water-gas-shift reaction.

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Introduction

Under at least three sets of circumstances a concentration of CO₂ relatively high in comparison to that of water may be encountered in the synthesis gas in a Fischer-Tropsch reactor.

(1) In the current technology as practiced at Sasol H₂S, CO₂ and other impurities in synthesis gas from coal gasification are removed by a Rectisol unit, involving low temperature scrubbing with methanol at elevated pressure. The exit CO₂ content is about 1% and conversion does not exceed 60-70%, so possible CO₂ inhibition is unimportant here. However, there is interest in developing an alternate process for selectively separating H₂S and leaving most of the CO₂ behind (Astarita, et al., p. 387). Such a process could yield substantial savings, since the higher H₂S concentration facilitates subsequent conversion in a Claus unit and minimizes CO₂ loading in the solvent, reducing energy costs for solvent regeneration. This leads to the question of possible effects on the Fischer-Tropsch synthesis of higher synthesis gas CO₂ concentrations.

(2) Water is formed as a primary product of the Fischer-Tropsch reaction, but on most K-promoted iron catalysts this reacts rapidly by the water-gas-shift reaction to form H₂ and CO₂. Therefore, at high conversions, a substantial concentration of CO₂ may exist.

(3) If synthesis gas is generated from CH₄, a high H₂/CO ratio is produced, greater than the H/C ratio of products from the synthesis. From material balance and water-gas-shift equilibrium constraints, oxygen must be rejected from the

plant as H₂O rather than as CO₂, the case for low H₂/CO syngas. If CO₂ is readily available from associated flue gas or natural gas, it may be desirable to feed CO₂ and a high H₂/CO synthesis gas into the Fischer-Tropsch reactor. Further the endothermicity of CO₂ reactions can help balance the exothermicity of the Fischer-Tropsch reaction.

Rate of Synthesis

Except for one early publication discussed below, all the kinetic expressions that have been published until recently for the rate of synthesis assume that there is no inhibiting effect of CO₂ on the rate. The rate expression of Anderson (1956, p. 227), frequently referenced, is:

$$-R_{H_2+CO} = \frac{a P_{H_2} P_{CO}}{P_{CO} + b P_{H_2O}} \quad (1)$$

Anderson noted that for a fixed temperature the two constants showed a definite, but undisclosed, trend with feed gas composition.

Huff and Satterfield (1983), using a well-mixed continuous flow slurry reactor, more recently developed an improved rate expression:

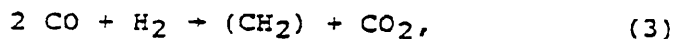
$$-R_{H_2+CO} = \frac{ab' P_{CO} P_{H_2}^2}{(P_{H_2O} + b' P_{CO} P_{H_2})} \quad (2)$$

In most previous kinetic studies the partial pressure of hydrogen did not vary significantly with conversion because the consumption of hydrogen was nearly offset by the reduction of gas volume accompanying the synthesis. Consequently the dependence of the rate on hydrogen pressure was not clearly established. In

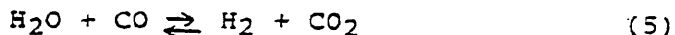
Equation (2), b' is a function of temperature only, but Equation (2) reduces to the form of Equation (1) if b in Equation 1 is inversely proportional to P_{H_2} . Both Equations (1) and (2) neglect possible inhibition by CO_2 and include that by H_2O only. Both equations reduce to the same form at low H_2O partial pressures.

The form of Equations 1 and 2 and a variety of experimental studies on iron catalysts show that CO and H_2O are strongly adsorbed onto iron catalysts and thereby inhibit the reaction. In an early paper Tramm (1952), in studies at $224-238^\circ C$ reported that addition of CO_2 in a fixed bed, gas phase reactor, with an iron catalyst, inhibited the conversion of $CO + H_2$, but the effect was less pronounced than that shown by an equivalent partial pressure of H_2O . As a very rough guide, Tramm's data suggested that water might have an inhibiting effect four times or so greater than CO_2 . In light of the present study we suspect that the inhibition they observed was not caused by CO_2 , but rather by water formed from CO_2 by the reverse water-gas-shift reaction (Equation (5)). In the development of Equation (2), the concentration of CO_2 did not seem to be an important variable, but conditions in which a high ratio of CO_2 to H_2O existed were not studied systematically.

Tramm (1952) and Brötz and Rottig (1952), all at Ruhrchemie A.G., Oberhausen-Holtten, presented expressions for the rate of consumption of CO in the Fischer-Tropsch synthesis, assuming that it proceeded by both



plus the water-gas-shift reaction,



Their expression is -

$$R_{\text{CH}_2} = k \cdot \frac{P_{\text{H}_2}^m}{P_{\text{CO}}} \cdot \frac{1}{\left[1 + c \left(\frac{P_{\text{CO}_2} + P_{\text{H}_2\text{O}}}{P_{\text{CO}} + P_{\text{H}_2}} \right)^n \right]} \quad (6)$$

where r is the rate of synthesis of "CH₂". The first ratio was taken to represent the intrinsic kinetics of the reaction in which $m = 1$ for Equation 3 and 2 for Equation 4. This kinetic expression is frequently reproduced incorrectly when referred to in subsequent publications by others. The water-gas-shift reaction was taken to be first order in H₂O and independent of CO.

