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THERMODYNAMICS OF COAL CONVERSION REACTIONS

PART 2. EFFECT OF PRESSURE ON WATER-GASIFICATION

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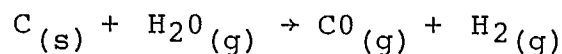
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Thermodynamics of Coal Conversion Reactions
Part 2. Effect of Pressure on Water-Gas Reaction

INTRODUCTION

In Part I "The Water-Gas Reaction" (Report ERP/ERL 78-50 (TR) it was shown that for the water-gas reaction



the free energy change for the reaction (ΔF) could be expressed as a function of temperature as follows: (1)

$$\Delta F = 31560 - 2.02 T \ln T + 0.91 \times 10^{-3} T^2 - 1.02 \times 10^5 / T - 20.73T$$

A program incorporating this equation was written for the NOVA computer and values of ΔF were calculated from 100°C to 1400°C in 5' intervals. The logarithm of the equilibrium constant ($\ln K$) and the equilibrium constant (K) also were calculated and tabulated simultaneously.

It was found that for this reaction the free energy change (ΔF) was positive and the equilibrium constant (K) was less than unity up to about 660°C. Above this temperature ΔF was negative and K was positive.

The amount of heat needed to heat the carbon to various temperatures also was calculated, using the following relationship:

$$H = -1972 + 4.1T + 0.00051T^2 + 210000/T$$

where H = heat contained in the carbon, above 298°K, in kcal/kg-mol.

The heat of reaction at temperature T was calculated from the following relationship:

$$HR = 31554 + 2.04T - 0.00091T^2 - 203000/T$$

Both these heat calculations covered the same range as the free energy study, ie. 100 - 1400°C.

Effect of Pressure on Water-Gas Reaction

It is a matter of some interest to know what happens in the water-gas reaction as the pressures of the gaseous reactant, H₂O, and the gaseous products, CO and H₂, change. An indication of this can be obtained from the following relationship:

$$F = RT \ln K_p + RT \ln \left(\frac{P_{CO} P_{H_2}}{P_{H_2O}} \right)$$

where R = gas constant (1.98647)

T = temp (°K)

K_p = equilibrium constant at temp T

P_{CO} = pressure of CO (atm)

P_{H₂} = pressure of H₂ (atm)

P_{H₂O} = pressure of H₂O (atm)

If P_{CO} = P_{H₂} = P_{H₂O} = 1, the quotient within the brackets equals unity, and since ln 1 = 0, this term = 0, i.e. we are at thermodynamic equilibrium. On the other hand, if the quotient of the terms within the brackets is less than unity, the term, RT ln $\left(\frac{P_{CO} P_{H_2}}{P_{H_2O}} \right)$, becomes negative and we have a negative value for the

free energy change for the reaction. This represents a driving force that tends to make the reaction proceed from left to right, as written. Conversely, if the quotient is greater than unity then $RT \ln \left(\frac{P_{CO} P_{H_2}}{P_{H_2O}^2} \right)$ is positive, making the overall free energy change positive i.e. we have a driving force tending to make the reaction proceed from right to left.

A program was written for the NOVA computer to do these calculations. Three temperatures were arbitrarily chosen for the study - 800, 900 and 1000°C. The pressure of the water vapour was arbitrarily varied from 10 atmospheres to 70 atmospheres in increments of 10 atmospheres, and those of the CO and H₂ were both varied from 5 atmospheres to 30 atmospheres in increments of 5 atmospheres.

These calculations resulted in a large number of points which would have been tedious to plot individually, so a program was written for the Hewlett-Packard calculator and plotter to plot the function in a continuous manner, using appropriate parameters for each case.

The results obtained at 800°C, where the logarithm of the equilibrium constant ($\ln K$) is 2.28 are shown in Figure 1. The pressure of the water vapour (in atmospheres) is plotted as the abscissa, and the "Excess Free Energy" in kcal per mol of carbon as the ordinate. The numbers 30, 25 and 20 on the graph refer to the values at which the pressures of CO and H₂ each were set for a particular calculation. It is obvious that ΔF , the "Excess Free Energy" is positive over most of the range shown in

this Figure, thus representing a strong driving force to make the reaction go from right to left as written. Only in the lower right corner of the figure are conditions reversed i.e. ΔF becomes negative at high pressures of water vapour (60-70 atm.) and low pressures of CO and H₂ (20 atm.).

