

**Answers to Problem Set - Pre-Course Preparation
Geochemistry for Ground-Water Systems**

$$1. \quad \text{formality } (f) = \frac{ppm}{1000 gfw} = \frac{400}{1000 \times 40.08} = 0.00998 \frac{mol}{kg \text{ soln}}$$

$$\text{molarity } (M) = \rho f = 1.023 \frac{kg \text{ soln}}{L} \times 0.00998 \frac{mol}{kg \text{ soln}} = 0.01021 \frac{mol}{L}$$

$$\text{molality } (m) = \frac{M}{\rho(1-S)} = \frac{f}{(1-S)}$$

$$S = 10^{-6} \times \sum_i ppm_i = 35,000 \times 10^{-6} = 0.035$$

$$m = \frac{0.00998}{1-0.035} = 0.01034 \frac{mol}{kg \text{ water}}$$

$$mg/L = M \times 1000 \times gfw = 0.01021 \times 1000 \times 40.08 = 409.2 \frac{mg \text{ Ca}}{L}$$

NOTE: if $\rho \approx 1.0$ (dilute solutions), then $f \approx m \approx M$ and $ppm \approx \frac{mg}{L}$.

$$2. \quad \frac{mg \text{ CaCO}_3}{L} \times \frac{1}{100.09 \frac{mg \text{ CaCO}_3}{mmol \text{ CaCO}_3}} \times 2 \frac{meq}{mmol \text{ CaCO}_3} = \frac{meq}{L}$$

$$100 \frac{mg \text{ CaCO}_3}{L} \times \frac{1}{100} \times 2 = 2.0 \frac{meq}{L}$$

$$\frac{mg \text{ HCO}_3^-}{L} = \frac{mg \text{ CaCO}_3}{L} \times \frac{2 \frac{meq}{mmol \text{ CaCO}_3}}{100.09 \frac{mg \text{ CaCO}_3}{mmol \text{ CaCO}_3}} \times 61.02 \frac{mg \text{ HCO}_3^-}{meq}$$

$$\frac{mg \text{ HCO}_3^-}{L} = \frac{mg \text{ CaCO}_3}{L} \times 1.2193$$

$$100 \frac{\text{mg } \text{CaCO}_3}{\text{L}} \times 1.2193 = 121.9 \frac{\text{mg } \text{HCO}_3^-}{\text{L}}$$

PHREEQC can be used to convert concentration units using either a gram formula weight (use “GFW” in the concentration definition) or a chemical formula (use “AS” in the concentration definition), from which it calculates a gram formula weight. This example uses the latter. The key is that, for alkalinity, a gram equivalent weight is needed and the equivalent weight for CaCO_3 is one-half of the gram formula weight (2 equivalents per mole of CaCO_3).

```
#
# Problem 2
#
TITLE Problem 2
SOLUTION 1
    -units mg/L
    Alkalinity 100 as Ca0.5(CO3)0.5
END
```

$$3. \quad C(0) = C(IV) + 4e^-$$

$$C(0) + 4e^- = C(-IV)$$

$$2C(0) = C(-IV) + C(IV), \text{ or}$$

$$2\text{CH}_2\text{O} = \text{CO}_2 + \text{CH}_4, \text{ electrons, charge, and oxygen balance.}$$

$$4. \quad C(0) = C(IV) + 4e^-$$

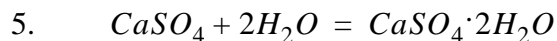
$$S(VI) + 6e^- = S(0)$$

$$3C(0) + 2S(VI) = 3C(IV) + 2S(0), \text{ or}$$

$$3\text{CH}_2\text{O} + 2\text{SO}_4^{-2} = 3\text{HCO}_3^- + 2\text{S}_{(s)}, \text{ electrons balance.}$$

$$3\text{CH}_2\text{O} + 2\text{SO}_4^{-2} = 3\text{HCO}_3^- + 2\text{S}_{(s)} + \text{OH}^-, \text{ charge balances}$$

