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CHEM 112 TEST 3
START TIME_________________ END TIME_________________ Name__________________

You are allowed 2 consecutive hours (no cutting classes) for this test. You may use your calculator but NO extra "scratch paper". Use the back of pages if necessary.

LECTURE (Multiple choice) 2 points each
1. Which of the following can be classified as Neutralizable?
a) A weak acid whose pKa < 8
b) A weak acid whose pKa > 8
c) A mixture of two acids, one having pKa = 1.5, the other having pKa = 3.5
d) The third proton in phosphoric acid, H₃PO₄
e) all of the above
f) three of the above

2. Which of the following can be classified as Titratable?
a) A strong acid such as HCl mixed with Acetic Acid
b) A weak acid whose pKa < 8
c) A weak acid whose pKa > 8
d) A mixture of two acids, one having pKa = 1.5, the other having pKa = 3.5
e) all of the above
f) three of the above

3. Which of the following can be classified as Separable?
a) A strong acid such as HCl mixed with Acetic Acid
b) A mixture of two acids, one having pKa = 1.5, the other having pKa = 3.5
c) The second and third protons in phosphoric acid, H₃PO₄ (pK₂ = 7.21, pK₃ = 12.33)
d) all of the above
e) only 2 of the above
f) none of the above

4. What is the principal requirement, with respect to bonding, for a polydentate ligand?
a) compact size
b) Soluble in water
c) high purity, approaching that of a primary standard
d) numerous lone pairs
e) the presence of a 3-bonded Nitrogen as part of the structure

5. Given a solution of the salt of a weak base and a weak acid (such as Ammonium Benzoate, NH₄OBz), which of the following reactions is the "defining reaction", the reaction which ultimately sets the pH of the solution?
a) NH₄⁺ + H₂O → H₃O⁺ + NH₃
b) OBz⁻ + H₂O → HOBz + OH⁻
c) NH₄⁺ + OBz⁻ → NH₃ + HOBz
d) Since you have the salt of a Weak Base and a Weak Acid, the pH will be set by the Kₗw reaction
   since you have a solution of a salt in water. The pH will turn out to be 7.00

6. In your Hardness of Water determination, the buffer action reaction which actually occurs during the titration is:
a) OH⁻ + H₂Y²⁻ = H₂O + HY⁻³
b) Ca⁺² + H₂Y²⁻ = CaY⁻² + 2H⁺
c) NH₄⁺ + H₂O = NH₃ + H₃O⁺
d) NH₃ + H₂O⁺ = NH₄⁺ + H₂O
Spontaneity. Please indicate whether the following processes are spontaneous in the
direction indicated (S), not spontaneous in the direction indicated (NS), or if there is
insufficient information to make a decision (?).

1. __S__ A process for which both ΔS and ΔH for the system are positive.
2. __NS__ Energy is transferred as heat from a hot body to a cold body
3. __S__ After a partition is removed, a gas expands into the unoccupied portions of a
   container.
4. __S__ A process at sufficiently high temperature for which both ΔS and ΔH for the
   system are positive.
5. __NS__ A process for which ΔS for the system is negative and ΔH for the surroundings
   is positive.
6. __S__ A gas expands isobarically such that ΔS for the universe is positive.
7. __NS__ Your room gets cleaner
8. __NS__ Water is heated over a fire at 1 atm and freezes
9. __?__ An exothermic chemical reaction
10. __?__ A chemical reaction produces a gas.

Short Answer:

1. What is the difference between a macrostate and microstate?
   A macrostate is a “generic” state of a system that can be described by a few macroscopic
   variables. A microstate is a specific configuration of the system that must be described
   in terms of every microscopic detail.

2. What is the best theoretical efficiency of a heat engine with a heat source at 523 K
   operating in an environment at 293 K?
   Efficiency = 1 - 293/523 = .440

3. What is the third law of thermodynamics?
   The third law of thermodynamics states that any system at equilibrium at absolute zero
   must have zero entropy.

4. A heat engine operating between the temperatures T_h and T_c transfers heat q_h
   to the engine which creates work (w') and transfers heat q_c out of the engine. What must
   be true mathematically about these quantities for the second law to be satisfied?

   \[ q_c/T_c - q_h/T_h > 0 \]
PROBLEMS. SHOW ALL WORK; NO “MAGIC” PERMITTED.

