Chemistry 1210 Spring 2023 Test 1

Wednesday, February 1, 2023   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 **45.5** marks available. Good luck!*

1) **[6.5 marks total]** The following initial rate data were collected for the reaction:

$$4A + 5B \longrightarrow 4C + 6D$$
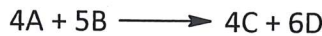
Run	[A] (M)	[B] (M)	$\frac{\Delta[A]}{\Delta t}$ $(\frac{M}{s})$	rate
1	0.50	0.64	-0.0800	0.02
2	0.80	0.64	-0.2048	0.0512
3	0.40	0.16	-0.0256	0.0064

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

$$\frac{run\,2}{run\,1} = \frac{0.0512}{0.02} = \frac{k(0.8)^m (0.64)^n}{k(0.5)^m (0.64)^n}$$

$$2.56 = \left(\frac{0.8}{0.5}\right)^m = 1.6^m$$

$$\Rightarrow m = 2$$

$$\frac{run\,3}{run\,2} = \frac{0.0064}{0.0512} = \frac{k(0.4)^2 (0.16)^n}{k(0.8)^2 (0.64)^n}$$

$$0.125 = \left(\frac{0.4}{0.8}\right)^2 \left(\frac{0.16}{0.64}\right)^n$$

$$= \frac{1}{4} \cdot \left(\frac{1}{4}\right)^n$$

$$0.5 = \left(\frac{1}{4}\right)^n \Rightarrow n = \frac{1}{2}$$

$$\boxed{rate = k[A]^2 [B]^{\frac{1}{2}}}$$

b) **[2 marks]** Determine the rate constant. Include units.

using run 1:

$$0.02 = k(0.5)^2(0.64)^{\frac{1}{2}}$$

$$\Rightarrow k = \boxed{0.1}$$

units:

$$\frac{M}{s} = k(M)^2(M^{\frac{1}{2}})$$

$$k = \boxed{M^{-1.5}s^{-1}}$$

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

$$2 + \frac{1}{2} = \boxed{2.5}$$

d) **[1 mark]** What is the value of $\frac{\Delta[D]}{\Delta t}$ for run 1?

$$0.02 \frac{\text{moles rxn}}{L \cdot s} \times \frac{6D}{1 \, \text{rxn}} = \boxed{0.12 \, \frac{M}{s}}$$

e) **[1 mark]** The reaction above does not occur in a single step. Give two reasons why this is so.
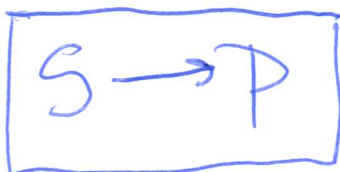
1) It would involve the collision of 9 particles, which is unlikely at best

2) If it did, the rate law would be $k[A]^4[B]^5$, and it isn't.

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2) **[9 marks total]** Michaelis and Menten have proposed the following mechanism for an enzyme (E) acting on a substrate (S) to produce a product (P) after production of the compound ES:

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \qquad \text{(fast)}$$

$$ES \overset{k_3}{\longrightarrow} E + P \qquad \text{(slow)}$$
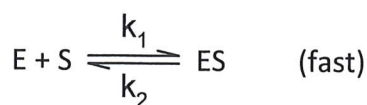
a) **[1 mark]** What is the overall reaction?

$$\cancel{E} + S + \cancel{ES} \longrightarrow \cancel{ES} + \cancel{E} + P$$

$$\boxed{S \longrightarrow P}$$

b) **[1 mark]** Which, if any, are the catalysts in the mechanism above?

$$E \text{ is a catalyst}$$

c) **[1 mark]** Which, if any, are the reactive intermediates in the mechanism above?

$$ES \text{ is a reactive intermediate}$$

d) **[1 mark]** Which, if any, are the termolecular steps in the mechanism above?