$$3\text{CH}_2\text{O} + 2\text{SO}_4^{-2} = 3\text{HCO}_3^- + 2\text{S}_{(s)} + \text{OH}^- + \text{H}_2\text{O}, \text{ oxygen balances}$$



$$\Delta G_r^o = \Delta G_{f, gyp}^o - \Delta G_{f, anhyd}^o - 2\Delta G_{f, water}^o$$

$$\Delta G_r^o = -1797.2 - (-1321.7) - 2(-237.18)$$

$$\Delta G_r^o = -1.14 \frac{kJ}{mol}$$

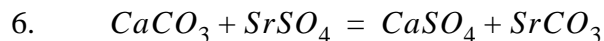
Therefore, the reaction will go as written. Gypsum is the stable phase relative to anhydrite and water at 25°C, 1 atmosphere total pressure (and all substances in their standard states, which is the case here.) If salts are present, water is not in its standard state and its activity is not unity. If equilibrium for the reaction is obtained then mass-action equation would be

$$K = 10^{\frac{-(-1.14)}{5.707}} = 1.584 = \frac{1}{a_{H_2O}^2}, \text{ which implies that } a_{H_2O} = 0.8. \text{ Thus, anhydrite would be}$$

stable in brines where the $a_{H_2O} \leq 0.8$.

With PHREEQC, pure water is defined as the initial solution (default pH 7, pe 4, temperature 25) and a phase assemblage with gypsum and anhydrite is defined. By default, equilibrium with each phase and an initial mass of 10 moles of each is defined. Implicitly the definition of a solution and a phase assemblage in the same simulation (everything before an END statement) are brought together and equilibrated. The output indicates that all the anhydrite dissolves and gypsum is formed.

```
#
# Problem 5
#
TITLE Problem 5
SOLUTION 1
EQUILIBRIUM_PHASES 1
    Gypsum
    Anhydrite
END
```

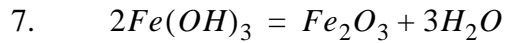


$$\Delta G_r^o = \Delta G_{f, anhydrite}^o + \Delta G_{f, strontianite}^o - \Delta G_{f, calcite}^o - \Delta G_{f, celestite}^o$$

$$\Delta G_r^o = -1321.7 + (-1137.6) - (-1128.8) - (-1341.0)$$

$$\Delta G_r^o = 10.5 \frac{kJ}{mol}$$

Therefore, calcite and celestite are the stable assemblage.



$$\Delta G_r^o = \Delta G_{f, Fe_2O_3}^o + 3\Delta G_{f, water}^o - 2\Delta G_{f, Fe(OH)_3}^o$$

$$\Delta G_r^o = -742.7 + 3(-237.18) - 2(-699)$$

$$\Delta G_r^o = -56.24$$

Hematite is stable relative to $Fe(OH)_3$. Similar calculation shows hematite stable relative to goethite.

I ran this problem with PHREEQC by equilibrating pure water with amorphous iron hydroxide and then looking at saturation indices. You find that goethite and hematite are very over saturated, which indicates they are more stable than the amorphous form.

