Introductory Chemical Engineering Thermodynamics

Chapter 18

Electrolytes

(18.01) Calcium chloride is used occasionally as an alternative …

Errata, US printings 1-3, International printing 1. Part (b) at 760 mmHg; (c) at 25 °C.
Solution:
(a) Basis: 100 g total, 5 g salt, 95 g water
NaCl, 58.44 g/mol
CaCl2, 110.98 g/mol
ΔH^{fus} (kJ/mol)= 6.01
95 g water = 95/18.02 = 5.272 mol
Rearranging Eqn. 14.23, $T = (1/T_m - R\ln x/\Delta H^{fus})^{-1}$

	mol	mol ion	x_{salt}	x_{H2O}	T
NaCl	0.085558	0.171116	0.031438	0.968562	269.8922
CaCl2	0.045053	0.135159	0.024997	0.975003	270.5618

5 wt% NaCl gives a melting pt about 0.65C lower. There are three ions in CaCl2, but the MW is higher, so the same mass give less melting depression.

(b) mol fractions are calculated above. The boiling point elevation assuming an ideal solution will be given by Raoult's law,
$P = x_{H2O} P^{sat}$
The mol fractions are given in (a). The temperature is adjusted until P = 760 mmHg.

	A	B	C	
water	8.07131	1730.63	233.426	
	xH2O	T(C)	Psat	P
NaCl	0.968562	100.8903	784.6681	760
CaCl2	0.975003	100.7045	779.4841	759.9995

NaCl give a boiling pt elevation about 0.2C higher for the same mass.

(a) by Eqn 11.71
$\Pi = -(RT/V)\ln x = -8.314\ (\text{MPa cm}^3/\text{mol-K})\ (298.15\ \text{K}) / (18.02\ \text{cm}^3/\text{mol}) \ln x$
using the x values from part (a).
NaCl, $\Pi = 4.4$ MPa
$CaCl_2$, $\Pi = 3.5$ MPa

(18.02) Ammonia is a weak base, as indicated by the pKa,A and pKa,B values...

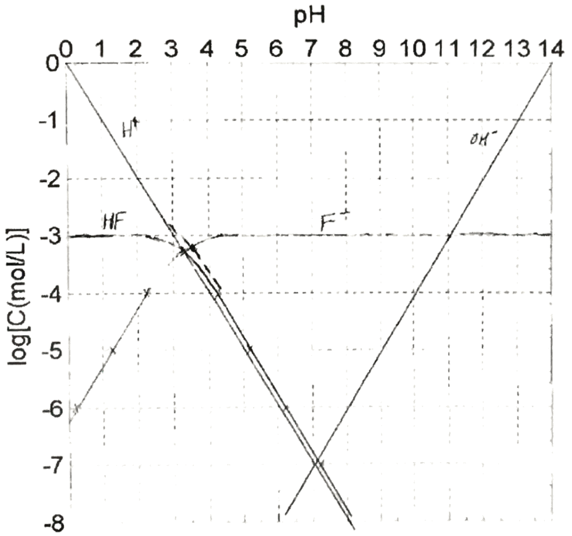
For ammonia, the acid reaction is
$NH_4^+ + H_2O = NH_3 + H_3O^+$ $pK_{a,A} = 9.245$
$K_{a,A} = [NH_3][H+]/[NH_4^+]$, where activity of water is 1.
Material balance – $[NH_3] + [NH_4^+] = C_A = 0.15$ m
Inserting the material balance to solve for the smaller quantity $[NH_3]$
$K_{a,A} = [NH_3][H+]/(C_A - [NH_3]) \rightarrow C_AK_{a,A} - K_{a,A}[NH_3] = [NH_3][H+] \rightarrow$
$[NH_3] = C_AK_{a,A}/(K_{a,A} + [H+])$
or the amount un-ionized is
$[NH_3]/C_A = K_{a,A}/(K_{a,A} + [H+]) = 10^{-9.245}/(10^{-9.245} + 10^{-pH})$
At pH 7, $[NH_3]/C_A = 5.66E-3$, and $[NH_4^+]/C_A = 0.99434$
At pH 1, $[NH_3]/C_A = 5.69E-09$, and $[NH_4^+]/C_A = 0.999999994$

(18.03) Sodium fluoride, NaF, is dissolved in water at an apparent...

$[Na^+] = 10^{-3}$ (1)
$[F^-] + [HF] = 10^{-3}$ or $[F^-] = 10^{-3} – [HF]$ (2)
charge balance: $[Na^+] + [H^+] = [F^-] + [OH^-]$ (3)
insert (1) and (2) into (3)
$[HF] + [H^+] = [F^-] + [OH^-]$ proton condition

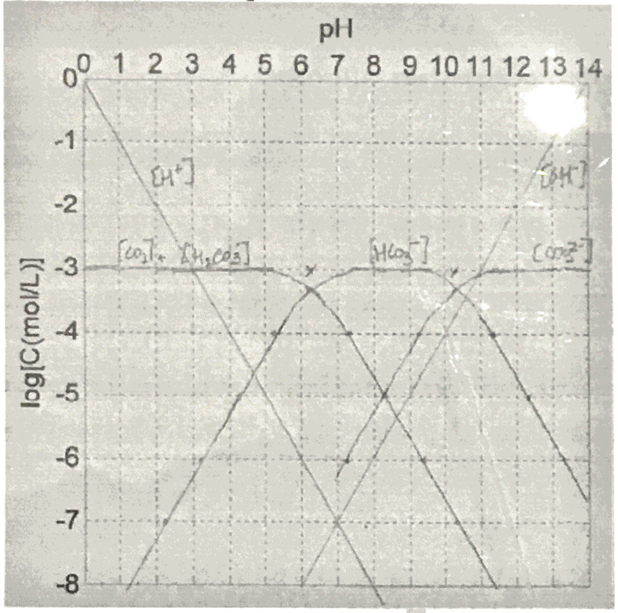
Note that F^- dominates negative charge between approx. 3.2 and 11.
The $[OH^-]$ can be dropped. H^+ and HF are very similar in size. The dotted line indicates the approximated

The pH ~ 3.5.



(18.04) A solution of NaHCO3 and HCl is prepared such that the total carbon...

Material Balance
10^{-3} = [Na^+] = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] (1)
2E-3 = [Cl^-] (2)
Charge Balance
[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [Cl^-] (3)
combine with the material balance for [Na^+] and [Cl^-]
10^{-3} + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + 2E-3 (4)
For CO_2, $pK_{a,A1} = 6.351$, $pK_{a,A2} = 10.329$, plot lines
Proton condition (4) becomes
[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + 1E-3 (5)
The only solution is at [H^+]= 1E-3, $\boxed{pH = 3}$.
At higher pH, the [H^+] is too small to satisfy (5).
Calculate partial pressure of CO_2,
[CO_2] + [H_2CO_3] = 10^{-3}.

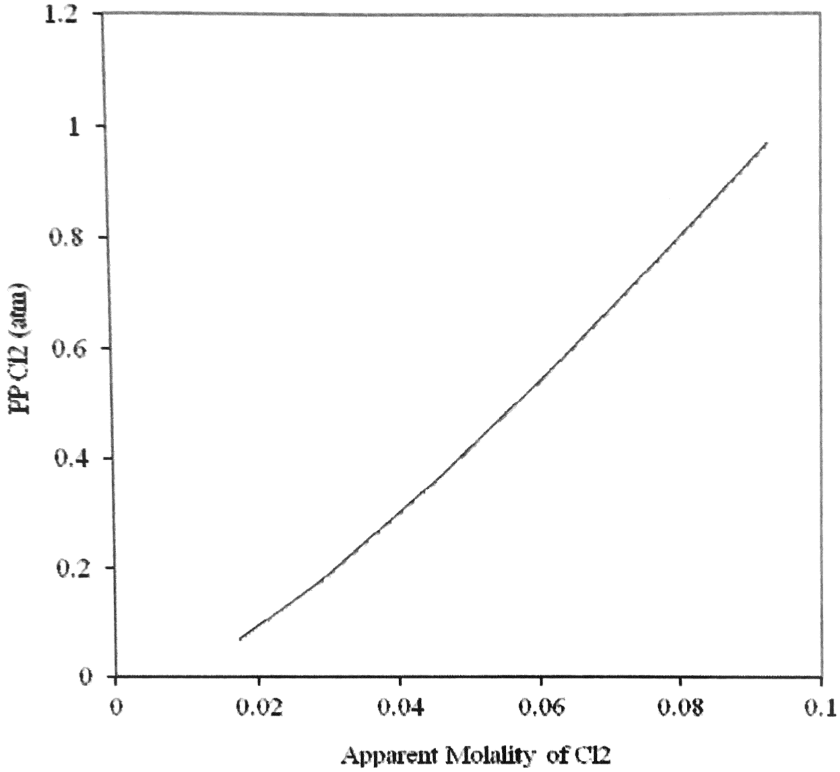


(a) $K_{H,CO2}$ from appendix E.
$K_{H,CO2} = 10^{-3}/(y_{CO2}P) \rightarrow y_{CO2}P = 10^{-3}/0.035 = 2.85E\text{-}2$ bar
The problem does not ask to compare, but normal ambient partial pressure of CO2 is approximately 3E-4 bar. If the solution is exposed to the atmosphere, the CO2 will come out of solution until Henry's law is satisfied

(b) Using MAB to predict Henry's Law, referring to Example 11.12(b), $\gamma_{CO2}^{\infty} = 57.4$. Using the fugacity from SCVP+, and the method of Ex 11.12(a), $f_{CO2}^{L} = 47$ bar. Henry's constant by the MAB model for CO2 in ~water is: $h_i = \gamma_i^{\infty} P_i^{sat} = 57.4*47 = 2698$ bar. From above, the concentration of molecular CO2 is 10^{-3}m. Noting the xs ~1 by Eq 18.148, then using Eq 18.147, $x_{CO2} = 0.001*0.001*1*18 = 18E\text{-}5$, and the partial pressure is $y_{CO2}P = x_{CO2}\gamma_{CO2}^{\infty} f_{CO2}^{L} = x_{CO2}h_{CO2}$ = 1.8E-5(2698 bar) = 4.86E-2 bar.

