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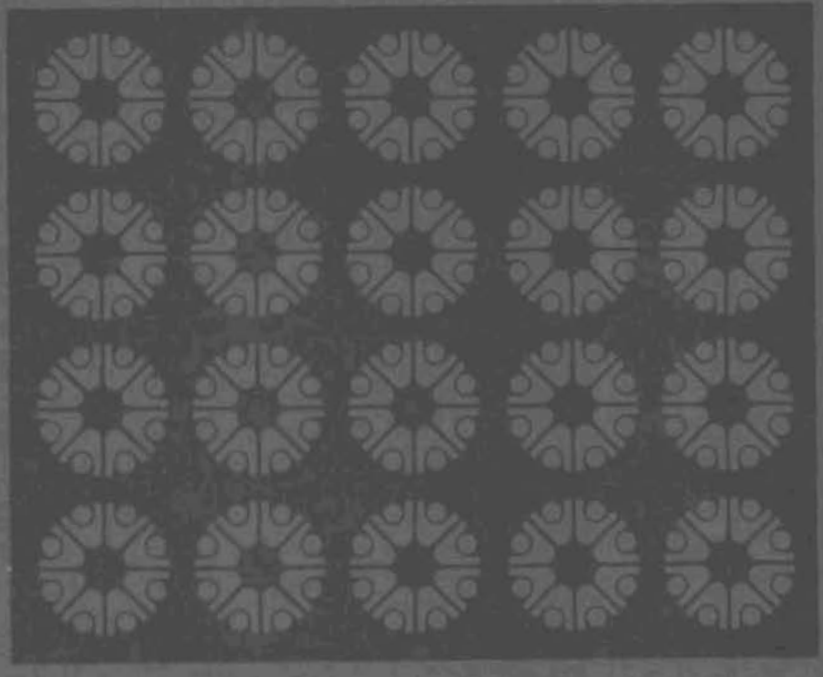
RADIOLYSIS OF HELIUM DILUTED MIXTURES OF CARBON MONOXIDE AND WATER VAPOR

JUNE 1972



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RADIOLYSIS OF HELIUM DILUTED MIXTURES OF CARBON MONOXIDE AND WATER VAPOR

By

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Ceramics and Graphite Section
Fuels and Materials Department

June 1972

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INTRODUCTION

The so-called water-gas shift reaction ($H_2O + CO \rightleftarrows H_2 + CO_2$) is of importance to the High Temperature Gas-Cooled Reactor (HTGR), which is graphite moderated and helium cooled. In a reactor, the total reaction may be conveniently considered as driven by an energy source composed of thermal and radiation components. At temperatures below approximately 500°C, the thermal reaction is not significant and the radiolytic reaction can be directly monitored. This report describes the results of a kinetic investigation of the radiolysis of mixtures of CO and H_2O in 1 atm of helium. The equimolar concentrations studied covered the range 10-940 vpm and results may be extrapolated with some confidence to the slightly lower concentrations expected in HTGR systems.

Although there has been considerable effort towards an understanding of the radiation chemistry of water and water vapor, there is little known about the radiolysis of mixtures of gases and less yet about the effects of dilution on the reaction kinetics. That the chemistry of radiation induced reactions is complex cannot be overemphasized. The variables to be considered in a meaningful study include impurities at a level ordinarily ignored, and possible surface catalysis by the containment vessel. Reported G values (molecules/100 eV) for the irradiation of pure water vapor, for example, vary over the incredible range from 0.015 to 5.9; the variability being explained as due to lack of control over the variables mentioned above.[1]

There have been some previous studies of the effect of inert gases on radiolytic reactions.[2] Sensitization by the inert gas is generally observed and is usually explainable in terms of charge or energy transfer from the inert gas to the reactive gases. Increased reactivity has, however, been observed in some cases even when the ionization potential of the inert gas is lower than that of the reactive gases and it is possible that the mechanism may be more complex than a simple energy exchange. Investigations of direct relevance to the current results include work by Tingey and co-workers[3-5,6,9] and a dissertation by Steinmann[7] on the radiolytic reaction of CO + H_2O both in the presence and absence of foreign gases. It was concluded from the latter work that the mechanism is essentially that obtained in the thermally induced reaction and was described by the rate expression:

$$\frac{dCO_2}{dt} = k[H_2O][CO]^{1/2}$$

Contrary to both previous and present results, Steinmann found $G_{CO_2}/G_{H_2} \rightarrow 1$ as $[CO] \rightarrow [H_2O]$. In an earlier study,[3] the radiolysis of a mixture of CO_2 and H_2 was investigated as a function of various diluting inert gases. Sensitization was observed in all cases and was described as due to charge exchange and excitation transfer mechanisms. The radiolysis of CO + H_2O was also investigated[3,4] as a function of He dilution but only to $[H_2O] \sim [CO] = 1500$ vpm. The present results are an extension to lower concentrations and various temperatures, $T < 500^{o}C$.

EXPERIMENTAL

The cobalt-60 source used in these experiments, which provides 1.33 and 1.17 MeV gamma rays, has been described earlier.[8] Dose rates were calculated assuming a 5.24 year half life for ^{60}Co following an earlier specific activity determination by methane dosimetry.[9]

The experimental apparatus is shown schematically in Figure 1. An open flow system was employed with flow rates in the range 30-180 cm^3/min. (standard temperature and pressure) giving product yields typically < 2% of the reactants. Commerically analyzed 940 vpm CO in He gas was passed over water maintained at $-21^{\circ}C \pm 0.5^{\circ}C$ in a large capacity refrigerated bath, thereby fixing water vapor pressure at approximately 940 vpm. The equimolar CO + H_2O mix was then diluted as desired with pure He, the dilution being determined roughly by a measurement of respective flow rates and more accurately by a direct chromatographic determination of the CO concentration. The mixed gas then passed through the quartz reaction bulb whose temperature was controlled to $\pm 5^{\circ}C$ using a Honeywell proportional controller. Following radiolysis, water vapor was removed from the gas before injection into the chromatograph by a dry ice-alcohol trap to prevent rapid moisture buildup on the chromatograph columns. The effluent gas was analyzed using a Varian Model 1532-2B Trace Gas Analyzer using He ionization detectors and molecular sieve packed columns. The unit was calibrated periodically using calibrated gas mixtures and an exponential dilution technique. Products of the reaction analyzed included CO_2, H_2, and CH_4, and CO, O_2, and N_2 could also be determined. Product yields were generally in the range 0.1-10 vpm. The instrument was reproducible to within 5% as determined by consecutive calibration experiments. Temperatures were measured using a "Rubicon" potentiometer (to 0.01 mv) and chromel-alumel thermocouples. The couple used for the refrigerated bath temperature measurement was checked at the freezing points of CO_2 and H_2O (-78 and $0^{\circ}C$) and the boiling point of water and found to be accurate to within $0.5^{\circ}C$.

Data were taken both isothermally by varying dilution and at constant dilution as a function of temperature, giving equivalent results, within the limits of error. Yields (G = molecules/100 eV) were not appreciably affected by variation of flow rates over the range employed.