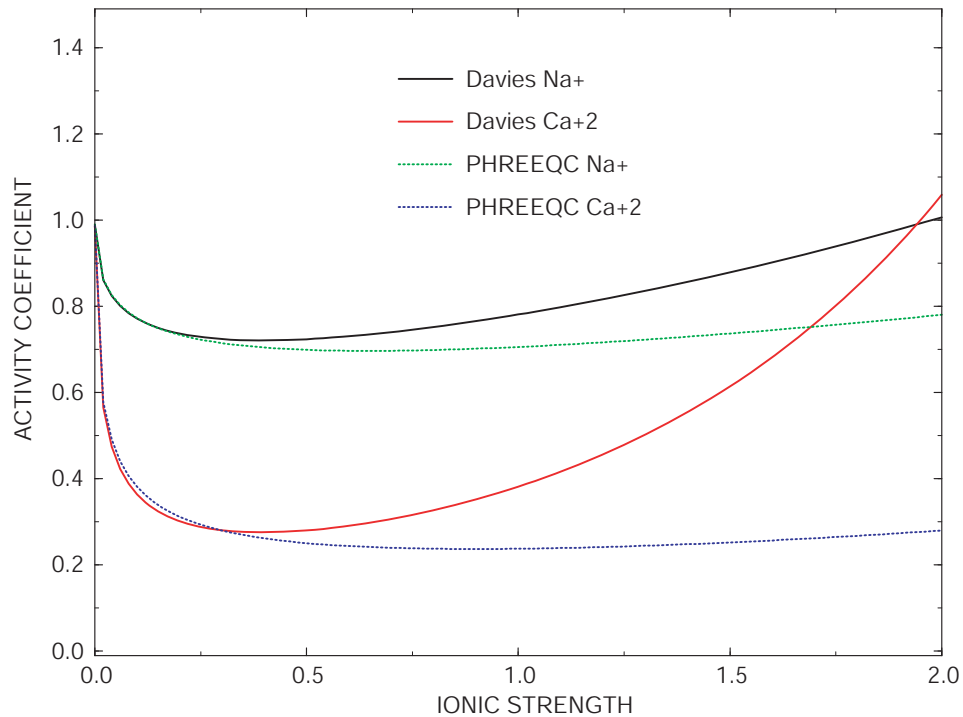
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#
# Problem 7
#
TITLE Problem 7
SOLUTION 1
EQUILIBRIUM_PHASES 1
    Fe (OH) 3 (a)
END
```

8. $0.01 \text{ m NaCl}, I = \frac{1}{2}(m_{Na^+} + m_{Cl^-}) = 0.01$

$$0.01 \text{ m CaCl}_2, I = \frac{1}{2}(4m_{Ca^{2+}} + m_{Cl^-}) = 0.5(0.04 + 0.02) = 0.03$$

$$0.01 \text{ m CaSO}_4, I = \frac{1}{2}(4m_{\text{Ca}^{2+}} + 4m_{\text{SO}_4^{2-}}) = 0.04$$

ACTIVITY COEFFICIENTS FOR Ca²⁺ AND Na⁺

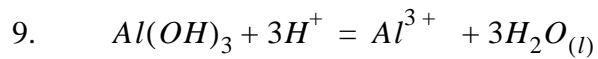


With PHREEQC, three solutions are defined, with NaCl, CaCl₂, and CaSO₄, each 0.01 molal. The ionic strength is printed in the output. Ionic strength for NaCl and CaCl₂ are identical to the hand calculation. Ionic strength for the CaSO₄ solution, 0.028 is much less than 0.04 because of ion pairing. The formation of the aqueous complex CaSO_{4(aq)} results in fewer charged species in solution and hence a smaller ionic strength. I used REACTION keyword to add NaCl to a dilute CaCl₂ solution. The addition of NaCl provided the desired ionic strength because it is univalent and has virtually no aqueous complexation. The USE keyword selected solution 4 to be the initial solution of the reaction, otherwise the first solution (SOLUTION 1) would have been used.

