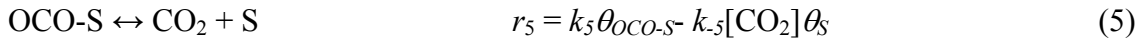
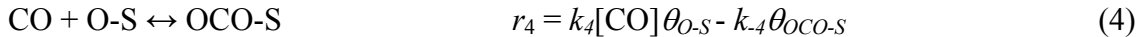
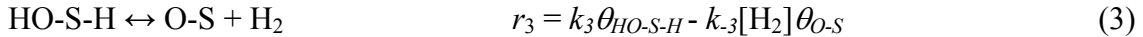
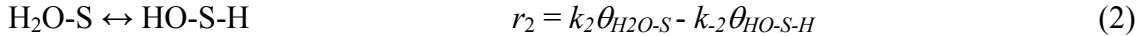
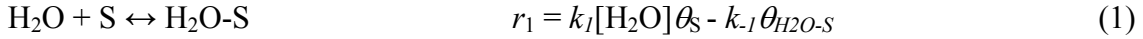


CE 561 Homework 8: (assigned 10/19/09, due 10/26/09)

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



where S is a surface site and H₂O-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?

In each case, the reaction rate is in units of moles per area per time. Dividing this by the concentration units (moles per volume for gas phase species, none for surface site fractions), we have the following:

$$k_1 = \text{length time}^{-1}, \text{ e.g. m s}^{-1}$$

$$k_{-1} = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_2 = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_{-2} = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_3 = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_{-3} = \text{length time}^{-1}, \text{ e.g. m s}^{-1}$$

$$k_4 = \text{length time}^{-1}, \text{ e.g. m s}^{-1}$$

$$k_{-4} = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_5 = \text{mol area}^{-1} \text{ time}^{-1}, \text{ e.g. mol m}^{-2} \text{ s}^{-1}$$

$$k_{-5} = \text{length time}^{-1}, \text{ e.g. m s}^{-1}$$

- (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.

If reaction 3 is rate limiting, then we can take the other reactions to be in pseudo-equilibrium. From the equilibrium of reaction (1), we get

$$\theta_{\text{H}_2\text{O-S}} = k_1/k_{-1} [\text{H}_2\text{O}] \theta_S$$

The equilibrium of reaction 2 then gives

$$\theta_{\text{HO-S-H}} = k_2/k_{-2} \theta_{\text{H}_2\text{O-S}} = (k_1 k_2)/(k_{-1} k_{-2}) [\text{H}_2\text{O}] \theta_S$$

The equilibrium of reaction 5 gives

$$\theta_{\text{OCO-S}} = k_{-5}/k_5 [\text{CO}_2] \theta_S$$

And, finally, the equilibrium of reaction 4 gives

$$\theta_{\text{O-S}} = (k_{-4} \theta_{\text{OCO-S}}) / (k_4 [\text{CO}]) = (k_{-5} k_{-4}) / (k_5 k_4) [\text{CO}_2] / [\text{CO}] \theta_S$$

The overall site balance gives

$$\theta_S + \theta_{\text{H}_2\text{O-S}} + \theta_{\text{HO-S-H}} + \theta_{\text{O-S}} + \theta_{\text{OCO-S}} = 1$$

$$(1 + k_1/k_{-1}(1 + k_2/k_{-2})[\text{H}_2\text{O}] + k_{-5}/k_5(1 + k_{-4}/(k_4 [\text{CO}])) [\text{CO}_2]) \theta_S = 1$$

Whence,

$$\theta_S = 1/(1 + k_1/k_{-1}(1 + k_2/k_{-2})[H_2O] + k_{-5}/k_5(1 + k_{-4}/k_4[CO])) [CO_2]$$

$$\theta_{HO-S-H} = (k_1k_2)/(k_{-1}k_{-2}) [H_2O]/(1 + k_1/k_{-1}(1 + k_2/k_{-2})[H_2O] + k_{-5}/k_5(1 + k_{-4}/k_4[CO])) [CO_2]$$

and

$$\theta_{O-S} = ((k_{-5}k_4)/(k_5k_4) [CO_2]/[CO])/ (1 + k_1/k_{-1}(1 + k_2/k_{-2})[H_2O] + k_{-5}/k_5(1 + k_{-4}/k_4[CO])) [CO_2]$$

So, the overall reaction rate, which is equal to the rate of reaction 3, is

$$r = (k_3(k_1k_2)/(k_{-1}k_{-2}) [H_2O] - k_{-3}((k_{-5}k_4)/(k_5k_4) [CO_2]/[CO])[H_2]) / (1 + k_1/k_{-1}(1 + k_2/k_{-2})[H_2O] + k_{-5}/k_5(1 + k_{-4}/k_4[CO])) [CO_2]$$

