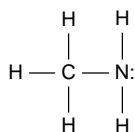# Chemistry 2000 Spring 2006 Test 2 Solutions

1. At the equivalence point, the base has been completely reacted, producing a solution of its conjugate acid. The solution will therefore be acidic, i.e. it will have a pH below 7.

   Bonus:
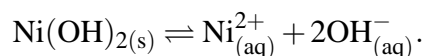

   Note the lone pair on the nitrogen atom in the Lewis diagram of methylamine. A Lewis base is an electron pair donor.

2.

$$Q = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{0.4^2}{0.5} = 0.32 < K.$$

   Since $Q < K$, the reaction will proceed as written, producing more NO_2 from N_2O_4.

3. (a) The equilibrium is

$$Ni(OH)_{2(s)} \rightleftharpoons Ni^{2+}_{(aq)} + 2OH^-_{(aq)}.$$

   At pH 10, there is more hydroxide in solution, which would tend to push the equilibrium back toward the reactant, i.e. depress the solubility. The solubility would therefore be higher at pH 4.

   (b)

$$
\begin{aligned}
K_{sp} &= (a_{Ni^{2+}})(a_{OH^-})^2. \\
a_{H^+} &= 10^{-7}. \\
\therefore a_{OH^-} &= \frac{K_w}{a_{H^+}} = \frac{10^{-14}}{10^{-7}} = 10^{-7}.
\end{aligned}
$$

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(Note that it's perfectly alright to just remember that $a_{OH^-} = 10^{-7}$ at pH 7 and 25°C.)

$$\therefore a_{Ni^{2+}} = \frac{K_{sp}}{a_{OH^-}^2} = \frac{6 \times 10^{-18}}{(10^{-7})^2} = 6 \times 10^{-4}.$$

The solubility is of nickel (II) hydroxide in a pH 7 buffer is therefore 6×10^{-4} mol/L.

4. The two K_a's are very different so only the first proton will be of any significance. The relevant equilibrium is

$$H_2Se_{(aq)} \rightleftharpoons HSe^-_{(aq)} + H^+_{(aq)}$$

for which we have

$$K_a = \frac{(a_{HSe^-})(a_{H^+})}{a_{H_2Se}}.$$

The equilibrium constant is relatively small, and the concentration of H_2Se is relatively large, so we can guess that our usual approximation that the acid will mostly remain undissociated will apply here. On the other hand, this is a sufficiently strong and concentrated acid that the dissociation of water is unlikely to be relevant. Proceeding on this basis, we have $a_{H_2Se} \approx 0.12$ and $a_{HSe^-} \approx a_{H^+}$.

$$\therefore 1.3 \times 10^{-4} \approx \frac{a_{H^+}^2}{0.12}.$$
$$\therefore a_{H^+}^2 \approx 1.56 \times 10^{-5}.$$
$$\therefore a_{H^+} \approx 3.95 \times 10^{-3}.$$

As anticipated, this is (a) much smaller than the H_2Se concentration, and (b) much larger than the amount of H^+ generated by the autodissociation of water. The pH is therefore

$$pH = -\log_{10} a_{H^+} = 2.40.$$

Bonus: If we try the above calculation with $a_{H_2Se} = 1.2 \times 10^{-4}$, we get $a_{H^+} = 1.25 \times 10^{-4}$, which is *larger* than the H_2Se concentration we started with. This nonsensical answer arose because the approximation that little of the acid dissociates is not valid in this case. We would have to use an initial/change/final table in this version of the problem.

5.

$$K_a = 10^{-pK_a} = 10^{-9.3} = 5.01 \times 10^{-10}.$$

This is the equilibrium constant for the dissociation

$$NH_{4(aq)}^+ \rightleftharpoons NH_{3(aq)} + H_{(aq)}^+.$$

Thus,

$$K_a = \frac{(a_{NH_3})(a_{H^+})}{a_{NH_4^+}} = \frac{10^{-9} a_{NH_3}}{a_{NH_4^+}}$$

since we want a pH of 9. The ratio of NH_3 to NH_4^+ is therefore

$$\frac{a_{NH_3}}{a_{NH_4^+}} = \frac{5.01 \times 10^{-10}}{10^{-9}} = 0.501.$$

The easiest way to make this buffer is just to add the appropriate amount of ammonium chloride directly to 500 mL of the ammonia solution. Note that

$$\frac{a_{NH_3}}{a_{NH_4^+}} = \frac{[NH_3]/c^\circ}{[NH_4^+]/c^\circ} = \frac{n_{NH_3}/V}{n_{[NH_4^+]}/V} = \frac{n_{NH_3}}{n_{[NH_4^+]}}.$$

