EXAM THREE
CHM 205 (Dr. Mattson)
23 MARCH 2011

Print your name:
Signature:

Instructions: Show all work whenever a calculation is required! You will receive credit for how you worked each problem as well as for the correct answer. If you need more space, you may use the back of your periodic table — Write: “See PT” in box and then attach the periodic table. BOX YOUR ANSWERS! Write legibly.

Useful acid dissociation constants for this exam:

\[
\begin{align*}
\text{HC}_2\text{H}_3\text{O}_2 &: \quad K_a = 1.8 \times 10^{-5} \quad \text{p}K_a = 4.74 \\
\text{H}_3\text{PO}_4: & \quad K_{a1} = 7.1 \times 10^{-3} \quad \text{p}K_{a1} = 2.15 \\
& \quad K_{a2} = 6.3 \times 10^{-8} \quad \text{p}K_{a2} = 7.20 \\
& \quad K_{a3} = 4.3 \times 10^{-13} \quad \text{p}K_{a3} = 12.37 \\
\end{align*}
\]

1. (4 pts) What is the pH of a 0.20 M NaH$_2$PO$_4$ solution?

2. (4 pts) What is the pH of a solution that is 0.30 M NaH$_2$PO$_4$ and 0.30 M Na$_2$HPO$_4$?

3. (4 pts) What is the numerical value of $K_n$ for the equilibrium:

\[
\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HPO}_4^{2-}
\]

4. (5 pts) Which of the following components when poured together will produce a buffer?

(a) 0.10 mol NaF and 100 mL 1.5 M HF
(b) 100 mL 0.40 M HCN and 50 mL 0.20 M NaOH
(c) 0.25 mol HBr and 0.25 mol NaBr
(d) 15 g NH$_4$Cl and 100 mL 1.0 M NH$_3$
(e) 0.24 mol HCl and 0.50 mol NaNO$_2$

5a. (4 pts) What is the pH of a buffer prepared by mixing 0.250 mol HC$_2$H$_3$O$_2$ with 0.400 mol NaC$_2$H$_3$O$_2$?

5b. (4 pts) Again considering the buffer above, what is the new pH if 0.020 mol NaOH were added?

6. (4 pts) What is the pH of a buffer prepared by mixing 0.500 mol HC$_2$H$_3$O$_2$ with 0.100 mol NaOH?

7a. (1 pt) Does the buffer described in Question 5a have a larger buffer capacity towards the addition of strong acid or strong base?

(a) strong acid
(b) strong base

7b. (1 pt) Does the buffer described in Question 6 have a larger buffer capacity towards the addition of strong acid or strong base?

(a) strong acid
(b) strong base

8. Consider Titration Curves 1, 2, and 3 for HA, HB, and HC, respectively. In each case, 50.00 mL of the weak acid was titrated with 0.1800 M NaOH(aq). These charts are on the data sheet.

8a. (1 pt) Which two weak acids have the same concentration?

HA & HB \quad HA & HC \quad HB & HC

8b. (2 pts) What is the $pK_a$ of HA?

8c. (1 pt) Which pair of acids could possibly be the same weak acid (but not necessarily the same concentration)?

HA & HB \quad HA & HC \quad HB & HC
8d. (3 pts) What is the molar concentration of HA, [HA] in the original sample?

8e. (1 pt) Identify the weakest acid (smallest $K_a$)?
(a) HA  (b) HB  (c) HC  
(d) HA and HB  (e) HA and HC  (f) HB and HC

9. Please refer to Titration Curve 4 on the data sheet. The acid titrated is H$_2$A.

9a. (4 pts) Give values for $pK_{a1}$ and $pK_{a2}$ for H$_2$A.

9b. (5 pts) What are the main species present at each point? Note: in some cases there is one answer and in other cases there is more than one answer.

(i) Point A: H$_2$A  HA$^-$  A$^{-2}$
(ii) Point B: H$_2$A  HA$^-$  A$^{-2}$
(iii) Point C: H$_2$A  HA$^-$  A$^{-2}$
(iv) Point D: H$_2$A  HA$^-$  A$^{-2}$
(v) Point 0*: H$_2$A  HA$^-$  A$^{-2}$

* The leftmost dot, at V = 0 mL NaOH

10. (2 pts) The pH at Point B is 6. What equation involving one or more $pK_a$ value(s) gives you the pH for Point B?

