Center for Applied Energy Research

at University of Kentucky

www.caer.uky.edu

Catalysis Research and Testing Center

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Anderson-Schulz-Flory Product Distribution – Can it be Avoided for Fischer-Tropsch Synthesis?

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The Schulz distribution function is applicable generally if there is a **constant** probability of chain growth, a, and $a < 1$; the latter requirement applies when some reaction limits the chain growth. The probability for chain growth, a, is defined as:

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$$a = r_p / (r_p + S\, r_t)$$

r_p = chain propagation

R_t = chain termination

Constant with carbon number

Mass fraction considered to be continuous function so can integrate rather than sum and leads to:

$$\log (m_P/P) = \log(\ln^2 a) + (\log a)P$$

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G. A. Huff, Jr. and C. N. Satterfield, J. Catal., 80 (1984) 370

$$m_n = x(1 - a_1)\, a_1^{n-1} + (1 - x)\,)\,(1 - a_2)\, a_2^{n-1}$$

M_n = mole fraction of carbon number n

a_1 and a_2 = chain growth probabilities on the two sets of sites

x = mole fraction of product synthesized on sites 1

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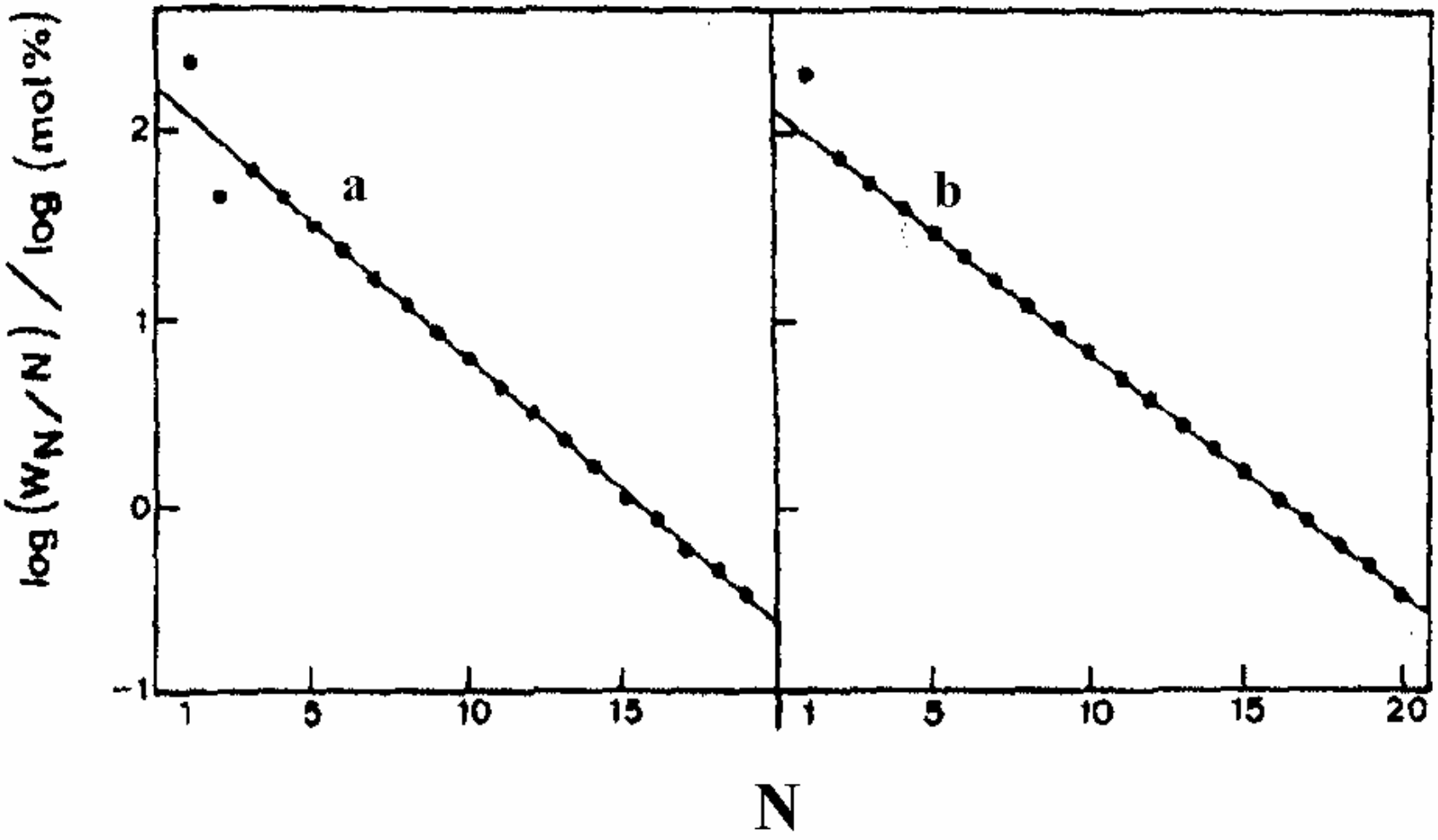

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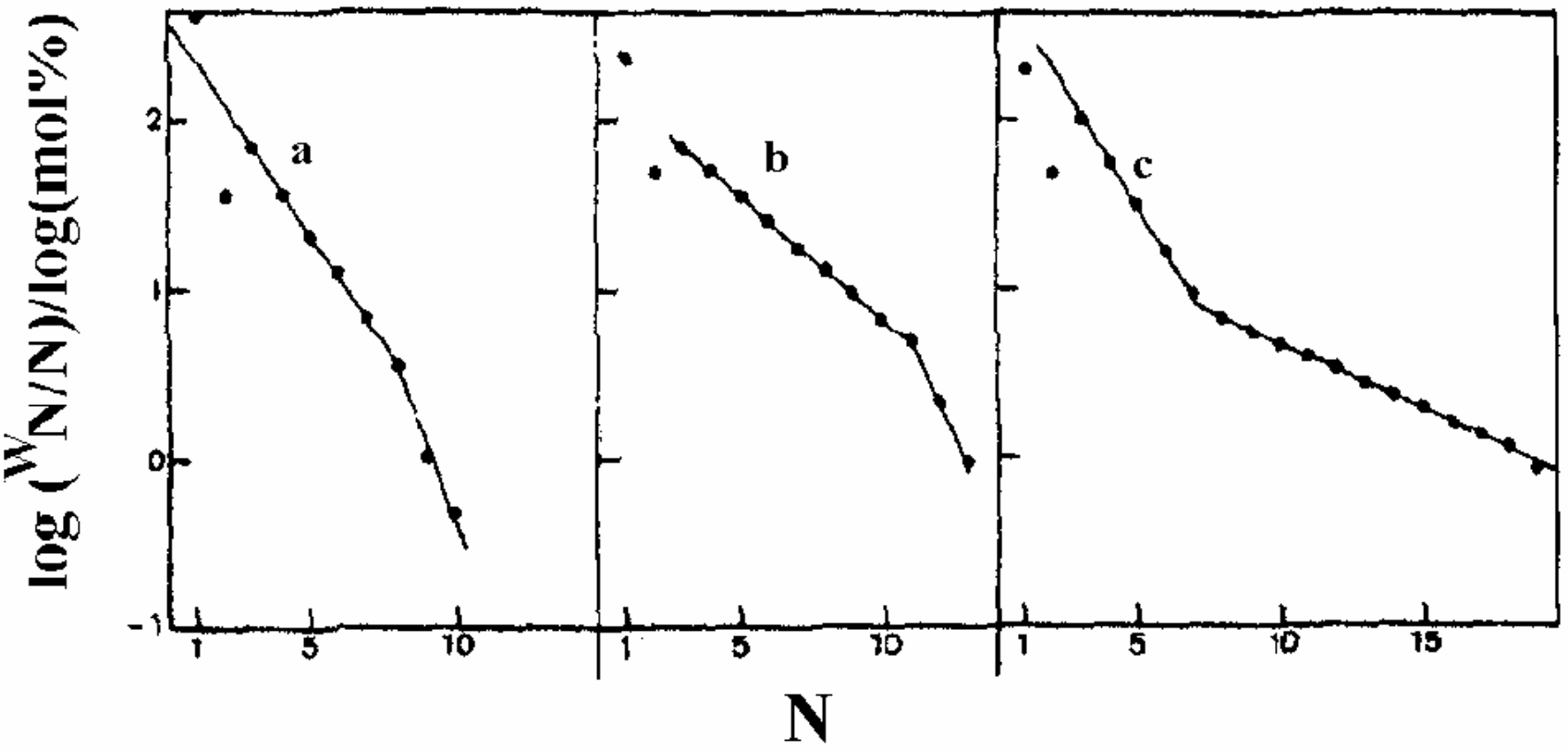

