Use of Adsorption Entropy to Choose between Kinetic Mechanisms and Rate Equations for Fischer–Tropsch Synthesis

INTRODUCTION

Recently Huff and Satterfield (*1*) obtained data on the rate of disappearance of H_2 and CO during Fischer–Tropsch synthesis using a reduced fused-magnetite catalyst over a wide range of temperatures, total and partial pressures, H_2/CO feed ratios and conversions. They concluded that the fit of their data to a rate equation following an enolic-type model was qualitatively (but not statistically) worse than that following a carbidic-type model or a combined enolic/carbidic-type model. Further, they recommended that the latter rate equation be used on the grounds that two, rather than three, adjustable parameters were involved, with the assertion that this did not imply that the enolic-type model was necessarily less realistic.

In the present work we compare the three models, and suggest that only the carbidic-type model is possible here. The comparison uses a concept originally suggested by Boudart, Mears, and Vannice (BMV) (*2*) and later improved by Knox and Dadyburjor (KD) (*3*). According to this concept, the experimental data is fitted to the rate expression obtained from the postulated model, to yield postulated adsorption equilibrium constants K_{exp} for reactants and/or products. Values of the adsorption entropy ΔS_{exp} can be obtained by a relation of the form

$$\ln K_{exp} = (\Delta S_{exp}/R) - (\Delta H_{exp}/R)(1/T), \quad (1)$$

where ΔH_{exp} is the adsorption enthalpy, R is the gas constant and T the absolute temperature. The validity of the model is then determined by noting if the "experimentally determined" value of ΔS_{exp} for each component falls between calculated values of upper and lower bounds of adsorption entropy for that component. The BMV and KD criteria differ in the way the sets of bounds are defined.

The BMV criteria are necessarily empirical, and can be combined into the following pair of inequalities for ΔS_{exp}:

$$\text{Max}[-S_A, 12.2 - 0.0014\,\Delta H_{exp}]$$
$$< \Delta S_{exp} < -10. \quad (2)$$

Here S_A is the entropy of the component in the fluid phase.

According to the KD criteria (*3*), a kinetic mechanism can be ruled out unless the corresponding ΔS_{exp} satisfies

$$\Delta S_{loc}^0 < \Delta S_{exp} < \Delta S_{2d}^0. \quad (3)$$

Here ΔS_{loc}^0 is the entropy change for adsorption as a localized species, and ΔS_{2d}^0 corresponds to adsorption as a two-dimensional gas. In other words, the two limiting cases of Eq. (3) consist of an adsorbate completely immobilized on the surface and an adsorbate completely free to move on the two-dimensional surface. The upper and lower bounds have been evaluated (*3*) using the equations of statistical thermodynamics. Of course either set of criteria, Eqs. (2) or (3), is a necessary but not sufficient condition for verifying a kinetic scheme.

We concentrate here on the KD criteria. Then the lower bound is given by (*3*)

$$\Delta S_{loc}^0 = -R\{4 + 6A + \ln[B_{loc}]\} \quad (4a)$$

with

489

$$A \equiv \ln\left[1 - \exp\left(-\frac{h\nu_0}{kT}\right)\right]$$
$$- \frac{(h\nu_0/kT)\exp[-h\nu_0/kT]}{1 - \exp[-h\nu_0/kT]}. \quad (4b)$$

If the molecule is nonlinear, the term B_{loc} is given by:

$$B_{loc} \equiv \frac{2^6\pi^5}{\sigma} \frac{m_A^{3/2}(I_x I_y I_z)^{1/2}(kT)^4}{h^6 P_A} \quad (4c)$$

whereas

$$B_{loc} \equiv \frac{2^{9/2}\pi^4}{\sigma} \frac{m_A^{3/2}I_x(kT)^{7/2}}{h^5 P_A} \quad (4d)$$

for a linear molecule. In Eqs. (4), h and k are the Planck and Boltzman constants, respectively; P_A is the component partial pressure in the vapor phase; m_A, σ, I_x, I_y, I_z are the mass, symmetry number, and three moments of inertia of the component molecule; and ν_0 is the vibration frequency with respect to the adsorption surface. Equations (4) have been derived assuming that the electronic contribution to the partition function is small, independent of temperature, and identical in the adsorbed and vapor phase states; and assuming that the frequency of the characteristic vibrations are identical in the adsorbed and vapor phase states, except for the vibration of the adsorbed molecule with respect to the surface.
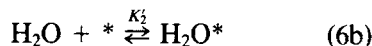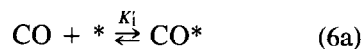
Similarly the upper bound is given by:

$$\Delta S_{2d}^0 = -R\left\{\frac{1}{2} + A\right.$$
$$\left. + \ln\left[(2\pi)^{1/2}\frac{m_A^{1/2}(kT)^{3/2}}{ahP_A}\right]\right\}, \quad (5)$$

where a is the surface area of an adsorption site, and the other parameters are as in Eqs. (4).

