Exam III Crib – CHM 152/154 – Fall 2005 – Dr. Smith – Form B

1. The Third Law of Thermodynamics states that:
   a. Energy cannot be created nor destroyed.
   b. Matter cannot be created nor destroyed.
   c. The entropy of a perfect crystalline solid at zero Kelvin is zero.
   d. The entropy of the universe is increasing.
   e. The entropy of an equilibrium process is zero.

2. Calculate ΔG^o_{rxn} at 25°C for this reaction: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ Given: ΔG^o_f for MgO(s) = -456.0 kJ/mol

Products – reactants
2(-456.0 kJ/mol) – (0) = -912.0 kJ/mol
Remember that ΔG^o_f for elements is zero.

3. Calculate ΔG^o_{rxn} at 25°C for this reaction: $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$. Given: ΔH^o_{rxn} = 128.9 kJ/mol and ΔS^o_{rxn} = 321 J/K·mol

ΔG^o_{rxn} = 128.9 kJ/mol – (298 K)(0.321 kJ/molK) = 33.2 kJ/mol

4. Calculate the equilibrium constant for a reaction that has ΔG^o_{rxn} = +2.34 kJ/mol.

2.34 kJ/mol (1000 J/kJ) = (-8.314 J/molK)(298 K) ln K
Ln K = -0.944447
K = 0.389

5. Which of the following reactions will result in an increase in entropy? (ΔS is +)
   a. $H_2O(g) \rightarrow H_2O(l)$
   b. $SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g)$
   c. $2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$
   d. Fe(s) at 50°C → Fe(s) at 0°C
   e. $3O_2(g) \rightarrow 2O_3(g)$

6. Calculate ΔS^o_{rxn} for the following reaction: $4\ Cr(s) + 3\ O_2(g) \rightarrow 2\ Cr_2O_3(s)$. Given: S^o for Cr(s) is 23.77 J/molK, S^o for $O_2(g)$ is 205.14 J/molK and S^o for $Cr_2O_3(s)$ is 81.20 J/molK.

ΔS^o_{rxn} = [2(81.20 J/molK)] – [4(23.77 J/molK) + 3(205.14 J/molK)] = -548.1 J/molK

7. The melting of a solid has a positive ΔS and a positive ΔH. This means that:
   a. This phase change is always spontaneous.
   b. This phase change is never spontaneous.
   c. This phase change is spontaneous at high temperatures but not at low temperatures.
   d. This phase change is spontaneous at low temperatures but not at high temperatures.

8. Which of the following, when mixed in water in equal molar amounts, would NOT result in a buffer solution?
   a. KF and HF b. CH_3COOH and $LiCH_3COO$ c. NH_3 and NH_4I **d. HNO_3 and KNO_3**

9. Which of the following statements is true regarding acid base titrations?
   a. The pH at the equivalence point for a strong acid/strong base titration is 7, and for a weak acid/strong base is less than 7.
   b. The pH at the equivalence point for a strong acid/strong base titration is 7, and for a weak acid/strong base is greater than 7.
   c. The pH at the equivalence point for a strong acid/strong base titration is 7, and for a weak acid/strong base is also 7.
   d. The pH at the equivalence point for a strong acid/strong base titration less than 7, and for a weak acid/strong base is greater than 7.
   e. The pH at the equivalence point for a strong acid/strong base titration is greater than 7, and for a weak acid/strong base is less than 7.

10. The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of PbI_2.

PbI_2 (s) ⇆ Pb^{2+}(aq) + 2 I^- (aq)

$K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
$1.4 \times 10^{-8}. = 4x^3$
$x = 1.5 \times 10^{-3}$ mol/L

11. The K_{sp} for barium sulfate is 1.1×10^{-10}. If 0.175 grams of barium sulfate is placed into 1.00 L of water:
   a. the solution is saturated and a precipitate forms.
   b. the solution is unsaturated.
   c. the solution is saturated but a precipitate does not form.
   d. all 0.175 grams sink to the bottom as barium sulfate is insoluble.
   e. the solution is unsaturated and a precipitate forms.

$BaSO_4$(s) ⇆ Ba^{2+}(aq) + SO_4^{2-}(aq)

0.175 g (mol / 233.36g) / 1.00L = 7.50×10^{-5} M
$x = 7.50 \times 10^{-5}$ M
$Q = x^2 = 5.62 \times 10^{-9}$
$Q > K_{sp}$

12. Which of the following reactions would have an equilibrium constant of K_f?
   a. $H_2PO_4^-$(aq) + H_2O(l) ⇆ HPO_4^{2-}(aq) + H_3O^+(aq)
   b. NH_3(aq) + H_2O(l) ⇆ NH_4^+(aq) + OH^-(aq)
   c. $2O_3$(g) ⇆ $3O_2$(g)
   d. Co^{3+}(aq) + 6 NH_3(aq) ⇆ $Co(NH_3)_6^{3+}$ (aq)
   e. $Ca_3(PO_4)_2$ ⇆ 3 Ca^{2+} (aq) + 2 PO_4^{3-}(aq)

13. Calculate the pH of a buffer solution that contains 0.15M H_3PO_4 and 0.033M NaH_2PO_4. Given: K_a for H_3PO_4 is 7.5×10^{-3}.

