An aqueous solution of 0.25 M trimethylamine has a pH of 11.63 . What's the experimental value of Kb ?

$$
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}+\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+} \\
\mathrm{K}_{3}=\frac{\left.\left[\mathrm{OH}^{-}\right]\left[\mathrm{CH}_{3}\right)_{3} \mathrm{NHt}^{+}\right]}{\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}\right]}
\end{gathered}
$$

How do we find Kb ? First, let's set up the traditional equilibrium calculation.

| Species | [Initial] | $\Delta$ | $\left[\epsilon_{\text {Guilibrium }}\right]$ |
| :---: | :---: | :---: | :---: |
| $O \mathrm{H}^{-}$ | $O$ | $+X$ | $X$ |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}$ | $O$ | $+X$ | $X$ |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$ | $0.2 S$ | $-X$ | $O .2 S-X$ |

$$
\begin{aligned}
& K_{b}=\frac{(x)(x)}{0.25-x} \\
& K_{b}=\frac{x^{2}}{0.25-x}
\end{aligned}
$$

If we want to find the value of the base ionization constant Kb, we need to find some other way of determining 'x'.

$$
K_{b}=\frac{x^{2}}{0.25-x}
$$

We know the pH, which gives us the HYDRONIUM ion concentration. We can calculate the HYDROXIDE ion concentration from the hydronium, and that will give us the value of ' $x$ ' we need!

$$
\begin{aligned}
& p H=11.63 \\
& \text { so }\left[H_{3} 0^{+}\right]=10^{-11.63}=2.34422882 \times 10^{-14}
\end{aligned}
$$

SALTS

- Compounds that result from the reaction of an acid and a base.
- Salts are strong electrolytes (completely dissociate in water) IF SOLUBLE (not all salts dissolve appreciably).
- Most ionic compounds are considered salts (they can be made by some reaction between the appropriate acid and base)
- Salts have acidic and basic properties! The ions that form when salts are dissolved can be acidic, basic, or neutral.
- Salts made from WEAK ACIDS tend to form BASIC solutions
- Salts made from WEAK BASES tend to form ACIDIC solutions

$$
\mathrm{Na}_{2} \mathrm{CO}_{3}: \mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow 2 \mathrm{Na}^{+}+\mathrm{CO}_{3}^{2-}
$$

Do any of these ions have acidic or basic properties?
$\mathrm{Na}^{+}$: neutral. Not a proton donor or a proton acceptor
$\mathrm{CO}_{3}{ }^{2-}$ : BASIC, since it can accept protons to form the weak acid CARBONIC ACID - in solution.

$$
\mathrm{H}_{2} \mathrm{CO}_{3} \mathrm{ACID}^{t} \mathrm{H}_{2} \mathrm{O} \rightleftharpoons 2 \mathrm{H}_{3} \mathrm{O}_{\mathrm{BASE}}^{t}+\mathrm{CO}_{3}^{-2}
$$

ex: $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$


For this reaction to occur, HA MUST be stable in water. In other words, a weak acid.
$\qquad$ The anion is a BASE. It can accept a proton from water to form the weak (therefore stable as a molecule!) acid HA

$$
\left.K_{b}=\frac{[\mathrm{HA}]\left[\mathrm{OH}^{-}\right]}{\left[A^{-}\right]} \right\rvert\, \text {This is the base ionization constant for } A^{-}
$$

Since $\bar{A}$ and HA are a conjugate pair, the ionization constants are related! You will generally not find both

$$
\begin{aligned}
& K_{w}=\left(K_{a, H A}\right)\left(K_{b, A^{-}}\right) \\
& 1.0 \times 10^{-14} \\
& \quad L_{1}=p K_{n}+p K_{b}
\end{aligned}
$$ can be easily converted to the other!

