Name KEY

Chemistry 121
Test 3
Spring 2021

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9.	_____/13
10.	_____/EC
Total	_____/100

Read this first: Don't panic. **This is a strictly timed exam. You must work quickly and accurately.** You have 54 minutes to complete the exam. If the space provided is insufficient for showing your work, continue on the back of the page. Don't forget to indicate where the work may be found. If there are questions ask the instructor not your neighbor. You may not share calculators. **Have fun.**

☐ Check here if you would like your approximate current course grade
This grade includes all exams, quizzes and homework scores to this point in the semester. It should be used only as a guide to help you determine your progress in the course and is subject to change depending upon further scores on exams, homework, and quizzes. Your grade will be in the lower right of the next page.

I. Descriptive: Select the best answer. Unless otherwise indicated, there is only one correct answer for each problem.

1. (3 pts.) Write the correct equilibrium constant expression, K_c, for the mass action

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$$

$$K_c = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6}$$

2. (3 pts.) Consider the reaction in question 1. If 1.0×10^{-2} mol $NiCl_2$ and 0.68 mol $Ni(NH_3)_6Cl_2$ are placed in a 250 mL beaker and dissolved in 150 mL of water, what will happen?

- ☐ Reaction proceeds to the right.
- ■ Reaction proceeds to the left.
- ☐ Nothing happens.
- ☐ It is not possible to determine that anything would happen without making actual measurements.

3. (10 pts) Calcium oxide has been used to scrub carbon dioxide out of smokestack gases from fossil fuel-fired electricity generating power plants. Consider the reaction at equilibrium in a closed container:

$$CO_2(g) + CaO(s) \rightleftharpoons CaCO_3(s) \quad \Delta H < 0$$

a. What effect would increasing the total mass of the calcium oxide in the container have on the equilibrium?

- ☐ Shift left
- ☐ Shift right
- ■ No change
- ☐ Need additional information to answer

b. What effect would increasing the partial pressure of $CO_2(g)$ have on the equilibrium?

- ☐ Shift left
- ■ Shift right
- ☐ No change
- ☐ Need additional information to answer

c. What effect would increasing the volume of the container have on the equilibrium?

- ■ Shift left
- ☐ Shift right
- ☐ No change
- ☐ Need additional information to answer

d. What effect would increasing the total pressure in the container to 3 atm with nitrogen gas have on the equilibrium?

- ☐ Shift left
- ☐ Shift right
- ■ No change
- ☐ Need additional information to answer

e. How would increasing the temperature affect the equilibrium?

- ■ Shift left
- ☐ Shift right
- ☐ No change
- ☐ Need additional information to answer

4. (4 pts.) The K_p for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$$

is 0.29 at 1000 K. The K_p for the reaction

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

is closest to

- ■ 11.9
- ☐ 3.4
- ☐ 1.86
- ☐ 1.7
- ☐ 1.2
- ☐ 0.58
- ☐ 0.29
- ☐ None of these. The correct value is _____

5. (3 pts.) Nitrogen monoxide gas reacts with oxygen at room temperature to form brown nitrogen dioxide gas according to the equation

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

The reaction is first order in oxygen and third order overall. What is the rate law?

- ☐ Rate = $k[NO]^2[O]^2$
- ☐ Rate = $k[NO]^2[O]$
- ☐ Rate = $3 \cdot k[NO]^2[O]$
- ■ Rate = $k[NO]^2[O_2]$
- ☐ Rate = $3 \cdot k[NO]^2[O_2]$
- ☐ Rate = $k[NO][O]^2$
- ☐ Rate = $k[NO][O_2]^3$
- ☐ Rate = $k([NO][O_2])^3$
- ☐ Cannot tell without knowing the units on k
- ☐ None of these are correct. The correct rate law is:

6. (6 pts.) The decomposition of hydrogen peroxide

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

obeys first-order kinetics. The reaction has a half-life of 34 s when 0.10 M H_2O_2 is allowed to decompose. Which of the following statements is true (check all that apply).

- ■ If the initial rate of the disappearance is 0.00204 M H_2O_2/s, the initial rate for the production of O_2 is 0.00102 M O_2/s.
- ■ The quantity of H_2O_2 remaining at 34 s is 0.050 M.
- ☐ The reaction is complete in 34 s.
- ☐ The reaction is complete in 68 s.
- ☐ The reaction is complete in 102 s.
- ■ Technically the reaction is never actually complete but nearly so in 5 half-lives.
- ☐ If the reaction is performed with 0.20 M H_2O_2, the half-life for the reaction is 17 s.
- ■ If the reaction is performed with 0.20 M H_2O_2, the half-life for the reaction is 34 s.
- ☐ If the reaction is performed with 0.20 M H_2O_2, the half-life for the reaction is 68 s.

7. (3 pts.) Radioactive isotopes decay obeying

- ☐ zeroeth order kinetics.
- ■ first order kinetics.
- ☐ second order kinetics.
- ☐ a kinetic order which depends upon the particular isotope.
- ☐ no simple order kinetics..

