Stuff to remember from yesterday:

$pH = -\log[H_3O^+]$ $\quad$ $pOH = -\log[OH^-]$

$pH + pOH = 14$ $\quad$ $[H_3O^+][OH^-] = 10^{-14}$

H_3O^+ produced → pH

Acids react with water: Acid dissociation reaction $\quad$ $HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + X^-$

Bases react with water: Base dissociation reaction $\quad$ $X^- + H_2O_{(l)} \rightleftharpoons HX_{(aq)} + OH^-$

pOH

-conjugate acid/base pairs: $\quad$ $HX \leftrightarrow X^-$ (acid ↔ base) $\quad$ $H_2O \leftrightarrow H_3O^+$ (base, acid) $\quad$ $H_2O \leftrightarrow OH^-$ (acid, base)

Strong Acid / Base reactions boil down to stoichiometry (no equilibrium)

Calculate the $[H_3O^+]$, $[OH^-]$, pH, and pOH of 1.3 mM HBr at 25°C

Start by writing out the reaction.

$$HBr_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$$

strong acid, so not an equilibrium

$$\frac{1.3 \text{ mmol HBr}}{L} \cdot \frac{1 \text{ mmol } H_3O^+}{1 \text{ mmol HBr}} \cdot \frac{10^{-3} \text{ mol}}{1 \text{ mmol}} = 1.3 \times 10^{-3} \text{ M } H_3O^+ = [H_3O^+]$$

$$pH = -\log[H_3O^+] = -\log 1.3 \times 10^{-3} = 2.87 = pH$$

$pH + pOH = 14$ $\quad$ $2.89 + pOH = 14$ $\quad$ $pOH = 11.11$

$[H_3O^+][OH^-] = 10^{-14}$ $\quad$ $[OH^-] = 10^{-14} / 1.3 \times 10^{-3} = 7.69 \times 10^{-12} = [OH^-]$

Don't be tricked by Really dilute acids or bases: acids must have pH < 7
bases must be pH > 7

example: what is the pH of 71 nM HCl?
strong acid

$71 \text{ nM HCl} \rightarrow 71 \text{ nM } H_3O^+ = 7.1 \times 10^{-8} \text{ M } H_3O^+$

$pH = -\log 7.1 \times 10^{-8}$
$pH = 7.14$?!?
↑
NO - this is an acid

* Remember that water contributes to $[H_3O^+]$ *

-for really dilute acid (or bases), we need to take this into consideration

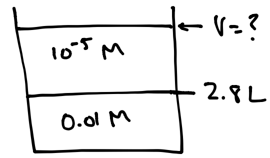
$$[H_3O^+]_{total} = [H_3O^+]_{water} + [H_3O^+]_{HCl} = 10^{-7} \text{ M} + 7.1 \times 10^{-8} \text{ M} = 1.71 \times 10^{-7} \text{ M}$$

$pH = 6.77$

You have 2.8 L of 10 mM HCl. How much water do you need to add to have a pH = 5?

10 mM = 0.01 M   pH = 2

current concentration   pH 5 $[H_3O^+] = 10^{-5} = [HCl]$



$$\underbrace{\frac{0.01\text{ mol}}{L}}_{\text{current concentration}}(2.8\text{ L}) = 0.028\text{ mol HCl}$$

$$\frac{0.028\text{ mol HCl}}{} \Big| \frac{1\text{ L}}{\underbrace{10^{-5}\text{ mol HCl}}_{\text{desired concentration}}} = 2800\text{ L!}$$

Need to add 2800 − 2.8 = 2797.2 L of H_2O

You have 2.8 L of 10 mM HNO_3. Your goal is to neutralize this solution by adding NaOH. If the NaOH you are adding is 1.00 M, calculate the volume that is needed. What is $[H_3O^+]$ at this point?

① How many moles of H_3O^+ are present?

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

$$\frac{2.8\text{ L } HNO_3}{} \Big| \frac{0.01\text{ mol}}{L} \Big| \frac{1\text{ mol } H_3O^+}{1\text{ mol } HNO_3} = 0.028\text{ mol } H_3O^+$$

So to neutralize this solution, 0.028 mol OH^- are needed (remember neutral is when $[H_3O^+] = [OH^-]$)

② Calculate volume of NaOH needed.

$$\frac{0.028\text{ mol } OH^-}{} \Big| \frac{1\text{ mol NaOH}}{1\text{ mol } OH^-} \Big| \frac{1\text{ L}}{1\text{ mol NaOH}} = 0.028\text{ L NaOH needed}$$