The results obtained at 900°C where $\ln K = 3.58$ are shown in Figure 2. These are much more favourable in that there is a much larger area of the graph where the "Excess Free Energy" is negative, representing a driving force for the reaction to go from left to right as written.

The results obtained at 1000°C, where $\ln K = 4.67$ are shown in Figure 3 and are much more favourable than those at 900°C. In all cases the "Excess Free Energy" is negative, representing a driving force available to drive the reaction from left to right as written.

CONCLUSIONS

It is not surprising that higher temperature, higher pressure of the reactant gas (H₂O), and lower pressures of the product gases (CO and H₂) all favour driving the reaction from left to right as written.

It must be remembered that the values for the temperatures and gas pressures used in this study were arbitrarily chosen merely to illustrate an effect, and the real values obtainable in practice may differ considerably from those used here.

Furthermore, this study has dealt only with the thermodynamics of the reaction and nothing can be learned from these results about the kinetics of the reaction. In the final analysis it will probably be the kinetic factors which will be the most important.

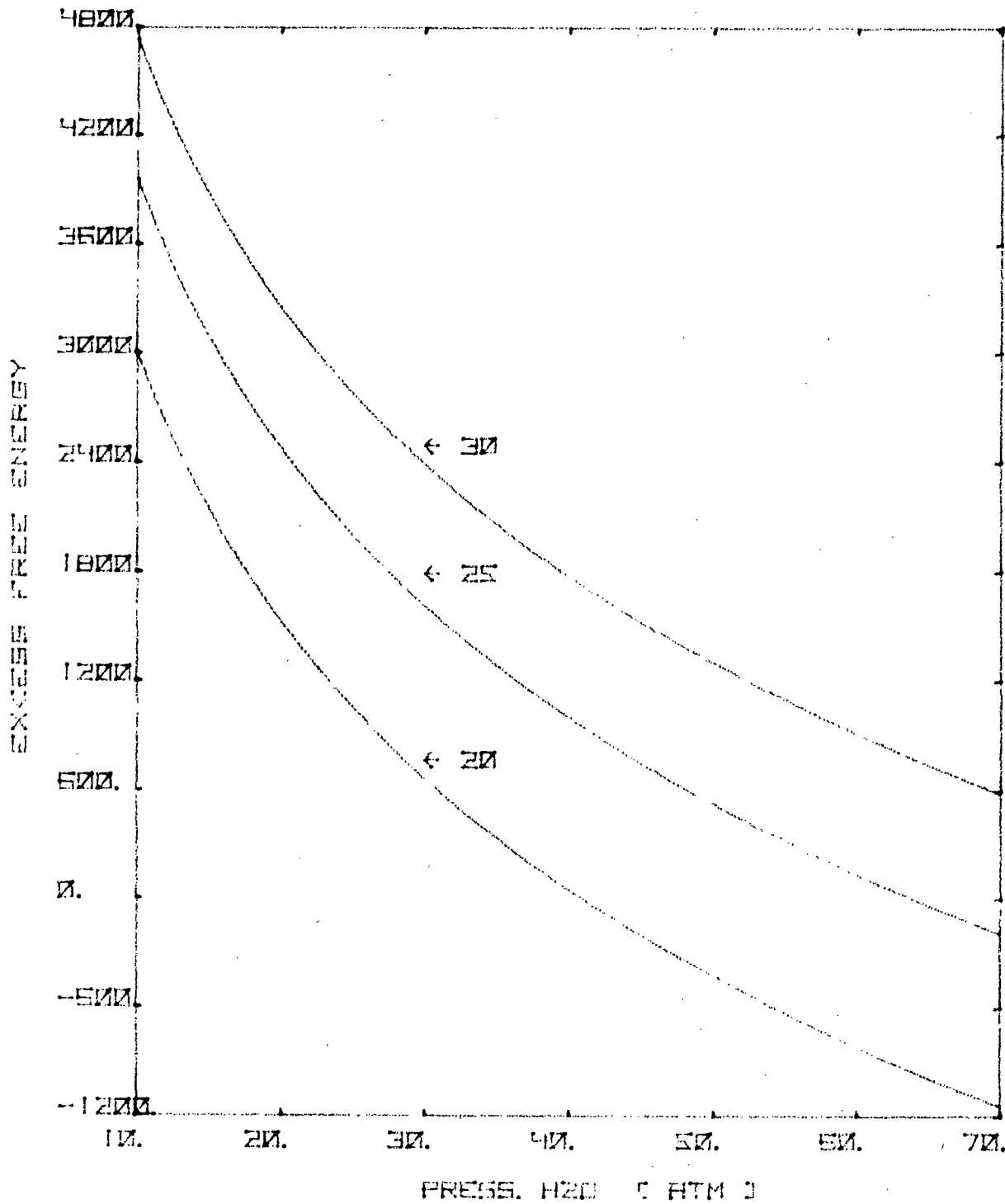


Figure 1. Excess Free Energy as a Function of Water-Vapour Pressure at 800°C, with $P_{CO} = P_{H_2}$ set at 30, 25 and 20 Atmospheres.