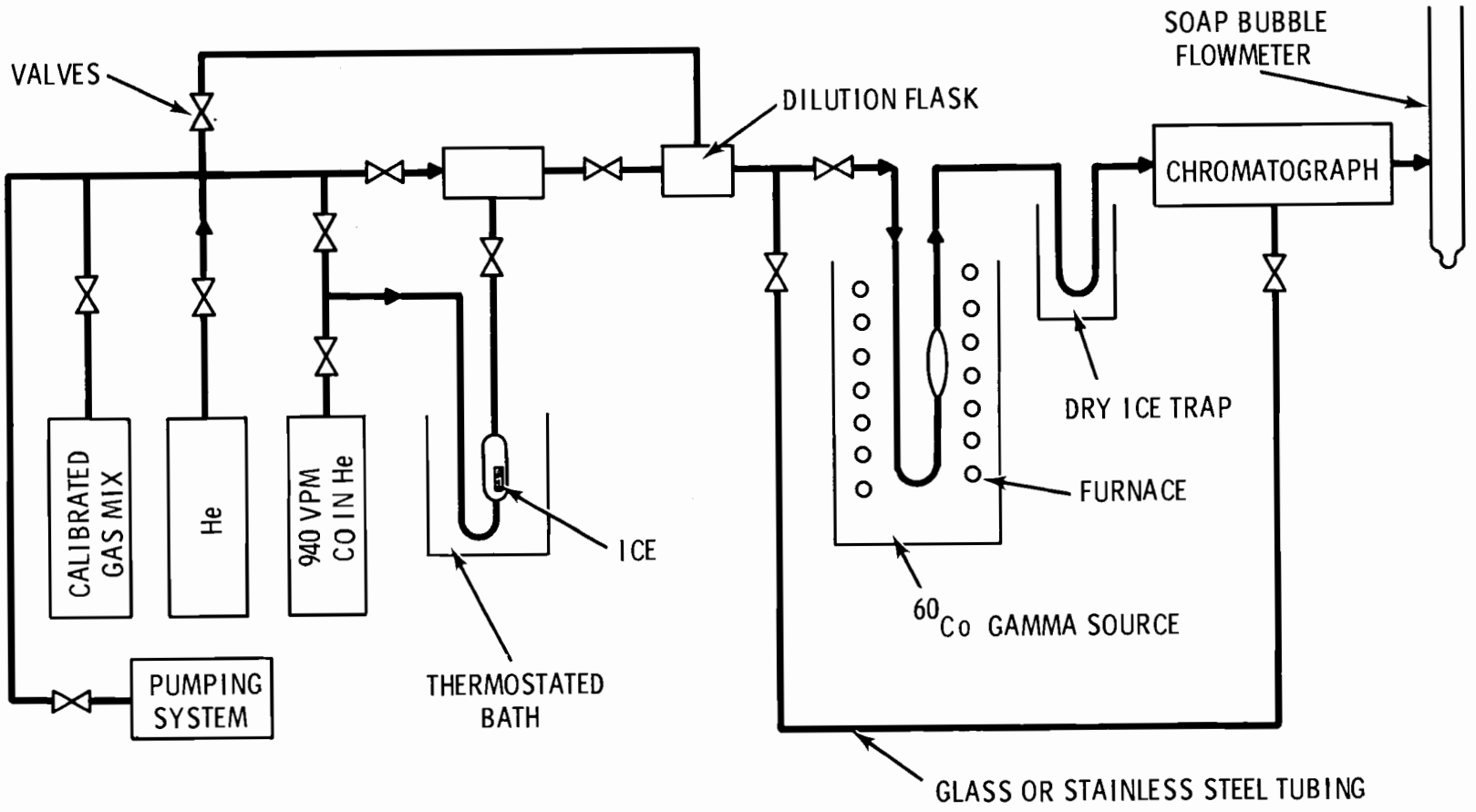

FIGURE 1. Experimental Apparatus for Gas Phase Radiolysis.

RESULTS AND DISCUSSION

The primary objective of this investigation was the accumulation of sufficient data to write a rate expression of the radiolysis reaction. A theoretical consideration of various equations which can be applied to such gas phase reactions* suggests, in this case, that the collision theory best describes the data:

$$d[CO_2]/dt = B\ T^{1/2}\ e^{-E/RT} \qquad (1)$$

Accordingly, a plot of $\ln [(d[CO_2]/dt)/T^{1/2}]$ versus $1/RT$ should be linear with slope (-E) as given in Figures 2 through 7 for equimolar concentrations of 10, 65, 100, 240, 465, and 940 vpm, respectively. Both major products (H_2 and CO_2) are plotted. The methane yields which are not shown, were low (approximately 0.5 ppm) and did not vary with temperature within the limits of measurement in agreement with previous work.[4] The data were fit by the method of least squares to equations of the form:

$$\ln (G/T^{1/2}) = (-E)(10^3/RT) + b$$

The constants and standard deviations obtained are listed in Table I. The trend to more negative activation energies with increasing dilution is quite clear as shown by the averaged values in Figure 8. It is to be noted that this concentration dependence is independent of the treatment employed to obtain the activation energy (see Appendix I for details.).

Considering the data isothermally (275°C), the yields are shown to vary regularly with concentration in Figure 9. We have used log (x) as a convenience rather than for theoretical or other reasons. While it is obvious that the so-called sensitization of the reaction cannot maintain

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* See Appendix I.

