Chemistry 212 Test 3 Name:____________________
Spring 2025

Multiple Choice (5 points each, Put answers in CAPS in the left margin.)
$R = 8.314$ J/mol•K = 0.0821 L•atm/mol•K

1. Which of the following pairs of reagents constitutes an aqueous buffer system?

A) KOH, KCl
B) $H_2PO_4^-$, HPO_4^{2-}
C) HCl, H_3PO_4
D) H_2CO_3, H_2O
E) NH_3, HCl

2. For the following equilibria (examine the 3 reactions carefully):

$$\begin{array}{lc} C_{(s)} + CO_{2\,(g)} \rightleftharpoons 2\,CO_{(g)} & K_1 \\ 2\,COCl_{2\,(g)} \rightleftharpoons 2\,CO_{(s)} + 2\,Cl_{2\,(g)} & K_2 \\ \hline C_{(s)} + CO_{2\,(g)} + 2\,Cl_{2\,(g)} \rightleftharpoons 2\,COCl_{2\,(g)} & K_T \end{array}$$

A) $K_T = K_1 + K_2$
B) $K_T = K_1 \div K_2$
C) $K_T = K_1 - K_2$
D) $K_T = K_1K_2$
E) $K_T = K_2 - K_1$

3. Which of the following is the best example of a Lewis base that is **not also** a Brønsted-Lowry base?

A) Ag^+
B) CH_4
C) CO_3^{2-}
D) Cl^-
E) NH_3

4. Addition of which of the following would have no effect on the solubility of AgCN?

A) HCl
B) NaCN
C) $AgNO_3$
D) $NaNO_3$
E) $HClO_4$

5. Which of the following complex ions is most stable in aqueous solution?

A) CdI_4^{2-} $K_f = 2.0 \times 10^6$
B) $Cu(CN)_4^{2-}$ $K_f = 1.0 \times 10^{25}$
C) $Cu(NH_3)_4^{2+}$ $K_f = 5.0 \times 10^{13}$
D) $HgCl_4^{2-}$ $K_f = 1.7 \times 10^{16}$
E) $Hg(CN)_4^{2-}$ $K_f = 2.5 \times 10^{41}$

6. Which of the following processes is entropically unfavorable (for the system)?

A) Scattering seeds in the wind.
B) Boiling water.
C) Expanding a gas into a vacuum.
D) The burning of coal.
E) Making a hard-boiled egg.

7. The small bags of silica gel you often see in a new shoe box are placed there to control humidity. Despite its name, silica gel is a solid. It is a chemically inert, highly porous, amorphous form of SiO_2. Water vapor readily adsorbs onto the surface of silica gel, so it acts as a desiccant.

A) $\Delta G < 0$, $\Delta H < 0$, $\Delta S < 0$
B) $\Delta G < 0$, $\Delta H > 0$, $\Delta S < 0$
C) $\Delta G < 0$, $\Delta H < 0$, $\Delta S > 0$
D) $\Delta G > 0$, $\Delta H > 0$, $\Delta S > 0$
E) $\Delta G > 0$, $\Delta H < 0$, $\Delta S < 0$

8. Which of the following is a statement of the second law of thermodymanics?
   - A) When reactants are converted into products, the change in enthalpy is independent of the number of steps taken.
   - B) The entropy of a perfect crystal of any substance at absolute zero is zero.
   - C) Energy can be converted from one form to another but cannot be created or destroyed.
   - D) State functions are properties that are determined by the state the system is in.
   - **E) The entropy of the universe is always increasing.**

9. Which of the following reactions shows a decrease in entropy?
   - A) $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2\,HCl_{(g)}$
   - **B)** $\mathbf{BaO_{(s)} + CO_{2\,(g)} \rightarrow BaCO_{3\,(s)}}$
   - C) $SiCl_{4\,(\ell)} + 2\,H_2O_{(l)} \rightarrow SiO_{2\,(s)} + 4\,HCl_{(aq)}$
   - D) $2\,CH_3OH_{(\ell)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(g)}$
   - E) $2\,SO_{3\,(g)} \rightarrow 2\,SO_{2\,(g)} + O_{2\,(g)}$

Discussion Questions: (You must show your work to receive credit.)

1. What is the pH of a__________ solution

a) 0.562 M HBrO ($K_a = 2.0 \times 10^{-9}$)

$HBrO \rightleftharpoons H^+ + BrO^-$

	HBrO	H^+	BrO^-
init	0.562	0	0
change	-x	x	x
equil	0.562 - x	x	x

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

$$2.0 \times 10^{-9} = \frac{(x)(x)}{(0.562 - x)}$$ Since $[HBrO]_i >> 100K_a$, assume x is negligible.

$$2.0 \times 10^{-9} = \frac{(x)(x)}{(0.562)}$$

$x^2 = 1.12 \times 10^{-9}$

$x = 3.35 \times 10^{-5} = [H^+]$ Check: $0.562 - 0.0000335 \approx 0.562$

$pH = -\log(0.0000335) = 4.47$

b) 1.20 M NaOCl ($K_a(HClO) = 3.0 \times 10^{-8}$)? (10 points)