1. (17 pts) Hess’s Law can be used to calculate energy changes that are difficult (or dangerous) to determine experimentally. An example is the generation of lethal Carbon Monoxide by the burning of carbon in a limited amount of oxygen: \[ 2 \text{C(graphite)} + \text{O}_2(g) \rightarrow 2 \text{CO(g)} \]

However, the Heats of Reaction for two other equations are known:

The usual combustion of graphite: \[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H_{\text{rxn}} = -393.5 \text{ KJ} \]

The combustion of Carbon Monoxide: \[ 2 \text{CO(g)} + \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) \quad \Delta H_{\text{rxn}} = -566.0 \text{ KJ} \]

\[ \begin{align*}
\text{a)} & \quad \text{Determine the Heat of Reaction for the reaction: } 2 \text{C(graphite)} + \text{O}_2(g) \rightarrow 2 \text{CO(g)} \\
& \quad 2 \text{C(graphite)} + 2 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) \quad \Delta H = 2(-393.5) \\
& \quad 2 \text{CO}_2(g) \rightarrow 2 \text{CO} + \text{O}_2(g) \quad \Delta H = -(-566.0) \\
& \quad 2 \text{C(graphite)} + \text{O}_2(g) \rightarrow 2 \text{CO} \quad \Delta H = -221 \text{ KJ}
\end{align*} \]

\[ \text{b)} \quad \text{Explain whether this reaction is exothermic or endothermic, and what those terms mean} \]

\[ \text{neg. sign} \rightarrow \text{exothermic reaction liberates heat} \]

\[ \text{c)} \quad \text{Do you get a greater heat effect per mole when you burn graphite to produce CO or when you burn graphite to produce CO}_2? \quad \text{Explain your reasoning.} \]

\[ \begin{align*}
\text{When you burn C to produce CO, you liberate: } & \quad -\frac{221125}{2} = -110562.5 \text{ KJ/mole} \\
\text{When you burn C to liberate CO}_2 & \quad -\frac{3930}{2} = -1965 \text{ KJ} \\
\text{greater heat effect with production of CO}_2
\end{align*} \]

\[ \text{d)} \quad \text{If you were to burn 240.0 grams of graphite (C, \text{ AW} = 12.00) to produce Carbon Monoxide, what would be the heat change, expressed in KJ?} \]

\[ (240g \text{ C})(\frac{1 \text{ C}}{12.00g \text{ C}})(-\frac{221125}{2} \text{ KJ} / \text{C} ) = -221012.5 \text{ KJ} \]

\[ \text{e)} \quad \text{What is the definition for the Heat of Formation for Carbon Monoxide, CO(g)? Show the appropriate equation.} \]

The heat of formation for CO in the heat of reaction when 1 mole of CO is formed from reactants in their standard states (at S.T.P.)

The reaction: \[ 2 \text{C(graphite)} + \frac{1}{2} \text{O}_2(g) \rightarrow 2 \text{CO(g)} \] so for 1 mole:

\[ \text{C(graphite)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO(g)} \]
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2. (10 pts) OK, so the weather is starting to get nicer, and it's about time, because in those days of cold and ice, you were getting very tired of having to chip ice off your windshield. You even found yourself attracted to an ad for MAGICMELT, a product which was being promoted which would not only free your windshield of ice, it would also clear it from dirt and grease. This sounded so good you bought a bottle and you talked 6 of your friends into each buying a bottle. When you opened the bottle, however, your chemistry knowledge told you that you'd been had (and you had better hope your friends have no chemistry knowledge), because what you smelled was nothing more than the unmistakable aroma of regular ammonia (NH₃, MW = 17.00, specific gravity = 0.987, Kₚ = 1.8 x 10⁻⁷). When you got over your frustration at having been suckered, you read the label more carefully and you noted yes, indeed, the magic ingredient was a 3.40% (by weight) solution of ammonia.

But, having been made suspicious of the whole MAGICMELT corporation, you've decided that maybe you'd better to check to see if they actually are putting in as much ammonia as is stated on the label. You go and collect all 7 bottles and carry out an analysis for ammonia employing your newly-acquired Chem 112 acid/base titration skills. What you obtain as % NH₃ values is the following: 3.38, 3.41, 3.21, 2.86, 3.26, 3.37, and 3.33.

With 95% confidence, can you state whether the MAGICMELT corporation can be held accountable for putting too little ammonia in their product? SHOW ALL YOUR WORK, COMPLETE WITH REASONING, AND STATE YOUR CONCLUSION IN A COHERENT STATEMENT. (A one word “Yes/No” type answer does not communicate and will cause a reduction in credit. I need to see that you understand what you're concluding here).

1. t-test for outliers:

   - Calculations:
     \[ t_{calc} = \frac{3.21 - 2.86}{3.41 - 2.86} = \frac{0.35}{0.55} = 0.636 \]

2. \[ t_{table}(n=7) = 1.569 \leq 2.86 \text{ value in to be discarded} \]

   - Using the other 6 values:
     \[ \bar{x} = 19.46, \bar{x} = 66.43, \bar{n} = 6 \]
     \[ t = 3.33, s = 0.07711, t(\bar{n}=6) = 2.571 \]

3. \[ t_{calc} = \frac{t(s_0)}{s} = \frac{(2.571)(0.07711)}{\sqrt{6}} = 0.081 < 0.08 \]

95% Confidence is 3.33 ± 0.08 = 3.25 ≤ 3.41

Conclusion: the 0.147 3.40 falls within the 95% Confidence Interval in no way to state, with 95% confidence, that the value of 3.33 is different from the stated value of 3.40, as the difference could be explained away by random error. Failing to find a real effect, conclude that there is not too little NH₃ in MAGICMELT.
3. (14 pts) In a solution whose volume is 100.0 mL is to be found the following: 2.0 mmole of HCl (MW = 36.50) and 1.0 mmole of Acetic Acid, HOAc (MW = 60.00, \( pK_a = 4.74 \))

You have on hand as much 0.10 M NaOH solution as you need and you are planning on reacting the acid mixture with the NaOH solution until no more Acid/Base reaction occurs.