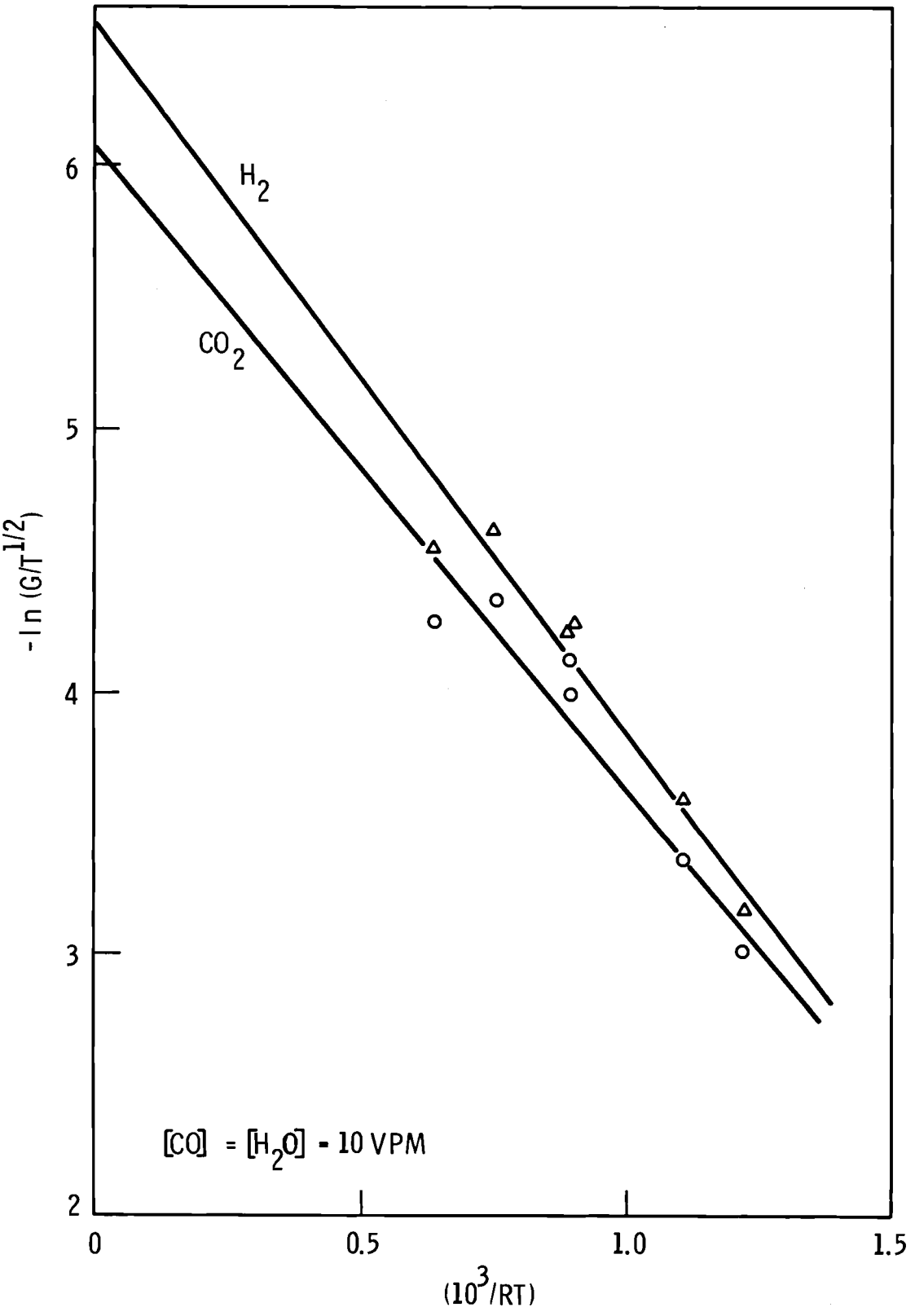


FIGURE 2. Product Yields Plotted as ln ($G/T^{1/2}$) versus $10^3/RT$ for 10 VPM Reactants.

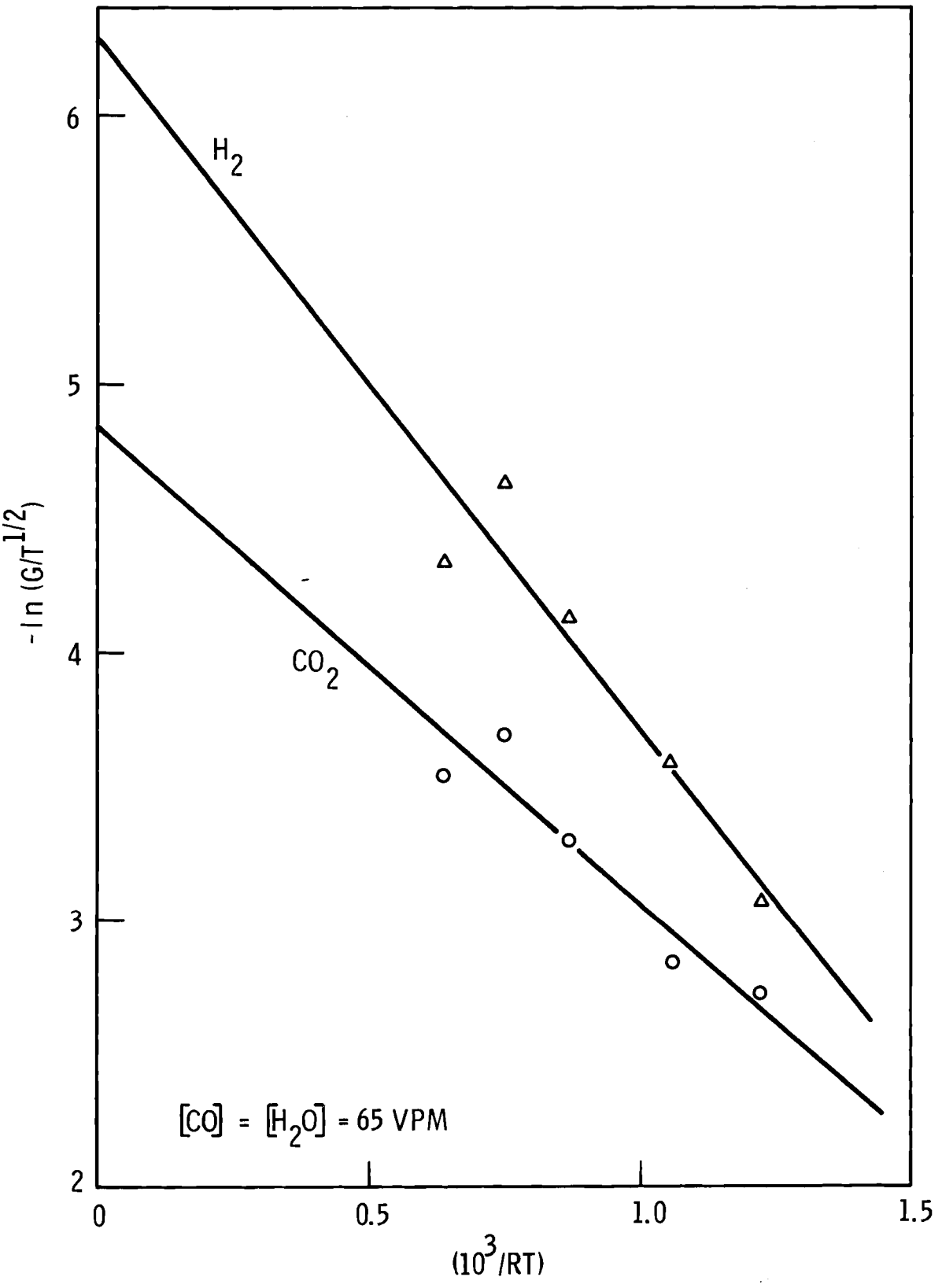


FIGURE 3. Product Yields Plotted as ln $(G/T^{1/2})$ versus $10^3/RT$ for 65 VPM Reactants.