II. Problems: Neatness and a logical approach count for as much as 25% of the partial credit. If the instructor can't follow the work quickly and easily or if the work leading to the solution is not mathematically true, partial credit will be completely forfeited. Sufficient units to demonstrate proper dimensionality throughout the solutions are required for full credit. **If you use any technological advantage for equation solving, please complete the setup of the problem to the point where you enter the equation or equation parameters into the calculator then indicate the method by which you solved the equation. Failure to follow these instructions will result in a non-negotiable 50% loss of credit on the problem. A free point will be added for putting an x in the line on the lower right of the previous page.**

1. (10 pts.) Consider the reaction

$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g) \qquad K_c = 113$$

When a 4.0 L glass vessel contains 0.040 mol of ammonia gas, 0.020 mol of nitrogen monoxide gas, 0.0060 mol of water vapor, and 0.050 mol of oxygen gas, are the gases at equilibrium? If not, which direction will the reaction proceed to achieve equilibrium?

INITIAL CONCS

$[NH_3] = 0.040\,mol / 4.0\,L = 0.010\,M$

$[NO] = 0.020\,mol / 4.0\,L = 0.005\,M$

$[H_2O] = 0.0060\,mol / 4.0\,L = 0.0015\,M$

$[O_2] = 0.050\,mol / 4.0\,L = 0.0125\,M$

$Q_c = \dfrac{(0.005)^4 (0.0015)^6}{(0.010)^4 (0.0125)^5}$

$= 2.3 \times 10^{-9}$

$Q_c < K_c$ REACTION PROCEEDS RIGHT

2. (8 pts.) When 0.0016 mol of formic acid was dissolved in sufficient water to make exactly 100 mL, the $[H_3O^+]$ was measured to be 1.5×10^{-3} M. From this information, calculate the value of the acid ionization constant, K_a. Formic acid = HCO_2H.

$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$

$[H_3O^+] = [HCO_2^-] = 0.0015\,M$

$[HCO_2H] = 0.016\,M - 0.0015\,M$
$= 0.0145\,M$

initial $C_{HCO_2H} = 0.0016\,mol / 0.1000\,L = 0.016\,M$

← REQUIRED SINCE $[H_3O^+]$ IS PRETTY BIG COMPARED TO ORIGINAL CONC.

$K_a = \dfrac{(0.0015)^2}{0.0145} = 1.55 \times 10^{-4}$

(w/o CORRECTION TO $C_{(HCO_2H)}$: $K_a = 1.41 \times 10^{-4}$)

Complete either problem 2 or problem 3. If you attempt both, indicate the one you wish graded. If you attempt both but don't indicate which to grade, problem 2 will be graded regardless of intention. Notice that problem 3 has 6 points of extra credit.

2. (12 pts.) N_2O_5 is an example of an odd compound that adopts different structures depending on the conditions. Most commonly it is a salt, but under some conditions it is a polar molecule. It can also be explosive. Consider the first-order decomposition reaction under controlled conditions:

$$N_2O_5(g) \rightarrow 2\,NO_2(g) + \tfrac{1}{2}O_2(g)$$

The following data were obtained:

Temp (°C)	k (h^{-1})
20.0	0.0308
40.0	0.462

Calculate the activation energy for this reaction.

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{0.0308}{0.462} = \frac{E_a}{8.314\ J/mol\,K}\left(\frac{1}{313.2\,K} - \frac{1}{293.2}\right)$$

$$-0.405 = \frac{E_a}{8.314\ J/mol\,K}\left(-2.178\times10^{-4}\,K^{-1}\right)$$

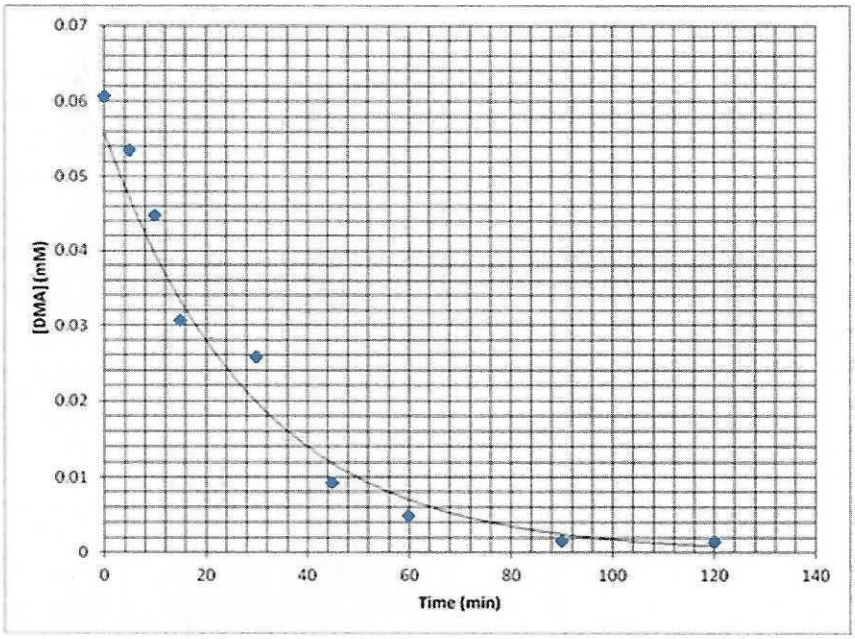
$$E_a = 15{,}500\ J/mol = 15.5\ kJ/mol$$