Therefore, we want

$$n_{NH_4^+} = \frac{n_{NH_3}}{0.501}.$$

500 mL of 1.5 M ammonia solution contains

$$
\begin{aligned}
n_{NH_3} &= (0.500\,L)(1.5\,mol/L) = 0.75\,mol. \\
\therefore n_{NH_4^+} &= \frac{0.75\,mol}{0.501} = 1.5\,mol. \\
\therefore m_{NH_4Cl} &= (1.5\,mol)(53.49\,g/mol) = 80\,g.
\end{aligned}
$$

We would therefore weigh out 80 g of ammonium chloride, and dissolve this in 500 mL of the ammonia solution.

6. The equilibrium expression is

$$K = 194 = \frac{a_{\beta CD-n}}{(a_{\beta CD})(a_n)},$$

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where I'm using 'n' as a shorthand for 'nicotine'. The initial concentrations of βCD and of nicotine are calculated as follows:

$$n_{\beta CD} = \frac{50 \times 10^{-3}\,\text{g}}{1134.98\,\text{g/mol}} = 4.4 \times 10^{-5}\,\text{mol}.$$

$$\therefore [\beta CD] = \frac{4.4 \times 10^{-5}\,\text{mol}}{1 \times 10^{-3}\,\text{L}} = 4.4 \times 10^{-2}\,\text{mol/L}.$$

$$n_{\text{nicotine}} = \frac{0.5 \times 10^{-3}\,\text{g}}{162.63\,\text{g/mol}} = 3.1 \times 10^{-6}\,\text{mol}.$$

$$\therefore [\text{nicotine}] = \frac{3.1 \times 10^{-6}\,\text{mol}}{1 \times 10^{-3}\,\text{L}} = 3.1 \times 10^{-3}\,\text{mol/L}.$$

The equilibrium constant is large but not huge. We're probably going to need an initial/change/final table (all concentrations in mol/L):

	$[\beta CD]$	$[\text{nicotine}]$	$[\beta CD - n]$
Initial	4.4×10^{-2}	3.1×10^{-3}	0
Change	$-x$	$-x$	x
Final	$4.4 \times 10^{-2} - x$	$3.1 \times 10^{-3} - x$	x

Substitute all of these quantities into the equilibrium expression (after dividing by $c^\circ = 1\,\text{mol/L}$ to convert concentrations to activities):

$$194 = \frac{x}{(4.4 \times 10^{-2} - x)(3.1 \times 10^{-3} - x)}.$$

$$\therefore x = 194(4.4 \times 10^{-2} - x)(3.1 \times 10^{-3} - x).$$

$$\therefore 0 = 194x^2 - 10.14x + 2.63 \times 10^{-2}.$$

$$\therefore x = \frac{10.14 \pm \sqrt{10.14^2 - 4(194)(2.63 \times 10^{-2})}}{2(194)}$$

$$= \frac{10.14 \pm 9.08}{2(194)}$$

$$= 4.95 \times 10^{-2} \quad \text{or} \quad 2.73 \times 10^{-3}.$$

The first answer doesn't make sense since it would make the nicotine concentration negative. The second answer must be the correct one:

$$x = 2.73 \times 10^{-3}.$$

This means that the concentration of free nicotine is $[\text{nicotine}] = 3.1 \times 10^{-3} - x = 3.4 \times 10^{-4}\,\text{mol/L}$ out of an initial $3.1 \times 10^{-3}\,\text{mol/L}$. The percentage of free nicotine is therefore

$$\frac{3.4 \times 10^{-4}\,\text{mol/L}}{3.1 \times 10^{-3}\,\text{mol/L}} \times 100\% = 11\%.$$