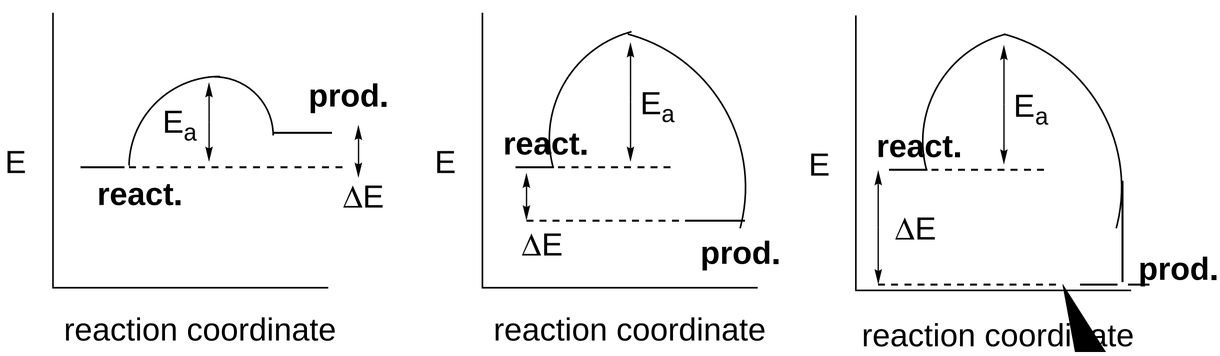
Chem 6 Sample Exam 1 brief answers

1. a. Consider the first 2 columns. Doubling [HI] quadruples the rate, so it must be **second order in HI**. Note that you get the same result by considering columns 2 and 3. So the rate law must be **rate = k[HI]^2**.
b. To get the rate constant, plug in some numbers. I used column 1:
rate = 7.5×10^{-4} Ms^{-1} = $k(0.005M)^2$
k = 30 $M^{-1}s^{-1}$
c. Plug in [HI] = 0.0020M to get
rate = $30M^{-1}s^{-1}(0.0020M)^2$
= $1.2\times10^{-4}Ms^{-1}$

2. These sketches are not to scale, and my drawing program is not good at making curves, but you should be able to get the idea from these pictures......
(a) $\Delta E = 10$, $E_a = 25$ (b) $\Delta E = -10$, $E_a = 50$ (a) $\Delta E = -50$, $E_a = 50$



Reaction (a) (the left-hand one) will be the fastest, since it has the lowest activation energy, and $k = Ae^{-Ea/RT}$

3. Michaelis-Menten. From class discussion of the Lineweaver-Burk plot, we saw that the maximum possible rate is $k_2[E]_o$. So half of that is $k_2[E]_o/2$. Set this equal to the rate expression to get
$k_2[E]_o/2 = \{k_2[E]_0[S]\}/[S] + K_M$
You can already see that this works when **[S] = K_M**
Or chug through the algebra:
$1/2 = [S]/[S] + K_M$
$1/2[S] + 1/2K_M = [S]$
$1/2K_M = 1/2[S]$
K_M = [S]

4. (a) Here are the steps labeled as initiation, propagation and termination.

$$C_2H_6 + I_2 \longrightarrow C_2H_5I + HI$$

proposed mechanism

I $I_2 \xrightarrow{k_1} 2I$

P $I + C_2H_6 \xrightarrow{k_2} C_2H_5 + HI$

P $C_2H_5 + I_2 \xrightarrow{k_3} C_2H_5I + I$

T $I + I \xrightarrow{k_{-1}} I_2$

(b) The rate is given by $-d/dt[C_2H_6] = k_2[C_2H_6][I]$
But [I] is an intermediate so we need to get rid of its concentration. Do this from steps 1 and 4, which define an equilibrium: $[I]^2/[I_2] = K_{eq} = k_1/k_{-1}$
So $[I] = \{[I_2]K_{eq}\}^{1/2}$
Plug in to get
Rate $= k_2[C_2H_6][I] = \mathbf{k_2[C_2H_6]\{[I_2]K_{eq}\}^{1/2}}$

Another approach to find [I] also works: doing the steady-state approximation on the concentrations of *both* the intermediates C_2H_5 and I. It would look like this, where the factors of 2 arise since you're either making or destroying 2 equivalents of I in steps 1 and 4.
$d/dt[I] = 0 = 2k_1[I_2] - k_2[I][C_2H_6] + k_3[C_2H_5][I_2] - 2k_{-1}[I]^2$
$d/dt[C_2H_5] = 0 = k_2[I][C_2H_6] - k_3[C_2H_5][I_2]$
Add these up; several terms will cancel out nicely, to give
$0 = 2k_1[I_2] - 2k_{-1}[I]^2$
$[I] = \{[I_2]K_{eq}\}^{1/2}$ where $K_{eq} = k_1/k_{-1}$, exactly the result from above.

5. a. The product ratio is given by the relative rates of formation of C and D. Thus $d/dt[C] = k_2[A]$ and $d/dt[D] = k_3[B]$, so
product ratio $= k_2[A]/k_3[B]$
But from the equilibrium, $[B]/[A] = K_{eq}$
Or, $[B] = [A]K_{eq}$
Plug this in to the product ratio expression to get
product ratio $= k_2[A]/k_3[A]K_{eq}$
product ratio = $\mathbf{k_2/k_3K_{eq}}$

b. **FALSE.** You can reach this conclusion in 2 ways. From the product ratio result of part a, even if K_{eq} is very small (favoring A), you can still get D as the major product if k_3 is bigger than k_2. Here are some numbers, for example. Suppose K_{eq} = 0.01 (i.e., a 100:1 mixture of A and B at equilibrium, k_2 is 1, and k_3 is 1000. This gives a product ratio of 0.1 (10:1 mixture of D and C).
Or, consider le Chatelier's principle. If an equilibrium mixture of A and B is perturbed by formation of D from B (which occurs faster than formation of C from A), you will drive the equilibrium from A to form B. If B continues to be drained by rapid formation of D, it should be clear this will be the major product even if the original equilibrium favored A.