Once the NaOH has been added, a neutralization reaction occurs:

$$NaOH(aq) + HNO_3(aq) \rightarrow H_2O(l) + NaNO_3(aq)$$

Since $[OH^-]_{added} = [H_3O^+]$ from HNO_3, only the autoionization of water matters

$$2H_2O(l) \rightleftharpoons [H_3O^+][OH^-] = 10^{-14}$$ $[H_3O^+] = 10^{-7}$ M

Acids and bases react with water - the 1st thing you should do when you think about these molecules is to react them with H_2O

$$HNO_{2(aq)} + H_2O_{(l)} \underset{}{\overset{K_a}{\rightleftharpoons}} H_3O^+_{(aq)} + NO_2^-{}_{(aq)}$$

K_a ← acid dissociation constant

Acid dissociation equilibrium

H_2O as a base

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

H_2O as an acid

$$NH_{3(aq)} + H_2O_{(aq)} \overset{K_B}{\rightleftharpoons} NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

K_B ← base dissociation constant

Base dissociation equilibrium

$$K_B = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

WEAK ACIDS/BASES

We saw above that 10 mM HCl has a pH of 2 → strong acid, so $[H_3O^+]$ = 10 mM

But what is the pH of 10 mM HF

NOT a strong acid!

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)} \qquad K_a = 6.3\times10^{-4}$$

	HF	H_3O^+	F^-
I	0.01	0	0
C	$-x$	$+x$	$+x$
E	$0.01-x$	x	x

This is an equilibrium problem

ICE

$$6.3\times10^{-4} = \frac{x^2}{0.01-x}$$

$$6.3\times10^{-6} - 6.3\times10^{-4}x = x^2$$

$$0 = x^2 + 6.3\times10^{-4}x - 6.3\times10^{-6}$$

$$x = \frac{-6.3\times10^{-4} + \sqrt{(6.3\times10^{-4})^2 - 4(-6.3\times10^{-6})}}{2} = 2.21\times10^{-3} = [H_3O^+]$$

$$pH = -\log[\,] = 2.65$$

= 10 mM F^-

What about 10 mM NaF? ⟶ NOTE that NaF is soluble ... in solution it is $Na^+ + F^-$

- we can't just reverse the K_a reaction – Bases react with H_2O, NOT H_3O^+!

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-$$

This is the K_b reaction!

- So to solve for $[OH^-]$, need K_b!

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} \qquad K_b = \frac{[OH^-][HF]}{[F^-]}$$

$$\boxed{K_a \cdot K_b = K_w!} \qquad \frac{[H_3O^+]\cancel{[F^-]}}{\cancel{[HF]}} \cdot \frac{[OH^-]\cancel{[HF]}}{\cancel{[F^-]}} = [H_3O^+][OH^-] = K_w$$

$$\boxed{pK_a + pK_b = 14}$$

K_a for HF = 6.3×10^{-4} $\qquad K_b = \frac{10^{-14}}{6.3\times10^{-4}} = 1.587 \times 10^{-11}$

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^- \qquad K_b = 1.587\times10^{-11}$$

	$F^-_{(aq)}$	$HF_{(aq)}$	OH^-
I	0.01	0	0
C	$-x$	$+x$	$+x$
E	$0.01 - x$	x	x

$$1.587\times10^{-11} = \frac{x^2}{0.01 - x}$$

$$x^2 = 1.587\times10^{-13} - 1.587\times10^{-11}x$$

$$0 = x^2 + 1.587\times10^{-11}x - 1.587\times10^{-13}$$

$$x = \frac{-1.587\times10^{-11} + \sqrt{(1.587\times10^{-11})^2 - 4(-1.587\times10^{-13})}}{2}$$

$x = 3.984\times10^{-7} = [OH^-]$

pOH = $-\log[OH^-]$ = 6.4

pH = 14 - pOH = 7.6

Salts + pH

A lot of salts, when dissolved in H_2O, will make a solution acidic or basic. The trick to understanding this is to recognize acids and bases

easy example

When $NaOH_{(s)}$ is dissolved in water, will the solution be acidic or basic?

$NaOH \rightarrow Na^+ + OH^-$

Na^+: ion, not acid or base

OH^-: strong base!

What about NaF?

$NaF \rightarrow Na^+ + F^-$

Na^+: ion

F^-: weak base (conjugate base of the weak acid HF)

Basic → F^- is a base

$NaCl \rightarrow Na^+ + Cl^-$

Na^+: ion

Cl^-: ion ← NOT a base because it is the conjugate "base" of a STRONG acid

$$HCl_{(aq)} + H_2O \longrightarrow H_3O^+ + Cl^-$$

not reversible

Cl^- will NOT react with H_2O to make OH^-!

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

NH_4^+: weak acid

Cl^-: ion

acidic

$NaHCO_3$

Na^+ HCO_3^-

ion acid <u>OR</u> base

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \quad K_b = 2.2 \times 10^{-8}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad K_a = 4.7 \times 10^{-11}$$

The base reaction (K_b) is more favored than the acid reaction! More OH^- will form ... $\boxed{\text{BASIC}}$