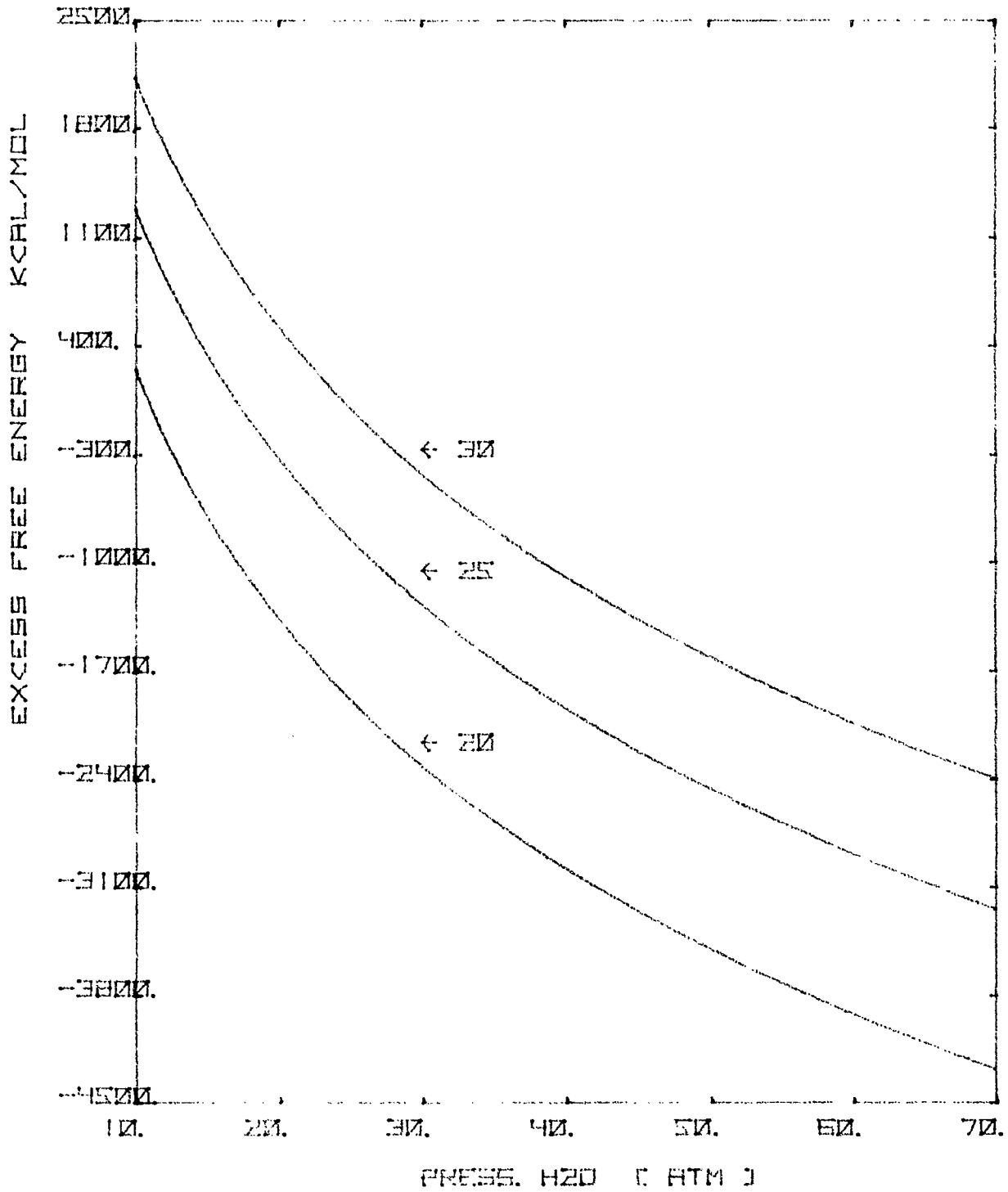


Figure 2. Excess Free Energy as a Function of Water-Vapour Pressure at 900°C, with $P_{CO} = P_{H_2}$ set at 30, 25 and 20 Atmospheres.

