

Read questions carefully before answering. No outside paper is allowed. Use the reverse side of your answer paper as scratch. Use the periodic table and important constants charts provided.

(Total points = ~~30~~ + 64 = 94).

21 + 50 = 71; Extra pt { 8 → 1, 16a → 2 }  
 { 9 → 1, 16b → 3 }  
 10 → 1

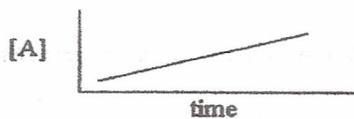
**MULTIPLE CHOICE.** Select the one alternative that best completes the statement or answers the question (3 pts each, if not mentioned otherwise).

- 1) Which of the following statements about gases is false? 1) B
- A) Distances between molecules of gas are very large compared to bond distances within molecules.
- B) All gases are colorless and odorless at room temperature.
- C) Gases expand spontaneously to fill the container they are placed in.
- D) Non-reacting gas mixtures are homogeneous.
- E) Gases are highly compressible.
- 2) Molecular compounds of low molecular weight tend to be gases at room temperature. Which of the following is most likely not a gas at room temperature? 2) B
- A) HCl B) LiCl C) Cl<sub>2</sub> D) H<sub>2</sub> E) CH<sub>4</sub>
- $1 + 35 = 36$   $7 + 35 = 42$   $35 \times 2 = 70$   $1 \times 2 = 2$   $12 + (1 \times 4) = 16$
- 3) What is the predominant intermolecular force in CBr<sub>4</sub>? 3) E
- A) hydrogen-bonding
- B) ion-dipole attraction
- C) ionic bonding
- D) dipole-dipole attraction
- E) London-dispersion forces
- :Br:  
:Br-C-Br: nonpolar  
|  
:Br:
- 4) Large intermolecular forces in a substance are manifested by \_\_\_\_\_. 4) E
- A) high heats of fusion and vaporization
- B) high boiling point
- C) low vapor pressure
- D) high critical temperatures and pressures
- E) all of the above
- 5) CsCl crystallizes in a unit cell that contains the Cs<sup>+</sup> ion at the center of a cube that has a Cl<sup>-</sup> at each corner. Each unit cell contains \_\_\_\_\_ Cs<sup>+</sup> ions and \_\_\_\_\_ Cl<sup>-</sup> ions, respectively. 5) E
- A) 2 and 2 B) 2 and 4 C) 1 and 8 D) 2 and 1 E) 1 and 1
- 6) Under constant conditions, the half-life of a first-order reaction \_\_\_\_\_. 6) E
- A) is constant
- B) is the time necessary for the reactant concentration to drop to half its original value
- C) does not depend on the initial reactant concentration
- D) can be calculated from the reaction rate constant
- E) All of the above are correct.

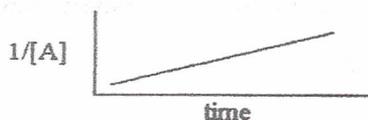
1 B  
2 B  
3 E  
4 E  
5 E  
6 E  
7 B  
8 A  
9 E  
10 D

7) Which one of the following graphs shows the correct relationship between concentration and time for a reaction that is second order in [A]? 7) B

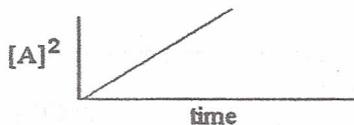
A)



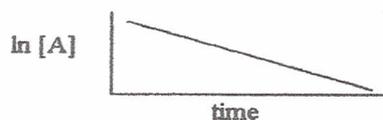
B)



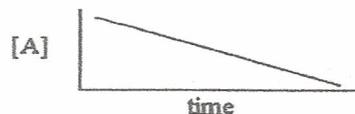
C)



D)



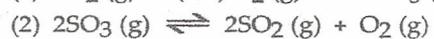
E)



8) At equilibrium, \_\_\_\_\_ 8) A

- A) the rates of the forward and reverse reactions are equal
- B) the rate constants of the forward and reverse reactions are equal
- ~~C) all chemical reactions have ceased~~
- ~~D) the value of the equilibrium constant is 1~~
- ~~E) the limiting reagent has been consumed~~

9) The equilibrium constant for reaction 1 is K. The equilibrium constant for reaction 2 is \_\_\_\_\_ 9) E



$$K_{c1} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$$

$$K_{c2} = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K^2}$$

- A) 2K      B)  $-K^2$       C)  $K^2$       D)  $1/2K$       E)  $1/K^2$

10) The equilibrium-constant expression depends on the \_\_\_\_\_ of the reaction.

- A) stoichiometry and mechanism
- B) the quantities of reactants and products initially present
- C) mechanism
- D) stoichiometry
- E) temperature

10) D

$$K_c = \frac{[\text{product}]_{eq}}{[\text{reactant}]_{eq}}$$

You will lose points if you don't show the (1) set up equation, (2) the raw data in the equation and (3) the appropriate units in your calculations.

