

Draw a CIRCLE around your symbolic answer and a BOX around your final numeric answer where appropriate. Clearly identify the quantity you are reporting and include the units if it is a numerical answer. Present your work neatly and in order beneath each question. Staple your answer sheets to the back of this sheet in the extreme left hand corner.

$$R = 8.31 \text{ (J/ K mol)} = 0.08206 \text{ (L atm/ K mol)} \quad N_A = 6.02 \times 10^{23}$$

$$1 \text{ atm} = 760 \text{ torr} = 1.01 \times 10^5 \text{ (N/ m}^2\text{)} = 1.01 \text{ bar} = 101 \text{ kPa}$$

$$h = 6.63 \times 10^{-34} \text{ J s} \quad c = 3.0 \times 10^8 \text{ m/s} \quad \text{SEE BOARD FOR ADDITIONAL INFO}$$

1a) In Sarah McCary's talk (day 1) on the NMR of binding of a neuropeptide to a lipid bilayer, it was observed that binding required

- a) NH_2 to be in the NH_3^+ form which was affected by pH
- b) Strong S-S bonds to form
- c) Amide bond formation

1b) In Albert Vaughn's talk (day 1) on protein folding within a lipid bilayer it was found that the key to the binding between the membrane and the protein was/were

- a) Al-Al metal bonds
- b) Boron-hydrogen bonding
- c) multiple tryptophans present in the protein
- d) lipid completely covering the protein

2a) In Aaron Evans' talk (day 2) palladium nanowires were formed

- a) in a spaghetti like mesh completely covering the basal planes of graphite
- b) in a vacuum chamber
- c) along the length of carbon nanotubes
- d) in parallel along the step edges of graphite planes that had been oxidized

2b) In Warren Shipley's talk (day 3) the ISC in $\text{Ir}(\text{piq})_3$ was found to be on a time scale of about

- a) 70 fs
- b) 70 ms
- c) 70 s
- d) 70 hr

3a) In Cynthia Groves' talk (day 4) gold nanoplates were formed

- a) by using dried lawn clippings
- b) by using dried seaweed
- c) in muffle furnace
- d) by laser ablation from a gold surface

3b) In Miyoung Kim's talk (day 4) inside TiO_2 nanotubes secondary nanotubes were formed from

- a) Al
- b) B
- c) C
- d) Si

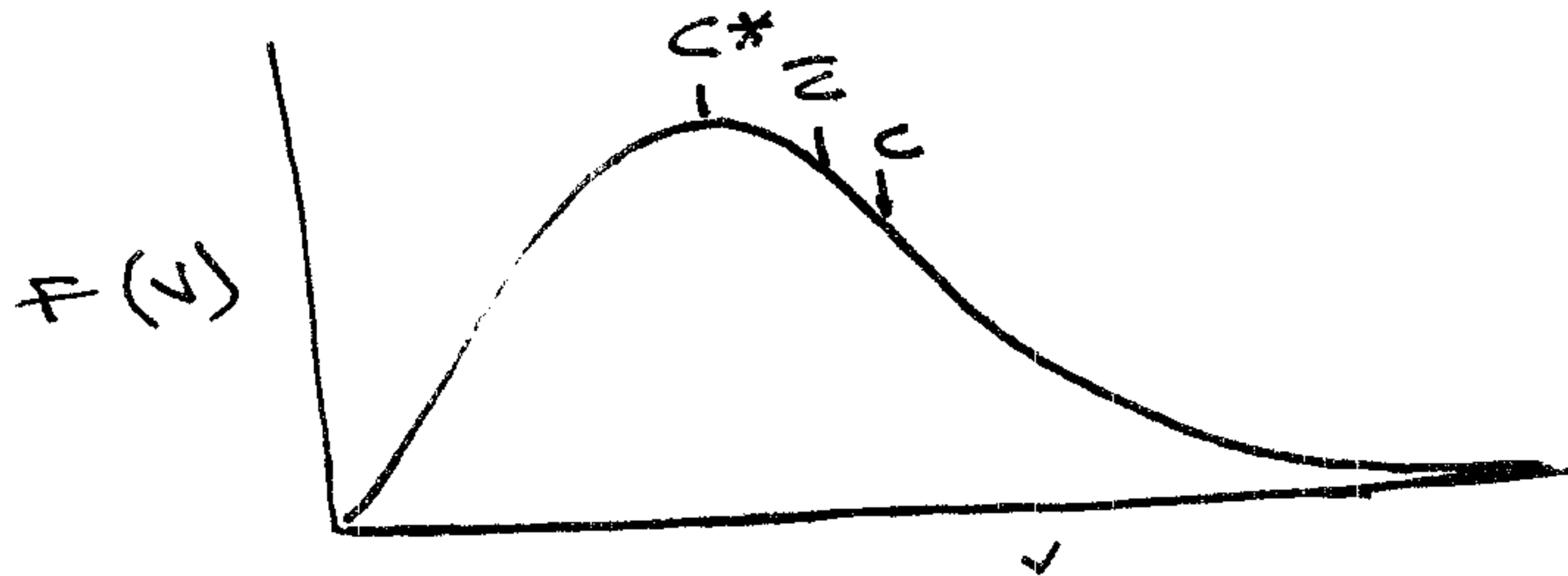
4) At the end of Brittany Pangburn's talk (day 5) we learned that fibrates are used to treat

