

Multiple Choice (5 points each, Put answers in CAPS in the left margin.)

1. What is the freezing point of a 0.37 *m* aqueous solution of aluminum chloride ( $K_b = 1.86\text{ }^\circ\text{C}/m$ )?  
 A)  $-0.69\text{ }^\circ\text{C}$       B)  $-1.38\text{ }^\circ\text{C}$       C)  $-2.05\text{ }^\circ\text{C}$       D)  $-2.75\text{ }^\circ\text{C}$       E)  $-3.44\text{ }^\circ\text{C}$

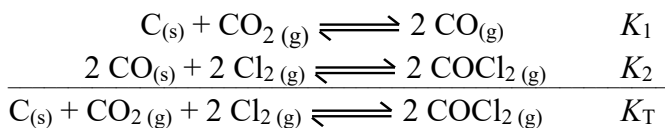
2. For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$  which of the following is a valid equation for rate (i.e. rate =)? (recall  $\Delta$  can be used for  $d$ , i.e.  $\Delta t$  for  $dt$ )

- A)  $\frac{d[\text{N}_2]}{dt}$       C)  $3\frac{d[\text{H}_2]}{dt}$       E)  $\frac{1}{2}\frac{d[\text{NH}_3]}{dt}$   
 B)  $-2\frac{d[\text{NH}_3]}{dt}$       D)  $\frac{1}{3}\frac{d[\text{H}_2]}{dt}$

3. For the reaction:  $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$  at equilibrium, some CO is added at constant volume. Which of the following is true for the new equilibrium?

- A)  $[\text{CO}]$ ,  $[\text{Cl}_2]$ , and  $[\text{COCl}_2]$  all increase.  
 B)  $[\text{CO}]$  and  $[\text{Cl}_2]$  increase and  $[\text{COCl}_2]$  decreases.  
 C)  $[\text{CO}]$  and  $[\text{Cl}_2]$  decrease and  $[\text{COCl}_2]$  increases.  
D)  $[\text{CO}]$  and  $[\text{COCl}_2]$  increase and  $[\text{Cl}_2]$  decreases.  
 E) Cannot determine from the information given.

4. For the following equilibria:



- A)  $K_T = K_1 + K_2$       C)  $K_T = K_1 - K_2$       E)  $K_T = K_2 - K_1$   
 B)  $K_T = K_1 \div K_2$       D)  $K_T = K_1 K_2$

4. Original: Answer = C, 278

5. Which of the following statements regarding chemical equilibrium is false?

- A) The concentrations of reactants and products are equal.  
 B) The concentrations of reactants and products remain constant.  
 C) Reactants are being converted to products and vice versa.  
 D) The rates of the forward and reverse reactions are equal.  
 E) Two of the statements (A-D) are false.

6. For the equilibrium  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  which of the following would result in a shift of the equilibrium to the right?

- A) Increasing pressure      C) Adding HI      E) Adding NaOH  
 B) Adding a catalyst      D) Decreasing pressure

7. For the reaction:  $\text{HOCl} + \text{C}_5\text{H}_5\text{N} \longrightarrow \text{C}_5\text{H}_5\text{NH}^+ + \text{OCl}^-$  (all species aqueous), which is the conjugate base to HOCl?  
 A) HOCl                      B)  $\text{C}_5\text{H}_5\text{N}$                       C)  $\text{C}_5\text{H}_5\text{NH}^+$                       D)  $\text{OCl}^-$                       E)  $\text{H}_2\text{O}$
8. Calculate the  $\text{H}^+$  ion concentration in  $8.8 \times 10^{-4} \text{ M Ca(OH)}_2$ .  
 A)  $8.8 \times 10^{-4} \text{ M}$                       C)  $2.2 \times 10^{-11} \text{ M}$                       E)  $5.7 \times 10^{-12} \text{ M}$   
 B)  $1.8 \times 10^{-3} \text{ M}$                       D)  $1.1 \times 10^{-11} \text{ M}$
9. Which of the following pairs of reagents constitutes an aqueous buffer system?  
 A) NaOH, NaCl                      C) HCl, HOAc                      E)  $\text{NH}_3$ , NaOH  
 B)  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$                       D)  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$

Discussion questions (You must show your work to receive credit!)

1. At  $273^\circ\text{C}$ , the reaction,  $2 \text{ NO} + \text{Br}_2 \longrightarrow 2 \text{ NOBr}$  (all gases), is observed to exhibit the following dependence of rate on concentration.

<u>[NO] (M)</u>	<u>[Br<sub>2</sub>] (M)</u>	<u>rate (M s<sup>-1</sup>)</u>
0.10	0.10	12
0.25	0.10	75
0.10	0.25	30

- a) What is the rate law for this reaction?  
 b) What is the rate constant for this reaction? (10 points)

General rate law:  $\text{rate} = k[\text{NO}]^x[\text{Br}]^y$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k(0.10 \text{ M})^x(0.10 \text{ M})^y}{k(0.25 \text{ M})^x(0.10 \text{ M})^y} = \frac{12 \text{ M/s}}{75 \text{ M/s}}$$

$$0.16 = \left(\frac{0.10}{0.25}\right)^x = (0.40)^x \Rightarrow x = 2$$

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k(0.10 \text{ M})^x(0.10 \text{ M})^y}{k(0.10 \text{ M})^x(0.25 \text{ M})^y} = \frac{12 \text{ M/s}}{30 \text{ M/s}}$$

$$0.40 = \left(\frac{0.10}{0.25}\right)^y = (0.40)^y \Rightarrow y = 1$$

Thus, the rate law is:  $\text{rate} = k[\text{NO}]^2[\text{Br}]$

b)  $12 \text{ M/s} = k(0.10 \text{ M})^2(0.10 \text{ M})$

$$k = 1.2 \times 10^4 \text{ M}^3\text{s}^{-1}$$

2. Explain your answer to Multiple Choice question #3. (6 points)

When CO is added to the reaction mixture, the forward reaction accelerates. This consumes both some of the added CO, but also some of the existing  $\text{Cl}_2$ . The result is a loss of  $\text{Cl}_2$  and a gain of CO, relative to what was there before the CO was added. Since the forward reaction accelerates, more product is formed leading to an increase in the concentration of  $\text{COCl}_2$ .

