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)	$N_2 + 2^* \rightleftarrows 2N^*$	1
(2)	$N^* + H^* \rightleftarrows NH^* + {}^*$	2
(3)	$NH^* + H^* \rightleftarrows NH_2^* + {}^*$	2
(4)	$NH_2^* + H^* \rightleftarrows NH_3 + 2^*$	2
(5)	$H_2 + 2^* \rightleftarrows 2H^*$	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:

$$N_2 + * \ \overset{k_1}{\underset{k_{-1}}{\mathrel{\rlap{\;\,\triangle}\rightleftarrows}}}\ N_2^*$$

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

Can you derive the rate expression?

Solution:

As described the mechanism is:

$$N_2 + * \ \overset{k_1}{\underset{k_{-1}}{\mathrel{\rlap{\;\,\triangle}\rightleftarrows}}}\ N_2^*$$

$$N_2^* + 3\,H_2 \ \overset{K_2}{\mathrel{\rlap{\,\bigcirc}=}}\ 2\,NH_3 + *$$

We start by writing the RDS:

$$r = k_1[N_2][*] - k_{-1}[N_2^*]$$

$$K_2 = \frac{[NH_3]^2[*]}{[H_2]^3[N_2^*]}$$

with the site balance:

$$[*]_0 = [*] + [N_2^*]$$

$$[*] = [*]_0 - \frac{[NH_3]^2[*]}{[H_2]^3K_2} \ \rightarrow\ [*] = \frac{[*]_0}{1 + \frac{[NH_3]^2}{[H_2]^3K_2}}$$

We can also use this to determine $[N_2^*]$:

$$[N_2^*] = [*]_0 - [*] = \frac{[*]_0 \frac{[NH_3]^2}{[H_2]^3K_2}}{1 + \frac{[NH_3]^2}{[H_2]^3K_2}} = \frac{[*]_0[NH_3]^2}{[H_2]^3K_2 + [NH_3]^2}$$

We can substitute both expressions into the rate equation:

$$r = k_1[N_2]\frac{[*]_0}{1 + \frac{[NH_3]^2}{[H_2]^3K_2}} - k_{-1}\frac{[*]_0[NH_3]^2}{[H_2]^3K_2 + [NH_3]^2}$$

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:

$$N_2 + 2^* \xrightarrow{k_1} 2N^*$$

$$H_2 + 2^* \underset{}{\overset{K_2}{\rightleftharpoons}} 2H^*$$

$$N^* + 3H^* \rightleftharpoons NH_3 + 4^*$$

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?

Solution:

We start with the RDS:

$$r = \frac{k_1[N_2][*]^2}{[*]_0}$$

The equilibrium reaction for the 2nd step must hold:

$$K_2 = \frac{[H^*]^2}{[*]^2\,[H_2]}$$

At such H_2 pressures, we can maybe assume that H* is the MARI. Let's test this out:

$$[*]_0 = [*] + [H^*]$$

$$[*] = \frac{[H^*]}{(K_2\,[H_2])^{1/2}} = \frac{[*]_0 - [*]}{(K_2\,[H_2])^{1/2}}$$

$$[*] = \frac{[*]_0}{1 + (K_2\,[H_2])^{1/2}}$$

If we plug this into the rate equation:

$$r = \frac{k_1[N_2][*]_0}{\left(1 + (K_2\ [H_2])^{\frac{1}{2}}\right)^2}$$

At high P_{H2}, we can assume that $(K_2\ [H_2])^{\frac{1}{2}} \gg 1$ and therefore the rate becomes:

$$r = \frac{k_1[N_2][*]_0}{K_2\ [H_2]}$$

This rate is first order in N_2 and inverse first order in H_2 as experimentally described. Interestingly, the following equilibrium does not enter into consideration at all because H* is assumed to be the MARI.

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?

Solution:

Let's assume that the RDS for the reaction is the transformation of adsorbed A to adsorbed B.

$$A + * \overset{\bigcirc}{\rightleftarrows} A^{*} \qquad (1)$$

$$A^{*} \xrightarrow{\wedge} B^{*} \qquad (2)$$

$$B^{*} \overset{\bigcirc}{\rightleftarrows} B \qquad (3)$$

The rate would be expressed as:

$$r = k_1 \left[A^{*}\right]$$

Let's express the adsorbed species:

$$K_A = \frac{\left[A^{*}\right]}{[A]\,[*]}$$

Which gives:

$$\left[A^{*}\right] = K_A [A]\,[*]$$

and

$$K_B = \frac{\left[B^{*}\right]}{[B]\,[*]}$$

Which gives:

$$\left[B^{*}\right] = K_B [B]\,[*]$$

$$[*]_0 = [*] + \left[A^{*}\right] + \left[B^{*}\right]$$

$$[*]_0 = [*] + [A]\,[*]K_A + [B]\,[*]K_B$$

$$\frac{[*]_0}{(1 + [A]K_A + [B]K_B)} = [*]$$

The rate becomes:

$$r = \frac{k_1 K_A [A][*]_0}{(1 + [A]K_A + [B]K_B)}$$

This is not exactly what we were aiming for. However the form of the equation looks right, we need a parameter in the form of:

$$\frac{[B]}{(1 + [A]K_A + [B]K_B)}$$

It looks very much like the expression of [B*]. This implies that the rate of reaction is likely to be expressed as the following:

$$r = k_1 \left[A^*\right]\left[B^*\right]$$

This means that the reaction is autocatalytic.
In order to convince ourselves, we can derive the new rate of reaction taking into account the autocatalytic step:

$$A^* + B^* \xrightarrow{\Lambda} 2B^*$$

Where the rate is equal to:

$$r = \frac{k_1[A*][B*]}{[*]_0}$$

With:

$$\left[A^*\right] = \frac{K_A [A][*]_0}{(1 + [A]K_A + [B]K_B)}$$

And

$$\left[B^*\right] = \frac{K_B [B][*]_0}{(1 + [A]K_A + [B]K_B)}$$

The rate becomes:

$$r = \frac{k_1 K_A K_B [A][B][*]_0}{(1 + [A]K_A + [B]K_B)^2}$$

Bingo ;)

Now if we add an inert but absorbing molecule at high pressure, a new equilibrium appears:

$$N + * \rightleftarrows N^{*}$$

N is not involved directly in the reaction but its adsorption will hinder the adsorption of A and B. It appears in the site balance:

$$[*]_0 = [*] + \left[A^{*}\right] + \left[B^{*}\right] + \left[N^{*}\right]$$

$$\text{or} \quad [*]_0 = [*] + [A]\,[*]K_A + [B]\,[*]K_B + [N]\,[*]K_N$$

With this, we can see that:

$$[*] = \frac{[*]_0}{(1 + [A]\,K_A + [B]\,K_B + [N]\,K_N)}$$

Which will lead to the following rate:

$$r = \frac{k_1 K_A K_B [A][B][*]_0}{(1 + [A]\,K_A + [B]\,K_B + [N]\,K_N)^2}$$

With N being at much higher pressure than A and B we can simplify the expression for adsorption sites:

$$[*] = \frac{[*]_0}{(K_4 N)}$$

And the rate becomes:

$$r = \frac{k_2 K_1 K_3 [A][B][*]_0^2}{(K_4 N)}$$

$$r = cst\,[A][B]$$