Application of Equilibrium Analysis to a Fischer–Tropsch Product

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In the Fischer–Tropsch (FT) process, synthesis gas is converted, *inter alia*, to aliphatic hydrocarbons, consisting predominantly of *n*-alkanes and *n*-alkenes, over iron- or cobalt-based catalysts. The product composition follows an Anderson–Schultz–Flory (ASF) distribution which can be expressed as

$$\ln x_i = i(\ln \alpha) + \ln\left(\frac{1 - \alpha}{\alpha}\right), \quad (1)$$

where x_i is the mole fraction of species with i carbon atoms and α is the probability of chain growth (*1*).

Equation (1) predicts a linear relationship between $\ln x_i$ and i, and is valid for a small range of carbon numbers (typically $4 < i < 10$). For higher carbon numbers, the experimental mole fractions often deviate from those predicted by Eq. (1). For example, Satterfield and co-workers (*2, 3*) studied the FT synthesis in a slurry reactor, and attributed their negative deviation to experimental artifacts such as temperature gradients and the difficulty of combining the products collected in the different traps.

Dictor and Bell (*4*) modeled an FT slurry reactor and demonstrated that their observed negative deviation could have resulted from mass transfer effects, in particular, from an accumulation of less volatile (higher molecular weight) hydrocarbons in the liquid phase. They suggested that this could explain the similar trends observed

using other types of reactors since such species should fill the pores and cover the external catalyst surface. In this paper, we demonstrate that the ASF distribution (Eq. (1)) can be derived from an equilibrium basis, and we discuss the consequences arising therefrom.

THEORY

The equilibrium chemical potential, μ_i, of an alkene (*o*) can be expressed as (*5*, pp. 46–47)

$$\mu_{io} = \mu_{io}^* + \ln x_{io} = i(\psi_{Co} + 2\psi_{Ho}), \quad (2)$$

where μ_i^* is the standard chemical potential of species i at temperature T and pressure P, i is the number of carbon atoms in the molecule, and ψ_C and ψ_H are the Lagrange multipliers of carbon and hydrogen, respectively. Similarly, the chemical potential of an alkane (*p*) can be expressed as:

$$\mu_{ip} = \mu_{ip}^* + \ln x_{ip} = i(\psi_{Cp} + 2\psi_{Hp}) + 2\psi_{Hp}. \quad (3)$$

Alberty (*6*) has demonstrated that the free energy of formation (Gibbs' function, ΔG_f^0) for the *n*-alkenes and for a "lumped" (*7*) mixture of alkene isomers of carbon number i can be expressed as

$$\Delta G_{fi}^0 = A + Bi. \quad (4)$$

Values of A and B for the *n*-alkenes for 400, 500, and 600 K, taken from (*6*) are listed in

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T (K)	n-alkenes		n-alkanes		
	A	B	A	B	R^2
400	22.01	18.49	−51.94	18.44	0.9999
500	7.20	28.74	−53.31	28.68	0.9999
600	−7.57	39.20	−54.32	39.11	0.9999

Table 1. We note that ΔG_f^0 for the n-alkanes can be expressed in such a fashion; Table 1 also lists values of A and B and the regression coefficient, R^2, for the linear regression of the ΔG_f^0 data for the n-alkanes taken from Alberty and Gehrig (9). As did Alberty (6) for the n-alkenes, we included in the regression only species with four or more carbon atoms.

Assuming ideal-gas behaviour for the aliphatic product (thus, $\mu_i^* = \mu_i^0 + \ln P$, where μ_i^0 is the standard chemical potential of species i at T), and taking $\mu_i^0 = \Delta G_{fi}^0/RT$ gives

$$\ln x_{io} = i(\psi_{Co} + 2\psi_{Ho} - B_o') - A_o' - \ln P, \quad (5)$$

and

$$\ln x_{ip} = i(\psi_{Cp} + 2\psi_{Hp} - B_p')$$
$$- A_p' - \ln P + 2\psi_{Hp}, \quad (6)$$

where A_o', B_o', A_p', and B_p' are the dimensionless constants (for use in Eq. (4)) of the n-alkenes and n-alkanes, respectively (i.e., $A_o' = A_o/RT$). Thus, at equilibrium, the distributions of n-alkenes and n-alkanes follow an ASF relationship. Equations (5) and (6) are valid both for systems containing solely n-alkenes or n-alkanes and for more complex mixed systems. In this development, we consider an FT product to be a partial equilibrium system; both the n-alkene and n-alkane homologous series achieve equilibrium among themselves, not with each other. Complete equilibrium among all the species does not occur.