Or, with nicer formatting:

$$r = \frac{k_1k_{-2}k_3[H_2O]/k_{-1}k_{-2} - k_{-3}k_{-4}k_{-5}[CO_2][H_2]/k_4k_5[CO]}{1 + \frac{k_1}{k_{-1}} \left(1 + \frac{k_2}{k_{-2}}\right) [H_2O] + \frac{k_{-5}}{k_5} \left(1 + \frac{k_{-4}}{k_4[CO]}\right) [CO_2]}$$

- (c) Derive an expression for the rate of the overall reaction assuming that CO₂ desorption is the rate limiting step.

If reaction 5 is rate limiting, then we can take the other reactions to be in pseudo-equilibrium. From the equilibrium of reaction (1), we get

$$\theta_{H_2O-S} = k_1/k_{-1} [H_2O] \theta_S$$

The equilibrium of reaction 2 then gives

$$\theta_{HO-S-H} = k_2/k_{-2} \theta_{H_2O-S} = (k_1k_2)/(k_{-1}k_{-2}) [H_2O] \theta_S$$

The equilibrium of reaction 3 gives

$$\theta_{O-S} = k_3\theta_{HO-S-H} / (k_{-3} [H_2]) = (k_1k_2k_3)/(k_{-1}k_{-2}k_{-3}) [H_2O]/[H_2] \theta_S$$

And, finally, the equilibrium of reaction 4 gives

$$\theta_{OCO-S} = k_4/k_{-4} \theta_{O-S}[CO] = (k_1k_2k_3k_4)/(k_{-1}k_{-2}k_{-3}k_{-4})[H_2O][CO]/[H_2] \theta_S$$

The overall site balance gives

$$\theta_S + \theta_{H_2O-S} + \theta_{HO-S-H} + \theta_{O-S} + \theta_{OCO-S} = 1$$

$$(1 + (k_1/k_{-1})[H_2O](1 + (k_2/k_{-2})(1 + k_3/(k_{-3}[H_2]) (1 + (k_4/k_{-4})[CO]))) \theta_S = 1$$

Whence,

$$\theta_S = 1/(1 + (k_1/k_{-1})[H_2O](1 + (k_2/k_{-2})(1 + k_3/(k_{-3}[H_2]) (1 + (k_4/k_{-4})[CO])))$$

and

$$\theta_{OCO-S} = (k_1k_2k_3k_4)/(k_{-1}k_{-2}k_{-3}k_{-4})[H_2O][CO]/[H_2]/(1 + (k_1/k_{-1})[H_2O](1 + (k_2/k_{-2})(1 + k_3/(k_{-3}[H_2]) (1 + (k_4/k_{-4})[CO])))$$

So, finally,

$$r = ((k_1k_2k_3k_4k_5)/(k_{-1}k_{-2}k_{-3}k_{-4})[H_2O][CO]/[H_2] - k_{-5}[CO_2]) / (1 + (k_1/k_{-1})[H_2O](1 + (k_2/k_{-2})(1 + k_3/(k_{-3}[H_2]) (1 + (k_4/k_{-4})[CO])))$$

Or, with nicer formatting:

$$r = \frac{k_1k_2k_3k_4k_5[H_2O][CO]/k_{-1}k_{-2}k_{-3}k_{-4}[H_2] - k_{-5}[CO_2]}{1 + \frac{k_1[H_2O]}{k_{-1}} \left(1 + \frac{k_2}{k_{-2}} \left(1 + \frac{k_3}{k_{-3}[H_2]} \left(1 + \frac{k_4[CO]}{k_{-4}}\right)\right)\right)}$$

- (d) Derive an expression for the rate of the overall reaction assuming that H₂O adsorption is the rate limiting step.

If reaction 1 is rate limiting, then we can take the other reactions to be in pseudo-equilibrium. It will work out best if we start from the reactions that directly involve the surface sites, because we ultimately want to write all the other fractional coverages in terms of the fractional coverage of empty sites.