(18.05) Plot the "apparent molality" of Cl2 against PP of Cl2.

Note that changing the moles of water or chlorine doesn't change anything because this system acts like a simple binary in terms of its degrees of freedom. Therefore change the total pressure to see the apparent molality change. Then its just a matter of running cl2H2O.xls a few times.



(18.06) Model a soft drink....

$CO2(g) = CO2(l)$ $K_H = ([CO2(l)] + [H2CO3])/(y_{CO2}P) = 0.035$
$H2O = H^+ + OH^-$ $K_w = [H^+][OH^-] = 1E\text{-}14$
$CO2 + H2O = HCO3^- + H^+$ $K_{a1} = 10^{-6.36} = [HCO3^-][H^+]/(([CO2(l)] + [H2CO3])a_{H2O})$
$HCO3^- + H2O = CO3^{2-} + H^+$ $K_{a2} = 10^{-10.33} = [CO3^{2-}][H^+]/([HCO3^-]a_{H2O})$
charge balance
$[H^+] = [HCO3^-] + 2[CO3^{2-}] + [OH^-]$

(a) at $y_{CO2}P = 3.5$ bar, using K_H, $([CO2(l)] + [H2CO3]) = 0.035(3.5) = 0.1225$ M
assuming m = M
Since this is constant, independent of pH, using K_{a1},
$[HCO3^-]=K_{a1}([CO2]+[H2CO3])/[H^+] = 10^{-6.36}(0.1225)/[H^+]$

$\log[HCO3^-] = -6.36 + \log(0.1225) + pH$
$\log[HCO3^-] = -7.27 + pH$ (this will have slope = 1) (1)

generate a few points

pH	$\log[HCO3^-]$ (by (1))
0	-7.27
2	-5.27
5	-2.27 Plot on graph

Now generate line for $[CO3^{2-}]$ using K_{a2},
$[CO3^{2-}] = K_{a2}[HCO3^-]/[H^+]$
$\log[CO3^{2-}] = \log K_{a2} + \log[HCO3^-] + pH$
$\log[CO3^{2-}] = -10.33 + \log[HCO3^-] + pH$, insert (1)
$= -10.33 - 7.27 + 2pH$
$\log[CO3^{2-}] = -17.6 + 2pH$ (this will have slope = 2) (2)

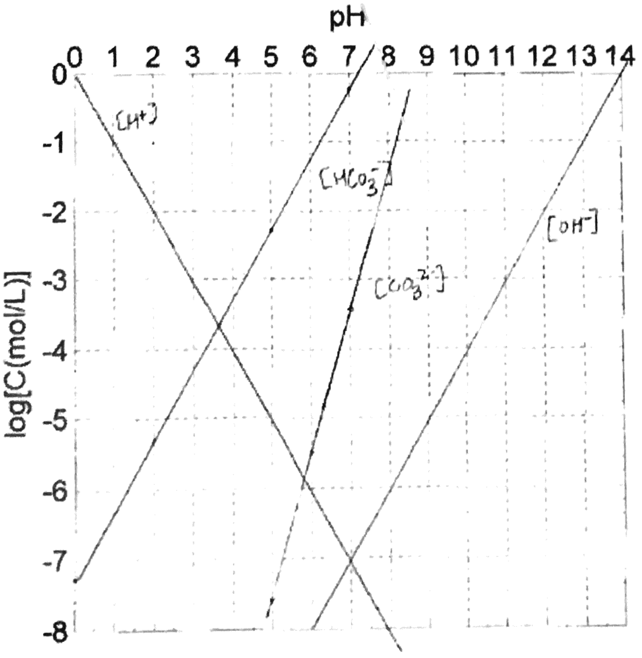
generate a few points

pH	$\log[CO3^{2-}]$
5	-7.6
6	-5.6
7	-3.6 Plot on graph

Note that $[HCO3^-] \gg [CO3^{2-}] \gg [OH^-]$ at all pH that come close to satisfying charge balance. A proton condition is not needed to find the answer.
$[H^+] = [HCO3^-] + \ldots$ at $\boxed{pH = 3.6}$

$[CO2] + [H2CO3] = 0.1225$
$[HCO3^-] = 10^{-3.6}M = 0.00025M$
$[CO3^{2-}] = 10^{(-17.6 + 2(3.6))} = 10^{-10.4}$ M
$[OH^-] = 10^{(-14 + 3.6)} = 10^{-10.4}$ M

Plot at 3.5 bar



(b) at $y_{CO2}P$ = 0.0003 bar, $[CO2] + [H2CO3] = K_H(y_{CO2}P)$= 0.035(3E-4)= 1.05E-5
using K_{a1}
$[HCO3^-] = 10^{-6.36}(1.05E-5)/[H^+]$
$\log[HCO3^-] = -6.36 - 4.979 + pH = -11.339 + pH$ (will have slope 1) (3)

generate a few points

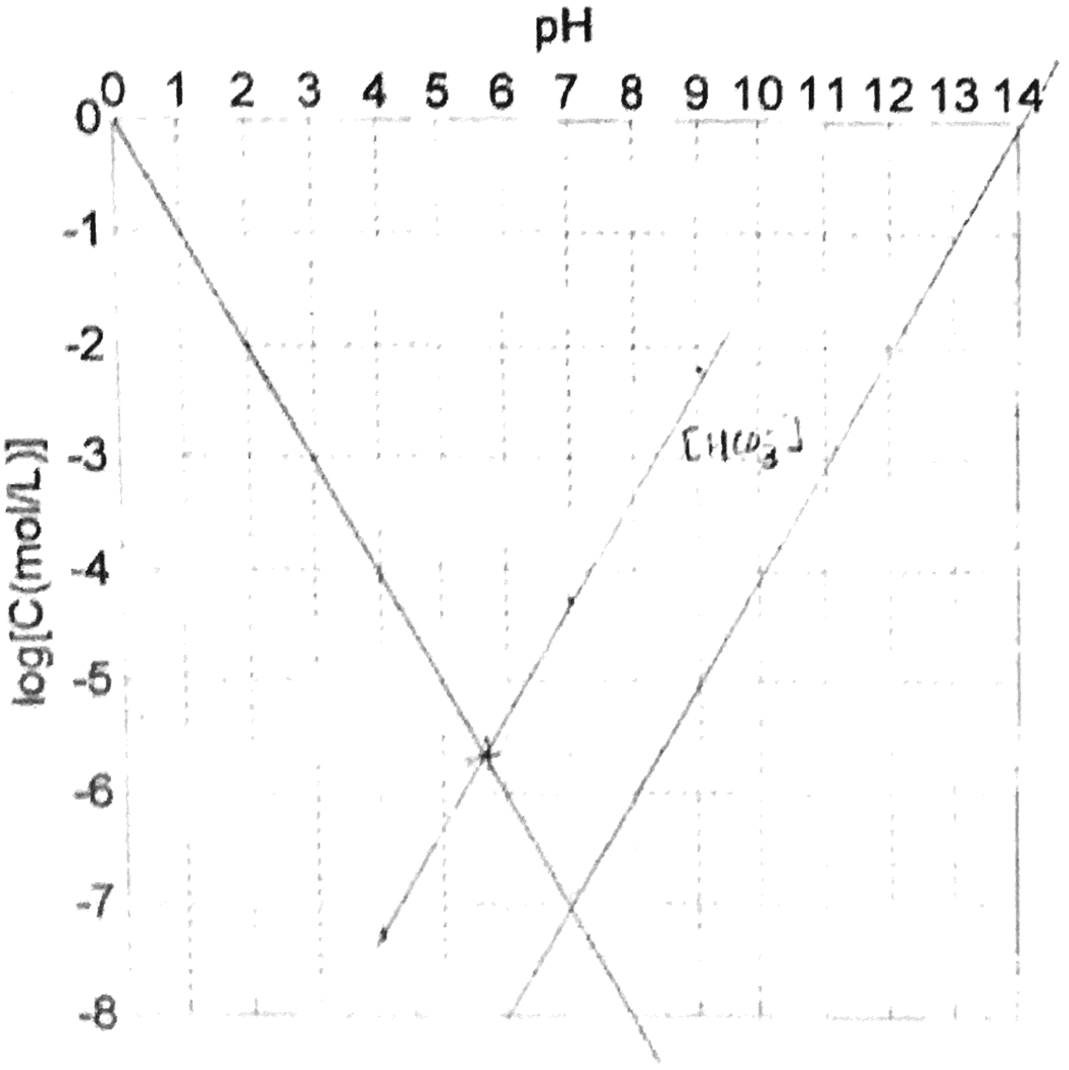
pH	log[HCO3⁻]
4	-7.34
7	-4.34
9	-2.34 Plot

Equation (2) becomes
$\log[CO3^{2-}] = -10.33 - 11.34 + 2pH$
$\log[CO3^{2-}] = -21.67 + 2pH$ (will have slope 2 (4)

as before, [HCO3⁻] is dominant anion, pH = 5.7 by same charge balance.

pH = 5.7
$[CO2] + [H2CO3] = 1.05E-5$
$[HCO3^-] = 2E-6$
$[CO3^{2-}]$ = 5E-11 by (2) using pH = 5.7
$[OH^-] = 10^{(-14+5.7)} = 10^{-8.3} = 5E-9$

Plot at $y_{CO2}P$ = 0.0003 bar



(18.07) Sodium bicarbonate, NaHCO3, commonly known as baking soda...

