MULTIPLE CHOICE – three (3) points each.

1. Which of the following statements is **true**?

a) For an endothermic reaction, the value of the equilibrium constant K increases as the temperature increases.

b) For a reaction at equilibrium, if the volume of the reaction container increases, the reaction must shift to the right to reestablish equilibrium.

c) Liquids are sometimes included in the K expression for a reaction.

d) At equilibrium, the rate of the forward reaction and the rate of the reverse reaction both equal zero.

e) Reactions that have mostly reactants at equilibrium with very little products present have large K values.

2. Consider the reaction of ethane with F_2:

$$C_2H_4(g) + 6\ F_2(g) \rightarrow 2\ CF_4(g) + 4\ HF(g) \qquad \Delta H_1 = ?$$

Assume the enthalpy change for the above reaction is ΔH_1. Using the following reactions and their enthalpy changes, one can construct a thermochemical cycle to determine ΔH_1.

$$H_2(g) + F_2(g) \rightarrow 2\ HF(g) \qquad \Delta H_2$$

$$C(s) + 2\ F_2(g) \rightarrow CF_4(g) \qquad \Delta H_3$$

$$2C(s) + 2\ H_2(g) \rightarrow C_2H_4(g) \qquad \Delta H_4$$

Which of the following expressions for ΔH_1 is correct?

a) $\Delta H_1 = 2\ \Delta H_2 - \Delta H_4 + 2\ \Delta H_3$

b) $\Delta H_1 = 2\ \Delta H_2 - 2\ \Delta H_4 + \Delta H_3$

c) $\Delta H_1 = \Delta H_3 + \Delta H_2 - 2\ \Delta H_4$

d) $\Delta H_1 = 6\ \Delta H_2 + 2\ \Delta H_3 - \Delta H_4$

e) $\Delta H_1 = \Delta H_4 - \Delta H_2 - \Delta H_3$

3. 100 mL of water is placed in a coffee cup calorimeter. When 1.0 g of a soluble ionic solid is added, the temperature increases from 21.5°C to 24.2°C as the solid dissolves. For the dissolving process, what are the correct signs for ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}?

	ΔS_{sys}	ΔS_{surr}	ΔS_{univ}
a)	–	–	–
b)	+	+	–
c)	+	–	+
d)	+	+	+
e)	–	–	+

4. For which process is $\Delta S°$ expected to be positive?

a) $I_2(g) \rightarrow I_2(s)$

b) $H_2O(l) \rightarrow H_2O(s)$

c) $CH_3OH(g) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

d) $O_2(g) + 2\ CO(g) \rightarrow 2\ CO_2(g)$

e) $N_2(g)$ at 2 atm $\rightarrow$ $N_2(g)$ at 1 atm (Assume constant T and n.)

5. A spontaneous chemical reaction is favored by which of the following?

a) increasing enthalpy and increasing entropy
b) decreasing enthalpy and increasing entropy
c) increasing enthalpy and decreasing entropy
d) decreasing enthalpy and decreasing entropy

6. Which of the following always describes a process at equilibrium?

a) $\Delta G = 1$ b) $\Delta H = T\Delta S$ c) $Q = 1$ d) $\Delta G = \Delta G°$ e) $K = 1$

7. Which of the following statements is **false**?

a) The equilibrium position represents the lowest free energy state available to a reaction.
b) Chemical reactions want to minimize free energy.
c) If the free energy of reactants is lower than the free energy of products, then the reverse reaction is spontaneous.
d) The value of the free energy change for a reaction is dependent on the temperature.
e) The process $H_2O(l) \rightarrow H_2O(g)$ is spontaneous at all temperatures and partial pressures of $H_2O(g)$.

8. Consider the following reaction at 298 K:

$$2\ HBr(g) + Cl_2(g) \rightarrow 2\ HCl(g) + Br_2(g) \qquad \Delta G° = -81.0\ kJ$$

Calculate ΔG at 298 K for this reaction at the following initial partial pressures.

