

NAME: _____

DATE: _____

There are 23 questions totaling 106.5 points (scored out of 100 pts). PLEASE look over the entire examination (12 pages, plus reference/scratch paper) BEFORE you begin to ensure your packet is complete. REMEMBER: The best place to start your exam may not be at the beginning! You have 2.75 hours to complete this examination and may only use a basic scientific calculator, the resource sheet and the periodic table provided. When specified, all work must be shown for credit AND all answers must be expressed with the proper amount of significant figures. Please sign the honor code at the end of the document, when complete. A scratch sheet will be provided by the instructor; please staple when you submit your exam. If you need further clarification, please speak with the instructor.

****I certify that the work presented in this examination is my own and that the rules set-forth for this exam were followed.***

Signature: _____

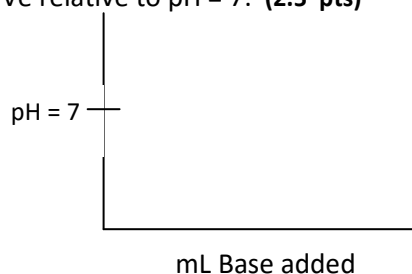
Please answer all exam questions. For Questions 1-16, unless otherwise stated, each blank/response is worth 1.5 pts. For Questions 17-21, all points are clearly labeled on each problem.

1. Determine the sign of ΔS_{sys} for each process:

Process	Sign of ΔS_{sys}
Dew forming	
Ammonium nitrate dissolves spontaneously and endothermally.	

2. True or False ? (circle one) High temperature conditions encourage a spontaneous reaction when ΔG° is positive.
3. At equilibrium, $\Delta G_{\text{rxn}} =$ _____. If ΔS_{univ} is negative, the sign of $\Delta G_{\text{rxn/sys}}$ is _____.
4. True or False ? (circle one) Low temperature conditions encourage a spontaneous reaction when entropy is favored and enthalpy is not favored.
5. In general, ionic compounds with small K_{sp} values have high or low (circle one) concentrations of dissolved ions in pure water. (2 pts)
6. If a reaction has a negative enthalpy value and a negative entropy value, which factor dominates: _____
 a. entropy b. enthalpy c. both dominate d. neither dominate
7. A buffer solution contains more weak base than weak acid. The pH of the buffered solution is greater than or less than or equal to (circle one) the pKa of the weak acid. (circle one).
8. For a reaction with an enthalpy = 54.0 kJ and entropy = 99.0 J/K, ΔG° at 25.0 °C = _____. (2.5 pts)
 This temperature range would yield **spontaneous** reaction: _____ (2.5 pts)
9. To ensure a K value that wildly favors products, the optimal ΔG° value would have a positive or negative sign, and be a small or large numeric value.

10. A student is considering making a buffer solution containing nitrous acid and sodium nitrite. The effective buffering pH range of this buffered solution is _____ to _____. (2 pts)
11. Which of the following reagents (HCl, CaS and NaCl) would INCREASE the solubility of CaF_2 ? (2 pts)
- _____
12. Consider three solutions: (a) 0.10 M weak monoprotic acid, (b) 0.10 M strong monoprotic acid, (c) 0.10 M diprotic acid. Each solution is titrated with 0.15 M NaOH. Which quantity is the same for all three solutions? Letter(s): _____
- The volume required to reach the final equivalence point.
 - The volume required to reach the first equivalence point.
 - The pH at the first equivalence point.
 - None of these are the same for all 3 solutions.
13. Rank the following in order of from highest to lowest standard molar entropy (S°): (3 pts)
- a. PCl_5 vapor b. water solid c. water vapor d. water liquid
- _____
- _____ \longrightarrow **Lowest S°**
14. Consider the reaction below, at 25 °C for the following questions. Without doing any calculations, the sign of $\Delta G^\circ_{\text{rxn}} =$ _____ $\text{CO}_2(g) \longrightarrow \text{C}(s) + \text{O}_2(g)$ $\Delta H = \text{endothermic}$
15. The mixture(s) below, dissolved in 1 L of water, that result in a buffer solution is/are (letters): _____. The solution that is the most effective buffer is solution (letter) _____ (4.5 pts total).
- 0.30 mol KCl and 0.15 mol HCl
 - 0.20 mol $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.10 mol NaOH
 - 0.90 mol $\text{HC}_2\text{H}_3\text{O}_2$ and 0.10 mol NaOH
 - 0.20 mol $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.40 mol HCl
16. Two monoprotic acids solutions (A and B) are titrated with identical NaOH solutions. The volume to reach the equivalence point for Solution A is twice the volume of required to reach the equivalence point for Solution B.
- The lower concentrated acid solution is: _____ (2.5 pts)
 - Sketch the titration curve for the titration of a weak acid with a strong base (titrant). Please be sure to accurately position V_e relative to $\text{pH} = 7$. (2.5 pts)



17. A student collects equilibrium K values at various temperatures for a reaction. They graph $\ln K$ vs. $(1/T)$ and the graph yields the following equation of the line : $y = -6.78 \times 10^4 x + 555$. The standard enthalpy value for the reaction is _____ (include units). Is this reaction spontaneous at all temperatures? _____ (5 pts total; 2.5 pts each)