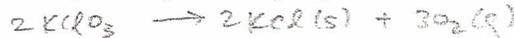
11) Oxygen gas is produced by decomposing  $\text{KClO}_3$  as follows:  $2 \text{KClO}_3 \rightarrow 2 \text{KCl (s)} + 3 \text{O}_2 \text{ (g)}$ . If 0.25 L of oxygen was collected over water at  $26^\circ\text{C}$  and 765 torr pressure, calculate the weight (in grams) of  $\text{KClO}_3$  decomposed. Vapor pressure of water at  $26^\circ\text{C}$  is 25 torr. (10 pts.)

11) 0.81 g  $\text{KClO}_3$

$\text{O}_2$   $V = 0.25 \text{ L}$   
over water:

$$T = 26^\circ\text{C} + 273 = 299 \text{ K}$$

$$P = 765 \text{ torr} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$



$$0.0066 \text{ moles KClO}_3 \times \frac{(39) + (35) + (16 \times 3) \text{ g}}{1 \text{ mole}} = 0.81 \text{ g KClO}_3$$

$$P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}} = 765 \text{ torr} - 25 \text{ torr} = 740 \text{ torr}$$

moles  $\text{O}_2$ :  $PV = nRT$

$$n = \frac{PV}{RT} = \frac{(740 \text{ torr})(0.25 \text{ L})}{(62.36 \frac{\text{L-torr}}{\text{mol-K}})(299 \text{ K})} = 0.0099 \text{ moles O}_2$$

$$\text{moles KClO}_3: 0.0099 \text{ moles O}_2 \times \frac{2 \text{ moles KClO}_3}{3 \text{ moles O}_2} = 0.0066 \text{ moles KClO}_3$$

$$= 0.81 \text{ g KClO}_3 \text{ decomposed}$$

12) A unit cell of LiF has 4  $\text{Li}^+$  and 4  $\text{F}^-$  ions and the edge length is  $4.02 \text{ \AA}$ , then calculate the density of LiF. (8 pts.)

12) 2.65  $\text{g/cm}^3$

Assuming that is a FCC unit cell, 4 of each atom.

$$\text{Volume of unit cell} = (\text{edge length})^3 = (4.02 \text{ \AA})^3 = 64.96 \text{ \AA}^3 \cdot \left(\frac{1 \text{ cm}}{10^8 \text{ \AA}}\right)^3 = 6.50 \times 10^{-23} \text{ cm}^3$$

$$\text{Mass of unit cell} = 4 \text{ Li atoms} \cdot \frac{6.94 \text{ amu}}{1 \text{ Li atom}} \cdot \frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}} = 4.61 \times 10^{-23} \text{ g Li}$$

$$4 \text{ F atoms} \cdot \frac{19.0 \text{ amu}}{1 \text{ F atom}} \cdot \frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}} = 1.26 \times 10^{-22} \text{ g F}$$

$$\text{mass Li} + \text{mass F} = 4.61 \times 10^{-23} \text{ g Li} + 1.26 \times 10^{-22} \text{ g F} = 1.72 \times 10^{-22} \text{ g LiF}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{1.72 \times 10^{-22} \text{ g LiF}}{6.50 \times 10^{-23} \text{ cm}^3} = 2.646153846 \text{ g/cm}^3$$

$$= 2.65 \text{ g/cm}^3$$

13) From the following data:

Calorimeter	130.765 g
Calorimeter + water	231.012 g $\rightarrow m_{H_2O} = 231.012 - 130.765 = 100.247g$
Initial water temperature	22.6°C
Final water temperature	5.8°C $\rightarrow \Delta T_{cool} = 5.8 - 22.6 = -16.8^\circ C$
Calorimeter + water + ice	250.21 g $\rightarrow m_{ice} = 250.21 - 231.012 = 19.198g$
Specific heat of water	4.184 J/g°C
Heat capacity of calorimeter	10.0 J/°C $\Delta T_{warm} = 5.8 - 0 = 5.8^\circ$

13) 87.2°C

a) Calculate the heat of fusion of ice (6 pts.)

$$q_{cool} = (C_p \cdot m_{H_2O} + C_{cup}) \cdot \Delta T_{cool}$$

$$= \left(4.184 \frac{J}{g \cdot ^\circ C} \times 100.247g\right) + 10.0 \frac{J}{^\circ C} \cdot (-16.8^\circ C)$$

$$= -7214.5 J$$

$$q_{warm} = C_p \cdot m_{ice} \cdot \Delta T_{warm}$$

$$= 4.184 \frac{J}{g \cdot ^\circ C} \times 19.198g \times 5.8^\circ C$$

$$= 465.882 J$$

$$q_{melt} + q_{warm} = -q_{cool}$$

$$q_{melt} = -q_{cool} - q_{warm} = -(-7214.5J) - 465.882J$$

$$q_{melt} = 7214.5J - 465.882J = 6748.605J$$

And  $q_{melt} = m_{ice} \cdot \Delta H_{fus}$

$$\therefore \Delta H_{fus} = \frac{q_{melt}}{m_{ice}} = \frac{6748.605J}{19.198g} = 351.53 J/g$$

b) Calculate the final temperature of water in this calorimeter if 40.7 kJ of heat is added to the system at 5.8°C (6 pts.)