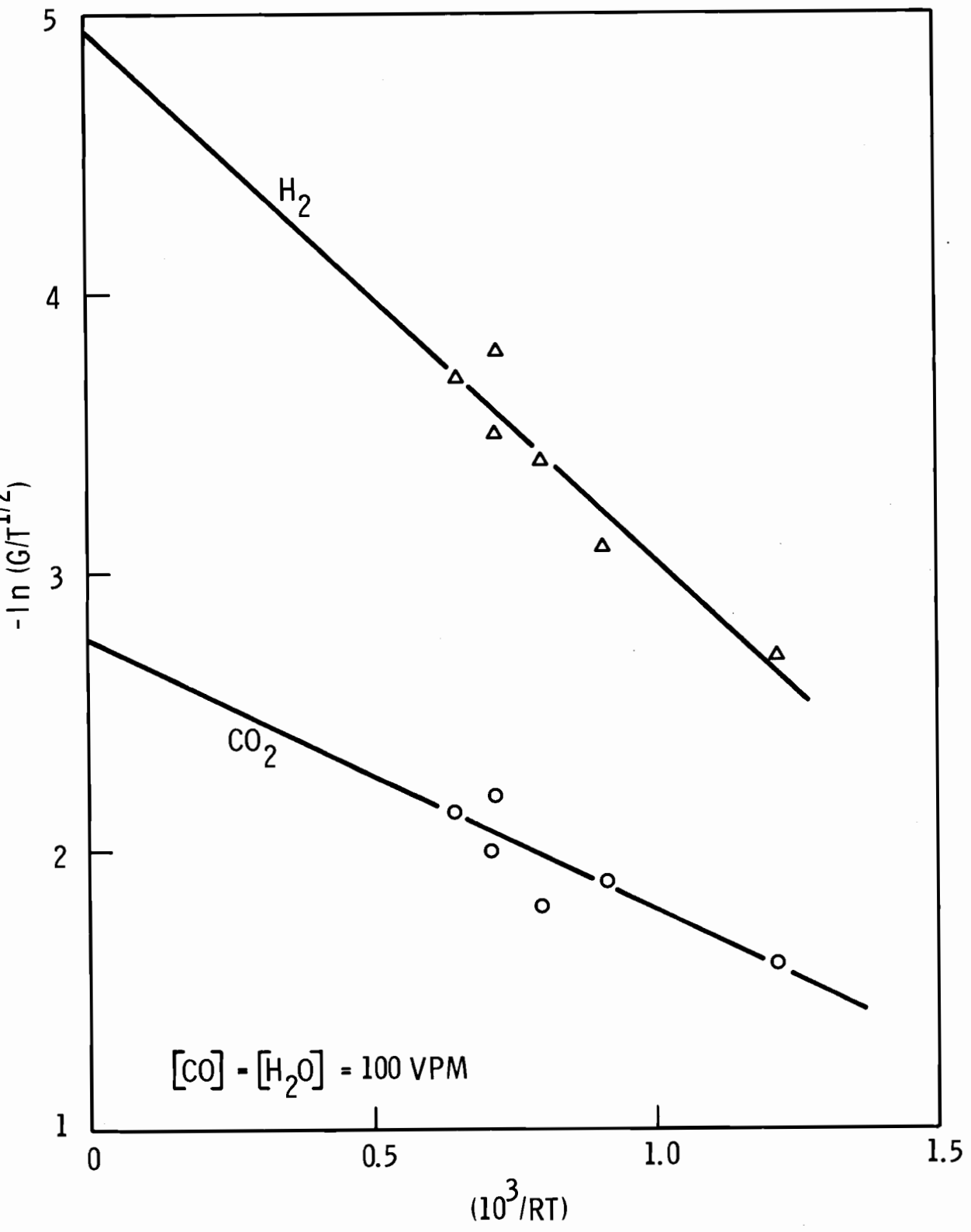


FIGURE 4. Product Yields Plotted as ln $(G/T^{1/2})$ versus $10^3/RT$ for 100 VPM Reactants.

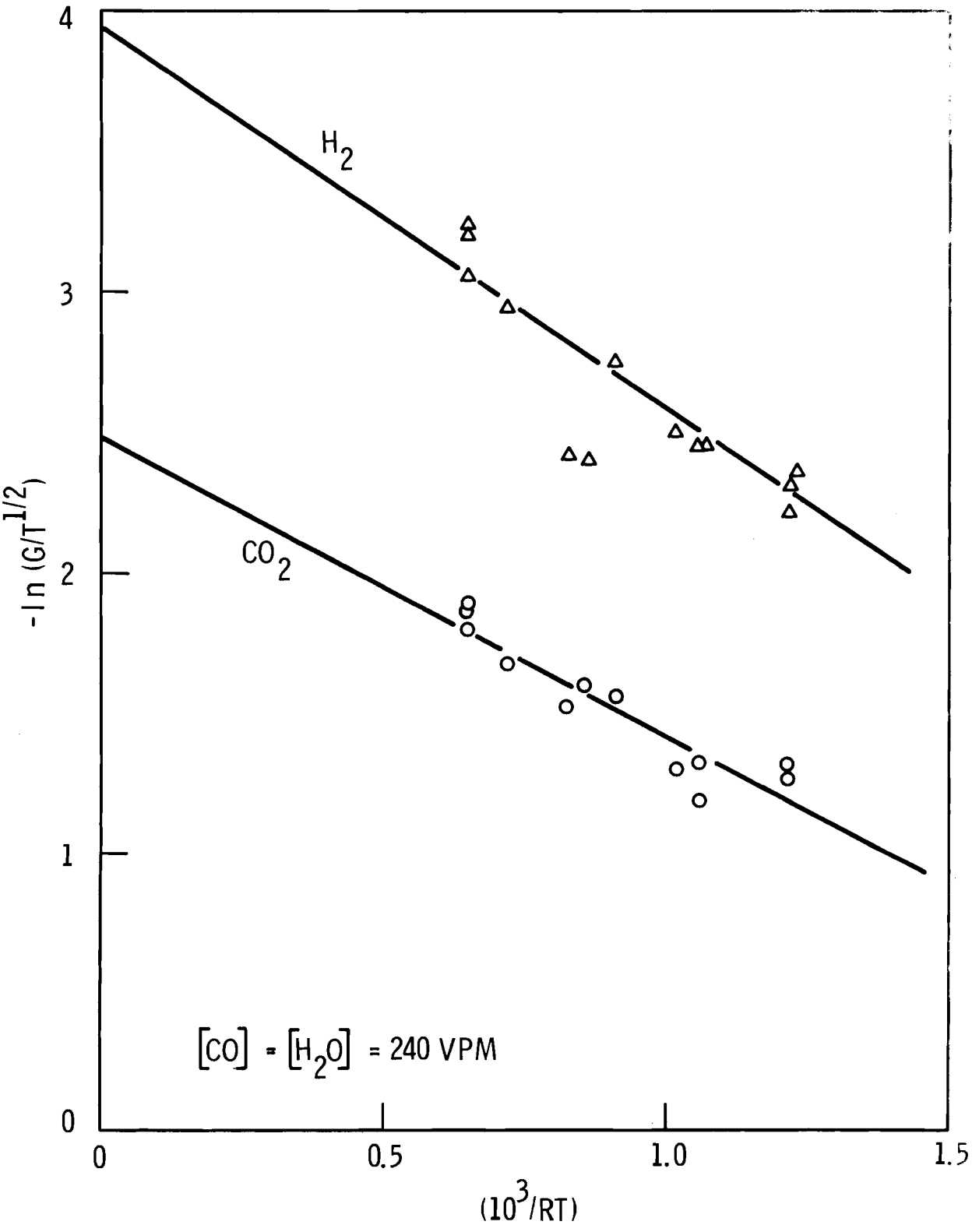


FIGURE 5. Product Yields Plotted as ln $(G/T^{1/2})$ versus $10^3/RT$ for 240 VPM Reactants.