There are no termolecular steps in the mechanism.

e) **[2 marks]** Derive the rate law predicted by the mechanism.

$$rate = k_3 [ES]$$

SSA on ES:

$$k_1 [E][S] = k_2 [ES] \text{ (ignoring slow step)}$$

$$[ES] = \frac{k_1 [E][S]}{k_2}$$

$$\boxed{So \ rate = k_3 \frac{k_1 [E][S]}{k_2}}$$

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f) **[3 marks total]** Sketch the energy diagram for the mechanism. On it, be sure to:

   i) **[0.5 marks]** Include proper labels and units for your axes.
   ii) **[0.5 marks]** Indicate the forward activation energies for each of the two steps above.
   iii) **[1.5 marks]** Include the appropriate number energy barriers with the appropriate relative heights.
   iv) **[0.5 marks]** The appropriate relative energies for all products and reactants. You may assume that both steps in the reaction, and the reaction as a whole, are exothermic.
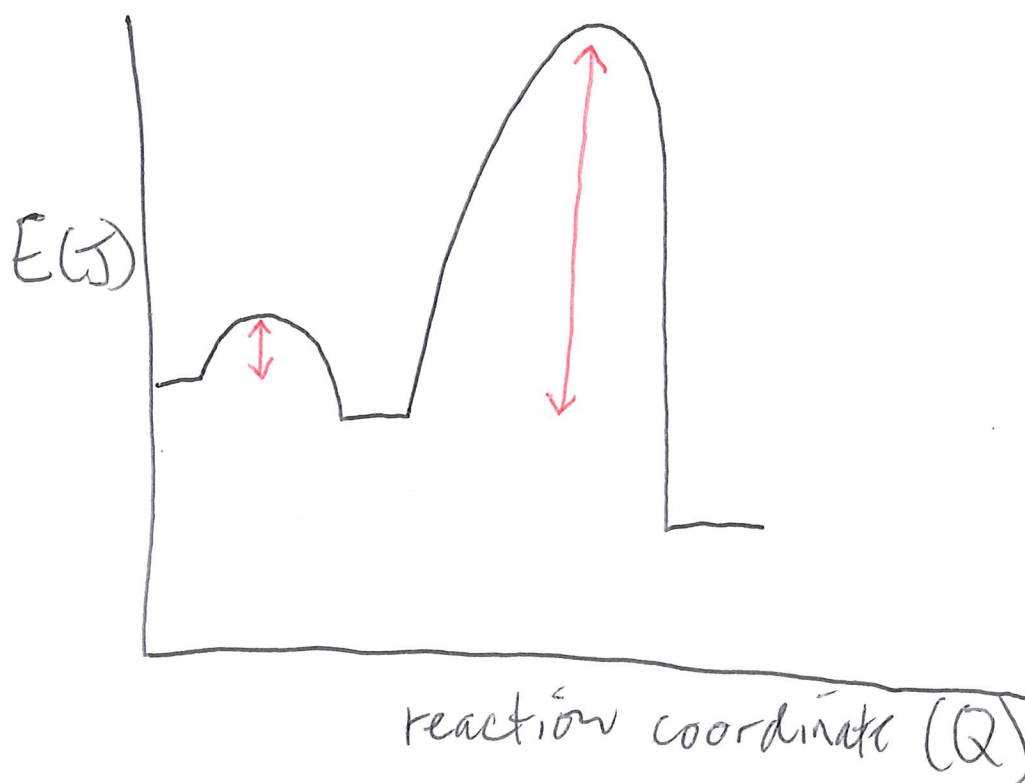
3) **[4 marks total]** It was found that the rate constant for a certain reaction followed the equation $lnk = 23.7 - \frac{12027}{T}$.

a) **[1 mark]** What is the pre-exponential factor (A)?

$$e^{23.7} = \boxed{1.96 \times 10^{10}}$$

b) **[1 mark]** What is the energy of activation for the reaction? Give your answer in kJ/mol.

$$12027 \times 8.31... \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \boxed{100 \frac{\text{kJ}}{\text{mol}}}$$

c) **[2 marks]** At what temperature will the rate constant be 1? (Give your answer in °C.)

