

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:	$P_{CO_2} = 10^{-3.5}$ atm $K_H = 10^{-1.5}$ M/atm
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1. Carbonate System.

(50% for all three parts) 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 ₃)	pH
#1	20	10	6.30
#2	10	350	9.50

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

Steps in solving the problem:

1. Calculate the alpha-1 and alpha-2 values for both waters using the known pH

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

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

2. Use the known alkalinity equation and alpha values to determine C_T for water #1 and water #2

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

So

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

3. Calculate the blended water Alk and C_T .

Water #1	Alk =	10	mg/L =	0.00020	equ/L			
	pH =	6.3			Flow =	20		
	pH	H+	alpha-0	alpha-1	alpha-2	alpha-3	OH-	CT
	6.3	5.01E-07	0.528727311	0.47123	4.4E-05	8.77E-49	2E-08	0.0004254
Water #2	Alk =	350	mg/L =	0.00700	equ/L			1 =
	pH =	9.5			Flow =	10		
	pH	H+	alpha-0	alpha-1	alpha-2	alpha-3	OH-	CT
	9.5	3.16E-10	0.000616345	0.87061	0.128773	4.07E-42	3.16E-05	0.0061768
Blended Water								
	CT =	0.002342504	M					
	Alk =	0.002466667	eq/L =	123.3333	mg/L			

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

There are many ways of solving this using some good simplifying assumptions, and thereby avoiding complicated numerical solutions. Here is one that I like. First, 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:

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

$$Alk[H^+]^2 + (Alk * K_1 - K_1C_T)[H^+] + (Alk * K_1K_2 - 2K_1K_2C_T) \approx 0$$

Now we can use the quadratic equation with:

$$A = Alk$$

$$B = (Alk * K_1 - K_1C_T) = (Alk - C_T)K_1$$

$$C = (Alk * K_1K_2 - 2K_1K_2C_T) = (Alk - 2C_T)K_1K_2$$

And the quadratic becomes:

$$[H^+] = \frac{-((Alk - C_T)K_1) \pm \sqrt{((Alk - C_T)K_1)^2 - 4Alk((Alk - 2C_T)K_1K_2)}}{2Alk}$$

simplified #1	assume H and OH are insignificant
	Alk-Ct = 0.000124163
	Alk-2Ct = -0.002218341
	B = (Alk-Ct)*K1= 5.54615E-11
	4AC = 4Alk((Alk-2Ct)K1K2 = -4.57297E-22
Quadratic	
	H = 8.06728E-10
	pH= 9.093

Note that the exact solution without the assumptions that H+ and OH- are insignificant would have gotten you a pH of 9.0527, which is reasonably close to the value above.

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

The easiest way to do this in my opinion is to start with the alkalinity equation

$$Alk = \alpha_1C_T + 2\alpha_2C_T + OH^- - H^+$$

And recognize that at the pH of interest alkalinity will be almost entirely bicarbonate, thus:

$$Alk \approx \alpha_1C_T$$

Then substitute in for the C_T using the Henry's law constant and the partial pressure of CO_2 as we normally do for open systems

$$Alk \approx \alpha_1 \frac{K_h p_{CO_2}}{\alpha_0}$$

And now recognize that the ratio of the two alphas is obtained from the quotient for K_1 .

$$\frac{\alpha_1}{\alpha_0} \equiv \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]}$$

And combining:

$$Alk \approx \frac{K_1 K_h p_{CO_2}}{[H^+]}$$

So:

$$[H^+] \approx \frac{K_1 K_h p_{CO_2}}{Alk}$$

And in this particular case, we have:

$$[H^+] \approx \frac{10^{-6.35} 10^{-3.5} 10^{-1.5}}{0.002466667} = 1.81088 \times 10^{-9}$$

So

$$pH = 8.742$$

which is very close to what one would get without ignoring H^+ and OH^- :

Exact Solution, ignoring carbonate			
	B = -	$K_1 * K_h * P_{CO_2} / Alk =$	-1.81088E-09
		C = $2K_2 * B =$	-1.69402E-19
		H =	1.90004E-09
		pH =	8.721

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 allows 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 =	0.002939	N				
	del Alk =	0.000472	N				
	NaOH =	0.018877	g/L =		18.9	mg/L	

2. Complexation

(50% total for all 4 parts) Fluoride forms few strong complexes. Aluminum 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 $\text{Al}^{+3} - \text{F}^-$ system. Using this graph determine the complete speciation in an acidified alum solution where the total aluminum concentration is 2 mM and the total fluoride concentration is 10 mM. Assume the pH of the 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.