It is now well established that CO₂ is formed by the water gas shift reaction rather than the primary synthesis. The quotient $P_{\text{H}_2}/P_{\text{CO}}$ in Equation 6 was formulated assuming that the reaction was proportional to the hydrogen surface coverage and inversely proportional to CO coverage; H₂ and CO coverages were assumed to be proportional to their respective partial pressures. It was also assumed that the structure of the catalyst changed as the gases in contact with it became more oxidizing in character (CO₂ and H₂O) and less reducing in character (CO + H₂). This effect was incorporated in their model by the parenthetical expression in the denominator with n taken to be between 5 and 7. These high values of n indicate that as the catalyst became more

oxidized its activity dropped greatly. No values of \underline{c} were reported.

Recently, Deckwer and co-workers have published three papers presenting kinetic studies obtained in a slurry reactor using either a fused magnetite catalyst or a precipitated iron catalyst promoted with K (Ledakowicz, et al., (1985), Deckwer et al., (1986), and Sanders and Deckwer, (1987)). Reaction conditions were in the general range of 220-260°C and 1 MPa for the fused catalyst. At H₂/CO inlet ratios of 0.8 and less, they concluded that water concentration was negligible on the basis of stoichiometric calculations, (Ledakowicz, et al., 1985), but this assumption was not tested experimentally. They correlated their data by the expression:

$$-R_{H_2+CO} = \frac{b_1 C_{H_2}}{1 + b_2 C_{CO_2}/C_{CO}} \quad (7)$$

This allows for inhibition by CO₂ and CO adsorption. Liquid-phase concentrations were used.

In terms of gas-phase partial pressures, an equivalent expression is:

$$-R_{H_2+CO} = \frac{ab P_{CO} \cdot P_{H_2}}{P_{CO_2} + b P_{CO}} \quad (8)$$

At higher inlet H₂/CO ratios or when water was introduced with the synthesis gas, it was found necessary to allow for water inhibition and the best correlation was obtained using the equivalent of Equation 2. A proposed kinetic expression containing inhibition terms for both H₂O and CO₂ was tried, but

found to be unsatisfactory.

Experimental

In view of the recommended correlation of Equation 7, it was desirable to examine possible inhibition effects of CO₂ by deliberately adding it to synthesis gas and analyzing for the actual water concentration present. Experiments were performed in a continuous-flow stirred autoclave reactor. We are not aware of any previous kinetic studies in recent years with deliberate CO₂ addition. A description of the apparatus and analytical procedures has been published (Huff and Satterfield, 1982a). By varying the synthesis gas flow rate, a wide range of conversion can be studied.

It is important in such studies to have good methods of analysis for H₂O and H₂ as well as CO, CO₂ and products. H₂O tends to tail in many g.c. columns, but we have worked out methods of determining it quantitatively (Huff, et al., 1983). H₂ is not detected in the g.c. apparatus, but is determined by a hydrogen transfer system through a palladium separator.

The catalyst used was reduced fused magnetite catalyst (United Catalysts Inc., C-73), so that results can be compared to a number of previously published studies on this catalyst. A subtlety that must be kept in mind in kinetic studies is that the form of the iron catalyst will change with reaction conditions (Satterfield, et al., 1986). Thus at high conversions the environment becomes more oxidizing and the ratio of oxide to carbide on the catalyst surface changes. This change in catalyst surface can affect the kinetics. Therefore, it is unclear

whether a change in gas composition affects solely the kinetics or both the kinetics and catalyst surface composition.

The slurry reactor was operated at 232°C and 263°C. The pressure was varied between 0.79 MPa (100 psig) and 1.48 MPa (200 psig) and flow between 0.6 and 3.6 NL/h/gFe. Material balances were conducted with synthesis gas alone, that had a H₂/CO feed ratio between 0.67 and 0.72, or with CO₂ added to comprise 20 or 50 mole % of the feed. To avoid sampling during transient reactor conditions, 24 hours were allowed to achieve steady state following a feed or pressure change and 48 hours following a temperature change. When CO₂ was added to the feed the total reactor pressure was increased so as to hold the inlet dry synthesis gas pressure constant. This was done to avoid dilution effects.

Only material balances having a 97-103% closure on oxygen were included in kinetic analysis. Returning to a given set of conditions periodically during the run indicated no significant loss in activity.

Kinetic Analysis

A comparison of Equation (8) and Equation (2) can be made by rearranging Equation (8) into the following form:

$$\frac{P_{H_2}}{-R_{H_2+CO}} = \frac{1}{C} + \frac{D}{C} \left(\frac{P_{CO_2}}{P_{CO}} \right) \quad (9)$$

Huff's equation (2), which allows for H₂O inhibition, but not CO₂, can be rearranged into

$$\frac{P_{H_2}}{-R_{H_2+CO}} = \frac{1}{A} + \frac{B}{A} \left(\frac{P_{H_2O}}{P_{H_2} \cdot P_{CO}} \right) \quad (10)$$

A large quantity of data obtained by Huff (1982) to generate Equation (2), without CO₂ addition, were used to compare Equation (8) and Equation (2) by plotting $P_{H_2}/-R_{H_2+CO}$ versus $P_{H_2O}/P_{H_2} \cdot P_{CO}$ or $P_{H_2}/-R_{H_2+CO}$ versus P_{CO_2}/P_{CO} . Plots of data at 232, 248 and 263°C were obtained. Those at 263°C are shown on Figures 1 and 2 as representative.

