

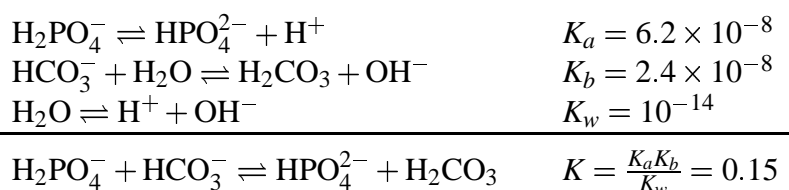
Chemistry 2000 Spring 2001 Section B Assignment 3

Solutions

1. A buffer is most effective when the target pH is close to the pK_a of the acid. The pK_a of hydrofluoric acid is 3.14 so an HF/F^- buffer would do nicely in at least some applications. (HF and fluoride ions are quite toxic at moderate concentrations so there are some contexts in which this buffer would not be appropriate.)
2. There are at least two possible reactions here:
 - (a) H_2PO_4^- acts as an acid and HCO_3^- acts as a base, or
 - (b) HCO_3^- is the acid and H_2PO_4^- is the base.

Let us take these two possibilities in turn:

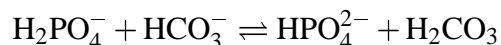
acid H_2PO_4^- /base HCO_3^- : The reaction is found by combining the following processes:



This is not a particularly small equilibrium constant, so we might reason, on this basis alone, that this reaction would occur. We should however think about what happens if we reverse the roles of the two species before we give our final answer (no reference to *Who Wants to be a Millionaire* intended).

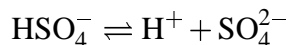
acid HCO_3^- /base H_2PO_4^- : Bicarbonate ($K_a = 4.8 \times 10^{-11}$) is a **much** weaker acid than H_2PO_4^- ($K_a = 6.2 \times 10^{-8}$). H_2PO_4^- ($K_b = 1.3 \times 10^{-12}$) is also a **much** weaker base than HCO_3^- ($K_b = 2.4 \times 10^{-8}$). We could calculate the equilibrium constant for this reaction, but it's clear what the result would be: The reaction of HCO_3^- acting as an acid with the base H_2PO_4^- will have a much smaller equilibrium constant than the previously considered case. Accordingly, we would predict that this reaction will not occur.

Our conclusion must therefore be that the reaction



will occur when the two reactants are mixed. Because of the moderate size of the equilibrium constant, all four species appearing in the reaction will be present in significant quantities at equilibrium.

3. HSO_4^- is, at least in principle, an amphoteric species. However, the conjugate acid of the hydrogen sulfate anion is a strong acid (sulfuric acid) so HSO_4^- will definitely not act as a base. The acid dissociation is



with

$$K_a = \frac{(a_{\text{H}^+})(a_{\text{SO}_4^{2-}})}{a_{\text{HSO}_4^-}}$$

The K_a of this acid is 1.2×10^{-2} (Kotz & Treichel, 4th ed., Table 17.4, p 799). This K_a is certainly large enough that we can ignore the dissociation of water. Thus, $a_{\text{H}^+} = a_{\text{SO}_4^{2-}}$. In fact, it is so large that a significant amount of the acid can be expected to dissociate. We are therefore going to have to work out the stoichiometry from a little table:

	$a_{\text{HSO}_4^-}$	$a_{\text{SO}_4^{2-}}$	a_{H^+}
initial	0.0053	0	0
final	$0.0053 - x$	x	x

Thus we have

$$\begin{aligned} K_a &= 1.2 \times 10^{-2} = \frac{x^2}{0.0053 - x} \\ \therefore x^2 &= 1.2 \times 10^{-2}(0.0053 - x) \\ \therefore 0 &= x^2 + 1.2 \times 10^{-2}x - 6.36 \times 10^{-5} \\ \therefore x &= a_{\text{H}^+} = 0.0040 \quad (\text{using the quadratic equation}). \\ \therefore \text{pH} &= -\log_{10} a_{\text{H}^+} = 2.40. \end{aligned}$$

4. Sulfuric acid is a strong acid so the first proton will come off quantitatively. If it weren't for the second proton, the pH would be about 2.3. This is reasonably close to the $\text{p}K_a$ of the second proton (1.9) so we have to solve the equilibrium problem for the second proton. The technique is very much as in the previous problem except that we have 0.0053 mol/L of protons before the second proton starts to come off. Here, I'll take the initial state to be what we get just after dissociation of the first proton:

	$a_{\text{HSO}_4^-}$	$a_{\text{SO}_4^{2-}}$	a_{H^+}
initial	0.0053	0	0.0053
final	$0.0053 - x$	x	$0.0053 + x$

The equilibrium relation now reads

$$K_a = 1.2 \times 10^{-2} = \frac{x(0.0053 + x)}{0.0053 - x}$$

$$\begin{aligned}
\therefore x(0.0053 + x) &= 1.2 \times 10^{-2}(0.0053 - x). \\
\therefore 0 &= x^2 + 0.0173x - 6.36 \times 10^{-5}. \\
\therefore x &= 0.0031 \quad (\text{using the quadratic equation}). \\
\therefore a_{\text{H}^+} &= 0.0053 + x = 0.0084. \\
\therefore \text{pH} &= -\log_{10} a_{\text{H}^+} = 2.07.
\end{aligned}$$

5. If the pH of the buffer is to be 5, we will have

$$a_{\text{H}^+} = 10^{-\text{pH}} = 10^{-5}.$$

The $\text{p}K_a$ is 4.6 so the K_a of the cation is

$$\begin{aligned}
K_a &= 10^{-\text{p}K_a} = 2.5 \times 10^{-5}. \\
&= \frac{(a_{\text{C}_6\text{H}_5\text{NH}_2})(a_{\text{H}^+})}{a_{\text{C}_6\text{H}_5\text{NH}_3^+}} \\
\therefore \frac{a_{\text{C}_6\text{H}_5\text{NH}_2}}{a_{\text{C}_6\text{H}_5\text{NH}_3^+}} &= \frac{K_a}{a_{\text{H}^+}} = 2.5.
\end{aligned}$$

At this point it is convenient to switch to thinking in terms of the number of moles since we will ultimately want to calculate how many moles of HCl we need. Note that

$$\frac{a_{\text{C}_6\text{H}_5\text{NH}_2}}{a_{\text{C}_6\text{H}_5\text{NH}_3^+}} = \frac{[\text{C}_6\text{H}_5\text{NH}_2]/c^\circ}{[\text{C}_6\text{H}_5\text{NH}_3^+]/c^\circ} = \frac{n_{\text{C}_6\text{H}_5\text{NH}_2}/V}{n_{\text{C}_6\text{H}_5\text{NH}_3^+}/V} = \frac{n_{\text{C}_6\text{H}_5\text{NH}_2}}{n_{\text{C}_6\text{H}_5\text{NH}_3^+}}$$

so we want

$$\frac{n_{\text{C}_6\text{H}_5\text{NH}_2}}{n_{\text{C}_6\text{H}_5\text{NH}_3^+}} = 2.5. \quad (1)$$

The solution initially contains a total of $(0.2 \text{ mol/L})(1 \text{ L}) = 0.2 \text{ mol}$ aniline. Reaction with HCl only converts this to the cation, so there is a conservation law:

$$n_{\text{C}_6\text{H}_5\text{NH}_2} + n_{\text{C}_6\text{H}_5\text{NH}_3^+} = 0.2 \text{ mol}. \quad (2)$$

We now have two equations (1 and 2) in the two mole numbers so we can solve for these quantities:

$$\begin{aligned}
n_{\text{C}_6\text{H}_5\text{NH}_2} &= 2.5n_{\text{C}_6\text{H}_5\text{NH}_3^+}. \\
\therefore 0.2 \text{ mol} &= 2.5n_{\text{C}_6\text{H}_5\text{NH}_3^+} + n_{\text{C}_6\text{H}_5\text{NH}_3^+}. \\
\therefore n_{\text{C}_6\text{H}_5\text{NH}_3^+} &= 0.057 \text{ mol} \\
\text{and } n_{\text{C}_6\text{H}_5\text{NH}_2} &= 0.2 - 0.057 \text{ mol} = 0.143 \text{ mol}.
\end{aligned}$$

For each mole of $\text{C}_6\text{H}_5\text{NH}_3^+$ to be produced, we need one mole of hydrogen ions. The HCl solution must therefore provide 0.057 mol of H^+ . The volume of HCl required is therefore

$$V_{\text{HCl}} = \frac{0.057 \text{ mol}}{5 \text{ mol/L}} = 0.011 \text{ L} \equiv 11 \text{ mL}.$$