$P_{HBr} = 1.00$ atm $P_{HCl} = 0.500$ atm $P_{Cl_2} = 5.00$ atm $P_{Br_2} = 0.200$ atm

a) –69.6 kJ b) –71.3 kJ c) –81.9 kJ d) –90.6 kJ e) –92.4 kJ

9. For a reaction at some initial concentrations and temperature, $Q > K$. Which of the following relationships must be **true** regarding this reaction at these conditions?

a) $\Delta G = 0$ b) $\Delta G° = 0$ c) $\Delta G > 0$ d) $K < 0$ e) $\Delta G < 0$

10. Which of the following indicates the **most acidic** solution?

a) pH = 1.2 b) $[H^+] = 1 \times 10^{-4}\ M$ c) $[H^+] = 0.3\ M$

d) pOH = 5.9 e) $[OH^-] = 0.5\ M$

11. The pOH of a sample of baking soda dissolved in water is 5.74 at 25ºC. Calculate the $[H^+]$ in this baking soda solution.

a) $1.0 \times 10^{-7}\ M$ b) $5.5 \times 10^{-9}\ M$ c) $1.8 \times 10^{-6}\ M$

d) $1.9 \times 10^{-9}\ M$ e) $6.2 \times 10^{-6}\ M$

12. How many of the following statements (I-IV) about a 1.0 M solution of weak acid is/are **true**?

I. As the K_a value increases, the pH of the solution decreases.
II. As the K_a value increases, the percent dissociation of the acid increases.
III. As the K_a value increases, the K_b value of the conjugate base decreases.
IV. As the K_a value increases, the $[H^+]$ in solution increases.

a) 0 (none) b) 1 c) 2 d) 3

e) 4 [All of the statements (I-IV) are true.]

13. Which of the following statements (a-d) is **false**?

a) The pH of a 10. *M* solution of KOH is 15.00.

b) The pH of a 1.0×10^{-12} *M* solution of HCl is 7.00.

c) The pH of a 0.20 *M* solution of $Ba(OH)_2$ is 13.30.

d) The pH of a 10. *M* solution of HCl is –1.00.

e) None of the above statements (a-d) is false.

14. Consider a 0.10 *M* solution of a weak acid HA. If pH = 3.00 for this solution, determine the equilibrium concentration of the conjugate base ($[A^-]$ = ?).

a) 1.0×10^{-4} *M* b) 1.0×10^{-3} *M* c) 1.0×10^{-2} *M* d) 1.0 *M* e) 1.0×10^{-5} *M*

15. What is the pH of a 0.015 *M* solution of aniline, $C_6H_5NH_2$? K_b for $C_6H_5NH_2$ is 3.8×10^{-10}.

a) 11.24 b) 7.00 c) 8.38 d) 2.76 e) 5.62

16. Arrange 0.10 *M* solutions of the following compounds by **increasing** pH:

$HC_2H_3O_2$ HCN $H_2NNH_3ClO_4$ NH_3

a) $HC_2H_3O_2 < H_2NNH_3ClO_4 < HCN < NH_3$
b) $HCN < HC_2H_3O_2 < H_2NNH_3ClO_4 < NH_3$
c) $HC_2H_3O_2 < HCN < NH_3 < H_2NNH_3ClO_4$
d) $HCN < HC_2H_3O_2 < NH_3 < H_2NNH_3ClO_4$
e) $H_2NNH_3ClO_4 < NH_3 < HCN < HC_2H_3O_2$

17. Which of the following reactions is **correctly** identified with the appropriate equilibrium constant?

a) $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$
K_a reaction for C_5H_5N

b) $NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$
K_b reaction for NH_3

c) $H_3O^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + H_2O(l)$
K_b reaction for H_3O^+

d) $HC_3H_5O_2(aq) + H_2O(l) \rightleftharpoons C_3H_5O_2^-(aq) + H_3O^+(aq)$
K_a reaction for $HC_3H_5O_2$

18. H_2CO_3 and H_2SO_4 are both diprotic acids. For H_2CO_3, $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 5.6 \times 10^{-11}$. For H_2SO_4, $K_{a_1} >> 1$ and $K_{a_2} = 1.2 \times 10^{-2}$. Which of the following statements concerning a 0.10 *M* H_2CO_3 solution and a 0.10 *M* H_2SO_4 solution is **true**?

a) The $[H^+]$ in the 0.10 *M* H_2CO_3 solution will be greater than the $[H^+]$ in the 0.10 *M* H_2SO_4 solution.

b) The $[H^+]$ in the 0.10 *M* H_2SO_4 solution will be less than 0.10 *M* ($[H^+] < 0.10$ *M*).

c) At equilibrium, the $[SO_4^{2-}]$ will be greater than the $[CO_3^{2-}]$ ($[SO_4^{2-}] > [CO_3^{2-}]$).

d) The pH of the 0.10 *M* H_2CO_3 solution will be less than 1.0 (pH < 1.0).

e) At equilibrium, $[H_2SO_4] > [HSO_4^-]$ in the 0.10 *M* H_2SO_4 solution.

19. Consider separate 0.25 *M* solutions of the following three salts:

KNO_2, $(C_2H_5)_3NHNO_3$, $(C_2H_5)_3NHNO_2$

Rank the three salt solutions in order of **increasing** pH (most acidic to most basic).
[K_a for $HNO_2 = 4.0 \times 10^{-4}$ and K_b for $(C_2H_5)_3N = 4.0 \times 10^{-4}$].

a) $(C_2H_5)_3NHNO_2 < KNO_2 < (C_2H_5)_3NHNO_3$

b) $KNO_2 < (C_2H_5)_3NHNO_3 < (C_2H_5)_3NHNO_2$

c) $KNO_2 < (C_2H_5)_3NHNO_2 < (C_2H_5)_3NHNO_3$

d) $(C_2H_5)_3NHNO_3 < KNO_2 < (C_2H_5)_3NHNO_2$

e) $(C_2H_5)_3NHNO_3 < (C_2H_5)_3NHNO_2 < KNO_2$

20. A chemist wishes to prepare a buffer at pH = 3.5 and has the following acids available, along with the potassium salts of their conjugate bases. Which acid/salt combination is the best choice for preparing the buffer?

a) $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$)/$KC_2H_3O_2$
b) HOCl ($K_a = 3.5 \times 10^{-8}$)/KOCl
c) HNO_2 ($K_a = 4.0 \times 10^{-4}$)/KNO_2
d) HCN ($K_a = 6.2 \times 10^{-10}$)/KCN
e) $HClO_2$ ($Ka = 1.2 \times 10^{-2}$)/$KClO_2$

21. Consider a buffer solution containing NaF and HF. Which of the following statements is **false**?

a) If $[F^-]$ = [HF], then the pH of the solution equals the pK_a value for HF.
b) If $[F^-]$ > [HF], then the pH of the solution is greater than the pK_a value for HF.
c) If [HF] > $[F^-]$, then the $[H^+]$ of the solution is greater than the K_a value for HF.
d) If HCl is added to the buffer, then the $[F^-]$ of the resulting solution should increase.
e) If NaOH is added to the buffer, then the pH of the resulting solution should increase.

22. Five different bases, all with the same initial concentration and volume, are each titrated with 0.1 *M* HNO_3. Which base titration has the **lowest** pH at the equivalence point?

a) CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$)
b) NH_3 ($K_b = 1.8 \times 10^{-5}$)
c) C_5H_5N ($K_b = 1.7 \times 10^{-9}$)
d) $C_6H_5NH_2$ ($K_b = 3.8 \times 10^{-10}$)
e) NaOH

23. Four different bases all with the same initial concentration and volume are each titrated with 0.1 *M* HNO_3. Which base titration has the **highest** pH at the halfway point to equivalence?

a) CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$)
b) NH_3 ($K_b = 1.8 \times 10^{-5}$)
c) C_5H_5N ($K_b = 1.7 \times 10^{-9}$)
d) $C_6H_5NH_2$ ($K_b = 3.8 \times 10^{-10}$)

Consider the titration of 30.0 mL of 0.30 *M* HCN by 0.10 *M* KOH for the next five questions.
K_a for HCN = 6.2×10^{-10}.