- a) high blood pressure
- b) high cholesterol
- c) high sodium levels
- d) brain seizures

In German Morera's talk (day 5) on IR kinetic flow studies we learned that quartz was used

- a) as part of tube containing bacteria used to absorb ions and minerals
- b) as part of a study of deep sea minerals
- c) as part a laser focusing device
- d) to study interaction of ions with sand

5) Draw a curve of the probability of speed $F(v)$ (on y axis) versus the speed v (on x axis) for a collection of gas molecules and on this Maxwell Boltzmann distribution curve show the relative position of root mean square speed c , most probable speed c^* , and mean speed \bar{c} or "c bar."



6) In deriving the ideal gas law if $pV = \frac{mN}{3} \langle v^2 \rangle$ select the appropriate speed expression for this equation and show how the final version of the ideal gas law is derived from this point. Clearly show each step.

$$pV = \frac{mN}{3} \langle v^2 \rangle \qquad c = \sqrt{\langle v^2 \rangle} = \left(\frac{3kT}{m} \right)^{1/2}$$

$$pV = \frac{mN}{3} \frac{3kT}{m} \qquad \langle v^2 \rangle = \frac{3kT}{m}$$

$$pV = NkT$$

$$pV = nN_A kT \qquad N = nN_A$$

$$pV = nRT \qquad R = N_A k$$

7) In deriving the collision frequency per molecule, z , there is a factor of $(2)^{1/2}$ that is introduced. Explain why.

The number of collisions is $\sqrt{2}$ greater when all molecules are moving instead of all being in fixed position except 1 moving.

8) Use the rate law $dA/dt = -kA^2$ and show step by step the derivation of the integrated rate law. Use the limits of time of 0 to t and limits of amount of x_0 to x . Place equations in derivational template.