## SALT OF A WEAK BASE

ex: $\mathrm{NH}_{4} \mathrm{Cl}$

$$
\begin{aligned}
& \mathrm{BHCl} \longrightarrow \mathrm{BH}^{+}+\mathrm{Cl}^{-} \mathrm{I}^{-} \text {The sail dissociates completely! }
\end{aligned}
$$

$$
\begin{aligned}
& \left.K_{a}=\frac{[\mathrm{B}]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{BH}^{+}\right]} \right\rvert\, \text {Acid ionization constant for } \mathrm{BH}^{+} \\
& \underset{1,0 \times 10^{-14}}{K_{w, ~}}=\left(K_{a H t}\right)\left(K_{b, B}\right)
\end{aligned}
$$

Find the pH for salt solutions just like you would find pH for any other weak acid or weak base solutions. Only trick is to find out whether the salt is actually acidic or basic!
$0.100 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl} \ldots$... Find the pH of the solution

$$
\mathrm{NH}_{4} \mathrm{Cl} \rightarrow \mathrm{Nr}_{4}^{+}+\mathrm{Cl}^{-}-\begin{aligned}
& \text { Is this salt acidic, basic, or neutral? Look at the } \\
& \text { ions... }
\end{aligned}
$$

$$
\mathrm{NH}_{4}{ }^{+} ; \quad \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Ammonia is a WEAK base. That means that it can exist in water. Since the product of the reaction is a water-stable molecule, ammonia is an ACIDIC ION.

$$
\mathrm{Cl}_{\mathrm{i}}^{-} \quad \mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCl}+\mathrm{OH}^{-}
$$

HCl is a STRONG acid. In other words, it ionizes completely in water. Since Cl - cannot hang onto the proton, it can't function as an effective base. NEUTRAL ION!
So, we will have to solve ammonia's acid equilibrium:

$$
\begin{array}{r}
\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \\
\mathrm{Ka}_{4}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}
\end{array}
$$

We need Ka! it's not listed in the book (pages A-13 and A-14), but we can find Kb for ammonia ... the conjugate of ammonium!

$$
\begin{aligned}
& K_{a} \times k_{b}=1.0 \times 10^{-14} \\
& K_{a}\left(1.8 \times 10^{-5}\right)=1.0 \times 10^{-14} \\
& K_{a}=5.56 \times 10^{-10}
\end{aligned}
$$

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$$
\begin{aligned}
& \mathrm{NH}_{4}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \mathrm{Ka}_{\mathrm{G}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}=5.56 \times 10^{-10}
\end{aligned}
$$

Once we find Ka , this problem is solved like any other weak acid problem!

| Species | [Initial] | $D$ |
| :--- | :---: | :---: |
| $\mathrm{NH}_{3}$ | 0 | $+X$ |
| $\mathrm{H}_{3} 0^{+}$ | 0 | $+X$ |
| $\mathrm{NH}_{4}{ }^{+}$ | 0.100 | $-x$ |
| $\frac{x^{2}}{0.100-x}=5.56 \times 10^{-10}$ |  |  |

$$
\begin{aligned}
& \downarrow \begin{array}{l}
\text { As sump } x<C 0.100 \\
\text { so } 0.100-x=0.100 \\
\frac{x^{2}}{0,100}=5.56 \times 10^{-10} \\
x=7.45 \times 10^{-6}=\left[H_{3} O^{+}\right]
\end{array}
\end{aligned}
$$

$$
S_{0} \rho H=5.13
$$

Compare:
$\mathrm{pH}=1.00$ for 0.100 M strong acid ( HCl )
$\mathrm{pH}=2.17$ for 0.100 M nitrous acid
$\mathrm{pH}=7.00$ for distilled water

$$
\begin{aligned}
& \mathrm{O} .100 \mathrm{M} \mathrm{NaC} \mathrm{NH}_{3} \mathrm{O}_{2} \text {, Find } \mathrm{pH} \\
& \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \rightarrow \mathrm{Na}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}-
\end{aligned}
$$

Check the ions formed by the salt to see if they have acidic or basic characteristics:
$\mathrm{Na}_{\mathrm{a}}+$ : Not a B-L acid (no H+ to donate). Not likely to be a B-L base due to its positive

- charge (would repel H+)
$\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }_{2}$ : Has hydrogen atoms, but is more likely a B-L base due to the negative charge:

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}
$$

LACETIC ACID is a weak acid, meaning it is water-stable. We expect, then, that acetate ion can function as a base by accepting a proton!

$$
\begin{aligned}
& \text { So, } \mathrm{Kb}_{b}=\frac{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]} \quad \begin{array}{l}
\text { As before, we wont find the } \mathrm{Kb} \text { for the ion } \\
\text { form in the chart, but we find a Ka for } \\
\text { its conjugate on page A-13 }
\end{array} \\
& \mathrm{Ka}_{1} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}=1.7 \times 10^{-5} \quad \text { So } K_{6}=\frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}}=5.89 \times 10^{-10}
\end{aligned}
$$

