US 1114 Exam 3. Wednesday, April 30.

Name Key

By submitting this exam, I certify that I have neither given nor received unauthorized aid.

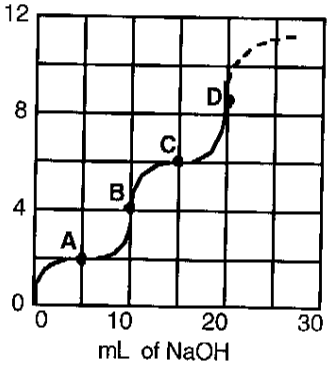
Useful information: $K_w = 1.00 \times 10^{-14}$, $K_a \bullet K_b = K_w$, $pH = -\log[H_3O^+]$, $pH = pK_a + \log\frac{[base]}{[acid]}$, $\Delta G^\circ = \Delta H^\circ - P\Delta V$, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $S = k \ln W$, $k = 1.38 \times 10^{-23}$ J/K, $\Delta G^\circ = -RT\ln K$, $R = 8.314$ J/molK, $pH = \frac{pK_{a1} + pK_{a2}}{2}$, $\Delta G = \Delta G^\circ + RT\ln Q$, $E = E^\circ - \frac{0.0592}{n}\log Q$

(1) A volume of 10.0 mL of 0.10 M H_3PO_4 was titrated with 0.10 M NaOH. The pH response to addition of various amounts of NaOH is shown. At point D, what is the composition of the solution (give species and concentration)?

D it is

HPO_4^{2-}

$[HPO_4^{2-}] = 0.033\,M$



(2) (4 points) ($K_{sp} = 4.9 \times 10^{-17}$)

(a) Solid $Fe(OH)_2$ is added to distilled water. What is $[Fe^{2+}]$ at equilibrium?

$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}_{(aq)} + 2\,OH^-_{(aq)}$ $K_{sp} = 4.9 \times 10^{-17}$

init	solid	0	0
final	solid	x	2x

$4.9 \times 10^{-17} = x(2x)^2 = 4x^3$

$2.3 \times 10^{-6}\,M = x = [Fe^{2+}]$

(b) $Fe(OH)_2$ solid is added to a pOH=1 buffer. What is the $[Fe^{2+}]$ at equilibrium?

$pOH = -\log[OH^-] = 1$

$[OH^-] = 0.10\,M$ $\quad 4.9 \times 10^{-17} = [Fe^{2+}][OH^-]^2$

$4.9 \times 10^{-17} = [Fe^{2+}][0.10\,M]^2 =$ $[Fe^{2+}] = 4.9 \times 10^{-15}\,M$

$K_{sp} = 7.4 \times 10^{-14}$

(3)(4 points) Solid $PbCO_3$ is added to a 0.200 M solution of Na_2CO_3.

(a) What is the $[Pb^{2+}]$ at equilibrium?

$PbCO_3(s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 7.4 \times 10^{-14}$

I.C.	same	0	0.200 M
Eq.	same	x	0.200 M

$7.4 \times 10^{-14} = x(0.200\,M)$

$x = 3.7 \times 10^{-13}\,M = [Pb^{2+}]$

(b) What happens if the solution is acidified to pH = 1 with HNO_3? (tricky) (qualitative, not quantitative answer)

more $PbCO_3$ will dissolve

(4)(6 points) State the three laws of thermodynamics that we have covered.

1st book

(5)(4 points) (a) What is the entropy of parking six cars in six spaces?

$S = k \ln w = 1.38 \times 10^{-23} \frac{J}{mK} \ln(6!) = 1.38 \times 10^{-23} \frac{J}{mK} \ln 720 = 9.1 \times 10^{-23} \frac{J}{K\,mol}$

(b) What is the entropy of 50 of coins with 2 coins heads and the rest tails?

$50.49 = w$

$S = 1.38 \times 10^{-23} \ln(50.49) = 1.05 \times 10^{-22} \frac{J}{mK}$

(6)(3 points) Circle the item in each pair that you would expect to have a higher entropy

(a) $S_8(s)$ or $8S_{(g)}$

(b) a full carton of one dozen eggs or a bag with 12 different marbles

(c) $Na_{(g)} + F_{(g)}$ or $NaF_{(s)}$

(7)(4 points) For the reaction below, $\Delta H^\circ = -92.2$ kJ and $\Delta S^\circ = -199$ J/K. When will this reaction be spontaneous? At what temperature does the reaction become nonspontaneous?

$N_{2(g)} + 3H_{2(g)} \text{---> } 2NH_{3(g)}$

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

$0 = -92,200J - T(-199 \frac{J}{K})$

$463K = T$ spontaneous below 463K

nonspontaneous at 463K

(8)(4 points) For the following reaction, determine the thermodynamic driving force (in kJ) under the following conditions at 298 K.