Both forms correlate the data, but a somewhat better fit is obtained by Equation (10) instead of Equation 9. A more stringent test is to examine presently-obtained data when CO₂ was added to the system in amounts of up to 50%. Figure 3 is a parity plot of present data compared to Equation (2) with the constants developed from earlier data by Huff (1982). At each of the two temperatures a two-fold variation in rate is covered. Water concentrations in the reactor ranged up to about 0.02 MPa. Figure 4 is a test of Equation (8) using the present data on fused magnetite with addition of CO₂. There is no effect of P_{CO_2}/P_{CO} on $P_{H_2}/-R_{H_2+CO}$ contrary to what would be expected from Equation (8). As a further test, Figure 5 for data at 263°C shows no effect of P_{CO_2} on $-r/P_{H_2}$ for CO₂ partial pressures up to 1.25 MPa. A similar lack of dependence on CO₂ was found at 232°C.

In contrast, Figure 6 presents data obtained by Hanlon (1985) at 248°C on fused magnetite, in which water was added to the synthesis gas. This showed a six-fold drop in $-R_{H_2+CO}/P_{H_2}$ as the partial pressure of H₂O in the reactor was increased from 0.04 MPa to 0.17 MPa. The figure in parenthesis beside each data point is the mole percent H₂O added to the feed.

A test was also made to see if an equation containing inhibition terms for both H₂O and CO₂ might give a more satisfactory correlation, using Huff's data (Huff, 1982). Multilinear regression was performed on a model of the form

$$\frac{P_{H_2}}{-R_{H_2} + CO} = A + B \left(\frac{P_{H_2O}}{P_{H_2} \cdot P_{CO}} \right) + C \left(\frac{P_{CO_2}}{P_{CO}} \right) \quad (11)$$

The results of the regression (44 data points) were:

T (°C)	A ¹ (MPa·gcat·min/mol)	B ¹ (MPa ² ·gcat·min/mol)	C ¹ (MPa·gcat·min/mol)	R ²
232	0.764 ± 0.11	0.983 ± 0.42	0.113 ± 0.10	0.90
248	0.434 ± 0.07	0.235 ± 0.08	0.031 ± 0.04	0.97
263	0.325 ± 0.08	0.093 ± 0.01	-0.006 ± 0.01	0.94

¹coefficient ± standard error of coefficient.

The standard errors of the coefficients B and C indicate that B is statistically more significant than C. Further, C is not statistically significant and has no physical significance at high temperatures.

It should be noted that P_{H₂O}/P_{H₂}·P_{CO} correlates highly with P_{CO₂}/P_{CO}:

T (°C)	R ²
232	0.87
248	0.95
263	0.92

Physically, this probably stems from the water-gas-shift equilibrium,

$$K_{WGS} = \frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}} \quad (12)$$

If the water-gas-shift reaction is at or close to equilibrium, then

$$\frac{P_{H_2O}}{P_{H_2} \cdot P_{CO}} = \frac{1}{K_{WGS}} \cdot \frac{P_{CO_2}}{P_{CO}^2} \quad (13)$$

The term P_{CO_2}/P_{CO}^2 is equal to Deckwer's inhibition term multiplied by $1/P_{CO}$. The two terms are therefore closely related.

The water-gas-shift equilibrium was closely attained here with the fused magnetite catalyst, as shown by Figure 7. It should be noted that equilibrium water vapor concentrations are relatively low compared to that of CO_2 . We conclude that the inhibition attributed to CO_2 in Equation (7) was instead caused by water formed from CO_2 by the reverse water-gas-shift reaction. Inhibition effects by H_2O swamp those possibly caused by CO_2 .

* * *

Acknowledgement

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Figure Captions

- Figure 1 Correlation of rate data in terms of inhibition by H_2O . Data of Huff (1982). $263^\circ C$.
- Figure 2 Correlation of rate data in terms of inhibition by CO_2 . Same data as in Figure 1.
- Figure 3 Parity plot comparison of present data with prediction from Equation (2). Solid line gives predicted values.
- Figure 4 No effect of P_{CO_2}/P_{CO} on $P_{H_2}/-R$, contrary to that expected from Equation (7). Present data.
- Figure 5 No effect of P_{CO_2} in reactor vapor on $-R_{H_2}/P_{H_2}$. Present data, $263^\circ C$, 25-70% conversion.
- Figure 6 Marked inhibition effect of H_2O in reactor vapor on $-R_{H_2}/P_{H_2}$. Data of Hanlon (1985), $248^\circ C$.
- Figure 7 Approach of reactor vapor concentrations to the water-gas-shift equilibrium. Present data.

