4) It follows from the above that the ratio of (olefin + remainder)/paraffin shows only two slopes with a break at C_{11}.

The following are postulated: Site 1 dominates between C_1 and C_9, on which over 90 mole % of the organic product is synthesized. The α for all organic groups on this site is about 0.68. Site 2 dominates the hydrocarbon product at C_{10}+. On Site 2, the average α over all reaction conditions is 0.93 for paraffins and 0.75 for olefins plus remainder. These α values appear to be independent of reaction conditions. Oxygenates are not formed on Site 2, since there is no break at C_{10}+ for this category. Even though the α for paraffins and olefins plus remainder are notably different on Site 2, a third site is not postulated based on the following argument. The break for both paraffins and olefins plus remainder occurs at the same carbon number, C_{10}. From a mechanistic standpoint, this behavior would be noted for only two different cases: 1) The bulk of paraffins and olefins plus remainder are formed on two different sites at C_{10}+. However, the fraction of sites producing each group would have to be exactly the same for the break to occur at only one carbon number; 2) Paraffins and olefins plus remainder are formed on the same site but with different α values. Since the first case seems highly improbable, the latter is chosen. However, the reason for the ratio of the rate of propagation to the rate of termination, namely α, being much higher for paraffins than olefins plus branched hydrocarbons on Site 2 is not readily apparent.

It is well documented that selectivity shifts towards heavier hydrocarbon production with increasing alkali content, expecially K_2O (Anderson, 1956). Potassium is a very strong base and so donates electrons to neighboring iron atoms. Since carbon tends to accept electrons, the carbon-iron bond is strengthened, and hence the statistical probability of chain growth increases (Dry et al., 1969). Since the fused-iron catalyst employed in this investigation was promoted with 0.5 to 0.8-wt % K_2O (Section I. D. 2.), several possibilities for site composition exist:

1) Iron without alkali: According to Dry and Ferreira (1967), it is conceivable that the distribution of alkali is heterogeneous; a high alkali concentration being on certain sites while others have little or no alkali present. Lighter products would be produced on the latter.
2) Iron promoted with alkali: Iron promoted with K_2O produces a high molecular weight organic product. Moreover, Anderson (1956) reports that basic promoters, especially K_2O, dispose the catalyst to form hydrocarbons instead of oxygenates.
3) Iron promoted with potassium silicate: In addition to potassium, the iron catalyst also contained SiO_2 (less than 0.4-wt %). Silica is present as an impurity in the iron oxide ore used in the preparation of the catalyst. While silica alone has no reported effect on selectivity, SiO_2 in the presence of K_2O

greatly affects both selectivity and activity of the catalyst (Dry, 1981). Silica apparently combines with bases, such as K_2O, to form a separate phase and so prevents K_2O from entering into solid solution with the iron during catalyst manufacture (Dry and Ferreira, 1967). Silica, being acidic, lowers the basicity of the system, and hence a shift to lighter products is observed (Dry and Oosthuizen, 1968). Also Anderson (1956) reports that acidic components, such as SiO_2, promote the formation of oxygenated molecules.

While the low-α site (#1) could be due to unalkalized iron, it is more likely iron promoted with potassium silicate, due to the large amount of SiO_2 present combined with the fact that both oxygenates and hydrocarbons are formed. Since both values of α for hydrocarbons on Site 2 are higher than for Site 1, and oxygenates are not formed on Site 2, Site 2 is probably iron promoted with alkali.

A break in the carbon number distributions at C_9 to C_{12} was also reported by Anderson (1956) for a variety of iron catalysts tested by Germany during WWII (Schwarzheide tests). While all of the catalysts were alkalized, no mention of silica content was made. The probability of chain growth α was 0.66 to 0.69 below C_9 and about 0.87 at $C_{12}+$. It would also appear that two sites were present on these catalysts.

I. G. Conclusions

The product distribution shows a break at about C_{10} above which hydrocarbons are produced with a much higher probability of chain growth while oxygenates are unaffected. This suggests that two kinds of sites are present for organic synthesis on the catalyst. The various groups of products each appear to follow the distribution derived by Flory for linear polymerization in which one carbon unit is added at a time on the terminus of the growing chain. However, product distributions based solely on material collected overhead of the reactor can be misleading due to significant accumulation of the C_{20}^{+} fraction in the liquid carrier.