```

#
# Problem 8
#
TITLE Problem 8
SOLUTION 1
    -units mol/kgw
    Na .01
    Cl .01
SOLUTION 2
    -units mol/kgw
    Ca .01
    Cl .02
SOLUTION 3
    -units mol/kgw
    Ca .01
    S(6) .01
SOLUTION 4
    -units mmol/kgw
    Ca .0001
    Cl .0002
REACTION
    NaCl 1
    .01 .1 .5 1. 2. moles
USE solution 4
END

```



$$\Delta G_r^o = \Delta G_{f, Al^+}^o + 3\Delta G_{f, H_2O}^o - \Delta G_{f, gibbs}^o - 3\Delta G_{f, H^+}^o$$

$$\Delta G_r^o = -489.4 + 3(-237.18) - (-1155) - 3(0.0)$$

$$\Delta G_r^o = -45.94$$

$$\log k = \frac{-\Delta G_r^o}{2.303RT} = -\frac{1}{2.3026 \times 0.008314 \times 298.15} \Delta G_r^o = -\frac{1}{5.708} \Delta G_r^o = -0.1752 \Delta G_r^o$$

$$\log k = -0.1752(-45.94) = 8.05$$

$$\log k = 8.05 = \log a_{Al^{3+}} + 3\log a_{H_2O} - 3\log a_{H^+} - \log a_{gibbs}$$

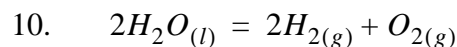
$a_{H_2O} \approx 1.0$ and $a_{gibbs} \equiv 1.0$, therefore,

$$\log k = 8.05 = \log a_{Al^{3+}} + 3pH, \text{ and for } a_{Al^{3+}} \approx 10^{-3},$$

$$pH = \frac{8.05 - (-3)}{3} = 3.68$$

In PHREEQC it is possible to adjust pH or the concentration of an element to achieve a specified saturation index (0.0 by default). Thus, Al is defined to be 1.0 mmolal and pH is adjusted to equilibrium with gibbsite. The calculated pH is 11.5, which is wildly different from 3.68 that was calculated by hand. The difference is in the faulty assumption in the hand calculation that Al^{+3} is the dominant aluminum species. In fact $Al(OH)_4^-$ is the dominant species and Al^{+3} is 24 orders of magnitude less abundant!

```
#
# Problem 9
#
TITLE Problem 9
SOLUTION 1
    pH 7.0 gibbsite
    Al 1.0 mmol/kgw
END
```



$$\Delta G_r^o = 2\Delta G_{f, H_{2(g)}}^o + \Delta G_{f, O_{2(g)}}^o - 2\Delta G_{f, H_2O}^o$$

$$\Delta G_r^o = 2(0.0) + 0.0 - 2(-237.18)$$

$$\Delta G_r^o = 474.36$$

$$\log k = -\frac{474.36}{5.708} = -83.10$$

$$\log k = -83.10 = 2\log P_{H_{2(g)}} + \log P_{O_{2(g)}}, \text{ assuming } a_{H_2O} = 1.0.$$

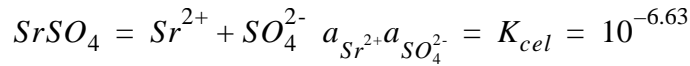
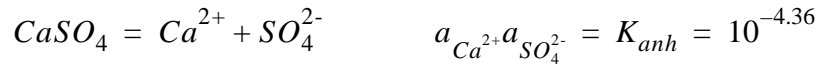
$$\text{If } P_{O_{2(g)}} = 1.0, \log P_{O_{2(g)}} = 0.0 \text{ and then } \log P_{H_{2(g)}} = -\frac{83.1}{2} = -41.6.$$

If $P_{H_{2(g)}} = 1.0$, $\log P_{H_{2(g)}} = 0.0$ and then $\log P_{O_{2(g)}} = -83.1$.

The pe can also be adjusted to obtain equilibrium with a phase. In this case, the pe of pure water with pH 7 was adjusted to obtain a partial pressure of 1.0 atmosphere of oxygen (log partial pressure 0.0). The partial pressure of hydrogen can be read from the list of saturation indices that follows the distribution of species. Same calculation is made for hydrogen partial pressure of 1.0 atm.