Application to Fischer–Tropsch mechanisms. We now apply Eqs. (4) and (5) to the various components of the Fischer–Tropsch reaction, and compare the calculated limiting cases of adsorption entropy with values obtained by fitting the experimental data to rate expressions corresponding to each of the three kinetic models con-

sidered in Ref. (*1*). We first consider the enol-type model, primarily because it was judged unsuitable in Ref. (*1*), and also because the analysis of this model is relatively straightforward. According to this model (II in the nomenclature of Ref. (*1*)), the sequence is

$$CO + * \underset{}{\overset{K_1'}{\rightleftarrows}} CO* \quad (6a)$$

$$H_2O + * \overset{K_2'}{\rightleftarrows} H_2O* \quad (6b)$$

$$H_2 + CO* \overset{k'}{\rightarrow} COH_2^*. \quad (6c)$$

Using the conventional assumptions of adsorption/desorption equilibrium in Eqs. (6a) and (6b), and taking Eq. (6c) to be the rate-determining step, the rate expression is

$$r = \frac{k'K_1'P_{CO}P_{H_2}}{1 + K_2'P_{H_2O} + K_1'P_{CO}}. \quad (6d)$$

Here asterisks denote surface sites, r is the rate of disappearance of H_2 and CO, k' is the rate constant in Eq. (6c), and K_1' and K_2' are the equilibrium adsorption constants for CO and H_2O, respectively. Fitting their experimental data to Eq. (6d), Huff and Satterfield (*1*) obtained best-fit values of k', K_1', and K_2' at different temperatures. Then the temperature variation of K_1' and K_2' via a relation of the form of Eq. (1) yields a value of $\Delta S_{exp}'$ for CO and H_2O, respectively. From Ref. (*1*), the experimentally fitted value of adsorption entropy for CO is apparently:

$$\Delta S_{exp}'(CO) \overset{?}{=} -66 \text{ cal/mol/}^\circ K. \quad (7a)$$

From Eqs. (4) and (5) the lower and upper bounds of adsorption entropy for CO can be calculated to be

$$\Delta S_{loc}^\circ(CO) = -43 \text{ cal/mol/}^\circ K \quad (7b)$$

$$\Delta S_{2d}^\circ(CO) = -22 \text{ cal/mol/}^\circ K. \quad (7c)$$

Details of these calculations and those following can be found in Ref. (*3*). Similarly for H_2O the experimental fit yields

$$\Delta S_{exp}'(H_2O) \overset{?}{=} -128 \text{ cal/mol/}^\circ K \quad (8a)$$

and the limiting cases are

$\Delta S^\circ_{loc}(H_2O) = -44$ cal/mol/°K (8b)

$\Delta S^\circ_{2d}(H_2O) = -23$ cal/mol/°K. (8c)

Neither Eqs. (7) nor (8) falls within the criteria of Eq. (3). Hence the corresponding model given by Eqs. (6) can be rejected. Huff and Satterfield (1) reached the same conclusion, but used a different argument.

Now consider the carbide-type model (model I in Ref. (1)) whereby

$$CO + 2* \underset{}{\overset{K_1}{\rightleftharpoons}} C* + O*$$ (9a)

$$O* + H_2 \underset{}{\overset{K_2}{\rightleftharpoons}} H_2O + *$$ (9b)

$$C* + H_2 \overset{k}{\rightarrow} CH_2^*$$ (9c)
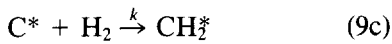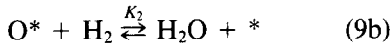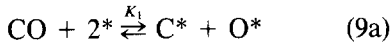
leads to the rate expression:

$$r = \frac{kK_1K_2P_{CO}(P_{H_2})^2}{P_{H_2O} + K_1K_2P_{CO}P_{H_2}}.$$ (9d)

Here K_1 represents the (dissociative) adsorption equilibrium constant for CO, while K_2 is the *desorption* equilibrium constant for H_2O. For this model, best fit values of the product K_1K_2 were obtained in Ref. (1). From the temperature dependence of this product, one can set

$\Delta S_{exp}(CO) - \Delta S_{exp}(H_2O)$

$$\overset{?}{=} 32$$ cal/mol/°K. (10a)

Since dissociative chemisorption leads to a less-ordered system than nondissociative chemisorption, the value of the upper bound for the adsorption entropy change will certainly increase. In other words, ΔS°_{2d} as calculated in Eq. (5) is no longer an upper bound for ΔS_{exp} in the case of dissociative chemisorption. However, a conservative upper bound can certainly be given by:

$$\Delta S^\circ_{2d,dissociative} \leq 0.$$ (10b)