(a) Material balances

$[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 10^{-2}$

$[Na^+] = 10^{-2}$

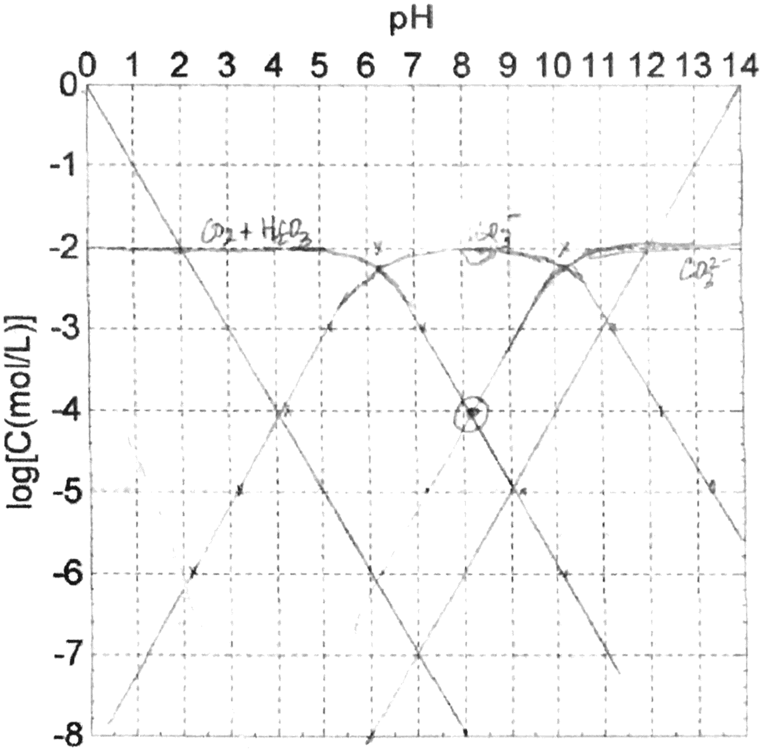
charge balance

$[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

insert C balance into charge balance for $[HCO_3^-]$, insert $[Na^+]$ balance into charge balance

$10^{-2} + \underset{\text{small}}{\cancel{[H^+]}} = 10^{-2} + [CO_3^{2-}] - [H_2CO_3] - [CO_2] + \underset{\text{small}}{\cancel{[OH^-]}}$

proton condition becomes $[CO_3^{2-}] = [H_2CO_3] + [CO_2]$ – see dot on plot below



concentrations are

$\boxed{[HCO_3^-] \sim 10^{-2}\text{ M}, [Na^+] = 10^{-2}\text{ M}, [H_2CO_3] + [CO_2] = [CO_3^{2-}] = 10^{-4}\text{ M}, \text{pH} = 8.2}$

(b) $K_H = ([CO_2] + [H_2CO_3]) / y_{CO2}P$ if saturated the concentration would be $([CO_2] + [H_2CO_3]) = 0.0003(0.035) = 1E\text{-}5$ mol/kg ~ mol/L

Yes, the CO2 will tend to come out of solution because the concentration in (a) is larger. The rate will be slow because the driving force is small.

(18.08) Sodium carbonate is mixed....

Errata: This problem is revised in the US 4th printing and International 2nd printing to use 0.05M Na+ and Acetate. The original problem statement did not have enough C to saturate the liquid and create the specified partial pressure.

Solution:

material balance

$[Na^+] = 0.05$ M

$[OAc^-] + [HOAc] = 0.05$ M

Acetic will follow $K_{a1} = [H^+][OAc^-]/[HOAc] = 10^{-4.76}$, plotted for total acetate

carbonate Henry's constant, $K_H = ([CO2] + [H2CO3])/(y_{CO2}P) = 0.035$

$CO2 + H2O = HCO3^- + H^+ \quad K_{a1} = 10^{-6.36} = [HCO3^-][H^+]/(([CO2]+[H2CO3])a_{H2O})$

$HCO3^- + H2O = CO3^{2-} + H^+ \quad K_{a2} = 10^{-10.33} = [CO3^{2-}][H^+]/([HCO3^-]a_{H2O})$

charge balance

$[H^+] + [Na^+] = [OAc^-] + [HCO3^-] + 2[CO3^{2-}] + [OH^-]$

Proton condition, substituting the material balances for Na and acetate,

$[H^+] + 0.05 = 0.05 - [HOAc] + [HCO3^-] + 2[CO3^{2-}] + [OH^-]$

$[H^+] + [HOAc] = [HCO3^-] + 2[CO3^{2-}] + [OH^-]$

start by assuming pH > 4.76

$[CO2] + [H2CO3] = 0.035(0.5) = 0.0175$

↓

using K_{a1}, $\log [HCO3^-] = -6.36 + \log(0.0175) + pH$

$\log [HCO3^-] = -8.117 + pH$ (will have slope 1) (1)

tabulate a few points

pH	$\log[HCO3^-]$
1	-7.117
3	-5.117
6	-2.117 Plot

$[CO3^{2-}]$ will be small

using K_{a2}; $\log[CO3^{2-}] = -10.33 + \log[HCO3^{2-}] + pH$ (insert (1))

$\log[CO3^{2-}] = -10.33 - 8.117 + 2pH = -18.447 + 2pH$ will have slope 2 (2)

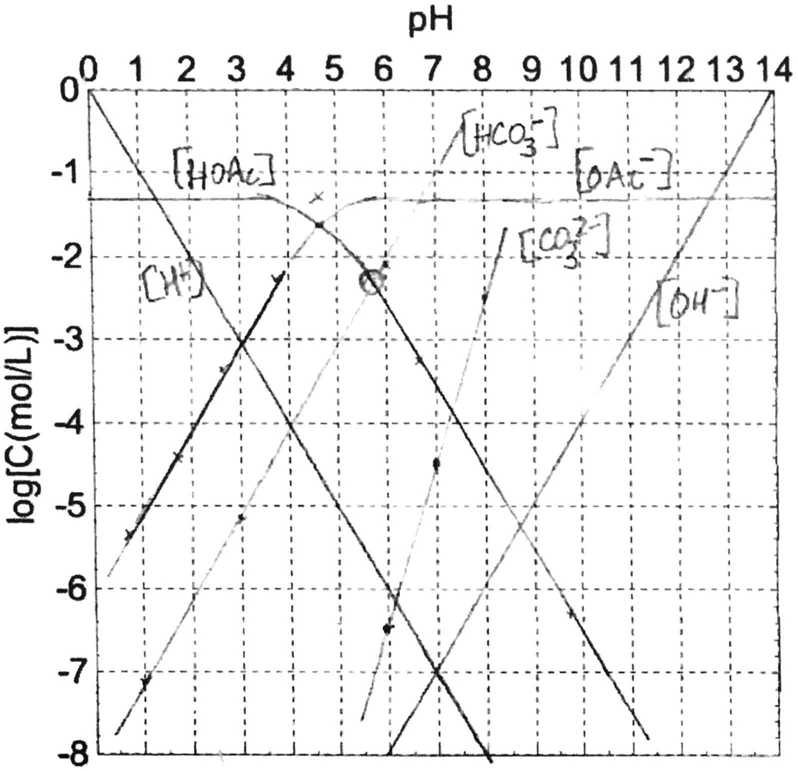
tabulate a few points

pH	$\log[CO3^{2-}]$
6	-6.45
7	-4.45
8	-2.45 Plot

looking at the plot and proton condition, the reasonable solution is
… + [HOAc] = [$HCO3^-$] + …