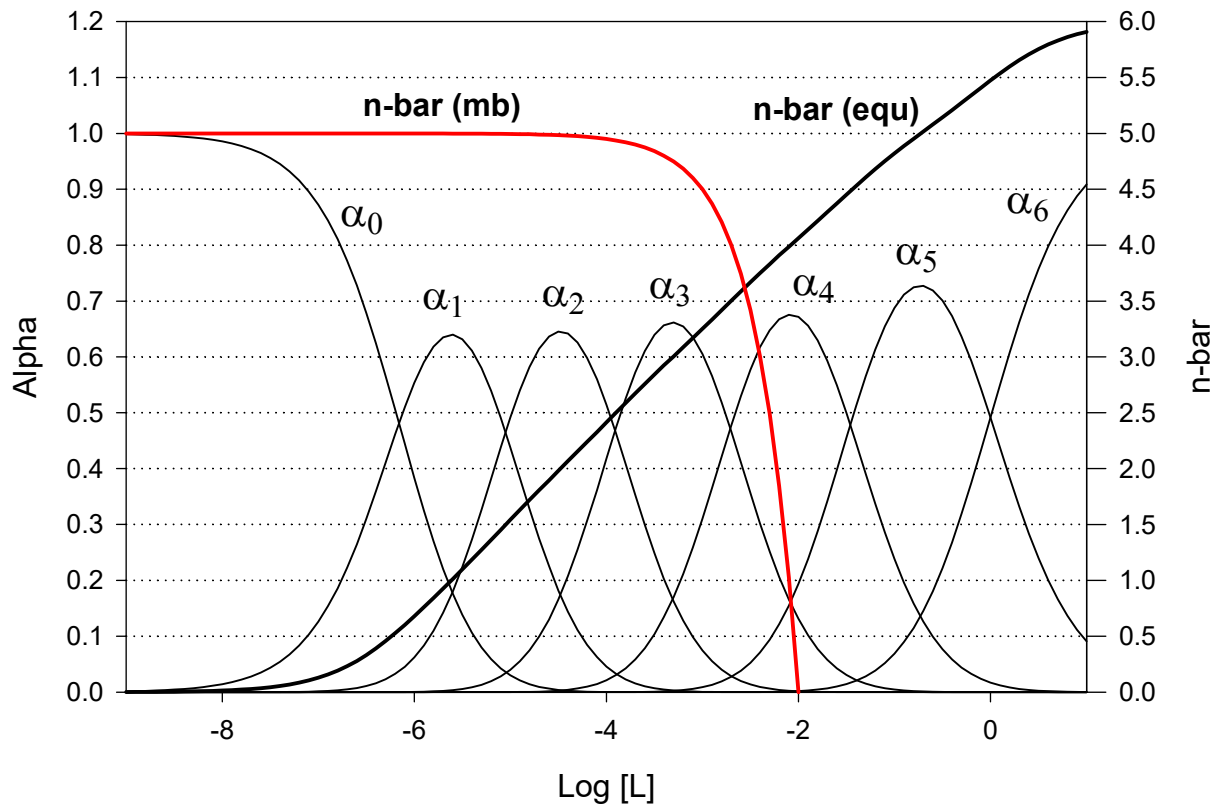
$$\bar{n}_{mb} = \frac{C_L - [L]}{C_M} = \frac{0.01 - [L]}{0.002} = 5 - 500[L]$$

From the graph the intersection is at $[L] = 10^{-2.57}$.

