Non-Dissociative and Dissociative Adsorption of Oxygen on Carbon: A Theoretical Comparison

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Introduction

The reaction of oxygen with carbon is a complex process of dissociative adsorption-desorption behavior that has been described mathematically in a number of different possible models [1]. For engineering purposes, however, to be able to include char oxidation behavior in complete coal flame models, in tractable mathematical form, some simplification or approximation is necessary. The two approximations most commonly used at this time are the empirical Freundlich/Frank-Kamanetskii *nth* order (FFK) expression [2], and the non-dissociative Langmuir. Of these two, the *nth* order (FFK) has been almost universally used in the flame models [3] but is increasingly being recognized as inadequate, particularly in contrast with the Langmuir.

The Langmuir itself, however, has nearly always been used in the non-dissociative form in combustion applications -- again for reasons of tractability -- and notably in the development of the "Extended Resistance Equation" (ERE) [4] which combines the Langmuir, Nusselt, and Thiele relations for predicting burning rates of spherical particles.

This now raises the issue of the accuracy of the approximation using the non-dissociative form of the Langmuir; and the objective in this paper is to compare idealized calculations for the non-dissociative and the dissociative Langmuir to evaluate the potential error in using the more tractable non-dissociative form.

Theoretical Basis

The theoretical basis for both forms of the Langmuir isotherm has a long history [reviewed, e.g., in 1], but is outlined here following Ref. 1. For a surface being covered by adsorbing oxygen in unsteady state, the rate of change in coverage, θ, is given by:

$$d\theta/dt = k_a \cdot y_{ox} (1 - \theta)^n - k_d \cdot \theta \qquad (1)$$

where: k_a, k_d, are the velocity constants for adsorption and desorption; y_{ox} is the ambient oxygen mole fraction; and $n = 1$ for non-dissociative and 2 for dissociative adsorption. At steady state, $\theta = \theta_{m(ax)}$, and the specific reaction rate, R_s, is proportional to the rate of decomposition of the film: $R_s = k_d \cdot \theta_m$. To obtain θ_m it is necessary to solve for θ [1] which, for $n = 2$, requires solving a quadratic in θ. For the two cases we then get:

Non-Dissociative Adsorption

$$R_s = (k_a \cdot y_{ox}) \cdot k_d / [k_a \cdot y_{ox} + k_d] \qquad (2)$$

which is the standard Langmuir Isotherm.

Dissociative Adsorption

$$R_s = (k_a \cdot y_{ox}) \cdot k_d / [(k_a \cdot y_{ox} + k_d/4)^{1/2} + (k_d/4)^{1/2}]^2 \qquad (3)$$

Analytical Evaluation

At the limits of small adsorption rates or of small desorption rates, the equations are substantially equivalent. For small k_d, the denominator of both Eqs. 2 and 3 reduce to $(k_a \cdot y_{ox})$, whence both equations become: $R_s = k_d$: i.e, zero order in oxygen concentration, and rate controlled by film decomposition. Likewise, for small $k_a \cdot y_{ox}$, the results are the same: in both equations, the denominator becomes k_d, which then cancels to give: $R_s = k_a \cdot y_{ox}$; i.e., the rate is first order in oxygen concentration, and controlled by adsorption. This result is standard for the non-

dissociative Langmuir, but is unexpected for the dissociative form. By comparison, for example, dissociative adsorption of hydrogen is well known to be half power [see 1].

Numerical Evaluation

Equations 2 and 3 have been compared by calculating the reaction rate from both equations, and the results are illustrated in Figs. 1 and 2. The numerical values of the rate coefficients were taken from Ref. 5 which used experimental data reported in Ref. 2.

Figure 1 is an Arrhenius plot of the calculated values, where the dotted line is calculated from the dissociative form, Eq. 3, and the full line is for the non-dissociative form, Eq. 2. There is a small but clear separation of the lines. The magnitude of the separation is obscured by the logarithmic scale, and the difference as a ratio is shown in Fig. 2. Nevertheless, comparison of this plot with the original data in Fig. 7 of Ref. 1 shows that the separation is well inside the experimental scatter.

