CEE 680 4 May 2018

FINAL EXAM

Closed book, three pages of notes allowed.

Answer any 3 of the 4 Questions. Each is worth 33% (you get an additional 1% for writing your name on the exam). Please indicate clearly which 3 questions you wish to be graded. State any important 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 cal/mole°K = 8.314 J/mole°K

Absolute zero = -273.15°C

1 joule = 0.239 calories

1. *Alkalinity & Buffering (33%)*

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 CaCO3)	pH
#1	20	5	6.30
#2	10	275	8.85

a) Describe how you would calculate the pH of the blended water. Include all steps in the process of making this calculation. Show equations where appropriate. There is no need to acutally do the calculation, however.

b) What will the alkalinity in of Water #1 be after addition of 35 mg/L of NaCl and 20 mg/L of Na_2CO_3? Present the answer in the traditional engineering units of mg/L alkalinity as $CaCO_3$.

c) What will the alkalinity of Water #2 be after addition of 150 mg/L of NaOH? Present the answer in the traditional engineering units of mg/L alkalinity as $CaCO_3$.

d) What will the pH be of Water #2 after addition of 150 mg/L of NaOH, assuming you've given it enough time to equilibrate with the atmosphere?

2. *Redox (33%)*

Lead is a contaminant of concern to drinking water utilities. It has a complex and incompletly defined redox, precipitation and complexation chemistry. The presence of Pb (+IV) deposits in distribution sytems has raised the concern that they may become reduced and enter into the more soluble Pb (+II) form. This question concerns the ability of chlorine to keep lead in the higher oxidation state.

a) Write a balanced equation for the oxidation of divalent lead to tetravalent lead oxide solid ($PbO_{2(s)}$) by reaction with hypochlorous acid (HOCl)

b) Determine the equilibrium constant (K) for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in a typical drinking water distribution system. How does pH affect the tendency of this reaction to proceed?

c) If the US lead standard (action level) is 0.015 mg/L, at what HOCl concentration will you just be able to meet the standard if the lead species are all in redox equilibrium with the HOCl/Cl- redox couple? Assume a pH of 7 and a chloride concentration of 1 mM (~35 mg/L). Please give your answer in mg/L as HOCl.

d) Assuming you have a drinking water distribution systems using free chlorine that maintains a residual of at least 0.071 mg/L (0.001 mM) of HOCl, how low can the pH be and still allow you to meet the lead standard (assume a 1 mM chloride concentration as in part c, and assume all species are in redox equilibrium).

e) Comment on the significance of this calculation and why the actual situation may not match your calculations.

3. Solubility (33%)

Lead carbonate ($PbCO_{3(s)}$) and red Lead Oxide ($PbO_{(s)}$) are two important solid phases that may control lead solubility in water[1]. Below is a solution leading to a lead oxide 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 oxide and lead carbonate. Assume the water has $\underline{10^{-4}\,M}$ total carbonates (i.e., 0.1 mM C_T). Show all soluble species along with the Pb_T line and indicate where precipitation will occur and the type of precipitate. Show your calculations for each line. Again, to help you, there is a full solubility diagram for lead oxide below. Feel free to work from this to prepare the combined carbonate-oxide diagram

b) Using this diagram, estimate the level of total carbonates needed to just meet the US lead action level (0.015 mg/L), presuming you're at the "optimum" pH. Also state what that "optimium" pH is.

c) Explain qualitatively how the solubility of lead would change if there were a souble dicarbonate species (i.e., $Pb(CO_3)_2^{-2}$) that could form.

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[1] Some mixed carbonate-hydroxide species may, in fact, be the most important, but they will not be considered here for the purpose of simplicity.