Let final temp. = T

$$\therefore q = m \cdot C_p \cdot \Delta T + C_{cup} \cdot \Delta T = (m_{H_2O} + m_{ice}) \cdot C_p \cdot \Delta T + C_{cup} \cdot \Delta T = \Delta T \left[ (m_{H_2O} + m_{ice}) \cdot C_p + C_{cup} \right]$$

$$\text{or } T - 5.8 = \frac{q}{(m_{H_2O} + m_{ice}) \cdot C_p + C_{cup}}$$

$$\text{or } T = \frac{q}{(m_{H_2O} + m_{ice}) \cdot C_p + C_{cup}} + 5.8$$

$$= \frac{40.7 \text{ kJ} \times \frac{1000 J}{1 \text{ kJ}}}{(100.247 + 19.198)g \times 4.184 \frac{J}{g \cdot ^\circ C} + 10 J} + 5.8$$

$$= \frac{40700^\circ C}{119.445 \times 4.184 + 10} + 5.8$$

$$= (81.44 + 5.8)^\circ C$$

$$T = 85.64^\circ C$$

14) The following experimental data were obtained at constant temperature for the reaction:

14) \_\_\_\_\_



Experiment	Initial Concentrations		Initial Rate M s <sup>-1</sup>
	[NO]	[NO <sub>2</sub> ] [O <sub>2</sub> ]	
1	0.0010	0.0010	7.0 x 10 <sup>-6</sup>
2	0.0010	0.0020	1.4 x 10 <sup>-5</sup>
3	0.0010	0.0030	2.1 x 10 <sup>-5</sup>
4	0.0020	0.0030	8.4 x 10 <sup>-5</sup>
5	0.0030	0.0030	1.9 x 10 <sup>-4</sup>

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

a. Calculate the order of the reaction with respect to each reactant (6 pts.).

$$\frac{\text{Mix 2}}{\text{Mix 1}} = \frac{1.4 \times 10^{-5}}{7.0 \times 10^{-6}} = \frac{k[0.0010]^m [0.0020]^n}{k[0.0010]^m [0.0010]^n} \quad \frac{\text{Mix 4}}{\text{Mix 3}} = \frac{k[0.0020]^m [0.0030]^n}{k[0.0010]^m [0.0030]^n} = \frac{8.4 \times 10^{-5}}{2.1 \times 10^{-5}}$$

$$2 = \left(\frac{0.0020}{0.0010}\right)^n = 2^n$$

$$n = 1$$

$$\left(\frac{0.0020}{0.0010}\right)^m = 4$$

$$2^m = 4$$

$$m = 2$$

Reaction order for O<sub>2</sub> = 1, NO = 2

b. Write the rate law for the reaction (2 pts.).

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]^1$$

$$\text{from exp 1: } k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]^1} = \frac{7.0 \times 10^{-6} \text{ M/s}}{(0.001)^2(0.001) \text{ M}} = 7000 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{rate} = 7000[\text{NO}]^2[\text{O}_2]^1$$

c. Calculate rate of NO<sub>2</sub> formation when [NO] = [O<sub>2</sub>] = 0.005 M (4 pts.)

$$\text{rate} = 7000 (0.005)^2 (0.005) = 8.75 \times 10^{-4} \text{ M/s}$$

$$\text{units: } (\text{M}^{-1} \text{s}^{-1})(\text{M})^2(\text{M}) = \text{M/s}$$

$$(k \text{ units} = \text{M}^{-1} \text{s}^{-1})$$

15) (Following question is modelled after Crystal Violet Kinetics expt.)