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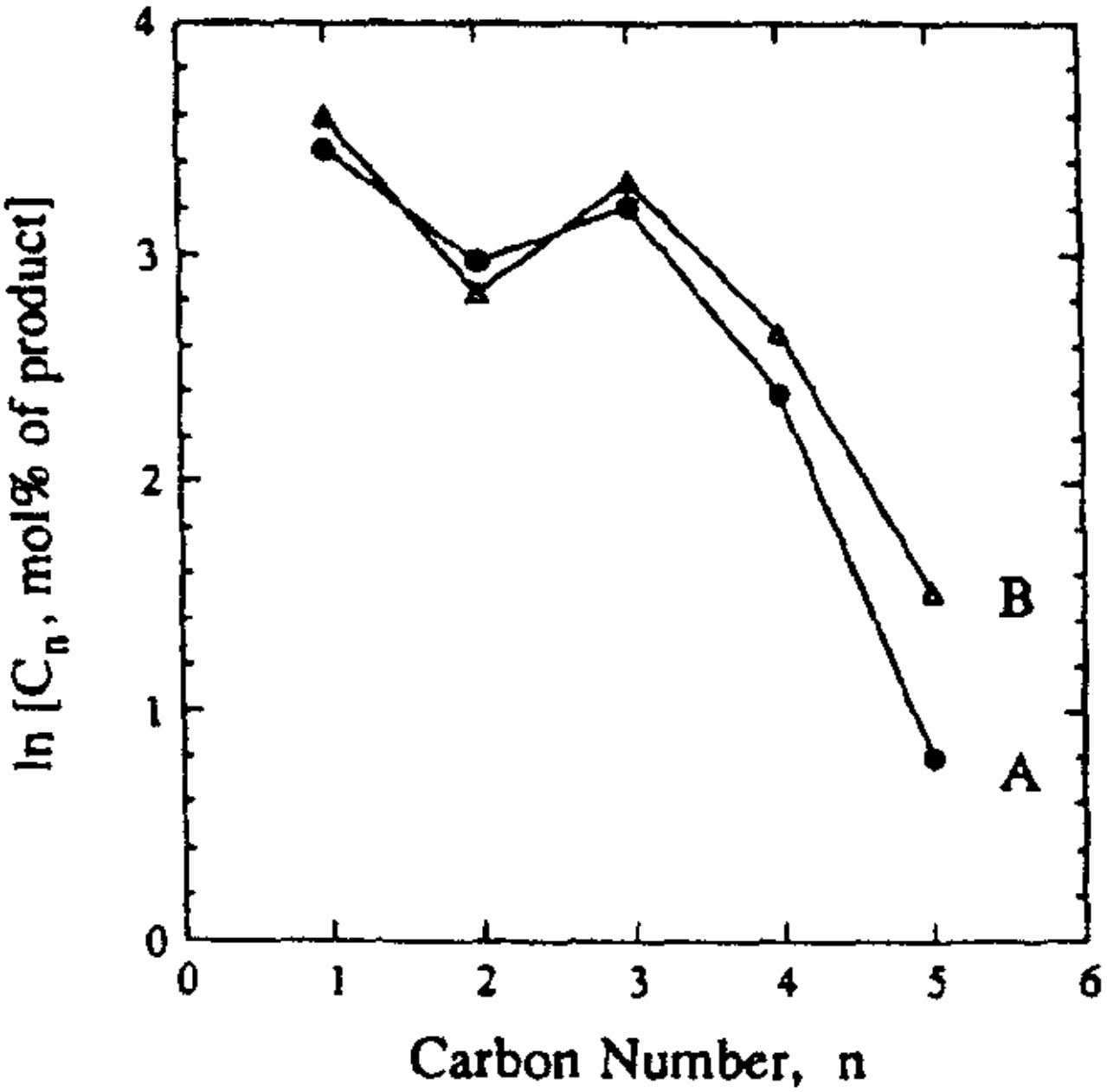

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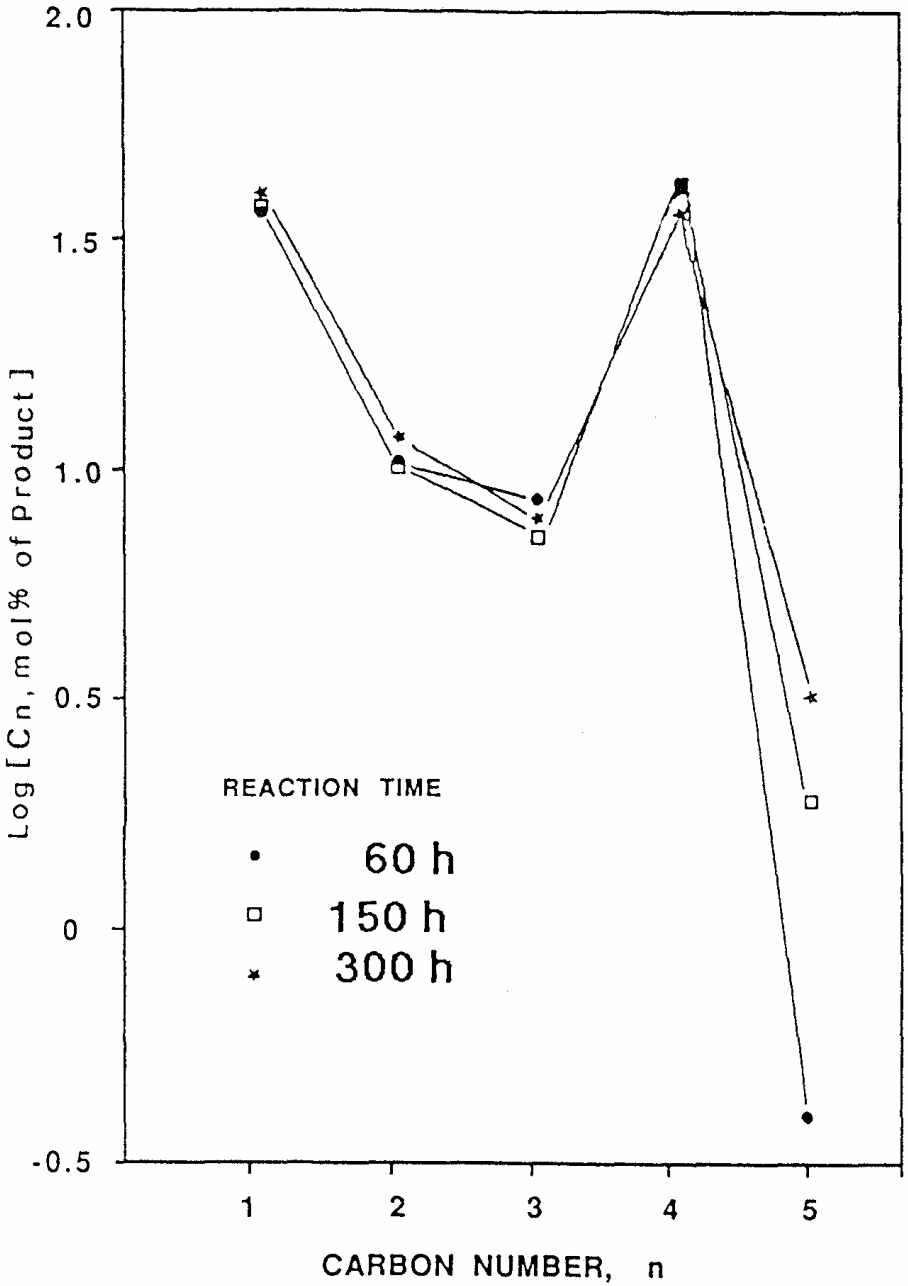

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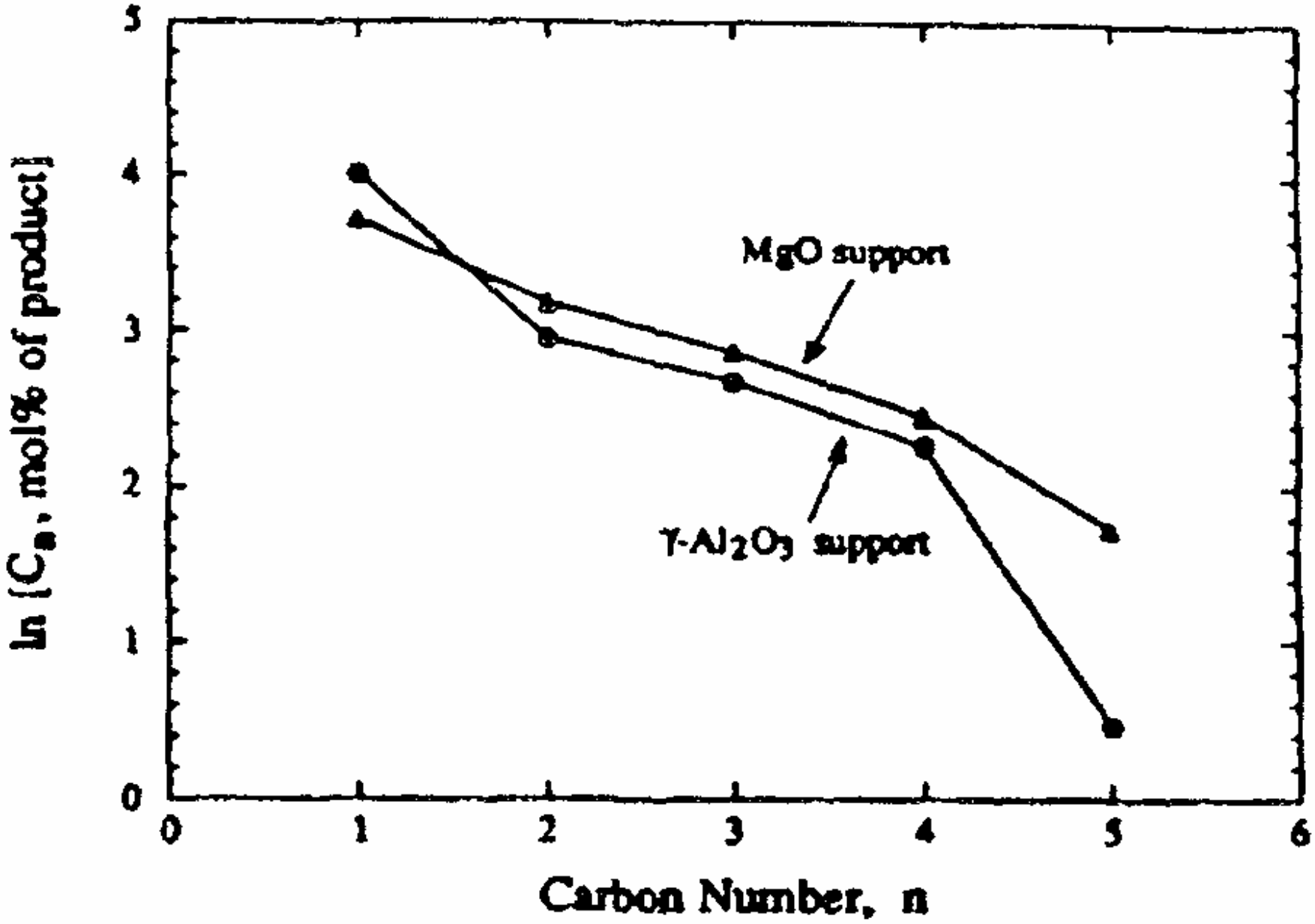