a) integral form with limits shown

$$\int_{x_0}^x A^{-2} dA = \int_0^t -k dt$$

b) results of integration with limits

$$-A^{-1} \Big|_{x_0}^x = -kt \Big|_0^t$$

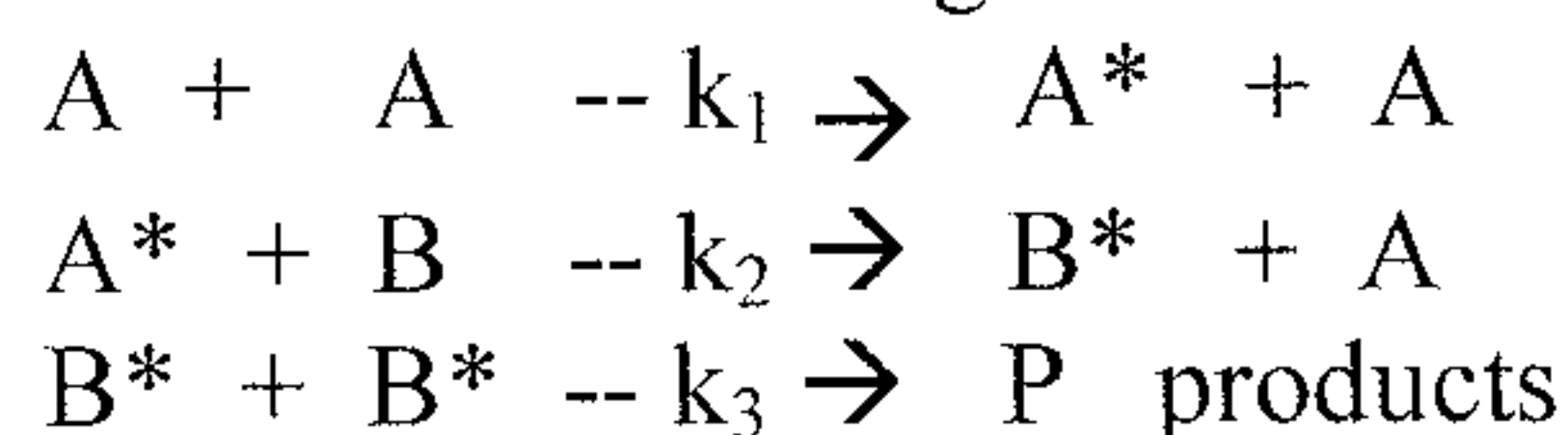
c) sub in limits

$$-\left(\frac{1}{x} - \frac{1}{x_0} \right) = -k(t-0)$$

d) final equation

$$\frac{1}{x} = \frac{1}{x_0} + kt$$

9) Consider the following mechanism where * indicates a short lived high energy species



Write expressions to show $d[A^*]/dt$ and $d[B^*]/dt$

$$d[A^*]/dt = k_1 [A]^2 - k_2 [A^*][B]$$

$$d[B^*]/dt = k_2 [A^*][B] - k_3 [B^*]^2$$

$$\left(\frac{k_2 k_1 [A]^2 [B]}{k_3 k_2 [B]} \right)^{1/2} = [B^*]$$

$$\left(\frac{k_1 [A]^2}{k_3} \right)^{1/2} = [B^*]$$

10) Apply the steady state approximation to $[A^*]$ and $[B^*]$ and use the two equations to solve for $[B^*]$ in terms of reactant molecules (no *'s)

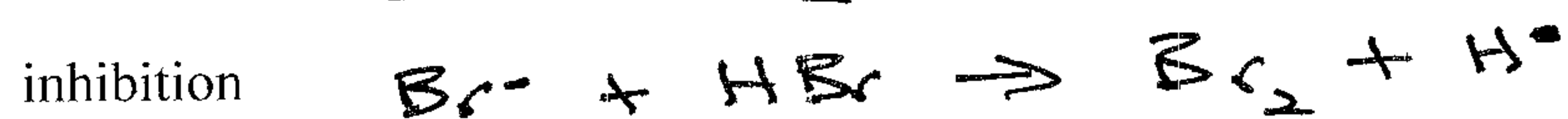
$$k_1 [A]^2 = k_2 [A^*][B] \Rightarrow \frac{k_1 [A]^2}{k_2 [B]} = [A^*]$$

$$k_2 [A^*][B] = k_3 [B^*]^2 \Rightarrow \left(\frac{k_2 [A^*][B]}{k_3} \right)^{1/2} = [B^*]$$

11) Write an expression for $d[P]/dt$ and then use the above to solve for $d[P]/dt$ and write the final rate law.

$$\frac{d[P]}{dt} = k_3 [B^*]^2 = k_3 \left(\frac{k_2 \frac{k_1 [A]^2}{k_2 [B]} [B]}{k_3} \right) = k_1 [A]^2$$

12) Br_2 and H_2 react to form HBr in a chain reaction mechanism where Br_2 is converted to free radicals $Br\cdot$ by light. Show one example of each of the following steps:



or other equivalent examples

13) Explain why a collision theory calculation based on numbers of collisions and energy of activation would give the rate constant $k(\text{theory})$ that are greater than experimental k for the reaction shown above

Rate constant k	Experiment	Theory
$2NOCl \rightarrow 2NO + Cl_2$	10^{10}	6×10^{10}

have to consider fraction of orientations that are suitable for reaction to occur even if collision is energetic enough.