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

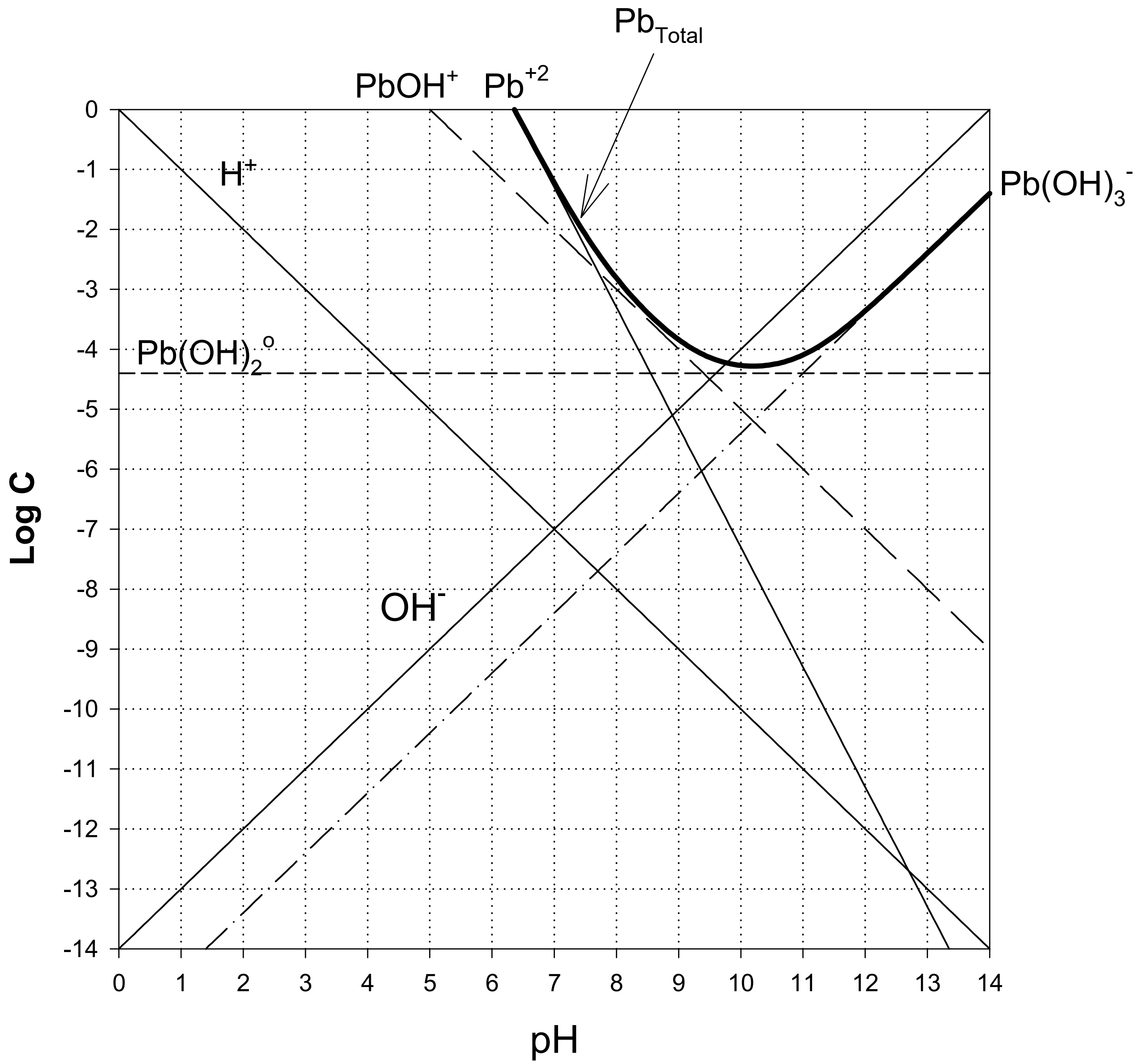
	OH^-		CO_3^{-2}	
Pb^{2+}	PbL	6.3		
	PbL_2	10.9	PbL • s	13.1
	PbL_3	13.9		
	PbL_2 • s	15.3		

They note that the numerical values are Log formation contstants.