6. For a 2nd-order reaction, the rate law is
rate = k $[C_2F_4]^2$ and we're given the value of k = $0.0896 M^{-1}s^{-1}$
Use the integrated form of the rate law:
$1/[[C_2F_4] = 1/[C_2F_4]_0 + kt$
Plug in the numbers provided
$1/[[C_2F_4] = 1/0.100M + (0.0896 M^{-1}s^{-1})(205s)$
$[C_2F_4] = 3.53x10^{-2}M$

7. I've reproduced the data table here and added columns for $\ln[N_2O_5]$ and $1/[N_2O_5]$ needed to see if it's first or 2nd order in N_2O_5.

	T = 338K			**T = 318K**		
Time (s)	**$[N_2O_5]$ (M)**	**$\ln[N_2O_5]$**	**$1/[N_2O_5]$**	**$[N_2O_5]$ (M)**	**$\ln[N_2O_5]$**	**$1/[N_2O_5]$**
0	$1.00x10^{-1}$	–2.30	10	$1.00x10^{-1}$	–2.30	10
100	$6.14x10^{-2}$	–2.79	16.3	$9.54x10^{-2}$	–2.35	10.5
300	$2.33x10^{-2}$	–3.76	42.9	$8.63x10^{-2}$	–2.45	11.6
600	$5.41x10^{-3}$	–5.22	185	$7.43x10^{-2}$	–2.60	13.5
900	$1.26x10^{-3}$	–6.68	794	$6.39x10^{-2}$	–2.75	15.6

By inspection, $\ln[N_2O_5]$ data vs time is linear (this is most easily seen from the 318K data, where it goes up by 0.05 every 100 seconds) and the $1/[N_2O_5]$ points are not linear. You didn't need to do this for both sets of data, but it's a nice check to confirm you're doing it right.
The linearity of the plot means it's first-order in N_2O_5. Now we extract the first-order rate constant from the equation
$\ln[N_2O_5] = \ln[N_2O_5]_o - kt$
Plug in data at 338K, with time = 0 and 100 seconds (of course, other choices should give the same answer, or plotting $\ln[N_2O_5]$ vs time and getting the slope of the line.)
$\ln(6.14x10^{-2}M) = \ln(1.00x10^{-1}M) - k(100s)$
$-2.79 = -2.30 - k(100s)$
$-0.49 = -k(100s)$

$k = 4.9x10^{-3}s^{-1}$
A similar analysis for the 318K data (same times) gives:
$-2.35 = -2.30 - k(100s)$
$k = 5x10^{-4}s^{-1}$
Now, to find E_a, apply one of the several forms of the Arrhenius equation. Most conveniently,
$\ln(k_2/k_1) = (E_a/R)x(1/T_1 - 1/T_2)$
$\ln(4.9x10^{-3}s^{-1}/5x10^{-4}s^{-1}) = (E_a/8.314J/molK)\{1/318K - 1/338K\}$
$2.28 = 2.24x10^{-5}J/mol(E_a)$
$E_a = 1.02x10^5$ J/mol = 102 kJ/mol

8. Photoelectric effect: $KE_{electron} = h\nu - h\nu_o$
Here instead of the usual work function $h\nu_o$ we have the ionization energy. To see if the light can remove the electron, we just have to find out if its energy $h\nu$ is greater than the ionization energy $h\nu_o$; thus it will work if $h\nu > h\nu_o$.
So, plug in the numbers, being careful with units.
$h\nu = hc/\lambda = (6.626x10^{-34}Js)(3x10^8m/s)/(225\ nm\ x\ 1m/10^9nm)$
$= 8.84x10^{-19}J$
convert to kJ/mol:
$8.84x10^{-19}J(1kJ/1000J)(6.02x10^{23}/mol) =$ **532kJ/mol**
Is $h\nu > h\nu_o$? Nope, not even close. So the answer is **NO**.

9. a. It can't go faster than the speed of light, so **the biggest uncertainty must be just that, c = $3x10^8$ m/s.** To make this more clear, possible speeds range from c to almost zero. How big an error could you get? Suppose you thought it had a velocity of zero, but it was really traveling at speed c. Then the uncertainty is c.
b. From the Heisenberg uncertainty principle, $\Delta x\Delta p \geq$h-bar/2. We want to find Δx and we have Δv; $\Delta p = m\Delta v$. Plug in the electron mass to get
$\Delta p = m\Delta v = (9.11x10^{-31}kg)(3x10^8m/s) = 2.73x10^{-22}$ kgm/s
Since $\Delta x\Delta p \geq$h-bar/2, then $\Delta x \geq$(h-bar/2)/(Δp)
$\Delta x \geq [(6.626x10^{-34}Js/2\pi)/2]/(2.73x10^{-22}\ kgm/s) = 1.93x10^{-13}Js^2/kgm$
since $1J = 1kgm^2/s^2$
$= 1.93x10^{-13}$ m, or, since there are 10^9 nm in a meter, **$1.93x10^{-4}$nm is the minimum uncertainty in position.**

10. 1. 268 hours is 4 half-lives. After 1 half-life, the initial 1 gram will decay to 0.5g; after 2, it's down to 0.25g, after 3, to 0.125g, and after 4, **0.0625g**. Thus the correct answer is **c**.
2. **d**
3. The slope of the lnk vs 1/T plot is $-E_a/R$. The steeper the slope, the bigger E_a, so **B** has a larger activation energy.
4. **a**
5. **b**