3. Consider an equilibrium whose forward reaction is exothermic. Which way will the equilibrium shift if the reaction is heated? Provide a physical explanation for your prediction. (7 points)

Exothermic reactions release heat, which essentially makes it a product of the reaction. Warming the reaction adds heat as if it were a reactant. The result is that warming the reaction leads to shift to reactants. The excess energy is usually used to break bonds leading to product formation.

4. Phosphorus pentachloride decomposes according to the chemical equation



A 0.1757 mol sample of  $\text{PCl}_5$  is injected into an empty 2.30 L reaction vessel held at  $250^\circ\text{C}$ . Calculate the concentrations of  $\text{PCl}_5$  and  $\text{PCl}_3$  at equilibrium. (10 points)

$$[\text{PCl}_5]_i = \frac{0.1757 \text{ mol}_{\text{PCl}_5}}{2.30 \text{ L}} = 0.07639 \text{ M}$$

$$[\text{PCl}_5]_e = 0.07639 - x \text{ M}, [\text{PCl}_3]_e = [\text{Cl}_2]_e = x \text{ M}$$

$$1.80 = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(x)(x)}{0.07639 - x}$$

$$x^2 + 1.80x - 0.1375 = 0$$

The quadratic equation yields two solutions: 0.07340 and -1.873. We can discard the latter root because negative concentrations have no physical meaning.

This yields  $[\text{PCl}_3]_e = [\text{Cl}_2]_e = 0.0734 \text{ M}$  and  $[\text{PCl}_5]_e = 0.07639 - 0.0734 \text{ M} = 0.00299 \text{ M}$

5. What is the pH of a \_\_\_\_\_ (12 points)

- a) 0.162 M  $\text{HBrO}$  ( $K_a = 2.0 \times 10^{-9}$ )

	$\text{HBrO}$	$\rightleftharpoons$	$\text{H}^+$	$+$	$\text{BrO}^-$	
init	0.162		0		0	
change	-x		x		x	
equil	0.162 - x		x		x	

$$K_a = \frac{[\text{H}^+][\text{BrO}^-]}{[\text{HBrO}]}$$

$$2.0 \times 10^{-9} = \frac{(x)(x)}{(0.162 - x)} \quad \text{Since } [\text{HBrO}]_i \gg 100K_a, \text{ assume } x \text{ is negligible.}$$

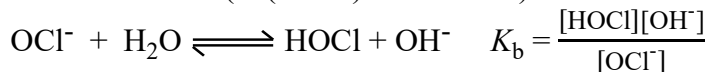
$$2.0 \times 10^{-9} = \frac{(x)(x)}{(0.162)}$$

$$x^2 = 3.24 \times 10^{-10}$$

$$x = 1.80 \times 10^{-5} = [\text{H}^+] \quad \text{Check: } 0.162 - 0.0000180 \approx 0.162$$

$$\text{pH} = -\log(0.0000180) = 4.74$$

- b) 0.100 M  $\text{NaOCl}$  ( $K_a(\text{HOCl}) = 3.0 \times 10^{-8}$ )?



$$\text{init} \quad 0.100 \text{ M} \quad 0 \text{ M} \quad 0 \text{ M}$$

$$\text{equil} \quad 0.100 - x \quad x \quad x$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$$

$$3.3 \times 10^{-7} = \frac{(x)(x)}{0.100 - x}$$

Since  $[\text{OCl}^-]_i \gg 100K_b$ , assume  $x$  is negligible in the denominator

$$3.3 \times 10^{-7} = \frac{x^2}{0.100}$$

$$x = [\text{OH}^-] = 1.82 \times 10^{-4} \text{ M} \quad (0.100 - 1.82 \times 10^{-4} \cong 0.100, \text{ so the assumption was OK})$$

$$\text{pOH} = -\log(1.82 \times 10^{-4}) = 3.74$$

$$\text{pH} = 14.00 - 3.74 = 10.26$$

6. Explain your answer to Multiple Choice question #6. (5 points)

The reaction has two molecules of gas on both the reactant and product sides of the reaction, so changing pressure will have no effect. By definition, catalysts have no effect on the position of equilibria. HI is a product, so adding more will shift the reaction to make more reactants, which is to the left. While NaOH is neither a reactant or product, it is a base and bases react with acids. The net effect is that the NaOH will react with the HI and remove it from the reaction mixture. That will cause the reaction to shift right.

7. Which is the stronger acid in non-aqueous solution and why: HBr or HCl? (In water, the two acids are equally strong, but in some other solvents one would be stronger.) (5 points)

HBr. There are two primary factors affecting acid strength: bond strength and bond polarity. In general, atoms in the same period have similar sizes leading to bonds that are comparably strong, meaning that bond polarity is more important. Going down a group atoms are of very different sizes meaning that bond strengths vary significantly and so bond strength is more important. HCl will have stronger bonds and so would be a weaker acid than HBr even though its bonds are more polar.