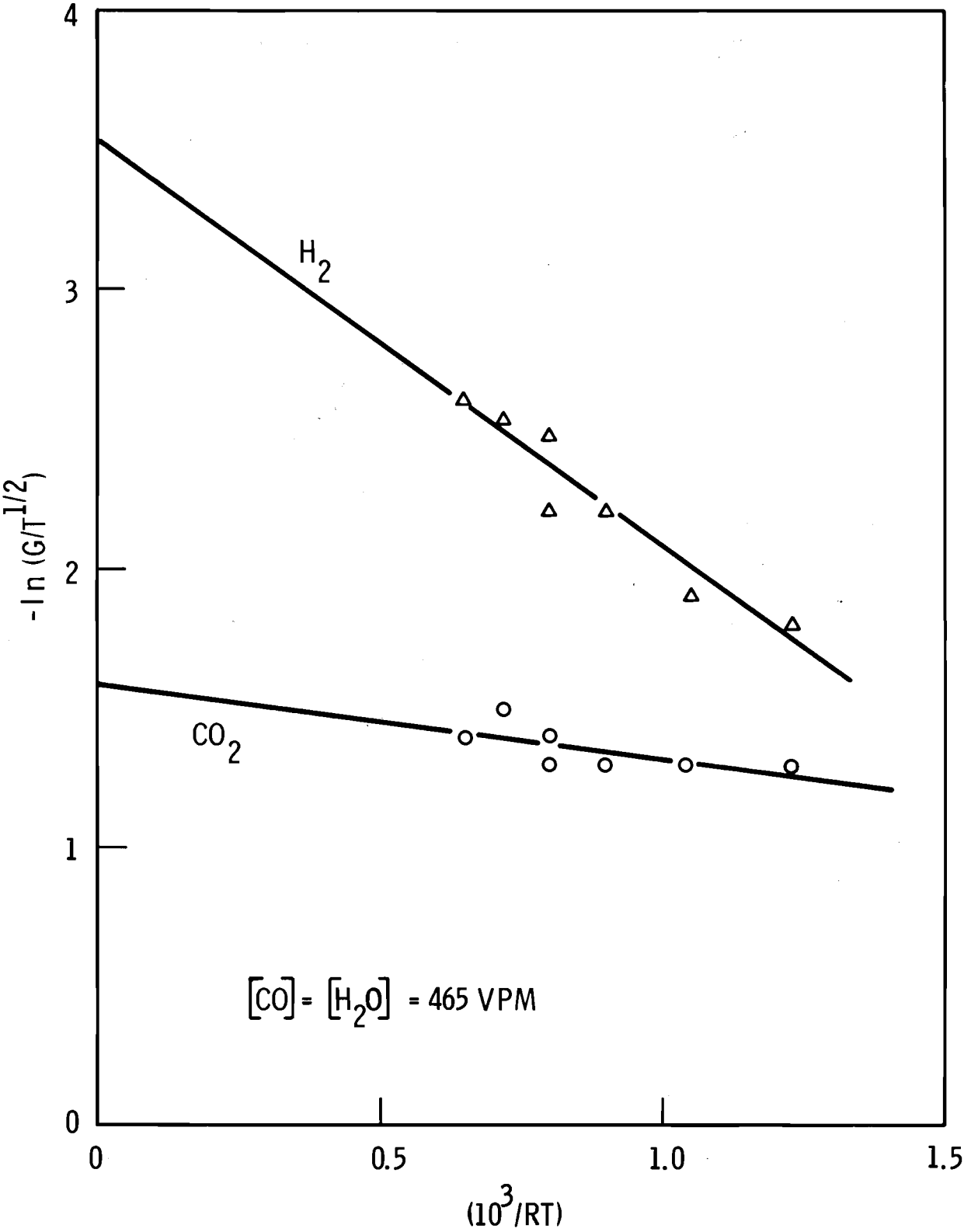


FIGURE 6. Product Yields Plotted as ln $(G/T^{1/2})$ versus $10^3/RT$ for 465 VPM Reactants.