4. (12 pts.) Below are the data for the TiO_2-mediated decomposition reaction of dimethylaniline (DMA), an important compound in the synthesis of agricultural chemicals, pharmaceuticals, and textiles. Accompanying the data is a plot of concentration versus time for the decomposition. The solid line through the data represents the best-fit line of the data.

Use any method you know to determine the reaction order and the rate constant for the reaction. A section of graph paper is supplied below, but may not be necessary. Simply guessing the order of the reaction and getting it correct receives one-half credit maximum.

Data

Time (min)	[DMA] (mM)	
0	0.0606	−2.80
5	0.0535	−2.93
10	0.0447	−3.11
15	0.0306	−3.49
30	0.0257	−3.66
45	0.0093	−4.68
60	0.0049	−5.32
90	0.0016	−6.44
120	0.0015	



(1) Check half lives

0.56 → 0.28 M $t_{1/2}$ = 20 min

0.28 → 0.14 $t_{1/2}$ = 20 min

Reaction is 1st order

Can't use actual data for this

$k = \frac{0.693}{20\,min} = 0.0347\,min^{-1}$

(2) Plot ln C vs t:

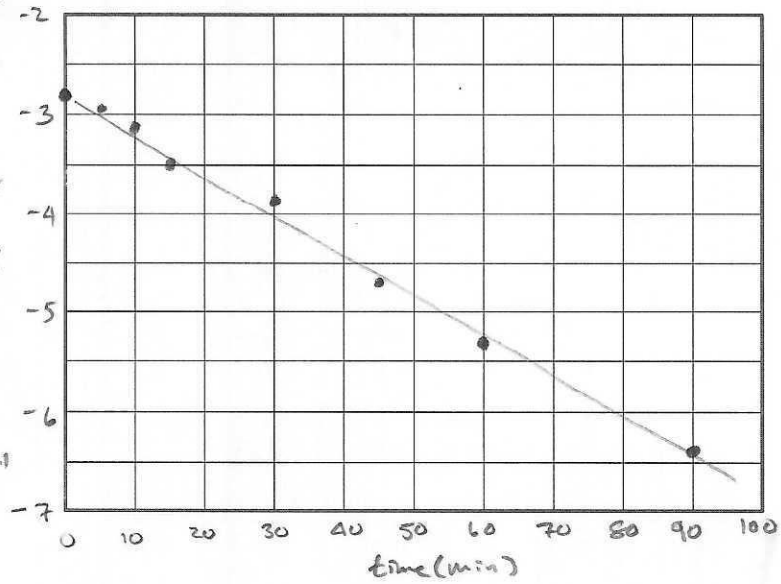
looks pretty straight

Slope = $\frac{-3.25-(-6)}{10\,min - 80}$

$= \frac{2.75}{-70\,min}$

$= -0.0393\,min^{-1}$

$k = 0.0393\,min^{-1}$



Rate Law	**Rate Constant**
Rate = k[DMA]	$k = 0.0347\,min^{-1}$

5. (13 pts.) The hydrolysis of sucrose ($C_{12}H_{22}O_{11}$) occurs slowly and is first order in sucrose and zeroeth order in water. The reaction occurs according to the equation

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2\ C_6H_{12}O_6(aq)$$

The reaction proceeds with a rate constant of 5.01×10^{-5}/min at room temperature. If a solution of sucrose is prepared to be 0.035 M, what will the concentration be in 168 hours?

$t = 168\,h \times \frac{60\,min}{1\,h} = 10,080\,min$

$C_t = 0.035M\,e^{-(5.01\times10^{-5}/min)(10,080\,min)}$

$= 0.621\,M$

6. (13 pts.) Consider the base hydrolysis of sodium acetate:

$$NaC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + NaOH(aq) \qquad K_c = 5.7 \times 10^{-10}$$

What is the calculated [NaOH] at equilibrium when 2.11 g of sodium acetate (82.03 g mol^{-1}) are dissolved in water to make 100.0 mL of solution? Water in the chemical equation is the solvent.

$$[NaC_2H_3O_2]_{initial} = \frac{2.11\,g / 82.03\,g/mol}{0.1000\,L} = 0.257\,M$$

$$K_c = \frac{x^2}{0.257 - x} \approx \frac{x^2}{0.257}$$

$x = 1.21 \times 10^{-5}\,M$ (Regardless of mathematical solution)