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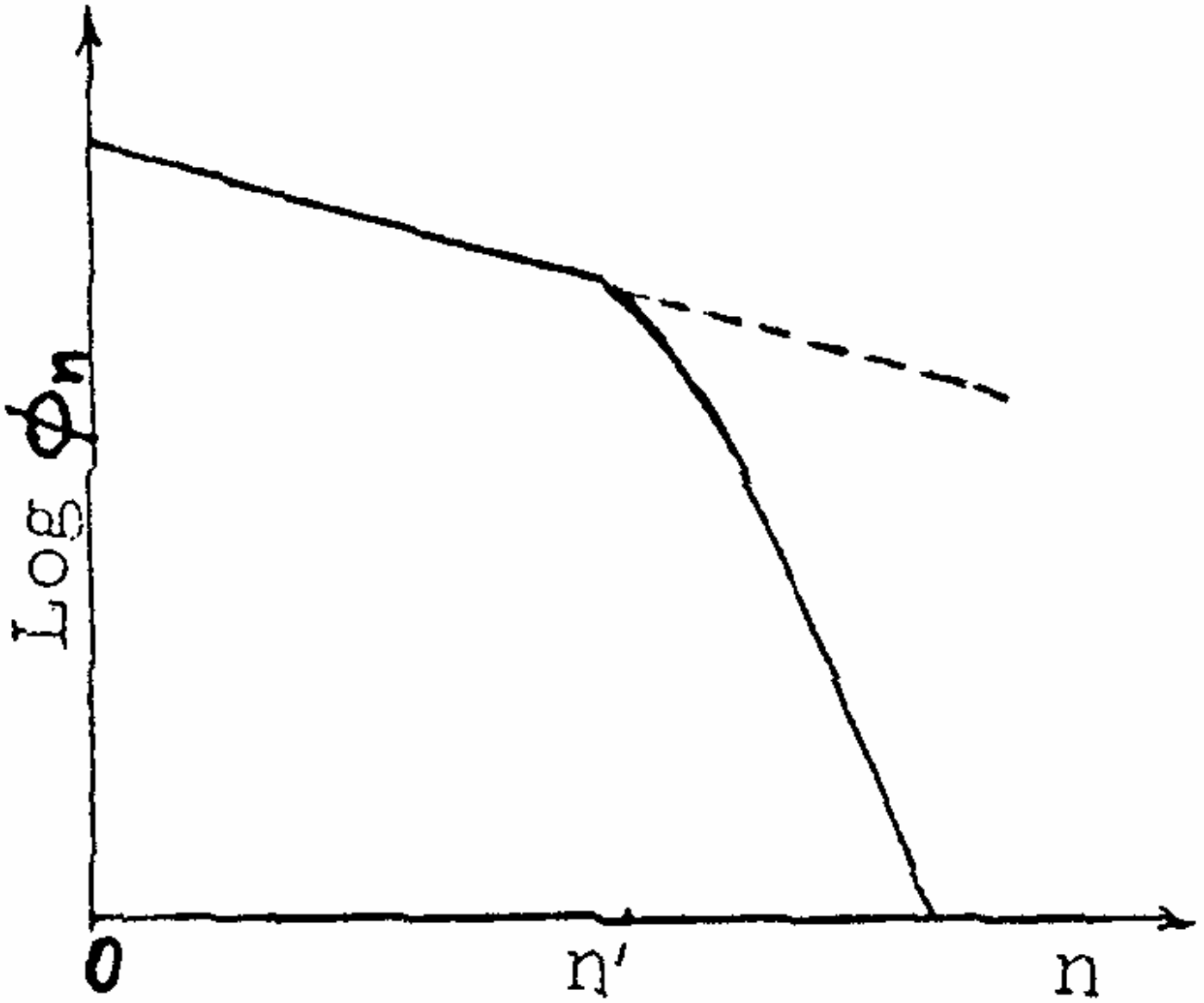

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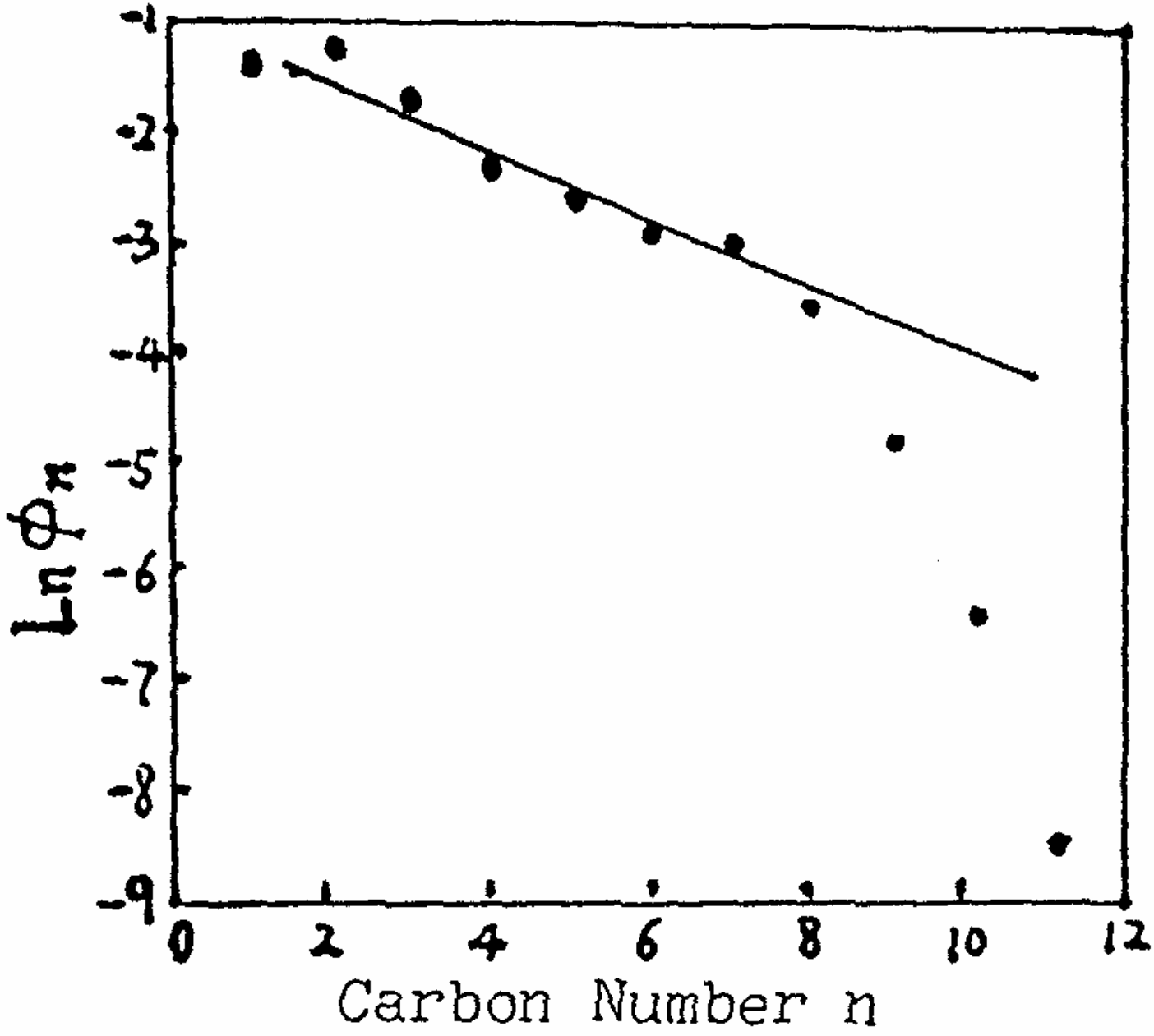

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H. G. Stenger, Jr., J. Catal., 92 (1985) 426

- Assumed a random distribution of sites and assigned this X.
- X is a dimensionless variable proportional to the concentration of K (promoter) on (iron) surface
- Assuming a normal distribution, fraction of sites with a potassium conc. X is:

$$F(X) = 1/(2)^{1/2} \exp((X - X_{sm})^2)$$

where X_{sm} is K conc. of maximum probability

- An exponential dependence of a on X is assumed

$$a(X) = 1 - (1 - a_0) \exp(-bX)$$

Where a_0 is chain growth probability at X = 0 (pure iron) and b represents the strength of interaction between neighboring K and Fe

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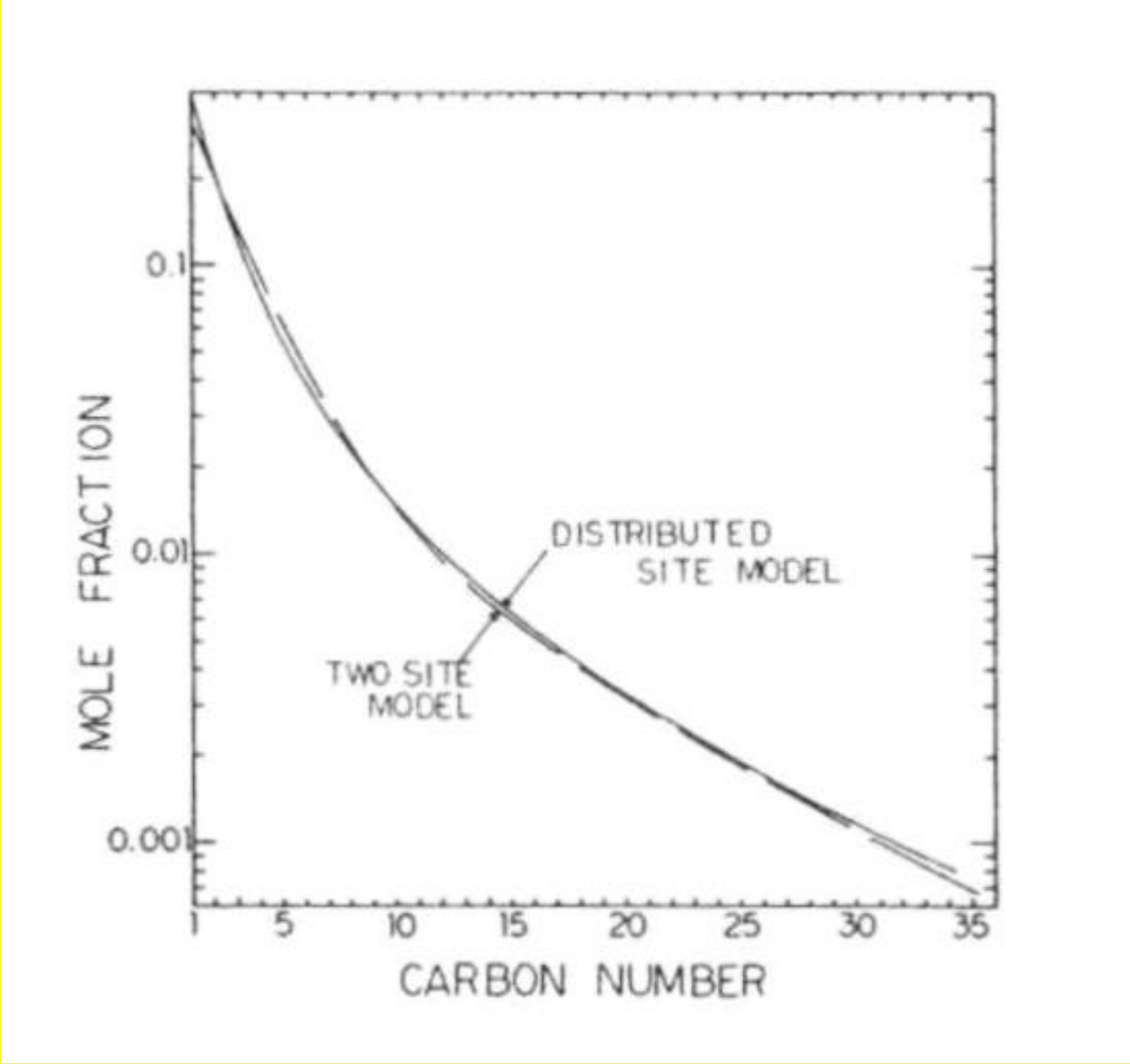
H. G. Stenger, Jr., J. Catal., 92 (1985) 426