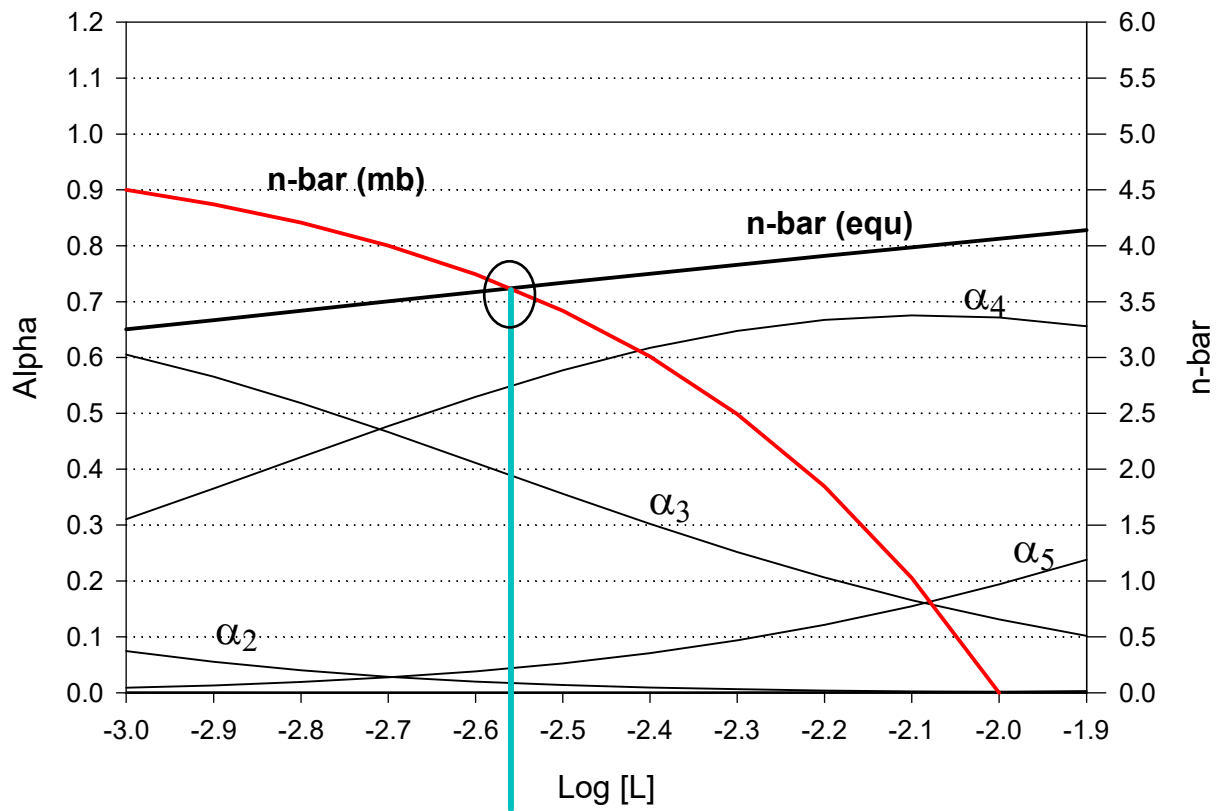
Graph Variable	Value	Species	Conc (M)
L	$10^{-2.57}$	F^-	2.7×10^{-3}
α_0	~ 0	Al^{+3}	~ 0
α_1	~ 0	AlF^{+2}	~ 0
α_2	0.02	AlF_2^+	4×10^{-5}

α_3	0.38	AlF_3	7.6×10^{-4}
α_4	0.55	AlF_4^-	1.1×10^{-3}
α_5	0.05	AlF_5^{-2}	1×10^{-4}
α_6	~ 0	AlF_6^{-3}	~ 0

Complexation



Complexation



- B.** (10%) Now explain in qualitative terms how the speciation would change if the alum solution 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 Al-OH complexes and thereby reduce the amount of Al available to complex with fluoride. This would change the effective \bar{n}_{mb} curve by raising the left asymptote. For example, let's assume an equilibrium ratio of $\Sigma \text{Al}(\text{OH})_x / \text{Al}^{+3}$ for all x (i.e., all possible OH complexes of aluminum), and we will call that ratio "R_{OH}". Since the free aluminum (Al^{+3}) is $\alpha_0 C_M$, then the amount of Al tied up by hydroxyl complexes is: $\alpha_0 C_M R_{OH}$. Then the amount of metal available for complexing fluoride 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 α_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 fluoride species to higher average numbers of fluoride bound per aluminum atom. However the total amount of aluminum bound to fluoride would go down as OH would be tying up some of the aluminum in the system. If there is an $\text{Al}(\text{OH})_3$ precipitate under these conditions, the \bar{n} would be further increased. Although not discussed in class, fluoride may be removed with an aluminum hydroxide precipitate through processes such as surface adsorption. Note that fluoride is a very weak base (HF has a pKa of about 3.2) so there would never be any appreciable formation of HF.

- C. (10%) Explain in qualitative terms how the speciation would change if the pH was high, and if 2 mM of EDTA was added. Note that EDTA does not form precipitates. Again, justify your answer using your knowledge of water chemistry.