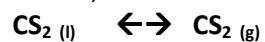
18. If the molar solubility of AlCl_3 is $2.44 \times 10^{-3} \text{ M}$ at 45°C , the K_{sp} at 45°C is _____.
Show all work for credit. (5 pts)

19. Solutions containing NaOH and $\text{Cu}(\text{NO}_3)_2$ are mixed. What precipitate can form? _____ (1.5 pts).
If the $[\text{Cu}(\text{NO}_3)_2] = 2.3 \times 10^{-8} \text{ M}$ and $[\text{NaOH}] = 1.9 \times 10^{-6} \text{ M}$, does a precipitate form? _____
Show your work for credit. (3.5 pts)

20. Determine the *molar solubility* of $\text{Ca}(\text{OH})_2$ in a solution **buffered to pH = 13.5**. (5 pts)

21. A 500.0 mL buffer solution initially contains 0.050 mol of HCHO_2 and 0.050 mol of NaCHO_2 . In order to adjust the buffer pH to 4.10, should you add NaOH or HCl to the buffer? **What mass of the correct reagent should you add?** (8 pts)

22. Carbon disulfide (CS_2) is a toxic, flammable substance. Consider the vaporization of CS_2 below. (19 pts total)



a. Calculate the $\Delta S^\circ_{\text{universe}}$ for this reaction at 25°C. Show all work for credit. (15 pts)

b. Is the reaction exothermic? _____ Is the reaction spontaneous at 25°C? _____ (3 pt total)

c. Calculate the partial pressure of CS_2 (P_{CS_2}) at equilibrium, at 25°C. (4 pts)

23. A 30.00-mL sample of 0.165 M propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$ is titrated with 0.300 M KOH. Calculate the pH of the solution after the following KOH additions are delivered to titration flask: **0.00, 8.25, 12.50, 16.50, and 25.00 mL**. For pH calculations, you DO NOT have to show work if $\text{pH} = \text{pKa}$, but you **MUST SHOW WORK FOR ALL titration calculations**. (15 pts total)

a. What is the pH after 0.00 mL of 0.300 M KOH is added? (3 pts)

23, cont. A 30.00-mL sample of 0.165 M propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$ is titrated with 0.300 M KOH.

b. What is the pH after 8.25 mL of 0.300 M KOH is added? ? (3 pts)

c. What is the pH after 12.50 mL of 0.300 M KOH is added? ? (3 pts)

23, cont. A 30.00-mL sample of 0.165 M propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$ is titrated with 0.300 M KOH.

d. What is the pH after 16.50 mL 0.300 M KOH is added? ? (3 pts)

e. What is the pH after 25.00 mL of 0.300 M KOH is added? ? (3 pts)

NAME _____

Reference Sheet:

$$[H^+][OH^-] = 1 \times 10^{-14}$$

$$pH = -\log [H_3O^+]$$

$$pH = pK_a + \log [A^-]/[HA]$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{surr} = -\Delta H_{rxn} / T$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q \quad \text{where } R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\Delta G^\circ_{rxn} = -RT \ln K$$

$$\ln K = [(-\Delta H^\circ_{rxn}/R) (1/T)] + (\Delta S^\circ_{rxn}/R)$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Dissociation Constants for Acids at 25 °C

Substance	Formula	K _{a1}	K _{a2}	K _{a3}
Acetic Acid	HC ₂ H ₃ O ₂	1.8 x 10 ⁻⁵		
Nitrous Acid	HNO ₂	4.6 x 10 ⁻⁴		
Propanoic acid	HC ₃ H ₅ O ₂	1.3 x 10 ⁻⁵		
Formic Acid	HCHO ₂	1.8 x 10 ⁻⁴		

Dissociation Constants for Bases at 25 °C

Substance	Formula	K _b
Ammonia	NH ₃	1.76 x 10 ⁻⁵
Nicotine	C ₁₀ H ₁₄ N ₂	1.0 x 10 ⁻⁶

Solubility Product Constants for Compounds at 25 °C

Substance	Formula	K _{sp}
Copper(II) hydroxide	Cu(OH) ₂	2.2 x 10 ⁻²⁰
Magnesium hydroxide	Mg(OH) ₂	2.06 x 10 ⁻¹³
Nickel (II) hydroxide	Ni(OH) ₂	5.48 x 10 ⁻¹⁶
Zinc (II) hydroxide	Zn(OH) ₂	3 x 10 ⁻¹⁷
calcium hydroxide	Ca(OH) ₂	7.2 x 10 ⁻¹⁵
Calcium phosphate	Ca ₃ (PO ₄) ₂	2.07 x 10 ⁻³³

Select Thermodynamic Values for Compounds at 25 °C

Substance	ΔH _f ^o (kJ/mol)	ΔG _f ^o (kJ/mol)
CS ₂ (l)	89.7	65.3
CS ₂ (g)	117.4	67.2