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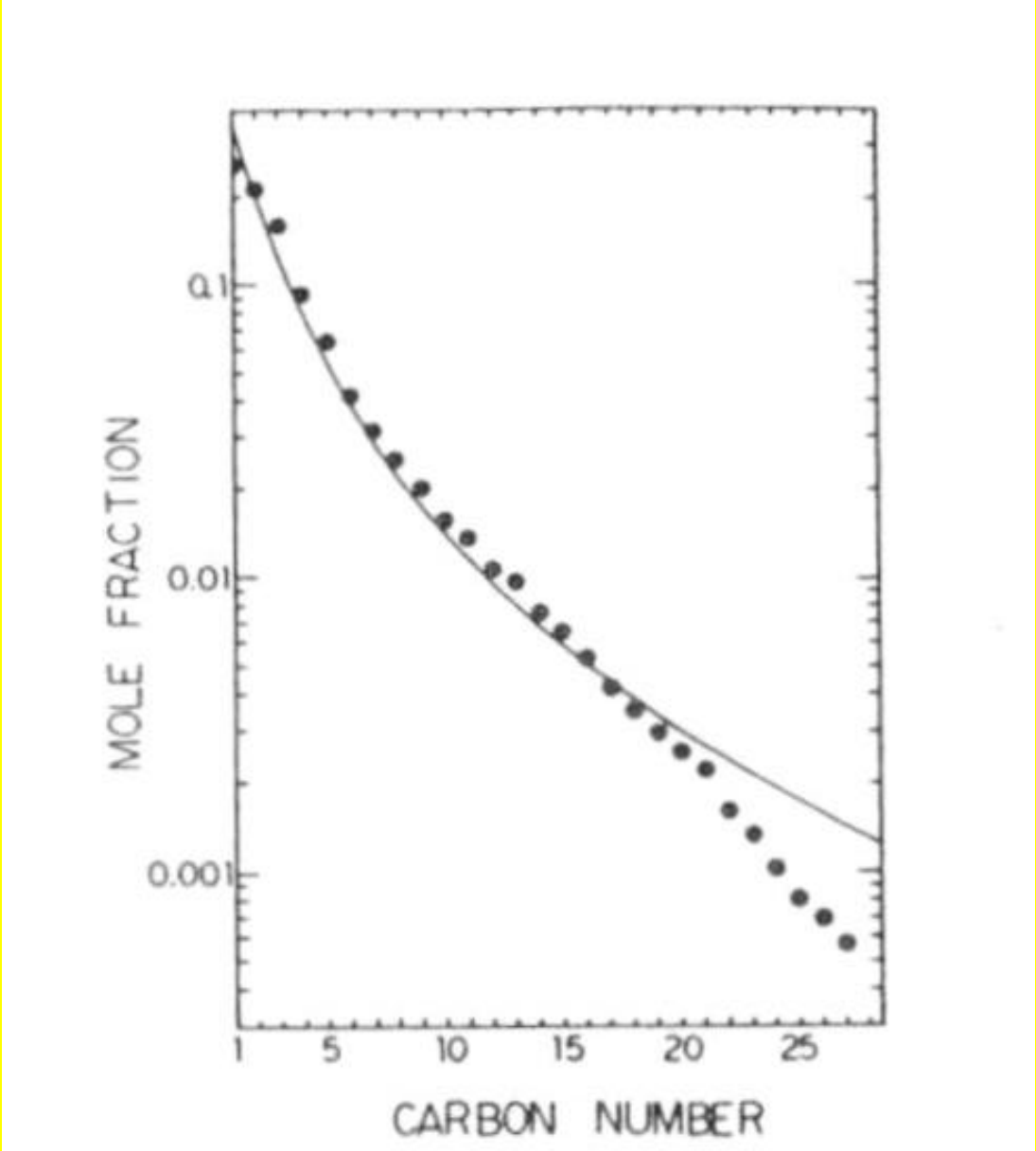

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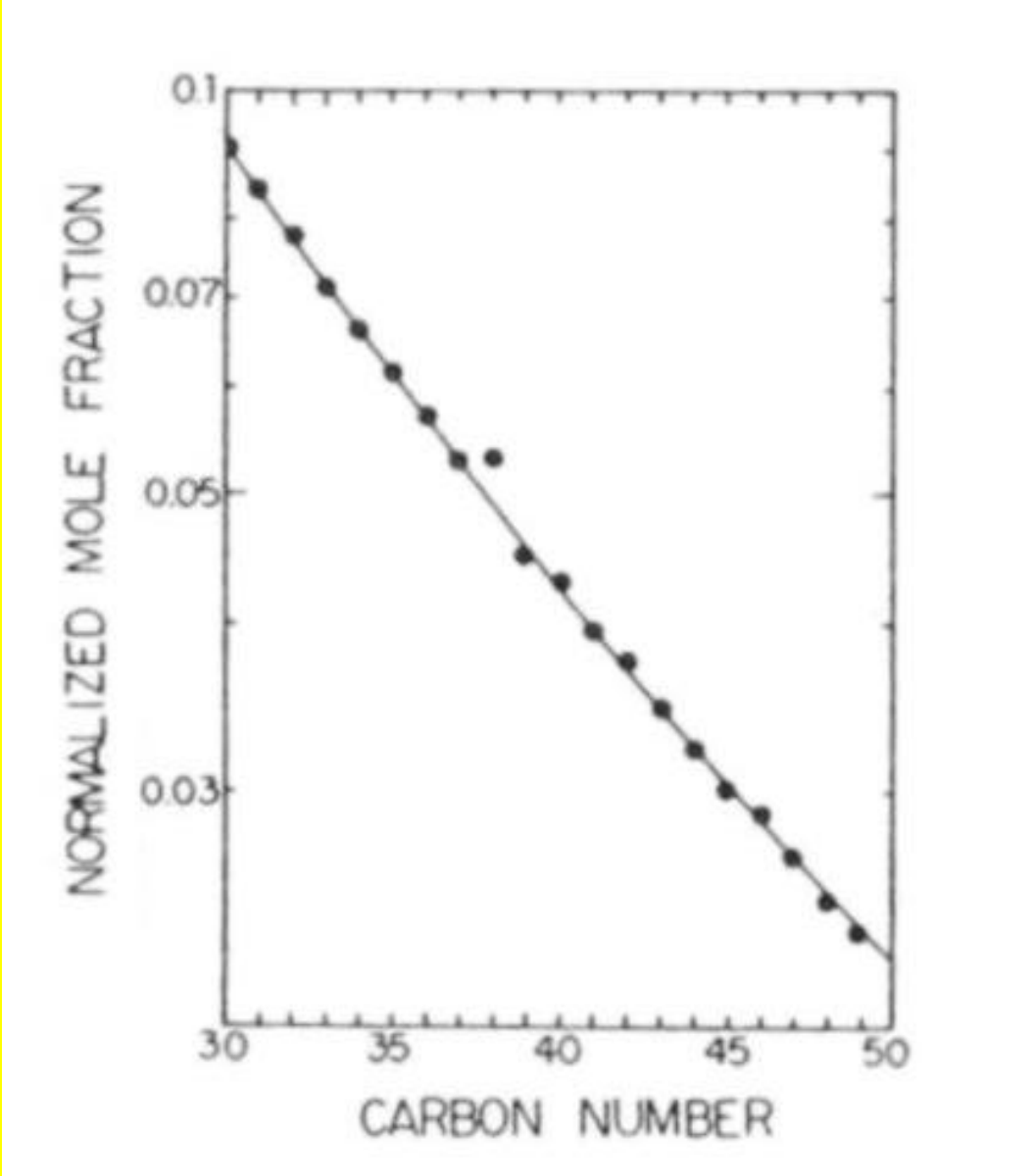

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R. Snel, Catal. Lett., **1** (1988) 327

- Reported first chemically induced negative deviation
- Degrade mixed metal (Fe:Ca = 1) citrate complex and then add Cs_2SO_4 (Fe:Cs = 33)
- Fixed-bed microreactor with on-line g.c. operated at 2.0 Mpa, 543 K, H_2/CO = 0.5 and VHSV = 1,000.
- Unpromoted sample followed ASF with a = 0.63.
- Negative deviation with promoted catalyst as in following figure

