

**FINAL EXAM**

Closed book, three pages of notes allowed.

**Answer Question #1, #2 and either #3 or #4.** Please state any additional assumptions you made, and **show all work**. If you don't have time to complete a section, please describe how you would solve the problem (without using a computer program such as MINEQL).

**Miscellaneous Information:**

$$R = 1.987 \text{ cal/mole}^\circ\text{K} = 8.314 \text{ J/mole}^\circ\text{K}$$

$$\text{Absolute zero} = -273.15^\circ\text{C}$$

$$1 \text{ joule} = 0.239 \text{ calories}$$

**1. Buffers (25%)**

You have prepared a 10 mM phosphate buffer designed to hold pH at 8.1 (25°C, assume  $I \approx 0$ ). The two chemicals at your disposal are  $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ .

- A. How much of each compound (in mM concentration) would you add to create your buffer?
- B. If you were to elevate the solution pH to 12.0, how much NaOH would you need to add (again in mM)?

**2. Redox (25%)**

Sulfide and sulfate are two forms of sulfur that commonly exist in the aquatic environment. They often are found in groundwaters with both reduced and oxidized iron.

- A. Write a balanced equation for the oxidation of hydrogen sulfide ( $\text{HS}^-$ ) to sulfate by reaction with amorphous ferric hydroxide, liberating free ferrous iron.
- B. Determine the net cell potential ( $E_{\text{net}}^\circ$ ) and the equilibrium constant for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in a typical groundwater and surface water systems.
- C. At what pH does the equilibrium rest half-way between the two sulfur species? Assume a free ferrous iron concentration of 0.56 mg/L. Which species (sulfate or bisulfide) will predominate at lower pHs?

### 3. Solubility (50%) Answer this or #4, your choice

Ferrous Sulfide (Troilite, a form of Pyrrhotite) is a rather insoluble mineral with a  $K_{so}$  of about  $10^{-18.1}$ . One would expect this to form in reduced groundwaters and sediments where ferrous iron and sulfide are major forms of Fe and S.  $Fe(OH)_{2(s)}$  would, of course form under the right conditions as well.

#	Reaction	pK
1 <sup>1</sup>	$FeS_{(s)} = Fe^{+2} + S^{-2}$	18.1
2	$Fe(OH)_{2(s)} + 2H^+ = Fe^{+2} + 2H_2O$	-12.9
3	$FeOH^+ + H^+ = Fe^{+2} + H_2O$	-9.5
4	$Fe(OH)_2^0 + 2H^+ = Fe^{+2} + 2H_2O$	-20.6
5	$Fe(OH)_3^- + 3H^+ = Fe^{+2} + 3H_2O$	-31.0

- Prepare a combined Ferrous Hydroxide and Ferrous Sulfide solubility diagram assuming you have a total sulfide concentration of  $10^{-6}M$ . The x-axis should be pH and the y-axis should be log concentration. Show lines for the four soluble iron species based on each precipitate. Identify the key precipitation zones with  $Fe_T$  lines.
- At what pH can both precipitates co-exist?
- If the sulfide concentration was to increase, would the pH where the precipitates co-exist increase or decrease?
- Describe in qualitative terms how the presence of  $10^{-3}M$  total carbonate would affect the hydroxide and sulfide precipitation zones.
- Describe in qualitative terms how the presence of  $10^{-6}M$  mercury would affect the hydroxide and sulfide precipitation zones

---

<sup>1</sup> Because of uncertainty over  $K_2$  for the sulfide system, this equilibrium are often expressed in terms of  $HS^-$  rather than  $S^{-2}$ . However, to be consistant, I have converted it to the more conventional  $K_{so}$  form in a way that is internally consistent with our value of  $10^{-13.9}$  for the sulfide  $K_2$ . These pK values were taken from Morel & Hering, 1993.

**4. Predominance (50%) Answer this or #3, your choice**

Lead carbonate ( $\text{PbCO}_{3(s)}$ ) and red Lead Oxide ( $\text{PbO}_{(s)}$ ) are two important solid phases that may control lead solubility in water<sup>2</sup>. In the attached pages is a detailed solution leading to a zinc hydroxide solubility diagram. Please use this to help solve the following problems.