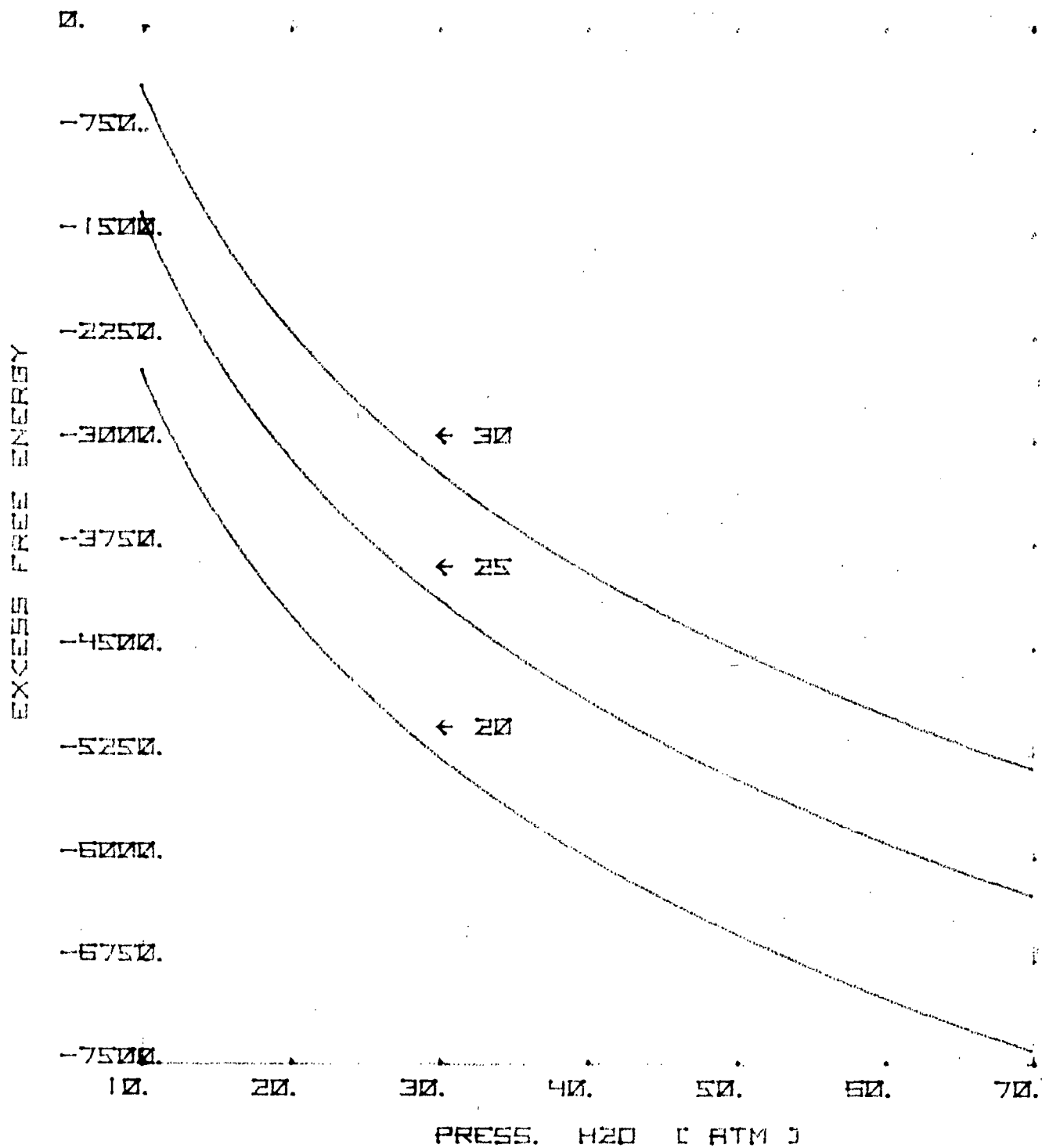


Figure 3. Excess Free Energy as a Function of Water-Vapour Pressure at 1000°C with $P_{CO} = P_{H_2}$ set at 30, 25 and 20 Atmosphere.

REFERENCES

1. Wicks, C.E. and Block, F.E. "Thermodynamic properties of 65 elements - their oxides, halides, carbides and nitrides"
U.S.B.M. Bull. 605. U.S. Government Printing Office, 1963.