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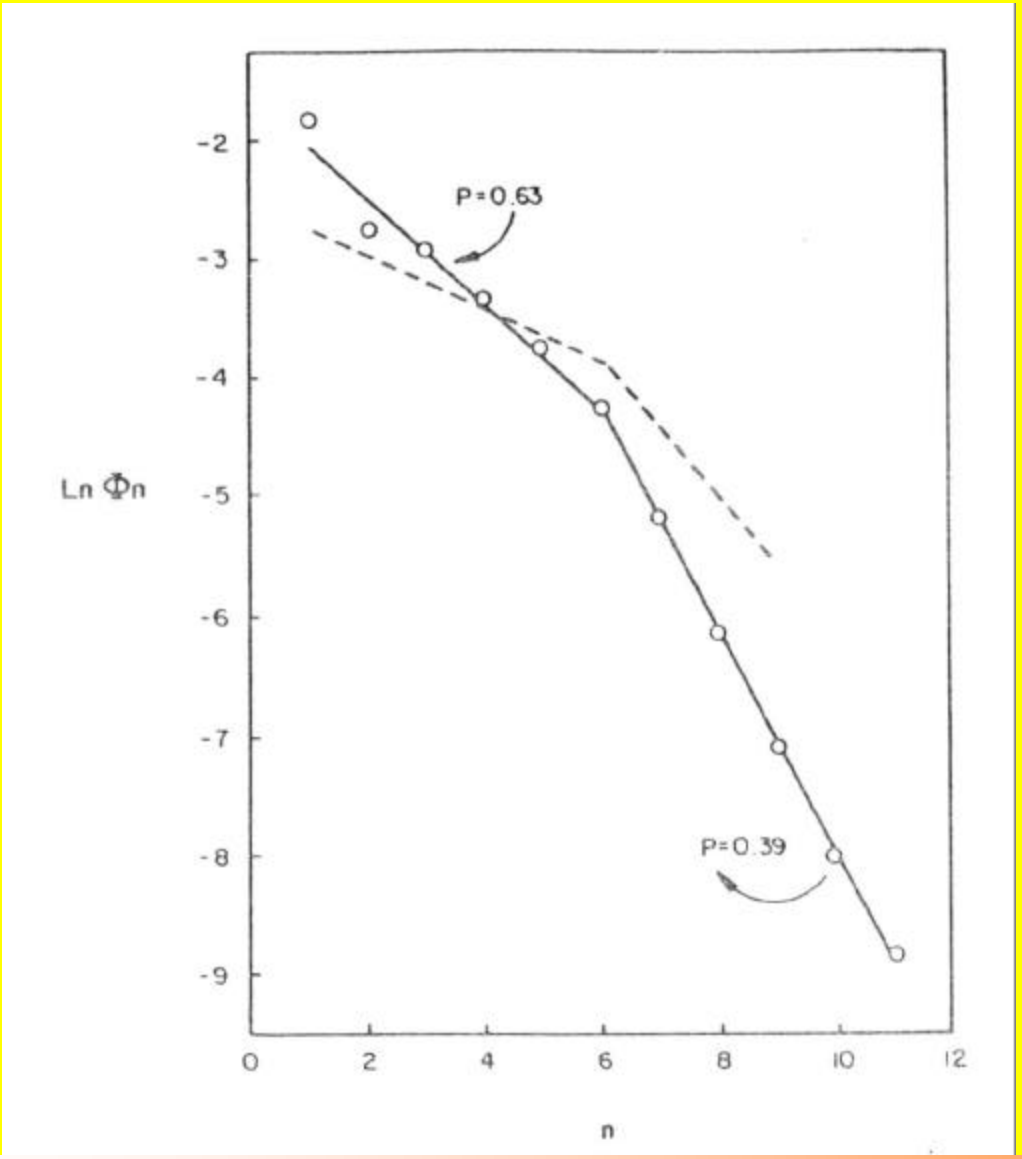
R. Snel, Catal. Lett., **1** (1988) 327



Chain Limiting (Cut Off)

Chain limiting, as used in the literature, may be divided into two broad categories. In many instances, the definition has not been given and considerable misunder-standing has resulted from the use of chain limiting.

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Low Alpha Distribution

This distribution is required for operation in a fluid-bed reactor. If liquid products are formed in the fluid-bed reactor, either the circulating as used initially at Sasol or fixed-bed as used in the Brownsville, Texas, the products are low molecular weight but follow a normal ASF distribution, or may have a slight positive deviation. If not, catalyst particles will adhere to each other and eventually become so large that they cannot be fluidized.

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Bifunctional Catalysis

The combination of FT synthesis with cracking or hydrocracking processes was commonly practiced in Germany during the 1930-1940 period; however, the two operations were obtained in separate processes. Obviously, cracking the heavier products to low molecular weight products can cause deviations from ASF.

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Bifunctional Catalysis

To our knowledge, the first to attempt to conduct the two processes in a single reactor were Gulf workers in the 1970s (14). They conducted the synthesis with a mixed bed of cobalt catalyst and a silicate cracking catalyst; the product distribution deviated from ASF. Mobil Oil workers conducted extensive studies in which they attempted to effect bifunctional catalysis in one reactor (15); eventually they settled on separate reactors for the two processes. Separate processes are also utilized at the commercial plant operated by Shell Middle Distillate Synthesis (16). However, the deviation from ASF is artificially introduced by cracking of heavier hydrocarbons and is not a deviation from the FT synthesis.

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Telomerization Model

I. Puskas, R. S. Hurlbut and R. E. Paul, J. Catal., **139** (1993) 591

- Precipitated promoted cobalt supported on diatomaceous earth reduced at 380^{o}C and used in fixed-bed reactor
- Feed was 17% CO, 34% H_2 and 49% N_2
- Products passed through wax trap and then on-line g.c.
- Model concepts:

  Primary products follow single alpha

  Deviations due to telomerization - new chain initiated by primary product

  Only hydrocarbons form in the reaction

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R. S. Hurlbut, I. Puskus and D. J. Schumacher, Energy & Fuels, **10** (1996) 537.

- Fixed-bed reactor (3/4 inch) using 1-3.3 mm or extruded catalyst particles.
- Nitrogen in the feed decreased the growth factor (alpha).
- Increasing space velocity increased the rate but did not impact alpha.
- Rate was a linear function of temperature.
- Results were considered to support:

  Multiplicity of chain growth probabilities (multi-value alpha)

  Diffusional limitations of the rates

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N. O. Egiebor, W. C. Cooper and B. W. Wojciechowski, Canadian J. Chem. Eng., **63** (1985) 826.

- Break at about C_{13} only due to alkanes, other products obey ASF
- Assert that primary products form at same rate but that termination is species specific
- Many observe the break at C_{13} and with many catalysts - the phenomenon is governed by the nature of the C_{13} molecule and the catalyst.

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Iron versus Cobalt Catalysts

- With an iron catalyst an alcohol initiates chain growth about 50-100 times as rapidly as the same carbon number alkene
- With a cobalt catalyst, alkenes can initiate chain growth but alcohols are nearly inert
- Implies different mechanism applies for iron and cobalt

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E. Iglesia, S. C. Reyes and R. J. Madon, 12th NAM, Abstract PC02, May 5-9, 1991

- Olefins readsorb to initiate surface chains that are indistinguishable those formed from CO/H_2
- Diffusion enhanced alkene readsorption increases alpha and alkane fraction
- Deviations from ASF described by transport effects within catalyst pores without requiring several chain growth sites.
- Experimental results were for a Ru catalyst by later papers indicate generality of model

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J. Eilers, S. A. Posthuma and S. T. Sie, Catal. Lett., 7 (1990) 127

- Close agreement with ASF with several hundred independent runs with various catalyst formulations under different operating conditions.
- Data represented in plot does not provide data over the carbon numbers that define the break point for a two alpha ASF

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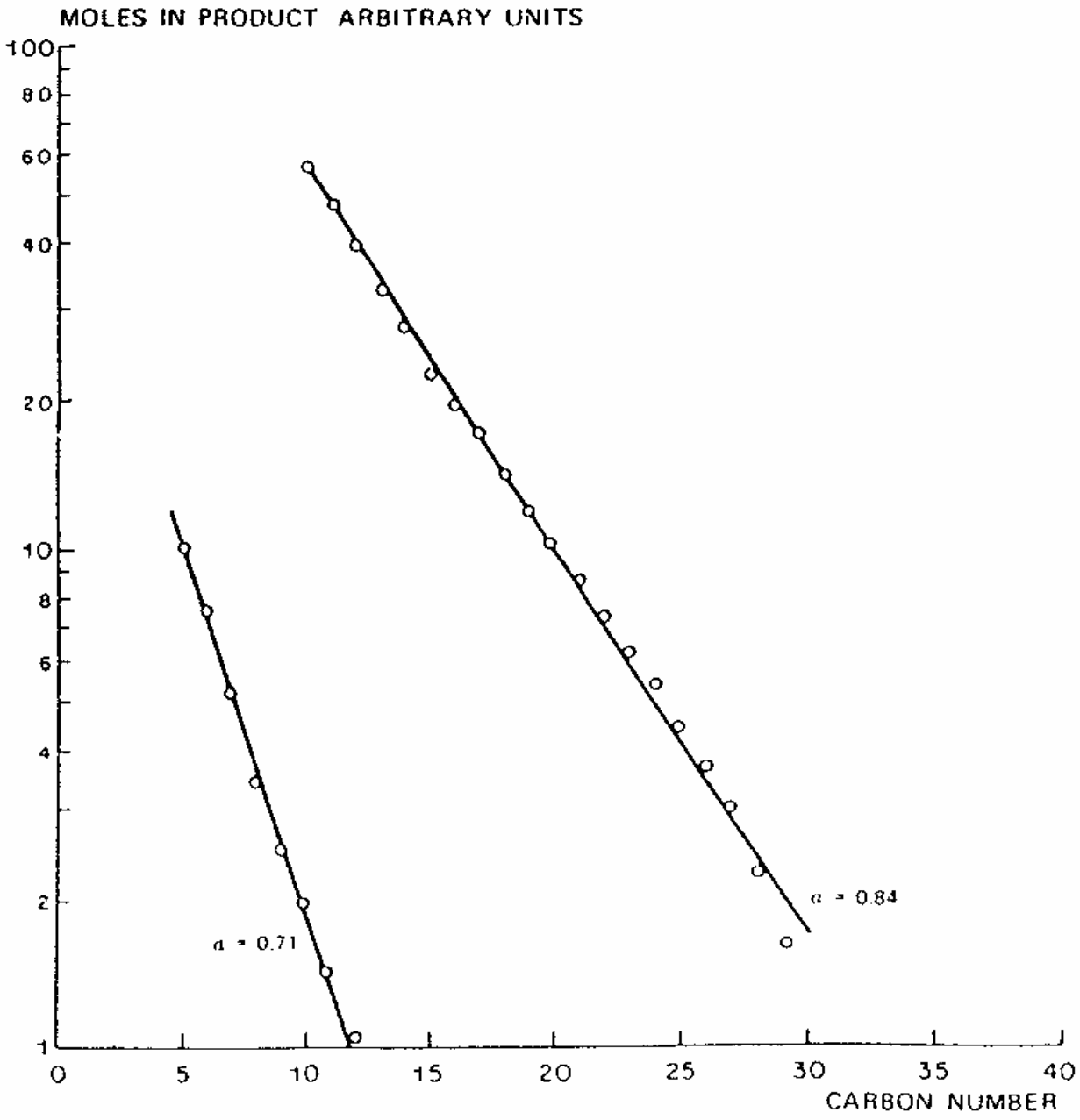