pH = 5.8
[HOAc] = $10^{-2.3}$ = 5E-3 M
[OAc] = 0.05 – 5E-3 = 0.045 M

Plot



(18.09) Thermodynamic data for Gibbs energy of formation …

$NaCl_{(s)} = Na^+ + Cl^-$

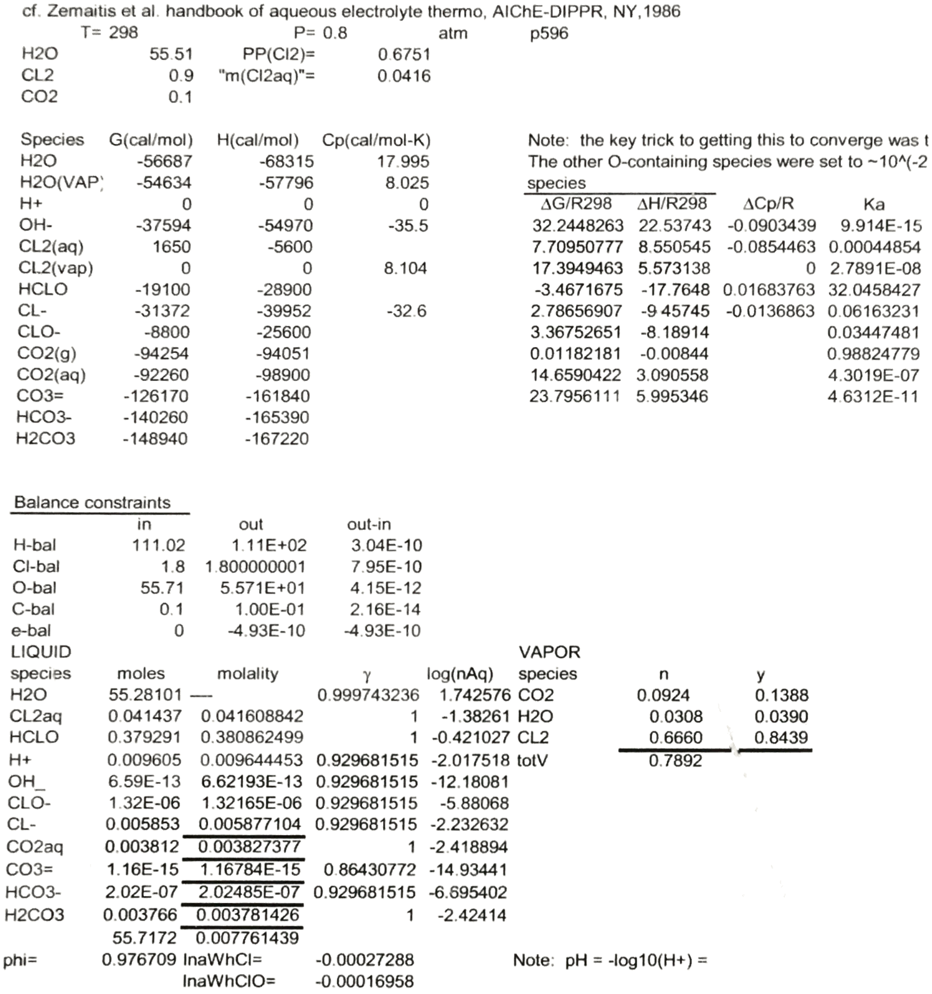
(a) ΔG = -261.905 – 131.228 + 384.138 = -8.753 kJ/mol
K_{sp} = exp(+8753/(8.314)/(298.15)) = 34.16 = [Na^+][Cl^-]
34.16 = $[Na^+]^2$ since [Cl^-] = [Na^+]
[Na^+] = 5.84 m

(b) total Cl^- in solution will be [Na^+] + 1 m
K_{sp} = [Na^+]([Na^+] + 1)
$[Na^+]^2$ + [Na^+] -34.16 = 0 solve by quad formula
[Na^+] = (-1 + sqrt(1+4(34.16))/2 = 5.36 m
[Na^+] = 5.36 m the presence of KCl causes NaCl to precipitate

(c) ΔG = -283.27 – 131.228 + 408.14 = 5.098 kJ/mol
K_{sp} = exp(5098/8.314/298.15) = 7.77
K_{sp} = [K^+][Cl^-]; [Cl^-] = 5.36 + 1 = 6.36 m
this is not saturated because

$$[K^+][Cl^-] = (1)(6.36) = 6.36 < 7.77 = K_{sp}$$

(18.10) Suppose 0.1 moles of CO2 were mixed with …



cf. Zemaitis et al. handbook of aqueous electrolyte thermo, AIChE-DIPPR, NY,1986

T= 298		P= 0.8		atm	p596
H2O	55.51	PP(Cl2)=	0.6751		
CL2	0.9	"m(Cl2aq)"=	0.0416		
CO2	0.1				

Species	G(cal/mol)	H(cal/mol)	Cp(cal/mol-K)
H2O	-56687	-68315	17.995
H2O(VAP)	-54634	-57796	8.025
H+	0	0	0
OH-	-37594	-54970	-35.5
CL2(aq)	1650	-5600	
CL2(vap)	0	0	8.104
HCLO	-19100	-28900	
CL-	-31372	-39952	-32.6
CLO-	-8800	-25600	
CO2(g)	-94254	-94051	
CO2(aq)	-92260	-98900	
CO3=	-126170	-161840	
HCO3-	-140260	-165390	
H2CO3	-148940	-167220	

Note: the key trick to getting this to converge was t
The other O-containing species were set to ~10^(-2
species

ΔG/R298	ΔH/R298	ΔCp/R	Ka
32.2448263	22.53743	-0.0903439	9.914E-15
7.70950777	8.550545	-0.0854463	0.00044854
17.3949463	5.573138	0	2.7891E-08
-3.4671675	-17.7648	0.01683763	32.0458427
2.78656907	-9.45745	-0.0136863	0.06163231
3.36752651	-8.18914		0.03447481
0.01182181	-0.00844		0.98824779
14.6590422	3.090558		4.3019E-07
23.7956111	5.995346		4.6312E-11

Balance constraints

	in	out	out-in
H-bal	111.02	1.11E+02	3.04E-10
Cl-bal	1.8	1.800000001	7.95E-10
O-bal	55.71	5.571E+01	4.15E-12
C-bal	0.1	1.00E-01	2.16E-14
e-bal	0	-4.93E-10	-4.93E-10

LIQUID					VAPOR		
species	moles	molality	γ	log(nAq)	species	n	y
H2O	55.28101	—	0.999743236	1.742576	CO2	0.0924	0.1388
CL2aq	0.041437	0.041608842	1	-1.38261	H2O	0.0308	0.0390
HCLO	0.379291	0.380862499	1	-0.421027	CL2	0.6660	0.8439
H+	0.009605	0.009644453	0.929681515	-2.017518	totV	0.7892	
OH_	6.59E-13	6.62193E-13	0.929681515	-12.18081			
CLO-	1.32E-06	1.32165E-06	0.929681515	-5.88068			
CL-	0.005853	0.005877104	0.929681515	-2.232632			
CO2aq	0.003812	0.003827377	1	-2.418894			
CO3=	1.16E-15	1.16784E-15	0.86430772	-14.93441			
HCO3-	2.02E-07	2.02485E-07	0.929681515	-6.695402			
H2CO3	0.003766	0.003781426	1	-2.42414			
	55.7172	0.007761439					
phi=	0.976709	lnaWhCl=	-0.00027288		Note: pH = -log10(H+) =		
		lnaWhClO=	-0.00016958				

18.11 Corrosion resistant alloys (such as nickel alloys and stainless steels)…

Correction in 4th and subsequent printings. In part (d), the values of Q should be Q_{11} and the statement is thus revised to ask:

(d) For Fe2+, log Q11 = –9.5, and for Ni2+, logQ11 = –10.5 and the hydrolyzed ion is soluble. Repeat (a) for each of these ions but relate pH to the ratio of ion concentrations.

Solution:

(a) Replacing x=1 and y=3 in Eq. 1:

$Cr^{3+} + 3H_2O \Leftrightarrow Cr(OH)_3 + 3H^+$

Similarly in Eq. 2: $\log Q_{13} = -4.6 = \log([H^+]^3/[Cr^{3+}])$. Rearranging:

$-4.6 = 3\log[H^+] - \log[Cr^{3+}]$. Recognizing that pH=-log[H⁺] $pH = 1.53 - \frac{1}{3}\log([Cr^{+3}])$.

(b) $[Cr^{3+}]$ = 10^(3*(1.53 - pH)). Values {pH, $[Cr^{3}]$}, {6, 3.9E-14}, {4, 3.9E-8},{2, 0.039}. The concentration goes up very fast as pH approaches 1.5.

(c) The hydrolysis product does not appear because it is considered 'pure' and as a pure solid the activity is 1.

(d) $Fe^{2+} + H_2O \Leftrightarrow Fe(OH)^+ + H^+$, $Fe^{2+} + H_2O \Leftrightarrow Fe(OH)^+ + H^+$

$\log Q_{11} = -9.5 = \log([Fe(OH)^+][H^+]/[Fe^{2+}])$

$\log Q_{11} = -10.5 = \log([Ni(OH)^+][H^+]/[Ni^{2+}])$

$-9,5 = \log[H^+] + \log([Fe(OH)^+]/[Fe^{2+}])$

$\log([Ni(OH)^+]/[Ni^{2+}]) = -9.5 + pH$. By inspection, we can write

$\log([Ni(OH)^+]/[Ni^{2+}]) = -10.5 + pH$

The hydrolysis of these ions will be very small at acidic pH.

(18.12) Ruthenium (Ru) is a strong oxidation catalyst ...