Using this and Eq. (7b) for CO, and Eqs. (8b) and (8c) for H_2O, a lower bound for $\{\Delta S_{exp}(CO) - \Delta S_{exp}(H_2)\}$ is given by:

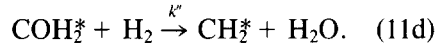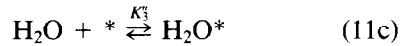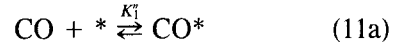$\Delta S^\circ_{loc}(CO) - \Delta S^\circ_{2d}(H_2O)$

$$= -20$$ cal/mol/°K (10c)

while an upper bound is given by

$\Delta S^\circ_{2d,dissociative} - \Delta S^\circ_{loc}(H_2O)$

$$= 44$$ cal/mol/°K. (10d)

Since the experimentally determined value of Eq. (10a) falls between the extreme cases of Eqs. (10c) and (10d), the model of Eqs. (9) cannot be rejected at this point.

Finally we consider the combined enolic/carbidic mechanism (model III in Ref. (1))

$$CO + * \underset{}{\overset{K''_1}{\rightleftharpoons}} CO*$$ (11a)

$$CO* + H_2 \underset{}{\overset{K''_2}{\rightleftharpoons}} COH_2^*$$ (11b)

$$H_2O + * \underset{}{\overset{K''_3}{\rightleftharpoons}} H_2O*$$ (11c)

$$COH_2^* + H_2 \overset{k''}{\rightarrow} CH_2^* + H_2O.$$ (11d)

The corresponding rate expression is

$$r = \frac{(k''K''_1K''_2/K''_3)P_{CO}(P_{H_2})^2}{P_{H_2O} + (K''_1K''_2/K''_3)P_{CO}P_{H_2}}.$$ (11e)

Here K''_1 and K''_3 represent (undissociated) adsorption equilibrium coefficients for CO and H_2O, respectively. K''_2 may be assumed to be approximately equivalent to an adsorption equilibrium coefficient for H_2, except that the "adsorption" occurs on an adsorbed CO molecule, rather than on the surface. With this assumption, the temperature dependence of the best-fit values of $(K''_1K''_2/K''_3)$ yields

$\Delta S''_{exp}(CO) + \Delta S''_{exp}(H_2) - \Delta S''_{exp}(H_2O)$

$$\overset{?}{=} 32$$ cal/mol/°K. (12a)

Note that since the functional forms of Eqs. (9d) and (11e) are identical, the best-fit values of the expressions (K_1K_2) and $(K''_1K''_2/K''_3)$ must be the same. Now a lower bound for the lefthand side of Eq. (12a) is given by:

$\Delta S^\circ_{loc}(CO) + \Delta S^\circ_{loc}(H_2) - \Delta S^\circ_{2d}(H_2O)$

$$= -49$$ cal/mol/°K (12b)

while the upper bound is

$\Delta S^\circ_{2d}(CO) + \Delta S^\circ_{2d}(H_2) - \Delta S^\circ_{loc}(H_2O)$

$$= 0$$ cal/mol/°K. (12c)

The upper and lower bounds for the adsorption entropy of H_2 are calculated in Ref.

(3). Further, the undissociated value of ΔS_{2d}° is used for CO in this case.

From Eqs. (12), this model can be ruled out as a reaction mechanism since the experimental values fall outside the expected bounds. Note that, since the calculated upper bound is exceeded by over 30 cal/mol/°K, our earlier assumption for K_2'' is not a critical one. Our assumption is not likely to be off by that large an amount.

CONCLUSIONS

The present results are consistent with those of Huff and Satterfield (1) in that the enol-type model for Fischer–Tropsch synthesis is rejected under these experimental conditions. However, rather than subjective criteria such as "goodness of fit" or number of adjustable parameters, the criterion of adsorption entropy bounds (3) is used.

It should be noted that, besides being more objective, the adsorption entropy bounds criterion has the added advantage of being able to discriminate between two different reaction mechanisms that give rise to rate expressions with identical dependences on reactant partial pressures. Ac-

cordingly, under the present experimental conditions, the combined enolic/carbidic model for Fischer–Tropsch synthesis does not meet the adsorption entropy criterion and must be rejected. On the other hand, the carbide-type model does meet the adsorption entropy criterion, and is a possible mechanism for Fischer–Tropsch synthesis.

REFERENCES

1. Huff, G. A., Jr., and Satterfield, C. N., submitted for publication.
2. Boudart, M., Mears, D. E., and Vannice, M. A., *Ind. Chim. Belg.* **32**, special issue, 281 (1967).
3. Knox, D., and Dadyburjor, D. B., *Chem. Eng. Commun.* **11**, 99 (1981).

DADY B. DADYBURJOR

*Department of Chemical Engineering
and Environmental Engineering
Rensselaer Polytechnic Institute
Troy, N.Y. 12181*