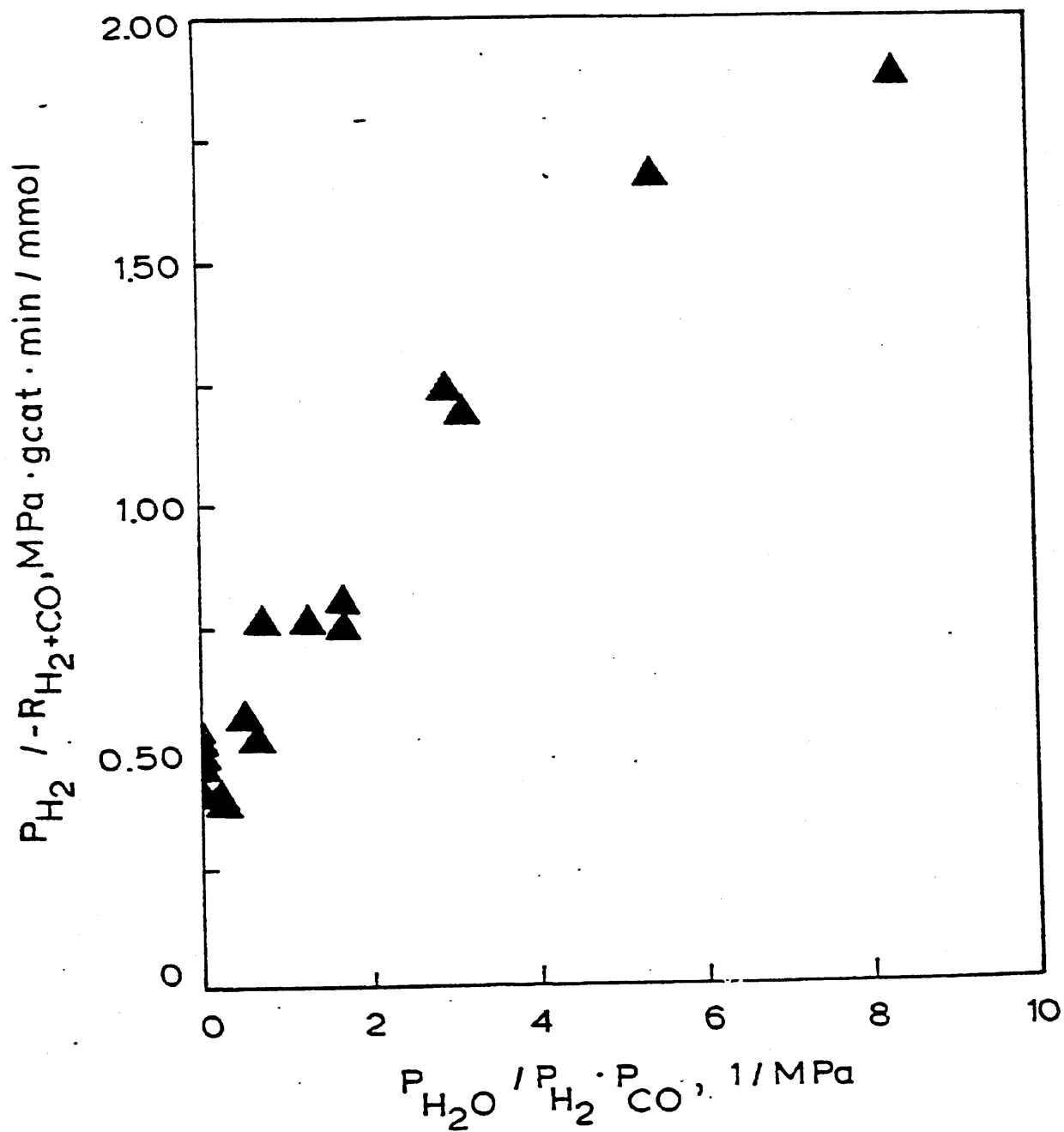


Figure 1

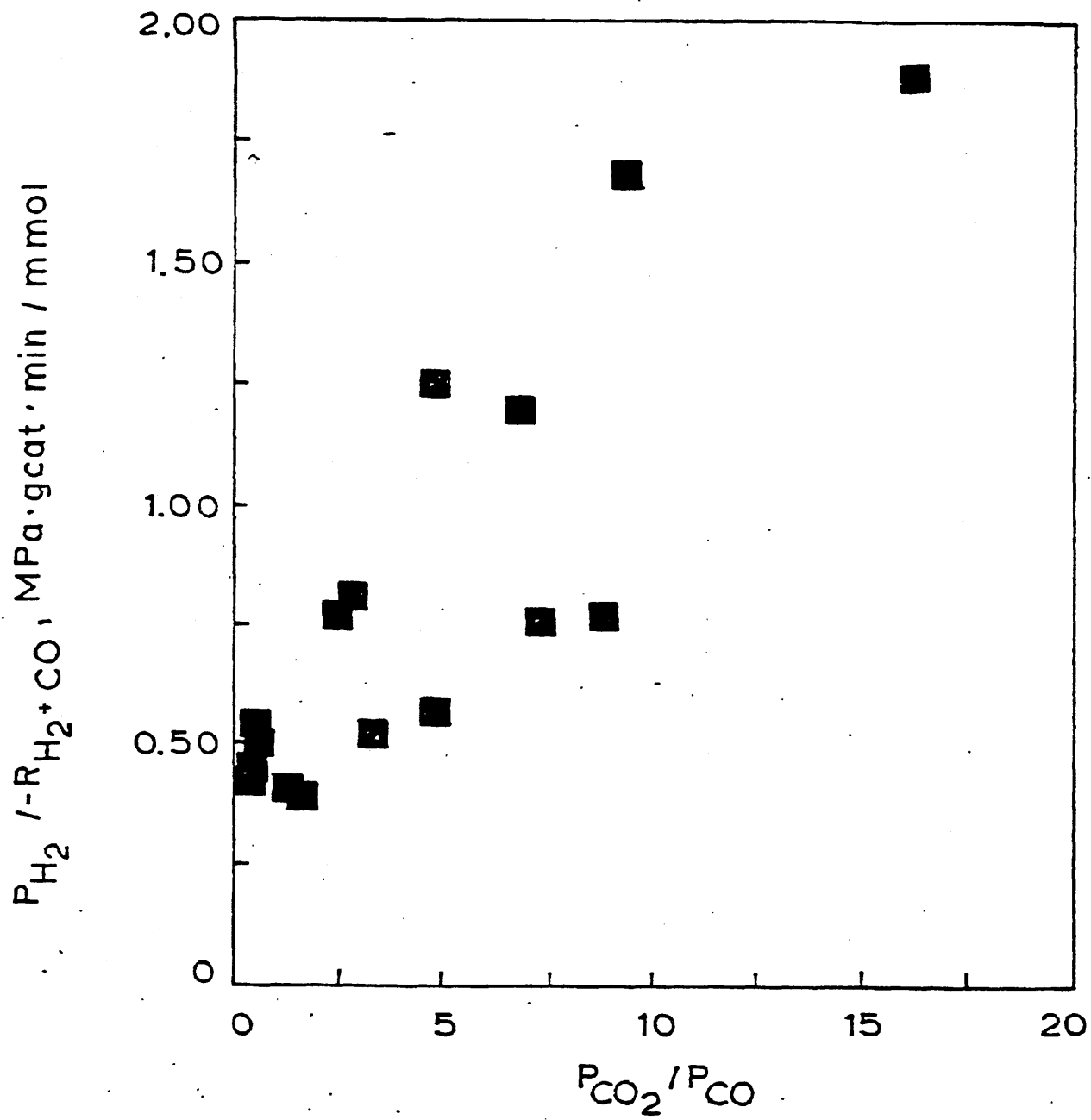