	E°	ΔG°
(a) (1) $RuO_{4(s)} + 4H^+ + 4e^- \Leftrightarrow RuO_{2(s)} + 2\,H_2O$	1.387	-4F(1.387)
(2) $2\{H_2O \Leftrightarrow \frac{1}{2}\,O_{2(g)} + 2\,H^+ + 2e^-\}$	1.229	4F(1.229)
$RuO_{4(s)} \Leftrightarrow RuO_{2(s)} + O_{2(g)}$	0.158	-0.632F

E° = 1.387 – 1.229 = 0.158, ΔG° = -nFE° 4(0.158)F = -0.632F < 0

or, can add Gibbs energies

ΔG° = - 4(1.387)F + 4(1.229)F = -0.632F = -60,978 J/mol

$\Delta G = \Delta G^o + RT \ln[(y_{O_2}P\, a_{RuO2})/a_{RuO4(s)}]$

activities are one, standard condition is $y_{O_2}P$ = 1 bar. Actual $y_{O_2}P$ is less, making ΔG more negative and spontaneous.

	E°	ΔG°
(b) $H_2RuO_{5(aq)} + 4H^+ + 4e^- \Leftrightarrow RuO_{2(s)} + 3H_2O$	1.4	-4F(1.4)
$2H_2O \Leftrightarrow O_{2(g)} + 4H^+ + 4e^-$	1.229	4F(1.229)
$H_2RuO_{5(aq)} \Leftrightarrow RuO_{2(s)} + O_{2(g)} + H_2O$	0.171	-0.684F

ΔG° = -nFE° = -4(96,485)(1.4-1.229) = -65,996 J/mol

$\Delta G = \Delta G^o + RT \ln[(a_{RuO2(s)}(y_{O2}P)\, a_{H2O})/[Ru_2O_{5(aq)}]] = 0$

activity $a_{RuO2(s)} = 1$, $a_{H2O} = 1$(LR rule),

$\ln[Ru_2O_{5(aq)}] = \Delta G^o/RT + \ln(y_{O2}P) = -65{,}996/8.314/298 + \ln(0.21)$

$\ln[Ru_2O_{5(aq)}] = -26.64 - 1.56 = -28.2 \rightarrow [Ru_2O_{5(aq)}] = 5.66E\text{-}13$ m, independent of pH.

(c)	E°	ΔG°
$4/2(\,RuO_{4(s)}^- + 4H^+ + 3e^- \Leftrightarrow RuO_{2(s)} + 2H_2O)$	1.533	-4F(1.533)
$RuO_{2(s)} + 3H_2O \Leftrightarrow H_2RuO_{5(aq)} + 4H^+ + 4e^-$	1.400	4F(1.400)
$4/3RuO_{4(s)}^- + 4/3H^+ + 1/3\,H_2O \Leftrightarrow 1/3RuO_{2(s)} + H_2RuO_{5(aq)}$	0.13	-0.532F

$0.532 = (RT/F) \ln\{[H_2RuO_{5(aq)}]/[RuO_{4(s)}^-]^{4/3}/[H^+]^{4/3}$

$0.532/0.0591*(3/4) = \log[H_2RuO_{5(aq)}]^{3/4}/[RuO_{4(s)}^-] + pH$

$\log[H_2RuO_{5(aq)}]^{3/4}/[RuO_{4(s)}^-] = 6.751 - pH$

$\boxed{a = 0.75;\ b = 6.751;\ c = -1}$

(d)

	E°	ΔG°
$3/2(\mathrm{RuO}_{4(s)}{}^{2-} + 4\mathrm{H}^+ + 3e^- \Leftrightarrow \mathrm{RuO}_{2(s)} + 2\mathrm{H_2O})$	2.005	-3F(2.005)
$\mathrm{RuO}_{2(s)} + 2\mathrm{H_2O} \Leftrightarrow \mathrm{RuO}_{4(s)}{}^- + 4\mathrm{H}^+ + 3e^-$	1.533	3F(1.533)
$3/2\mathrm{RuO}_{4(s)}{}^{2-} + 2\mathrm{H}^+ \Leftrightarrow 1/2\mathrm{RuO}_{2(s)} + \mathrm{RuO}_{4(s)}{}^- + \mathrm{H_2O}$	0.472	-1.416F

$1.416/0.0591 = \log \{[\mathrm{RuO}_{4(s)}{}^-]/[\mathrm{RuO}_{4(s)}{}^-]^{3/2}/[\mathrm{H}^+]^2\}$

$23.959 = -\log \{[\mathrm{RuO}_{4(s)}{}^-]^{3/2}/[\mathrm{RuO}_{4(s)}{}^-]\} + 2\mathrm{pH}$; $\log \{[\mathrm{RuO}_{4(s)}{}^-]^{3/2}/[\mathrm{RuO}_{4(s)}{}^-]\} = -23.959 + 2\mathrm{pH}$

$\boxed{a = 1.5;\ b = -23.959;\ c = 2}$

(18.13) (a) Rank the following molecules in order of increasing oxidation

Errata in US printings 1-3 and International printing 1. The primary alcohol was written incorrectly; it should be –CH2OH. The aldehyde will be written –CHO future printings.

Solution:

(a)

Moiety	Oxidation states of other atoms	C oxidation state
CH4	+4	-4
-CH3	+3	-3
-CH2-	+2	-2
-CH2OH(alcohol)	-2 + 3 = +1	-1
-COH(aldehyde),	-2 + 1 = -1	+1
-CO-(ketone)	-2	+2
-COOH	2(-2) + 1 = -3	+3
CO2	2(-2) = -4	+4

(b)

Moiety	Structure	Degree of reduction
pentane	C5H12	(5(4)+12)/5 = 6.4
1-pentanol	C5H12O	(5(4) + 12 – 2)/5 = 6
Ethyl propyl ether	C5H12O	(5(4) + 12 – 2)/5 = 6
2-methyl butanol	C5H12O	(5(4) + 12 – 2)/5 = 6
2-pentanone	C5H10O	(5(4)+10-2)/5 = 5.6
1-pentanal	C5H10O	(5(4)+10-2)/5 = 5.6
Valeric acid	C5H10O2	(5(4)+10-2(2))/5 = 5.2

(18.14)The human body processes ethanol by oxidizing it to acetaldehyde...

(a) the heat of reaction is

$\Delta H = -42.9 - 214.1 + 11.9 + 291.2 = 46.1$ kJ/mol

since the MW of ethanol is about 46, the heat requirement is about 1 kJ/g.

(b)

$K = \exp(-\Delta G/RT)$

$\Delta G = 1231 + 43.2 - 1163.9 - 91.45 = 18.85$ kJ/mol

This is unfavorable at standard state conditions.

$K = \exp(-18850/8.31447/310) = 6.67\mathrm{E}{-4}$.

If the ratio of the two forms of NAD are near 1, then very little acetaldehyde will inhibit the reaction from proceeding. Fortunately the body converts acetaldehyde to acetic acid using an enzyme, so the reaction can continue to go forward by keeping the acetaldehyde concentration very low.

(18.15) The first step in biological glycolysis….

(a) $\Delta G_{rxn}'^{o} = -1319 - 156 + 427 + 1060 = 12$ kJ/mol
$\Delta H_{rxn}'^{o} = -2279 - 286 + 1299 + 1267 = 1$ kJ/mol

$\Delta G_{rxn}' = \Delta G_{rxn}'^{o} + RT \ln (C_{gluc6}/(C_{gluc}C_{Pi}))$ (water uses L-R rule)
$= 12{,}000 + 8.314(298.15)\ln[8.3E\text{-}5/5E\text{-}3/1E\text{-}3] = 18964$ J/mol, very unfavorable.
$\Delta H_{rxn}'^{o}$ almost zero (within roundoff)

(b)
$\Delta G_{rxn}'^{o} = -1426 - 1060 + 2298 + 156 = -32$ kJ/mol
$\Delta H_{rxn}'^{o} = -2622 - 1299 + 3605 + 285 = -30$ kJ/mol

$\Delta G_{rxn}' = -32{,}000 + 8.314(298.15)\ln[(1.4E\text{-}4)(1E\text{-}3)/(1.85E\text{-}3)] =$
$-55{,}522$ J/mol, very favorable
$\Delta H_{rxn}'$ exothermic

(c) coupling – can add rxns and go through steps, or add overall results.

$\Delta G_{rxn}' = 18{,}964 - 55{,}522 = -36{,}558$ J/mol, favorable
$\Delta H_{rxn}' = 1 - 30 = -29$ kJ/mol exothermic

(18.16) When we discussed H3PO4 in Section 18.9, we developed a recurring…

Errata US printing 1-3, International printing 1. Part (a) shoul dask for Eqn. 18.90.