The rate of the Fischer-Tropsch synthesis is approximately first-order in hydrogen concentration and zero-order in carbon monoxide concentration. The intrinsic activation energy of 20 kcal/mol found here falls in the middle of the range 17 to 25 kcal/mol reported for fixed-bed reactors. Water inhibits the synthesis rate and is apparently strongly adsorbed on the catalyst surface. Although a Flory plot suggests that there are two kinds of sites, the intrinsic kinetics mostly reflect the activity of the first site as it produces 90+ mole % of the product (C_1 to C_9).

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Table 1-1

Range of Experimental Conditions

Temperature	232 - 269°C
Total Pressure	275 - 1480 kPa
Space Velocity	1100 - 8500 hr^{-1}
Inlet H_2/CO	0.34 - 1.81
Outlet H_2/CO	0.24 - 40
Outlet H_2O/CO_2	0.0040 - 0.42
H_2 Conversion	16 - 68%
CO Conversion	16 - 98%

Table 1-2

Fitted Parameters for Langmuir-Hinshelwood Kinetic Rate Models

	Eqn. (1-11)
k	E_a = 21 kcal/mol
K_{CO}	ΔH_{ads} = +31 kcal/mol
K_{H_2O}	ΔH_{ads} = +63 kcal/mol
	Eqn. (1-12)
k	E_a = 20 kcal/mol
$\frac{K_{COH_2}K_{CO}}{K_{H_2O}}$	ΔH_{ads} = -24 kcal/mol