14) If you double the amount of reactant B and the rate law increase by a factor of 8 then the reaction is 3rd order with respect to B.

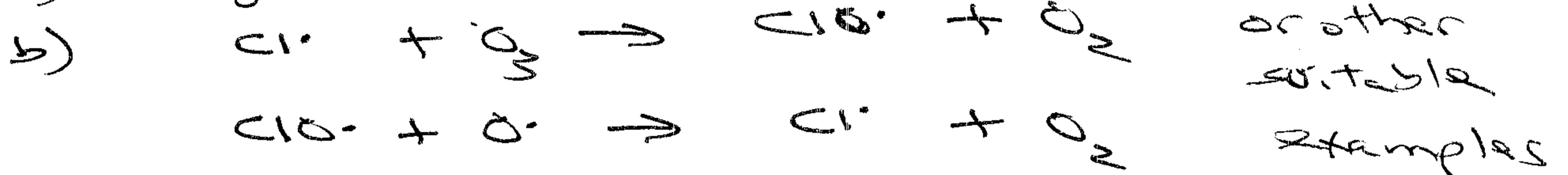
$$2^0 \quad 2^1 \quad 2^2 \quad \textcircled{3} = 8$$

15) How does a temperature increase affect the Maxwell-Boltzmann distribution and why does this in turn increase the rate of a gas phase reaction?

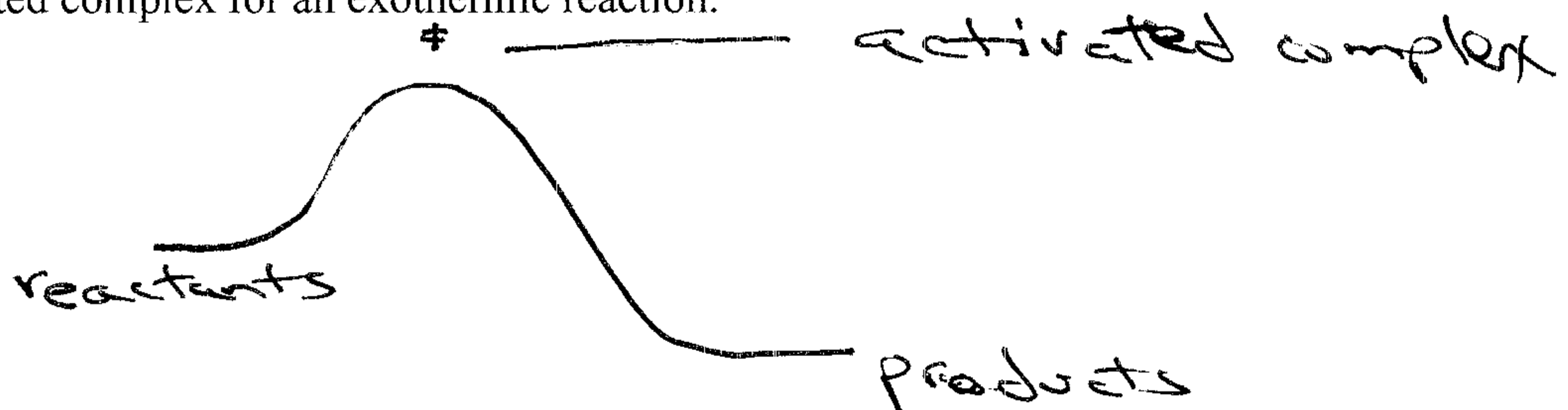
It shifts curve to right (higher energy - higher velocity) and this shifts pops a higher percentage of collisions above minimum required, E_a .