```
#
# Problem 10
#
TITLE Problem 10
SOLUTION 1
    pH 7.0
    pe 1    O2 (g) 0.0
SOLUTION 2
    pH 7.0
    pe 1    H2 (g) 0.0
END
```

11.



$$a_{Sr^{2+}} a_{CO_3^{2-}} = \frac{a_{Sr^{2+}} a_{SO_4^{2-}} a_{Ca^{2+}} a_{CO_3^{2-}}}{a_{Ca^{2+}} a_{SO_4^{2-}}} = \frac{K_{cel} K_{cal}}{K_{anh}} = 10^{-6.63 + (-8.48) - (-4.36)} = 10^{-10.75}$$

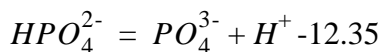
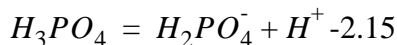
$$SI_{stront} = \log \frac{a_{Sr^{2+}} a_{CO_3^{2-}}}{K_{stront}} = -10.75 - (-9.271) = -1.48$$

The water is undersaturated with respect to strontianite. As long as the water remains saturated with calcite, celestite, and anhydrite, strontianite will tend to dissolve until its mass is completely dissolved. The reaction will form calcite and celestite while dissolving anhydrite. The reaction would change if the anhydrite mass were completely dissolved; then strontianite would dissolve to equilibrium and the resulting water would be undersaturated with anhydrite.

Here, a solution is equilibrated with calcite, anhydrite, and celestite. The stability of strontianite in this solution can be determined from the saturation index. The saturation index for strontianite is -1.48, which indicates that strontianite is unstable relative to the other phases.

```
#
# Problem 11
#
TITLE Problem 11
SOLUTION 1
EQUILIBRIUM_PHASES 1
    Calcite
    Anhydrite
    Celestite
END
```

12. Reaction log K



$$\frac{a_{H_2PO_4^-} a_{H^+}}{a_{H_3PO_4}} = 10^{-2.15}, \text{ if } a_{H_2PO_4^-} = a_{H_3PO_4}, \text{ then pH} = 2.15.$$

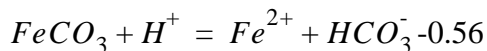
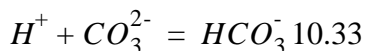
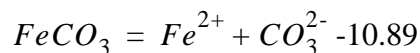
Likewise, $a_{H_2PO_4^-} = a_{HPO_4^{2-}}$ at pH = 7.21 and $a_{HPO_4^{2-}} = a_{PO_4^{3-}}$ at pH 12.35.

Molalities of the phosphate species change exponentially with pH. Thus at very low pH the dominant species is H_3PO_4 ; between 2.15 and 7.21, the dominant species is $H_2PO_4^-$; between 7.21 and 12.35, the dominant species is HPO_4^{2-} ; and above pH 12.35, the dominant species is PO_4^{3-} . For natural waters (pH 6-9), the dominant species are $H_2PO_4^-$ and HPO_4^{2-} .

With PHREEQC it is only necessary to fix the pH and look at the distribution of species for phosphorus. At pH 7 the predominant species is $H_2PO_4^-$, with slightly less HPO_4^{2-} .

```
#
# Problem 12
#
TITLE Problem 12
SOLUTION 1
    pH      7
    P       1 mmol/kgw
END
```

13. Reaction Log K

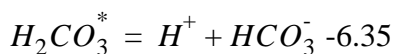


eq. a:

$$\log a_{Fe^{2+}} + \log a_{HCO_3^-} + pH = -0.56$$

eq. b:

$$C_t = m_{H_2CO_3} + m_{HCO_3^-} = 10^{-2.5}, \text{ ignoring complexes and carbonate ion.}$$



eq. c:

$$\frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3^*}} = 10^{-6.35}$$

From eq. c, pH = 6.0, and activity coefficients equal 1.0:

$$m_{H_2CO_3^*} = 10^{0.35} m_{HCO_3^-}.$$

Substituting in eq. b:

$$10^{-2.5} = m_{HCO_3^-} (10^{0.35} + 1)$$

$$m_{HCO_3^-} = \frac{10^{-2.5}}{(10^{0.35} + 1)} = 9.76 \times 10^{-4}$$

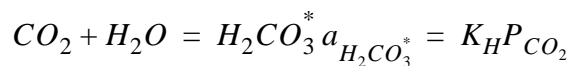
$$\log m_{HCO_3^-} = \log a_{HCO_3^-} = -3.01$$

Substituting into eq. a:

$$\log a_{Fe^{2+}} = -0.56 - (-3.01) - 6.0 = -3.55$$

In PHREEQC, the pH and C concentrations are set to the specified values and the concentration of iron is allowed to vary to obtain equilibrium with siderite. The total iron concentration is found to be 0.36 mmol/kgw, which includes some ion-pairing effects.