The equilibrium of reaction 5 gives

$$\theta_{OCO-S} = k_5/k_5 [CO_2] \theta_S$$

The equilibrium of reaction 4 then gives

$$\theta_{O-S} = (k_4 \theta_{OCO-S}) / (k_4 [CO]) = (k_5 k_4) / (k_5 k_4) [CO_2] / [CO] \theta_S$$

The equilibrium of reaction 3 then provides

$$\theta_{HO-S-H} = (k_3/k_3) [H_2] \theta_{O-S} = (k_5 k_4 k_3) / (k_5 k_4 k_3) [H_2] [CO_2] / [CO] \theta_S$$

Finally, the equilibrium of reaction 2 gives

$$\theta_{H_2O-S} = k_2/k_2 \theta_{HO-S-H} = (k_5 k_4 k_3 k_2) / (k_5 k_4 k_3 k_2) [H_2] [CO_2] / [CO] \theta_S$$

Substituting all of these into the overall site balance gives

$$\theta_S + \theta_{OCO-S} + \theta_{O-S} + \theta_{HO-S-H} + \theta_{H_2O-S} = 1$$

$$(1 + k_5 [CO_2] / k_5 (1 + k_4 / (k_4 [CO]) (1 + k_3 [H_2] / k_3 (1 + k_2 / k_2)))) \theta_S = 1$$

And

$$\theta_S = 1 / (1 + k_5 [CO_2] / k_5 (1 + k_4 / (k_4 [CO]) (1 + k_3 [H_2] / k_3 (1 + k_2 / k_2))))$$

So, the rate of reaction (1), which gives the overall rate, is

$$r = k_1 [H_2O] - (k_5 k_4 k_3 k_2 k_1) / (k_5 k_4 k_3 k_2) ([H_2] [CO_2] / [CO]) / (1 + k_5 [CO_2] / k_5 (1 + k_4 / (k_4 [CO]) (1 + k_3 [H_2] / k_3 (1 + k_2 / k_2))))$$

Or, with nicer formatting:

$$r = \frac{k_1 [H_2O] - \frac{k_5 k_4 k_3 k_2 k_1 [CO_2] [H_2]}{k_2 k_3 k_4 k_5 [CO]}}{1 + \frac{k_5 [CO_2]}{k_5} \left(1 + \frac{k_4}{k_4 [CO]} \left(1 + \frac{k_3 [H_2]}{k_3} \left(1 + \frac{k_2}{k_2} \right) \right) \right)}$$

- (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.

I did not even try to do this one by hand, but simply put the equations into Maple and tried solving it. The Maple sheet is posted below and linked [here](#).

```
> restart;
r1:=k1*C_h2o*theta_s-km1*theta_h2o;
r2:=k2*theta_h2o-km2*theta_hoh;
r3:=k3*theta_hoh-km3*C_h2*theta_o;
r4:=k4*C_co*theta_o-km4*theta_oco;
r5:=k5*theta_oco-km5*C_co2*theta_s;
r1 := k1 C_h2o theta_s - km1 theta_h2o
r2 := k2 theta_h2o - km2 theta_hoh
r3 := k3 theta_hoh - km3 C_h2 theta_o
```

$$r4 := k4 C_co \theta_o - km4 \theta_{oco}$$

$$r5 := k5 \theta_{oco} - km5 C_co2 \theta_s$$

> eqs:={r1-r2=0,r2-r3=0,r3-r4=0,r4-r5=0,theta_s+theta_h2o+theta_hoh+theta_o+theta_oco=1};

$$\begin{aligned} eqs := \{ & \theta_s + \theta_{h2o} + \theta_{hoh} + \theta_o + \theta_{oco} = 1, \\ & k2 \theta_{h2o} - km2 \theta_{hoh} - k3 \theta_{hoh} + km3 C_{h2} \theta_o = 0, \\ & k4 C_{co} \theta_o - km4 \theta_{oco} - k5 \theta_{oco} + km5 C_{co2} \theta_s = 0, \\ & k3 \theta_{hoh} - km3 C_{h2} \theta_o - k4 C_{co} \theta_o + km4 \theta_{oco} = 0, \\ & k1 C_{h2o} \theta_s - km1 \theta_{h2o} - k2 \theta_{h2o} + km2 \theta_{hoh} = 0 \} \end{aligned}$$

> sols:=simplify(solve(eqs,{theta_s,theta_h2o,theta_hoh,theta_o,theta_oco}));