$$ln(1) = 23.7 - \frac{12027}{T}$$

$$\Rightarrow 23.7 = \frac{12027}{T} \Rightarrow T = 507.46 K = \boxed{234.32 °C}$$

4) **[2 marks]** If the rate of a reaction doubles when the temperature is increased from 6.85°C to 16.85°C, then the energy of activation for that reaction is:

a) 0.67 J/mol   b) 46.8 kJ/mol   c) 66.5 J/mol   d) 468 J/mol

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5) **[4 marks]** Suppose the way Pat's cat Jimmy eats his food follows first-order kinetics. Further suppose the half-life of a meal of his is 150 seconds. If, after 200 seconds, he has eaten 44 grams of food, how much was his total serving?

$$k = \frac{\ln 2}{t_{1/2}} = 4.62 \times 10^{-3} \, s^{-1}$$

$$[A]_0 = X$$

then $[A]_t = X - 44$

$$\ln\left(\frac{X}{X-44}\right) = 4.62 \times 10^{-3} \times 200$$

$$\Rightarrow \frac{X}{X-44} = 2.5198\ldots$$

$$\frac{X}{X-44} = a$$

$$X = aX - 44a$$

$$X - aX = -44a$$

$$44a = aX - X$$

$$44a = X(a-1)$$

$$X = \frac{44a}{a-1} = \boxed{72.95 \, g}$$

6) **[2 marks]** Given the following data:

[A] (M)	t (s)
	0
1	20
0.5	30
0.25	40

What was $[A]_0$? How do you know? (No marks for guessing. 😊)

$t_{1/2}$ is constant (10 s)

∴ at 10 s [A] must have been 2M
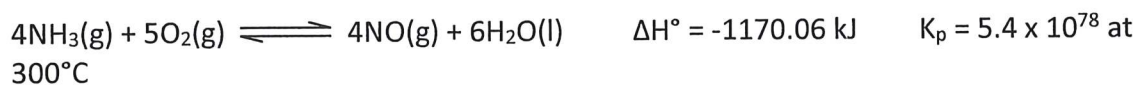
and at 0 s [A] must have been 4M

$$\boxed{4M}$$

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7) **[4 marks]** Given the following equilibrium:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \quad \Delta H° < 0 \text{ (exothermic)}$$
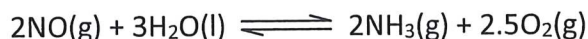
Predict the effect that each of the changes given below would have on the value of K and on the moles of Cl_2 present in a fresh system initially at equilibrium. Your choices are **Increase** from the starting value, **Decrease** from the starting value, or **Not Change** from the starting value. You may assume that, unless explicitly stated otherwise, the changes were carried out at constant temperature.

	Effect on:					
	K_p			Cl_2		
Adding some H_2	I	D	(NC)	I	D	NC
Cooling the reaction mixture	(I)	D	NC	I	(D)	NC
compressing the reaction mixture	I	D	(NC)	I	D	(NC)
Adding some He(g)	I	D	(NC)	I	D	(NC)

8) **[8 marks]** Given the equilibrium:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l) \quad \Delta H° = -1170.06 \text{ kJ} \quad K_p = 5.4 \times 10^{78} \text{ at } 300°C$$

a) The value of K_p for

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

at 300°C should be:

i) 3.7×10^{-79}
ii) 4.3×10^{-40}
iii) -2.3×10^{39}
iv) -2.7×10^{78}

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b) The value of K_c for the reaction

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l) \quad \Delta H° = -1170.06 \text{ kJ} \quad K_p = 5.4 \times 10^{78} \text{ at } 300°C$$
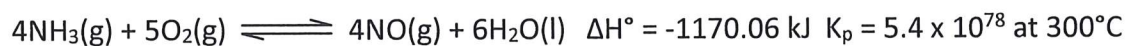
at 300°C should be:

i) 2.2×10^{60}
ii) 2.2×10^{70}
iii) 1.1×10^{75}
iv) 1.1×10^{77}
v) 2.6×10^{80}
vi) 2.6×10^{82}
vii) 1.3×10^{87}
viii) 1.3×10^{97}