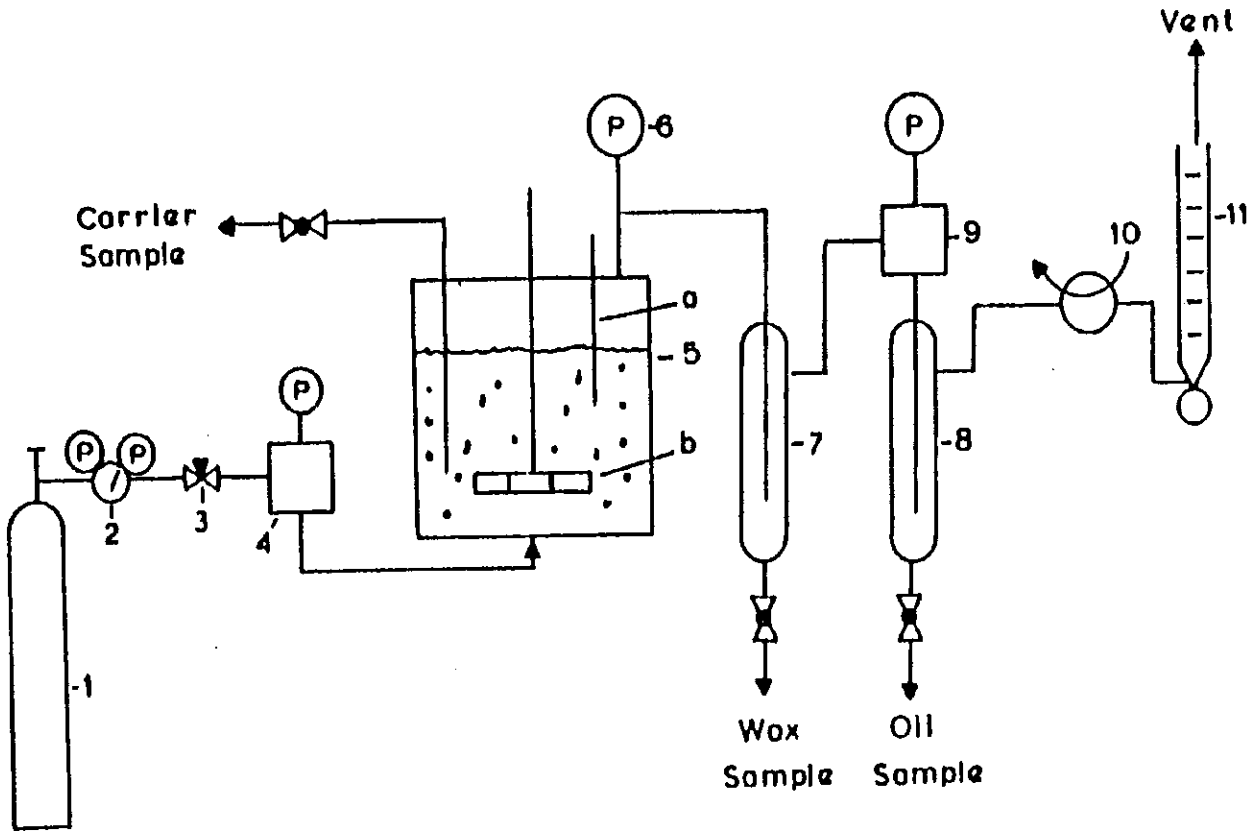

Figure 1-1. Slurry Reactor Apparatus: (1) Gas Cylinder with Premixed CO/H_2 Mixture; (2) Pressure Regulator; (3) Automated Flow Controller; (4) Back-Pressure Regulator; (5) 1-Liter, Mechanically Stirred Autoclave with Thermocouple at (a) and Turbine Impeller at (b); (6) Pressure Gauge; (7) Wax Receiver; (8) Ice-cooled Receiver; (9) Back-Pressure Regulator; (10) Gas Sample Valve; (11) Soap-film Flowmeter.

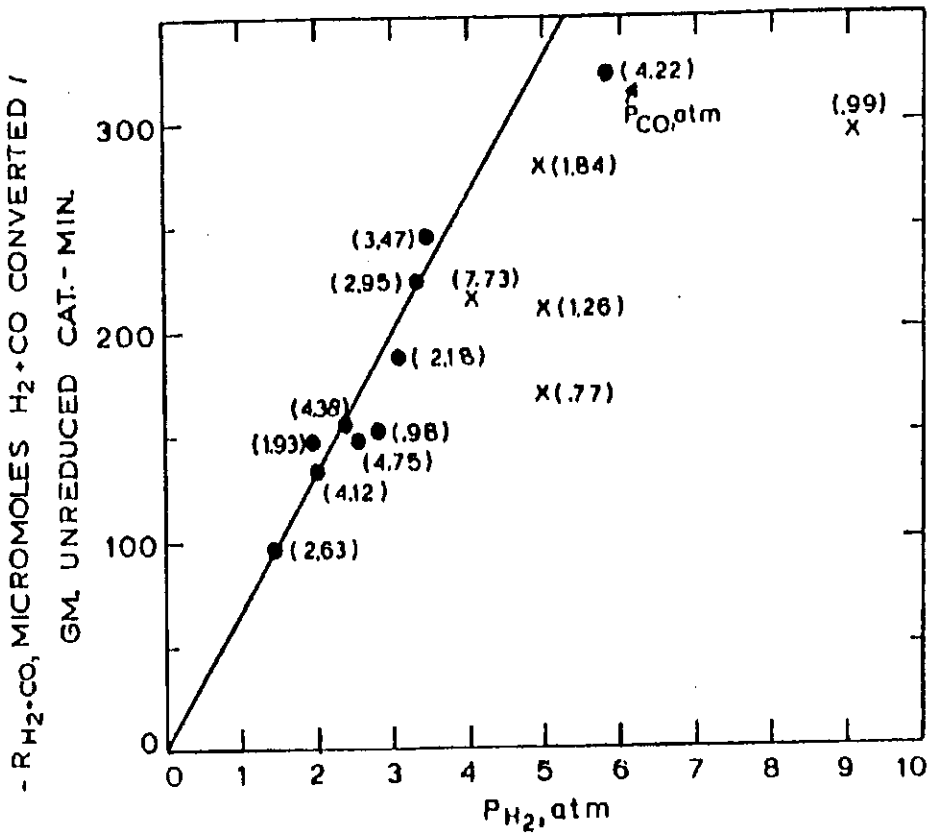

Figure 1-2. Rate of Synthesis Gas Conversion at 232°C as a Function of Hydrogen Partial Pressure; Run 9. "X" Denotes an Effluent Water Partial Pressure Above 0.1 atm (10 kPa).