$$\begin{aligned} sols := \{ & \theta_o = (km5 C_{co2} km1 k3 km4 + k1 C_{h2o} k2 k3 k5 + km5 C_{co2} k2 k3 km4 \\ & + km5 C_{co2} km1 km2 km4 + k1 C_{h2o} k2 k3 km4) / (km5 C_{co2} km1 k3 km4 + km5 C_{co2} k2 k3 km4 \\ & + k1 C_{h2o} k2 k3 k5 + km5 C_{co2} km1 km2 km4 + k1 C_{h2o} k2 k3 km4 + km5 C_{co2} k2 k3 k4 C_{co} \\ & + km4 km1 km2 km3 C_{h2} + k5 km1 km2 km3 C_{h2} + k5 k2 k3 k4 C_{co} \\ & + k2 km4 km5 C_{co2} km3 C_{h2} + km4 km5 C_{co2} km1 km3 C_{h2} + k5 km1 k3 k4 C_{co} \\ & + km4 km2 km5 C_{co2} km3 C_{h2} + km5 C_{co2} km1 km2 km3 C_{h2} + k5 km1 km2 k4 C_{co} \\ & + km5 C_{co2} km1 k3 k4 C_{co} + k1 C_{h2o} k2 k3 k4 C_{co} + km5 C_{co2} km1 km2 k4 C_{co} \\ & + k1 C_{h2o} k5 km2 km3 C_{h2} + k1 C_{h2o} k2 km4 km3 C_{h2} + k1 C_{h2o} k5 km2 k4 C_{co} \\ & + k1 C_{h2o} k5 k3 k4 C_{co} + k1 C_{h2o} k2 k5 km3 C_{h2} + k1 C_{h2o} k2 k5 k4 C_{co} \\ & + k1 C_{h2o} km4 km2 km3 C_{h2}), \theta_{hoh} = (k1 C_{h2o} k2 k5 km3 C_{h2} + k1 C_{h2o} k2 k5 k4 C_{co} \\ & + k1 C_{h2o} k2 km4 km3 C_{h2} + k2 km4 km5 C_{co2} km3 C_{h2} + km4 km5 C_{co2} km1 km3 C_{h2}) / \\ & (km5 C_{co2} km1 k3 km4 + km5 C_{co2} k2 k3 km4 + k1 C_{h2o} k2 k3 k5 + km5 C_{co2} km1 km2 km4 \\ & + k1 C_{h2o} k2 k3 km4 + km5 C_{co2} k2 k3 k4 C_{co} + km4 km1 km2 km3 C_{h2} \\ & + k5 km1 km2 km3 C_{h2} + k5 k2 k3 k4 C_{co} + k2 km4 km5 C_{co2} km3 C_{h2} \\ & + km4 km5 C_{co2} km1 km3 C_{h2} + k5 km1 k3 k4 C_{co} + km4 km2 km5 C_{co2} km3 C_{h2} \\ & + km5 C_{co2} km1 km2 km3 C_{h2} + k5 km1 km2 k4 C_{co} + km5 C_{co2} km1 k3 k4 C_{co} \\ & + k1 C_{h2o} k2 k3 k4 C_{co} + km5 C_{co2} km1 km2 k4 C_{co} + k1 C_{h2o} k5 km2 km3 C_{h2} \\ & + k1 C_{h2o} k2 km4 km3 C_{h2} + k1 C_{h2o} k5 km2 k4 C_{co} + k1 C_{h2o} k5 k3 k4 C_{co} \\ & + k1 C_{h2o} k2 k5 km3 C_{h2} + k1 C_{h2o} k2 k5 k4 C_{co} + k1 C_{h2o} km4 km2 km3 C_{h2}), \theta_s = (k5 \\ & km1 km2 km3 C_{h2} + k5 km1 km2 k4 C_{co} + km4 km1 km2 km3 C_{h2} + k5 km1 k3 k4 C_{co} \\ & + k5 k2 k3 k4 C_{co}) / (km5 C_{co2} km1 k3 km4 + km5 C_{co2} k2 k3 km4 + k1 C_{h2o} k2 k3 k5 \\ & + km5 C_{co2} km1 km2 km4 + k1 C_{h2o} k2 k3 km4 + km5 C_{co2} k2 k3 k4 C_{co} \\ & + km4 km1 km2 km3 C_{h2} + k5 km1 km2 km3 C_{h2} + k5 k2 k3 k4 C_{co} \\ & + k2 km4 km5 C_{co2} km3 C_{h2} + km4 km5 C_{co2} km1 km3 C_{h2} + k5 km1 k3 k4 C_{co} \end{aligned}$$

