

Derivation of Thermodynamically Consistent Reaction Rate Expressions for Equilibrium Limited Gas-Solid Reactions

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Highlights

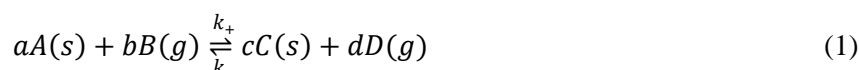
- New reaction rate derivation approach for equilibrium limited gas solid reactions
- Different rate expressions for the forward and reverse reaction rate
- Numerical problems arise which can be addressed by relaxation techniques

1. Introduction

Many homogeneous gas phase reactions are equilibrium limited. Starting from either side of chemical equilibrium, they proceed until the reaction rates of the forward and reverse reaction are equal, i.e. until chemical equilibrium is reached. Therefore, the theoretically achievable conversion is limited and there is always a certain amount of reactants remaining at chemical equilibrium. When modeling equilibrium limited reaction systems, this fact is recognized by using thermodynamically consistent reaction rate expressions. Reaction rate equations are commonly termed as thermodynamically consistent when they satisfy two conditions: (1) they are positive in the direction of decreasing Gibbs energy, (2) they vanish (i.e. $r = 0$) at chemical equilibrium [1]. However, equilibrium limitation is often disregarded for heterogeneous gas-solid reactions. This is a valid approximation for gas-solid reactions that are essentially irreversible, i.e. where chemical equilibrium is so far on the product side that the reverse reaction can be neglected (e.g. combustion reactions of solid matter). Nonetheless, there are industrially important gas-solid reactions with marked equilibrium limitations. Examples are the Boudouard reaction, the calcination of limestone and the reverse water-gas shift chemical looping using iron as an oxygen storage material [2]. Sohn [3] found that the rate expression for the hydrogen reduction of magnetite particles was different from the rate expression for the re-oxidation of iron particles produced from the same reduction reaction. He argued that the forward and reverse reaction of equilibrium limited gas-solid reactions generally follow different reaction mechanisms. In this work, a new approach is proposed for the derivation of thermodynamically consistent equilibrium limited gas-solid reaction rates that accounts for the differences in the forward and reverse direction.

2. Methods

The overall reaction rate of equilibrium limited homogeneous reactions is generally expressed as the difference of the forward and reverse reaction rate. Assuming that the overall reaction rate vanishes at equilibrium, the law of mass action can be used to derive thermodynamically consistent reaction rate expressions, which are valid for the forward and reverse reaction direction. In this work, an arbitrary equilibrium limited gas-solid reaction is considered:



Here, A and C are solid components, B and D are gaseous components and a, b, c and d are stoichiometric coefficients. The kinetic coefficients of the forward and reverse reaction rates are denoted by k_+ and k_- , respectively. For the derivation of reaction rates for equilibrium limited gas-solid reactions of the form of equation (1) a similar workflow to the derivation of homogeneous reaction rate expressions is applied for both reaction directions. Thus, two distinct rate expressions are derived for describing the reaction rate coming from the left and the right side of chemical equilibrium.

3. Results and discussion

The new approach yields reaction rate expressions of the form

$$r = \begin{cases} f_1(\mathbf{x})f_2(\mathbf{y}) & \text{if } \mathbf{y} < \mathbf{y}_{eq} \\ g_1(\mathbf{x})g_2(\mathbf{y}) & \text{if } \mathbf{y} > \mathbf{y}_{eq} \end{cases} \quad (2)$$

Here, \mathbf{x} is the solid phase composition vector, \mathbf{y} the gas phase composition vector and \mathbf{y}_{eq} the equilibrium composition vector. Thus, coming from the left side of equilibrium ($\mathbf{y} < \mathbf{y}_{eq}$) the reaction rate may take a different functional form than coming from the right side of equilibrium ($\mathbf{y} > \mathbf{y}_{eq}$). Figure 1 illustrates the idea in comparison to conventional reaction rates which are valid coming from both sides of equilibrium.

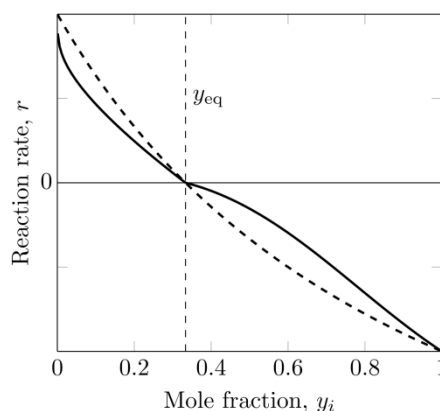


Figure 1. Reaction rates as a function of gas phase composition. Dashed: conventional reaction rate valid on both sides of chemical equilibrium. Solid: proposed reaction rate expression with different reaction mechanisms coming from either side of chemical equilibrium. The kink in the dashed line at y_{eq} indicates the change of the reaction mechanism.

Due to the non-smooth change in the reaction rate, numerical problems may arise using the proposed reaction rates in the conditional form of equation (2) for simulation and optimization problems which often involve solving ODE or PDE systems. In this work, it is shown how these problems can be addressed by using relaxation techniques.

4. Conclusions

The derivation presented in this work is an extension of the theory of homogeneous reaction rates toward heterogeneous equilibrium limited gas-solid reaction rates. Important technical examples are used to argue why the rate expressions for these reactions must necessarily be more complex than the ones conventionally used to accurately describe these processes. Necessary mathematical properties are illustrated that equilibrium limited reaction rate equations for gas-solid reactions must have to be able to describe a different reaction behavior coming from either side of chemical equilibrium while remaining thermodynamically consistent. More refined kinetics can be derived by including mechanistic steps like adsorption and desorption but they must fulfill the form of equation (2).

References

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Keywords

chemical kinetics; gas-solid reactions; reversible reactions; reaction rate expressions