$K_p = K_c (RT)^{-5}$

$K_c = K_p (RT)^{5}$

c) The value of K_p for the reaction

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l) \quad \Delta H° = -1170.06 \text{ kJ} \quad K_p = 5.4 \times 10^{78} \text{ at } 300°C$$
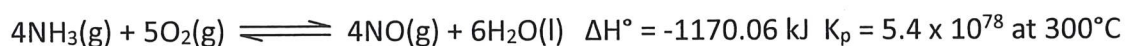
at 400°C should be:

i) 6.3×10^{27}
ii) 7.8×10^{62}
iii) 4.8×10^{78}
iv) 5.2×10^{78}

d) Given the additional reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_p = 0.01 \text{ at } 300°C$$
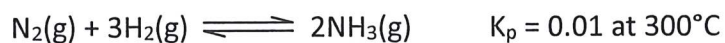
$(0.01)^2 \times 5.4 \times 10^{78}$

Calculate K_p (at 300°C) for the reaction:

$= 5.4 \times 10^{74}$

$$2N_2(g) + 6H_2(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$$
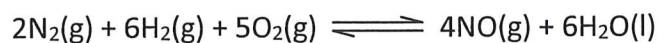
9) **[2 marks]** Ethanol has a vapour pressure of 58.9 torr at 25°C and a normal boiling point of 78.4°C. Its enthalpy of vaporization (in kJ/mol) should be:

a) 7.8 J/mol
b) 417 J/mol
c) 780 J/mol
d) 41.7 kJ/mol

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10) **[4 marks total]** A flask was charged with 0.1 bar of H_2O, 0.1 bar of Cl_2O, and 0.2 bar of HOCl, and the equilibrium

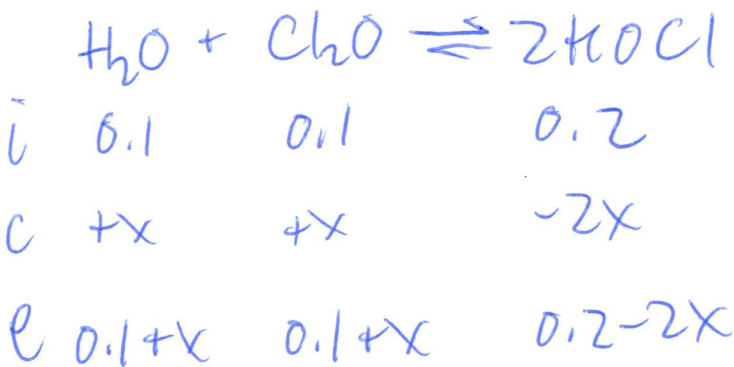$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K = 2.25 \text{ at } 252.7°C$$

established.

a) **[1 mark]** In which direction did the reaction proceed to establish equilibrium? How do you know? (No marks for guessing. ☺)

$$Q = \frac{(0.2)^2}{(0.1)(0.1)} = 4 \quad \text{too big, rxn} \leftarrow$$

b) **[3 marks]** Calculate the equilibrium partial pressures of all species.

$$H_2O + Cl_2O \rightleftharpoons 2HOCl$$

i	0.1	0.1	0.2
c	+x	+x	−2x
e	0.1+x	0.1+x	0.2−2x

$$\frac{(0.2-2x)^2}{(0.1+x)^2} = 2.25$$

$$\frac{0.2 - 2x}{0.1+x} = 1.5$$

$$0.2 - 2x = 0.15 + \overset{1.5}{\cancel{}}x$$

$$2x + \overset{1.5}{\cancel{}}x = 0.2 - 0.15$$

$$\overset{3.5}{\cancel{}}x = 0.05$$

$$x = \cancel{}\ldots$$
$$0.0142\ldots$$

$$P_{H_2O,e} = P_{Cl_2O,e} = \cancel{}$$
$$\cancel{}$$
$$\approx 0.1142 \text{ bar}$$

$$P_{HOCl,e} = \cancel{} \ldots$$
$$0.1714$$
$$\text{bar}$$