ChE-403 Problem Set 2.3

Week 7

Problem 1

We just saw that ammonia synthesis proceeded through the following sequence:

Step		$\overline{\sigma}_i$
(1)	$N_2 + 2* \rightleftharpoons 2N*$	1
(2)	$N* + H* \rightleftharpoons NH* + *$	2
(3)	$NH* + H* \rightleftharpoons NH_2* + *$	2
(4)	$NH_2* + H* \rightleftharpoons NH_3 + 2*$	2
(5)	$H_2 + 2* \rightleftharpoons 2H*$	3
	$N_2 + 3H_2 = 2NH_3$	

We saw in class that step 1 was the rate determining step (RDS) and that all other steps could be expressed as a pseudo-equilibrated reaction. What would the mechanism be if the first and rate determining step was actually:

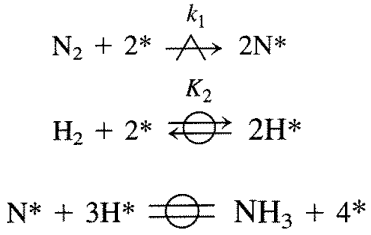
$$N_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2^*$$

With N_2* being the most abundant reaction intermediate (MARI).

Can you derive the rate expression?

Problem 2

The ammonia synthesis reaction can occur over Ru. At high H_2 pressure and low N_2 pressure (49 bar H_2 1 bar N_2) and a reaction far from equilibrium, we see the following mechanism:



The resulting rate appears to be in first order in [N_2] and inverse first order in [H_2]. The final concentration of ammonia (at these low conversions) seems to have no effect. Can you derive a rate that explains these results at these conditions?

Problem 3

For the reaction of A to B over a solid catalyst, the reaction rate has the following form:

$$r = \frac{cst\ P_A\ P_B}{(1 + K_A P_A + K_B P_B)^2}$$

Can you suggest a mechanism that would correspond to this reaction?

What would happen to the rate expression if a large pressure of an inert molecule P_N (with $P_N >> P_A$ and P_B) was introduced that could adsorb on the catalyst similarly to A and B?