

Work independently. Do not look at others' exams.

Do not allow your exam responses to be shared.

1. (30 points) Circle ALL correct answers, or fill in the blank, as appropriate. You may skip **THREE** of the sub-questions a–m. Write **SKIP** clearly in the left margin corresponding to your choice. If you do not, the first sub-question (a) will be skipped.

Element	Molecular weight (g/mol)	Collisional diameter (Å)
H (hydrogen)	1.00	2.5
I (iodine)	127	30

- a) At 298 K and 1 atm, the root mean square velocity of H₂ is (**greater than / equal to / less than**) that of I₂.

greater than $\frac{\sqrt{\langle u_{H_2}^2 \rangle}}{\sqrt{\langle u_{I_2}^2 \rangle}} = \frac{\sqrt{\frac{3RT}{M_{H_2}}}}{\sqrt{\frac{3RT}{M_{I_2}}}} = \frac{\sqrt{\frac{1}{M_{H_2}}}}{\sqrt{\frac{1}{M_{I_2}}}} = \sqrt{\frac{M_{I_2}}{M_{H_2}}}$

- b) At 298 K and 1 atm, the number of collisions each H₂ encounters per second is (**greater than / equal to / less than**) that of I₂.

Less than $\frac{z_{H_2}}{z_{I_2}} = \frac{4\sqrt{\pi} \frac{N}{V} \sigma_{H_2}^2 \sqrt{\frac{RT}{M_{H_2}}}}{4\sqrt{\pi} \frac{N}{V} \sigma_{I_2}^2 \sqrt{\frac{RT}{M_{I_2}}}} = \frac{\sigma_{H_2}^2 \sqrt{\frac{1}{M_{H_2}}}}{\sigma_{I_2}^2 \sqrt{\frac{1}{M_{I_2}}}} = \frac{\sigma_{H_2}}{\sigma_{I_2}}^2 \sqrt{\frac{M_{I_2}}{M_{H_2}}}$

$$\frac{z_{H_2}}{z_{I_2}} = \frac{2.5}{30}^2 \sqrt{\frac{254}{2}} = (0.0833)^2 \sqrt{127} = 0.078$$

- c) At 298 K and 0.1 atm, the number of collisions each H₂ encounters per second is (**greater than / equal to / less than**) that of I₂.

Less than (pressure contributes the same to each, ratio same as above)

- d) At 298 K and 1 atm, the translational kinetic energy of 1 mol of H₂ is (**greater than / equal to / less than**) that of 1 mol of I₂.

equal to (kinetic energy depends *only* on Temperature and the number of moles)

- e) At 298 K, the translational kinetic energy of 1 mol of H₂ at 0.1 atm is (**greater than / equal to / less than**) that of 1 mol of H₂ at 10 atm.

equal to (kinetic energy depends *only* on Temperature and the number of moles)

- f) The sedimentation coefficient of a spheroidal particle is (**greater than / equal to / less than**) that of a particle with the same density and mass, but with a prolate (elongated) shape.

greater than (a sphere presents the least resistance, friction)

g) The units for a second order rate constant are ($\text{s}^{-1} / \text{M s}^{-1} / \text{M}^{-1} \text{s}^{-1}$).
 $\text{M}^{-1} \text{s}^{-1}$

h) Given the stoichiometry of a reaction, one (**can / might be able to / cannot**) deduce the rate law.
 cannot

i) Given the rate law for a reaction, one (**can / might be able to / cannot**) deduce the stoichiometry.
 cannot

j) The kinetics of a reaction are observed to be first order in A and first order in B. Select the mechanism(s) below which is/are consistent with this observation.

(a)	(b)	(c)	(d)	(e)
$A + B \rightarrow C$	$A \xrightarrow{\text{fast}} A^* \xrightarrow{\text{slow}} A^* + B \rightarrow C$	$B \xrightarrow{\text{fast}} B^* \xrightarrow{\text{slow}} A + B^* \rightarrow C$	$A \xrightarrow{\text{slow}} A^* \xrightarrow{\text{fast}} A^* + B \rightarrow C$	$B \xrightarrow{\text{slow}} B^* \xrightarrow{\text{fast}} A + B^* \rightarrow C$

a, b, and c

k) The Arrhenius pre-factor, A, is thought to represent:

The rate at zero temperature

The rate at infinite temperature

The rate at zero pressure

The rate at dilute concentrations of A

infinite temperature

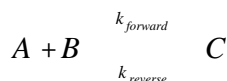
l) Describe briefly in words, from Arrhenius/kinetic theory considerations, WHY raising the temperature of a reaction increases the overall velocity of a reaction

raising the average energy of molecular collisions, thereby allowing more reactions to overcome the activation energy. To a lesser extent, it also increases the frequency of collisions

m) Describe briefly in words, from Eyring's transition state theory, WHY raising the temperature of a reaction increases the overall velocity of a reaction

Shifting the equilibrium from the reactants toward the transition state. In particular, for reactions which increase their rate with temperature, it is proposed that there is an unfavorable entropy in forming the transition state. Increasing the temperature overcomes this unfavorable entropy.