Solution:

(a)

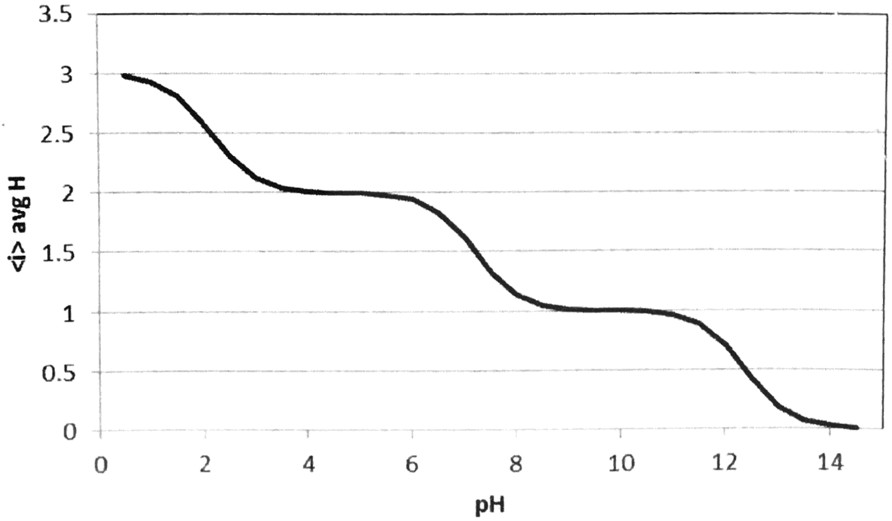
$[PO_4^{3-}] + [H^+] = [HPO_4^{2-}] \quad K_{a1} = [HPO_4^{2-}]/[PO_4^{3-}]/[H^+] \rightarrow K_{a1}[H^+] = [HPO_4^{2-}]/[PO_4^{3-}]$ (1)
$[HPO_4^{2-}] + [H^+] = [H_2PO_4^-] \quad K_{a2} = [H_2PO_4^-]/[HPO_4^{2-}]/[H^+] \rightarrow K_{a2}[H^+] = [H_2PO_4^-]/[HPO_4^{2-}]$ (2)
$[H_2PO_4^-] + [H^+] = [H_3PO_4] \quad K_{a3} = [H_3PO_4]/[H_2PO_4^-]/[H^+] \rightarrow K_{a3}[H^+] = [H_3PO_4]/[H_2PO_4^-]$ (3)
$C = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$ (4)
$C/[PO_4^{3-}] = 1 + [HPO_4^{2-}]/[PO_4^{3-}] + [H_2PO_4^-]/[PO_4^{3-}] + [H_3PO_4]/[PO_4^{3-}]$ (5)

Multiplying (1)(2)(3), $K_{a1}K_{a2}K_{a3}[H^+]^3 = ([HPO_4^{2-}]/[PO_4^{3-}])([H_2PO_4^-]/[HPO_4^{2-}])([H_3PO_4]/[H_2PO_4^-])$
$= [H_3PO_4]/[PO_4^{3-}]$. (6)
Multiplying (1)(2)
$K_{a1}K_{a2}[H^+]^2 = ([HPO_4^{2-}]/[PO_4^{3-}])([H_2PO_4^-]/[HPO_4^{2-}]) = [H_2PO_4^-]/[PO_4^{3-}]$ (7)
Inserting (1), (6), (7) into (5)
$C/[PO_4^{3-}] = 1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+]^3$ (8)
$\boxed{C = [PO_4^{3-}](1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+]^3) \qquad (9)}$
The binding K's are the reciprocal of the association K's. All K's here are the binding K's.

(b)
The binding polynomial is
$P = (1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+]^3)$
$\langle i \rangle = (K_{a1}[H^+] + 2K_{a1}K_{a2}[H^+]^2 + 3K_{a1}K_{a2}K_{a3}[H^+]^3)/P$
$K_{a1} = 1/K_{a3}^{dissoc} = 1/10^{-12.375} = 10^{12.375}$; $K_{a2} = 1/K_{a2}^{dissoc} = 1/10^{-7.198} = 10^{7.198}$; $K_{a3} = 1/K_{a1}^{dissoc} = 1/10^{-2.148} = 10^{2.148}$

Ka1	2.37E+12	Ka2	15776112.7	Ka3	140.6048

pH	[H$^+$]	P	numerator	<i>
0.5	0.316228	1.7E+20	5.06506E+20	2.978004
1	0.1	5.6E+18	1.65287E+19	2.933601
1.5	0.031623	2E+17	5.73846E+17	2.816389
2	0.01	9E+15	2.32628E+16	2.584376
2.5	0.003162	5.4E+14	1.24725E+15	2.307764
3	0.001	4.3E+13	9.0605E+13	2.12321
3.5	0.000316	3.9E+12	7.98199E+12	2.04237
4	0.0001	3.8E+11	7.64239E+11	2.013232
4.5	3.16E-05	3.8E+10	75396130870	2.002426
5	0.00001	3.8E+09	7521706020	1.995105
5.5	3.16E-06	3.8E+08	756219142.4	1.980793
6	0.000001	4E+07	77209271.88	1.940531
6.5	3.16E-07	4491167	8232604.999	1.833066
7	1E-07	611254	985374.3276	1.612053
7.5	3.16E-08	112402	149812.0376	1.332828
8	1E-08	27455.8	31195.9646	1.136223
8.5	3.16E-09	7874.05	8247.163769	1.047385
9	1E-09	2409.78	2446.195839	1.01511
9.5	3.16E-10	754.635	757.3764216	1.003632
10	1E-10	238.511	237.8855918	0.997376
10.5	3.16E-11	76.0268	75.06424305	0.987339
11	1E-11	24.7175	23.72121927	0.959694
11.5	3.16E-12	8.49932	7.499690315	0.882387
12	1E-12	3.37141	2.371448528	0.703399
12.5	3.16E-13	1.7499	0.749901692	0.42854
13	1E-13	1.23714	0.237138119	0.191683
13.5	3.16E-14	1.07499	0.074989496	0.069758
14	1E-14	1.02371	0.023713745	0.023164
14.5	3.16E-15	1.0075	0.007498943	0.007443



(18.17) Write a binding polynomial for CO2 in aqueous systems and determine...

Errata: US printing 1-3 and International printing 1 omit the specification to perform the calculation at 25°C.

Solution:

$[CO_3^{2-}] + [H^+] = [HCO_3^-]$ $\qquad K_{a1}[H^+] = [HCO_3^-]/[CO_3^{2-}]$ $\qquad$ (1)

$[HCO_3^-] + [H^+] = [H_2CO_3] + [CO_2]$ $\qquad K_{a2}[H^+] = \{[H_2CO_3] + [CO_2]\} /[HCO_3^-]$ $\quad$ (2)

$C = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [CO_2]$ $\qquad$ (3)

$C/[CO_3^{2-}] = 1 + [HCO_3^-]/[CO_3^{2-}] + \{[H_2CO_3] + [CO_2]\}/[CO_3^{2-}]$ $\qquad$ (4)

multiplying (1)(2),

$K_{a1}K_{a2}[H^+]^2 = ([HCO_3^-]/[CO_3^{2-}])(\{[H_2CO_3] + [CO_2]\}/[HCO_3^-]) = \{[H_2CO_3] + [CO_2]\}/[CO_3^{2-}]$ $\quad$ (5)

Inserting (5) and (1) into (4),

$C = [CO_3^{2-}](1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2)$

$P = (1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2) = (1 + K_{a1}' + K_{a1}'K_{a2}')$

Using Gprimecalc.xls at 298.15K

	$\Delta G'^{o}_{f,298}$ (kJ/mol)
CO2(g)	-394.36
CO_3^{2-}	-531.049
HCO_3^-	-546.814
H_2CO_3	-541.578

where the entry for H_2CO_3 represents the molecular CO2 also.

So for Eq (1), $\Delta G'^{o}_{298} = -546.814 + 531.049 = -15.769$ kJ/mol

$K_{a1}' = \exp(-\Delta G'^{o}_{298}/RT) = \exp(15769/8.31447/298.15) = 578.90$

For Eq (2), $\Delta G'^{o}_{298} = -541.578 + 546.814 = 5.236$ kJ/mol

$K_{a2}' = \exp(-\Delta G'^{o}_{298}/RT) = \exp(-5236/8.31447/298.15) = 0.12097$

$\boxed{P = 1 + 578.9 + 0.12097 = 580.02}$

The fractions in each form are given by the fractional contributions to the binding polynomial,

$$\boxed{\begin{array}{l} [CO_3^{2-}]/C = 1/P = 0.0017 \\ [HCO_3^-]/C = 578.9/580.02 = 0.9981 \\ \{[H_2CO_3] + [CO_2]\}/C = 0.12097/580.02 = 0.0002 \end{array}}$$

The Gibbs energy of the CO2 psuedoisomer is

$\boxed{\Delta G_f'^{o}{}_{298} = -531.049 - 0.00831447(298.15)\ln 580.02 = -546.82 \text{ kJ/mol}}$

(18.18) Write the binding polynomial...