- A. Prepare a solubility diagram (log C vs pH) for a water that is potentially in equilibrium with lead hydroxide and lead carbonate. Assume the water has  $10^{-3}\text{M}$  total carbonates (i.e., 1 mM  $\text{C}_T$ ). Show all soluble species along with the  $\text{Pb}_T$  line and indicate where precipitation will occur and the type of precipitate. To help you, there is a full solubility diagram for lead hydroxide only below. Feel free to work from this to prepare the combined carbonate-hydroxide diagram
- B. Below is a partially completed predominance diagram for the lead oxide – lead carbonate system. This was prepared for a total soluble lead concentration of  $10^{-4}\text{M}$  (i.e., 0.1 mM  $\text{Pb}_T$ ). Please complete this diagram showing the line(s) separating the two precipitates (C lines) and also determine and show the last remaining B line that separates the  $\text{PbCO}_3$  precipitation zone from the  $\text{Pb(OH)}_3^-$  zone (no precipitate). Show your work.

Stumm & Morgan Present the following data in Table A6.1

	$\text{OH}^-$		$\text{CO}_3^{-2}$
$\text{Pb}^{2+}$	PbL	6.3	
	PbL <sub>2</sub>	10.9	PbL • s
	PbL <sub>3</sub>	13.9	
	PbL <sub>2</sub> • s	15.3	

They note that the numerical values are Log formation constants.

Using these data you can rearrange the equilibrium quotients to get the following

In equilibrium with  $\text{PbO}(s)$ :

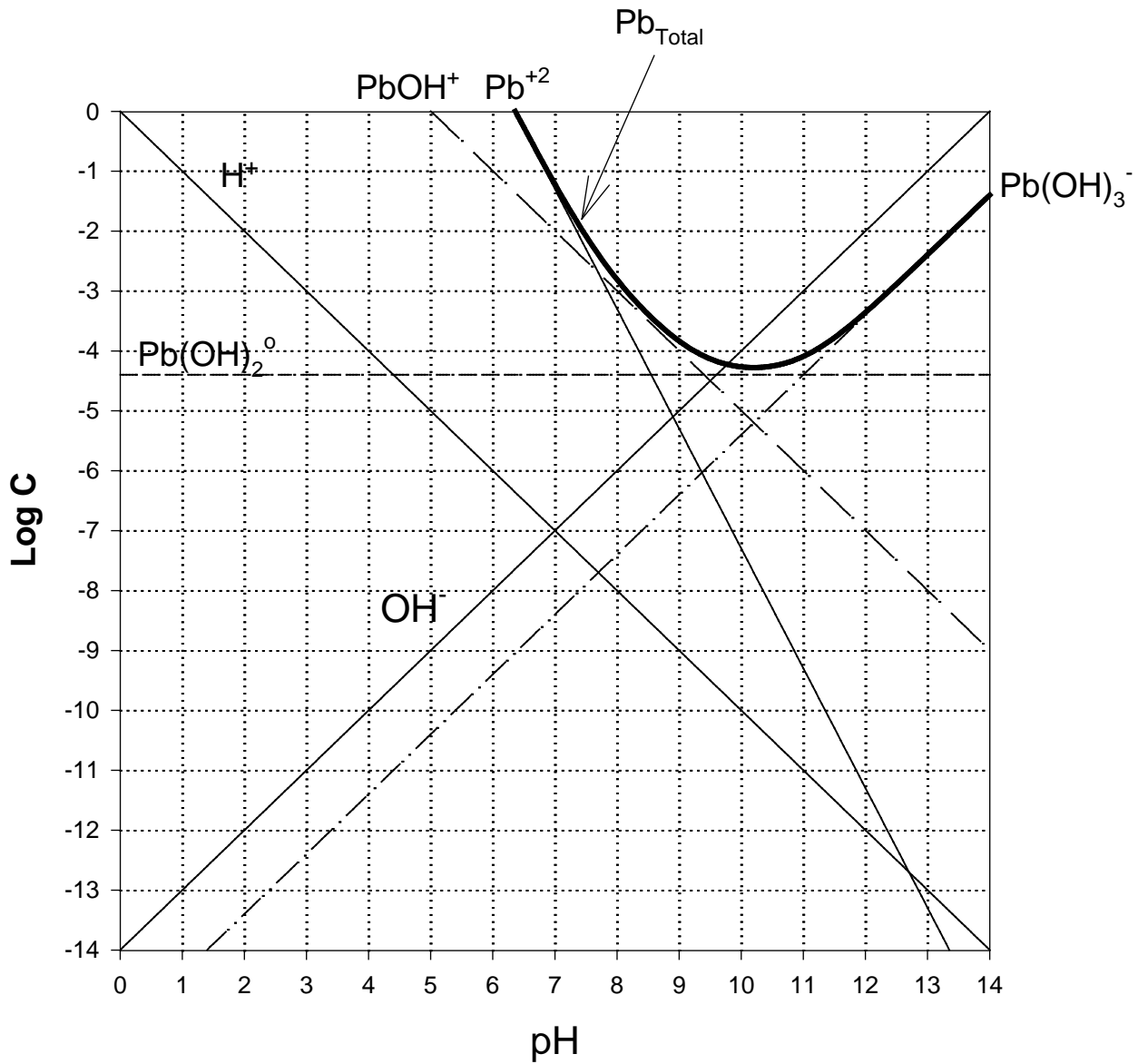
$$\text{Log}[\text{Pb}^{+2}] = +12.7 - 2\text{pH}$$