Figure 2 is the ratio of the dissociative to the non-dissociative calculated value with the ratio dropping from about 0.8 to 0.7 with increasing temperature. The rate is reduced by dissociation.

The effective reaction order was also examined using a plot (not given) based on Eq. 2 of data calculated from Eq. 3. The standard plot for the non-dissociative Langmuir as in Ref. 6, is of reciprocal reaction rate $(1/R_s)$ against reciprocal oxygen mole fraction $(1/y_{ox})$, at constant temperature. The plots developed show a *linear* variation, in spite of the dissociative structure of the source equation (Eq. 3).

Conclusions

The difference between predicted reaction rates, calculated from the dissociative and the non-dissociative forms of the Langmuir rate expression, is real but relatively small. In absolute values, the non-dissociative form predicts values that are 70% to 80% lower than calculated from the dissociative form. Nevertheless, this difference is small compared with experimental scatter typically reported. A further result is the evident linearity of the dissociative predictions for the dependence of

reaction rate on oxygen concentration. These results suggest that rate constants obtained using the non-dissociative rate equation are probably not substantially different from those using the dissociative form. This suggests a direction for further analysis.

References
1. Essenhigh. R.H.: Ch. 19 in *Chem. Coal Utilzn.: 2nd. Suppl. Vol.*; Wiley, NY, 1981
2. Monson, C.R., Germane, G.J., Blackham, A.U., & Smoot, L.D.: *Comb. Flame*, 100: 669 (1995)
3. Smoot, L.D. (Ed.) *Fundamentals of Coal Combustion*, Elsevier, NY, 1993
4. Essenhigh. R.H.: *22nd. Symp. (Internat.) on Combustion*, pp. 89-96, Comb. Inst., 1988
5. Essenhigh. R.H. and Mescher, A.M.: *26nd. Symp. (Intrenat.) on Combustion*, pp. 3085-3094, Comb. Inst., 1996
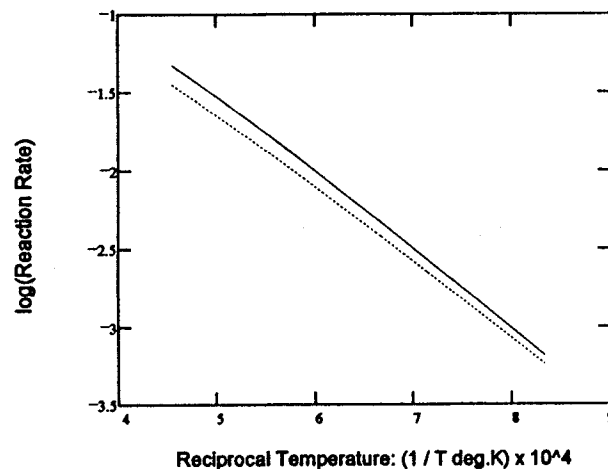6. Essenhigh. R.H.: *Energy and Fuels*, 5:41-46 (1961)

Fig. 1 Arrhenius plot of reaction rate against (reciprocal) temperature. *Solid* line, non-dissociative Eq. 2; *dotted* line, dissociative Eq. 3
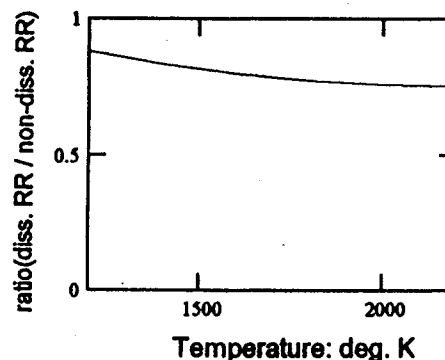

Fig. 2 Ratio of dissociative predicted rates to non-dissociative predicted rates, varn. with temperature