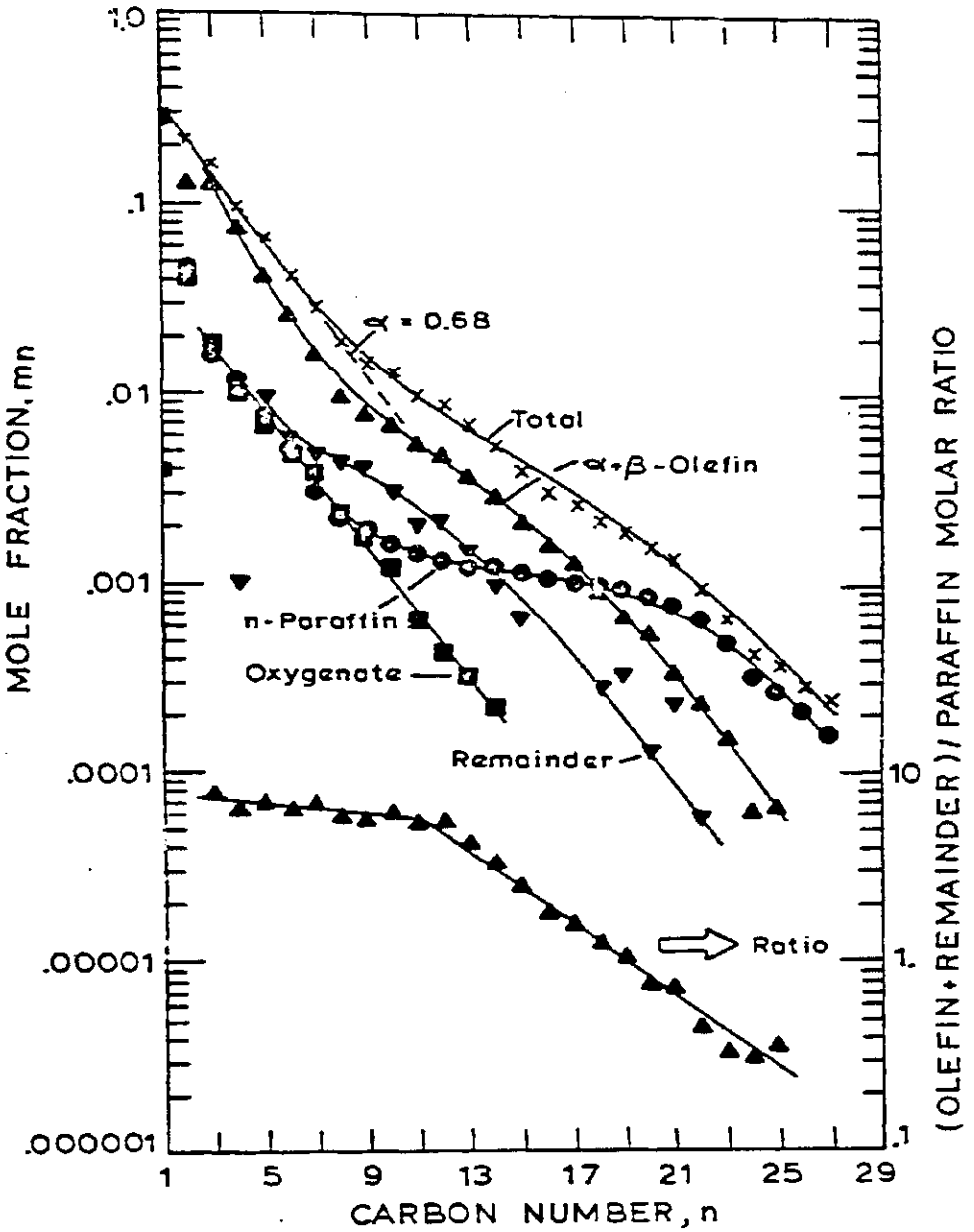

Figure 1-3. Carbon Number Distribution by Organic Class; Run 9-45 (620 Hours on Stream) at 263°C, 790 kPa Total Pressure, H_2/CO Feed Ratio of 0.55, and Space Velocity of 2320 hr^{-1}.