```
#
# Problem 13
#
TITLE Problem 13
SOLUTION 1
    pH      6
    -units  mmol/kgw
    C       3.2
    Fe      1      Siderite  0.0
END
```



$$H_2CO_3^* = H^+ + HCO_3^- \frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3^*}} = 10^{-6.35}$$

Charge balance:

$m_{HCO_3^-} \approx m_{H^+}$, ignoring carbonate ion. Assuming activity coefficients equal 1.0, then

$$a_{HCO_3^-} \approx a_{H^+}.$$

Substituting in the second mass action equation gives:

$$\frac{a_{H^+}^2}{a_{H_2CO_3^*}} = 10^{-6.35}$$

Substitution into the first mass action equation gives:

$$a_{H^+}^2 = 10^{-6.35} \times K_H \times P_{CO_2}$$

$\log P_{CO_2}$ is given to be -1.5 and $\log K_H$ calculated from Nordstrom et al analytical expression is -1.47 at 25°C (298.15°K).

Therefore,

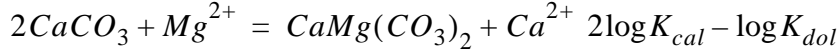
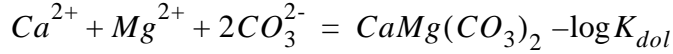
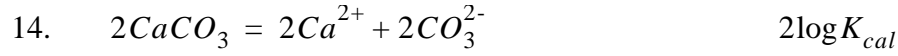
$$a_{H^+}^2 = 10^{-6.35 + (-1.47) + (-1.5)} = 10^{-9.32} = 4.79 \times 10^{-10}$$

and

$$a_{H^+} = 2.19 \times 10^{-5} \text{ and } pH = 4.66$$

All that is needed is the composition of water in equilibrium with a carbon dioxide log partial pressure of -1.5. Here, the concentration of carbon is adjusted to produce the specified partial pressure and the pH is adjusted to achieve charge balance. The resulting pH is 4.66.

```
#
# Problem 14
#
TITLE Problem 14
SOLUTION 1
    pH      7      charge
    temp    25
    C       3.2    CO2 (g) -1.5
END
```



Calcite: $\log K_{cal} = -171.9065 - 0.077993T + \frac{2839.319}{T} + 71.595\log T$, T is °K.

Dolomite: $\log K_{dol, T} = \log K_{dol, 298.15} - \frac{\Delta H_{r, 298.15}^o}{2.303 \times 0.001987} \left(\frac{298.15 - T}{298.15T} \right)$

Dolomite (ordered): $\log K_{dol_{orde}, 298.15} = -17.09$, $\Delta H_{r, 298.15}^o = -9.436 \frac{kcal}{mol}$

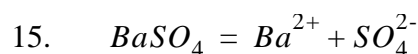
Dolomite (disordered): $\log K_{dol_{dis}, 298.15} = -16.54$, $\Delta H_{r, 298.15}^o = -11.09 \frac{kcal}{mol}$

Table 1: Ca/Mg ratio in solution for dolomite at varying temperature

T	$\log K_c$	$\log K_{d,o}$	$\log K_{d,d}$	a_{Ca}/a_{Mg} ratio	
				order	disorder
0	-8.38	-16.46	-15.80	0.49	0.11
10	-8.41	-16.72	-16.11	0.80	0.19
20	-8.45	-16.97	-16.40	1.16	0.31
25	-8.48	-17.09	-16.54	1.35	0.38
30	-8.51	-17.20	-16.67	1.53	0.45
40	-8.58	-17.42	-16.93	1.83	0.59
50	-8.66	-17.63	-17.17	1.99	0.70
60	-8.76	-17.82	-17.39	1.99	0.75
70	-8.87	-18.00	-17.61	1.83	0.74
80	-8.99	-18.17	-17.81	1.55	0.67

In PHREEQC, it is possible to use the EQUILIBRIUM_PHASES and REACTION_TEMPERATURE keyword data blocks to calculate the composition of the aqueous solution in equilibrium with dolomite at different temperatures. Here, the initial solution is pure water and reaction of pure water with dolomite at three temperatures, 10, 25, and 40 C are defined.