The aliphatics distribution can be determined from

$$\ln x_l \equiv \ln(x_{io} + x_{ip}) = -\ln P$$
$$+ \ln\{\exp[i(\psi_{Co} + 2\psi_{Ho} - B_o')]\exp(-A_o')$$
$$+ \exp[i(\psi_{Cp} + 2\psi_{Hp} - B_p')]$$
$$\exp(-A_p' + 2\psi_{Hp})\}. \quad (7)$$

Equation (7) reduces to the form of Eq. (1) for $B_o' \cong B_p'$, as is the case for n-alkanes and n-alkenes, and $(\psi_{Co} + 2\psi_{Ho}) \cong (\psi_{Cp} + 2\psi_{Hp}) \equiv (\psi_C + 2\psi_H)$:

$$\ln x_l = i(\psi_C + 2\psi_H - B_o') - \ln P$$
$$+ \ln[\exp(-A_o') + \exp(-A_p' + 2\psi_{Hp})]. \quad (8)$$

Thus, a linear relationship between i and $\ln x_l$, the basis of the ASF distribution, can be derived from a thermodynamic basis.

DISCUSSION

Anderson (8) performed global equilibrium analyses for the FT synthesis and demonstrated that global equilibrium is not achieved. The implication of Eqs. (7) and (8) is that an FT product could be a system at partial equilibrium; some but not all species equilibrate. Such an equilibrium would occur if reaction kinetics controlled the yield of CO_2 and aliphatics, and equilibrium controlled the aliphatics distribution. Thus, the chain growth/equilibration step must be fast relative to the rate of formation of the initial hydrocarbon species.

Equation (8) is valid for the case $\psi_{Co} \cong \psi_{Cp}$ and $\psi_{Ho} \cong \psi_{Hp}$, which corresponds to hydrogenation equilibrium between the alkenes and alkanes. This case requires complete saturation of the aliphatic product which, typically, is not observed. Equation (8) also is valid for the case $(\psi_{Co} + 2\psi_{Ho}) \cong (\psi_{Cp} + 2\psi_{Hp})$ with $\psi_{Co} \neq \psi_{Cp}$ and $\psi_{Ho} \neq \psi_{Hp}$. In this case, both the alkenes and the alkanes achieve equilibrium among themselves (i.e., their distributions follow Eqs. (5) and (6), respectively) and hydrogenation equilibrium does not occur. This is consistent with the primary product being an al-

kene, and with chain growth reactions being more rapid than hydrogenation reactions.

We note that for the case $(\psi_{Co} + 2\psi_{Ho}) \neq (\psi_{Cp} + 2\psi_{Hp})$ or $B'_o \neq B'_p$, Eq. (7) can not be reduced to ASF form. In this case $\ln x_l$ is not linear in i, but both the alkene and alkane homologous series are still in equilibrium among themselves. This case could provide an equilibrium explanation for a "double α" ASF distribution and would correspond either to a significant degree of isomerization within the alkenes and alkanes or to a change in the isomeric distribution of the product at a given carbon number.

An algorithm which solved Eq. (8) for ψ_C and ψ_H was written in BASICA and implemented on an IBM PC. The two unknown Lagrange multipliers were calculated for given values of slope, α, and intercept, $\ln(1 - \alpha)/\alpha$. The equilibrium distribution of n-alkanes and n-alkenes was then determined using Eqs. (2) and (3); literature values of the standard chemical potentials of methane, ethane, propane (9), ethene, and propene (10) were used and Eq. (4) with the data of Table 1 was used to determine the chemical potentials of the C_4–C_{20} species. The final section of the program determined $\sigma^2_{\ln x_l}$, the variance of the uncertainty in $\ln x_l$, using the techniques which have been discussed previously (11, Eqs. (2) to (5)) and which are not repeated here for brevity. We have used