$$\text{Log}[\text{PbOH}^+] = +5.0 - \text{pH}$$

$$\text{Log}[\text{Pb(OH)}_2] = -4.4$$

$$\text{Log} [\text{Pb(OH)}_3^-] = -15.4 + \text{pH}$$

<sup>2</sup> Some mixed carbonate-hydroxide species may, in fact, be the most important, but they will not be considered here for the purpose of simplicity.



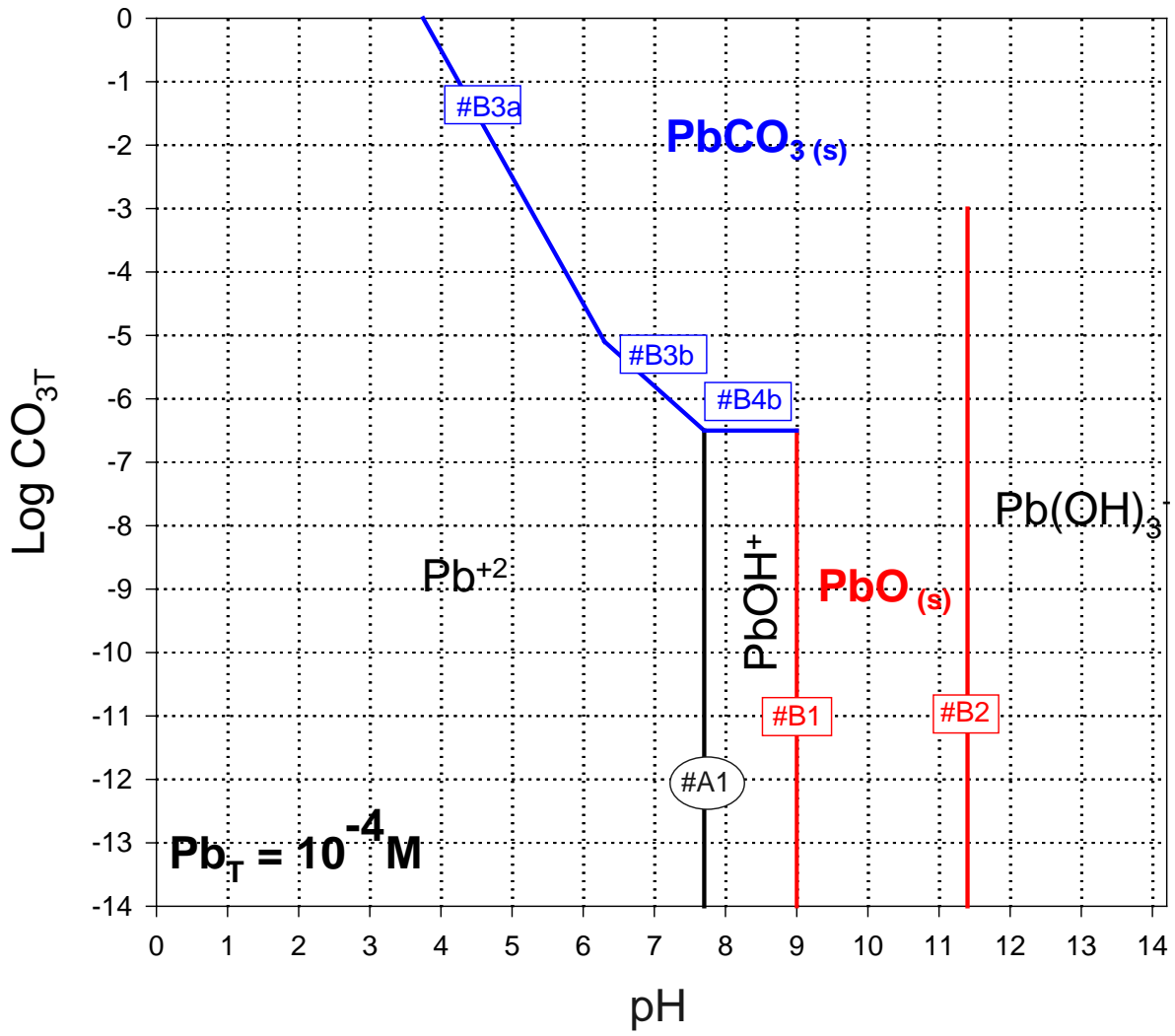
In equilibrium with  $PbCO_3(s)$ :