$$\begin{aligned}
& + km4 km2 km5 C_co2 km3 C_h2 + km5 C_co2 km1 km2 km3 C_h2 + k5 km1 km2 k4 C_co \\
& + km5 C_co2 km1 k3 k4 C_co + k1 C_h2o k2 k3 k4 C_co + km5 C_co2 km1 km2 k4 C_co \\
& + k1 C_h2o k5 km2 km3 C_h2 + k1 C_h2o k2 km4 km3 C_h2 + k1 C_h2o k5 km2 k4 C_co \\
& + k1 C_h2o k5 k3 k4 C_co + k1 C_h2o k2 k5 km3 C_h2 + k1 C_h2o k2 k5 k4 C_co \\
& + k1 C_h2o km4 km2 km3 C_h2), \theta_{h2o} = (k1 C_h2o k5 km2 km3 C_h2 \\
& + k1 C_h2o k5 km2 k4 C_co + k1 C_h2o km4 km2 km3 C_h2 + km4 km2 km5 C_co2 km3 C_h2 \\
& + k1 C_h2o k5 k3 k4 C_co) / (km5 C_co2 km1 k3 km4 + km5 C_co2 k2 k3 km4 + k1 C_h2o k2 k3 k5 \\
& + km5 C_co2 km1 km2 km4 + k1 C_h2o k2 k3 km4 + km5 C_co2 k2 k3 k4 C_co \\
& + km4 km1 km2 km3 C_h2 + k5 km1 km2 km3 C_h2 + k5 k2 k3 k4 C_co \\
& + k2 km4 km5 C_co2 km3 C_h2 + km4 km5 C_co2 km1 km3 C_h2 + k5 km1 k3 k4 C_co \\
& + km4 km2 km5 C_co2 km3 C_h2 + km5 C_co2 km1 km2 km3 C_h2 + k5 km1 km2 k4 C_co \\
& + km5 C_co2 km1 k3 k4 C_co + k1 C_h2o k2 k3 k4 C_co + km5 C_co2 km1 km2 k4 C_co \\
& + k1 C_h2o k5 km2 km3 C_h2 + k1 C_h2o k2 km4 km3 C_h2 + k1 C_h2o k5 km2 k4 C_co \\
& + k1 C_h2o k5 k3 k4 C_co + k1 C_h2o k2 k5 km3 C_h2 + k1 C_h2o k2 k5 k4 C_co \\
& + k1 C_h2o km4 km2 km3 C_h2), \theta_{oco} = (km5 C_co2 k2 k3 k4 C_co \\
& + km5 C_co2 km1 km2 km3 C_h2 + km5 C_co2 km1 k3 k4 C_co + k1 C_h2o k2 k3 k4 C_co \\
& + km5 C_co2 km1 km2 k4 C_co) / (km5 C_co2 km1 k3 km4 + km5 C_co2 k2 k3 km4 \\
& + k1 C_h2o k2 k3 k5 + km5 C_co2 km1 km2 km4 + k1 C_h2o k2 k3 km4 + km5 C_co2 k2 k3 k4 C_co \\
& + km4 km1 km2 km3 C_h2 + k5 km1 km2 km3 C_h2 + k5 k2 k3 k4 C_co \\
& + k2 km4 km5 C_co2 km3 C_h2 + km4 km5 C_co2 km1 km3 C_h2 + k5 km1 k3 k4 C_co \\
& + km4 km2 km5 C_co2 km3 C_h2 + km5 C_co2 km1 km2 km3 C_h2 + k5 km1 km2 k4 C_co \\
& + km5 C_co2 km1 k3 k4 C_co + k1 C_h2o k2 k3 k4 C_co + km5 C_co2 km1 km2 k4 C_co \\
& + k1 C_h2o k5 km2 km3 C_h2 + k1 C_h2o k2 km4 km3 C_h2 + k1 C_h2o k5 km2 k4 C_co \\
& + k1 C_h2o k5 k3 k4 C_co + k1 C_h2o k2 k5 km3 C_h2 + k1 C_h2o k2 k5 k4 C_co \\
& + k1 C_h2o km4 km2 km3 C_h2) \}
\end{aligned}$$

> assign(sols);

> simplify(factor(expand(r1)));

$$\begin{aligned}
& (k1 C_h2o k3 k5 k4 C_co k2 - km1 km2 km5 C_co2 km3 C_h2 km4) / (k4 C_co k3 k5 k1 C_h2o \\
& + km2 k4 C_co k5 k1 C_h2o + km2 km3 C_h2 km4 k1 C_h2o + km2 km3 C_h2 k5 k1 C_h2o \\
& + km2 km5 C_co2 km3 C_h2 km4 + k3 k5 k4 C_co km1 + k3 k5 k4 C_co k2 + km2 k5 k4 C_co km1 \\
& + k5 k1 C_h2o k3 k2 + km4 k1 C_h2o k3 k2 + km4 km5 C_co2 k3 km1 + k1 C_h2o km3 C_h2 km4 k2 \\
& + km4 km5 C_co2 k3 k2 + k1 C_h2o km3 C_h2 k5 k2 + k4 C_co km5 C_co2 k3 k2 \\
& + km5 C_co2 km3 C_h2 km4 k2 + k4 C_co k1 C_h2o k3 k2 + k4 C_co km5 C_co2 k3 km1 \\
& + km2 km3 C_h2 km4 km1 + k4 C_co k1 C_h2o k5 k2 + km2 k4 C_co km5 C_co2 km1
\end{aligned}$$

$$+ k_2 k_4 k_5 C_{CO_2} k_1 + k_2 k_3 C_{H_2} k_5 k_1 + k_2 k_3 C_{H_2} k_5 C_{CO_2} k_1 \\ + k_3 C_{H_2} k_5 C_{CO_2} k_4 k_1)$$

The final expression for the reaction rate is a bit long, but not so long as to be completely impractical. I did not try simplifying it to get any of the other expressions from parts b, c, and d.

