CEE 680 Spring 2020

Homework #4 Solution

1. Thermodynamics #1

Based on only the following information, determine the standard free energy change $^{\Delta}G°$ and K value at 25°C and 1 atm for the dissociation of carbonic acid, $H_2CO_3 = H^+ + HCO_3^-$.

Available information:

Reaction	K (@25°C, 1 atm)
$H_2CO_3 = CO_{2(aq)} + H_2O$	630

Species	$^{\Delta}G°_f$ (@25°C, 1 atm) (kJ/mol)
$CO_{2(aq)}$	-386.22
H_2O	-237.18
H^+	0.0
HCO_3^-	-586.85

1 point

Solution to 1:

First we determine ΔG for the hydrolysis reaction ($H_2CO_3 = CO_2$ (aq) + H_2O):

$$^{\Delta}G^o = -2.303RT\log K$$
$$= -2.303\left(0.008314 kJ/mol{-}^oK\right)298.15^0K\left(\log 630\right)$$
$$= -15.973 kJ/mol$$

Then using this information we can determine ΔG of formation for carbonic acid

$$^{\Delta}G^o = \sum \nu_i\, ^{\Delta}G^o_f$$
$$^{\Delta}G^o = {}^{\Delta}G^o_{f-CO_2(aq)} + {}^{\Delta}G^o_{f-H_2O} - {}^{\Delta}G^o_{f-H_2CO_3}$$
$$-15.973 kJ/mol = -386.22 kJ/mol - 237.18 kJ/mol - {}^{\Delta}G^o_{f-H_2CO_3}$$
$$-607.427 kJ/mol = {}^{\Delta}G^o_{f-H_2CO_3}$$

Finally we use this to get the ΔG for the first proton loss reaction:

$$^{\Delta}G^o = \sum \nu_i\, ^{\Delta}G^o_f$$
$$^{\Delta}G^o = {}^{\Delta}G^o_{f-H^+} + {}^{\Delta}G^o_{f-HCO_3^-} - {}^{\Delta}G^o_{f-H_2CO_3}$$
$$^{\Delta}G^o = (0 - 586.85 - (-607.427)) kJ/mol$$
$$^{\Delta}G^o = 20.577 kJ/mol$$

And the corresponding K:

$$\log K = -\frac{\Delta G^o}{2.303RT}$$
$$= -\frac{20.577 kJ/mol}{2.303(0.008314 kJ/mol{-}^O K)298.15^0 K}$$
$$= -3.605$$

or:

$$K = 10^{-3.605}$$
$$= 2.49x10^{-4}$$

2. Thermodynamics #2

Estimate the value of K_W at 20°C and 1 atm. Assume that at 25°C and 1 atm, the following is true:

Equation	Equilibrium Constant (K_w)
$H_2O = H^+ + OH^-$	1.01×10^{-14}

Species	$H°_f$ (kJ/mol)
H^+	0
OH^-	-230.0
H_2O	-285.83

1 point

Solution to 2

First we calculate the ΔH at 20°C:

$$\Delta H^o = \sum \nu_i \Delta H_f^o$$
$$\Delta H^o = \Delta H^o_{f-H^+} + \Delta H^o_{f-OH^-} - \Delta H^o_{f-H_2O}$$
$$\Delta H^o = (0 - 230.0 - (-285.83)) kJ/mol$$
$$\Delta H^o = 55.83 kJ/mol$$

Then assuming ΔH remains constant with small changes in temperature, we use one of the many forms of the Arrhenius equation:

$$Ln\frac{K_2}{K_1} = -\frac{\Delta H^o(T_2 - T_1)}{RT_1T_2}$$

or

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{K_{20}}{1.01x10^{-14}} = -\frac{55.83kJ/mol}{0.008314kJ/mol{-}^oK}\left(\frac{1}{293.15} - \frac{1}{298.15}\right)$$

$$K_{20} = 0.688x10^{-14}$$

or:

$$\log K_{20} = -14.16$$

3. *Acid/Base Equilibria II: MINEQL method*

Solve the problems from question #1 in homework #3 (1A and 1B copied below) using MINEQL[1]. Present the MINEQL-based concentrations in a table. Compare your MINEQL results with the approximate solutions you obtained from your graphs in problem homework #3 (note: when solving problems with the carbonate system, you will have to send aqueous CO_2 to the Type VI category just as you did for H^+. When we work with open carbonate systems, you won't have to do this.)

A). Consider a 0.10 F phosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}) system. Using MINEQL, calculate the pH and the concentration of all species in the following solutions:

i) 0.10 F NaH_2PO_4

ii) 0.10 F Na_2HPO_4

iii) 0.10 F Na_3PO_4

B) Consider a 0.10 F carbonate system (H_2CO_3, HCO_3^-, CO_3^{-2}) and 0.20 F ammonia system (NH_4^+, NH_3), and use MINEQL to calculate pH and composition of the following systems:

i) 0.10 F $NaHCO_3$

ii) 0.10 F $NaHCO_3$ + 0.20 F NH_4Cl

iii) 0.10 F $(NH_4)_2CO_3$

iv) 0.10 F Na_2CO_3

2 points

i) 0.10 F NaH2PO4

Solution Composition

[1] You may also use other chemical equilibria programs besides MINEQL, if you prefer. Examples of others include ChemEQL and MINTEQ.

