Aq Chem
PS #2

1) a) $[HCl]_T = 3\times 10^{-4} M$

$[NaOH]_T = 5\times 10^{-4} M$

$[OH^-] = [NaOH]_T - [HCl]_T = 2\times 10^{-4} M = 10^{-3.7} M$

$[H^+] = K_w/[OH^-] = 10^{-14}/10^{-3.7} = 10^{-10.3} M$; $pH = 10.3$

$[H^+] = 5\times 10^{-11} M$

$[Na^+] = 5\times 10^{-4} M$; $[Cl^-] = 3\times 10^{-4} M$

The HCl and NaOH dissociated completely.
H^+ reacted with OH^- to form H_2O.
The equilibrium $[H^+]$ is given by the $[OH^-]$ + Kw, where the $[OH^-]$ is given by the excess of strong base over strong acid.

b) $[NaHCO_3]_T = 10^{-3} M$

$[HCl]_T = 2\times 10^{-4} M$

$NaHCO_3 \rightarrow Na^+ + HCO_3^-$

$HCl \rightarrow H^+ + Cl^-$

$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ $\quad K_{a_1} = [HCO_3^-][H^+]/[H_2CO_3^*] = 10^{-6.3}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\quad K_{a_2} = [CO_3^{2-}][H^+]/[HCO_3^-] = 10^{-10.3}$

$H^+ + OH^- \rightleftharpoons H_2O$ $\quad K_w = [H^+][OH^-] = 10^{-14}$

$[H_2CO_3^*] = [HCl]_T = 2\times 10^{-4} M = 10^{-3.7} M$

$[HCO_3^-] = [NaHCO_3]_T - [H_2CO_3^*] = 8\times 10^{-4} M = 10^{-3.1} M$

$$K_{a_1} = 10^{-6.3} = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]}$$

$$[H^+] = \frac{(10^{-6.3})[H_2CO_3^*]}{[HCO_3^-]} = \frac{(10^{-6.3})(10^{-3.7})}{(10^{-3.1})} = 10^{-6.9} M = 1.25\times 10^{-7} M$$

$$[OH^-] = K_w/[H^+] = \frac{10^{-14}}{10^{-5.7}} = 10^{-7.1} M = 7.98\times 10^{-8} M$$

$[Na^+] = 10^{-3} M$; $[Cl^-] = 2\times10^{-4} M$

$$[CO_3^{2-}] = \frac{K_{a_2}[HCO_3^-]}{[H^+]} = \frac{(10^{-10.3})(10^{-3.1})}{(10^{-6.9})} = 10^{-6.5} M$$

$[H^+] = 10^{-6.9} M = 1.25\times10^{-7} M$ $[HCO_3^-] = 10^{-3.1} M = 8\times10^{-4} M$

$[OH^-] = 10^{-7.1} M = 7.98\times10^{-8} M$ $[CO_3^{2-}] = 10^{-6.5} M = 3.21\times10^{-7} M$

$[H_2CO_3^*] = 10^{-3.7} M = 2\times10^{-4} M$ $[Cl^-] = 2\times10^{-4} M$

$[Na^+] = 10^{-3} M$

The $NaHCO_3$ and HCl dissociated completely; H^+ then added to HCO_3^- to form $H_2CO_3^*$. The equilibrium $[H^+]$ is then given by the mass law expression for the dissociation of $H_2CO_3^*$ (K_{a_1}), $[HCO_3^-]$, and $[H_2CO_3^*]$.

c) $[CO_2]_T = 10^{-2} M$; $[NaOH]_T = 2\times10^{-3} M$

$CO_2(g) \rightarrow CO_2(aq)$ complete dissol'n

$NaOH \rightarrow Na^+ + OH^-$ complete dissol'n

Let $[H_2CO_3^*] = [CO_2] + [H_2CO_3]$,

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

$[H_2CO_3^*] = [H_2CO_3^*]_T - [NaOH]_T = 8\times10^{-3} M = 10^{-2.1} M$

$[HCO_3^-] = [NaOH]_T = 2\times10^{-3} M = 10^{-2.7} M$

We assume complete dissol'n of CO_2, which forms $H_2CO_3^*$ in H_2O. NaOH dissociates completely and OH^- abstracts a proton from $H_2CO_3^*$, forming HCO_3^-, the equilibrium $[H^+]$ is then determined by the mass law expression (K_{a_1}), $[H_2CO_3^*]$, and $[HCO_3^-]$.

(As in previous example).

$$[H^+] = \frac{(10^{-6.3})[H_2CO_3^*]}{[HCO_3^-]} = \frac{(10^{-6.3})(10^{-2.1})}{10^{-2.7}} = 10^{-5.7} M = 2\times10^{-6} M$$

$$[OH^-] = K_w/[H^+] = 10^{-14}/10^{-5.7} = 10^{-8.3} M = 5\times10^{-9} M$$

$[Na^+] = 2\times10^{-3} M$

$$[CO_3^{2-}] = \frac{K_{a_2}[HCO_3^-]}{[H^+]} = \frac{(10^{-10.3})(10^{-2.7})}{10^{-5.7}} = 10^{-7.3} M = 5\times10^{-8} M$$

d) $pCO_2 = 10^{-2.5}$ atm $\quad [NaOH]_T = 10^{-3}$ M
⇒ open system

$$\begin{array}{l|cccc}
 & H_2O & H^+ & H_2CO_3^* & Na^+ \\
\hline
H_2O & 1 & 1 & & \\
H^+ & & -1 & & \\
OH^- & 1 & & 1 & \\
 & & & 1 & \\
H_2CO_3^* & & -1 & 1 & \\
HCO_3^- & & -2 & & 1 \\
CO_3^{2-} & & & & \\
Na^+ & & & & \\
\hline
 & 1 & & & \\
H_2O_T & & & 1 & \\
[CO_2]_T & -1 & -1 & & 1 \\
[NaOH]_T & 1 & & & \\
\end{array}$$

$$\text{TOT H: } [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] = -[NaOH]_T$$

Possible solutions

i) $[OH^-] = 10^{-3}$ M $\gg [H^+], [HCO_3^-], [CO_3^{2-}]$

ii) $[HCO_3^-] = 10^{-3}$M $\gg [H^+], [CO_3^{2-}], [OH^-]$

iii) $2[CO_3^{2-}] = 10^{-3}$M $\gg [H^+], [HCO_3^-], [OH^-]$

You can use your plot form PS#1, Question 3 (from 2e - open system), noting that $[H_2CO_3^*] = (10^{-2.5} \text{ atm})(10^{-1.46} \text{ M/atm}) = 10^{-3.96}$ M now (and $[H_2CO_3^*] = (10^{-1.5} \text{ atm})(10^{-1.46} \text{ M/atm}) = 10^{-2.96}$ M before).

ii) looks like an appropriate soln . . .

$$[HCO_3^-] = 10^{-3} \text{ M}$$

$$[H_2CO_3^*] = pCO_2 * K_H = (10^{-2.5} \text{ atm})(10^{-1.46} \text{ M/atm}) = 10^{-3.96} \text{ M}$$

From Ka_1:
$$[H^+] = \frac{(Ka_1)[H_2CO_3^*]}{[HCO_3^-]} = \frac{(10^{-6.3})(10^{-3.96})}{(10^{-3})} = 10^{-7.26} \text{ M}$$

pH = 7.26.

$[H^+] = 10^{-7.26}$ M

$[OH^-] = 10^{-6.74}$ M

$[H_2CO_3^*] = 10^{-3.96}$ M

$[HCO_3^-] = 10^{-3}$ M

$$[CO_3^{2-}] = (Ka_2)[HCO_3^-]/[H^+] = \frac{(10^{-10.3})(10^{-3})}{(10^{-7.26})} = 10^{-6.04} \text{ M}$$

$[Na^+] = 10^{-3}$M

In this system, OH^- reacts with $H_2CO_3^*$ to form HCO_3^-. As there is an unlimited supply of $H_2CO_3^*$ (from pCO_2), the system is buffered and the pH is controlled by the $H_2CO_3^* : HCO_3^-$ ratio (and only slightly alkaline in spite of 10^{-3}M strong base!).

PROBLEM #2

$$CaCO_3(s) \rightleftarrows Ca^{2+} + CO_3^{2-}$$

a)

$\Delta G_{rxn} = \mu_{rxn} = \sum_i \nu_i \mu_i$

$\nu_i = \frac{dn_i}{d\xi}$, so $\nu_i > 0$ for products, $\nu_i < 0$ for reactants

$\mu_i = \mu_i^\circ + RT \ln\{i\}$

$\mu_{CaCO_3} = \mu^\circ_{CaCO_3}$

$\nu_{Ca^{2+}} = \nu_{CO_3^{2-}} = 1$

$\nu_{CaCO_3} = -1$

$\mu_{Ca^{2+}} = \mu^\circ_{Ca^{2+}} + RT \ln\{Ca^{2+}\}$

$\mu_{CO_3^{2-}} = \mu^\circ_{CO_3^{2-}} + RT \ln\{CO_3^{2-}\}$

$$\mu_{rxn} = \sum_i \nu_i \mu_i = -\mu^\circ_{CaCO_3} + \mu^\circ_{Ca^{2+}} + RT\ln\{Ca^{2+}\} + \mu^\circ_{CO_3^{2-}} + RT\ln\{CO_3^{2-}\}$$

$$\Delta G_{rxn} = \mu_{rxn} = -\mu^\circ_{CaCO_3} + \mu^\circ_{Ca^{2+}} + \mu^\circ_{CO_3^{2-}} + RT\ln\{Ca^{2+}\}\{CO_3^{2-}\}$$

$\Delta G_{rxn} = 0$ at equil., so

$$\mu^\circ_{Ca^{2+}} + \mu^\circ_{CO_3^{2-}} - \mu^\circ_{CaCO_3} = -RT\ln\{Ca^{2+}\}\{CO_3^{2-}\}$$

$$e^{-(\mu^\circ_{Ca^{2+}} + \mu^\circ_{CO_3^{2-}} - \mu^\circ_{CaCO_3}/RT)} = K_{eq} = K_{sp} = \{Ca^{2+}\}\{CO_3^{2-}\}$$ ✓

b) at $T = 298$, $P = 1\,atm$

$\mu_{Ca^{2+}} = -553.58$ kJ/mol

$\mu_{CO_3^{2-}} = -527.81$ kJ/mol

$\mu_{CaCO_3} = -1128.79$ kJ/mol

Then

$$K_{sp} = e^{-((-553.58 - 527.81 + 1128.79\,kJ/mol)/(298K \cdot 0.0083145\,kJ/mol\,K))} = 4.92 \times 10^{-9}$$

$$= \boxed{10^{-8.31}}$$ ✓

c) $K_2 = K_1 e^{-\Delta H^\circ/R \left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

$\Delta H_{rxn} = n\Delta H^\circ_{prd} - n\Delta H^\circ_{react} = \Delta H^\circ_f(Ca^{2+}) + \Delta H^\circ_f(CO_3^{2-}) - \Delta H^\circ_f(CaCO_3(s))$

$= (-542.83 - 677.14 + 1206.92)\,kJ/mol$

$= -13.05\ kJ/mol$

$$K_2(277K) = K_1(298K)\, e^{-\left(\frac{-13.05\times10^3\ J/mol}{8.31451\ J/mol\cdot K}\right)\left(\frac{1}{277} - \frac{1}{298}\right)}$$

$$= \left(10^{-8.31}\right)\left(1.49\right) = 7.30\times10^{-9} = \boxed{10^{-8.14}}\ ✓$$

so solubility ↑ as T↓, makes sense, as rxn is exothermic.

In this calculation, we are assuming that ΔH° is constant over the considered temperature range.

In Fig 2.5 (p.88), the slope of the line gives ΔH°/R, so a fairly straight line over ΔT indicates a fairly constant ΔH°. For $CaCO_3(s)$, the line is fairly straight from 4°C to 25°C, and so our assumption was likely acceptable, but introduced some error.

d) $K_{sp} = \{Ca^{2+}\}\{CO_3^{2-}\} = \gamma_{Ca^{2+}}[Ca^{2+}]\,\gamma_{CO_3^{2}}[CO_3^{2-}]$

$$[Ca^{2+}][CO_3^{2-}] = \frac{K_{sp}}{\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}} = K_{apparent}$$

$$\log\gamma_i = -0.5(z_i^2)\left[\frac{I^{1/2}}{1+I^{1/2}} - 0.2\,I\right]$$, choosing $B = 0.2$ in the Davies E

$A = \frac{1.17}{\ln 10} = 0.5$

$I = 0.0004\ M$

$$\left[\frac{I^{1/2}}{1+I^{1/2}} - 0.2\,I\right] = 1.95\times10^{-2}$$

Then $\log\gamma_{Ca^{2+}} = -0.5(2)^2[1.95\times10^{-2}] = -3.9\times10^{-2}$

$\log\gamma_{CO_3^{2-}} = -3.9\times10^{-2}$, as it has the same charge magnitude as Ca^{2+}.

Then $$K_{app} = \frac{10^{-8.31}}{10^{-0.039}\,10^{-0.039}} = \boxed{10^{-8.23}}$$ ✓

$I = 0.2\ M$

$$\left[\frac{I^{1/2}}{1+I^{1/2}} - 0.2\,I\right] = 2.69\times10^{-1}$$

Then $\log\gamma_{Ca^{2+}} = \log\gamma_{CO_3^{2-}} = -0.5(2)^2[2.69\times10^{-1}] = -0.54$

$$K_{app} = \frac{10^{-8.31}}{10^{-0.54}\,10^{-0.54}} = \boxed{10^{-7.23}}$$ ✓

Problem 2 e.

Ksp values for a given temperature and ionic strength

Ionic Strength (M)	T=298K	T=277K
0	**$10^{-8.31}$**	**$10^{-8.14}$**
0.0004	**$10^{-8.23}$**	**$10^{-8.06}$**

Lake temperature variations from 4 to 25°C correspond to K_{sp} variations of ±0.17 log units, so neglecting the effect of lake temperature on K_{sp} could introduce errors that exceed the "inherent" uncertainty of ±0.05 log units. Similarly, it is important to recognize the effect of ionic strength on K_{sp}, as assuming I= 0 M would result in errors as great as 0.08 log units.

Problem 3

a) $K_{eq} = ?$

$\Delta G° = -RT\ln K$ at equilibrium

$= \Sigma \mu_i^{\circ} \nu_i = \mu^{\circ}_{H^+} + \mu^{\circ}_{Ac} - \mu^{\circ}_{HAc} = (0 - 369.3 + 396.5)$ kJ/mol

$= 27.2$ kJ/mol

$$K = e^{-\Delta G°/RT} = e^{\left(-27.2 \overset{(kJ/mol)}{} / (\underset{(K)}{298} \cdot \underset{(kJ/mol\cdot K)}{0.0083145})\right)} = 1.71\times10^{-5} = \boxed{10^{-4.77} = K_a}$$

b) Let $\xi = \frac{[Ac^-]}{10^{-3}M}$; representing the progress of the rxn.

Let $Q = \frac{[prod]}{[react]} = \frac{[Ac^-][H^+]}{[HAc]}$. In terms of $[Ac^-]$, $Q = \frac{[Ac^-]^2}{[10^{-3}M - [Ac^-]]}$ (1).

Then $\Delta G = \Delta G° + RT\ln Q = (27.2\ kJ/mol) + (298K \cdot 0.0083145\ kJ/mol\cdot K)\ln Q$. (2).

Plot of ΔG vs. ξ was generated by varying $[Ac^-]$ from 0 to 10^{-3}M,
solving Q in terms of $[Ac^-]$ (Eqn 1),
then solving for ΔG (Eqn 2).

If $G = \Sigma \mu_i n_i$ and $\mu_i = \mu_i^{\circ} + RT\ln[i]$

Then $G = n_{H^+}\mu^{\circ}_{H^+} + n_{Ac^-}\mu^{\circ}_{Ac^-} + n_{HAc}\mu^{\circ}_{HAc}$

$+ n_{H^+} RT\ln[H^+] + n_{Ac^-} RT\ln[Ac^-] + n_{HAc} RT\ln[HAc]$.

3b (con't)

Subsituting

n_{H^+}, n_{Ac^-} from 0 to 10^{-3} mol,

n_{HAc} from 10^{-3} to 0 mol,

$[H^+], [Ac^-]$ from 0 to 10^{-3} M,

$[HAc]$ from 10^{-3} M to 0 M,

$\mu^\circ_{H^+} = 0$, $\mu^\circ_{Ac^-} = -369.3$, $\mu^\circ_{HAc} = -396.5$,

$R = 0.00831451$ kJ/mol·K, $T = 298K$,

we generated the plot of G vs. ξ.

c) The equilibrium is where $\Delta G = 0$,

$K = 10^{-4.77}$ (as shown in part a)

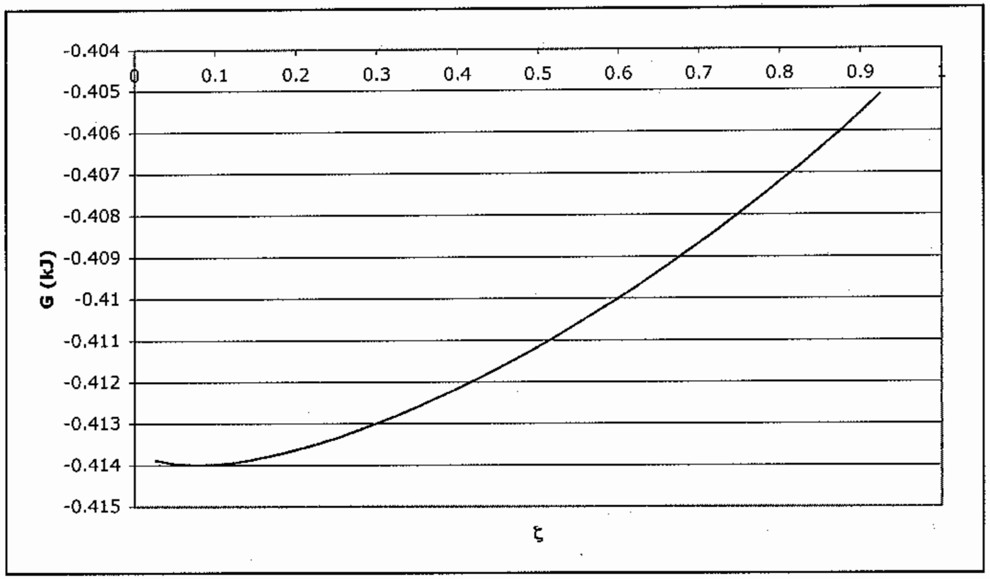
$$10^{-4.77} = \frac{[H^+][Ac^-]}{[HAc]} = \frac{x^2}{(10^{-3} - x)}$$

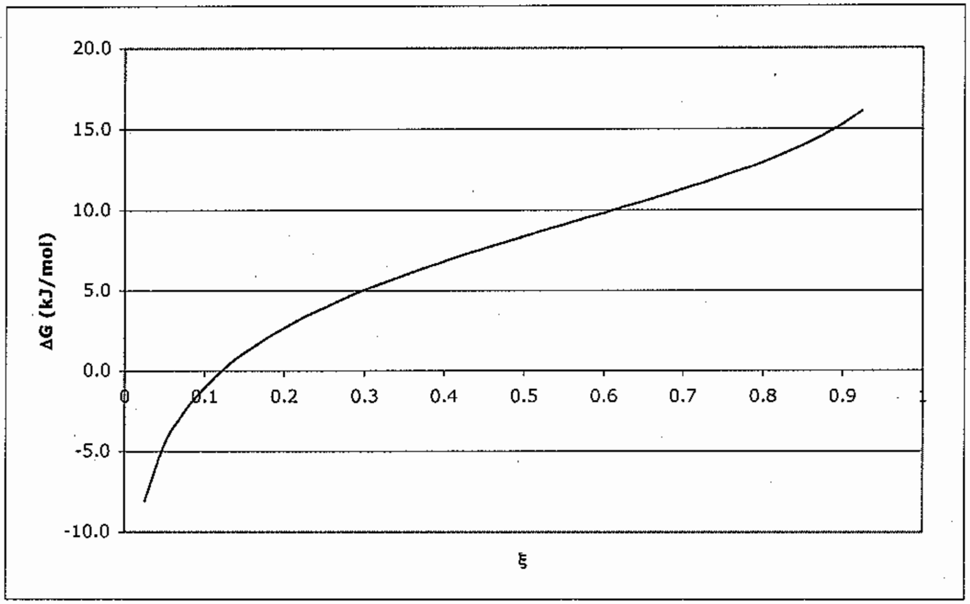
$$x^2 - (10^{-4.77})(10^{-3}) + 10^{-4.77}x = 0$$

$$x = [Ac^-] = [H^+] = 1.22 \times 10^{-4} \text{ M} = 10^{-3.91} \text{ M}$$

$$[HAc] = 10^{-3} - 10^{-3.91} = 10^{-3.06} \text{ M}$$

ξ	G	ΔG	[A-] (M)	Q
0			0.00E+00	
0.025	-4.14E-01	-8.1	2.50E-05	6.4E-07
0.05	-4.14E-01	-4.6	5.00E-05	2.6E-06
0.075	-4.14E-01	-2.6	7.50E-05	6.1E-06
0.1	-4.14E-01	-1.1	1.00E-04	1.1E-05
0.125	-4.14E-01	0.1	1.25E-04	1.8E-05
0.15	-4.14E-01	1.1	1.50E-04	2.6E-05
0.175	-4.14E-01	1.9	1.75E-04	3.7E-05
0.2	-4.14E-01	2.7	2.00E-04	5.0E-05
0.225	-4.13E-01	3.3	2.25E-04	6.5E-05
0.25	-4.13E-01	3.9	2.50E-04	8.3E-05
0.275	-4.13E-01	4.5	2.75E-04	1.0E-04
0.3	-4.13E-01	5.0	3.00E-04	1.3E-04
0.325	-4.13E-01	5.5	3.25E-04	1.6E-04
0.35	-4.13E-01	5.9	3.50E-04	1.9E-04
0.375	-4.12E-01	6.4	3.75E-04	2.3E-04
0.4	-4.12E-01	6.8	4.00E-04	2.7E-04
0.425	-4.12E-01	7.2	4.25E-04	3.1E-04
0.45	-4.12E-01	7.6	4.50E-04	3.7E-04
0.475	-4.11E-01	8.0	4.75E-04	4.3E-04
0.5	-4.11E-01	8.4	5.00E-04	5.0E-04
0.525	-4.11E-01	8.7	5.25E-04	5.8E-04
0.55	-4.11E-01	9.1	5.50E-04	6.7E-04
0.575	-4.10E-01	9.5	5.75E-04	7.8E-04
0.6	-4.10E-01	9.8	6.00E-04	9.0E-04
0.625	-4.10E-01	10.2	6.25E-04	1.0E-03
0.65	-4.09E-01	10.6	6.50E-04	1.2E-03
0.675	-4.09E-01	10.9	6.75E-04	1.4E-03
0.7	-4.09E-01	11.3	7.00E-04	1.6E-03
0.725	-4.08E-01	11.7	7.25E-04	1.9E-03
0.75	-4.08E-01	12.1	7.50E-04	2.3E-03
0.775	-4.08E-01	12.5	7.75E-04	2.7E-03
0.8	-4.07E-01	13.0	8.00E-04	3.2E-03
0.825	-4.07E-01	13.4	8.25E-04	3.9E-03
0.85	-4.06E-01	14.0	8.50E-04	4.8E-03
0.875	-4.06E-01	14.6	8.75E-04	6.1E-03
0.9	-4.06E-01	15.3	9.00E-04	8.1E-03
0.925	-4.05E-01	16.1	9.25E-04	1.1E-02
0.95	-4.05E-01		9.50E-04	0.01805





PROBLEM #4

$\Delta G^\circ = -RT\ln K$

$K = e^{-\Delta G^\circ/RT}$; $R = 8.31451 \text{ J/mol}\cdot\text{K} = 8.31451\times10^{-3} \text{ kJ/mol K}$

$T = 298 \text{ K} = 273 + 25$

$\Delta G^\circ = \sum_i \nu_i \mu_i^\circ$; ν_i = stoichiometric coefficients $= \frac{dn_i}{d\xi}$ $\Rightarrow$ so $\nu_i < 0$ for reactants, $\nu_i > 0$ for products

Recipe

$[HCN]_T$

$[NaCl]_T$

$[NaOH]_T$

$[H_2O]_T$

$HCN \rightleftarrows H^+ + CN^-$ $\quad K_{HCN} = \frac{\{H^+\}\{CN^-\}}{\{HCN\}}$

$NaCl \rightleftarrows Na^+ + Cl^-$ $\quad K_{NaCl} = \frac{\{Na^+\}\{Cl^-\}}{\{NaCl\}}$

$NaOH \rightleftarrows Na^+ + OH^-$ $\quad K_{NaOH} = \frac{\{Na^+\}\{OH^-\}}{\{NaOH\}}$

$HCl \rightleftarrows H^+ + Cl^-$ $\quad K_{HCl} = \frac{\{H^+\}\{Cl^-\}}{\{HCl\}}$

$H_2O \rightleftarrows OH^- + H^+$ $\quad K_{H_2O} = \{H^+\}\{OH^-\}$

$HCN \rightleftarrows H^+ + CN^-$

$\Delta G^\circ = \sum \nu_i \mu_i = \mu^\circ_{H^+} + \mu^\circ_{CN^-} - \mu^\circ_{HCN} = 52.7 \text{ kJ/mol}$

$K = e^{-\Delta G^\circ/RT} = e^{(-52.7 \text{ kJ/mol})/((8.31451\times10^{-3} \text{ kJ/mol}\cdot\text{K})(298\text{K}))} = \boxed{5.8\times10^{-10} = 10^{-9.24}}$

$\Rightarrow$ should consider this rxn.

$NaCl \rightleftarrows Na^+ + Cl^-$

$K = e^{-\Delta G^\circ/RT} = e^{-(-23.2)/RT} = 1.17\times10^4 = \boxed{10^4}$

$\Rightarrow$ rxn goes to completion.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$\Delta G^\circ = -9.1 \text{ kJ/mol}$$

$$K = e^{-\Delta G^\circ/RT} = 39.4 = \boxed{10^{1.6}}$$

$$K = \frac{\{Na^+\}\{OH^-\}}{\{NaOH(aq)\}} = 10^{1.6}$$

$$\frac{\{Na^+\}}{\{NaOH(aq)\}} = \frac{10^{1.6}}{\{OH^-\}}$$

if $pH \leq 13$ $\{OH^-\} \leq 10^{-1}$, so

$$\frac{\{Na^+\}}{\{NaOH(aq)\}} \geq \frac{10^{1.6}}{10^{-1}} = 10^{1.6}$$

, so $\{Na^+\} \geq 10^{2.6}\{NaOH(aq)\}$, and it is safe to assume that all the NaOH is dissociated.

$\Rightarrow$ rxn not considered.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$\Delta G^\circ = -16.3 \text{ kJ/mol}$$

$$K = 719.5 = 10^{2.86}$$

$$K = \frac{\{H^+\}\{Cl^-\}}{\{HCl(aq)\}} = \boxed{10^{2.86}}$$

$$\frac{\{Cl^-\}}{\{HCl(aq)\}} = \frac{10^{2.86}}{\{H^+\}}$$

if $pH = 1$, $\frac{\{Cl^-\}}{\{HCl(aq)\}} = \frac{10^{2.86}}{10^{0}} = 10^{2.86}$

$\{Cl^-\} = 10^{2.86}\{HCl(aq)\}$, so we can assume HCl is fully dissociated if $pH \geq 1$.

$\Rightarrow$ rxn not considered

$\underline{H_2O \rightleftharpoons H^+ + OH^-}$

$\Delta G^\circ = 79.9\ kJ/mol$

$K_{H_2O} = K_w = 9.9 \times 10^{-15} = \boxed{10^{-14}}$ ⇒ should consider rxn (dissociation not complete)

4b) make appropriate ionic strength corrections:

We will correct the rxns of interest: K_{H_2O}, K_{HCN} ,

$$K_{H_2O} = \{H^+\}\{OH^-\} \qquad K_{HCN} = \frac{\{H^+\}\{CN^-\}}{\{HCN(aq)\}}$$

as $\{i\} = \gamma_i [i]$, we can substitute;

$$K_{H_2O} = \gamma_{H^+}[H^+]\,\gamma_{OH^-}[OH^-] \qquad K_{HCN} = \frac{\gamma_{H^+}[H^+]\,\gamma_{CN^-}[CN^-]}{\gamma_{HCN}[HCN(aq)]}$$

Rearrange to find $K_{app} = {}^cK = {}'K = \frac{[prod]}{[react]}$ (concentrations, not activities):

$$\frac{K_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}} = [H^+][OH^-] = K_{app,H_2O}. \qquad (\text{Eqn } 1)$$

$$\frac{K_{HCN}\,\gamma_{HCN}}{\gamma_{H^+}\,\gamma_{CN^-}} = \frac{[H^+][CN^-]}{[HCN(aq)]} = K_{app,HCN}. \qquad (\text{Eqn } 2)$$

We know K_{H_2O}, K_{HCN}. We must find γ_{H^+}, γ_{HCN}, γ_{CN^-}, γ_{OH^-} from the Davies eqn:

$$\log \gamma_i = -A z_i^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - bI \right] ; \qquad A = 0.5, \quad b = 0.3.$$

We must find I for Recipe 1 and Recipe 2.

4b (con't)

$I = \frac{1}{2}\sum_i z^2[i] = \frac{1}{2}\left[[Na^+](1)^2 + [Cl^-](-1)^2\right] = 1\times10^{-1}M$, as $[Na^+], [Cl^-] \gg [H^+], [OH^-], [CN^-]$

Alternately, you can use the recipe concentrations

For Recipe 1: $[HCN]_T = 10^{-3}M$; $[NaCl]_T = 10^{-1}M$, $[NaOH]_T = 0\,M$

$$I = \frac{1}{2}\left[(10^{-3}M)(1)^2 + (10^{-3}M)(-1)^2 + (10^{-1}M)(1)^2 + (10^{-1}M)(-1)^2\right]$$

$$= 1.01\times10^{-1}M \simeq 1.\underline{0}\times10^{-1}M$$

For Recipe 2: $[HCN]_T = 10^{-3}M$; $[NaCl]_T = 10^{-1}M$, $[NaOH]_T = 10^{-3}\,M$

$$I = \frac{1}{2}\left[(10^{-3}M)(1)^2 + (10^{-3}M)(-1)^2 + (10^{-1}M)(1)^2 + (10^{-1})(-1)^2 + (10^{-3}M)(1)^2 + (10^{-3}M)(-1)^2\right]$$

$$= 1.02\times10^{-1}\,M \simeq 1.\underline{0}\times10^{-1}M$$

As $I_{recipe\,1} \simeq I_{recipe\,2}$; $\gamma_{recipe\,1} = \gamma_{recipe\,2}$ for all species.

For the spp w/ $z = \pm 1$:

$$\log \gamma_i = -0.5(\pm1)^2\left[\frac{(1.0\times10^{-1})^{1/2}}{1+(1.0\times10^{-1})^{1/2}} - 0.3(2.0\times10^{-1})\right]$$

$$= -0.105$$

$$\boxed{\gamma_i = 10^{-0.105} \text{ for } H^+, CN^-, OH^-.}$$

For HCN (neutral); $\boxed{\gamma_{HCN} = 1}$ (as Davies gives $\log\gamma = 0$) $(\gamma = e^{\log\gamma} = e^0 = 1)$.

Plug into Eqn 1:

$$K_{app,H_2O} = [H^+][OH^-] = \frac{K_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}} = \frac{10^{-14}}{10^{-0.105}\,10^{-0.105}} = 10^{-13.79}\;K_{app,H_2O}$$

Plug into Eqn 2:

$$K_{app,HCN} = \frac{[H^+][CN^-]}{[HCN]} = \frac{K_{HCN}\,\gamma_{HCN}}{\gamma_{H^+}\,\gamma_{CN^-}} = \frac{(10^{-9.24})(1)}{(10^{-0.105})(10^{-0.105})} = 10^{-9.03} = K_{app,H_2O}$$

4c) solve (incase you haven't had enough)

Recipe 1: $[HCN]_T = 10^{-3}M$
$[NaOH]_T = 0\ M$
$[NaCl]_T = 10^{-1}M$

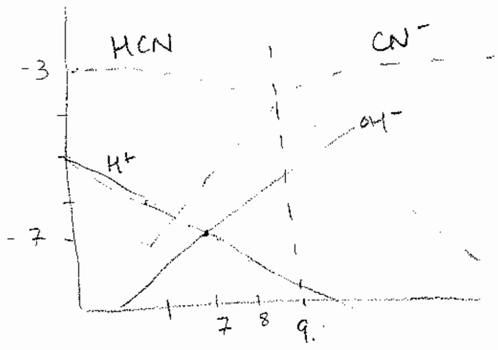
$H_2O \rightleftarrows OH^- + H^+ \quad K_w = 10^{-13.79}$
$HCN \rightleftarrows H^+ + CN^- \quad K_{HCN} = 10^{-9.03}$

$Na^+, Cl^-, OH^-, H^+, H_2O, CN^-, HCN$ ← expect pH<9, choose HCN as cmpt.

7 unknowns − 2 eqns = 5 cmpts

	H_2O	H^+	HCN	Na^+	Cl^-
H_2O	1				
H^+		1			
OH^-	1	-1			
HCN			1		
CN^-		-1	1		
Na^+				1	
Cl^-					1
$[H_2O]_T$	1				
$[HCN]_T$			1		
$[NaCl]_T$				1	1

sketch.



TOT H^+: $[H^+] - [OH^-] - [CN^-] = 0$ ⇒ 2 spps dominate.

Possibilities: i) $[H^+] = [OH^-] \gg [CN^-]$

@ pH = 7, Then $\frac{[CN^-]}{[HCN]} = \frac{10^{-9.03}}{10^{-7}} = 10^{-2.03}$

if $[HCN] \simeq [HCN]_T = 10^{-3}$ (at pH=7, this is ok assump,)

Then $[CN^-] = (10^{-2.03})(10^{-3}) = 10^{-5.03}$

$\gg 10^{-7} = [OH^-], [H^+]$

So this sol'n is not valid.

ii) $[H^+] = [CN^-] \gg [OH^-]$

From K_{HCN}; $[CN^-] = \frac{[HCN]10^{-9.03}}{[H^+]}$

Then $[H^+] = \frac{[HCN]\,10^{-9.03}}{[H^+]}$; ~~$]$~~ as $[HCN] \simeq [HCN]_T = 10^{-3}M$

$[H^+]^2 = (10^{-3})(10^{-9.03}) = 10^{-12.03}$

$[H^+] = 10^{-6.0}$ ⇒ $\boxed{pH = 6.0}$

4c) (cont)

Recipe 2: $[HCN]_T = 10^{-3} M$; $[NaOH]_T = 10^{-3} M$; $[NaCl]_T = 10^{-1} M$

expect pH to go up, added strong base, so CN^- might dominate and I will choose it as a component.

	H_2O	H^+	CN^-	Na^+	Cl^-
H_2O	1				
H^+		1			
OH^-	1	-1			
HCN		1	1		
CN^-			1		
Na^+				1	
Cl^-					1
$[H_2O]_T$	1				
$[HCN]_T$		1	1		
$[NaOH]_T$	1	-1		1	
$[NaCl]_T$				1	1

TOT HCN: $[HCN] + [CN^-] = [HCN]_T$

TOT H: $[H^+] - [OH^-] + [HCN] = [HCN]_T - [NaOH]_T = 10^{-3} - 10^{-3} = 0.$

Possible solutions

(i) $[H^+] = [OH^-] >> [HCN]$

@ pH = 7, $[HCN] \simeq [HCN]_T = 10^{-3} M$

$\Rightarrow$ not possible.

(ii) $[OH^-] = [HCN] >> [H^+]$

From TOT HCN: $[HCN]_T = [HCN] + [CN^-]$

Use K_{HCN} to replace $[CN^-]$: $[HCN]_T = [HCN] + \frac{[HCN]K_{HCN}}{[H^+]}$

$$[HCN]_T = [HCN]\left(1 + \frac{K_{HCN}}{[H^+]}\right)$$

$$[HCN] = [HCN]_T \Big/ \left(1 + \frac{K_{HCN}}{[H^+]}\right)$$; plug this into (ii)

$$[OH^-] = [HCN]_T \Big/ \left(1 + K_{HCN}/[H^+]\right)$$

Use K_w to replace $[OH^-]$:

$$\frac{K_w}{[H^+]} = [HCN]_T \Big/ \left(1 + \frac{K_{HCN}}{[H^+]}\right)$$

$$[HCN]_T = \frac{K_w}{[H^+]} + \frac{K_{HCN} K_w}{[H^+]^2}$$

$$[HCN]_T [H^+]^2 - K_w [H^+] - K_{HCN} K_w = 0$$

$$10^{-3} [H^+]^2 - 10^{-13.79} [H^+] - (10^{-9.03})(10^{-13.79}) = 0$$

$$[H^+] = 1.3\underline{1} \times 10^{-10}$$

$$\boxed{pH = 9.88}$$

Problem #5. *Solution by Prof. B. Voelker*

The first law says that the total energy of the universe is conserved, while the second law says that all usable forms of energy (for example, energy stored in chemical reactions, which have the capacity to do work) eventually become useless (for example, chemical reactions proceed and generate heat instead of doing work).

The second law implies that if no energy were able to enter or leave earth, life would not be possible. Chemical reactions should spontaneously proceed to their equilibrium state. For example, organic carbon plus oxygen would become carbon dioxide and water, and there would be no going back. So the energy entering earth in the form of sunlight makes life possible. Some of this light is absorbed pretty efficiently by molecules in plants to make an energetically unfavorable reaction proceed (photosynthesis: using carbon dioxide and water to make oxygen and organic carbon). The fact that sunlight heats some parts of the planet more than others also gives us other processes doing work on the planet: global oceanic and atmospheric currents, for example. So all of the biogeochemical cycles on the surface of the earth are driven by the energy from the sun.

The first and second laws together imply that all this energy entering the planet from the sun should eventually be dissipated as heat. If no energy were leaving the planet, it should keep getting hotter here. In fact, energy is leaving the planet at pretty much the same rate at which it is entering it, not as heat, but as *blackbody radiation*, light that is emitted according to a body's temperature. (The energy can't leave the earth very easily as heat, because heat conduction from the earth to outer space means that earth is getting molecules in outer space moving faster, and there are very few molecules in outer space). By the way, the light is radiated from the earth's atmosphere. The light radiated from the surface of the earth is absorbed by the *green house gases* in the atmosphere. So even though the amount of energy the planet receives from the sun determines what blackbody temperature the earth has to have, the earth's surface will be warmer if we increase the amount of greenhouse gases (global warming).

Everything else that is going on with energy on the planet, e.g. evaporation and condensation of water in the hydrological cycle, photosynthesis and respiration, etc. is part of a closed loop: energy is shuffled from place to place, and turned from more useful to less useful forms, but it is not gained or lost.

The previous three paragraphs neglect that there is also a significant amount of stored energy on this planet: the heat at the earth's core. This heat drives geological processes, and makes biogeochemical cycles possible on geological time scales of many millions of years. Once this energy is lost to outer space, life on earth will also no longer be possible (unless humans can build sunlight-powered machines to replace geological processes).