$$\text{Log}[Pb^{+2}] = -13.1 - \text{log}[CO_3^{-2}]$$

$$\text{Log}[PbOH^+] = -20.8 + \text{pH} - \text{log}[CO_3^{-2}]$$

$$\text{Log}[Pb(OH)_2] = -30.2 + 2\text{pH} - \text{log}[CO_3^{-2}]$$

$$\text{Log}[Pb(OH)_3] = -41.2 + 3\text{pH} - \text{log}[CO_3^{-2}]$$



Some important equilibrium constants:

<u>Equilibria</u>	<u>Log K</u>
$\text{Mg(OH)}_2(s) = \text{Mg}^{+2} + 2\text{OH}^-$	-11.6
$\text{Mg}^{+2} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.44
$\text{MgCO}_3(s) = \text{Mg}^{+2} + \text{CO}_3^{-2}$	-7.5
$\text{CaCO}_3(s) = \text{Ca}^{+2} + \text{CO}_3^{-2}$	-8.34
$\text{Ca(OH)}_2(s) = \text{Ca}^{+2} + 2\text{OH}^-$	-5.19
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) = \text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$	-4.62
$\text{CaOH}^+ = \text{Ca}^{+2} + \text{OH}^-$	-1.15
$\text{FeCO}_3(s) = \text{Fe}^{+2} + \text{CO}_3^{-2}$	-10.7
$\text{AlOH}^{+2} = \text{Al}^{+3} + \text{OH}^-$	-9.01
$\text{CdOH}^+ = \text{Cd}^{+2} + \text{OH}^-$	-3.92
$\text{CoOH}^+ = \text{Co}^{+2} + \text{OH}^-$	-4.80
$\text{CuOH}^+ = \text{Cu}^{+2} + \text{OH}^-$	-6.00
$\text{HgOH}^+ = \text{Hg}^{+2} + \text{OH}^-$	-10.60
$\text{NiOH}^+ = \text{Ni}^{+2} + \text{OH}^-$	-4.14
$\text{PbOH}^+ = \text{Pb}^{+2} + \text{OH}^-$	-6.29
$\text{ZnOH}^+ = \text{Zn}^{+2} + \text{OH}^-$	-5.04
$\text{HgS}(s) = \text{Hg}^{+2} + \text{S}^{-2}$	-42.7