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Hydrogenolysis

Operation with an iron catalyst and ^{14}C-labeled C_{28} alkane, no evidence for hydrogenolysis was obtained for gas phase products or for n-1, n-2, etc liquid products

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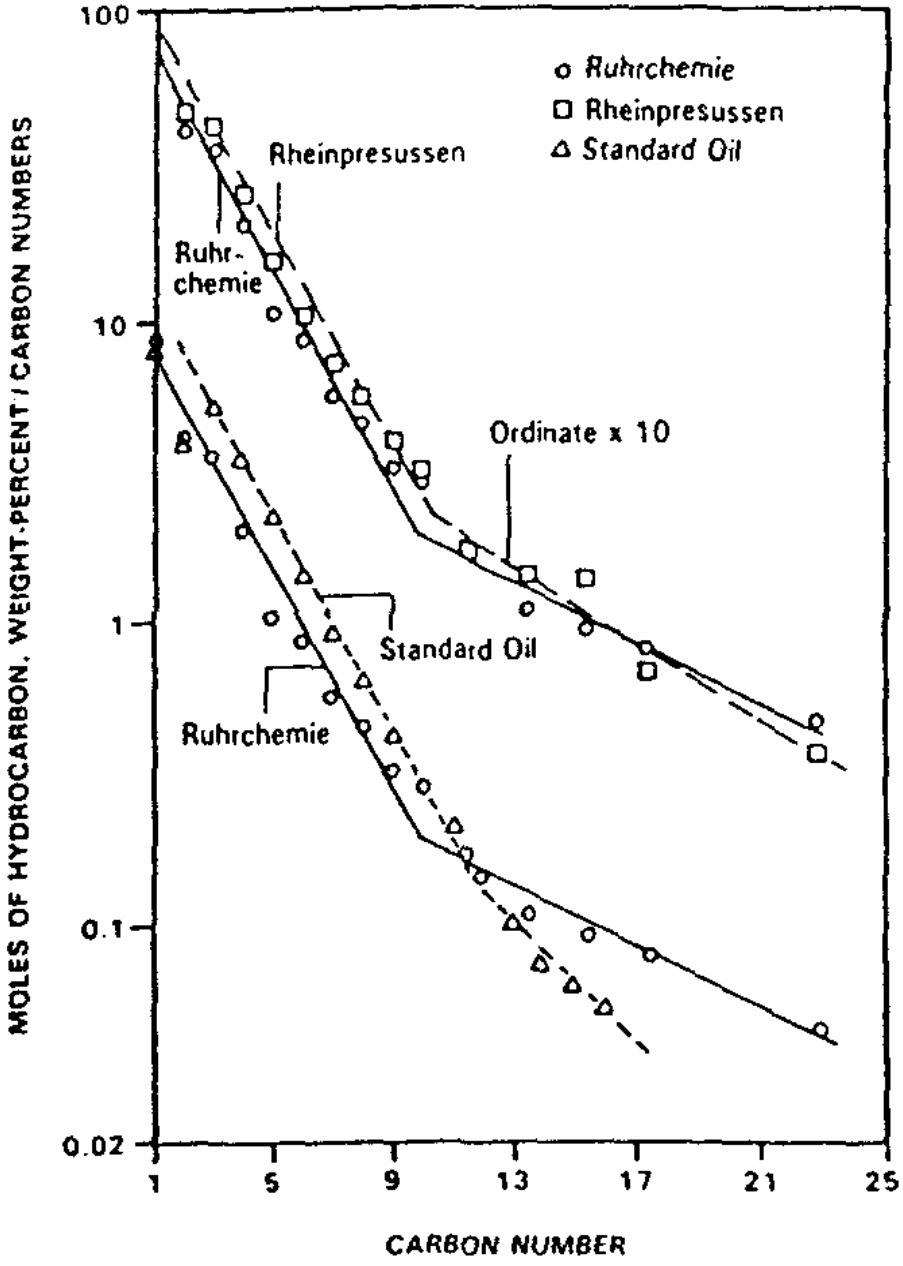

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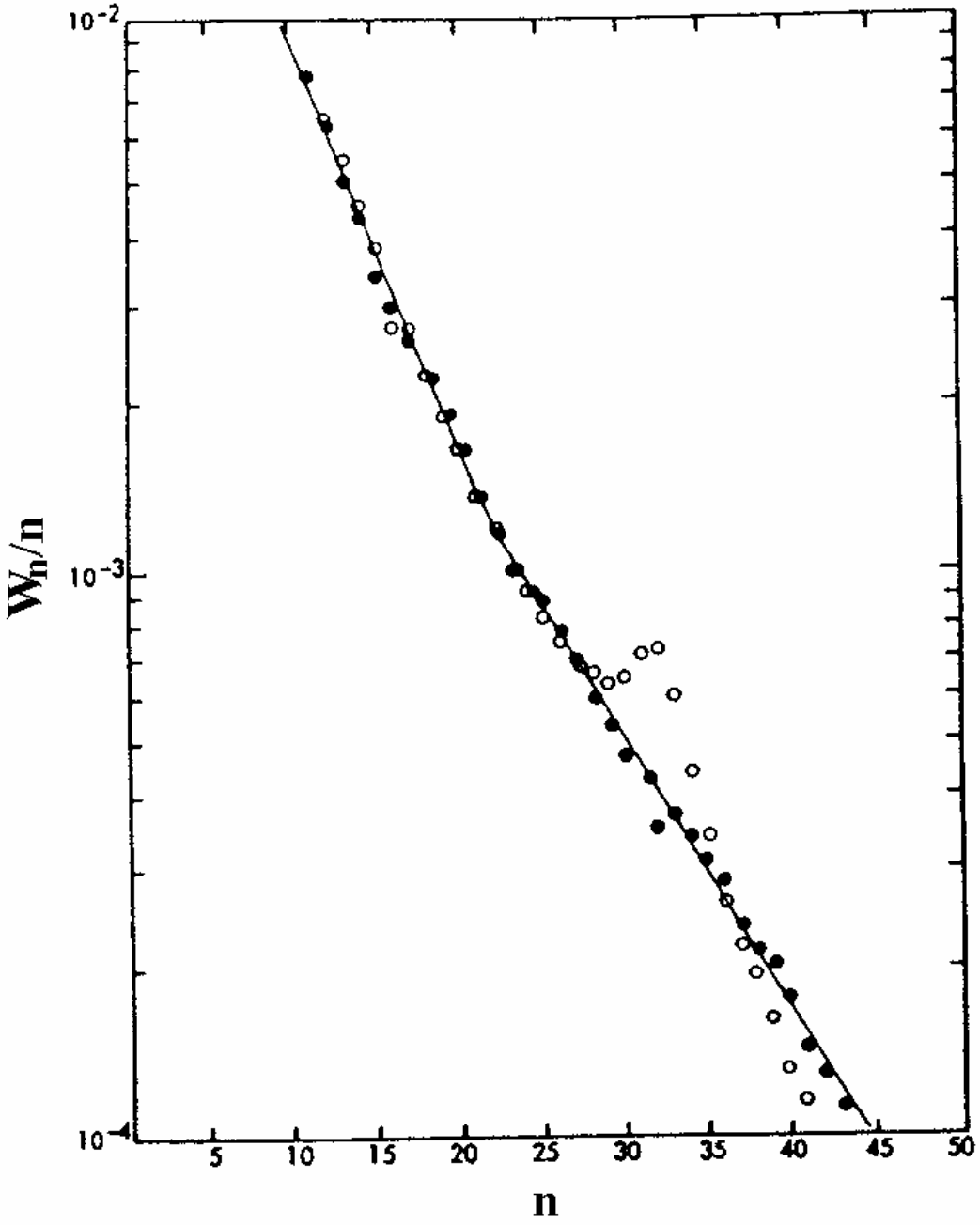