	$N_{2(g)}$ +	$3H_{2(g)}$ --->	$2NH_{3(g)}$
concentration	0.100 M	0.500 M	1.0 M

$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.0)^2}{(0.1)(0.5)^3} = 80$

$\Delta G^\circ = -92,200\ J - (298K)(-199\ J/K)$

$\Delta G^\circ = -32,900\ J$

$\Delta G = \Delta G^\circ + RT \ln Q =$

$\Delta G = -32,900\ J + (8.314\ J/mol\ K)(298K) \ln 80 =$

$-22,000\ J$

$-22.0\ kJ$

(9) (9 points) In a titration, 0.100 NaOH was added to 10.0 mL of a 0.250 M solution of HClO. What is the pH at the following points ($K_a = 3.5 \times 10^{-8}$) $pK_a = 7.46$

(a) after 6.0 mL of base is added

$(0.250\ M)(0.0100\ L) = 2.50 \times 10^{-3}\ mol_a\ HClO$

$HClO + NaOH \longrightarrow ClO^- + Na^+ + H_2O$

	$HClO$	$NaOH$	ClO^-	Na^+	H_2O
init	2.50×10^{-3} mol	6.0×10^{-4} mol	0	0	–
final	1.90×10^{-3} mol	0	6.0×10^{-4} mol	–	–

$pH = pK_a + \log \frac{[base]}{[acid]} = 7.46 + \log \frac{6.0 \times 10^{-4}\ mol}{1.90 \times 10^{-3}\ mol} = 6.96$

(b) after 25.0 mL of acid is added 2.50×10^{-3} mol

$HClO + OH^- \longrightarrow ClO^- + H_2O$

	$HClO$	OH^-	ClO^-	H_2O
init	2.50×10^{-3} mol	2.50×10^{-3} mol	0	–
final	0	0	2.50×10^{-3} mol	

$[ClO^-]_{final} = \frac{2.50 \times 10^{-3}\ mol}{0.035\ L} = 0.0714\ M$

$ClO^- K_b = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.86 \times 10^{-7}$

$ClO^- + H_2O \rightleftharpoons OH^- + HClO \quad K_b = 2.9 \times 10^{-7}$

	ClO^-	H_2O	OH^-	$HClO$
init	0.0714	–	0	0
fin	0.0714 – x		x	x

$\frac{x^2}{0.0714} = 2.86 \times 10^{-7}$

$x = [OH^-] = 1.4 \times 10^{-4}\ M$

$pOH = 3.85$

$pH = 10.15$

(10) (4 points) (a)What is the pH of a 100.0 mL solution that is 0.200 M HF and 0.010 M NaF?

$K_a = 3.5 \times 10^{-4}$ $pK_a = 3.46$

$pH = 3.46 + \log \frac{[F^-]}{[HF]} = 3.46 + \log \frac{0.010}{0.200} = \boxed{2.16}$

(b) If 5.00 mL of 3.00 M NaOH is added to the solution above, what is the new pH?

$(0.0050\,L)\left(3.00 \frac{mol}{L}\right) = 1.5 \times 10^{-2}$ mols OH^-

0.0200 mols HF, 1.0×10^{-3} mols F^-

$HF + OH^- \rightarrow F^- + H_2O$

	HF	OH^-	F^-	H_2O
init	0.0200 mols	0.0150 mols	1.0×10^{-3} mols	—
Final	0.005 mols	0	0.016 mols	

$pH = 3.46 + \log \frac{0.016 \text{ mols}}{0.005 \text{ mols}} =$

3.97

(12)(3 points) Find a way to separate a solution of 0.100 M Ca^{2+}, 0.100 M Pb^{2+}, and 0.100 M Ni^{2+} using precipitation reactions.

Add Cl^- to precipt $PbCl_2$

Add OH^- to precip $Ni(OH)_2$ first.

(Extra Credit)(4 points) If the concentrations of the reagents in the following reaction are 1.00 M $SnCl_4$, 1.0 M H_2O, 1.0 M HCl, and 5g SnO_2, What is K and what is ΔG for the reaction? What will the concentration of the three gaseous reagents be when ΔG = -10 kJ?

$$SnCl_{4(g)} + 2H_2O_{(g)} \text{ ---> } 4HCl_{(g)} + SnO_{2(s)}$$

$\Delta G = [(1 mole)(-519.7 kJ/mol) + (4 moles)(-431.2 kJ/mol)] - [(1 mole)(-432.2 kJ/mol) + (2 moles)(-228.6 kJ/mol)]$

$\Delta G = -155$ kJ/mole

$-155,000 J = (-8.314 J/mol K)(298 K) \ln K$

$62.6 = \ln K$

$1.5 \times 10^{27} = K$

	$SnCl_4$	$+2H_2O$	$\to 4HCl$	$+SnO_2$
init	1.00	1.00	1.00	
fin	1.00-x	1.00-2x	1.00+4x	
	y	2y	5.00	

$\frac{5.00M}{(y)(2y)^2} = 2.6 \times 10^{25}$

$\frac{4y^3}{5} = 3.8 \times 10^{-26}$

$y = 3.6 \times 10^{-9}$

$\Delta G = \Delta G^\circ + RT \ln Q$ when $\Delta G = -10$ kJ

$-10,000 J = -155,000 J + (8.314 J/mol K)(298 K) \ln Q$

$145,000 J = (8.314 J/mol K)(298 K) \ln Q$

$58.5 = \ln Q$

$2.6 \times 10^{25} = Q = \frac{[HCl]^4}{[SnCl_4][H_2O]^2}$

Find

$[SnCl_4] = 3.6 \times 10^{-9} M$

$[H_2O] = 7.2 \times 10^{-9} M$

$[HCl] = 5 M$