Chemistry 1210 Spring 2024 Test 1

Friday, February 2, 2024 Time: 1 hour 50 minutes

Name: ANSWERS Student #: ____________________

*This test consists of **nine** pages of questions, the formula sheet, and a periodic table. Please ensure that you have a complete test and, if you do not, obtain one from me **immediately**. There are **35.5** marks available. Good luck!*

1) **[9.5 marks total]** For the reaction

$$3A + 2B \longrightarrow C + 6D$$

The following data were collected:

Run	[A] (M)	[B] (M)	$\frac{\Delta[B]}{\Delta t}(\frac{M}{s})$
1	0.1	0.2	-5.091×10^{-5}
2	0.2	0.2	-1.440×10^{-4}
3	0.3	0.3	-3.240×10^{-4}

a) **[2 marks]** Determine the rate law for the reaction.

$$\frac{\text{run 2}}{\text{run 1}} = \frac{k(0.2)^x(0.2)^y}{k(0.1)^x(0.2)^y} = \frac{-1.440\times10^{-4}}{-5.091\times10^{-5}}$$

$$2^x = 2.828...$$

$$x \ln 2 = \ln(2.828)$$

$$x = 1.5$$

So $\boxed{\text{rate} = k[A]^{1.5}[B]^{0.5}}$

$$\frac{\text{run 3}}{\text{run 2}} = \frac{-3.240\times10^{-4}}{-1.440\times10^{-4}} = \frac{k(0.3)^{1.5}(0.3)^y}{k(0.2)^{1.5}(0.2)^y}$$

$$2.25 = (1.5)^{1.5}(1.5)^y$$

$$1.2247... = 1.5^y$$

$$\ln(1.2247...) = y\ln(1.5) \Rightarrow y = 0.5$$

b) **[3 marks]** Determine the rate constant for the reaction. Include units.

using run 2:

$1.440\times10^{-4}\frac{M}{s}\times\frac{1\,rxn}{2B} = k(0.2)^{1.5}(0.2)^{0.5}$

$\Rightarrow \boxed{k = 1.8\times10^{-3}\,M^{-1}s^{-1}}$

units:

$\frac{M}{s} = k(M)^{1.5}(M)^{.5}$

$\Rightarrow k = M^{-1}s^{-1}$

c) **[1 mark]** What will be the value of $\frac{\Delta[D]}{\Delta t}$ (in M/s) in run 3?

$3.240\times10^{-4}\frac{M}{s}\times\frac{6D}{2B} = \boxed{9.72\times10^{-4}\frac{M}{s}}$

d) **[2 marks]** This reaction cannot occur in a single step. Give two reasons why.

If it did: 1) rate law would be $k[A]^3[B]^2$. It's not.

2) 5 Particles would have to collide at once, which is unlikely.

e) **[0.5 marks]** What is the overall order of the reaction kinetics?

$1.5 + 0.5 = \boxed{2}$

f) **[1 mark]** What is the order of the reaction kinetics with respect to compound C? How do you know? (No marks for guessing. 😊)

Zero. C does not appear in the rate law, and the only way that can happen is if the rate law has $[C]^0$ in it.

2) **[10 marks total]** The following mechanism has been proposed for the decomposition of ozone in the atmosphere:

$$Cl\cdot + O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ClO\cdot + O_2 \quad \text{(fast)}$$

$$ClO\cdot + O_3 \xrightarrow{k_3} Cl\cdot + 2O_2 \quad \text{(slow)}$$

a) **[1 mark]** What is the overall reaction for the decomposition of ozone?

$2O_3 \rightleftharpoons 3O_2$

b) **[0.5 marks]** Are there any catalysts? If so, what are they?

$Cl\cdot$

c) **[0.5 marks]** Are there any reactive intermediates? If so, what are they?

$ClO\cdot$

d) **[1 mark]** If you add more ozone (O_3) to the reaction above, the rate will increase, but past a certain amount of added ozone the rate will not increase any more. Why? (No marks for guessing. 😊)

All the Cl· will be occupied.

e) **[2 marks]** What rate law is predicted by the mechanism?