Figure 2

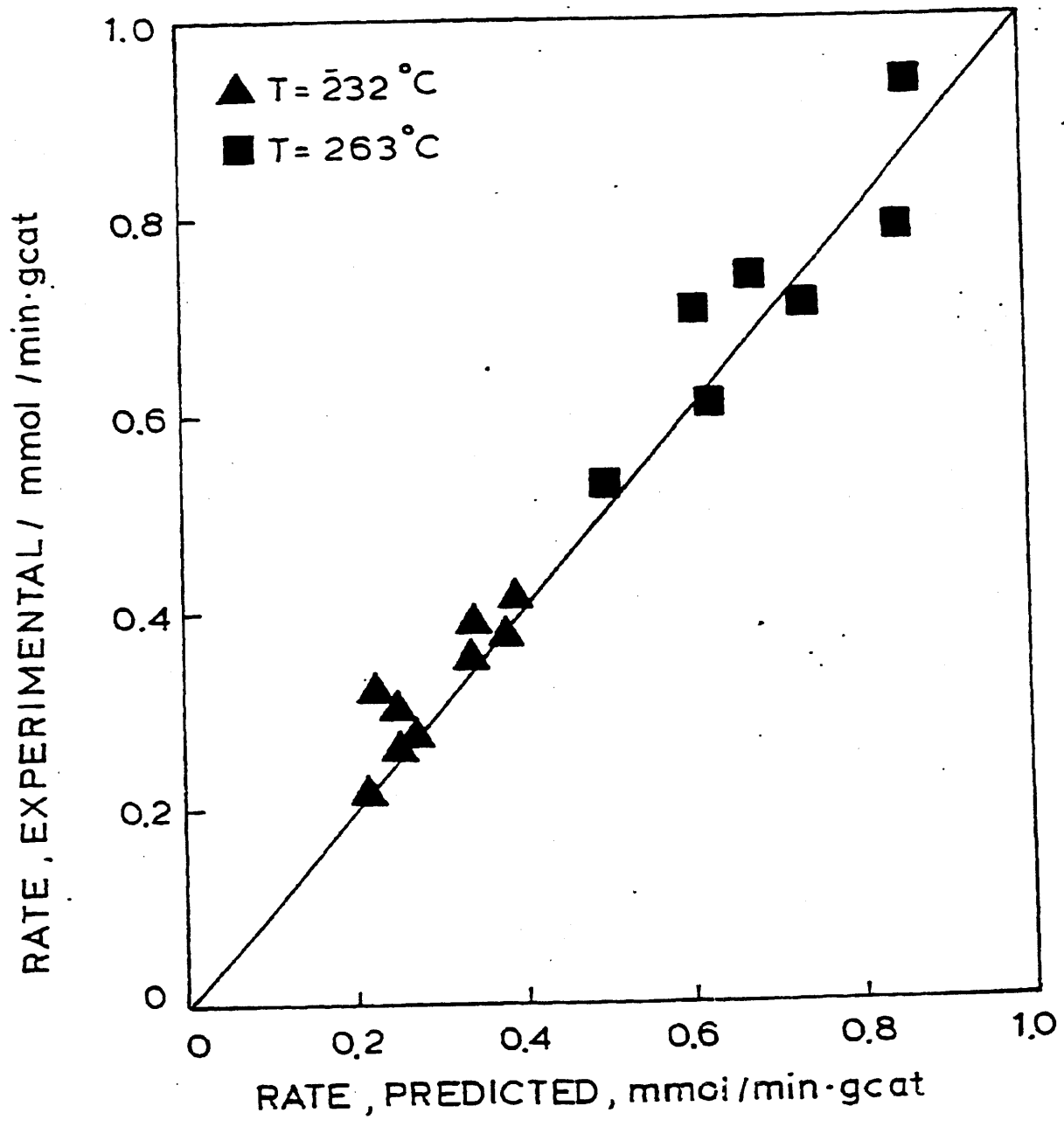