24. Calculate the pH when 0.0 mL of KOH has been added.

a) 9.73 b) 4.27 c) 3.61 d) 4.87 e) 5.29

25. Calculate the pH after 15.0 mL of KOH has been added.

a) 9.21 b) 8.51 c) 12.50 d) 7.70 e) 9.91

26. Calculate the pH after 45.0 mL of KOH has been added.

a) 8.30 b) 10.11 c) 9.09 d) 4.79 e) 9.21

27. Calculate the pH at the equivalence point in this titration.

a) 11.04 b) 10.33 c) 12.08 d) 8.83 e) 7.00

WRITTEN OUT PROBLEMS – Show all work for partial credit.

28. Consider the following reaction and data:
(12 pts.)

$$2\ SO_2(g)\ +\ O_2(g) \rightarrow 2\ SO_3(g)$$

Compound	$\mathbf{\Delta H_f^o}$	**S°**
$SO_3(g)$	–396 kJ/mol	257 J/K•mol
$SO_2(g)$	–297 kJ/mol	248 J/K•mol
$O_2(g)$	?	205 J/K•mol

a) Calculate the value of ΔG° for the reaction at 25°C.

b) Assuming ΔH° and ΔS° are temperature independent, calculate the temperatures at which this reaction is spontaneous (assuming all gases are at 1 atm).

c) At standard conditions, this reaction is allowed to react to reach equilibrium. If, at equilibrium, the partial pressures of $O_2(g)$ and $SO_3(g)$ are 0.50 atm and 2.0 atm respectively, calculate the equilibrium partial pressure of $SO_2(g)$. Note: T = 25°C

29. Consider the following equilibrium constant vs. temperature data for some reaction:
(7 pts)

K	Temp
2.54×10^4	109°C
5.04×10^2	225°C
6.33×10^1	303°C
2.25×10^{-1}	412°C
3.03×10^{-3}	539°C

a) Is this reaction spontaneous at standard concentrations and T = 25°C? Explain.

b) Predict the signs of $\Delta H°$ and $\Delta S°$ for the reaction. Explain.

30. The gas arsine, AsH_3, decomposes by the following reaction:
(8 pts)

$$2\ AsH_3(g) \rightleftharpoons 2\ As(s) + 3\ H_2(g)$$

In an experiment, pure $AsH_3(g)$ of unknown initial concentration is placed into a 2.0 L container. After equilibrium is reached, 6.0 moles of $H_2(g)$ is produced and 12.0 moles of $AsH_3(g)$ is also present. Determine the initial concentration of $AsH_3(g)$ before the reaction took place ($[AsH_3]_{initial}$ = ?). Also, calculate the value of the equilibrium constant for this reaction (K = ?). Show all work for credit.

31. A 0.10 *M* solution of the salt NaX has a pH of 11.50. Calculate the pH of a 1.0 *M* solution of HX.
(6 pts)

32. Consider 1.0 L of a solution composed of 1.60 *M* $HONH_2$ ($K_b = 1.1 \times 10^{-8}$) and 0.80 *M* $HONH_3NO_3$.

(8 pts)

a) Calculate the pH of this solution.

b) In order for this 1.0 L of solution to have pH = pK_a, would you add HCl or KOH? What quantity (moles) of HCl or KOH would you add to the solution in order to get pH = pK_a?

33. Consider the titration of 200.0 mL of 0.10 *M* HNO_3 titrated by 0.10 *M* $Ca(OH)_2$. Sketch the titration curve for this titration. On your plot, label the axis and indicate the pH and volume of the equivalence point. Also indicate the initial pH before any $Ca(OH)_2$ has been added as well as the pH at 150.0 mL of $Ca(OH)_2$ added.

(9 pts)