11. (5 pts) Entropy in the Spring! Predict the sign of $\Delta S$ for each of these activities that occur in the Spring. Circle either 0 < $\Delta S$ or $\Delta S$ < 0 for each choice. If you cannot predict, circle the group “0 < $\Delta S$ < 0”
0 < $\Delta S$ < 0 Birds gathering sticks to build nests
0 < $\Delta S$ < 0 Snow and ice melting
0 < $\Delta S$ < 0 Photosynthesis (basically: CO$_2$(g) + H$_2$O(l) $\rightarrow$ (CH$_2$O)$_x$ + O$_2$(g) where (CH$_2$O)$_x$ is a large carbohydrate, the main component of a leaf.)
0 < $\Delta S$ < 0 Birds gathering in large flocks to fly north together
0 < $\Delta S$ < 0 Water vapor condensing into rain drops

12. (6 pts) In class we saw this reaction, which produced red-brown NO$_2$(g):
2 NO(g) + O$_2$(g) $\rightarrow$ 2 NO$_2$(g)
(a) Is this reaction entropy favored?  Yes or No
(b) Is this reaction spontaneous at 25 $^\circ$C? Yes or No
(c) Is this reaction exothermic or endothermic?
  Circle: Exothermic  Endothermic  Cannot predict

13. (4 pts) Another reaction, familiar to us from our study of kinetics and gas-phase equilibrium is:
N$_2$O$_4$(g) $\rightarrow$ 2 NO$_2$(g)  $\Delta H = 57$ kJ
(a) Is this reaction entropy favored?  Yes or No
(b) Is this reaction spontaneous?
  Yes, at all temperatures  No, never spontaneous
  Only at high temperatures; not at low temperatures
  Only at low temperatures; not at high temperatures

14. Consider the reaction:
2 HI(g) $\rightarrow$ H$_2$(g) + I$_2$(s)  $\Delta H^0$ = -53 kJ  $\Delta S^0$ = -166 J/K

14a. (3 pts) Calculate $\Delta G^0$

14b. (3 pts) Estimate $\Delta G$ at 400 K

14c. (3 pts) Calculate $\Delta G$ at 298 K if P$_{HI}$ = 0.10 atm, P$_{H_2}$ = 1.0 atm

14d. (3 pts) Calculate K$_p$ at 298 K

14e. (3 pts) Estimate the temperature when the reaction becomes spontaneous?

Subtotal from exam: ___________
Homework: ___________
Total: ___________

Useful equations:
$\Delta G^0 = \Delta H^0 - T \Delta S^0$
$\Delta G = \Delta H - T \Delta S$
$\Delta G^0 = -RT \ln Q$
$\Delta G = \Delta G^0 + RT \ln Q$

R = 8.314 J/mol K = 0.0821 L atm/mol K
**Please note:** Vol of NaOH added is in units of mL

**Titration Curve 1.** 50.00 mL HA with 0.1800 M NaOH

**Titration Curve 2.** 50.00 mL HB with 0.1800 M NaOH

**Titration Curve 3.** 50.00 mL HC with 0.1800 M NaOH

**Titration Curve 4.** For Question 9. Please note regarding x-axis label: “0.1 F NaOH” is the same as 0.1 M NaOH
Answers:

1. 3.95
2. 7.20
3. 6.3 \times 10^6
4. a, b, d, and e:
   (a) 0.10 mol NaF and 100 mL 1.5 M HF: Recipe 1
   (b) 100 mL 0.40 M HCN and 50 mL 0.20 M NaOH: Recipe 2a
   (c) not a buffer
   (d) 15 g NH₄Cl and 100 mL 1.0 M NH₃: Recipe 1
   (e) 0.24 mol HCl and 0.50 mol NaNO₂: Recipe 2b

5a. 4.94
5b. 5.00
6. 4.14
7a. a
7b. b
8a. HB & HC
8b. 4.00
8c. HA & HB
8d. 0.11 M
8e. (c)
9a. pK_{a1} = 4.0 and pK_{a2} = 8.0
9b.
   (i) Point A: \[H_2A \quad HA^-\]
   (ii) Point B: \[HA^-\]
   (iii) Point C: \[HA^- \quad A^{-2}\]
   (iv) Point D: \[A^{-2}\]
   (v) Point 0*: \[H_2A\]
10. \[\text{pH} = \left(\frac{pK_{a1} + pK_{a2}}{2}\right)\]
11. 
   \(\Delta S < 0\) Birds gathering sticks to build nests
   \(0 < \Delta S\) Snow and ice melting
   \(0 < \Delta S < 0\) Photosynthesis (cannot predict \(\Delta S\) because \(\Delta n = 0\))
   \(\Delta S < 0\) Birds gathering in large flocks to fly north together
   \(\Delta S < 0\) Water vapor condensing into rain drops
12. (a) No; (b) Yes; (c) Exothermic
13. (a) Yes; (b) Only at high temperatures; not at low temperatures
14a. \[\Delta G^0 = -3.53 \text{ kJ}\]
14b. \[\Delta G^{400 K} = +13.4 \text{ kJ}\]
14c. \[\Delta G = 7.88 \text{ kJ}\]
14d. \[K_p = 4.16\]
14e. 319 K