Figure 3

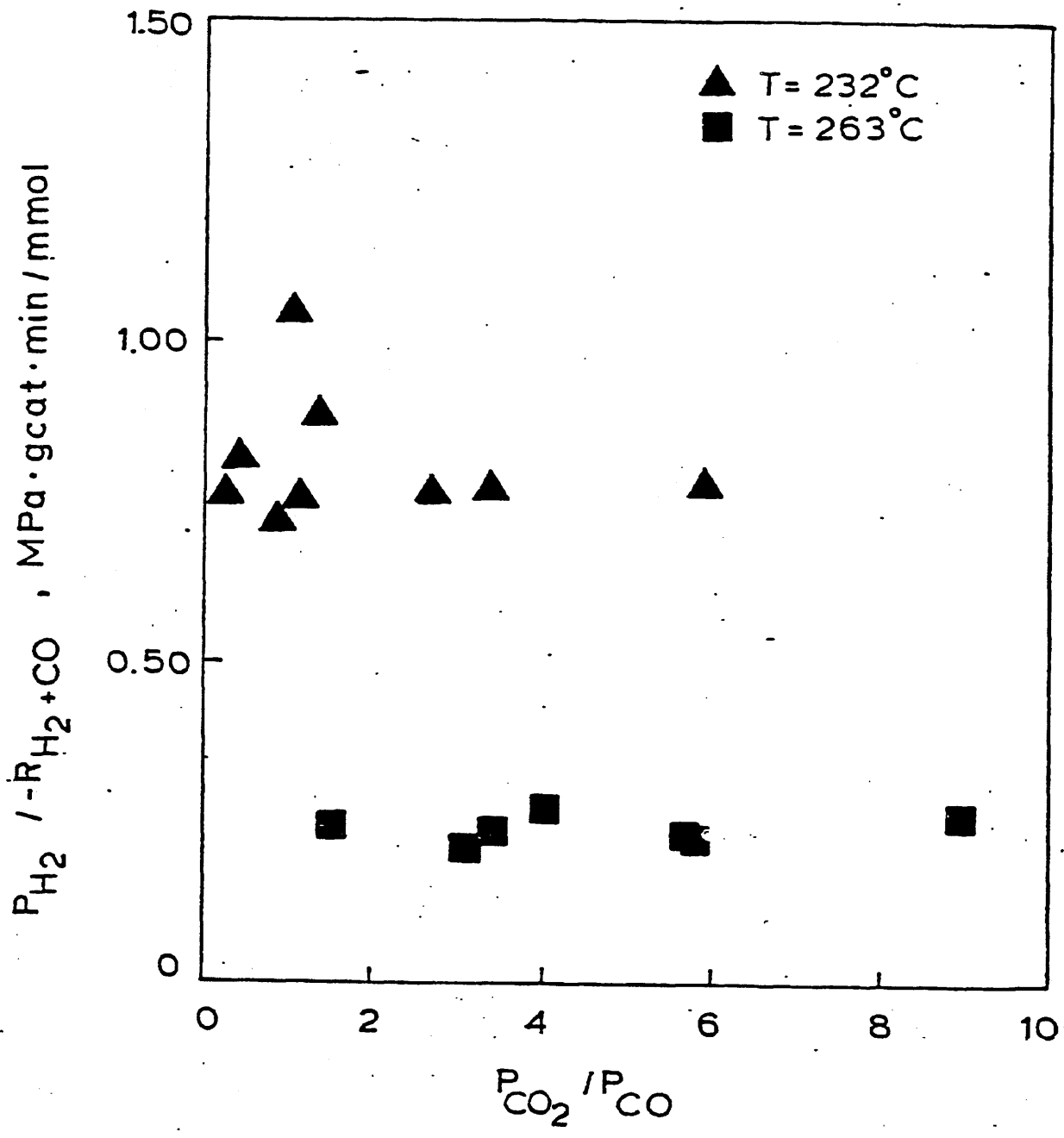


Figure 4

