## **Derivation of Rate Equations From Reaction Mechanism**

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This proposed mechanism for methanol synthesis was the basis for the UKRON-I Test Problem developed by Berty, Lee, and Szeifert of the Chemical Engineering Department of the University of Akron and discussed at International Workshops on Kinetic Model Development at the 1983 Denver and 1985 Chicago AIChE meetings.

$$2 [H_{2} + S = H_{2} - S]$$
  

$$CO + H_{2} - S = H_{2}CO - S$$
  

$$H_{2}CO - S + H_{2} - S = CH_{3}OH - S + S$$
  

$$CH_{3}OH - S = CH_{3}OH + S$$

 $2H_2 + CO = CH_3OH$  overall pathway

Abbreviations:

## $H = H_2$ C = CO $F = H_2CO$ $M = CH_3OH$

The Test Problem gave data from a steady-state reactor that functioned as a CSTR: an internal recycle reactor or "Berty reactor" for catalyst studies. Since we have a steady-state reactor, the steady-state approximation (SSA) applies to all species, since they really are at steady-state.

Since the gas is probably non ideal at the high-pressure conditions inside the reactor, we should use fugacities instead of partial pressures in the rate equations for the individual steps. However, by assuming that the fugacity coefficients in this system are constant over the range of conditions specified, we can "absorb" the fugacity coefficients into the rate coefficients and use partial pressures in the rate equations.

Prof. Berty and coworkers derived a rate equation (rate as function of gas concentrations) without applying the partial equilibrium approximation nor assuming a rate limiting step. There are 4 steps, each with two rate coefficients. For varying temperature, there is also an activation energy for each step.

Their result is given on the next page. The rate equation is the quadratic solution equation given at the top of the page. The a,b,c values in the quadratic solution are given by the equations below on the page. A lot of algebra!

Berty and coworkers then generated a set of hypothetical "experimental data" from this rate equation for a variety of operating conditions including different temperatures.. Participants were given the mechanism and data and told to come up with a rate equation that fit the data. They were not given the rate equation on the next page. The rate equations generated by the participants were much simpler than the one on the next page. The goal was to develop a rate equation that fit the data with the least error.



No rate limiting step assumption is involved!

By applying the partial equilibrium approximation to each step except one – the rate determing step (RDS) – we can simplify the algebra and derive a rate equation. There are four possibilities for the rate limiting step, so we can derive four rate equations to test. Here we will show the derivation for one possibility.

Model 1 – specify that Step 1 is the RDS:

$$r_M = 0.5 (k_1 P_H \theta_V - k_{-1} \theta_H)$$

The rate of methanol formation is proportional to the net forward rate of step 1, since we have specified that it is the rate determining step (RDS) in this model. Note that the rate of methanol formation at steady-state is one-half the rate of step 1, since step 1 has to occur twice for every methanol molecule formed.

Apply the partial equilibrium approximation (PEA) to steps 2-4 so that we can express the fractional surface coverages,  $\theta_i$ , in terms of partial pressures:

Step 2: 
$$\theta_F = K_2 P_C \theta_H$$

Step 3: 
$$\theta_F = \frac{\theta_M \theta_V}{K_3 \theta_H}$$

Step 4:  $\theta_M = \frac{P_M \theta_V}{K_4} = K_M P_M \theta_V$   $K_M = \frac{k_{-4}}{k_4} = \frac{1}{K_4}$ 

Set the relationships for steps 2 and 3 equal to each other,

$$K_2 P_C \theta_H = \frac{\theta_M \theta_V}{K_3 \theta_H} \qquad \qquad \theta_H^2 = \frac{\theta_M \theta_V}{K_2 K_3 P_C}$$

then insert the relationship for step 4,

$$\theta_H^2 = \frac{P_M}{K_2 K_3 K_4 P_C} \theta_V^2$$
$$\theta_H = \left(\frac{P_M}{K_2 K_3 K_4 P_C}\right)^{0.5} \theta_V$$

Now substitute this last equation into the relationship for step 2:

$$\theta_F = \left(\frac{K_2 P_C P_M}{K_3 K_4}\right)^{0.5} \theta_V$$

Then substitute these results for  $\theta_H$ ,  $\theta_F$  and  $\theta_M$  in terms of  $\theta_V$  into the "site balance":

$$\begin{split} 1 &= \theta_V + \theta_H + \theta_F + \theta_M \\ 1 &= \theta_V + \left(\frac{P_M}{K_2 K_3 K_4 P_C}\right)^{0.5} \theta_V + \left(\frac{K_2 P_C P_M}{K_3 K_4}\right)^{0.5} \theta_V + \left(\frac{P_M}{K_4}\right) \theta_V \\ \theta_V &= \frac{1}{1 + \left(\frac{1}{K_2 K_3 K_4}\right)^{0.5} \left(\frac{P_M}{P_C}\right)^{0.5} + \left(\frac{K_2}{K_4 K_3}\right)^{0.5} P_C^{0.5} P_M^{0.5} + \left(\frac{1}{K_4}\right) P_M} \end{split}$$