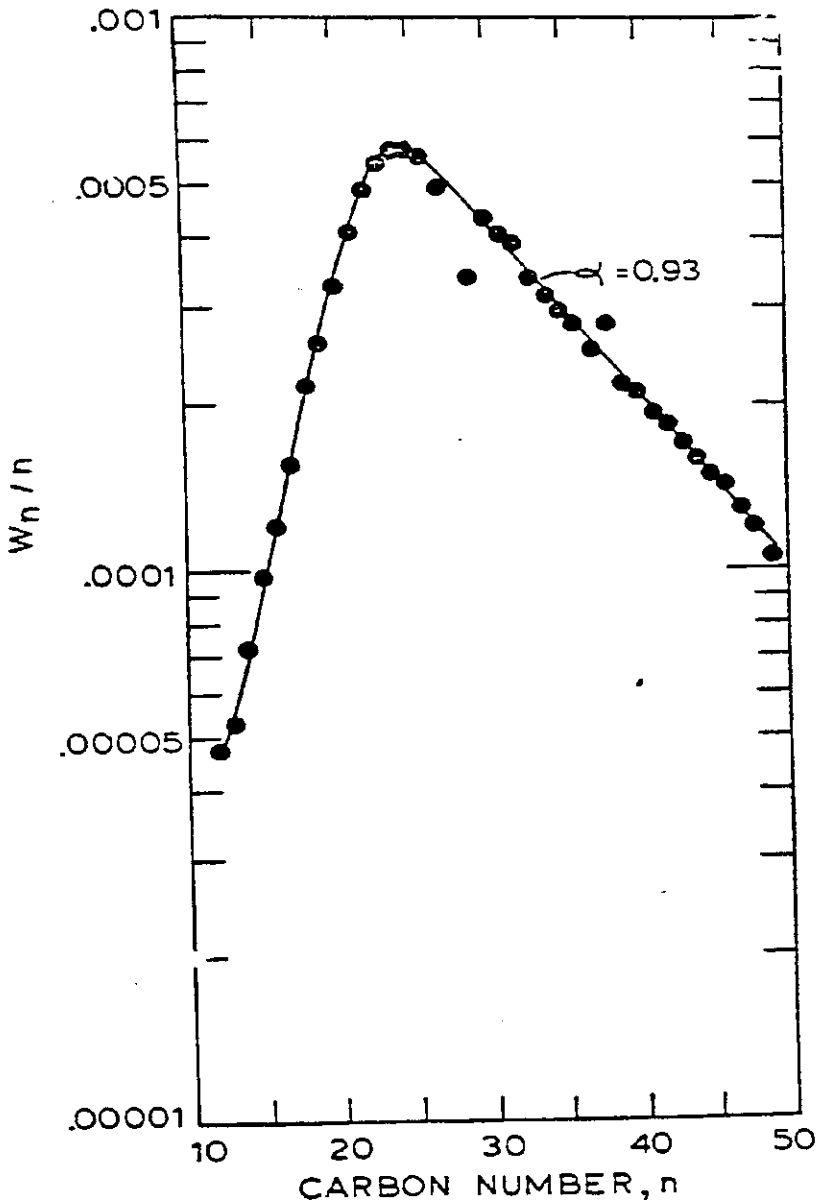

Figure 1-4. Carbon Number Distribution of Liquid Carrier After Run 9 (680 Hours on Stream).