15) \_\_\_\_\_

Nitrogen dioxide and carbon monoxide react at high temperatures according to the equation:



$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

a) Determine and write the rate law (rate equation) for this reaction given the following information. Clearly state any conclusions and show any and all calculations or reasoning used for full credit (8 pts).

i) Run 1 of the experiment was performed with  $[\text{CO}]_0 = 0.15 \text{ M}$  and  $[\text{NO}_2]_0 = 1.75 \times 10^{-3} \text{ M}$ . For this run, a plot of  $1/[\text{NO}_2]_t$  versus  $t$  produced a straight line with a slope of  $0.12 \text{ M}^{-1}\text{s}^{-1}$ .

thus, can we assume CO in excess, so we can rewrite the equation using  $k' = k[\text{CO}]_0^n$   
 $\text{rate} = k'[\text{NO}_2]^m$

ii) Run 2 of the experiment was performed with  $[\text{CO}]_0 = 0.30 \text{ M}$  and  $[\text{NO}_2]_0 = 1.75 \times 10^{-3} \text{ M}$ . For this run, the slope of the  $1/[\text{NO}_2]_t$  versus  $t$  plot was the same as the slope of the plot for run 1.

	Initial Concentrations	
	$[\text{CO}]_0$	$[\text{NO}_2]_0$
①	0.15 M	$1.75 \times 10^{-3} \text{ M}$
②	0.30 M	$1.75 \times 10^{-3} \text{ M}$

i) this is a second-order reaction

$$\frac{1}{[\text{NO}_2]_t} = k't + \frac{1}{[\text{NO}_2]_0}$$

$$k' = \text{slope} = 0.12 \text{ M}^{-1}\text{s}^{-1}$$

$$k'_1 = k'_2$$

$\therefore$  reaction order for  $[\text{NO}_2]$  is 2.

order of  $[\text{CO}]$   $\frac{k'_2}{k'_1} = \frac{k[0.30\text{M}]^n}{k[0.15\text{M}]^n}$

$$1 = \left(\frac{0.30}{0.15}\right)^n = 2^n$$

$$\log 1 = n \log 2$$

$$0 = n \log 2$$

$$0 = n$$

so reaction order of CO being 0, it has no effect on reaction rate.

true rate constant  $k = \frac{k'}{[\text{CO}]_0^n} = k'$  since  $[\text{CO}]^0 = 1$

$$\text{rate} = 0.12 \text{ M}^{-1}\text{s}^{-1} [\text{NO}_2]^2 [\text{CO}]^0 = 0.12 \text{ M}^{-1}\text{s}^{-1} [\text{NO}_2]^2$$

16) For the equilibrium reaction given below:  
 $\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \leftrightarrow \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$

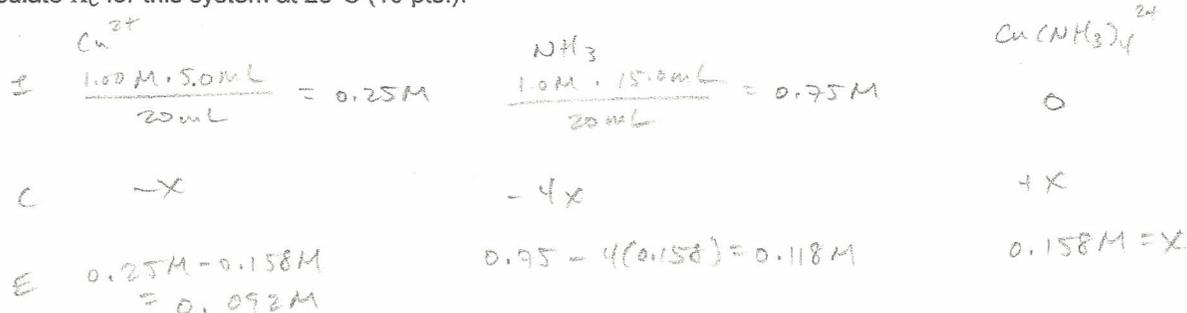
16) \_\_\_\_\_

a) Write the equilibrium constant expression for this reaction (4 pts.).

$$K_c = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]_{\text{eq}}}{[\text{Cu}^{2+}]_{\text{eq}} [\text{NH}_3]_{\text{eq}}^4}$$

To measure the equilibrium constant, 5.0 mL of 1.00 M  $\text{Cu}(\text{NO}_3)_2(\text{aq})$  solution was mixed with 15.0 mL of 1.0 M  $\text{NH}_3(\text{aq})$  at 25°C. When the equilibrium reached, the absorbance of  $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$  at equilibrium was determined using spectroscopy to be 0.31. A standard curve of  $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$ , plotting the absorbance (y-axis) vs. the concentration (x-axis) gave a straight line with a slope of 1.948 and intercept of 0.0018.

b) Calculate  $K_c$  for this system at 25°C (10 pts.).



$$[\text{Cu}(\text{NH}_3)_4^{2+}] = \frac{\text{Absorbance} - b}{m} = \frac{0.31 - 0.0018}{1.948} = 0.1582135524 = 0.158 \text{ M}$$

$$K_c = \frac{(0.158)}{(0.092)(0.118)^4} = 8858.113291 = 8.9 \times 10^3$$