Physical Chemistry HW 3

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1. a. The rate equation here is
$$\frac{d[A]}{dt} = -k_1[A] + k_2[B][C]$$
which has to equal 0 at equilibrium. We also know that $[A]+[B] = 1$ and $[B] = [C]$. Substituting this in gives
$$0 = -2k_2[A] - k_2(1-[A])^2 \rightarrow 2[A] = (1-[A])^2$$
Solving this for $[A]$ gives
$$[A] = 0.26M$$

   b. The decomposition of D creates B, which is a product in the decomposition of A. Thus, when D is added, the amount of A increases and the amount of C decreases.

   c. The rate equation for B is
$$\frac{-d[B]}{dt} = k_2[B][C] - k_1[A] + k_4[B][E] - k_3[D]$$
which equals 0 at equilibrium. Thus,
$$0 = k_2[B][C] - k_1[A] + k_4[B][E] - k_3[D]$$
Solving for [B] gives
$$[B] = \frac{k_1[A] + k_3[D]}{k_2[C] + k_4[E]}$$

2. The number of edge sites in the nanoparticle is
$$12N - 16$$
and the number of face sites is
$$6(N-2)^2$$
We also can express the total fraction of occupied sites as
$$\theta = x_{face}\theta_{face} + x_{edge}\theta_{edge}$$
where x_{face} and x_{edge} represent the probabilities of a space being a face or an edge, respectively. We also know that
$$K_1 = \frac{k_{adsorption}}{k_{desorption}}, K_1 * k_{desorption} = k_{adsorption}$$
for the edge sites, and
$$K_2 = \frac{k_{adsorption}}{k_{desorption}}, K_1 * k_{desorption} = k_{adsorption}$$
First, we can solve for the respective probabilities
$$x_{face} = \frac{N_{face}}{N_{total}} = \frac{6(N-2)^2}{6(N-2)^2 + 12N - 16} = \frac{3N^2 - 12N + 12}{3N^2 - 6N + 4}$$

$$x_{edge} = \frac{N_{edge}}{N_{total}} = \frac{12N - 16}{6(N-2)^2 + 12N - 16} = \frac{6N - 8}{3N^2 - 6N + 4}$$

Then, to find the two θ values, we can apply the langmuir equilibrium expression

$$\theta = \frac{k_{adsorption} C_M}{k_{desorption} + k_{adsorption} C_M}$$

Substituting in the previous expression with K_1 gives

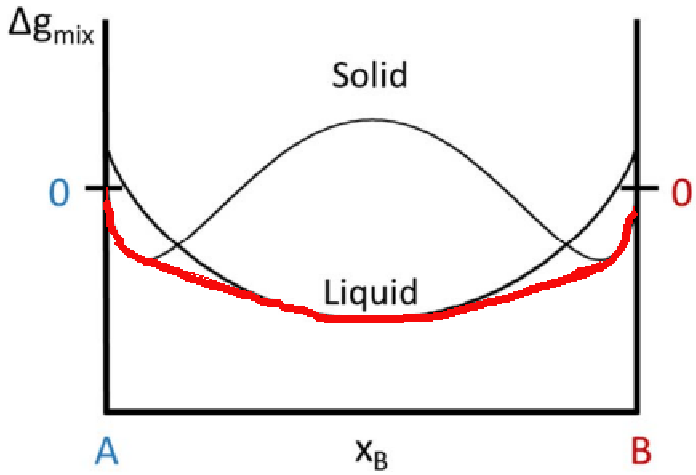
$$\theta_{edge} = \frac{K_1 k_{desorption} C_M}{k_{desorption} + K_1 k_{desorption} C_M} = \frac{K_1 C_{CO}}{1 + K_1 C_{CO}}$$

We can derive a similar expression for θ_{face}

$$\theta_{face} = \frac{K_2 C_{CO}}{1 + K_2 C_{CO}}$$

Finally, combining everything gives

$$\theta = \frac{K_1 C_{CO}}{1 + K_1 C_{CO}} * \frac{6N - 8}{3N^2 - 6N + 4} + \frac{K_2 C_{CO}}{1 + K_2 C_{CO}} * \frac{3N^2 - 12N + 12}{3N^2 - 6N + 4}$$



3.

4. The rate equation here is

$$\frac{d[A]}{dt} = -k[A][C]$$

Solving the differential equation gives

$$[A] = [A]_0 e^{-k[C]t}$$

At t=5, this becomes

$$[A] = e^{-0.1*5*2} = e^{-1} = 0.367$$

Thus, the concentration of B would be

$$[B] = 1 - [A] = 0.632$$