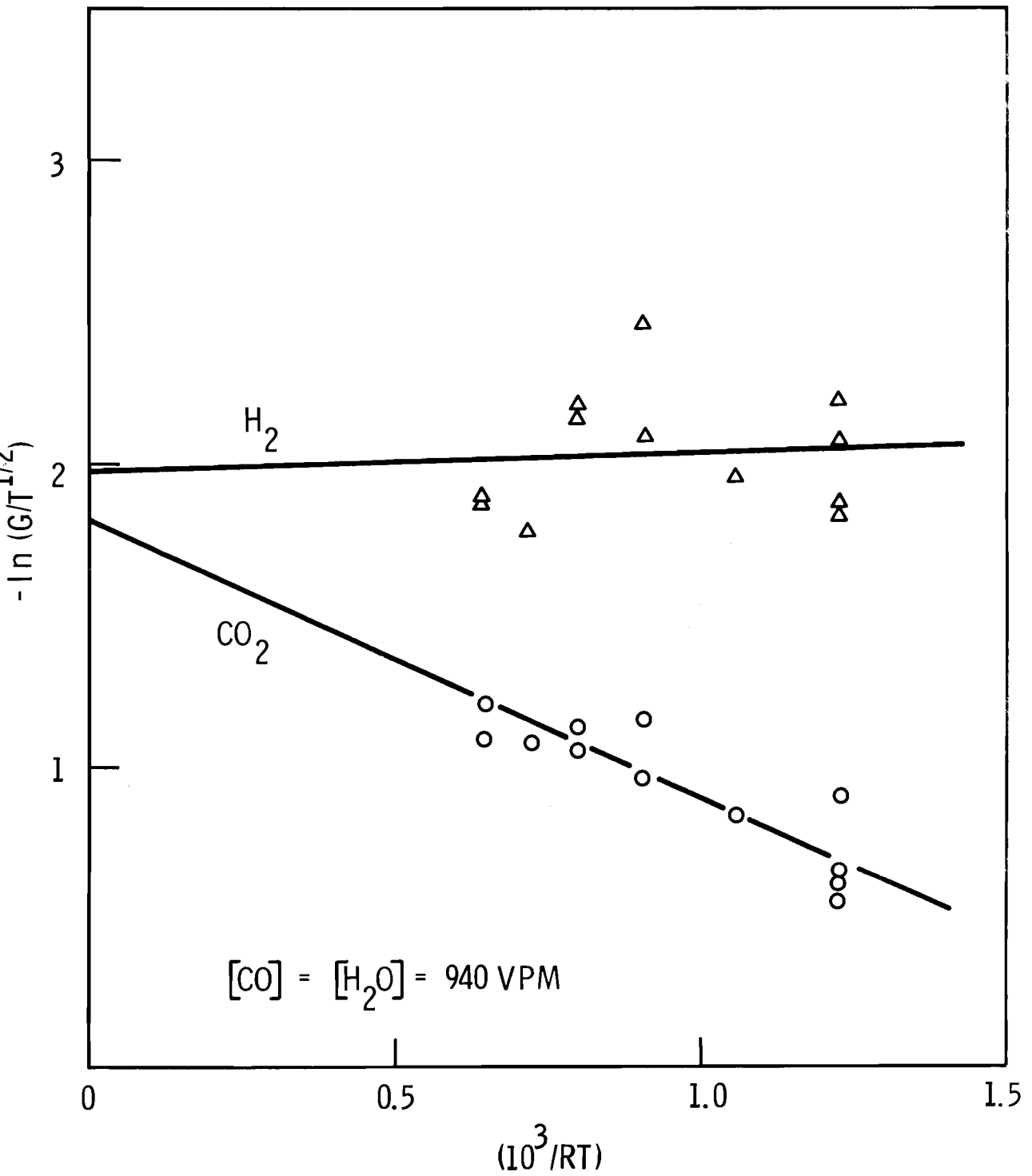


FIGURE 7. Product Yields Plotted as ln $(G/T^{1/2})$ versus $10^3/RT$ for 940 VPM Reactants.

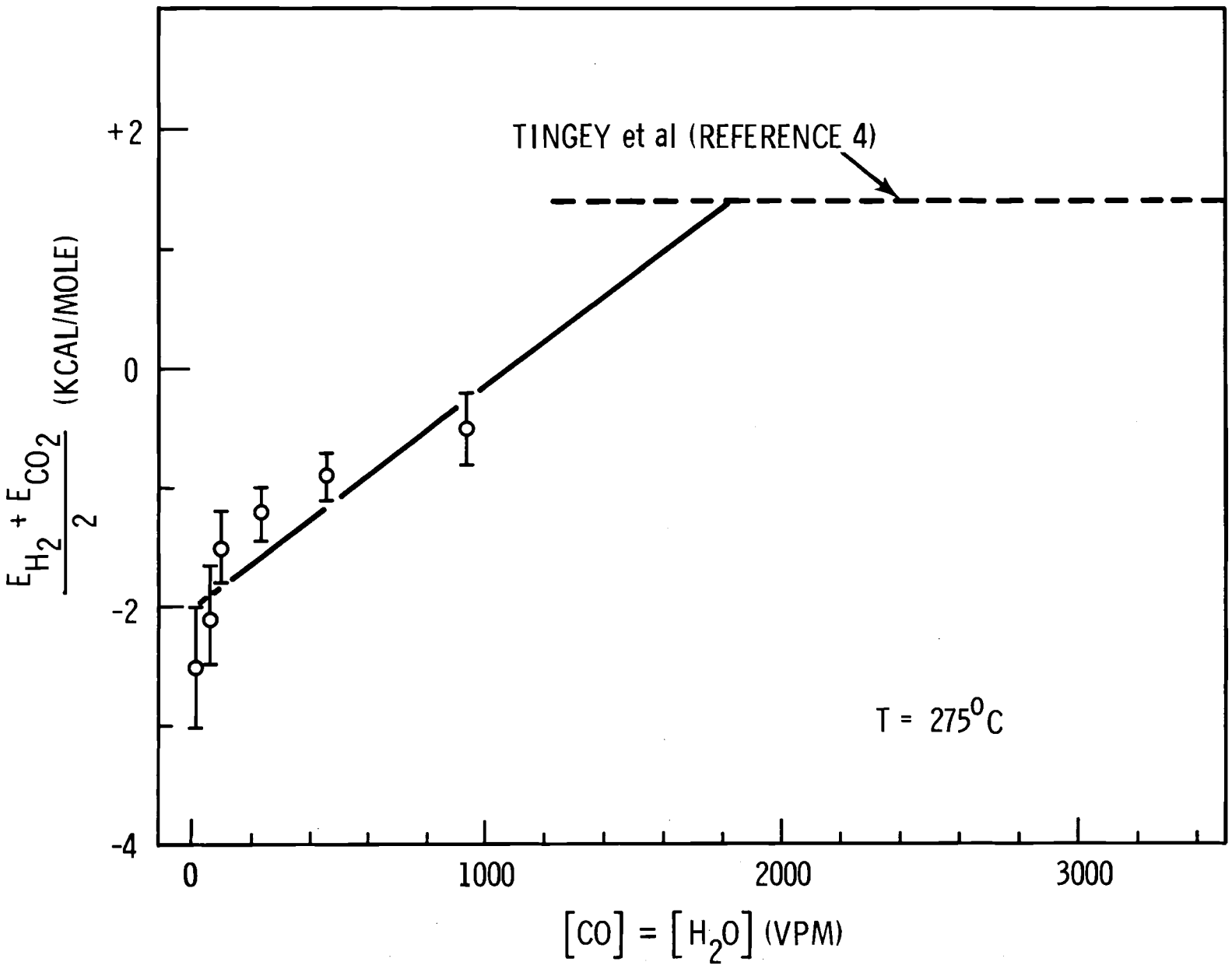


FIGURE 8. Mean Activation Energy Plotted as a Function of Reactant Concentration for T = 275°C.

TABLE I. Least Squares Data Fit For
$\ln (G/T^{1/2}) = (-E)(1/RT) + b$

vpm	x	-b	-E(cal)	σ*
10	H_2	6.45	2600	0.20
	CO_2	6.07	2400	0.15
65	H_2	6.28	2500	0.19
	CO_2	4.80	1700	0.12
100	H_2	4.94	1900	0.11
	CO_2	2.74	1000	0.10
240	H_2	3.95	1400	0.16
	CO_2	2.48	1000	0.08
465	H_2	3.56	1500	0.09
	CO_2	1.59	300	0.05
940	H_2	1.97	- 100	0.20
	CO_2	1.82	1000	0.13

* σ of ± 0.2 for $\ln(G/T^{1/2})$ implies: G ± 1.2, E ± 400.

yields at the plateau values to extremely high dilutions, the exact point of decreasing yields ($\lesssim 10^4$ vpm in this case) is not yet predictable. The convergence of the yields ($G_{CO_2}/G_{H_2} = 1$) at approximately 10^2 vpm indicates that competing reactions such as production of C_3O_2 and CH_4, for example, apparently become insignificant at the higher dilutions.

It is well to point out here the possibility of spurious effects due to O_2 impurities. During the experiments, there were two major sources of oxygen, one of which was decomposition of the carbon - suboxide. This product is apparently formed during an overnight run at 135°C and subsequently decomposed by heating to higher temperatures. By carrying out the runs from high to low temperatures or isothermally, this problem could be controlled to some extent. The other source (air in leakage) was generally minimal. The bulk of the data nevertheless represents gas mixtures usually containing between 1 and 3 vpm O_2. These levels are obviously a serious problem for the most dilute runs at $[CO] = [H_2O] = 10$ vpm, but for the 240 vpm data and higher, the effects (if any) appear not to be large. We have determined, under somewhat higher levels of O_2 (> 3 vpm) and approximately 80 vpm reactants, that H_2 yields are decreased by increasing O_2 concentrations presumably by the reaction ($H_2 + O_2 \rightarrow 2\ H_2O$, while CO_2 yields are increased from the reaction $2\ CO + O_2 \rightarrow 2\ CO_2$). The effect was not, however, reproducible and we have not attempted correcting for O_2 effects. Although the reasonably self-consistent results obtained do not in themselves preclude interference by O_2, it can be said that the problem is not of major proportions.