```
#
# Problem 15
#
TITLE Problem 15
SOLUTION 1
EQUILIBRIUM_PHASES
    Dolomite
REACTION_TEMPERATURE
    10    25    40
END
```



From Nordstrom and others (1990), $\log K_{bar, 298.15} = -9.97$, and $\Delta H_r^o = 6.35 \frac{kcal}{mol}$.

Using the van't Hoff equation,

$$\log K_{barite, 348.15} = -9.97 - \frac{6.35}{2.303 \times 0.001987} \left(\frac{298.15 - 348.15}{298.15 \times 348.15} \right) = -9.30$$

In pure water, no complexing, activity coefficients equal 1.0, barite solubility equals $\sqrt{K_{barite}}$, because for these assumptions $K_{barite} = a_{Ba^{2+}} a_{SO_4^{2-}} = m_{Ba^{2+}} m_{SO_4^{2-}}$ and $m_{Ba^{2+}} = m_{SO_4^{2-}}$. The ratio of the solubilities in pure water at the two temperatures is

$$\frac{\sqrt{K_{348.15}}}{\sqrt{K_{298.15}}} = \sqrt{\frac{10^{-9.30}}{10^{-9.97}}} = 2.16. \text{ Barite is twice as soluble at } 75^\circ\text{C} \text{ as at } 25^\circ\text{C. Barite should precipitate upon cooling.}$$

The heat exchanger will be clogged with barite after prolonged use. Note that ΔH_r^o is positive, indicating solubility will increase with increasing temperature. As written, the reaction is endothermic.

Again EQUILIBRIUM_PHASES and REACTION_TEMPERATURE are used to equilibrate pure water with barite at 75 and 25 degrees. At 75 degrees, the solubility is 0.018 mmol/kgw, which is greater than the solubility at 25 degrees, 0.011 mmol/kgw.