$$\sigma^2_{\ln x_l} = \sigma^2_{\ln x_{io}} + \sigma^2_{\ln x_{ip}}, \qquad (9)$$

where $\sigma^2_{\ln x_{io}}$ and $\sigma^2_{\ln x_{ip}}$, the variance of the uncertainties in $\ln x_{io}$ (n-alkene) and $\ln x_{ip}$ (n-alkane), respectively, were calculated using an uncertainty of $\sigma_{\mu_i^0} = 0.7i$ for $i \geq 7$ (equivalent to an uncertainty of ~1% in the free energy of formation) and $\sigma_{\mu_i^0} = 0$ for $i \leq 6$ on the basis that the chemical potentials of these low molecular weight species are well known.

Figure 1 presents the ASF plot of the equilibrium composition calculated using Eq. (8) at 600 K, 10 atm with $\alpha = 0.67$, and the data listed in Table 1. The 95% confidence region is within the solid bands. The dramatic in-
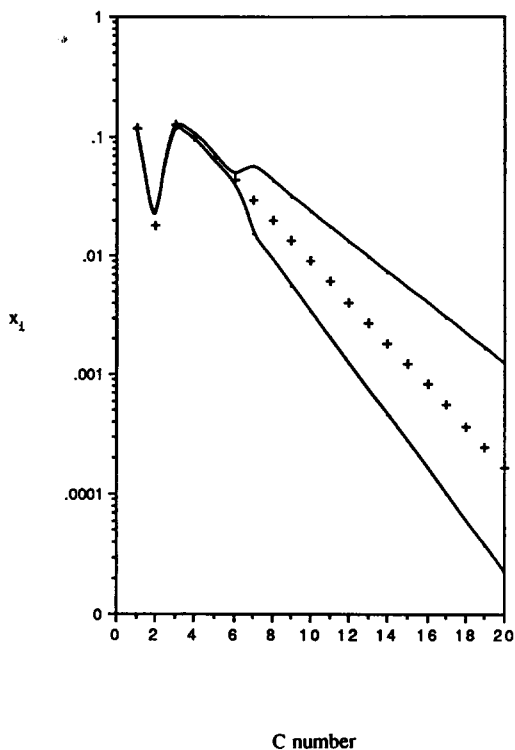

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FIG. 1. ASF Distribution 600 K, 10 atm, $a = 0.67$; (+) distribution calculated from Eq. (8); solid lines represent the 95% confidence interval.

crease in the size of the confidence region at $i = 7$ is a consequence of the effect of uncertainty in a species' chemical potential being greatest on its own mole fraction (11); thus little uncertainty exists for $i \leq 6$. The uncertainty of 1% in the free energy data results in a large uncertainty in the calculated equilibrium composition (20% in $\ln x_l$). Hence, small uncertainties in the thermodynamic data have a large impact on the calculated product distribution.

The partial equilibrium model requires the use of free energy data and kinetics/mass transfer models require the use of rate constants and mass transfer coefficients. Sensitivity analysis provides a means for estimating the uncertainty in the calculated product distribution resulting from uncertainties in the underlying data. If an experimental product distribution falls within the uncer-

tainty region of a linear ASF distribution (i.e., Eq. (8) or a single α model) then use of the more complex Eq. (7) or double α model is not justified unless other experimental evidence exists. The effect of small uncertainties on the FT product distribution demonstrates that sensitivity analysis should be an integral component of any mathematical model of FT product distributions, particularly since the mole fractions of higher molecular weight species are very small, and subject to significant experimental uncertainties.

The equilibrium analysis coupled with the sensitivity analysis presented herein demonstrates that the ASF distribution, Eq. (1), the mass-transfer limited model of Dictor and Bell (4), the recent kinetic model of Basini (12) and the partial equilibrium model, Eq. (8), provide equally acceptable fits of FT product distributions. That a mathematical model fit experimental data is a necessary but not a sufficient proof of a model (13). However, the results of this work indicate that equilibrium may have a greater role in determining the product distribution of the FT process than has been thought previously. Indeed, since the observed n-alkene distribution (1) often is linear, consistent with that for equilibrium (Eq. (5)), the partial equilibrium model should not be readily discounted.