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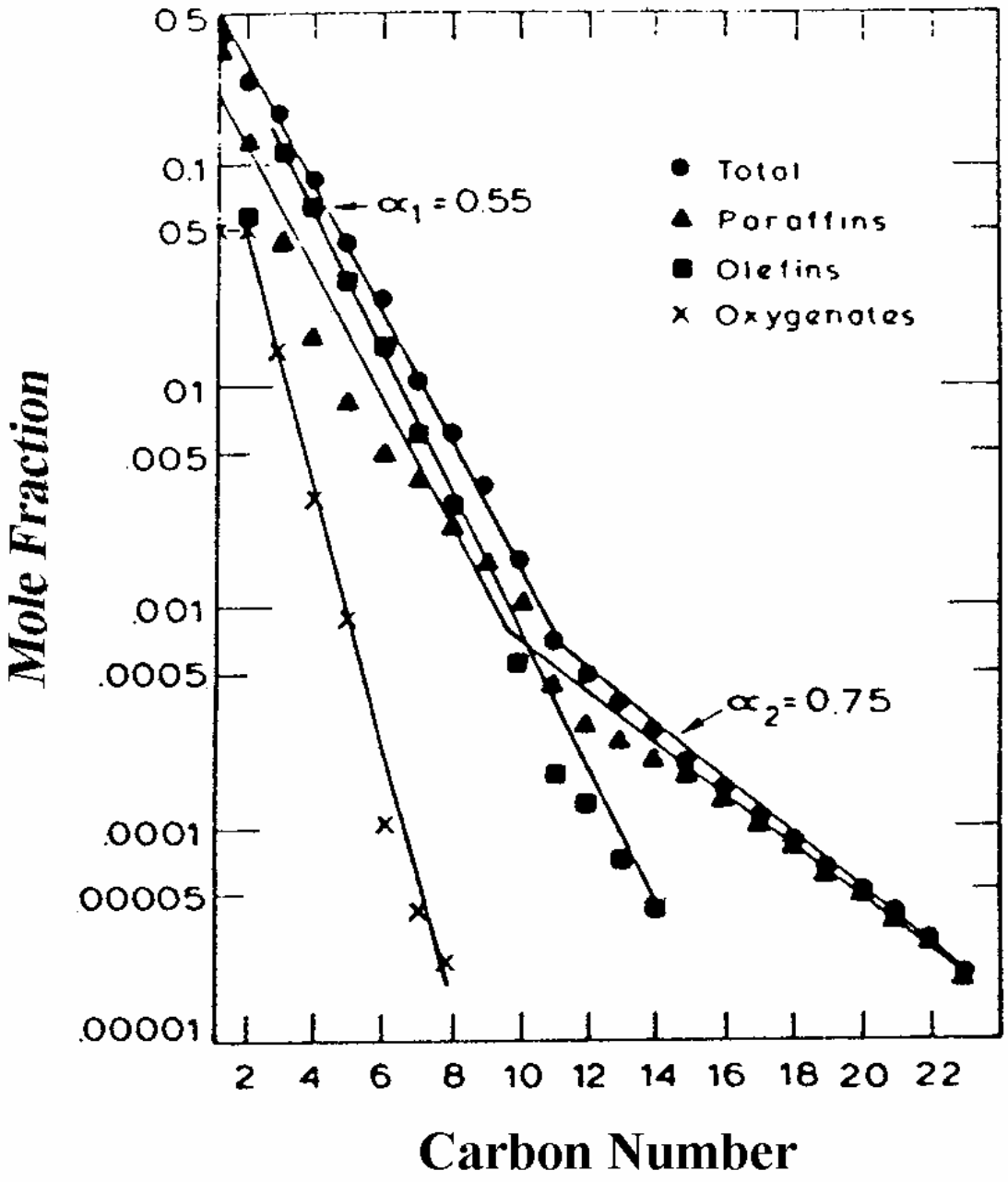

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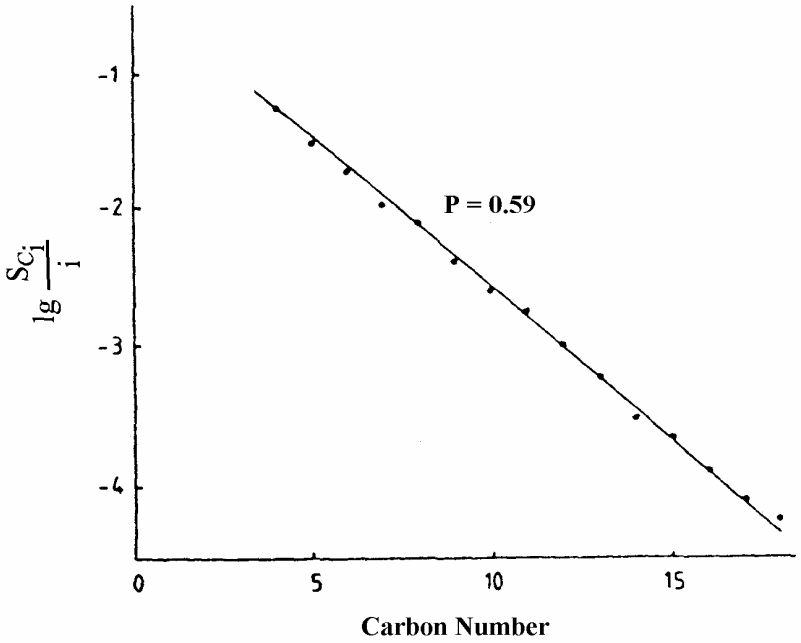

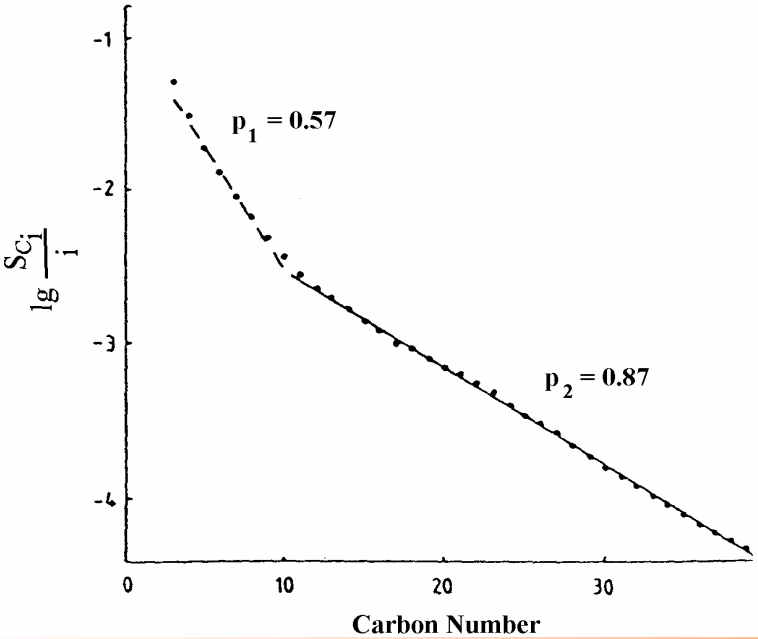

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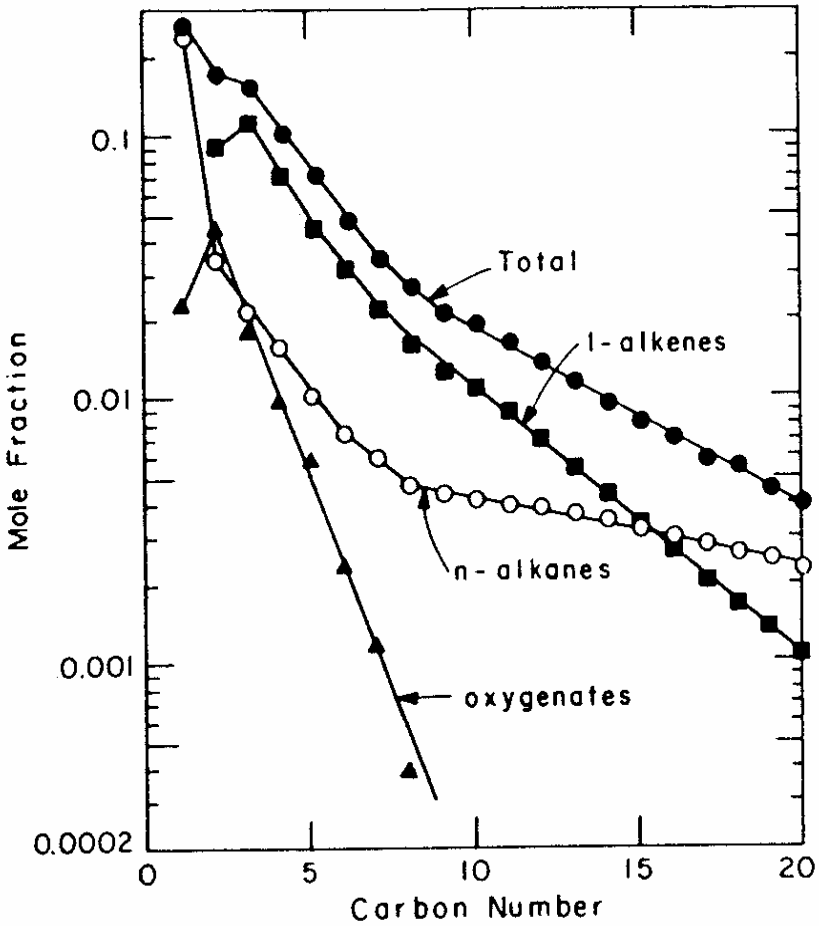