Here we would have a competing ligand for the metal and a very strong ligand at that. This would effectively lower the available metal (C_M) for complexation with fluoride much like the hydroxide did. The degree to which it would be lowered would depend on the ligand (i.e., EDTA) to aluminum ratio. This would cause a decrease in the \bar{n} for Al-F complexes. As pH goes down, the EDTA becomes more protonated and the protonated forms are less effective as ligands and would be less able to compete with high levels of fluoride.

If the pH were high enough for $\text{Al}(\text{OH})_3$ to precipitate, then EDTA might just result in higher levels of solubilized Al in the form of Al-EDTA complexes and less hydroxide precipitate. If there isn't enough EDTA to cause all of the $\text{Al}(\text{OH})_3$ precipitate to dissolve, the residual Al^{+3} concentration will be determined only by the hydroxide solubility product relationship and in that case EDTA would not affect Al-F complexes.

- 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 ideal 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 Al^{+3} and F^- and thereby decrease the K_1 value. This would have the effect of shifting the α_1 curve to higher free ligand concentrations. For analogous reasons the K_2 and K_3 would be changed in the same way, but not as much. The K_4 would not appreciably change. In contrast, the K_5 and K_6 would increase, and therefore, the α_4 , α_5 , and α_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. multiple choice

(50%) Answer all 20 of the following questions. The first 10 are multiple choice. Please indicate which of the options is the best choice.

1. Pearson is:
 - a. the first name of your textbook's author
 - b. the founder of modern environmental chemistry
 - c. the originator of a discredited theory
 - d. the one who developed the hard and soft acid concept**
 - e. none of the above
2. When a solution spontaneously absorbs CO₂ from the atmosphere it:
 - a. results in higher total carbonate
 - b. drops in pH
 - c. approaches equilibrium
 - d. all of the above**
 - e. none of the above
3. Phosphate
 - a. is a tetradentate ligand
 - b. is a deadly poison
 - c. is insoluble
 - d. is the drug of choice for malaria
 - e. has been used as a "builder" in detergents**
4. H₂CO₃*:
 - a. is composed mostly of aqueous CO₂**
 - b. is always conservative, even in open systems
 - c. is a toxic substance
 - d. all of the above
 - e. complexes very strongly with sodium
5. Ion pairs:
 - a. are always charged
 - b. are larger than Bartlett pears
 - c. are illegal in Alabama
 - d. are outer-sphere complexes**
6. The value of n-bar:
 - a. is usually 6 or less
 - b. depends on the free ligand concentration
 - c. can be used to solve complexation problems graphically
 - d. all of the above**
 - e. none of the above

7. The buffer intensity of the open carbonate system:
- is independent of the alkalinity
 - is independent of the C_T
 - is always higher than the p_{CO_2}
 - is at a minimum where the $pH < pK_1$**
 - is at a minimum where the $pH = pK_2$
8. Detergent “builders” are used to:
- help solubilize grease
 - complex trace metals
 - take hardness cations from the surfactants**
 - elevate the acidity
 - reduce the caloric content
9. EDTA
- stands for ethylenediamine tetraacetic acid**
 - is most commonly used as a pH buffer
 - forms precipitates with most metals
 - is commonly used to enhance the impacts of copper on algae
 - is a tetra-dentate ligand
10. The Irving Williams Series
- is a means of estimating alkalinity
 - describes the inverse proportionality of acidity to alkalinity
 - includes a number of books, such as The Chapman Report, and The Prize
 - provides a comprehensive description of ligand structure
 - follows the increase in ligand affinity from Mn(II) to Cu(II)**

The 10 below are true/false. Mark each one of the following statements with either a “T” or an “F”

11. _____ **T** Mercury forms stronger complexes with iodide than with chloride .
12. _____ **T** As metals become more oxidized, they tend to be more prone to hydrolysis
13. _____ **F** Most complexation reactions essentially result in complete conversion to products or no conversion at all when at equilibrium
14. _____ **T** Phosphate forms stronger complexes than Hydrogen phosphate

15. _____ **F** Environmental systems are far more likely to be at equilibrium with respect to precipitation reactions than with respect to acid/base (e.g., proton) equilibrium.

16. _____ Oxidation state almost always changes with ligand number.

Not counted

17. _____ **T** The oxidation state of phosphorus in the environment is almost always +V.

18. _____ **F** As pH increases, so does the ligand number

19. _____ **T** An effective way to keep metals in solution is to add strong ligands like EDTA.

20. _____ **T** For the ferrous/ferric systems, oxidation results in stronger complexation.

Additional Information:

For a diprotic acid:

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

Some additional equilibria

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

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

NAME	FORMULA	pK _a
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