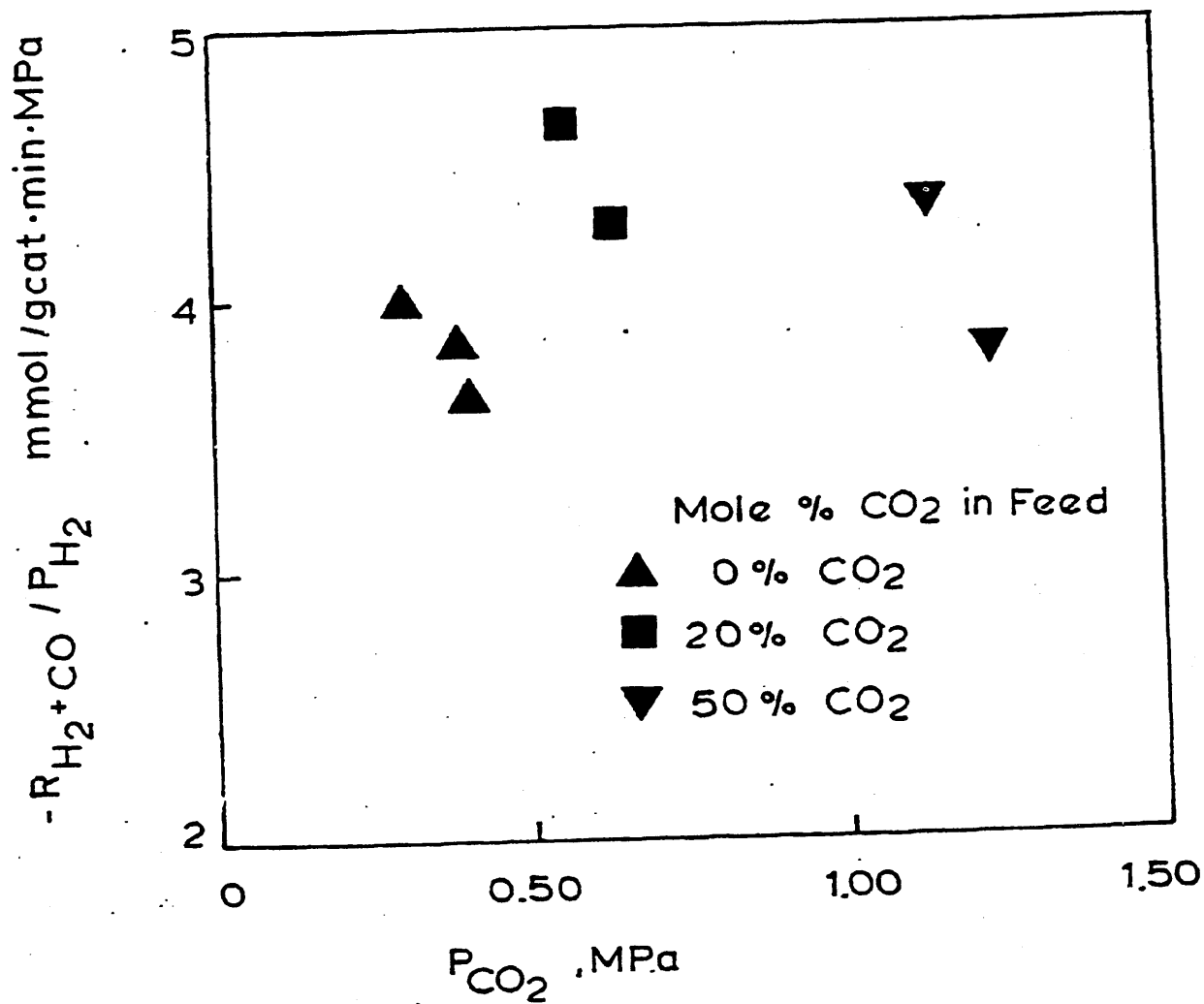


Figure 5

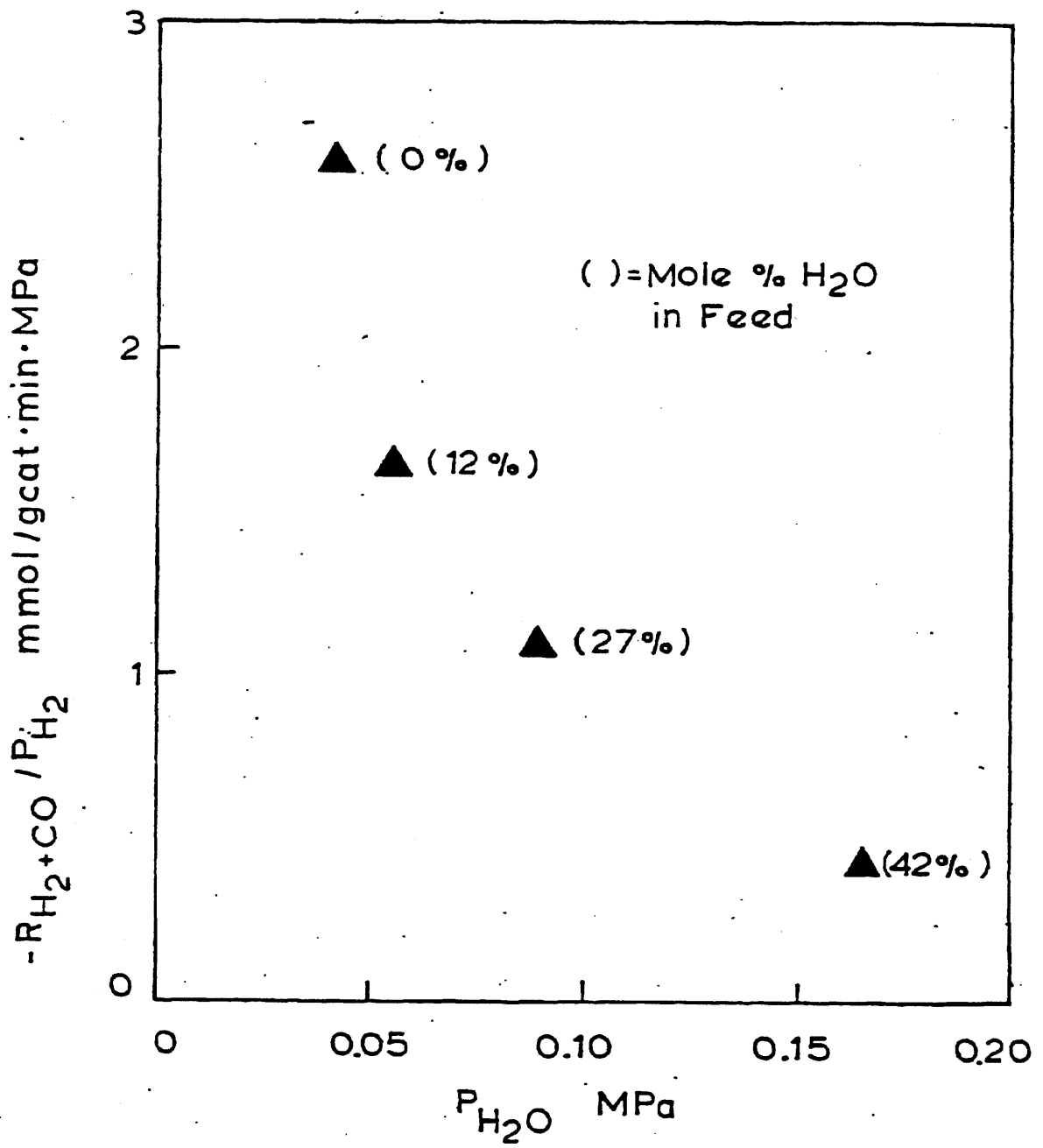


