Ionization of Water

DEMONSTRATION OF CONDUCTIVITY OF TAP WATER AND DISTILLED WATER

- Pure distilled water still has a small conductivity. Why?
- There are a few ions present.
- Almost all the pure water is H₂O molecules.
- But every once in a while, this happens:





[H₃O⁺] & [OH⁻] in Neutral Water

<u>At 25°C</u> (NOTE: Assume Temp = 25° C unless otherwise noted)

$$[H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

and $[H_3O^+] = [OH^-]$ if water is <u>neutral</u>.

(If "water" is mentioned in a problem, it can be assumed to be NEUTRAL unless otherwise stated!)

(substitute. $[H_3O^+]$ for $[OH^-]$)

 $[H_3O^+]$ $[H_3O^+] = 1.00 \times 10^{-14}$

$$[H_3O^+]^2 = 1.00 \text{ x } 10^{-14}$$

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} M$$

Also
$$[OH^{-}] = [H_3O^{+}] = \underline{1.00 \times 10^{-7}}$$
 M

At Higher Temp

Given: Kw at 60° C = 9.55 x 10^{-14}

Calculate $[H_3O^+]$ & $[OH^-]$ at 60^0C

[H₃O⁺] & [OH⁻] in Acids and Bases

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$





Add base, $[OH^-]$ increases, so the equilibrium shifts LEFT and $[H_3O^+]$ decreases.

Finding [H₃O⁺] and [OH⁻] in Acids and Bases

<u>At 25°C</u>



At Other Temps

- you'd be given Kw

eg.) Kw at 60° C = 9.55 x 10^{-14}

Calculate $[OH^-]$ in 0.00600 M HNO₃ at 60^0 C.

$$[H_3O^+][OH^-] = Kw$$

 $[H_3O^+][OH^-] = 9.55 \times 10^{-14}$

 $[OH^{-}] = \frac{9.55 \text{ x } 10^{-14}}{0.00600} = 1.59 \text{ x } 10^{-11} \text{ M}$

Rd. pg. 126-127 Ex. 28-30 pg. 127 of SW.

pН

-Shorthand method of showing acidity (or basicity, alkalinity)

If $[H_3O^+] = 0.10 \text{ M} (1.0 \text{ x} 10^{-1} \text{ M}) \text{ pH} = 1.00$ $[H_3O^+] = 0.00010 \text{ M} (1.0 \text{ x} 10^{-4} \text{ M}) \text{ pH} = 4.00$

Definition of pH

 $\mathbf{pH} = -\log_{10} [\mathbf{H}_{3}\mathbf{O}^{+}] \quad (\text{assume log} = \log_{10})$

If $[H_3O^+] = 1.0 \times 10^{-7}$

 $pH = -log (1.0 \times 10^{-7})$

Regular Scientific Calculator. Enter: 1 \rightarrow EXP \rightarrow 7 \rightarrow +/- \rightarrow LOG \rightarrow +/- and the answer should be 7

For DAL (Sharp) calc. Enter: $+/- \rightarrow \log \rightarrow 1 \rightarrow \exp \rightarrow +/- \rightarrow 7 \rightarrow =$ and the answer should be 7

For a TI 83 Enter (-) \rightarrow LOG \rightarrow 1 \rightarrow 2nd \rightarrow EE \rightarrow (-) \rightarrow 7 \rightarrow ENTER and the answer should be 7

Use the (-) button at the bottom right of the white pad. NOT the "—" on the far right

NOTE: If you are using a DAL or a TI 83 calculator and the number you want to find the pH of is the answer to a an ongoing calculation, leave the answer to your calculation in the calculator and press (-) or +/- $\rightarrow \log \rightarrow 2^{nd} \rightarrow ANS \rightarrow ENTER$ (or =).

Practice finding pH's on your own calculator. You will be doing many of these in the rest of this unit and it's important that you can do it quickly and easily and accurately!





Enter: $11.612 \rightarrow +/- \rightarrow 2^{nd} \rightarrow \log$ The calculator answer should be 2.443430553 x 10⁻¹²

The original pH had 3 SD's, so the answer must also have 3 SD's (Remember the answer is NOT a pH, so digits to the LEFT of the decimal point <u>are</u> also significant!). Remember that concentration also has a <u>unit</u>!. So the answer would be reported as:



For a DAL or TI 83 enter: $2^{nd} \rightarrow \log \rightarrow (-) (or +/-) \rightarrow 11.612 \rightarrow ENTER (or =)$

If pH = 3.924 calculate [H₃O⁺]

Logarithmic Nature of pH

A change of 1 pH unit \rightarrow a factor of 10 in [H₃O⁺] or (acidity)

eg.)
$$pH = 3.0 \quad [H_3O^+] = 1 \times 10^{-3} \text{ M}$$

 $pH \text{ goes}$
 $down 1 \text{ unit}$
 $pH = 2.0 \quad [H_3O^+] = 1 \times 10^{-2} \text{ M}$

How many times more acidic is pH 3 than pH 7?

pH 7
$$[H_3O^+] = 1 \times 10^{-7}$$

pH 3 $[H_3O^+] = 1 \times 10^{-3}$

рн 3

or taking antilog of difference in pH 7 - 3 = 4antilog $4 = 10^4 = 10,000$ times

(remember lower pH more acidic)

Natural rainwater pH ~ 6 Extremely acidic acid rain pH ~ 3 diff = 3 & antilog $(3) = 10^3$ (1,000) So, the acid rain is 1000 times more acidic than natural rain water!

pOH

Calculate the pOH of 0.0020 M KOH

$$[OH^{-}] = 2.0 \text{ x } 10^{-3} \text{ M}$$

pOH = -log (2.0 x 10⁻³) = 2.70

Find the pH of the same solution:

$$\begin{split} [OH^{-}] &= 2.0 \text{ x } 10^{-3} \text{ M} \\ [H_3O^+] &= \frac{1.00 \text{ x } 10^{-14}}{2.0 \text{ x } 10^{-3}} = 5.0 \text{ x } 10^{-12} \\ \text{pH} &= 11.30 \end{split}$$

Notice: pH + pOH = 14.00

From Math: If $a \times b = c$ Then: $\log_a + \log_b = \log_c$

Eg.) $10 \times 100 = 1000$ Log(10) + log(100) = log(1000)2 1 + = 3

So since

 $[H_3O^+] [OH^-] = Kw$ $log[H_3O^+] + log[OH^-] = log (Kw)$

or make everything *negative*

 $-\log[H_3O^+] + -\log[OH^-] = -\log Kw$



See pOH scale & pH scale. Pg. 140 S.W.

These are very

you study these!

important? Make sure

When not at 25°C

Eg.) At 60° C Kw = 9.55 x 10^{-14}

Find the pH of neutral water at 60° C.

One way: Calculate pKw $pKw = -\log Kw = -\log (9.55 \times 10^{-14})$ <u>At 60⁰C</u> <u>pKw = 13.020</u>

For <u>*neutral*</u> water pH = pOH ([H₃O⁺] = [OH⁻])

pH + pOH = pKw (substitute pH for pOH) pH + pH = 13.020 2pH =13.020 → so pH = $\frac{13.020}{2}$ = 6.510

Is pH always 7.00 in neutral water?_____

At higher temp:

 $2H_2O + heat \quad \leftrightarrows \quad H_3O^+ + OH^-$

$$\begin{split} [{\rm H}_{3}{\rm O}^{+}] > 1.0 \ x \ 10^{-7} & {\rm so} \ p{\rm H} < 7 \\ [{\rm OH}^{-}] > 1.0 \ x \ 10^{-7} \ {\rm so} & p{\rm OH} < 7 \end{split}$$

Summary:

In <u>neutral</u> water <u>pH = pOH at any temp.</u> pH & pOH = 7.00 at 25^oC only. At lower temps pH and pOH are > 7 At higher temps pH and pOH are < 7

At any temp: pH + pOH = pKwAt $25^{\circ}C$: pH + pOH = 14.000

Read p. 134-141 in SW. Do ex. 49-53 + 55-57 (p. 139-141 S.W.) Do Worksheet 4-3 pH and pOH Calculations

K_a & K_b for Weak acids and Bases

Reminder: pH of SA's

[H₃O⁺]=[acid] *strong* means 100% ionized

so, to find pH of 0.100 M HCl

 $[H_3O^+] = 0.100 \text{ M}$ **pH = 1.000** For weak acids $[H_3O^+] \ll [acid]$

Eg.) What is pH of 0.10 M HF?

Look at equilibrium for Weak Acid HF



 $Keq = \frac{[H_3O^+][F^-]}{[HF]}$ for WA's Keq is called **K**_a (*acid* ionization constant)

- see acid table for list of Ka's.

higher Ka \rightarrow stronger acid lower Ka \rightarrow weaker acid

For SA's (eg. HCl)Ka = $[H_3O^+]$ [Cl]= called "very large!"[HCl]Essentially zero
molecular HCl

-Discuss Relative Strengths of Oxyacids

[H₃O⁺] from Ka (pH from Ka)

1. $[H_3O^+]$ from Ka and Original concentration (Co)

- eg.) Find the $[H_3O^+]$ in 0.10 M HF WA
- 1. Write out equilibrium equation for *ionization*

$$HF + H_2O \rightleftharpoons H_3O^+ + F$$

2. <u>Ice table</u>



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Do ex. 74 & 75 Pg. 152
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After Questions 74 & 75



NOTE: Ions which act as acids can come from compounds.

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Eg.) See table ~ ammonium ion NH_4^+
- can be found in NH_4NO_3, NH_4Cl, NH_4Br, etc....
ferric ( hexaaquoiron) Fe^{3+} ( Fe(H_2O)_6^{3+}) could be found in Fe(H_2O)_6 Br_3 (also called FeBr_3)
or Fe(H_2O)_6 (NO_3)_3 (also called Fe(NO_3)_3)
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Aluminum (hexaaquoaluminum) $Al^{3+}(Al(H_2O)_6^{3+})$ could be found in $Al(H_2O)_6Cl_3$ (also called AlCl₃)

Do ex. 79 & 81, Pg. 152

More Ka Calculations:

Ka from pH

NOTE: the pH is to 3 SD's so your final answer cannot have more than 3 SD's.

Eg.) a 0.350 M Solution of the weak acid HA has a pH of 1.620. Find the Ka of HA.



Now, you can see that the change in concentration [C] of $[H_3O^+]$ is + 2.399 x 10⁻² M and using the mole ratios (mole bridges) in the balanced equation, you can figure out the [C]'s for the A⁻ and the HA:

	-2.399 x 10 ⁻² M		+ 2.	.399 x 10 ⁻² M	+ 2	.399 x 10 ⁻² M
	HA	+ H ₂ O	与	H_3O^+	+	A
[I]	0.350			0		0
[C]	- 2.399 x 10 ⁻²		+ 2.	399 x 10 ⁻²	+ 2.	.399 x 10 ⁻²
[E]			2.3	99 x 10 ⁻²		

Now, we can figure out the equilibrium concentrations of HA and A^{\cdot}. There are no "x"s in the table so we don't need to make any assumptions. It is best to use your calculator to figure out the equilibrium [HA], because the [C] may or MAY NOT be insignificant. Using a calculator 0.350 –2.399 x 10⁻² = 0.32601. Don't round it off too much here. I would keep it in a memory in my calculator. BUT BECAUSE THE "0.350" IS 3 DECIMAL PLACES AND YOU ARE SUBTRACTING, THE [E] OF "HA" CANNOT HAVE MORE THAN 3 DECIMAL PLACES (although you should use 0.32601 in your calculator) JUST REMEMBER THAT IN THE NEXT CALCULATION, THE 3 DECIMAL PLACES IN THE ICE TABLE TRANSLATES TO 3 SD'S, SO YOUR FINAL ANSWER CANNOT HAVE MORE THAN 3 SD'S.

-2.399 x 10 ⁻² M			+ 2.399 x 10 ⁻²	M + 2.399 x 10^{-2} M
	HA ·	+ H ₂ O	$rac{}{rac{}}$ H ₃ O ⁺	+ A ⁻
[I]	0.350		0	0
[C]	- 2.399 x 10 ⁻²		+ 2.399 x 10 ⁻²	+ 2.399 x 10 ⁻²
[E]	0.326		2.399×10^{-2}	2.399×10^{-2}

3. Write Ka expression & substitute values.

Ka = $\frac{[H_3O^+][A^-]}{[HA]} = \frac{(2.399 \times 10^{-2})^2}{0.326}$ = 1.7653 x 10⁻³ and expressing in 3SD's, the answer is:

$$Ka = 1.77 \times 10^{-3}$$

For those that want a short-cut for multiple choice:



Do Ex. 77 & 80 on p. 152 SW

To Calculate Co (conc. of acid needed) form pH & Ka

Eg. Find the concentration of HCOOH needed to form a solution with pH = 2.69

- 1. First change pH to $[H_3O^+]$ $[H_3O^+] = antilog (-pH)$ = antilog (-2.69) $[H_3O^+] = 2.0417 \times 10^{-3} M$ (notice that the given pH limits us to 2SD's, but keep more in your calculations.)
- 2. Write out ionization equilibrium with an ICE TABLE. You can insert 2.0417 x 10^{-3} for equilibrium [H₃O⁺]. And since our **unknown** is the initial [HCOOH], we put in an "C₀" for the [I] of HCOOH:

	HCOOH +	- H₂O ±	$\overline{\bullet}$ H ₃ O ⁺	+	HCOO ⁻
[I]	Co		0		0
[C]					
[E]			2.0417 x 10 ⁻³		

Now we can see that the change in concentration [C] of $[H_3O^+]$ is " + 2.0417 x 10⁻³" and the [C] of HCOO⁻ will be the same. The [C] of HCOOH will be " - 2.0417 x 10⁻³"

	HCOOH +	- H ₂ O ±	\rightarrow H ₃ O ⁺ -	HCOO ⁻
[I]	Co		0	0
[C]	-2.0417×10^{-3}		$+ 2.0417 \times 10^{-3}$	$+ 2.0417 \times 10^{-3}$
[E]			2.0417 x 10 ⁻³	

We can now calculate the equilibrium concentrations [E] of HCOOH and HCOO⁻.

	HCOOH +	H ₂ O	\dashv H ₃ O ⁺	+ HCOO ⁻
[I]	Co		0	0
[C]	- 2.0417 x 10 ⁻³		+ 2.0417 x 10 ⁻³	+ 2.0417 x 10 ⁻³
[E]	C _o - 2.0417 x 10 ⁻³		2.0417 x 10 ⁻³	2.0417×10^{-3}

The next step will be to write the K_a expression and substitute the equilibrium concentrations in:

3. Write Ka expression. Substitute equilibrium concentrations in. Find Ka for HCOOH on the acid table:

$$Ka = [H_3O^+] [HCOO^-]$$
Find Ka on Acid
[HCOOH]
Find Ka on Acid
Table

 $1.8 \times 10^{-4} = \frac{(2.0417 \times 10^{-3})^2}{(\text{ Co} - 2.0417 \times 10^{-3})}$

Now we can solve for Co (the original concentration of the acid):

Co- 2.0417 x $10^{-3} = \frac{(2.0417 \text{ x } 10^{-3})^2}{1.8 \text{ x } 10^{-4}}$

 $Co - 2.0417 \times 10^{-3} = 2.3159 \times 10^{-2}$

 $Co = 2.3159 \text{ x } 10^{-2} + 2.0417 \text{ x } 10^{-3}$

 $Co = 2.52 \times 10^{-2} M$

 $Co = 2.5 \times 10^{-2} M or 0.025 M$ (remember, we are restricted to 2 SD's)

Do Ex. 76 & 78 on p. 152 of SW.

Now For Bases

<u>Base ionization</u> $NH_3 \rightarrow very \text{ common weak base. It partially ionizes in water to form <math>NH_4^+$ and OH^- :

 $NH_{3(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+_{(aq)} + OH_{(aq)}^-$

Equilibrium constant - called base ionization constant (Kb)

 $NH_{3(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

Kb expression: $Kb = \frac{[NH_4^+] [OH^-]}{[NH_3]}$

NOTE: Ions can also act as a weak bases. The reaction of an <u>ion</u> with water to form OH⁻ is called <u>base hydrolysis</u>. Equilibrium constant is still called Kb.

Eg.) Hydrolysis of CN



Ionization of N_2H_4 (weak base)



Do Ex 32 on p. 128 of SW.

How to Find Kb using Acid Table

(not shown directly)

 $\frac{\text{Derivation}}{- \text{Look at hydrolysis of base } F: F + H_2O \Rightarrow HF + OH$ $Kb_{(F-)} = \frac{[HF][OH]}{[F]}$ $- \text{Look at ionization the weak acid HF: } HF + H_2O \Rightarrow H_3O^+ + F$ $Ka_{(HF)} = \frac{[H_3O^+][F]}{[HF]}$ $- \text{Multiply } Ka_{[HF]} \times Kb_{[F^-]} = Conj. \text{ base}$ $Ka_{[HF]} \times Kb_{[F^-]} = \frac{[H_3O^+][F]}{[HF]} \times \frac{[HF][OH]}{[F]} = [H_3O^+][OH^-] \text{ (notice that [HF] and [F] will cancel.)}$ or $Ka_{(HF)} \times Kb_{[F^-]} = Kw$

 $Ka_{(HF)} \times Kb_{(F)} = Kw$

Or
$$Kb_{(F)} = Kw$$

 $Ka_{(HF)}$

In general:



Using Acid Table:

- 1. Find base on *right* side (if amphiprotic -locate base on <u>right</u> side only)
- 2. It's conjugate acid will be across from it on the left side.
- 3. The Ka of it's conjugate acid is on the **far right** of the same line.
- 4. Use equation: $Kb_{(base)} = \underline{Kw}$

Ka(conj. acid)

Eg.) Calculate the Kb for HCO_3^- : (find HCO_3^- on **<u>RIGHT</u>** SIDE)



Find Kb of SO₃²⁻

Similarly : If Kb (base) given

Ka (weak acid) = Kw
Kb(it's conj. Base)Eg.) The Kb for base B⁻ is 2.73 x 10⁻⁹Find the Ka for the acid HB3 sig. Digs.Ka(HB) = Kw
Kb(B⁻) = $\frac{1.00 \times 10^{-14}}{2.73 \times 10^{-9}} = \frac{3.66 \times 10^{-6}}{2.73 \times 10^{-9}}$

NOTES:

- > Table only states Ka values. For questions like this Kb will have to be calculated if not given.
- ➢ All Ka's on table are 2 SD's—limits any calculation using them to 2 SD's maximum.
- > The larger the Kb, the "stronger" the weak base the more OH^{-} produced.
- The smaller the Ka of an acid, the larger the Kb of its conjugate Base. (Weaker acids have stronger conjugate bases)

Calculations Involving Kb

Given: Find or find or find [Base] & Kb \rightarrow [OH⁻] \rightarrow pOH \rightarrow pH

eg.) Find [OH⁻] in a 0.20 M solution of KNO₂ (this is a salt, so it must be dissociated into it's ions first)



2. Hydrolysis (if ion) or ionization (if molecule) equation followed by an ICE table:

	NO ₂ +	- H ₂ O ±	\rightarrow HNO ₂	+	OH
[I]	0.20		0		0
[C]					
[E]					

We can let "x" equal the moles/L of NO_2 which hydrolyze as the reaction reaches equilibrium. Using the mole ratios in the equation and calculating [E]'s we get:

	NO ₂ +	- H ₂ O ≒	HNO ₂ +	· OH ⁻
[I]	0.20		0	0
[C]	-X		+x	+x
[E]	0.20 - x		Х	Х

3. <u>K_b Expression:</u>

 $K_{b} = \underline{[HNO_{2}] [OH^{-}]}$ at equilibrium [NO₂⁻]

On the next page, we substitute the [E]'s into the Kb expression (*Don't forget, we are in "baseland" not "acidland" now!*)



NOTE: In many problems, finding [OH⁻] is only the first step. Often you have to find the pH. Then you would use the process $[OH^-] \rightarrow pOH \rightarrow pH$

Kb From pH and Concentration

Eg.) At a certain temp, a 0.20 M solution of K_2SO_3 has a pH of 10.25. Calculate the Kb of SO_3^{2-} at this temp.

- 1. Identify SO_3^{2-} as a <u>weak base</u> (When K_2SO_3 is dissociated, it yields $K^+(a \text{ spectator})$ and SO_3^{2-})
- 2. $[OH^{-}]$ can be obtained from pH $(pH \rightarrow pOH \rightarrow [OH^{-}])$

pH = 10.25 so pOH = 14.00 - 10.25 = 3.75[OH⁻] = antilog (-pOH) = antilog (-3.75) = $1.778 \times 10^{-4} \text{ M}$

3. Write <u>hydrolysis</u> equation and an ICE table. (It is called *hydrolysis* this time because $SO_3^{2^-}$ is an <u>ion</u>.) We know the *initial* $[SO_3^{2^-}]$ is 0.20M and the *equilibrium* $[OH^-]$ is 1.778 x 10^{-4} M:

	SO_3^{2-} +	- H ₂ O 与	HSO ₃	+ OH ⁻
[I]	0.20		0	0
[C]				
[E]				1.778 x 10 ⁻⁴

So, from this, the change in conc. [C] of OH^{-} is "+ 1.778 x 10⁻⁴" and using the coefficient ratios we can insert the [C]'s for the other species and calculate the equilibrium concentrations [E]'s:

	SO_3^{2-} +	- H ₂ O 3	\Leftrightarrow HSO ₃	+	OH-
[I]	0.20		0		0
[C]	- 1.778 x 10 ⁻⁴		+ 1.778 x 10 ⁻⁴		+ 1.778 x 10 ⁻⁴
[E]	0.1998		1.778 x 10⁻⁴		1.778 x 10⁻⁴

4. Now we write the Kb expression and substitute the values from the [E]'s in our ICE table:



- Do worksheet on Ka, Kb calculations