3.091: Introduction to Solid State Chemistry
Maddie Sutula, Fall 2018
Recitation 24

1 pH and pOH

The concentration of ions in solution can be quite high– and can differ from solution to solution by many orders of magnitude. For this reason, it is useful to refer to a logarithmic scale. We will use an operator p defined to be the negative log (base 10) of the value it precedes: for example, pH= $-\log_{10}[H^+]$.

The pH of a solution is a measure of how acidic it is: a pH of 7 indicates the solution is neutral, while lower values are acidic and higher values are basic. The compliment to pH is pOH, a measure of the concentration of hydroxide ions: pOH= $-\log_{10}[OH^-]$. A high pOH corresponds to an acidic solution, while a low pOH indicates a basic solution. pH and pOH are related as

$$pH + pOH = 14$$

Example: The K_a for nitrous acid, HNO_2, is 4.0×10^{-4}. Determine the pH and pOH of 0.1 M nitrous acid.

First, let's write an expression for the dissociation of nitrous acid:

$$HNO_2(aq) + H_2O(l) \rightarrow NO_2^-(aq) + H_3O^+(aq)$$

Then, we can write an expression for the acid dissociation constant:

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

To find the pH, we need to determine the concentration of H^+ ion (equivalently H_3O^+). The initial concentration of nitrous acid is 0.1 M: we can set up an ICE table to solve for the final concentrations:

	$[HNO_2]$	$[NO_2^-]$	$[H_3O^+]$
Initial	0.1	0 M	0 M
Change	$-x$ M	$+x$ M	$+x$ M
Final	$0.1 - x$ M	x M	x M

Plugging in the final values to the expression for K_a, we can solve for x to find the concentration of hydrogen ions:

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{x^2}{0.1 - x} = 4.0 \times 10^{-4}$$

$$x^2 = 4.0 \times 10^{-5} - x(4.0 \times 10^{-4})$$

$$x^2 + x(4.0 \times 10^{-4}) - 4.0 \times 10^{-5} = 0$$

$$[H_3O^+] = x \approx 0.006$$

Finally, we can solve for pH:

$$pH = -log[H^+] = -log[H_3O^+] = -log(0.006) = 2.21$$

The value of pOH follows using the relation that pH + pOH = 14:

$$pOH = 14 - pH = 11.79$$

Example: What is the pH of 0.04 M HI, which is a strong acid?

The key phrase to solving this problem is 'strong acid.' When we have a strong acid, we don't need an acid dissociation constant because we know it fully dissociates! Here, the concentration of hydrogen ion simply equals the initial concentration of acid:

$$pH = -log[H^+] = -log(0.04) = 1.4$$

2 $\mathbf{pK_a}$ and $\mathbf{pK_b}$

In the same way that it is convenient to express the concentration of hydronium or hydroxide ions as a logarithmic value, it can be useful to express the acid and base dissociation constants as pK_a and pK_b, since they can again differ by many orders of magnitude between species. The definition of p as an operator remains the same, so pK_a=$-\log_{10}(K_a)$ and pK_b=$-\log_{10}(K_b)$.

Example: For an 0.2 M solution of pyridine (C_5H_5N), a base with a pH of 9.28, determine the pK_b.

First, let's write a dissociation equation for pyridine:

$$C_5H_5N(aq) + H_2O(l) \rightarrow C_5H_5NH^+(aq) + OH^-$$

Then, we can convert the pH to a pOH, since pyridine is a base:

$$pOH = 14 - pH = 14 - 9.28 = 4.72$$

Next, we can convert the pOH into a concentration of hydroxide ions:

$$pOH = -log_{10}[OH^-]$$

$$[OH^-] = 10^{-pOH} = 10^{-4.72} = 1.89 \times 10^{-5}$$

Then, we can write an expression for the base dissociation constant:

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

And write our ICE table: Plugging these final values into the expression from above for K_b:

	$[C_5H_5N]$	$[C_5H_5NH^+]$	$[OH^-]$
Initial	0.2	0 M	0 M
Change	$-x$ M	$+x$ M	$+x$ M
Final	$0.2 - x$ M	x M	x M

$$K_b = \frac{x^2}{0.2 - x}$$

Above, we determined the value of x=$[OH^-]$=1.89×10^{-5} , so we can simply plug in to solve for K_b:

$$K_b = \frac{(1.89 \times 10^{-5})^2}{0.2 - 1.89 \times 10^{-5}} = 1.8 \times 10^{-9}$$

Finally,

$$pK_b = -log(K_b) = 8.74$$

3.091 Introduction to Solid-State Chemistry
Fall 2018