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

In equilibrium with PbO(s):
Log[Pb^{+2}] = +12.7 -2pH
Log[$PbOH^+$] = +5.0 –pH
Log[$Pb(OH)_2$] = -4.4
Log [$Pb(OH)_3$] = -15.4 +pH

In equilibrium with $PbCO_3$(s):
Log[Pb^{+2}] = -13.1 –log[CO_3^{-2}]
Log[$PbOH^+$] = -20.8 +pH –log[CO_3^{-2}]
Log[$Pb(OH)_2$] = -30.2 +2pH –log[CO_3^{-2}]
Log [$Pb(OH)_3$] = -41.2 +3pH –log[CO_3^{-2}]


Pb$_{Total}$
PbOH$^+$
Pb^{+2}
Pb(OH)$_3^-$
H$^+$
Pb(OH)$_2^o$
OH$^-$
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
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14

4. Multiple Choice and True/False (33%)

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

1. The first endpoint of an alkalinity titration:
    - a. is at pH 4.5
    - b. can be determined with phenolphthalein indicator
    - c. is highly dependent on total carbonate concentration
    - d. is when all carbonates are converted to carbonic acid
    - e. none of the above

2. When a solution spontaneously absorbs CO_2 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 strong acid
    - b. has two different types of ligand atoms
    - c. is a strong ligand
    - d. is readily oxidized by chlorine
    - e. has been used as a “surfactant” in detergents

4. H_2CO_3*:
    - a. is composed mostly of aqueous CO_2
    - 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. Ionic strength:
    - a. increases with increasing salinity
    - b. can affect chemical equilibria
    - c. is related to electrical conductivity
    - d. all of the above
    - e. none of the above

6. Most Metal Hydroxide precipitates:
    - a. become more soluble as pH decreases below 4
    - b. decrease in solubility as the oxidation state of the metal increases
    - c. readily form the zero valent metal at very low pHs
    - d. all of the above
    - e. none of the obove

7. The buffer intensity of the open carbonate system:
   - a. is independent of the alkalinity
   - b. is independent of the C_T
   - c. is always higher than the p_{CO2}
   - d. is at a minimum where the pH is just below the pK_1
   - e. is at a minimum where the pH = pK_2

8. Detergent “builders” are used to:
   - a. help solubilize grease
   - b. complex trace metals
   - c. take hardness cations from the surfactants
   - d. elevate the acidity
   - e. reduce the caloric content

9. A Galvanic Cell
   - a. is a device that produces hydrogen gas from water
   - b. must always be carefully buffered
   - c. can be used to determine a oxidation half cell potential
   - d. all of the above
   - e. none of the above

10. The Irving Williams Series
   - a. is a means of estimating alkalinity
   - b. describes the inverse proportionality of acidity to alkalinity
   - c. includes a number of books, such as The Chapman Report, and The Prize
   - d. provides a comprehensive description of ligand structure
   - e. 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. _____ Silver forms stronger complexes with with chloride than with fluoride.

12. ______ As metals become more oxidized, they tend to be more prone to hydrolysis

13. ______ Most complexation reactions essentially result in complete conversion to products or no conversion at all when at equilibrium

14. ______ Phosphate forms weaker complexes than Hydrogen phosphate

15. ______ 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. ______ A substance is oxidized when it gains electrons.

17. ______ The oxidation state of phosphorus in the environment is almost always +V.

18. ______ Increasing ligand concentrations always result in greater amount of metal precipitation

19. ______ For the ferrous/ferric systems, oxidation results in higher solubility.

20. ______ For the ferrous/ferric systems, oxidation results in stronger complexation.

Some important equilibrium constants:

Equilibria	Log K
$Mg(OH)_{2\ (s)} = Mg^{+2} + 2OH^-$	-11.6
$Mg^{+2} + H_2O = MgOH^+ + H^+$	-11.44
$MgCO_{3\ (s)} = Mg^{+2} + CO_3^{-2}$	-7.5
$CaCO_{3(s)} = Ca^{+2} + CO_3^{-2}$	-8.34
$Ca(OH_2)_{(s)} = Ca^{+2} + 2OH^-$	-5.19
$CaSO_4 \cdot 2H_2O_{(s)} = Ca^{+2} + SO_4^{-2} + 2H_2O$	-4.62
$CaOH^+ = Ca^{+2} + OH^-$	-1.15
$FeCO_{3(s)} = Fe^{+2} + CO_3^{-2}$	-10.7
$AlOH^{+2} = Al^{+3} + OH^-$	-9.01
$CdOH^+ = Cd^{+2} + OH^-$	-3.92
$CoOH^+ = Co^{+2} + OH^-$	-4.80
$CuOH^+ = Cu^{+2} + OH^-$	-6.00
$HgOH^+ = Hg^{+2} + OH^-$	-10.60
$NiOH^+ = Ni^{+2} + OH^-$	-4.14
$PbOH^+ = Pb^{+2} + OH^-$	-6.29
$ZnOH^+ = Zn^{+2} + OH^-$	-5.04
$HgS_{(s)} = Hg^{+2} + S^{-2}$	-42.7

Some important half-cell reactions

Equ#	Half Cell Reaction	ΔE° (Volts)
1	$O_2(aq) + 4H^+ + 4e^- = 2H_2O$	+1.23
2	$Mn^{+3} + e^- = Mn^{+2}$	+1.51
3	$Mn^{+4} + e^- = Mn^{+3}$	+1.65
4	$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$	+1.49
5	$Fe^{+3} + e^- = Fe^{+2}$	+0.77
6	$Cu^{+2} + e^- = Cu^+$	+0.16
7	$\frac{1}{2}HOBr + \frac{1}{2}H^+ + e^- = \frac{1}{2}Br^- + \frac{1}{2}H_2O$	+1.33
8	$O_{3\ (g)} + 2H^+ + 2e^- = O_{2\ (g)} + H_2O$	+2.07
9	$Al^{+3} + 3e^- = Al_{(s)}$	-1.68
10	$\frac{1}{2}HOCl + \frac{1}{2}H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	+1.48
11	$\frac{1}{2}OCl^- + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	+1.64
12	$BrO_3^- + 5H^+ + 4e^- = HOBr + 2H_2O$	+1.45
13	$\frac{1}{2}NH_2Cl + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}NH_4^+$	+1.40
14	$Fe(OH)_{3(am)} + 3H^+ + e^- = Fe^{+2} + 3H_2O$	+0.95
15	$SO_4^{-2} + 9H^+ + 8e^- = HS^- + 4H_2O$	+0.25
16	$S_{(s)} + 2H^+ + 2e^- = H_2S_{(g)}$	+0.17
17	$Zn^{+2} + 2e^- = Zn(s)$	-0.76
18	$Ni^{+2} + 2e^- = Ni(s)$	-0.24
19	$Pb^{+2} + 2e^- = Pb(s)$	-0.126
20	$ClO_2 + e- = ClO_2-$	+0.95
21	$PbO_2(s) + 4H^+ + 2e^- = Pb^{+2} + 2H_2O$	+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[2]
Nitrogen (N_2)	780,840 ppmv (78.084%)	6.1×10^{-4}
Oxygen (O_2)	209,460 ppmv (20.946%)	1.3×10^{-3}
Argon (Ar)	9,340 ppmv (0.9340%)	1.4×10^{-3}
Carbon dioxide (CO_2)	387 ppmv (0.0387%)	3.4×10^{-2}
Neon (Ne)	18.18 ppmv (0.001818%)	4.5×10^{-4}
Helium (He)	5.24 ppmv (0.000524%)	3.7×10^{-4}
Methane (CH_4)	1.79 ppmv (0.000179%)	
Krypton (Kr)	1.14 ppmv (0.000114%)	
Hydrogen (H_2)	0.55 ppmv (0.000055%)	7.8×10^{-4}
Nitrous oxide (N_2O)	0.3 ppmv (0.00003%)	
Xenon (Xe)	0.09 ppmv (9×10^{-6}%)	