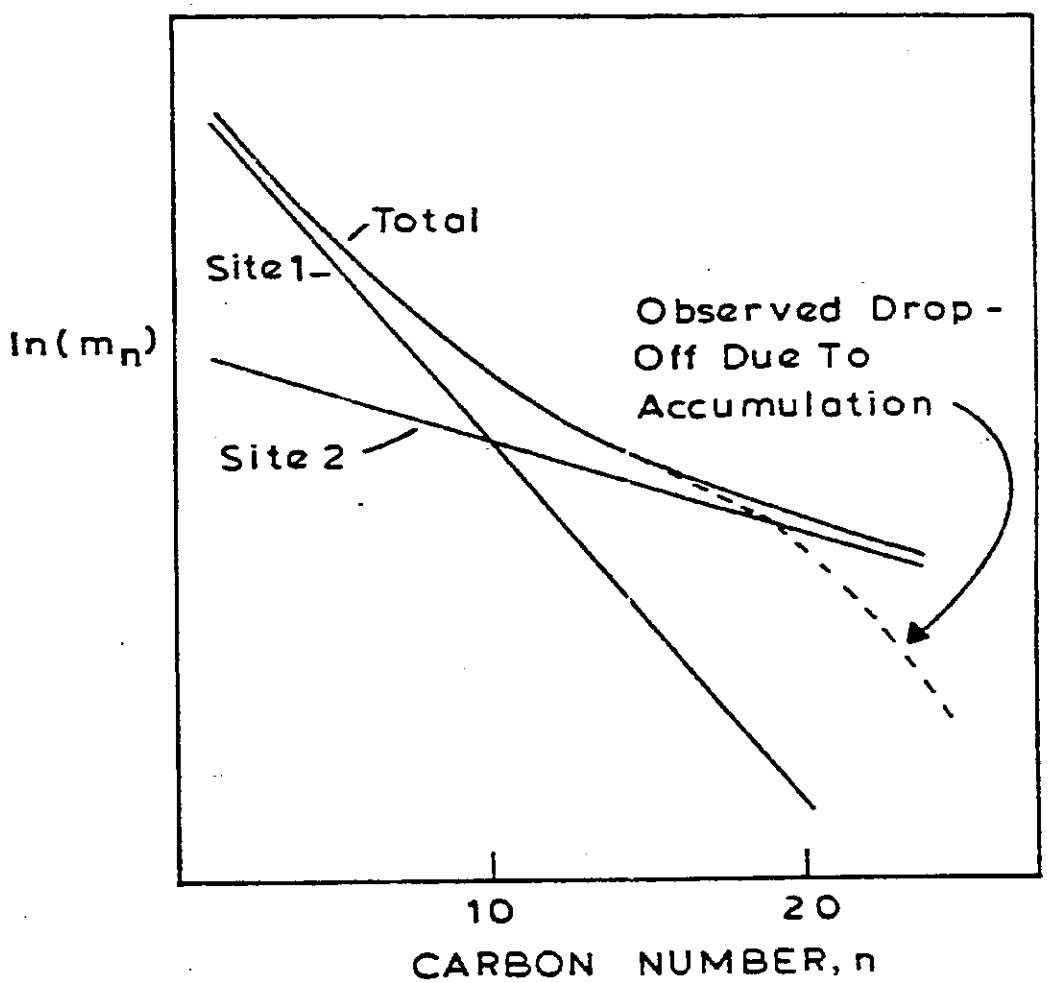

Figure 1-5. Form of Flory Plot Postulated for 2-Site Reaction and Accumulation of Products in Liquid Carrier.