- (2) A particular catalyst has a void fraction of 0.40, an internal surface area of 180 m²/g, and a pellet density of 1.40 g/cm³. 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.

Computation of the effective pore diameter is relatively simple. If the specific surface area is 180 m²/g = 1.8 × 10⁶ cm²/g, and the pellet density is 1.4 g/cm³, then the surface to volume ratio is (1.8 × 10⁶ cm²/g) * (1.4 g/cm³) = 2.52 × 10⁶ cm⁻¹. The surface to volume ratio of a cylinder is 4/d_p (where d_p is the cylinder, or pore, diameter). So, we have 4/d_p = 2.52 × 10⁶ cm⁻¹, from which d_p = 1.6 × 10⁻⁶ cm = 16 nm.

Estimating the diffusion coefficient is more complex. One estimate of the diffusion coefficient can be obtained from the Fuller equation, which is given in Perry's Handbook, which says:

"For prediction of the gas diffusivity of **binary air-hydrocarbon or nonhydrocarbon gas mixtures at low pressures**, the method of Fuller et al., given by Eq. (2-152) is recommended.

$$D_{12} = \frac{0.1013T^{1.75} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{0.5}}{P \left[(\sum v_1)^{1/3} + (\sum v_2)^{1/3} \right]^2}$$

Units of *T* and *P* are K and Pa, respectively, with the resulting diffusivity in m²/sec. All *v_i* are group contribution values for the subscript component summed over atoms, groups, and structural features given in Table 2-400."

The relevant volume increments are 16.5 for carbon atoms, 1.98 for H atoms, 17.0 for S atoms, and -20.2 for a heterocyclic ring. So, for thiophene, we have

$$\sum v_1 = 4 * 16.5 + 4 * 1.98 + 17.0 - 20.2 = 70.72$$

For H₂, a diffusion volume is given directly in the table from which the above values were obtained, and it is $\sum v_2 = 7.07$. The molecular weights of thiophene and hydrogen are 84.14 and 2.02 amu, respectively. So, at 600 K and 1 bar (10⁵ Pa) we have

$$D_{12} = \frac{0.1013(600)^{1.75} \left(\frac{1}{84.14} + \frac{1}{2.02} \right)^{0.5}}{10^5 \left[(70.72)^{1/3} + (7.07)^{1/3} \right]^2} = 0.0014 \text{ m}^2 \text{ s}^{-1} = 14.3 \text{ cm}^2/\text{s}$$

The next thing to consider is whether the pores are sufficiently small that Knudsen diffusion will be important. As we discussed in class, the Knudsen diffusion coefficient can also be estimated from an equation in Perry's handbook (eq. 16-66). Taking only the Knudsen diffusion part of it, we get

$$D_K = \frac{2d_p}{3} \left(\frac{2RT}{\pi M} \right)^{0.5} = \frac{2 * 1.6 \times 10^{-8}}{3} \left(\frac{2 * 8.314 * 600}{\pi * 0.08414} \right)^{0.5} = 2.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} = 0.021 \text{ cm}^2 \text{ s}^{-1}$$

The effective diffusion coefficient for the combination of the two is given by the geometric mean of the two ($D_{12}D_K/(D_{12} + D_K) = 0.021 \text{ cm}^2/\text{s}$). Only the smaller of the two matters.

Finally, to get the effective diffusion coefficient in the porous material, we must multiply by the void fraction and divide by the tortuosity. Guessing a tortuosity of 3, we have $D_e = 0.6 * 0.021/3 = 0.004 \text{ cm}^2/\text{s}$.

For a spherical catalyst pellet, we have:

$$\eta = \frac{3 \phi \coth(\phi) - 1}{\phi} \text{ with } \phi = R \sqrt{\frac{S_g \rho_c k_r}{D_e}}$$

Or

$$\eta = \frac{1}{\phi} \frac{3 \phi \coth(3\phi) - 1}{3\phi} \text{ with } \phi = \frac{R}{3} \sqrt{\frac{S_g \rho_c k_r}{D_e}}$$

These are equivalent, but one must make sure to use the expression for the effectiveness factor with the correct corresponding definition of the Thiele modulus that is used.