15) (a) Is quantum efficiency large or small for the destruction of ozone molecules in the upper atmosphere. (b) Show propagation steps in a mechanism that explains how a chlorine free radical can destroy ozone.

a) large



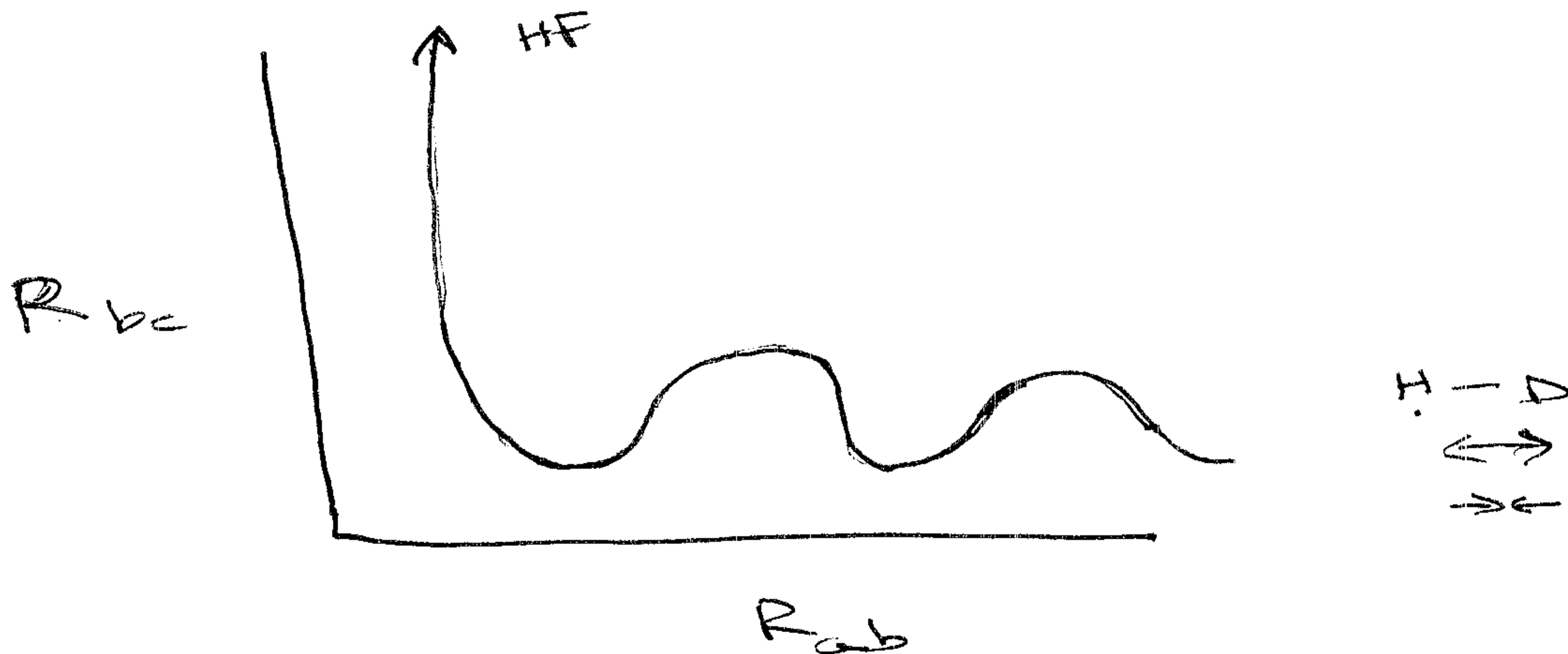
16) Draw a potential energy versus reaction coordinate diagram and show the position of reactants, products, and activated complex for an exothermic reaction.



17) Show a plot of R_{bc} (y axis) versus R_{ab} (x axis) for the reaction



and show a vibrational reaction with sufficient energy to form non-vibrational product.



18) Attach homework

19) Attach homework

20) Attach homework