$pK_a = 2.125$
pH = 2.125 + log (0.033 / 0.15) = 1.47

14. Consider this acid dissociation equation: $HCOOH \leftrightarrows H^+ + HCOO^-$. What will happen if NaHCOO is added to an aqueous formic acid (HCOOH) solution?
    a. The reaction will shift to the left increasing the acid dissociation and the pH will decrease.
    b. The reaction will shift to the right increasing the acid dissociation and the pH will increase.
    c. The reaction will shift to the left decreasing the acid dissociation and the pH will increase.
    d. The reaction will shift to the right decreasing the acid dissociation and the pH will decrease.
    e. The reaction will shift to the left decreasing the acid dissociation and the pH will decrease.

15. Calculate the pH when 25.0 mL of 0.100M HCl has been titrated with 13.5 mL of 0.120M KOH.

Beginning moles HCl is 0.0025 and KOH is 0.00162
Once reacted moles HCl is 0.00088 and KOH is all gone, note volume is 25.0 + 13.5 mL now
$[H^+]$ = 0.00088mol / 0.0385L = 0.022857
pH = -log H^+ = 1.64

16. Which of the following is more soluble in acidic solution?
    a. **$Ca(OH)_2(s)$** b. LiBr(s) c. $NaNO_3(s)$ d. $NH_4Cl(s)$ e. $CaSO_4(s)$

17. When electrical energy from an external source is used to force a reaction to go in the non-spontaneous direction the cell is called a _____ cell.
    a. **electrolytic** b. galvanic c. voltaic d. concentration e. fuel

18. Which of the following batteries is used in most automobiles?
    a. mercury **b. lead storage** c. fuel d. dry cell e. lithium

19. What is the oxidizing agent in this reaction? 2 Na(s) + 2 **HCl(aq)** → 2 NaCl(aq) + $H_2(g)$

H in HCl goes from +1 to zero in H_2 (g). So it is reduced, thus the ox agent.

20. Calculate the standard Gibb's free energy for this galvanic cell: Ni(s) | Ni^{2+} || Au^{3+} | Au(s).

E^o_{cell} = 0.25 + 1.50 = 1.75 V
ΔG^o = -(6 mol e)(96500 J/Vmol e)(kJ/1000 J)(1.75 V) = -1010 kJ

21. Consider this electrochemical cell: Ag(s) |$AgNO_3$(0.01 M) || $AgNO_3$(1.5 M) | Ag(s). Which of the following statements is true?
    a. Electrons will flow from left to right, causing a decrease in the $AgNO_3$ concentration in the left cell, and an increase in the $AgNO_3$ concentration in the right cell.
    b. Electrons will flow from right to left, causing an increase in the $AgNO_3$ concentration in the left cell, and a decrease in the $AgNO_3$ concentration in the right cell.
    c. Electrons will flow from left to right, causing an increase in the $AgNO_3$ concentration in the left cell, and a decrease in $AgNO_3$ concentration in the right cell.
    d. Electrons will flow from right to left, causing a decrease in the $AgNO_3$ concentration in the left cell, and an increase in the $AgNO_3$ concentration in the right cell.
    e. There will be no electron flow because the reduction potential at both electrodes is the same.

22. Calculate the cell potential at 25°C for a galvanic cell made of solid Be in $Be(NO_3)_2$ solution and solid Cr in $Cr(NO_3)_3$ solution if $[Be(NO_3)_2]$ = 0.97M and $[Cr(NO_3)_3]$ = 0.12M.

E^o_{cell} = 1.85 + 0.74 = 2.59 V

The overall cell rxn is $3\ Be^{2+} + 2\ Cr(s) \rightarrow 3Be(s) + 2Cr^{3+}$ *thus n = 6 electrons*
$E = 2.59 - [\ (8.314\ J/molK)(298K) / (6\ mol\ e)(96500\ J/Vmol\ e)\ ]\ \ln (0.12^2 / 0.97^3) = 2.61\ V$

23. A galvanic cell is constructed from a Fe electrode in 1.0 M $Fe(NO_3)_2(aq)$ and a Ni electrode in 1.0 M $Ni(NO_3)_2$. Which statement is true?
    a. Ni(s) is the anode
    b. Electrons flow from the iron electrode to the nickel electrode through a wire.
    c. The iron electrode will gain mass.
    d. Negative ions will flow from the salt bridge into the nickel(II) nitrate solution.
    e. Electrons will flow from the anode to the cathode through the salt bridge.

The iron rxn must be reversed and become the oxidation, so iron is the anode and nickel is the cathode.

24. Which of the following is most likely to undergo reduction?
    a. Au(s) **b. $Br_2(l)$** c. Cr(s) d. Cr^{3+} e. Ni^{2+}

25. What is the standard cell potential for a galvanic cell composed of Be(s) in $Be(NO_3)_2$ solution and Pb(s) in $Pb(NO_3)_2$ solution?

Lead is the anode and the oxidation process so the $E^o_{ox} = 0.13V$. Be will be the cathode and the reduction, $E^o_{red} = 1.85V$. So the total cell potential is 1.98V.

Bonus 1: Rubidium has a heat of vaporization of 69.0 kJ/mol and an entropy of vaporization of 71.9 J/molK. Calculate the boiling point of rubidium. *(Hint: what is ΔG during a phase change?)*

$0 = 69.0\ kJ/mol - T(0.0719\ kJ/molK)$
$T = 9.60 \times 10^2\ K$ or 687^oC

Bonus 2: Which of the following when put in water would make an acidic solution?
    a. KF
    b. KCl
    c. NH_4I
    d. $LiHCO_3$
    e. NH_4F

Bonus 3: Calculate the pH when 25.0 mL of 0.155M acetic acid has been titrated with 10.0 mL of 0.100M NaOH. Given K_a for acetic acid is 1.75×10^{-8}.