(1) $\qquad\qquad$ (2)

$ATP^{4-} + H^+ = HATP^{3-}$ $\quad K_{1,\,bind} = [HATP^{3-}]/([ATP^{4-}][H^+]) = \exp(\,-(\Delta G_{f(2)}{}^{o} - \Delta G_{f(1)}{}^{o}\,)/RT)$

$= \exp(\,-(-2811.5 + 2768.1)/0.008314/298.15) = 3.984E7$

(3) $\qquad\qquad$ (4)

$HATP^{3-} + H^+ = H_2ATP^{2-}$ $K_{2,\text{ bind}} = [H_2ATP^{2-}]/([HATP^{3-}][H^+]) = \exp(-(\Delta G_{f(4)}^{o} - \Delta G_{f(3)}^{o})/RT)$
$= \exp(-(-2838.2 - 2811.5)/0.008314/298.15) = 4.763E4$

$K_{2,\text{ bind}} = [H_2ATP^{2-}]/([HATP^{3-}][H^+]) = [H_2ATP^{2-}]/(K_{1,\text{bind}}[HATP^{4-}][H^+]^2)$

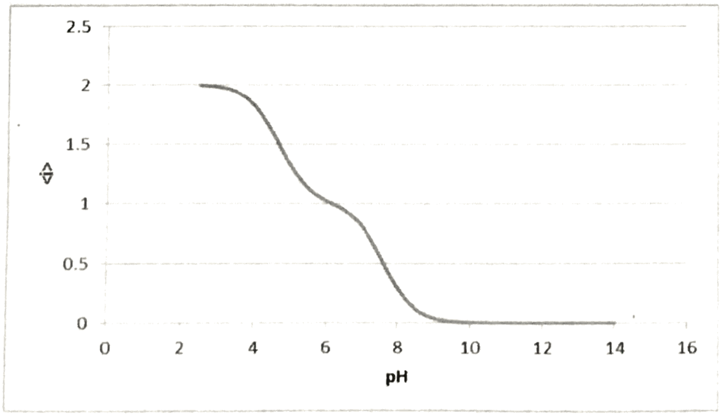
note that $K_{i,\text{ bind}} = 1/K_{(i+1)\text{dissoc}}$, the pK's for dissociation are 7.6 and 4.68
$<i> = (K_{1,\text{ bind}}[H^+] + 2K_{1,\text{bind}}K_{2,\text{ bind}}[H^+]^2 + \ldots)/P$ = 'numerator'/P
$P = (1 + K_{1,\text{ bind}}[H^+] + K_{1,\text{bind}}K_{2,\text{ bind}}[H^+]^2 + \ldots)$
Prepare a table. Note that each protonation is half way at pH = $pK_{a,\text{dissoc}}$ where $<i> = 0.5, 1.5$ respectively.
At pH 7.6, P = 2.0018, if C is the apparent concentration of ATP,

$[ATP^{4-}]/C = 1/P = 1/(2.0018) = 0.49956$
$[HATP^{3-}]/C = K_{1,\text{ bind}}[H^+]/P = (3.984E7)(10^{-7.6})/2.0018 = 0.49992$
$[H_2ATP^{2-}]/C = 2K_{1,\text{bind}}K_{2,\text{ bind}}[H^+]^2/P = 2(3.984E7)(4.763E4)10^{-15.2}/2.0018 = 0.0012$

	species	reaction		
	$\Delta G^{o}_{f,298}$	$\Delta G^{o}_{rxn,298}$		
	kJ/mol	kJ/mol	Ka,bind	
ATP,4-	-2768.1			
ATP,3-	-2811.48	-43.38	39835481.79	-7.60027
ATP,2-	-2838.18	-26.7	47631.89959	-4.6779

pH	P	numerator	<i>
14	1.0000004	3.98355E-07	3.98355E-07
13.5	1.0000013	1.25971E-06	1.25971E-06
13	1.000004	3.98355E-06	3.98353E-06
12.5	1.0000126	1.25971E-05	1.25969E-05
12	1.0000398	3.98355E-05	3.98339E-05
11.5	1.000126	0.000125971	0.000125955
11	1.0003984	0.000398355	0.000398197
10.5	1.0012597	0.001259712	0.001258127
10	1.0039836	0.003983586	0.00396778
9.5	1.0125973	0.012597465	0.012440745
9	1.0398374	0.039839277	0.038312988
8.5	1.1259898	0.126008803	0.111909362
8	1.3985446	0.398734306	0.285106615

pH	P	numerato	<i>
7.6	2.001819	1.003016	0.501052
7.5	2.261606	1.263503	0.558675
7	5.002523	4.021497	0.803894
6.5	13.78683	12.97657	0.94123
6	42.73292	43.63036	1.021001
5.5	145.9453	163.9196	1.123158
5	589.0988	777.8428	1.320394
4.68	1661.544	2488.806	1.497888
4.5	3158.148	5054.588	1.600491
4	22958.94	41932.34	1.826405
3.5	202342.1	392085	1.937734
3	1937276	3834715	1.979436
2.5	19100369	38074764	1.993405



(18.19) Repeat problem 18.18, but use ADP.

(1) (2)

$ADP^{3-} + H^+ = HADP^{2-}$ $K_{1,\text{bind}} = [HADP^{2-}]/([ADP^{3-}][H^+]) = \exp(-(\Delta G_{f(2)}^{\circ} - \Delta G_{f(1)}^{\circ})/RT)$

$= \exp(-(-1947.1 + 1906.13)/0.008314/298.15) = 1.5067E7$

(3) (4)

$HADP^{2-} + H^+ = H_2ADP^-$ $K_{2,\text{bind}} = [H_2ADP^-]/([HADP^{2-}][H^+]) = \exp(-(\Delta G_{f(4)}^{\circ} - \Delta G_{f(3)}^{\circ})/RT)$

$= \exp(-(-1971.98 + 1947.1)/0.008314/298.15) = 2.2858E4$

$K_{2,\text{bind}} = [H_2ADP^-]/([HADP^{2-}][H^+]) = [H_2ADP^-]/(K_{1,\text{bind}}[ADP^{3-}][H^+]^2)$

note that $K_{i,\text{bind}} = 1/K_{(i+1)\text{dissoc}}$, the pK's for dissociation are 7.178 and 4.359

$<i> = (K_{1,\text{bind}}[H^+] + 2K_{1,\text{bind}}K_{2,\text{bind}}[H^+]^2)/P =$ 'numerator'/P

$P = (1 + K_{1,\text{bind}}[H^+] + K_{1,\text{bind}}K_{2,\text{bind}}[H^+]^2)$

Prepare a table. Note that each protonation is half way at pH = $pK_{a,\text{dissoc}}$ where <i> = 0.5, 1.5 respectively.

At pH 7.6, P = 1.37869, if C is the apparent concentration of ADP,

$[ADP^{3-}]/C = 1/P = 1/1.37869 = 0.7253$

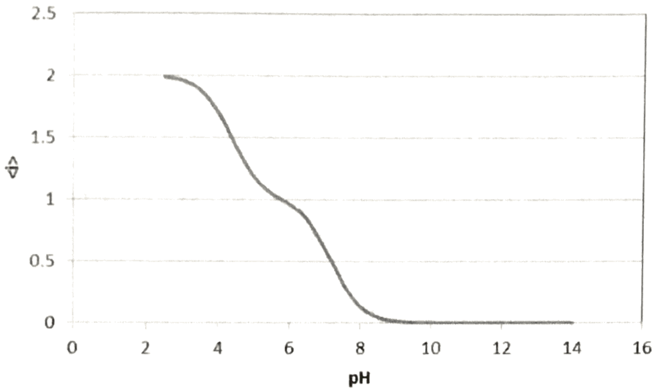
$[HADP^{2-}]/C = K_{1,\text{bind}}[H^+]/P = (1.5067E7)(10^{-7.6})/1.37869 = 0.2745$

$[H2ADP^-]/C = 2K_{1,\text{bind}}K_{2,\text{bind}}[H^+]^2/P = 2(1.5067E7)(2.2858E4)10^{-15.2}/1.37869 = 3E-4$

ADP binding as a function of pH

	species	reaction		
	$\Delta G^{o}_{f,298}$	$\Delta G^{o}_{rxn,298}$		
	kJ/mol	kJ/mol	Ka,bind	pK
ADP,3-	-1906.13			
HADP,2-	-1947.1	-40.97	15067210	-7.17803
H2ADP-	-1971.98	-24.88	22857.56	-4.35903

pHc	P	numerato	<i>
14	1	1.51E-07	1.51E-07
13.5	1	4.76E-07	4.76E-07
13	1.000002	1.51E-06	1.51E-06
12.5	1.000005	4.76E-06	4.76E-06
12	1.000015	1.51E-05	1.51E-05
11.5	1.000048	4.76E-05	4.76E-05
11	1.000151	0.000151	0.000151
10.5	1.000476	0.000476	0.000476
10	1.001507	0.001507	0.001504
9.5	1.004765	0.004765	0.004742
9	1.015068	0.015068	0.014844
8.5	1.04765	0.047654	0.045486
8	1.150707	0.150741	0.130999
7.6	1.378689	0.378906	0.274831
7.5	1.476811	0.477156	0.323099
7.178	2.001593	1.00311	0.501156
6.5	5.79911	4.83355	0.833499
6	16.41161	15.75601	0.960053
5.5	52.0907	54.5347	1.046918
5	186.1121	219.552	1.179677
4.5	821.8668	1165.266	1.417829
4.359	1319.493	1977.762	1.49888
4	4951.718	8394.716	1.695314
3.5	39205.64	73644.62	1.878419
3	359467.9	703866.7	1.958079
2.5	3491645	6935641	1.986354



(18.20) Beginning with the untransformed (ADP)...

To obtain the transformed Gibbs energies, we repeat the calculations performed on GprimeCalc. For each species, take the Gibbs energy of formation relative to the most bare form,

$K_{a,bind} = \exp(-(\Delta G^o_{f,i} - \Delta G^o_{f,ADP^{3-}})/(RT))$

Because the $[H^+]$ and $[Mg^{2+}]$ are already included in the transform, the binding polynomial is $P = 1 + K_{bind1} + K_{bind2} + K_{bind3} + K_{bind4}$

THIS NOTATION DIFFERS FROM EQ 18.124 BECAUSE K_{bind2} INCLUDES TWO REACTIONS, K_{bind3} INCLUDES THREE REACTIONS, ETC.