Finally, use these relationships in the rate equation for the RDS:

$$r_{M} = \frac{0.5k_{1} \left(P_{H} - \left(\frac{P_{M}}{K_{1}^{2}K_{2}K_{3}K_{4}P_{C}}\right)^{0.5}\right)}{1 + \left(\frac{1}{K_{2}K_{3}K_{4}}\right)^{0.5} \left(\frac{P_{M}}{P_{C}}\right)^{0.5} + \left(\frac{K_{2}}{K_{4}K_{3}}\right)^{0.5}P_{C}^{0.5}P_{M}^{0.5} + \left(\frac{1}{K_{4}}\right)P_{M}}$$

At the moment, we have five adjustable parameters,  $k_1$  and the four K. We can use our knowledge of equilibrium to reduce this to four.

At equilibrium,  $r_M = 0$ , and therefore the numerator of the rate equation = 0 at equilibrium.

$$P_{H} - \left(\frac{P_{M}}{K_{1}^{2}K_{2}K_{3}K_{4}P_{C}}\right)^{0.5} = 0 \quad \text{at equilibrium}$$
$$K_{1}^{2}K_{2}K_{3}K_{4} = \frac{P_{M}}{P_{C}P_{H}^{2}} \quad \text{at equilibrium}$$

We also know from equilibrium that

$$\Delta G_{rxn}^0(T) = -RT \ln K_{eq} \qquad K_{eq} = \frac{P_M}{P_C P_H^2} \phi_0^2 \qquad \text{at equilbrium}$$

where we assume ideal gas behavior (should be checked) and where  $\phi_0 = 1$  atm = 101.325 kPa is the standard-state fugacity, selected to match the pressure units used for the partial pressures. K<sub>eq</sub> is dimensionless. K<sub>eq</sub><sup>\*</sup> has dimensions of inverse pressure squared, and has a different numeric value from K<sub>eq</sub> when  $\phi_0$  is not 1 atm, e.g., when  $\phi_0 = 101.325$  kPa.

$$K_{eq}^{*} = \frac{K_{eq}}{\phi_{0}^{2}} = K_{1}^{2}K_{2}K_{3}K_{4} = \frac{P_{M}}{P_{C}P_{H}^{2}}$$
 at equilibrium

However, since all the *K*'s are constant at a given temperature, the relationship between the *K*'s holds at all extents of reaction, not just at equilibrium.

$$K_{eq}^* = \frac{K_{eq}}{\phi_0^2} = K_1^2 K_3 K_2 K_4$$
 at all extents of reaction

This means we can replace the product of the unknown *K*'s in the numerator of the rate equation with  $K_1^2 K_2 K_3 K_4 = K_{eq}^*$ . The value of  $K_{eq}^*$  can be obtained using the known Gibbs free energy of reaction obtained from thermodynamic tables. The effect is to eliminate  $K_1$  as an unknown.

$$r_{M} = \frac{0.5k_{1} \left( P_{H} - \left( \frac{P_{M}}{K_{eq}^{*} P_{C}} \right)^{0.5} \right)}{1 + \left( \frac{1}{K_{2} K_{3} K_{4}} \right)^{0.5} \left( \frac{P_{M}}{P_{C}} \right)^{0.5} + \left( \frac{K_{2}}{K_{4} K_{3}} \right)^{0.5} P_{C}^{0.5} P_{M}^{0.5} + \left( \frac{1}{K_{4}} \right) P_{M}}$$

Grouping parameters to simplify notation,

$$r_{M} = \frac{k_{f} \left( P_{H} - \left( \frac{P_{M}}{K_{eq}^{*} P_{C}} \right)^{0.5} \right)}{1 + K_{1}^{'} \left( \frac{P_{M}}{P_{C}} \right)^{0.5} + K_{2}^{'} P_{C}^{0.5} P_{M}^{0.5} + K_{M} P_{M}}$$
 Step 1 is RDS

We have four adjustable parameters with which to fit this equation to isothermal data:  $k_f$ ,  $K_1'$ ,  $K_2'$  and  $K_M$ . The value of  $K_{eq}^*$  at the reaction temperature can be obtained using the known Gibbs free energy of reaction obtained from thermodynamic tables. All of the models derived from the mechanism also have four adjustable parameters. Each of these four parameters are temperature dependent, so there is also an activation energy parameter for each.