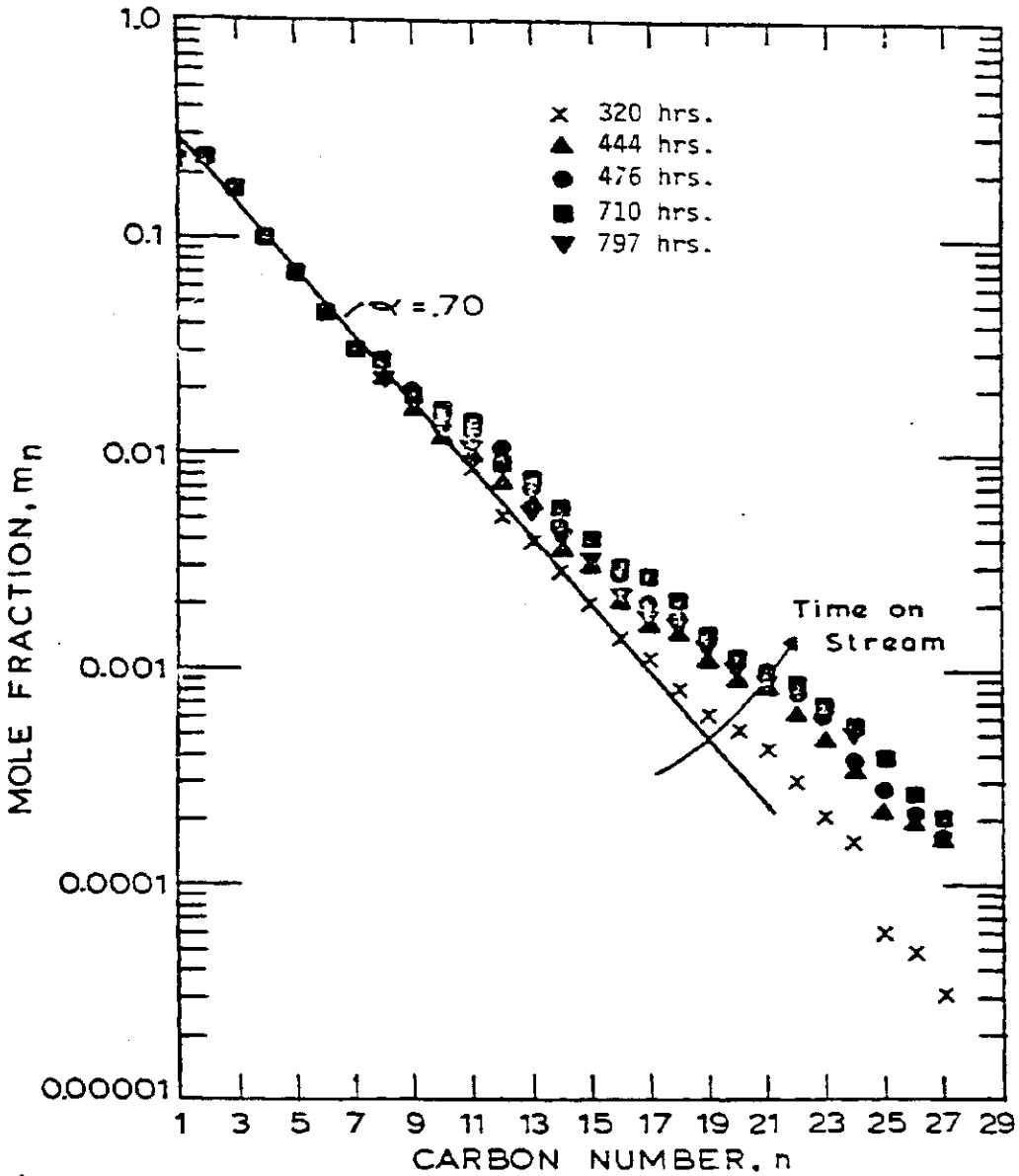

Figure 1-6. Effect of Time on Stream on Carbon Number Distribution; Run 8 at 263°C, 790 kPa Total Pressure, H_2/CO Feed Ratio of 0.69, and Space Velocity of 3300 hr^{-1}.

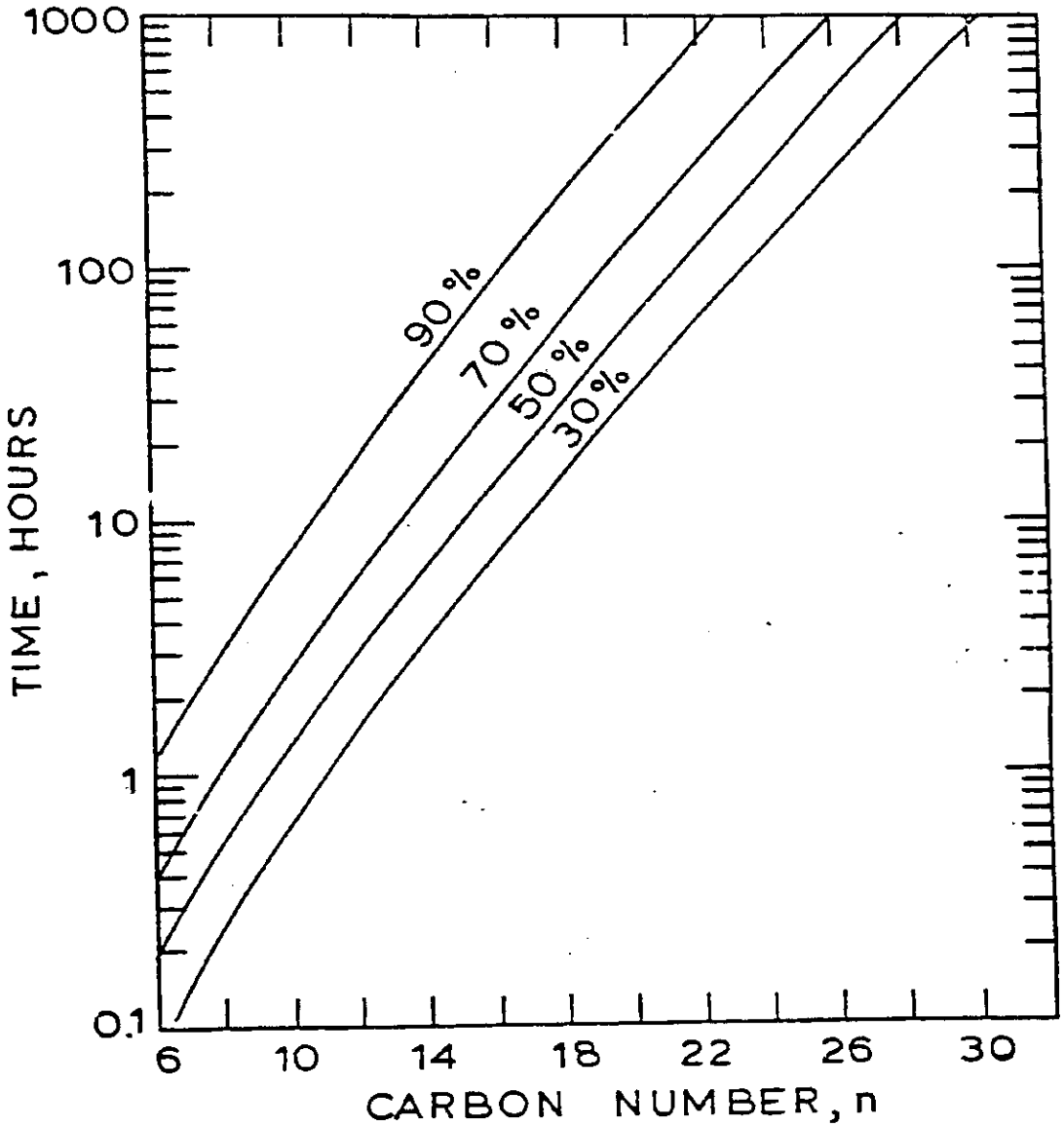

Figure 1-7. Time Required for Specified Percent of Carbon Number n to Have Appeared Overhead.