Some important half-cell reactions

<u>Equ#</u>	<u>Half Cell Reaction</u>	<u><math>\Delta E^\circ</math> (Volts)</u>
1	$\text{O}_2(\text{aq}) + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+1.23
2	$\text{Mn}^{+3} + \text{e}^- = \text{Mn}^{+2}$	+1.51
3	$\text{Mn}^{+4} + \text{e}^- = \text{Mn}^{+3}$	+1.65
4	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{+2} + 4\text{H}_2\text{O}$	+1.49
5	$\text{Fe}^{+3} + \text{e}^- = \text{Fe}^{+2}$	+0.77
6	$\text{Cu}^{+2} + \text{e}^- = \text{Cu}^+$	+0.16
7	$\frac{1}{2}\text{HOBr} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Br}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.33
8	$\text{O}_3(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
9	$\text{Al}^{+3} + 3\text{e}^- = \text{Al}(s)$	-1.68
10	$\frac{1}{2}\text{HOCl} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.48
11	$\frac{1}{2}\text{OCl}^- + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.64
12	$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- = \text{HOBr} + 2\text{H}_2\text{O}$	+1.45
13	$\frac{1}{2}\text{NH}_2\text{Cl} + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{NH}_4^+$	+1.40
14	$\text{Fe(OH)}_3(\text{am}) + 3\text{H}^+ + \text{e}^- = \text{Fe}^{+2} + 3\text{H}_2\text{O}$	+0.95
15	$\text{SO}_4^{-2} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$	+0.25
16	$\text{S}(s) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{S}(g)$	+0.17
17	$\text{Zn}^{+2} + 2\text{e}^- = \text{Zn}(s)$	-0.76
18	$\text{Ni}^{+2} + 2\text{e}^- = \text{Ni}(s)$	-0.24
19	$\text{Pb}^{+2} + 2\text{e}^- = \text{Pb}(s)$	-0.126
20	$\text{ClO}_2 + \text{e}^- = \text{ClO}_2^-$	+0.95
21	$\text{PbO}_2(s) + 4\text{H}^+ + 2\text{e}^- = \text{Pb}^{+2} + 2\text{H}_2\text{O}$	+1.451

Properties of Selected Elements

Element	Symbol	Atomic #	Atomic Wt.	Valence	Electronegativity
Aluminum	Al	13	26.98	3	1.47
Bromine	Br	35	79.904	1,3,5,7	2.74
Calcium	Ca	20	40.08	2	1.04
Carbon	C	6	12.01	2,4	2.50
Chlorine	Cl	17	35.453	1,3,5,7	2.83
Copper	Cu	29	63.54	1,2	1.75
Hydrogen	H	1	1.01	1	2.20
Iron	Fe	26	55.845	0,2,3	1.83
Magnesium	Mg	12	24.31	2	1.23
Manganese	Mn	25	54.94	2,3,4,6,7	1.60
Nitrogen	N	7	14.0047	3,5	3.07
Oxygen	O	8	16.00	2	3.50
Potassium	K	19	39.10	1	0.91
Sodium	Na	11	22.99	1	1.01
Strontium	Sr	38	87.62	2	0.99
Sulfur	S	16	32.06	2,4,6	2.44
Zinc	Zn	30	65.39	2	1.65
Lead	Pb	82	207.19	2,4	

Atmospheric Gases

Gas	Atmospheric Abundance	Henry's Law Const <sup>3</sup>
<a href="#">Nitrogen</a> (N <sub>2</sub> )	780,840 ppmv (78.084%)	6.1 x 10 <sup>-4</sup>
<a href="#">Oxygen</a> (O <sub>2</sub> )	209,460 ppmv (20.946%)	1.3 x 10 <sup>-3</sup>
<a href="#">Argon</a> (Ar)	9,340 ppmv (0.9340%)	1.4 x 10 <sup>-3</sup>
<a href="#">Carbon dioxide</a> (CO <sub>2</sub> )	387 ppmv (0.0387%)	3.4 x 10 <sup>-2</sup>
<a href="#">Neon</a> (Ne)	18.18 ppmv (0.001818%)	4.5 x 10 <sup>-4</sup>
<a href="#">Helium</a> (He)	5.24 ppmv (0.000524%)	3.7 x 10 <sup>-4</sup>
<a href="#">Methane</a> (CH <sub>4</sub> )	1.79 ppmv (0.000179%)	
<a href="#">Krypton</a> (Kr)	1.14 ppmv (0.000114%)	
<a href="#">Hydrogen</a> (H <sub>2</sub> )	0.55 ppmv (0.000055%)	7.8 x 10 <sup>-4</sup>
<a href="#">Nitrous oxide</a> (N <sub>2</sub> O)	0.3 ppmv (0.00003%)	
<a href="#">Xenon</a> (Xe)	0.09 ppmv (9x10 <sup>-6</sup> %)	

<sup>3</sup> In: moles/L/atm

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
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	0
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
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48
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
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{+3} = \text{H}^+ + \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{+2}$	4.8
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02
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
Hypobromous acid	$\text{HOBr} = \text{H}^+ + \text{OBr}^-$	8.71
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
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
Sulfide	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9

$\alpha_2$  for a diprotic acid:

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