The Gibbs energy of formation for the pseudoisomer is then

$$\boxed{\Delta G^o_{f,ADP} = \Delta G^o_{f,ADP^{3-}} - RT\ln P = -1424.23 - 0.008314*298.15*\ln(2.103) = -1426.07 \text{ kJ/mol}}$$

The fraction of each species can be calculated by

$1/P$, K_{bind1}/P, K_{bind2}/P, K_{bind3}/P, K_{bind4}/P

or equivalently by

$\exp((\Delta G^o_{f,ADP} - \Delta G^o_{f,i})/RT)$

Summary of calculations:

T(K)	298.15
I (mol/kg)	0.25
pH_c	7
pMg_c	3

R	8.31451	J/molK
pH_a	7.141851	

$\alpha = A_\gamma(\ln(10))$	1.175849
sqrt(I)/(1+Bsqrt(I)	0.277778
dα/dT	0.002006

transform	$\Delta G^o_{f,298}$ (kJ/mol)	$\Delta H^o_{f,298}$ (kJ/mol)	$\Delta G^o_{f,T}$ (kJ/mol)	G transform correction kJ/mol	G Debye-Hu correction (kJ/mol)	G transform value kJ/mol	H Debye-Hu correction (kJ/mol)	H transformed value kJ/mol	
Mg2+	-455.3	-467	-455.3	-17.1241	-3.23877	-475.663	1.647702	-465.352	per Mg2+
H+	0	0	0	-39.9563	-0.80969	-40.766	0.411925	0.411925	per H+

Name	$\Delta G^o_{f,298}$ (kJ/mol)	$\Delta H^o_{f,298}$ (kJ/mol)	z_i	N_H	N_{Mg}	$\Delta G^o_{f,T}$ (kJ/mol)	G, D-H correction (kJ/mol)	H, D-H correction (kJ/mol)	Transformed Props $\Delta G'^o_{f,298}$ (kJ/mol)	$\Delta H'^o_{f,298}$ (kJ/mol)
ADP,3-	-1906.13	-2626.54	-3	12	0	-1906.13	-7.28724	3.707329	-1424.23	-2627.78
HADP,2-	-1947.1	-2620.94	-2	13	0	-1947.1	-3.23877	1.647702	-1420.38	-2624.65
H2ADP-	-1971.98	-2638.54	-1	14	0	-1971.98	-0.80969	0.411925	-1402.07	-2643.9
MgADP-	-2387.97	-3074.54	-1	12	1	-2387.97	-0.80969	0.411925	-1423.92	-2613.72
MgHADP	-2416.67	-3075.44	0	13	1	-2416.67	0	0	-1411.05	-2615.44

	Ka,bind	P	Psuedo-isomer G_{form}(adp)	fraction using G_{form}	fraction using P
ADP,3-				0.475516	0.475516
HADP,2-	0.212072512			0.100844	0.100844
H2ADP-	0.000131172			6.24E-05	6.24E-05
MgADP-	0.885857745			0.42124	0.42124
MgHADP	0.004916489			0.002338	0.002338
		2.102978	-1426.068		

(18.21) Repeat problem 18.20, but use H3PO4

To obtain the transformed Gibbs energies, we repeat the calculations performed on GprimeCalc. For each species, take the Gibbs energy of formation relative to the most bare form,

$K_{a,bind} = \exp(-(\Delta G^o_{f,i} - \Delta G^o_{f,PO_4^{3-}})/(RT))$

However, in this case, data for PO_4^{3-} are not available. It is insignificant at the pH of interest anyway. We will use HPO_4^{2-} as the 'most bare form'.

$K_{a,bind} = \exp(-(\Delta G^o_{f,i} - \Delta G^o_{f,HPO_4^{2-}})/(RT))$

Because the $[H^+]$ and $[Mg^{2+}]$ are already included in the transform, the binding polynomial is $P = 1 + K_{bind1}$

The Gibbs energy of formation for the pseudoisomer is then

$$\boxed{\Delta G^o_{f,P_i} = \Delta G^o_{f,HPO_4^{2-}} - RT\ln P = -1058.57 - 0.008314*298.15*\ln(1.4472) = -1059.5 \text{ kJ/mol}}$$

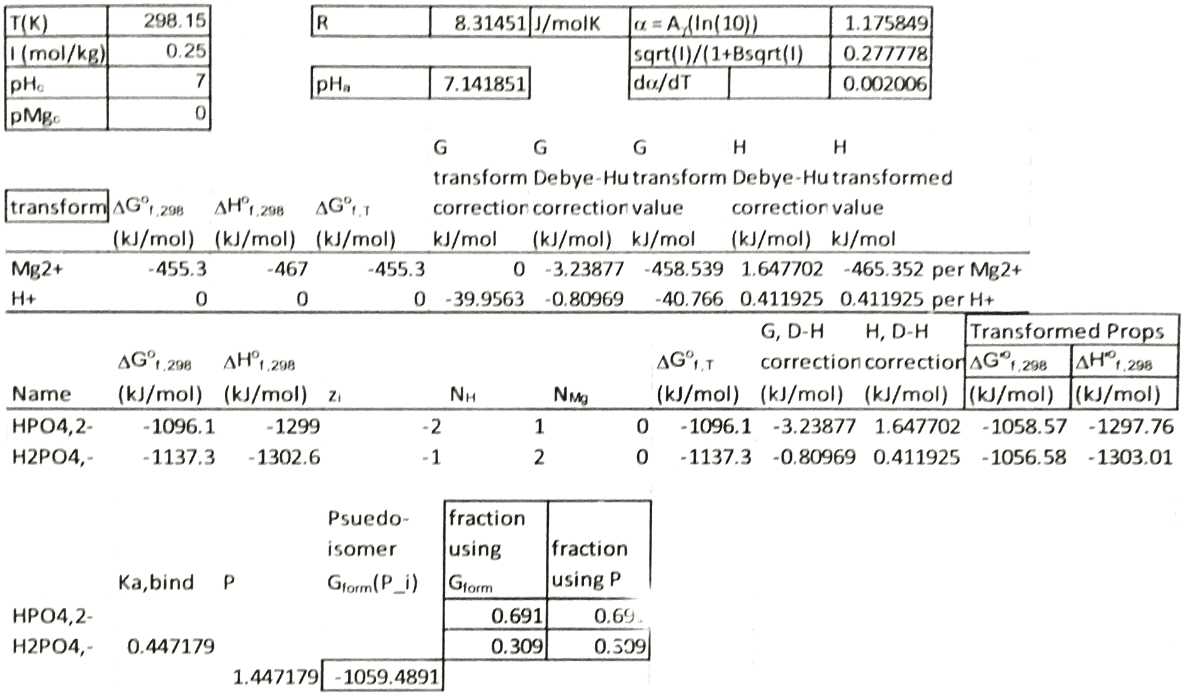
The fraction of each species can be calculated by

$1/P$, K_{bind1}/P

or equivalently by

$\exp((\Delta G^o_{f,P_i} - \Delta G^o_{f,i})/RT)$

Summary of calculations:



T(K)	298.15
I (mol/kg)	0.25
pH_c	7
pMg_c	0

R	8.31451	J/molK
pH_a	7.141851	

$\alpha = A_\gamma(\ln(10))$	1.175849
sqrt(I)/(1+Bsqrt(I)	0.277778
dα/dT	0.002006

transform	$\Delta G^o_{f,298}$ (kJ/mol)	$\Delta H^o_{f,298}$ (kJ/mol)	$\Delta G^o_{f,T}$ (kJ/mol)	G transform correction kJ/mol	G Debye-Hu correction (kJ/mol)	G transform value kJ/mol	H Debye-Hu correction (kJ/mol)	H transformed value kJ/mol	
Mg2+	-455.3	-467	-455.3	0	-3.23877	-458.539	1.647702	-465.352	per Mg2+
H+	0	0	0	-39.9563	-0.80969	-40.766	0.411925	0.411925	per H+

Name	$\Delta G^o_{f,298}$ (kJ/mol)	$\Delta H^o_{f,298}$ (kJ/mol)	z_i	N_H	N_{Mg}	$\Delta G^o_{f,T}$ (kJ/mol)	G, D-H correction (kJ/mol)	H, D-H correction (kJ/mol)	Transformed Props $\Delta G'^o_{f,298}$ (kJ/mol)	 $\Delta H'^o_{f,298}$ (kJ/mol)
HPO4,2-	-1096.1	-1299	-2	1	0	-1096.1	-3.23877	1.647702	-1058.57	-1297.76
H2PO4,-	-1137.3	-1302.6	-1	2	0	-1137.3	-0.80969	0.411925	-1056.58	-1303.01

	Ka,bind	P	Psuedo-isomer G_{form}(P_i)	fraction using G_{form}	fraction using P
HPO4,2-				0.691	0.69
H2PO4,-	0.447179			0.309	0.309
		1.447179	-1059.4891		

(18.22) This is the same problem as 18.17 with different wording.