Figure 6

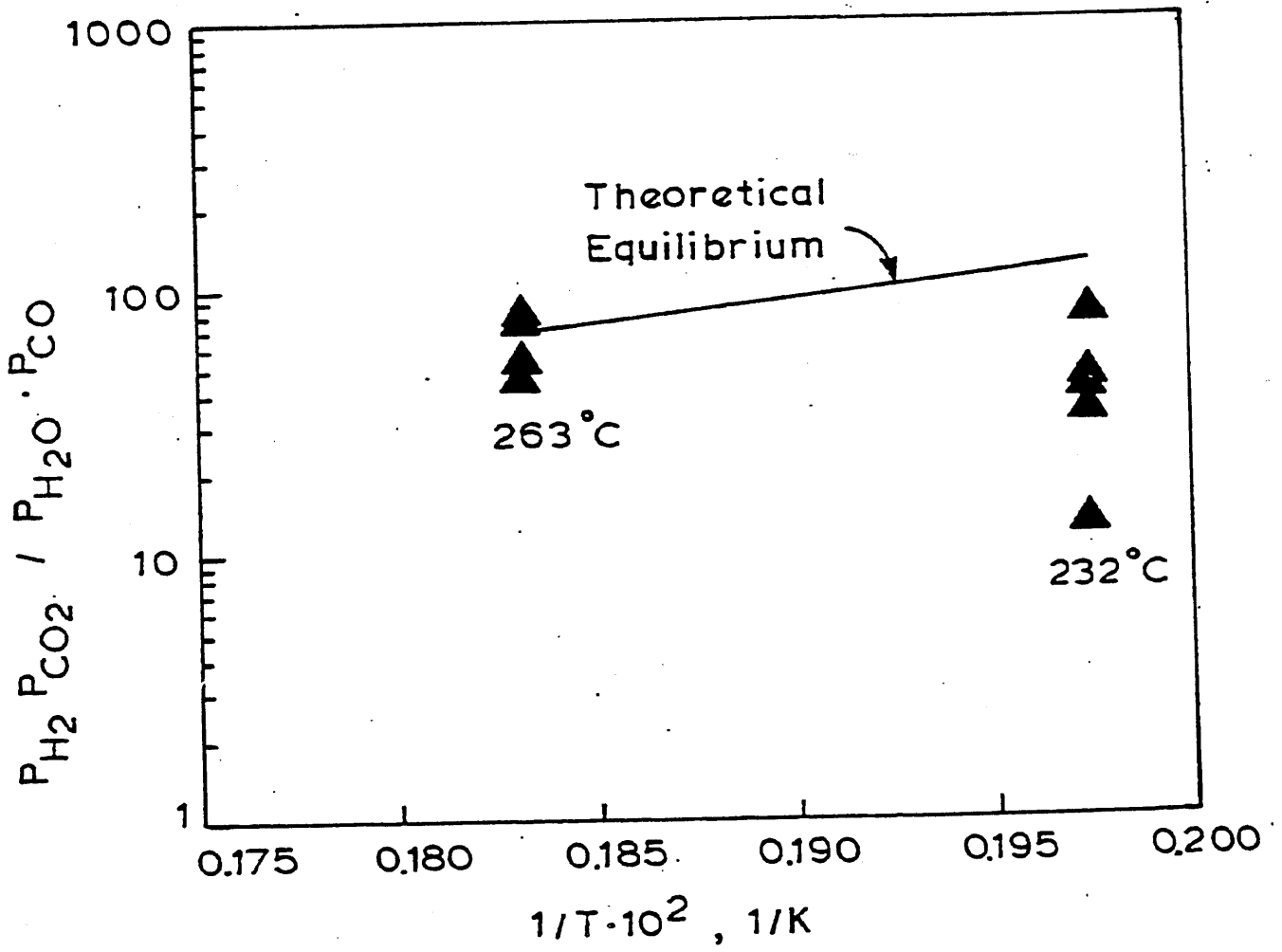


Figure 7