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$$
\begin{aligned}
& \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \stackrel{\mathrm{HC}}{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-} \\
& \mathrm{K}_{6}=\frac{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}=5.89 \times 10^{-10}
\end{aligned}
$$

| Species | $[$ Initial $]$ | $\Delta$ | $[$ Gqulibrivm $]$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | 0 | $+X$ | $x$ |
| $\mathrm{OH}^{-}$ | 0 | $+x$ | $x$ |
| $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}-$ | 0.100 | $-x$ | $0.100-x$ |
| $\frac{x^{2}}{0.100-x}=5.89 \times 10^{-10}$ |  |  |  |

$$
\begin{aligned}
& \not \begin{array}{l}
\text { assume } x<0.100-x \approx 0.100 \\
0.100 \\
\frac{x^{2}}{0.100}=5.89 \times 10^{-10} \\
x=7.67 \times 10^{-6}=\left[0 H^{-}\right]
\end{array}
\end{aligned}
$$

We need pH, but we've found HYDROXIDE concentration ... convert.

$$
\begin{aligned}
p O H & =\log _{10}\left(7.67 \times 10^{-6}\right) \\
& =5.12 \\
p H & =14.00-5.12 \\
p H & =8.88
\end{aligned}
$$

For comparison:
0.100 M sodium acetate, $\mathrm{pH}=8.88$
0.100 M ammonia, $\mathrm{pH}=11.13$
0.100 M NaOH (strong base), $\mathrm{pH}=13.00$

The acetate ion is basic, but it's a very weak base!

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$$
\begin{aligned}
& \text { O. } 100 \mathrm{M} \mathrm{NaCl}, \text { Find } \mathrm{pH} \\
& \mathrm{NaCl} \longrightarrow \mathrm{Na}^{+}+\mathrm{Cl}^{-}
\end{aligned}
$$

check the ions formed by the salt to see if they're acidic or basic.
$\mathrm{Na}^{+}$: Not a B-L acid since it has no H+ to donate. Not likely a B-L base, as the positive charge would repel $\mathrm{H}+$
$\left(1^{-}\right.$: Not a B-L acid, but it might be a proton acceptor.

$$
\mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \overrightarrow{\mathrm{HCl}}+\mathrm{OH}^{-}
$$

This is hydrochloric acid (a STRONG ACID) - which completely ionizes in water. That means chloride ion is not good at holding on to $\mathrm{H}+\ldots$ and cannot function as a base.

Since neither sodium nor chloride affect pH , the pH of the solution is set by the water equilibrium itself. Therefore, the pH of the solution is 7.00 ... same as for distilled water.

161 POLYPROTIC ACIDS
Find pH of $\mathrm{O}_{1} 10 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$
... what's special about phosphoric acid?
(1) $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

Phosphoric acid has THREE acidic protons!
(2) $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HPO}_{4}^{2-}+\mathrm{H}_{3} \mathrm{O}^{+}$
(3)

$$
\left.\mathrm{HPO}_{4}^{2-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{PO}_{4}^{3-}+\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

$$
K_{a_{3}}=4.8 \times 10^{-13}
$$

The first dissociation is dominant here, and for simple calculations of phosphoric acid in water, we will simply use the first ionization and ignore the other two.

Remember: This is a weak acid. It exists in water mostly as undissociated phosphoric acid molecules.

Solve the equilibrium of phosphoric acid's FIRST proton:

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} ; \mathrm{Ka}=6.9 \times 10^{-3} \\
& \mathrm{~K}_{4}=\frac{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]}=6.9 \times 10^{-3}
\end{aligned}
$$

| Species | [Initial] | $\Delta$ | [Equilibrium] |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | 0 | $+x$ | $x$ |
| $\mathrm{H}_{3} \mathrm{O}^{+}$ | 0 | $+x$ | $x$ |
| $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 0.10 | $-x$ | $0.10-x$ |
| $x^{2}$ |  |  |  |

$$
\begin{aligned}
& \frac{x^{2}}{0.10-x}=6.9 \times 10^{-3} \\
& \qquad \begin{array}{l}
\text { assume } x \ll 0.10 \\
\text { so } 0.10-x
\end{array} 0.10
\end{aligned}
$$

$$
\text { So, } p H=-\log (0.0262678511)
$$

$$
p H=1.58
$$