Concerning the general reasonableness of the results, the plot of Figure 9 and others which could be constructed at other temperatures do indicate as required a tailing of yields to G = 0 at [x] = 0 and extrapolate well to the values obtained earlier at higher concentrations by a sealed ampule technique. The decrease in activation energy with increasing dilution parallels a similar decrease found in an earlier study[5] of the radiolysis of ($CO_2 + H_2$) from + 11.0 Kcal at $[H_2] = [CO_2] = 5 \times 10^5$ vpm to + 2.0 Kcal at $[H_2] = [CO_2] = 60$ vpm. The temperature coefficient (a) in $G = aT^{1/2}\ e^{-E/RT}$

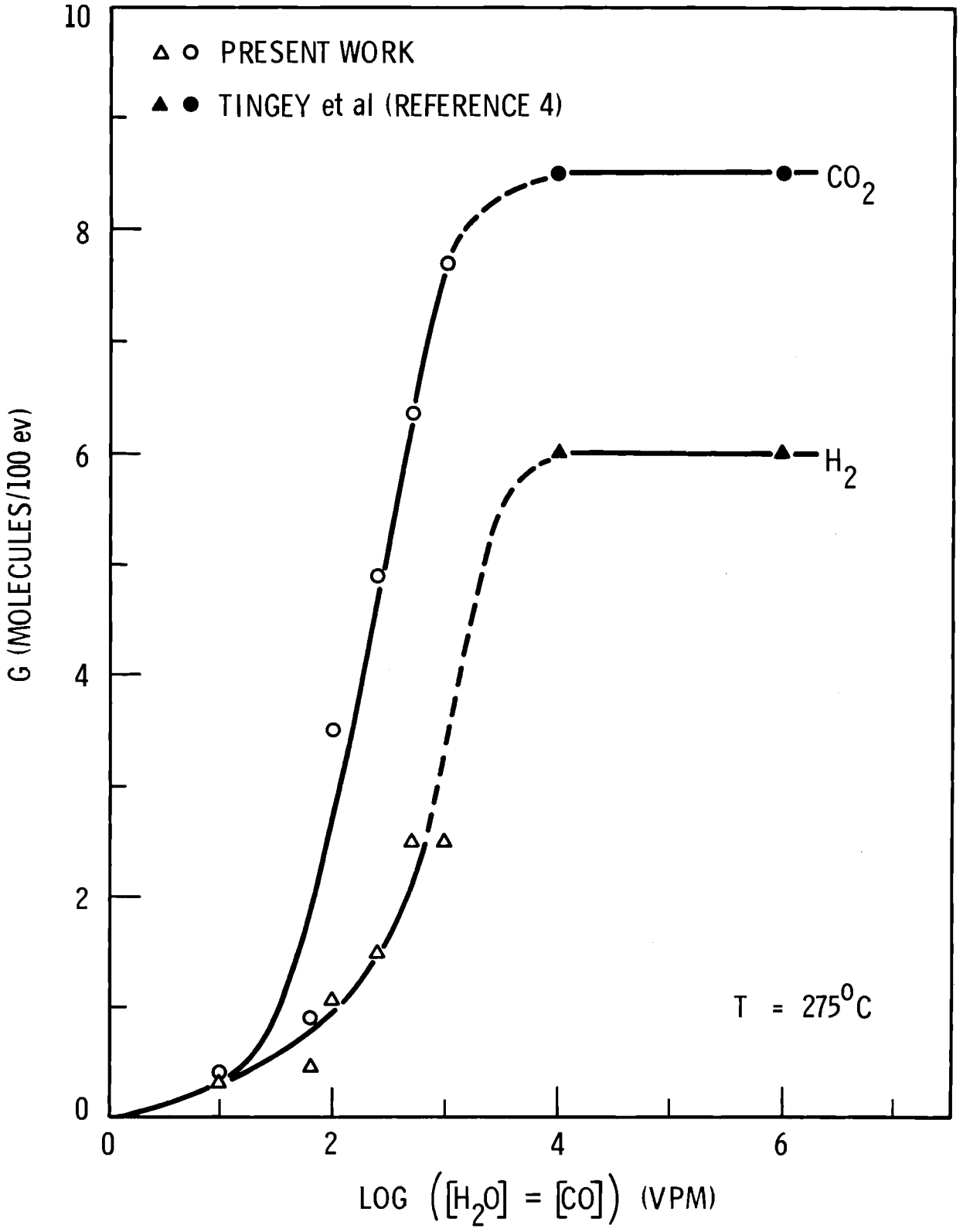


FIGURE 9. Yields Plotted as a Function of Reactant Concentrations for T = 275°C.

decreased in the latter study with increasing dilutions as was also observed for the present reaction.

The explanations given[5] are applicable here. When no helium is present, the reactive gases are excited directly by the radiation and a variety of ionic and excited species are formed. In a diluted mixture, the vast majority of energy is absorbed by the helium (98.8% for $[H_2O] = [CO] =$ 1000 vpm). Since no stable species are formed with the excited helium, much of this energy is transferred to the reactive gases. Since the excitation mechanism is different, the excited states are likely to be different and a different temperature coefficient and activation energy should be ovserved. That negative activation energies have been obtained in the present case is unusual but quite possible in reactions governed by competing mechanisms. If we consider that mechanism A is followed down to moderate dilution and B at very high dilution, then the intermediate concentrations 10-1000 vpm may also reflect the change by a regular variation (as observed) for the temperature coefficient and activation energy (Table I).

SUMMARY

The results and interpretations may be summarized as follows:

1. Product yields for the radiolysis regularly decrease for $[CO] = [H_2O] < 10^4$ vpm, but are constant at $G_{H_2} = 6.0$ and $G_{CO_2} = 8.5$ for all higher concentrations.

2. At high dilution (< 100 vpm), a stoichiometric ratio of products is obtained such that $G_{H_2} = G_{CO_2} = 0.012\ [x]$ for $[x] = [H_2O] = [CO]$.

3. Product yields decrease with increasing temperature such that $\Delta G/\Delta T \sim 1/500$, where G is molecules/100 eV and T is ^{o}C. This suggests that the activation energy is negative as obtained by the treatment employed.

4. The absolute value of activation energy is a function of the treatment used, but regardless of the approach, the values decrease with increasing dilution.

5. A thermally unstable oxygen-containing product (probably C_3O_2) and CH_4 were observed as significant products in addition to CO_2 and H_2.

