A First Course on Kinetics and Reaction Engineering Practice Problem 10.2

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It also shows how and why heterogeneous catalytic reactions can have atypical rate expressions.

Problem Statement

Assume that methane partial oxidation, equation (1), takes place on a metal catalyst according to the simplified mechanistic scheme given in equations (1a) through (1d).

$2 \text{ CH}_4 + \text{O}_2 \rightarrow 2 \text{ CH}_3\text{OH}$	(1)
$CH_4 + * \rightleftharpoons CH_4 - *$	(1a)
$O_2 + 2 \approx arrow 2 O- st$	(1b)
CH_4 -* + O-* \rightarrow CH_3OH -*	(1c)
CH₃OH-* ⇄ CH₃OH + *	(1d)

Step (1c) may be assumed to be the rate-limiting step. Develop a rate expression for the overall reaction in terms of only the concentrations of the gas phase species (methane, oxygen, and methanol) and the equilibrium and rate constants. If it is assumed that the surface of the catalyst is almost completely covered with adsorbed O (which is the most abundant surface intermediate), how does this simplify the rate expression? Comment upon the result.