$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$ $\quad K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$

	OCl^-	HOCl	OH^-
init	1.20 M	0 M	0 M
equil	0.100 – x	x	x

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

$$3.3 \times 10^{-7} = \frac{(x)(x)}{1.200 - x}$$

Since $[OCl^-]_i >> 100K_b$, assume x is negligible in the denominator

$$3.3 \times 10^{-7} = \frac{x^2}{1.20}$$

$x = [OH^-] = 6.29 \times 10^{-4}\ M$ ($1.20 - 1.82 \times 10^{-4} \approx 1.20$, so the assumption was OK)

$pOH = -\log(6.29 \times 10^{-4}) = 3.20$

$pH = 14.00 - 3.20 = 10.80$

2. When Lewis acids and bases interact, a coordinate covalent bond typically forms. How is it different from a “normal” covalent bond? Functionally, how is a coordinate covalent bond different from a “normal” covalent bond? (i.e. What effect(s) arise in the CCB, not in a NCB)?) (6 points)

   A covalent bond is a shared pair of electrons. In a “normal” covalent bond, the bound atoms each contribute one electron to the bond. In a CCB, typically resulting from a Lewis acid/base pairing, the Lewis base contributes both electrons to the bond. An outcome is that a formal charge is created with the Lewis base developing a -1 formal charge and the Lewis acid gaining a +1 formal charge.

3. The K_{sp} of $PbBr_2$ is 6.60×10^{-6}. (i) What is the molar solubility of $PbBr_2$ in pure water? (ii) What is the solubility of $PbBr_2$ in 0.500 M KBr solution? (12 points)

   a) $[Pb^{2+}][Br^-]^2 = 6.60 \times 10^{-6}$

   Let $[Pb^{2+}] = x$, $[Br^-] = 2x$, then $x(2x)^2 = 6.60 \times 10^{-6}$

   $4x^3 = 6.60 \times 10^{-6}$

   $x = 1.18 \times 10^{-2}$

   $[PbBr_2] = [Pb^{2+}] = 1.18 \times 10^{-2}\ M$

   b) $[Pb^{2+}](0.500)^2 = 6.60 \times 10^{-6}$

   $[Pb^{2+}] = 2.64 \times 10^{-5}\ M$

   $$\text{solubility}_{PbBr2} = \left(\frac{2.64 \times 10^{-5}\ \text{mol}_{PbBr2}}{L}\right)\left(\frac{367.0\ \text{g}_{PbBr2}}{\text{mol}_{PbBr2}}\right) = 9.69 \times 10^{-3}\ g$$

4. For the complex ion $Cu(NH_3)_4^{2+}$ write out the chemical reaction for its formation constant (K_f) and the formation constant expression (equation). (6 points)

   $$Cu^{2+}_{(aq)} + 4\ NH_{3\ (aq)} \rightleftharpoons Cu(NH_3)_4^{2+} \quad K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

5. Why is it that increasing the entropy of a system necessarily increases the entropy of the universe. Focus your answer on a system that would result in a decrease in the system entropy. For example, you could use freezing a liquid, crystallization of a salt from solution, etc. (5 points)

   Some systems directly increase the entropy of the universe because their ΔS is positive. Any system the produces more gas molecules than it starts with would be an example of this. For systems with a negative ΔS, however, the overall entropy has to more than compensate for the loss in system entropy. Here, energy must be expended to create order within the system and the use of that energy creates the additional disorder outside of the system. Thus, for example, using a freezer to solidify water into ice results in greater universe entropy because the compressor heats the air around the freezer. The faster moving air molecules more than compensates for the limit in movement of the liquid water molecules when they freeze.

6. Consider the equilibrium $N_2O_{4\,(g)} \longrightarrow 2\ NO_{2\,(g)}$. $\Delta G^o = 5.30$ kJ/mol and $\Delta H^o = 57.9$ kJ/mol for this reaction. What are ΔS^o and K_p for the forward reaction. (T = 25 ºC) At what temperature does the equilibrium shift to the right? Is your answer for ΔS^o expected or not and why? (16 points)

   $\Delta G^o = -RT\ln K_{eq}$
   5.30 kJ/mol = (8.314 J/mol•K)(1 kJ/1000 J)(2998 K)lnK_{eq}
   $\ln K_{eq} = -2.14$
   $K_{eq} = 0.118$

   $\Delta G^o = \Delta H^o - T\Delta S^o$
   5.30 kJ•mol^{-1} = 57.9 kJ•mol^{-1} - (298 K)ΔS^o
   ΔS^o = 0.176 kJ/mol•K = 176 J/mol•K

   The equilibrium shifts from left to right when $\Delta G^o = 0$.
   0 = (57.9 kJ/mol)(1000 J/kJ) -T(176 J/mol•K)
   T(176 J/mol•K) = 57,900 J•mol^{-1}
   T = 329 K = 56 ºC

   Yes. One gas molecule becomes two gas molecules during the reaction. This suggests that ΔS^o should be both positive and relatively large.