CHEM102 Exam III (Aug 13 2009).
$33\frac{1}{3}$ points / problem with maximum of 100 points.

1.

a) After adding NaOH (strong base) the concentrations are as follows (n is the number of moles of HA and A^-):

$$a \equiv [\mathrm{HA}]_0 = \frac{n - 0.050 \text{ mol}}{0.150 \text{ L}}, b \equiv \left[\mathrm{A}^-\right]_0 = \frac{n + 0.050 \text{ mol}}{0.150 \text{ L}}$$

The initial pH of the solution is 5 (= pK_a) because it has equal amounts of HA and A^-. This yields $\left[\mathrm{H_3O^+}\right] = 10^{-5}$ M. The new equilibrium reaction to consider is:

$$\mathrm{HA{+}H_2O \rightleftharpoons A^- + H_3O^+}$$

Set up the ICE table:

	HA	A^-	H_3O^+
I	a	b	10^{-5} M
C	$+x$	$-x$	$-x$
E	$a+x$	$b-x$	$10^{-5}-x$

Note that $x > 0$ with this choice of signs on row C. To remain a good buffer, the pH must remain within ±1 of pK_a. So, adding base to the solution can at most increase the pH from 5 to 6 ($\left[\mathrm{H_3O^+}\right] = 10^{-6}$ M). This gives $x = 10^{-5} - 10^{-6} = 9.0 \times 10^{-6}$. Write the equilibrium expression:

$$K_a = \frac{(10^{-5} - x)(b - x)}{a + x} = 10^{-5}$$

Inserting $x = 9.0 \times 10^{-6}$ into the above equation, rearranging, and solving for n gives 0.061 mol. The minimum concentration is therefore:

$$0.061 \text{ mol}/0.100 \text{ L} = 0.61 \text{ M}$$

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b) The pK$_a$ value indicates that this is a strong acid and as such does not make a buffer.

2.

a) Initial pH: 0.050 L of 1.0 M NH_3(aq) with pK$_a$ = 9.25 (for NH_4^+). This gives pK$_b$ = 14 − 9.25 = 4.75 (at room temperature) and $K_b = 1.778 \times 10^{-5}$. The reaction to consider is:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Set up the ICE table:

	NH_3	NH_4^+	OH^-
I	1.0	0.0	0.0
C	$-x$	$+x$	$+x$
E	$1.0 - x$	x	x

The expression for equilibrium constant is:

$$K_b = \frac{x^2}{1.0 - x} \approx x^2 = 1.778 \times 10^{-5} \Rightarrow x = 0.0042$$

Note that 0.0042 is less than 5% of 1.0. Thus $\left[OH^-\right] = 0.0042$ M and pOH = log(0.0042) = 2.375. This gives pH = 14 − 2.375 = 11.6 (basic solution as it should be).

b) Equivalence point: 0.25 M HCl (strong acid). Match the moles of base and acid:

$$0.25 \text{ mol/L} \times V = 1.0 \text{ mol/L} \times 0.050 \text{ L}$$

This gives $V = 0.20$ L = 200 mL.

c) Adding 250 mL of HCl takes the system past the equivalence point. The first 200 mL is used to eliminate the base (equivalence point) and the additional 50 mL will change the pH to be more acidic. The number of moles of acid in this amount of liquid is 0.25 mol/L× 0.050 L = 0.0125 mol. The new volume is (0.250 + 0.050) L = 0.300 L. This gives the final $\left[H_3O^+\right] = 0.0417$ M and pH = $-\log(0.0417) = 1.38$.

d) pK$_a$ can be located half-way to the equivalence point (e.g., at 100 mL). pK$_b$ = 14−pK$_a$.

e) In order to choose a suitable indicator, we need to find pH at the equivalence point. The number of moles of both added acid and base in the liquid are equal, 0.050 mol, and the new volume after addition is 0.250 L. This gives the NH_4^+ concentration as 0.2 M. This will establish a new equilibrium:

$$\mathrm{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+}$$

The corresponding ICE table is:

	NH_4^+	NH_3	H_3O^+
I	0.2 M	0	0
C	$-x$	$+x$	$+x$
E	$0.2 - x$	x	x

The equilibrium is: $K_a = 5.6 \times 10^{-10} = \frac{x^2}{0.2-x} \approx x^2 \Rightarrow x = 1.1 \times 10^{-5}$. Then $\mathrm{pH} = -\log(1.1 \times 10^{-5}) = 4.96$. Thus, an indicator that changes its color around this pH should be used.

3.

a) Half reactions (everything under standard condition; oxidation of OH^- driven rather than H_2O when $\mathrm{pH} > 7$):

$$\mathrm{O_2 + 2H_2O} + 4e^- \leftarrow \mathrm{4OH^-}(\text{ oxidation; }+), E_L^\circ = 0.4\text{ V}$$

$$\mathrm{4H_2O} + 4e^- \rightarrow \mathrm{2H_2 + 4OH^-}\ (\text{reduction; -}), E_R^\circ = -0.83\text{ V}$$

b) The EMF is $E^\circ = -0.83\text{ V} - 0.4\text{ V} = -1.23\text{ V}$.

c) Based on b) at least 1.23 V is needed to run the cell.

d) Current = (number of electrons)×(electron charge) / time. Solving for the number of electrons gives 6.7×10^{22}.

e) Four moles of electrons are required per one mole of O_2 produced.

f) The number of O_2 molecules produced is $(6.7\times10^{22}) / 4 = 1.68\times10^{22}$. Use Avogadro's constant to convert to moles, 0.028 mol.

g) $V = 1.00\text{ m}^3$, $n = 0.028$ mol, $T = 298$ K, $R = 8.314$ J/(K mol), $P =?$. Ideal gas law $\Rightarrow P = 69.$ Pa.