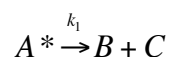
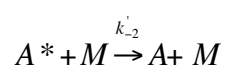
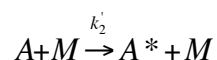
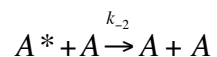
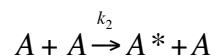


NAME: _____

Score _____/15

1. (10 points)

Consider the following reaction mechanism:



- a. Write an expression for the rate of reaction in terms of the concentration of the activated complex A^* .

$$\frac{d[B]}{dt} = k_1[A^*]$$

- b. Applying an appropriate approximation, determine the reaction rate in terms of the various rate constants, the concentration of A, and the concentration of M.

$$\frac{d[A^*]}{dt} = k_2[A]^2 - k_{-2}[A][A^*] + k_2'[A][M] - k_{-2}'[A^*][M] - k_1[A^*]$$

Apply steady-state approximation

$$\frac{d[A^*]}{dt} \approx 0$$

$$[A^*] = \frac{k_2[A]^2 + k_2'[A][M]}{k_1 + k_{-2}[A] + k_{-2}'[M]}$$

$$\text{Rate} = \frac{d[B]}{dt} = k_1[A^*] = k_1 \frac{k_2[A]^2 + k_2'[A][M]}{k_1 + k_{-2}[A] + k_{-2}'[M]}$$

If $[M]=0$, we have the Lindemann mechanism.

- c. What is the effective rate in the limit of very large concentrations of M?

For [M] large :

$$\text{Rate} = \frac{d[B]}{dt} = k_1[A^*] = k_1 \frac{k_2[A]}{k_{-2}}$$

Rate is first - order in [A], independent of values of [M] and [A]

(as long as [M] is relatively larger than other terms in rate expression)

d. What is the reaction rate if there is virtually no “self-activation”; that is, all activation occurs through collisions of A with M?

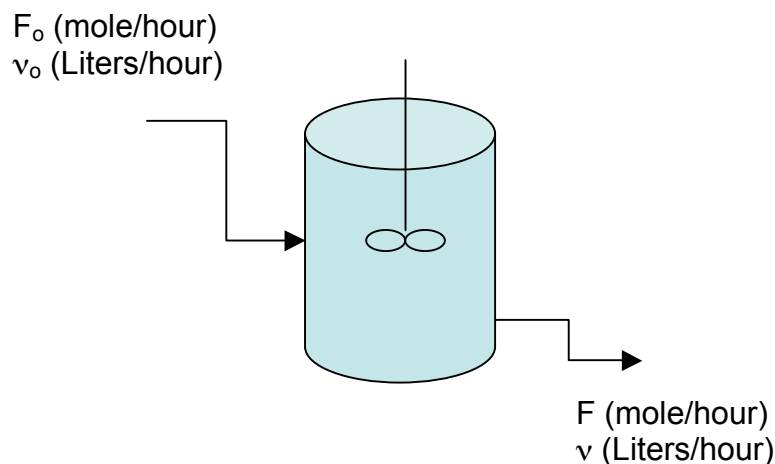
for no self - activation (and deactivation), we can take k_2 and k_{-2} to be 0 :

$$\text{Rate} = \frac{d[B]}{dt} = k_1[A^*] = k_1 \frac{k_2[A][M]}{k_1 + k_{-2}[M]}$$

In this situation, the reaction is first order in [A] and depends explicitly on [M]

2. (5 points)

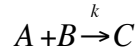
Consider a simplified model of a continuously stirred tank reactor (CSTR) with volume V shown schematically in the figure below:



There is one flow stream into the tank, F_o ; one flow stream out of the tank, F . The units for F are in (moles/hour). The volumetric flowrates for the streams are labeled v_o and v for the inlet and outlet

streams, respectively. For the current purposes, the inlet stream contains only reactants of a chemical reaction, and the output stream contains products and unreacted reactants. There is complete mixing such that the concentrations of all species are constant throughout the reactor volume, V.

Now consider the following reaction:



We can see that the differential rate of accumulation of C in the tank is equal to the sum of three things: 1. The rate of flow into the tank, 2. The rate of flow out of the tank, and 3. The rate at which C is created in the tank.

Assuming steady state operation of the tank, determine a relation between the required tank volume to achieve a fractional conversion of X and the rate constant for this reaction. The expression may contain other properties of the system in addition to the two mentioned.

Consider the mole balance for species C; assume a stoichiometric feed ratio of A and B:

rate of change of moles of C in tank = rate of production via reaction - amount exiting in outlet stream

$$\frac{dC}{dt} = V \frac{d[C]}{dt} - v[C]$$

$$0 = V k[A][B] - v[C]$$

$$V = \frac{v[C]}{\left(\frac{d[C]}{dt}\right)} = \frac{v[C]}{k[A][B]}$$

For a conversion of A (or B) by a fraction X, the concentrations of A, B, C in the tank (and thus exiting) are:

$$[A] = (1 - X)[A_0]$$

$$[B] = (1 - X)[B_0]$$

$$[C] = X[A_0]$$

Plugging in the expressions for the concentrations we obtain the tank volume as:

$$\text{Volume}_{\text{Tank}} = \frac{v[C]}{k[A][B]} = \frac{vX[A_0]}{k(1-X)[A_0](1-X)[B_0]}$$

$$\text{Volume}_{\text{Tank}} = \frac{v[C]}{k[A][B]} = \frac{vX[A_0]}{k[A_0]^2(1-X)^2} \quad (\text{recalling stoichiometric feed of A and B})$$

We see that the required tank volume is inversely proportional to the rate constant which is intuitively consistent.