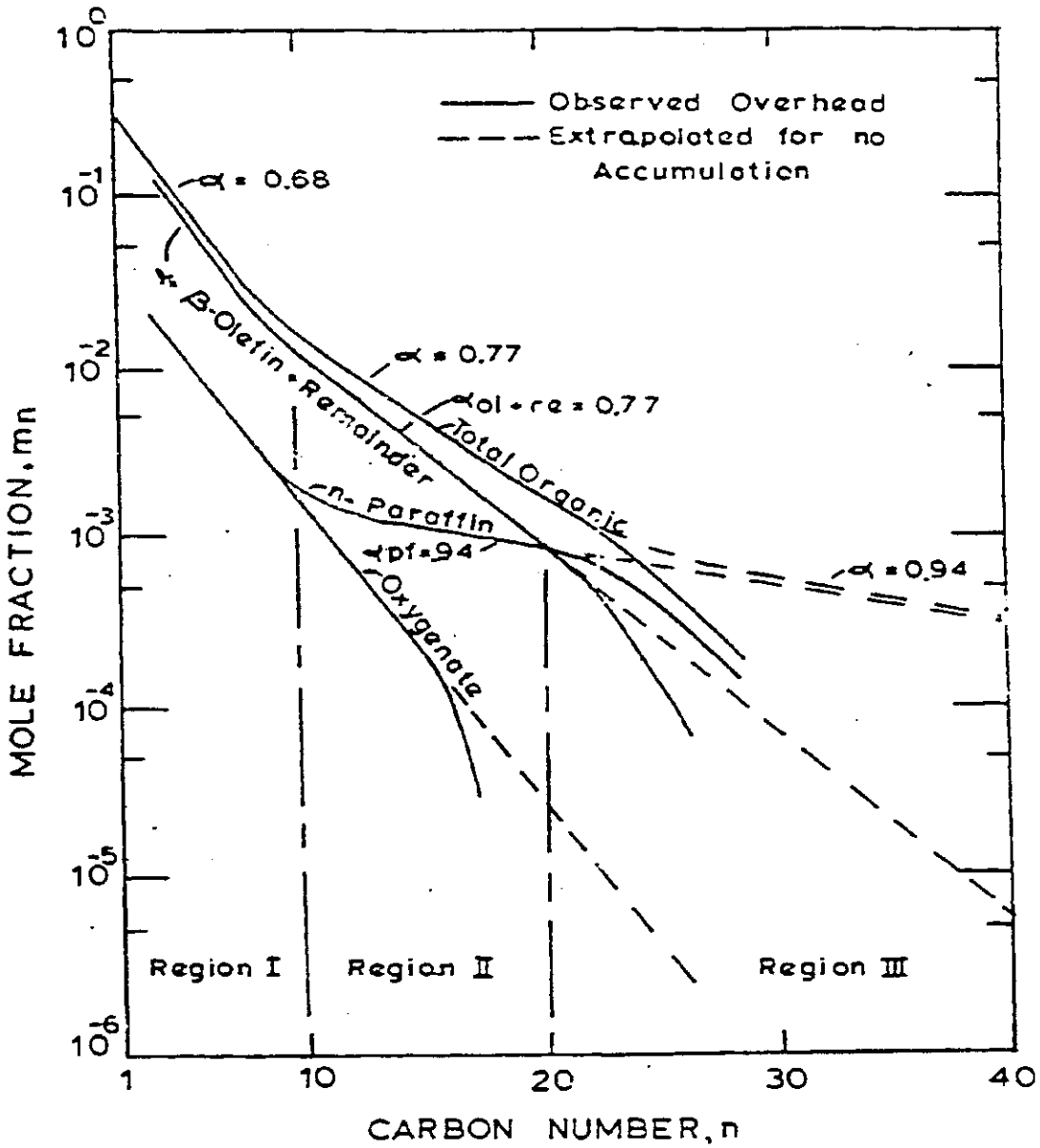

Figure 1-8. General Form of Observed Flory Plot.