Using the first version of the effectiveness factor and Thiele modulus given above and iterating to find the Thiele modulus that gives $\eta = 0.5$ leads to

$$\phi = R \sqrt{\frac{S_g \rho_c k_r}{D_e}} = 0.25 \sqrt{\frac{1.8 \times 10^6 * 1.4 k_r}{0.004}} = 4.73$$

With units of g, cm, and s for mass, length, and time, respectively. Solving this gives $k_r = 5.7 \times 10^{-7} \text{ cm/s}$.

If we had ignored Knudsen diffusion and used the bulk diffusion coefficient, then this would be higher by a factor of $14.3/0.021 = 680$, which would give $k_r = 4 \times 10^{-7} \text{ cm/s}$. So, it is very important that we correctly evaluate the Knudsen diffusion coefficient and use it.

- (1) 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 $C_{As} = 3 \times 10^{-4} \text{ mol/cm}^3$.

DATA:

- | | | | | |
|--|------|-------|-------|--------|
| Diameter of sphere (cm) | 0.25 | 0.075 | 0.025 | 0.0075 |
| r_{obs} (mol hr ⁻¹ cm ⁻³) | 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_{obs} for a commercial *disk-shaped* catalyst pellet 1 cm in diameter and 0.3 cm thick

(a) For reactions in a spherical porous catalyst pellet, we have a relationship between the effectiveness factor and Thiele modulus that can be expressed as

$$\eta = \frac{1}{\phi} \frac{(3\phi)\coth(3\phi) - 1}{3\phi}, \text{ where the Thiele modulus is defined by}$$

$$\phi = \frac{R}{3} \sqrt{\frac{\rho_c S_g k_r}{D_{eA}}} = \text{‘factor’} * R$$

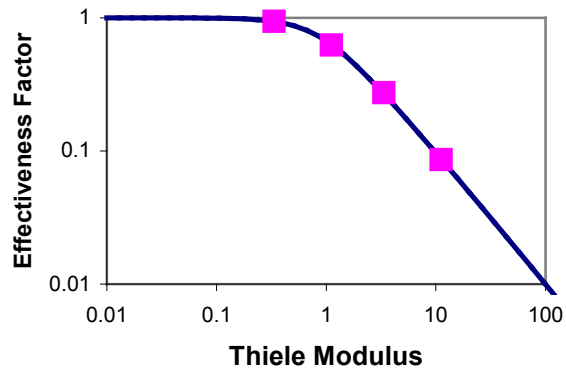
By definition, the effectiveness factor is equal to the observed rate divided by the ‘true rate’ (the rate if there were no pore diffusion limitations). So, if we knew the ‘factor’

$\left(\frac{1}{3} \sqrt{\frac{\rho_c S_g k_r}{D_{eA}}}\right)$ and the true reaction rate ($=k_r C_{As}$) then we could plot the data on an

effectiveness factor vs. Thiele modulus plot, and we would expect it to fit the above expression. So, what we will do is guess the ‘factor’ and the ‘true rate’, calculate the resulting effectiveness factor and Thiele modulus, and then adjust the ‘factor’ and ‘true rate’ to minimize the error between the model curve and the one derived from the data. This is done in the spreadsheet below.

Sphere Diameter (cm)	R/3 (=diameter/6) (cm)	Observed Rate (mol hr ⁻¹ cm ⁻³)	Thiele Modulus =factor*R/3	Effectiveness Factor =Obs rate/ True rate	Effectiveness Factor (fit)	Squared Error
0.2500	0.0417	0.3300	11.1860	0.0861	0.0867	4.09E-07
0.0750	0.0125	1.0500	3.3558	0.2739	0.2684	3.07E-05
0.0250	0.0042	2.4000	1.1186	0.6261	0.6298	1.31E-05
0.0075	0.0013	3.6000	0.3356	0.9392	0.9384	7.27E-07
	factor	268.4650			Sum of Errors	4.5E-05
	True rate	3.8330				

A plot of the resulting effectiveness factor curve looks like



All of the data points are affected by diffusion limitations. The data point with the smallest catalyst size is only slightly affected, while the last two points are near the diffusion-controlled regime.

From the above analysis, the 'true' rate constant (defined in terms of the rate per catalyst volume) is $k_r = (\text{true rate})/(C_{As}) = 3.833 \text{ mol cm}^{-3} \text{ hr}^{-1} / 3 \times 10^{-4} \text{ mol cm}^{-3} = 1.28 \times 10^4 \text{ hr}^{-1} = 3.55 \text{ s}^{-1}$.