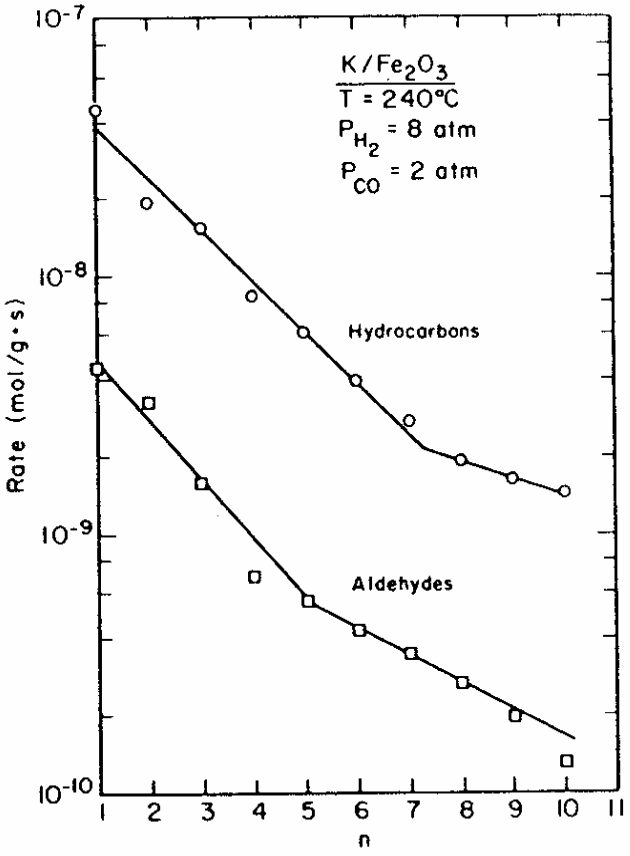

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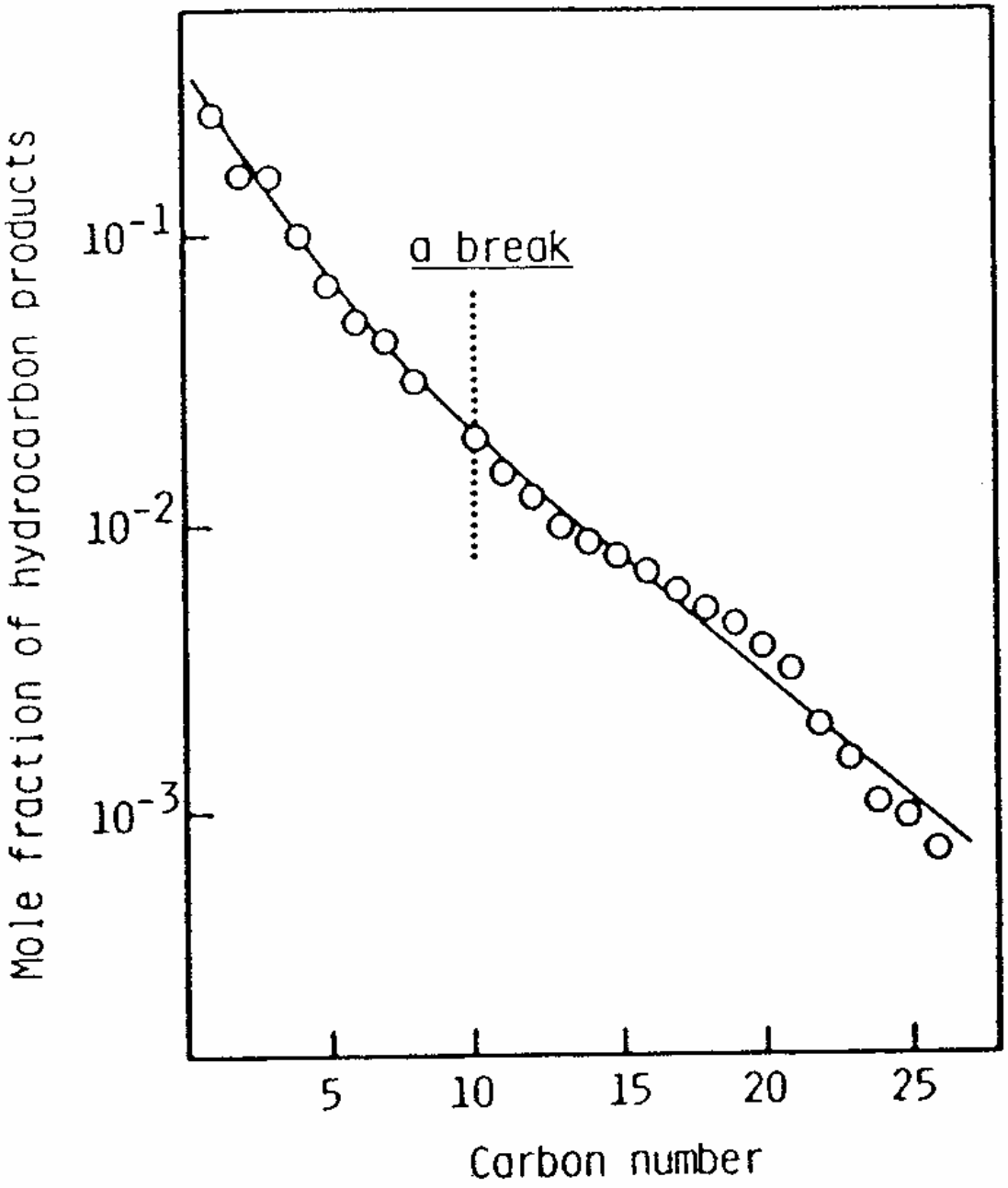

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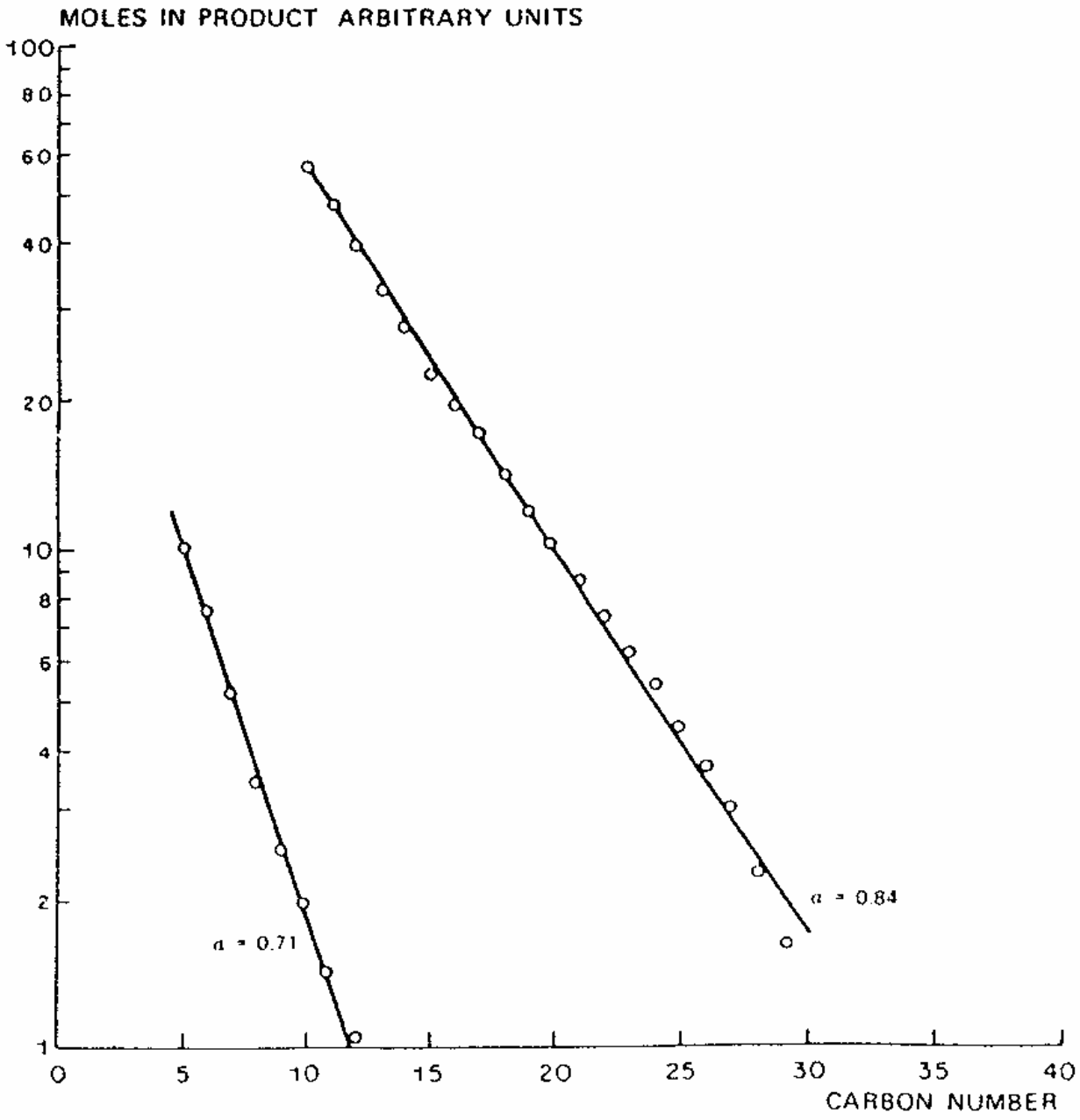

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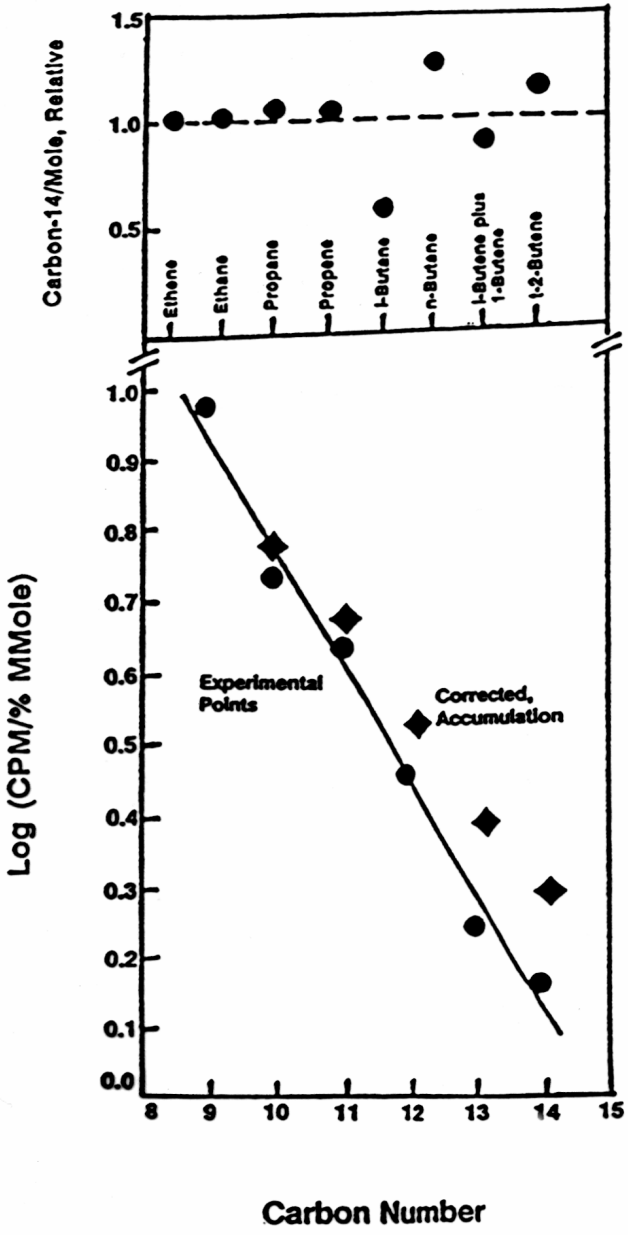

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Conclusions

- Negative deviations are believed to be due to experimental artifacts and no reliable evidence is available for a departure from ASF at some specific carbon number
- Positive deviations are observed frequently and for a variety of catalysts but these are considered to be impacted frequently by reactor disguise
- Positive deviations are frequently due to accumulation of heavier products in catalyst pores and/or the reactor void volume

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