$rate = k_3[ClO\cdot][O_3]$ (from slow step)

need SSA for ClO·

$k_1[O_3][Cl\cdot] = k_2[O_2][ClO\cdot]$ (ignore slow step)

$[ClO\cdot] = \frac{k_1}{k_2}\frac{[O_3][Cl\cdot]}{[O_2]}$

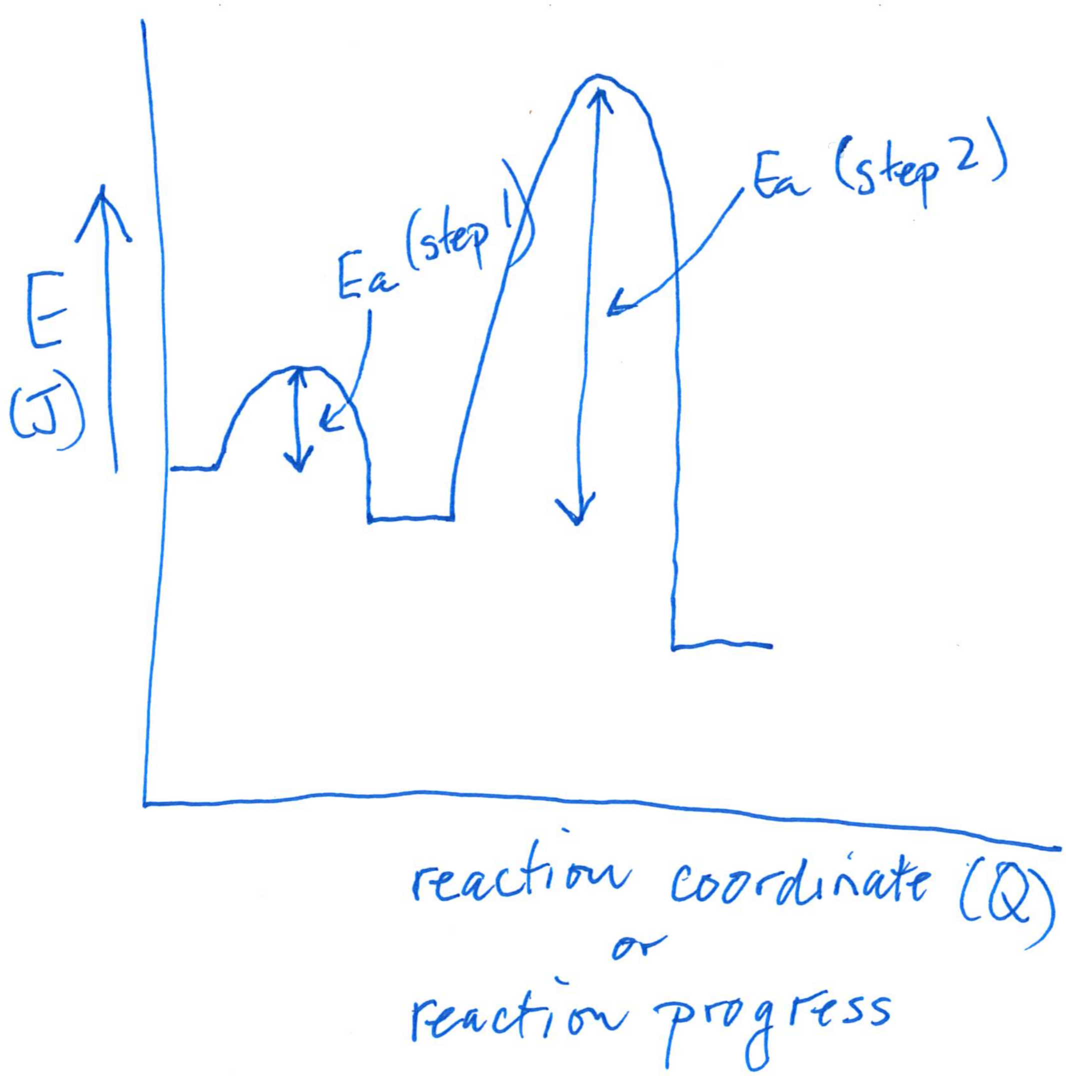
So $\boxed{rate = k_3\frac{k_1}{k_2}\frac{[O_3]^2[Cl\cdot]}{[O_2]}}$

f) **[1 mark]** If the experimental rate law was determined to be rate = $k[O_3][O_2]^{-1}$, would the mechanism above be "good"? How do you know? (No marks for guessing. 😊)

No. The rate law predicted by the mechanism doesn't match the experimental one.

g) **[4 marks]** Sketch (not necessarily to scale) the energy diagram for the mechanism above. On your graph, be sure to include:

i) **[0.5 marks]** Proper axes labels with appropriate units.
ii) **[2 marks]** The appropriate number of energy barriers.
iii) **[0.5 marks]** The appropriate relative heights for the energy barriers.
iv) **[0.5 marks]** A label for the forward activation energy for each step.
v) **[0.5 marks]** The proper relative energies of reactants and products for each step. Assume that both steps are exothermic.