In terms of this rate per catalyst volume, the Thiele modulus is

$$\phi = \frac{R}{3} \sqrt{\frac{k_r}{D_{eA}}}, \text{ so the 'factor' is } \sqrt{\frac{3.55 \text{ s}^{-1}}{D_{eA} \text{ cm}^2 \text{ s}^{-1}}} = 268 \text{ cm}$$

From which the effective diffusion coefficient is

$$D_{eA} = 4.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

(b) The disk-shaped catalyst has a geometry that is closer to being a slab than an infinite cylinder. So, we will use the slab solution, but with the 'length' given by the actual volume to surface ratio (V/s) of the catalyst disk. If the disk has thickness t and diameter d then

$$(V/S) = (\pi(d/2)^2 t) / (2\pi(d/2)^2 + \pi d t) = dt / (2d + 4t)$$

So, the appropriate generalized Thiele modulus is

$$\phi = \frac{dt}{2d + 4t} \sqrt{\frac{k_r}{D_{eA}}}$$

Substituting the dimensions of this particular catalyst and the values of k_r and D_A from part A, we have

$$\phi = \frac{1 \cdot 0.3}{2(1.0) + 4(0.3)} \sqrt{\frac{3.55}{4.9 \times 10^{-5}}} = 0.09375 \cdot 268 = 25.1$$

The effectiveness factor is then

$$\eta = \tanh(25.1)/25.1 = 1/25.1 = 0.040$$

For the commercial pellet size, the reaction is strongly diffusion limited. Based on this effectiveness factor, we expect the observed rate per unit volume to be

$$r_{obs} = 0.040 * 3.833 \text{ mol cm}^{-3} \text{ hr}^{-1} = 0.153 \text{ mol cm}^{-3} \text{ hr}^{-1} = 4.3 \times 10^{-5} \text{ mol cm}^{-3} \text{ s}^{-1}$$

(2) 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 1×10^{-6} mol cm^{-3} . The diameter is 2 mm, and the effective diffusion coefficient of the reactant in the pores is estimated to be $0.2 \text{ cm}^2/\text{s}$.

- (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?

(a) First, we should realize that measuring the concentration profile inside the catalyst is a tremendously difficult task, so this must be a hypothetical problem made up by a professor (possibly a professor at the University of Michigan, whose name starts with F?). But, assuming that we did somehow measure the concentration inside the particle and found that the concentration halfway between the external surface and the center of the pellet was 0.1 times the concentration at the surface, we can directly compute the Thiele modulus. For a spherical porous catalyst pellet, the concentration profile is given by

$$C_A(r) = C_{As} \left(\frac{R}{r} \right) \frac{\sinh(\lambda r)}{\sinh(\lambda R)}, \text{ where } \lambda = \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \varepsilon_s^2}}$$

In terms of the Thiele modulus, $\phi = R\lambda = R \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \varepsilon_s^2}}$, this is

$$\frac{C_A(r)}{C_{As}} = \left(\frac{R}{r} \right) \frac{\sinh\left(\phi \left(\frac{r}{R} \right)\right)}{\sinh(\phi)}.$$

For the conditions described above, this is

$$0.1 = (2) \frac{\sinh(0.5\phi)}{\sinh(\phi)}, \text{ or } 0.05 \sinh(\phi) = \sinh(0.5\phi)$$

This can be solved by trial and error to get $\phi = 6.0$

There are strong diffusion limitations (as we knew without actually doing the calculation, since there was a strong drop in concentration in the outer part of the pellet).

The effectiveness factor is

$$\eta = \frac{3 \phi \coth(\phi) - 1}{\phi}$$

and for $\phi = 6.0$, this gives $\eta = 0.42$. Diffusion limitations have reduced the rate to less than half of what it would be without diffusion limitations.

(b) At a position 0.2 mm from the surface (0.8 mm from the center, or $r/R = 0.8$), we have

$$C_A(0.8 \text{ mm}) = C_{As} (1.25) \frac{\sinh(6.0(0.8))}{\sinh(6.0)} = 0.38 C_{As} = 3.8 \times 10^{-7} \text{ mol cm}^{-3}$$

(d) To have an effectiveness factor of 0.8, we need to have

$$\eta = \frac{3\phi \coth(\phi) - 1}{\phi} = 0.8$$

This can be solved by trial and error (getting an initial guess from graphs of the effectiveness factor shown in the notes or textbook) to get $\phi = 2.04$.

With a sphere diameter of 2 mm, we had $\phi = 6.0$. The Thiele modulus is proportional to the sphere diameter, so to get a Thiele modulus of 2.04, we need a sphere diameter of $2.0 \text{ mm} * 2.04 / 6.0 = 0.68 \text{ mm}$.