Species	Graph		MINEQL		MINEQL[2]
	C	pC	C	pC	C
H^+	2.2e-5	4.65	2.01e-5	4.70	3.02e-5 (pH 4.52)
OH^-	4.5e-10	9.35	4.98e-10	9.30	3.33e-10
H_3PO_4	2.8e-4	3.55	2.87e-4	3.54	4.21e-4
$H_2PO_4^-$	1e-1	1.0	9.94e-2	1.00	9.91e-2
HPO_4^{-2}	2.8e-4	3.55	3.07e-4	3.51	2.08e-4
PO_4^{-3}	8e-12	11.1	6.88e-12	11.16	2.90e-12
Na^+	1e-1	1	1e-1	1	9.98e-2
$NaHPO_4^-$	N/A	N/A	N/A	N/A	2.44e-4

ii) 0.10 F Na2HPO4

Solution Composition

Species	Graph		MINEQL (old version)		MINEQL
	C	pC	C	pC	C
H^+	1.7e-10	9.75	1.85e-10	9.73	2.09e-10 (pH 9.68)
OH^-	5.6e-5	4.25	5.43e-5	4.27	4.82e-5
H_3PO_4	8e-12	11.1	7.88e-12	11.10	3.68e-12
$H_2PO_4^-$	2.8e-4	3.55	2.97e-4	3.53	1.25e-4
HPO_4^{-2}	1e-1	1	9.95e-2	1.00	3.80e-2
PO_4^{-3}	2.8e-4	3.55	2.42e-4	3.62	7.68e-5
Na^+	2e-1	0.7	2e-1	0.70	1.38e-1
$NaHPO_4^-$	N/A	N/A	N/A	N/A	6.18e-2

iii) 0.10 F Na3PO4

Solution Composition

Species	Graph		MINEQL (old version)		MINEQL
	C	pC	C	pC	C
H^+	2.5e-13	12.6	2.69e-13	12.57	1.65e-13 (pH 12.78)
OH^-	4e-2	1.4	3.74e-2	1.43	6.10e-2
H_3PO_4	1e-17	17	6.25e-18	17.20	9.25e-18
$H_2PO_4^-$	2e-7	6.7	1.62e-7	6.79	3.98e-7
HPO_4^{-2}	4e-2	1.4	3.74e-2	1.43	1.53e-2
PO_4^{-3}	6.3e-2	1.2	6.26e-2	1.20	3.90e-2
Na^+	3e-1	0.5	3e-1	0.52	2.54e-1
$NaHPO_4^-$	N/A	N/A	N/A	N/A	4.57e-2

[2] Different versions of MINEQL apparently give slightly different answers to the sodium phosphate system, probably because of different considerations & constants for soluble sodium complexes.

B) Calculate pH and composition of the following systems:
i) 0.10 F $NaHCO_3$
ii) 0.10 F $NaHCO_3$ + 0.20 F NH_4Cl
iii) 0.10 F $(NH_4)_2CO_3$
iv) 0.10 F Na_2CO_3

i) 0.10 F $NaHCO_3$

Solution Composition

Species	**Graph**		**MINEQL**	
	C	pC	C	pC
H^+	5e-9	8.3	7.57e-9	8.12
OH^-	2e-6	5.7	1.33e-6	5.88
H_2CO_3	1e-3	3	1.56e-3	2.81
HCO_3^-	1e-1	1	9.1e-2	1.04
CO_3^{-2}	1e-3	3	1.56e-3 **	3.25
Na^+	1e-1	1	1e-1	1.00

** this is the sum of $[CO_3^{-2}]$ (5.69e-4) and $[NaCO_3^-]$ (9.93e-4).

ii) 0.10 F $NaHCO_3$ + 0.20 F NH_4Cl

Solution Composition

Species	**Graph**		**MINEQL**	
	C	pC	C	pC
H^+	2.5e-8	7.6	2.45e-8	7.61
OH^-	4e-7	6.4	4.08e-7	6.39
H_2CO_3	5e-3	2.3	4.94e-3	2.31
HCO_3^-	1e-1	1	8.98e-1	1.05
CO_3^{-2}	1.8e-4	3.75	1.71e-4	3.77
NH_4^+	2e-1	0.7	1.96e-1	0.71
NH_3	5e-3	2.3	4.47e-3	2.35
Cl^-	2e-1	0.7	2e-1	0.70
Na^+	1e-1	1	1e-1	1.00

iii) 0.10 F $(NH_4)_2CO_3$

Solution Composition

Species	Graph		MINEQL	
	C	pC	C	pC
H^+	5.6e-10	9.25	6.4e-10	9.19
OH^-	1.8e-5	4.75	1.57e-5	4.81
H_2CO_3	7e-5	4.2	1.34e-4	3.87
HCO_3^-	1e-1	1	9.31e-2	1.03
CO_3^{-2}	8e-3	2.1	6.8e-3	2.17
NH_4^+	1e-1	1.0	1.07e-1	0.97
NH_3	1e-1	1.0	9.33e-2	1.03

iv) 0.10 F Na_2CO_3

Solution Composition

Species	Graph		MINEQL	
	C	pC	C	pC
H^+	2.2e-12	11.65	4.0e-12	11.4
OH^-	4.5e-3	2.35	2.5e-3	2.6
H_2CO_3	2e-8	7.7	2.1e-8	7.68
HCO_3^-	4.5e-3	2.35	2.4e-3	2.62
CO_3^{-2}	1e-1	1	9.7e-2 **	1.01
Na^+	2e-1	0.7	2e-1	0.70

** this is the sum of [CO_3^{-2}] (2.8e-2) and [$NaCO_3^-$] (6.9e-2).