The assumption of ideal-gas behaviour was considered by Anderson (8) to be acceptable and any errors introduced by neglecting nonideal effects can be estimated with sensitivity analysis. The values of the constants A and B for Eq. (4) depend on the number of and the specific isomers considered by the model and can be altered depending on the composition of the product. However, given that the FT aliphatic product contains predominantly n-alkanes and n-alkenes, the data used herein are acceptable.

Finally, we note that the thermodynamic data of Alberty et al. (14) for the n-alkanols can be expressed in the linear form of Eq. (4). The value of B differs from those for the

n-alkanes and n-alkenes by less than 1%. Equation (8) can be extended to include the n-alkanols as

$$\ln x_l = i(\psi_C + 2\psi_H - B_o') - \ln P$$
$$+ \ln[\exp(-A_o') + \exp(-A_p' + 2\psi_{Hp})$$
$$+ \exp(-A_a' + 2\psi_{Ha} + \psi_{Oa})]. \quad (10)$$

Thus, the equilibrium approach to the ASF distribution can be extended to products containing alcohols (or indeed any oxygenated species) in addition to aliphatic hydrocarbons. The mole fraction of one of the alcohol species would be required for determination of the third Lagrange multiplier.

CONCLUSIONS

The ASF distribution has been shown to have an equilibrium basis. This is consistent with chain growth being fast relative to the formation of the initial carbonaceous species, the primary product being an alkene, and hydrogenation reactions being slow relative to chain growth. The equilibrium model provides an equally acceptable mathematical fit of observed product distributions as do kinetics/mass transfer models. Deviations from an ASF distribution can be attributed to uncertainties in underlying data; consequently, sensitivity analysis is an important component of any mathematical model of the FT process.

APPENDIX: NOMENCLATURE

A, B	constants for Eq. (4)
A', B'	constants for Eq. (4), dimensionless
ΔG_{fi}^0	free energy (Gibbs' function) of formation of species i, kJ mol^{-1}
P	pressure, atm
R	gas constant
R^2	regression coefficient
T	temperature, K
x_i	mole fraction of species i

Greek Letters

α	probability of chain growth
ψ_k	Lagrange multiplier for element k
σ^2	variance of the uncertainty
μ_i	chemical potential of species i

μ_i^* standard chemical potential of species i at (T, P), dimensionless

μ_i^0 standard chemical potential of species i at (T), dimensionless

Subscripts

a alkanol
i carbon number
o alkene
p alkane

REFERENCES

1. Anderson, R. B., "The Fischer–Tropsch Synthesis," Chap. 5 and references therein. Academic Press, New York, 1984.
2. Satterfield, C. N., and Huff, G. A., *J. Catal.* **73**, 187 (1982).
3. Satterfield, C. N., Huff, G. A., and Longwell, J. P., *Ind. Eng. Chem. Process Des. Dev.* **21**, 465 (1982).
4. Dictor, R. A., and Bell, A. T., *Ind. Eng. Chem. Process Des. Dev.* **22**, 681 (1983).
5. Smith, W. R., and Missen, R. W., "Chemical Reaction Equilibrium Analysis: Theory and Algorithms." Wiley-Interscience, New York, 1982.
6. Alberty, R. A., *J. Phys. Chem.* **87**, 4999 (1983).
7. Smith, W. R., and Missen, R. W., *Canad. J. Chem. Eng.* **52**, 280 (1974).
8. Anderson, R. B., *in* "Catalysis" (P. H. Emmett, Ed.), Vol IV, p. 1. Reinhold, New York, 1956.
9. Alberty, R. A., and Gehrig, C. A., *J. Phys. Chem. Ref. Data* **13**, 1173 (1984).
10. Alberty, R. A., And Gehrig, C. A., *J. Phys. Chem. Ref. Data* **14**, 803 (1985).
11. Norval, G. W., Phillips, M. J., Missen, R. W., and Smith, W. R., *Appl. Catal.* **54**, 37 (1989).
12. Basini, L., *Ind. Eng. Chem. Res.* **28**, 659 (1989).
13. Boudart, M., *Ind. Eng. Chem. Fundam.* **25**, 656 (1986).
14. Alberty, R. A., Chung, M. B., and Flood, T. M., *J. Phys. Chem. Ref. Data* **16**, 391 (1987).