## Lecture Notes P: Acid-Base Chemistry III

## 1) Who wants protons more (or who wins in a fight for protons)

Mix HF with NaCN , or mix NaF with HCN

$$
\begin{array}{llll}
\mathrm{HF}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons & \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{F}^{-} & \mathrm{K}_{\mathrm{a}}=6.6 \times 10^{-4} & \mathrm{pKa}=3.18 \\
\mathrm{HCN}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons & \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{CN}^{-} & \mathrm{K}_{\mathrm{a}}=6.17 \times 10^{-10} & \mathrm{pKa}=9.21
\end{array}
$$

## concept

You have 50 ml of a complex mixture of weak acids that contains some HF and some HCN. Which is larger, [ $\left.\mathrm{F}^{-}\right] /[\mathrm{HF}]$ or $\left[\mathrm{CN}^{-}\right] /[\mathrm{HCN}]$ ?
(a) $\left[\mathrm{F}^{-}\right] /[\mathrm{HF}]$
(b) $\left[\mathrm{CN}^{-}\right] /[\mathrm{HCN}]$
(c) can't tell from available information

## 2) Once you know the pH , what does a weak acid look like.

If you know the temperature of Pittsburgh, you can say what it feels like. This is much easier than calculating/predicting the temperature of Pittsburgh.


## Concept

Some side chains in proteins contain sites that can exchange protons with the surrounding water (i.e. they are weak acids). Consider a protein with the following side chains,

| Amino Acid | side-chain | Amino Acid | side-chain |
| :--- | :--- | :--- | :--- |
|  |  |  |  |
| Arginine | $\mathrm{pK}_{\mathrm{a}}=12.48$ | Histidine | $\mathrm{pK}_{\mathrm{a}}=6.04$ |
| Aspartic Acid | $\mathrm{pK}_{\mathrm{a}}=3.90$ | Lysine | $\mathrm{pK}_{\mathrm{a}}=10.79$ |
| Cysteine | $\mathrm{pK}_{\mathrm{a}}=8.33$ | Tyrosine | $\mathrm{pK}_{\mathrm{a}}=10.13$ |
| Glutamic acid | $\mathrm{pK}_{\mathrm{a}}=4.07$ |  |  |

Given that the pH of blood is about 7.3, how many of the above side chains would be in their ionic form $\left(\mathrm{A}^{-}\right)$in blood?
A) 2
B) 3
C) 4
D) 5

## 3) pH indicators

Consider an indicator that is a weak acid with $\mathrm{K}_{\mathrm{a}}=1.4 \times 10^{-9}\left(\mathrm{pK}_{\mathrm{a}}=8.8\right)$. The protonated form (HIn) is colorless, and the deprotonated form ( $\mathrm{In}^{-}$) is pink. [This is similar to the indicator Phenolphtalein.]

Who is controlling the pH , and who is being controlled by the pH ?


What is the ratio between the protonated and deprotonated forms ([HA]/[A$])$ when the pH is 7.8 ?

What is the ratio between the protonated and deprotonated forms ([HA]/[ $\left.\mathrm{A}^{-}\right]$) when the pH is 8.8 ?

What is the ratio between the protonated and deprotonated forms ([HA]/[ $\left.\mathrm{A}^{-}\right]$) when the pH is 9.8 ?

## 4) How buffers work.

As the pH changes, the ratio of $\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]$ changes.
Corollary: To change the pH you have to change the ratio $\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]$.
So if you have a bunch of [ $\mathrm{A}^{-}$] and [HA] present, and you want the pH to go up, you have to convert most of the HA into $\mathrm{A}^{-}$.

Consider starting with 100 ml of a mixture in which $\left[\mathrm{A}^{-}\right]=[\mathrm{HA}]=1 \mathrm{M}$.

Now add enough $\mathrm{OH}^{-}$to convert half the HA into $\mathrm{A}^{-}(50 \mathrm{ml}$ of 1 M NaOH$)$.

$$
\mathrm{HA}+\mathrm{OH}^{-} \leftrightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \quad \mathrm{~K}=1 / \mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{a}} / \mathrm{K}_{\mathrm{w}} \gg 1
$$

If you had added 50 ml of 1 M NaOH to 100 ml of water, the pH would be:

Similarly, if you add enough $\mathrm{H}_{3} \mathrm{O}^{+}$to convert half the $\mathrm{A}^{-}$into $\mathrm{HA}(50 \mathrm{ml}$ of 1 M HCl$)$.

$$
\mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \longleftrightarrow \mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \quad 1 / \mathrm{K}_{\mathrm{a}} \gg 1
$$

If you had added 50 ml of 1 M NaOH to 100 ml of water, the pH would be:

