

**SECOND EXAM**

Closed book, two pages of notes allowed.

Answer any two of the three questions. Please state any additional assumptions you made, and show all work.

Some useful constants:	$P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ $K_{\text{H}} = 10^{-1.5} \text{ M/atm}$
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**1. Carbonate System.**

Two raw drinking waters are mixed as they enter the headworks of a water treatment plant. The two are characterized as follows:

Water	Flow (MGD)	Alkalinity (mg/L as CaCO <sub>3</sub> )	pH
#1	20	5	6.30
#2	10	275	8.85

A. What will the pH of the blended water be immediately after mixing?

Steps in solving the problem:

1. Calculate the alpha-1 and alpha-2 values for both waters using the known pH
2. Use the known alkalinity equation and alpha values to determine  $C_T$  for water #1 and water #2

$$\text{Alk} = \alpha_1 C_T + 2\alpha_2 C_T + \text{OH}^- - \text{H}^+$$

So

$$C_T = \frac{\text{Alk} - \text{OH}^- + \text{H}^+}{\alpha_1 + 2\alpha_2}$$

3. Calculate the blended water Alk and  $C_T$ .

Water #1	Alk =	5	mg/L =	0.0001	equ/L			
	pH =	6.3			Flow =	20		
	<b>pH</b>	<b>H+</b>	<b>alpha-0</b>	<b>alpha-1</b>	<b>alpha-2</b>	<b>alpha-3</b>	<b>OH-</b>	<b>CT</b>
	6.3	5.01E-07	0.528727311	0.47123	4.4E-05	8.77E-49	2E-08	0.0002132
Water #2	Alk =	275	mg/L =	0.0055	equ/L			1 =
	pH =	8.85			Flow =	10		
	<b>pH</b>	<b>H+</b>	<b>alpha-0</b>	<b>alpha-1</b>	<b>alpha-2</b>	<b>alpha-3</b>	<b>OH-</b>	<b>CT</b>
	8.85	1.41E-09	0.00305158	0.96499	0.031954	2.26E-43	7.08E-06	0.0053386
Blended Water								
	CT =	0.001921669	M					
	Alk =	0.0019	eq/L =	95	mg/L			

4. From these two calculate the blended water pH, as shown below:

Start with the full alkalinity equation:

$$Alk = \alpha_1 C_T + 2\alpha_2 C_T + OH^- - H^+$$

In most cases you can ignore the OH and H, so:

$$Alk \approx \alpha_1 C_T + 2\alpha_2 C_T$$

Now working with the alpha values you have

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

and

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

Now substituting in for the alphas:

$$Alk \approx \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} C_T + 2 \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} C_T$$

So multiplying both sides by the denominator:

$$Alk([H^+]^2 + K_1[H^+] + K_1K_2) \approx K_1[H^+]C_T + 2K_1K_2C_T$$

And factoring it out:

$$Alk[H^+]^2 + Alk * K_1[H^+] + Alk * K_1K_2 \approx K_1[H^+]C_T + 2K_1K_2C_T$$

And combining the like terms:

$$Alk[H^+]^2 + Alk * K_1[H^+] - K_1[H^+]C_T + Alk * K_1K_2 - 2K_1K_2C_T \approx 0$$

$$Alk[H^+]^2 + (Alk * K_1 - K_1 C_T)[H^+] + (Alk * K_1 K_2 - 2K_1 K_2 C_T) \approx 0$$

Now we can use the quadratic equation with:

$$A = Alk$$

$$B = (Alk * K_1 - K_1 C_T) = (Alk - C_T)K_1$$

$$C = (Alk * K_1 K_2 - 2K_1 K_2 C_T) = (Alk - 2C_T)K_1 K_2$$

And the quadratic becomes:

$$[H^+] = \frac{-((Alk - C_T)K_1) \pm \sqrt{((Alk - C_T)K_1)^2 - 4Alk((Alk - 2C_T)K_1 K_2)}}{2Alk}$$

simplified #1	assume H and OH are insignificant
	Alk-Ct = -2.16694E-05
	Alk-2Ct = -0.001943339
	B = (Alk-Ct)*K1= -9.67937E-12
	4AC = 4Alk((Alk-2Ct)K1K2 = -3.08576E-22
	Quadratic
	H = 7.82525E-09
	pH= <b>8.107</b>

- B. What will the pH of the blended water be after it has reached equilibrium with the bulk atmosphere?

Exact Solution, ignoring carbonate	
	B = - K1*Kh*Pco2/Alk = -2.35097E-09
	C = 2K2*B = -2.19926E-19
	H = 2.44106E-09
	pH = <b>8.612</b>

- C. How many mg/L of caustic soda (NaOH) must be added to the unequilibrated blended water in part "A" to raise the pH to 9.80 ?

Here you are back to a closed system. Therefore you must assume  $C_T$  to be conservative again. You need to calculate the new alpha values for pH 9.8. Then use that information to calculate the new alkalinity. From here you get the increase in alkalinity required (delta Alk). This allow you to calculate how much NaOH is needed, which is the source of that new alkalinity.

		H+	alpha-0	alpha-1	alpha-2	alpha-3	OH-
Target pH	9.8	1.58E-10	0.000273887	0.77192	0.227809	1.44E-41	6.31E-05
	Alk =	0.002422 N					
	del Alk =	0.000522 N					
	NaOH =	0.02088 g/L =		20.9 mg/L			

## 2. Complexation

(50% total for all 4 parts) Bromide forms few strong complexes. Silver is one exception. The following two part problem concerns complexes of this metal-ligand combination..

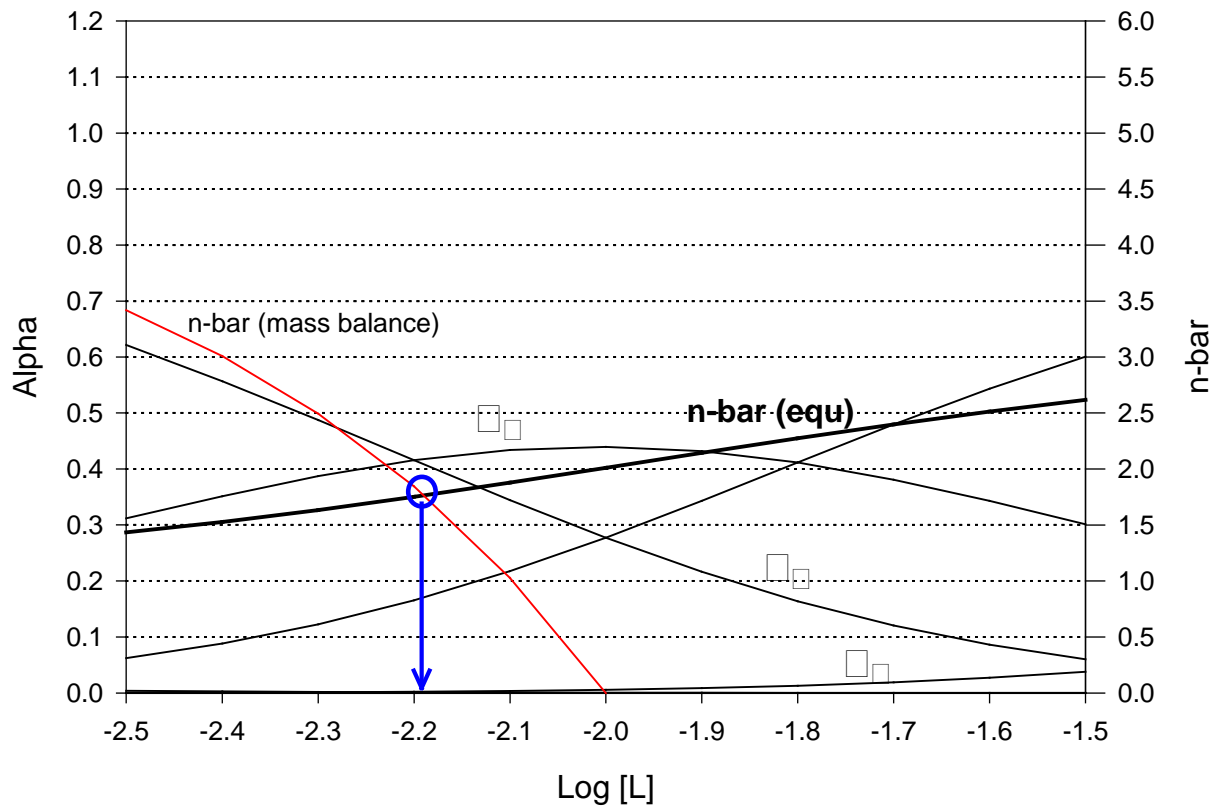
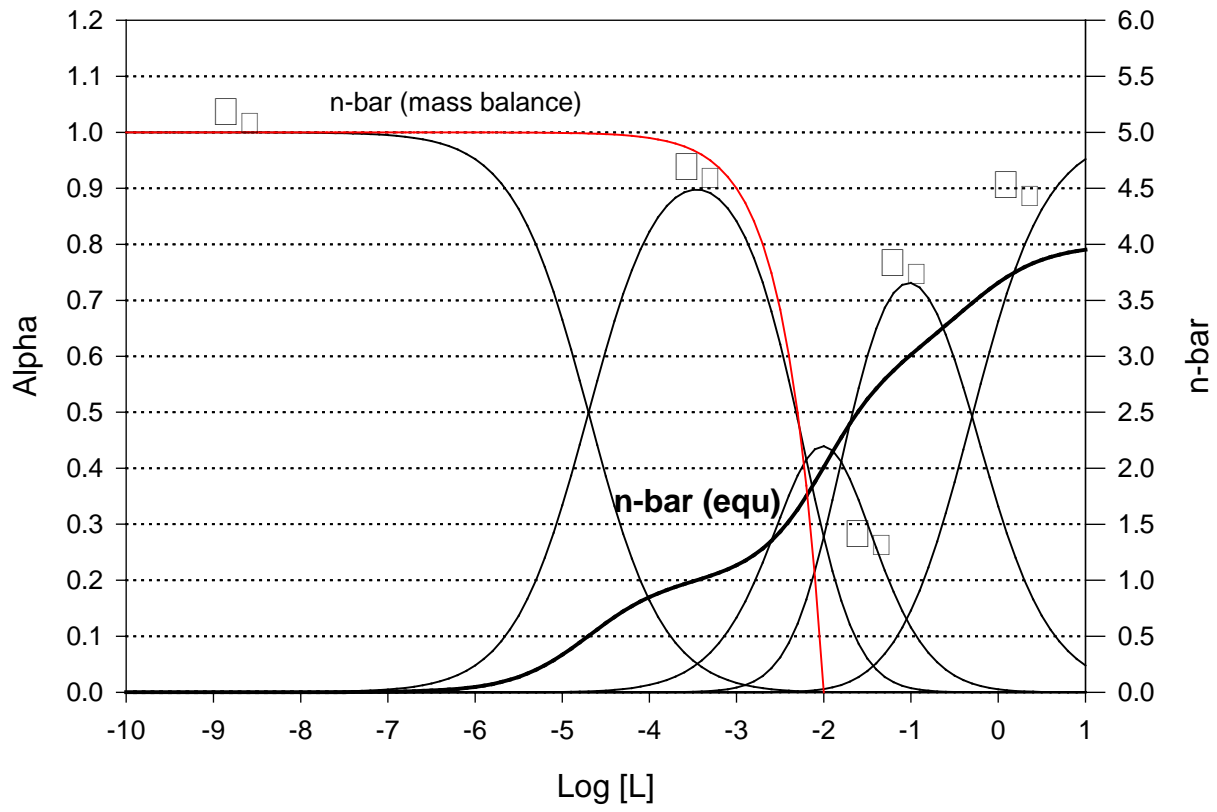
- A. (25%) Below is an “accurate” alpha graph for the  $\text{Ag}^+ - \text{Br}^-$  system. Using this graph determine the complete speciation in a waste brine where the total silver concentration is 2 mM and the total bromide concentration is 10 mM. Assume the pH of the brine is low enough to render any hydroxide complexes insignificant.

Draw the two n-bar lines (equilibrium line and mass balance line). Find the intersection of the two lines and draw a vertical at that point. Then read off the alpha values and determine concentrations. Below is an expanded view of the graph to aide in finding the best values. For the purposes of your exam, you only needed to draw the line over the full sized graph and locate the points as best you can by eye. The correct values are presented in the table below.

$$\bar{n}_{mb} = \frac{C_L - [L]}{C_M} = \frac{0.01 - [L]}{0.002} = 5 - 500[L]$$

From the graph the intersection is at  $[L] = 10^{-2.19}$ .

Graph Variable	Value	Species	Conc (M)
L	$10^{-2.19}$	$\text{Br}^-$	$6.5 \times 10^{-3}$
$\alpha_0$	~0	$\text{Ag}^+$	~0
$\alpha_1$	0.42	$\text{AgBr}$	$8.4 \times 10^{-4}$
$\alpha_2$	0.42	$\text{AgBr}_2^-$	$8.4 \times 10^{-4}$
$\alpha_3$	0.17	$\text{AgBr}_3^{-2}$	$3.4 \times 10^{-4}$
$\alpha_4$	~0	$\text{AgBr}_4^{-3}$	~0



- B. (10%) Now explain in qualitative terms how the speciation would change if the brine wastewater pH was substantially elevated so that hydroxide complexes became important and justify your answer using your knowledge of water chemistry

The higher level of hydroxide would create more Ag-OH complexes and thereby reduce the amount of Ag available to complex with bromide. This would change the effective  $\bar{n}_{mb}$  curve by raising the left asymptote. For example, let's assume an equilibrium ratio of  $\Sigma Ag(OH)_x / Ag^+$  for all x (ie.g., all possible OH complexes of silver), and we will call that ratio " $R_{OH}$ ". Since the free silver ( $Ag^+$ ) is  $\alpha_0 C_M$ , then the amount of Ag tied up by hydroxyl complexes is:  $\alpha_0 C_M R_{OH}$ . Then the amount of metal available for complexing bromide is  $(C_M - \alpha_0 C_M R_{OH})$  or  $C_M (1 - \alpha_0 R_{OH})$ . This complicates the  $\bar{n}_{mb}$  equation and makes it a function of  $\alpha_0$ :

$$\bar{n}_{mb} = \frac{C_L - [L]}{C_M (1 - \alpha_0 R_{OH})} = \frac{0.01 - [L]}{0.002(1 - \alpha_0 R_{OH})}$$

While the x-intercept wouldn't change, the y-intercept would go up and the overall effect would be to shift the bromide species to higher average numbers of bromide bound per silver atom. If there is an AgOH precipitate under these conditions, the  $\bar{n}$  would be further increased.

- C. (10%) Explain in qualitative terms how the speciation would change if the groundwater pH remained low, but if 10 mM of  $Hg^{+2}$  was added. Note that  $Hg^{+2}$  is another metal ion that strongly complexes bromide. Again, justify your answer using your knowledge of water chemistry.

Here we would have a competing metal for the ligand. This would effectively lower the available ligand ( $C_L$ ) much like the hydroxide lowered the available metal ( $C_M$ ). The degree to which it would be lowered would again depend on the amount of free ligand and the amount of available mercury. This would cause a decrease in the  $\bar{n}$  for Ag-Br complexes. Note that bromide is a very weak base (HBr has a pKa of about -8) so there would never be any appreciable formation of HBr.

- D. (5%) Finally explain in qualitative terms how the speciation would change if you took into account the impacts of high ionic strength. Note that the alpha graph as shown is based on the idea infinite dilution case (i.e., no ionic strength). Again, justify your answer using your knowledge of water chemistry.

Higher ionic strength would mask the charge attraction between  $Ag^+$  and  $Br^-$  and thereby decrease the  $K_1$  value. This would have the effect of shifting the  $\alpha_1$  curve to higher free ligand concentrations. For analogous reasons the  $K_2$  would be little changed, but the  $K_3$ ,  $K_4$ ,  $K_5$  and  $K_6$  would increase, and therefore, the  $\alpha_3$ ,  $\alpha_4$ ,  $\alpha_5$ , and  $\alpha_6$  curves would shift to the left. The exact change could be calculated using an ionic strength correction on the K values, assuming some model like Debye-Huckel. All of this would change the  $\bar{n}_{equ}$  curve and the intersection between the two  $\bar{n}$  curves.

### 3. pH, metals and lake liming

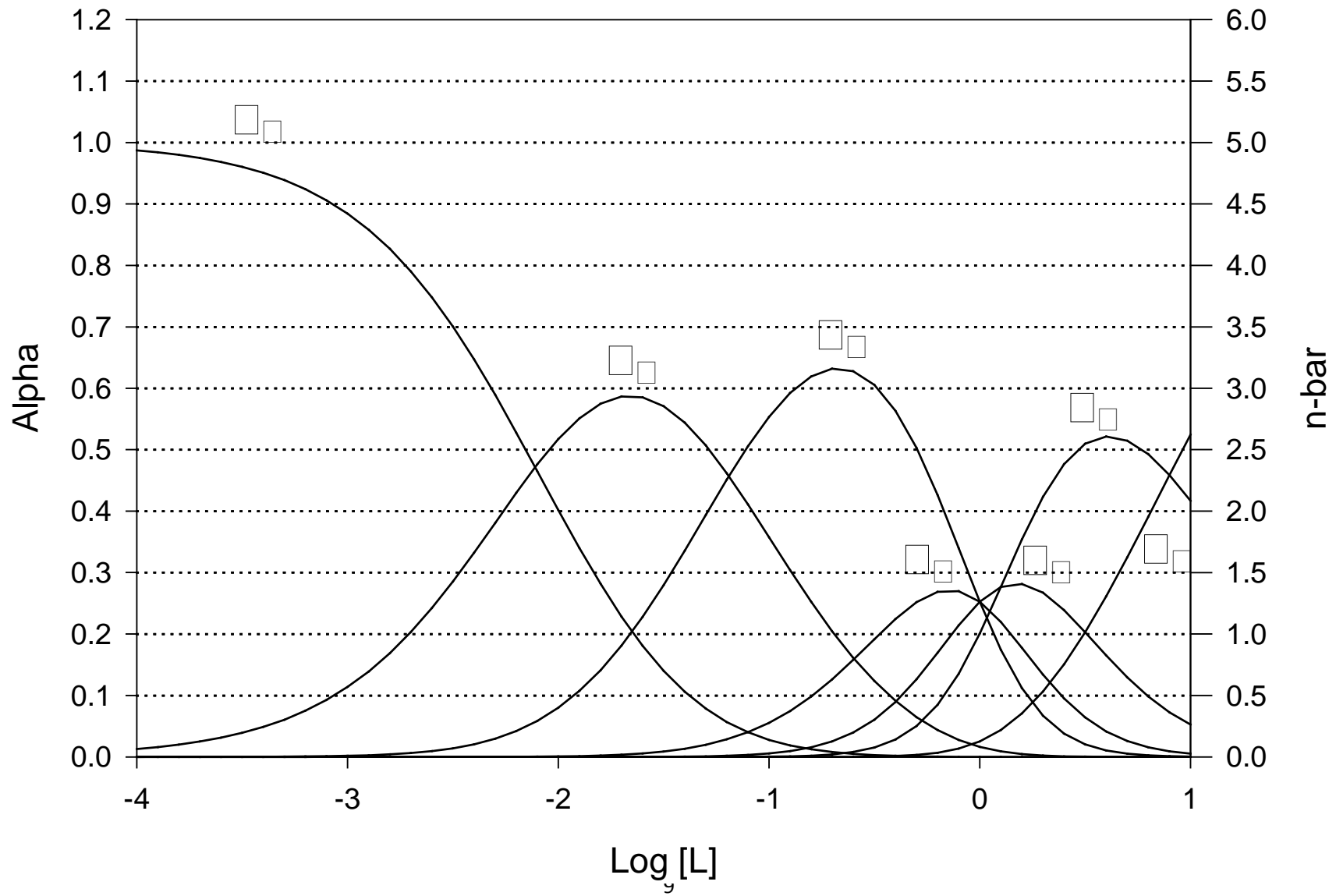
(50 % for all 3 parts) There are many lakes in NY and New England that are naturally acidic and impacted by acid precipitation. One of these is Lake Alcoa. This popular vacation spot now has a pH of 4.7, an alkalinity of -0.95 mg/L, and a total carbonate concentration ( $C_T$ ) of  $5 \times 10^{-5}$  M (assume 25°C,  $\sim 0$  ionic strength). Local officials have proposed lime  $\{Ca(OH)_2\}$  as a solution to the low pH problem.

- a. How much lime must be added (in moles/liter) to raise the pH to 8.3 after initial mixing?
- b. Calculate the ratio of  $[FeOH^{+2}]/[Fe^{+3}]$  and  $[Fe(OH)_2^+]/[Fe^{+3}]$  in the lake after lime addition (i.e., at pH 8.3)
- c. If this lake is allowed to reach equilibrium with the bulk atmosphere, what will its final pH be?

**No-one did this problem**









Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK <sub>a</sub>
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7 STRONG
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3 (&2) ACIDS
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-0
Hydronium ion	$\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$	0
Trichloroacetic acid	$\text{CCl}_3\text{COOH} = \text{H}^+ + \text{CCl}_3\text{COO}^-$	0.70
Iodic acid	$\text{HIO}_3 = \text{H}^+ + \text{IO}_3^-$	0.8
Thiocyanic Acid	$\text{HSCN} = \text{H}^+ + \text{SCN}^-$	1.1
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15 (&7.2,12.3)
Citric acid	$\text{C}_3\text{H}_5\text{O}(\text{COOH})_3 = \text{H}^+ + \text{C}_3\text{H}_5\text{O}(\text{COOH})_2\text{COO}^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$\text{HF} = \text{H}^+ + \text{F}^-$	3.2
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Propionic acid	$\text{C}_2\text{H}_5\text{COOH} = \text{H}^+ + \text{C}_2\text{H}_5\text{COO}^-$	4.87
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35 (&10.33)
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02 (&13.9)
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Boric acid	$\text{B}(\text{OH})_3 + \text{H}_2\text{O} = \text{H}^+ + \text{B}(\text{OH})_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Hydrocyanic acid	$\text{HCN} = \text{H}^+ + \text{CN}^-$	9.3
Phenol	$\text{C}_6\text{H}_5\text{OH} = \text{H}^+ + \text{C}_6\text{H}_5\text{O}^-$	9.9
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^- = \text{H}^+ + \text{C}_6\text{H}_4(\text{O})\text{COO}^{2-}$	9.92
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3
Bisulfide ion	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9
Water	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	14.00
Methane	$\text{CH}_4 = \text{H}^+ + \text{CH}_3^-$	34

Some additional equilibria

Equilibrium	Constant
$\text{FeOH}^{+2} = \text{Fe}^{+3} + \text{OH}^{-}$	$K_1 = 10^{-11.8}$
$\text{Fe}(\text{OH})_2^{+} = \text{FeOH}^{+2} + \text{OH}^{-}$	$K_2 = 10^{-10.5}$
$\text{Fe}(\text{OH})_4^{-} = \text{Fe}(\text{OH})_2^{+} + 2\text{OH}^{-}$	$K_3 = 10^{-12.1}$
$\text{Fe}_2(\text{OH})_2^{+4} = 2\text{Fe}^{+3} + 2\text{OH}^{-}$	$K_{22} = 10^{-25.05}$