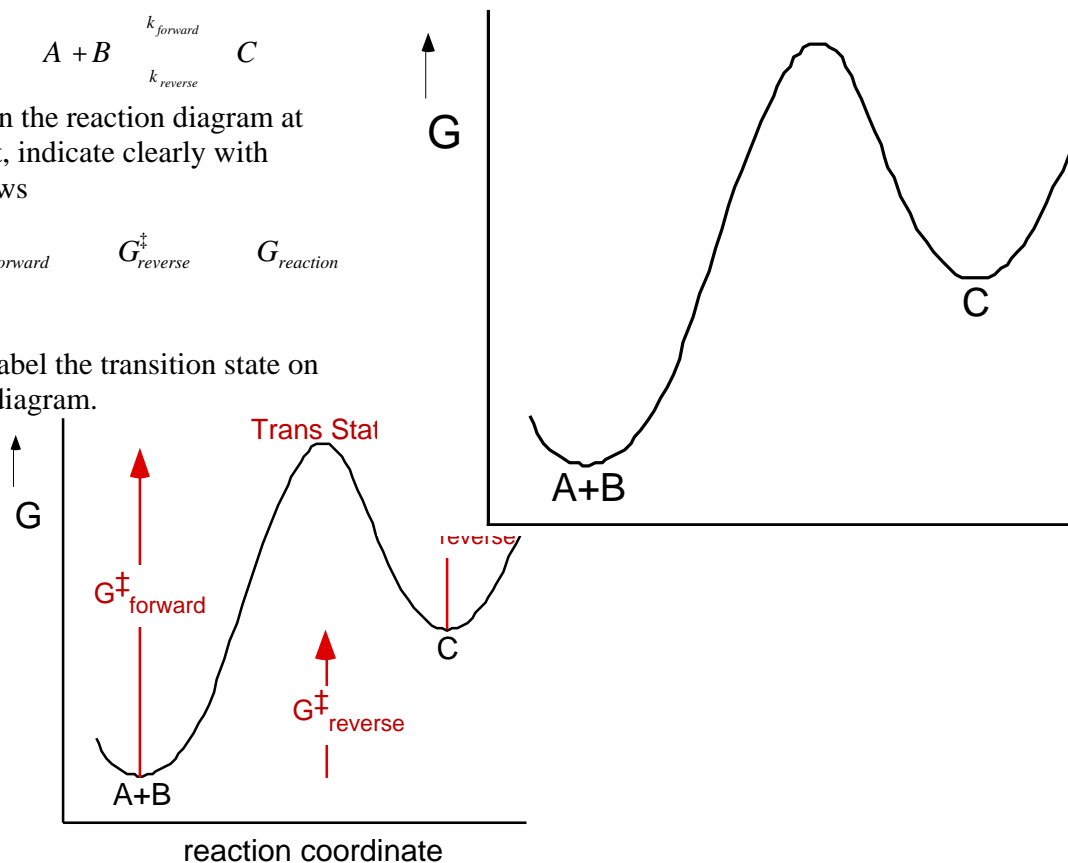
2. (10 points) Consider the reaction:



a) On the reaction diagram at right, indicate clearly with arrows



b) Label the transition state on the diagram.



3. (20 points) Consider the kinetic mechanism shown at right.

a) Place A, B, C, D, E, and F into the following categories:

Reactants:

B

Intermediates:

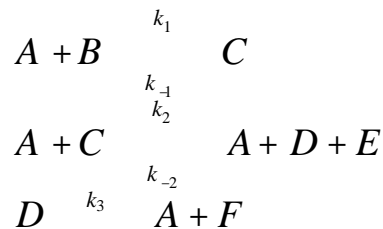
C, D

Products:

E, F

Catalysts:

A



b) Complete the following

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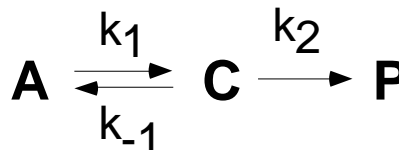
$$\frac{dC}{dt} =$$

$$\frac{dC}{dt} = k_1 AB - k_{-1} C - k_2 AC + k_{-2} ADE$$

$$\frac{dA}{dt} =$$

$$\frac{dA}{dt} = -k_1 AB + k_{-1} C + k_3 D$$

4. Consider the reaction mechanism shown at right. In each case below, the reaction is started by addition of A to a total concentration of A_o , with no C or P initially present. The rate of the reaction is observed at early times (the concentration of P remains much less than that of A and C). This is not looking for the integrated rate equation, but rather at the initial rate, when only a small amount of P has formed.



