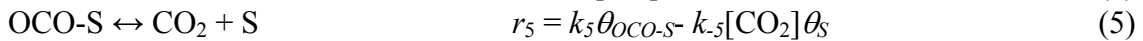
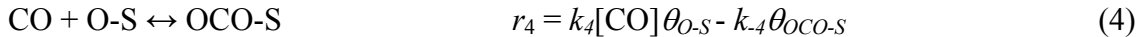
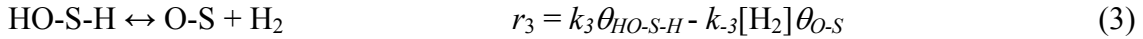
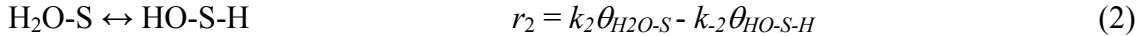
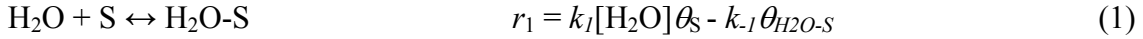


**CE 561 Homework 8: (assigned 10/19/09, due 10/26/09)**

A proposed mechanism for the water-gas shift reaction on ferrochrome catalysts at high temperatures is



where S is a surface site and H<sub>2</sub>O-S, HO-S-H, O-S and OCO-S are surface bound species.

- (a) What are the units of the ten elementary rate constants for these five reversible reactions?
  - (b) Derive an expression for the rate of the overall reaction ( $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$ ) in terms of the gas phase concentrations, assuming that reaction 3 is the rate limiting step.
  - (c) Derive an expression for the rate of the overall reaction assuming that CO<sub>2</sub> desorption is the rate limiting step.
  - (d) Derive an expression for the rate of the overall reaction assuming that H<sub>2</sub>O adsorption is the rate limiting step.
  - (e) Try to derive an expression for the rate of the overall reaction without assuming a rate-limiting step (you could, in principle, do this one first, and simplify the result to get answers for (b), (c), and (d)). You may still assume that the surface concentrations are in steady-state.
- (2) A particular catalyst has a void fraction of 0.40, an internal surface area of 180 m<sup>2</sup>/g, and a pellet density of 1.40 g/cm<sup>3</sup>. Compute the effective pore diameter in this catalyst. Estimate the effective diffusion coefficient for dilute thiophene in hydrogen at a pressure of 1 bar and temperature of 600 K within this catalyst. If this catalyst is formed into spherical pellets with a diameter of 5 mm, estimate the value of the surface reaction rate constant for which internal diffusion limitations will reduce the reaction rate by a factor of 2.
- (3) A series of experiments were performed using various sizes of crushed catalyst to determine the importance of pore diffusion. The reaction may be assumed to be first order and irreversible. The surface concentration of reactant was  $C_{As} = 3 \times 10^{-4}$  mol/cm<sup>3</sup>.

DATA:

Diameter of sphere (cm)	0.25	0.075	0.025	0.0075
-------------------------	------	-------	-------	--------

- |   |      |      |      |      |
|---|------|------|------|------|
| $r_{\text{obs}}$ (mol hr <sup>-1</sup> cm <sup>-3</sup> ) | 0.33 | 1.05 | 2.40 | 3.60 |
|---|------|------|------|------|
- (a) Determine the “true” rate constant  $k_r$  and the effective diffusivity  $D_{eA}$  from the above data.
- (b) Predict the effectiveness factor and the expected rate of reaction  $r_{\text{obs}}$  for a commercial *disk-shaped* catalyst pellet 1 cm in diameter and 0.3 cm thick

- (4) A first-order heterogeneous irreversible reaction is taking place within a porous spherical catalyst pellet. The reactant concentration halfway between the external surface and the center of the pellet (i.e. at  $r = R/2$ ) is equal to one tenth of the reactant concentration at the external surface of the pellet. The concentration at the external surface is  $1 \times 10^{-6}$  mol cm<sup>-3</sup>. The diameter is 2 mm, and the effective diffusion coefficient of the reactant in the pores is estimated to be 0.2 cm<sup>2</sup>/s.
- (a) What are the values of the Thiele modulus and the effectiveness factor for the reaction under these conditions?
- (b) What is the concentration of reactant 0.2 mm from the external surface?
- (c) What sphere diameter will give an effectiveness factor of 0.8?