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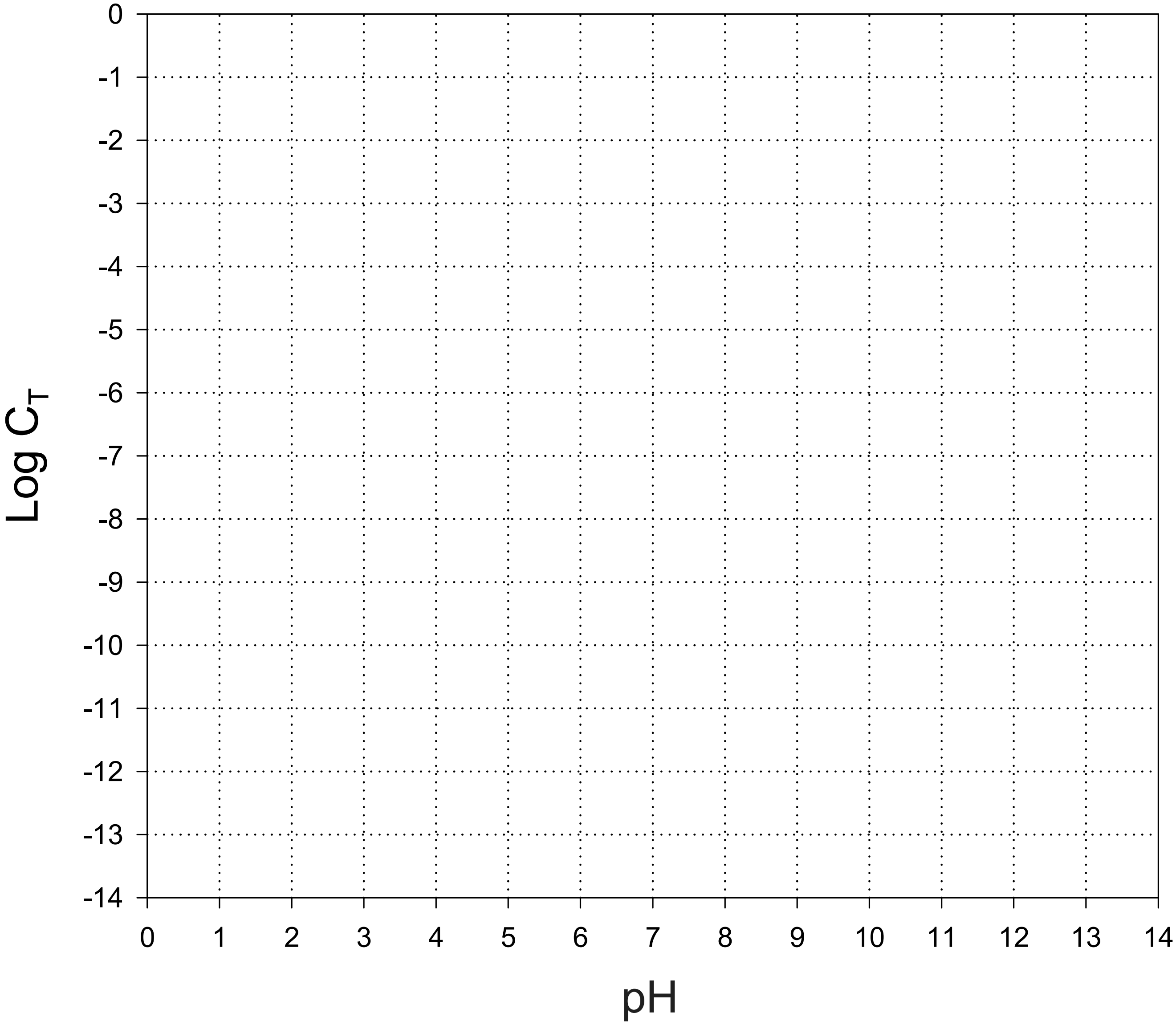
[2] In: moles/L/atm

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

NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3
Nitric acid	$HNO_3 = H^+ + NO_3^-$	0
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Aluminum ion	$Al(H_2O)_6^{+3} = H^+ + Al(OH)(H_2O)_5^{+2}$	4.8
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Hypobromous acid	$HOBr = H^+ + OBr^-$	8.71
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Sulfide	$HS^- = H^+ + S^{-2}$	13.9

α_2 for a diprotic acid:

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