- a) (15 points) Assuming that fast equilibrium is established between A and C (k_2 is much less than k_{-1}), express the initial velocity dP/dt as a function of A_o and the rate constants.

$$\frac{dP}{dt} = k_2 C$$

$$A_o = A + C + P \quad A + C$$

$$K = \frac{k_1}{k_{-1}} = \frac{C}{A} \quad A = \frac{1}{K} C$$

$$A_o = \frac{1}{K} C + C$$

$$C = \frac{1}{1 + \frac{1}{K}} A_o \quad \frac{dP}{dt} = k_2 \frac{1}{1 + \frac{1}{K}} A_o = \frac{k_2}{1 + \frac{1}{K}} A_o$$

- b) (15 points) Assuming instead, that C reaches steady state (k_2 is comparable to k_{-1}), express the initial velocity dP/dt (at steady state) as a function of A_o and the rate constants.

$$\frac{dP}{dt} = k_2 C$$

$$A_o = A + C + P \quad A + C$$

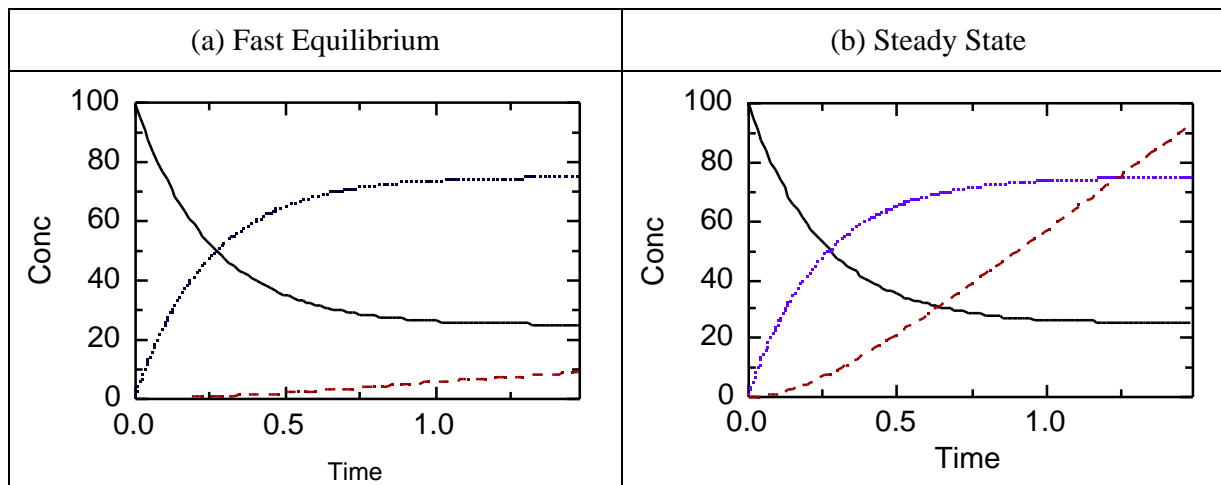
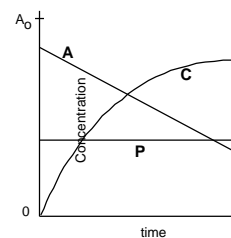
$$\frac{dC}{dt} = 0 = k_1 A - k_{-1} C - k_2 C$$

$$k_1 A = (k_{-1} + k_2) C \quad A = \frac{k_{-1} + k_2}{k_1} C$$

$$A_o = \frac{k_{-1} + k_2}{k_1} C + C$$

$$C = \frac{1}{1 + \frac{k_{-1} + k_2}{k_1}} A_o \quad \frac{dP}{dt} = k_2 \frac{1}{1 + \frac{k_{-1} + k_2}{k_1}} A_o = \frac{k_2}{1 + \frac{k_{-1} + k_2}{k_1}} A_o$$

- c) (10 points) The equations derived above describe the kinetics of the reaction only within a certain time window. In the graphs below, plot qualitatively (you don't need a calculator) for each of (a) and (b) above, the concentrations of A, C, and P from time $t=0$ up through some reasonable time (not until the end of the reaction). For part (b) include behavior before and including the steady state phase. An example is shown at right.



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