3) **[2 marks]** For a certain reaction, a plot of lnk vs. 1/T was made. The y-intercept was found to be 21.4313, and the slope was -6013.62 K. Determine the rate constant for the reaction at 26.85°C, including units for the rate constant. Assume the reaction is first order.

$$\ln k = 21.4313 - 6013.62\left(\frac{1}{T}\right)$$

For T = 300K:

$$\ln k = 21.4313 - \frac{6013.62}{300}$$

$$= 1.3859 \Rightarrow \boxed{k = 3.998\ldots\ (\simeq 4)\,s^{-1}}$$

4) **[2 marks]** A certain reaction runs 1.90909 times faster at 36.85°C than it does at 26.85°C. What is the energy of activation for the reaction? Give your answer in kJ/mol.

$k_1 = 1$ $T_1 = 300\text{ K}$

$k_2 = 1.90909$ $T_2 = 310\text{ K}$

$$\ln(1.90909) = \frac{E_a}{8.3144\ldots}\left(\frac{310-300}{310 \times 300}\right)$$

$$\Rightarrow E_a = 50{,}000\ \frac{J}{mol}$$

$$= \boxed{50.0\ \frac{kJ}{mol}}$$

5) **[3 marks]** For a certain reaction a plot of $1/[A]_t$ vs. t resulted in a straight line with a slope of $0.25\ M^{-1}s^{-1}$ and a y-intercept of $10\ M^{-1}$. Find the half-life of the reaction.

2nd order IRL kinetics:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

y-int ↑ ($\frac{1}{[A]_0}$), slope = k = 0.25 ↑ (kt)

$$10 = \frac{1}{[A]_0} \Rightarrow [A]_0 = 0.1\ M$$

At the half-life...

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\Rightarrow \frac{1}{[A]_0} = kt_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{1}{k[A]_0} = \boxed{40\,s}$$

6) **[2 marks]** The (radioactive) breakdown of elements follows first-order kinetics. One element that breaks down this way is Technitium-96, which has a half-life of 4.3 days. How many hours will it take for 10 percent of a sample of Technitium-96 to break down?

For 1st order, $t_{1/2} = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{t_{1/2}}$

So: $\ln\left(\frac{100}{90}\right) = \frac{\ln 2}{4.3} \cdot t$

↑ 10 gone, 90 left

$\Rightarrow t = 0.65$ days

$= \boxed{15.68\ \text{hours}}$

7) **[1 mark]** Write a reaction for which the equilibrium expression is $K = P_{CO2,e}$.

Many are possible. One is

$$CO_2(s) \rightleftharpoons CO_2(g)$$

8) **[6 marks]** For the reaction:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l) \qquad K_p = 9.4 \times 10^{88} \text{ at } 250°C$$

a) Calculate K_c at 250°C

$T = 523.15\,K$

$\Delta n = 4 - 9 = -5$

$9.4 \times 10^{88} = K_c (0.08314\ldots \times 523.15)^{-5}$

$K_c = 1.4636\ldots \times 10^{97}$

b) Calculate the value of K_p for the reaction

$2NO(g) + 3H_2O(l) \rightleftharpoons 2NH_3(g) + 2.5O_2(g)$

$$\left(\frac{1}{9.4\times10^{88}}\right)^{\frac{1}{2}} = \boxed{3.2616\times10^{-45}}$$

c) Given the additional reaction

$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$ $K_p = 9.8 \times 10^{-41}$ at 250°C

Calculate K_p for the reaction

$4NH_3(g) + 2O_2(g) \rightleftharpoons 4NO(g) + 6H_2(g)$

$4NH_3 + \cancel{5}^{2}O_2 \rightleftharpoons 4NO + \cancel{6H_2O}$ $K_p = 9.4\times10^{88}$

$\cancel{6H_2O} \rightleftharpoons 6H_2 + \cancel{3O_2}$ $K_p = (9.8\times10^{-41})^3$

$4NH_3 + 2O_2 \rightleftharpoons 4NO + 6H_2$

$$K_p = 9.4\times10^{88} \times (9.8\times10^{-41})^3 = \boxed{8.8472\times10^{-32}}$$