APPENDIX I

The primary interest in this investigation was the accumulation of sufficient data to write a rate expression for the radiolysis reaction and necessitated some consideration of the form of the equation to be applied. Consider a rate expression of the form:

$$d(CO_2)/dT = k'[CO][H_2O].$$

If we use the classical kinetic theory of gases (a Maxwellian distribution of velocities are imposed on a hard sphere model), the collision frequency for both two and three body collisions is proportional to the square root of the absolute temperature. This means, $k' \quad T^{1/2}$. According to the Arrhenius equation, k' is given by

$$k' = Ae^{-E/RT} .$$

The pre-exponential term, A, has been called the "frequency factor" or "collision number" and E is the activation energy.

Then, combining the results of both, we get

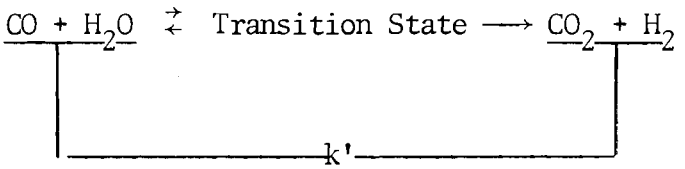
$$k' = BT^{1/2} e^{-E/RT} .$$

It follows then, that E can be determined from the slope of a plot of

$$\ln [d(CO_2)/dT)/T^{1/2}] \text{ vs. } 1/KT \qquad (1)$$

Alternatively, we can consider the more recent statistical treatment of Eyring and co-workers.[10] The approach is summarized and simplified as follows for the particular reaction in question.

The reaction is



The equilibrium constant is given by

$$K = [T.S.]/[CO][H_2O] =$$

$$F_{T.S.}/F_{CO}\ F_{H_2O}$$

where F_i = grand partition functions in units of concentration/volume. For simplicity, we can consider the molecular counterpart, f_i, and its translational, vibrational, and rotational components given by

$$f_i = f_{trans.} \cdot f_{rot.} \cdot f_{vib.}$$

Then assuming unit transmission (every activated molecule converts to product), it can be shown that

$$k' = \frac{kT}{h}\ ; K = \frac{kT}{h}\ \left(\frac{f_{T.S.}}{f_{CO} \cdot f_{H_2O}}\right) e^{-E/RT}$$

For our purpose, all $f_{vib.} \sim 1$

$f_{trans.} = C_i T^{3/2}$ in all cases.

$f_{rot.} = C'_i T$ for a linear molecule.

$f_{rot.} = C''_i T^{3/2}$ for a non-linear molecule.

where C_i, C'_i, and C''_i are constants.

Then, assuming a nonlinear transition state

$$k' = \frac{kT}{h} \left[\frac{C_{TS}\, T^{3/2} \cdot C''_{TS}\, T^{3/2}}{C_{CO} T^{3/2} \cdot C'_{CO} T \cdot C_{H_2O} T^{3/2} \cdot C''_{H_2O}{}^{3/2}} \right] e^{-E/RT}$$

$$k' = \frac{C_*}{T^{3/2}}\ e^{-E/RT}$$

It follows that the plot to be used to obtain an activation energy should be

$$\ln\, [d(CO_2)/dT) \cdot T^{3/2}]\ \text{vs.}\ 1/RT \qquad (2)$$

If, as has been suggested by Steinmann,[7] the radiolytic reaction is described by $d(CO_2)/dT = k'[H_2O][CO]^{1/2}$, the partition function for CO is raised to the 1/2 power and the plot

$$\ln\, [d(CO_2)/dT) \cdot T^{1/4}]\ \text{vs.}\ 1/RT \qquad (3)$$

should have slope = -E.

If we assume a three-body reaction is operative (He being the third, for example) and unit dependence for [CO], we get

$$\ln[(d(CO_2)/dT \cdot T^3]\ \text{vs.}\ 1/RT \qquad (4)$$

or helium and $(CO)^{1/2}$

$$\ln\, [d(CO_2)/dT) \cdot T^{7/4}]\ \text{vs.}\ 1/RT \qquad (5)$$

Often, the accuracy of kinetic data and indeed the theoretical soundness of the inclusion of a T^y term has led to deletion of the term and the plot to be considered is simply

$$\ln\, [d(CO_2)/dT]\ \text{vs.}\ 1/RT \qquad (6)$$

Of all these, (1), (2), (3), and (6) are the more likely possibilities. The treatments all give standard deviations of the order of ± 0.4 Kcal so an obvious choice is not present. We have chosen as the form of treatment

$$\frac{d(CO_2)}{dT} = kT^{1/2}\, e^{-E/RT}$$

and the plots to be considered are

$$\ln\left(\frac{d(CO_2)}{dT}/T^{1/2}\right) \text{ vs. } 1/RT \qquad (1)$$

The basis for this choice is primarily as the least demanding on prior assumptions with the exception of (6). Treatments (2) and (3) require a sure knowledge of reaction order which is not available. The assumption of a simple bimolecular reaction (2) is particularly hard to justify in view of the non-unity ratio obtained for products, i.e., $G_{CO_2}/G_{H_2} = 1$ except at very high dilution where the data are least trustworthy.[2] By employing (1) which is also applicable to three body reactions, these ambiguities are not imposed. As far as the dependence on dilution is concerned, the rate of change of the activation energy is unaffected, but the position of the entire curve E = f (conc.) shifts in absolute magnitude along the E axis, depending on the treatment used. The $T^{3/2}$ fit (2) and the $1/T^{1/2}$ fit (1) are at the extremities with $E_2 - E_1 = +2.2$ Kcal.

REFERENCES

1. A. R. Anderson and J. A. Winter, Radiation Research, June-July 167, (1966).

2. S. C. Lind, Radiation Chemistry of Gases, Reinhold Publishing Co., New York, New York, 1962.

3. G. L. Tingey, "Inert Gas Sensitization in the Radiolysis of Gaseous Mixtures," BNWL-SA-590, March 1966, Battelle-Northwest, Richland, Washington.

4. G. L. Tingey, R. C. Giberson, and E. D. Jensonm "Reactions of Coolant Impurities with Graphite in a HTGR," Chem. Eng. Prog. Symp. Ser. 66 No. 104, 73, 1970.

5. G. L. Tingey and D. E. Clark, "Technical Activities Quarterly Report, AEC Reactor Development and Technology Program, Section 8," BNWL-1522-1, Battelle-Northwest, Richland, Washington.

6. G. L. Tingey, "Radiolysis of Mixtures of Carbon Monoxide and Water Vapor," HW-SA-3440 (General Electric), April 1964.

7. R. Steinmann, "The Radiation Induced Reaction Between Carbon Monoxide and Water," Dissertation Abstracts 23, 1534 (1962).

8. R. E. Nightingale (ed.), Nuclear Graphite (1962), Academic Press, New York, New York, p. 250.

9. G. L. Tingey, "The Radiolysis of a Mixture of Carbon Dioxide and Hydrogen," BNWL-SA-591, April 1966, Battelle-Northwest, Richland, Washington.

10. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Inc., New York (1941).

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