**NOTE:** this space for setting up the pH line if you decide it's a good idea.

\[
\begin{align*}
\text{100 mL} & \quad \text{2.0 mmol HCl} \\
& \quad \text{1.0 mmol HOAc}
\end{align*}
\]

a) How much NaOH solution, in mL, will be needed to complete all the A/B reactions that can occur?

To react all 3.0 mmoles/acid you will need 3.0 mmoles OH

\[
\frac{3.0}{0.10} = 30 \text{ mL}
\]

b) If you were to consider adding the NaOH employing a titration strategy, show whether or not this system could be titrated, and if it can, what the resulting titration curve would look like.

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\[
\begin{align*}
\text{N.B. curve will not be flat. You titrate a strong acid} \\
\text{2.41 pH at 180 mL}
\end{align*}
\]

c) If you decide that a titration is possible, determine the pH values for any equivalence points that would show up during the course of the titration. Make clear your reasoning through this whole process. Simply writing down numbers won’t be enough. I need to see how you’ve thought your way through this problem.

at the 1st p. (comes at 20 mL vol) you have 1.00 mmole HOAc in a vol of 100+20 = 120 mL. This is an \( x^2 = K_a \) calculation

\[
K_a = 1.8 \times 10^{-5} \implies x = [\text{H}_3\text{O}^+] = 3.89 \times 10^{-4} \implies \text{pH} = 3.41
\]

When you begin titrating the HOAc at 25 mL you have an \( x^2 = K_a \) calculation

\[
\text{at the 1st equivalence pt. pH = 4.17}
\]

at the 2nd eq. Point you have 1.0 mmole DAc in 130 mL total

\[
K_a = 4.17 \implies K_b = 9.26 \implies K_b = 10^{-5.14}
\]

So \( K_b = 5.56 \times 10^{-10} = \frac{x^2}{130} \implies x = [\text{OH}^-] = 2.07 \times 10^{-5} \implies \text{pH} = 5.68 \implies \text{pOH} = 8.32
\]
4. (18 pts) We've said in class that the phosphoric acid system (H₃PO₄, MW = 98.00, pK₁ = 2.12, pK₂ = 7.21, pK₃ = 12.33) is often used to prepare buffer solutions. 

NOTE: this space for setting up the pH line if you decide it’s a good idea.

a) Suppose you are told you wish to prepare a buffer solution with the pH value of 7.50. Which member or members of the phosphoric acid family do you use in preparing this buffer?

At pH = 7.50 you need H₂PO₄⁻ and HPO₄²⁻, the HPO₄²⁻ will be present in greater amount.

b) If you decide more than one component of the phosphoric acid family is needed, what will be the ratio of the components you choose?

\[
7.50 = 7.21 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \rightarrow \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{1}{1.95} = 0.5129
\]

\[
0.29 = \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \rightarrow \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.29} = 1.95
\]

c) Which member of the Phosphoric Acid family will be present in greatest amount? 

What is the % of this member present?

\[
\%	ext{ HPO}_4^{2-} = \frac{\sum [\text{HPO}_4^{2-}]}{\sum [\text{H}_2\text{PO}_4^-] + \sum [\text{HPO}_4^{2-}]} = 0.5129
\]

\[
\%	ext{ HPO}_4^{2-} = \frac{1}{1.5129} = 66.1%	ext{ HPO}_4^{2-}
\]

d) Suppose you are told that the sum of the buffer components needs to add up to a total molarity of 0.5 M. What would be the concentrations of the buffer components needed to prepare your desired buffer?

\[
\frac{1}{0.5} \times \frac{x}{1.95 - x} = 1.95 \rightarrow x = 0.975 - 1.95x \\
2.95x = 0.975 \rightarrow x = 0.33 M = [\text{HPO}_4^{2-}] \\
0.5 - x = 0.17 M = [\text{H}_2\text{PO}_4^-]
\]

e) What would be the buffer capacity of the buffer solution in step (d) above toward added base?

\[
8.50 = 7.21 + \log \frac{(0.33 + x)}{(0.17 - x)}
\]

\[
1.29 = \log \frac{(0.33 + x)}{(0.17 - x)} \rightarrow \frac{(0.33 + x)}{(0.17 - x)} = 10^{1.29} = 19.5x \\
19.5x = 0.33 + x \rightarrow 19.5x - x = 0.33 + x \rightarrow 18x = 0.33 + x \rightarrow x = 0.1455 \rightarrow 0.15M
\]

Pledge: I have neither given nor received any unacknowledged aid on this test.