```
#
# Problem 16
#
TITLE Problem 16
SOLUTION 1
EQUILIBRIUM_PHASES
    Barite
REACTION_TEMPERATURE
    75    25
END
```

16.

pH	mV	
Buffer	6.86	-41.3
Buffer	4.00	-209.6
Unknown	(7.61)	2.9

$$E = E^o + slope \times \log a_H^+ = E^o - slope \times pH$$

$$slope = -\left(\frac{E_2 - E_1}{pH_2 - pH_1}\right) = -\left(\frac{-209.6 - (-41.3)}{4.00 - 6.86}\right) = -58.8$$

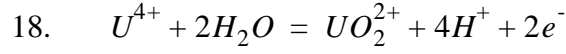
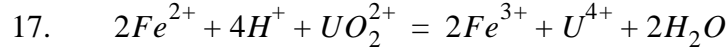
$$E^o = E_1 - slope \times pH_1 = -41.3 - 58.8 \times 6.86 = -444.7$$

Theoretical slope is

$$\frac{(-2.303)RT}{nF} = \frac{-2.303 \times 0.001987 \times 298.15}{1 \times 23.06} = -0.05916V = -59.16mV .$$

Percent Nernstian slope is $\frac{-58.8}{-59.16} \times 100 = 99.4\%$; the electrode is working well.

$$pH_{sample} = \frac{E_{sample} - E^o}{-slope} = \frac{2.9 - (-444.7)}{58.8} = 7.61$$



$$Eh = E^o + \frac{0.059}{2} \log \left(\frac{a_{UO_2^{2+}} a_{H^+}^4}{a_{U^{4+}} a_{H_2O}^2} \right)$$

Find the line on an Eh-pH diagram where $a_{UO_2^{2+}} = a_{U^{4+}}$, in which case

$$Eh = E^o - \frac{4 \times 0.059}{2} pH$$

$$\Delta G_r^o = \Delta G_{f, UO_2^{2+}}^o + 4\Delta G_{f, H^+}^o + 2\Delta G_{f, e^-}^o - \Delta G_{f, U^{4+}}^o - 2\Delta G_{f, H_2O}^o$$

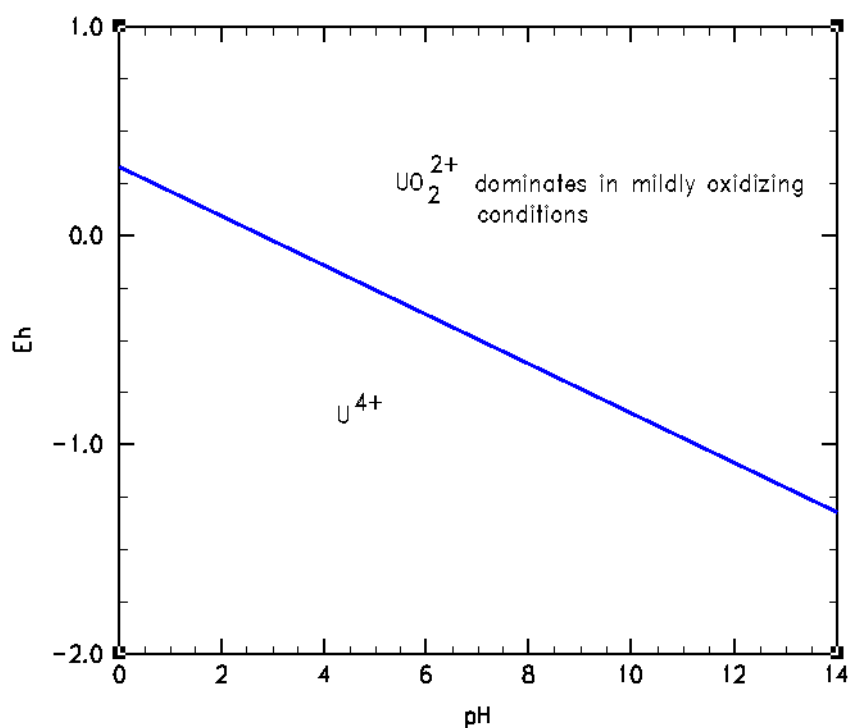
$$\Delta G_r^o = -989.1 + 4(0.0) + 2(0.0) - (-579.1) - 2(-237.18) = 64.36$$

$$\Delta G_r^o = nE^o F = 2E^o \times \left(23.06 \times 4.184 \frac{kJ}{kcal} \right) \text{ and } E^o = \frac{64.36}{2 \times 23.06 \times 4.184} = 0.33 V.$$

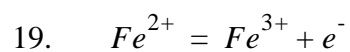
The equation for $a_{UO_2^{2+}} = a_{U^{4+}}$ is $Eh = 0.33 - 0.118pH$.

A log partial pressure of oxygen of -4.0 was chosen to represent mildly oxidizing. At pH 7 and this redox environment, all of the uranium is found to be in the U(VI) state from the distribution of species.

Stability of UO_2^{2+} vs U^{4+}



```
#
# Problem 19
#
TITLE Problem 19
SOLUTION 1
    pH      7
    pe      7      O2 (g) -4.0
    U       1 mmol/kgw
END
```



$$\Delta G_r^0 = \Delta G_{f, \text{Fe}^{3+}}^0 + \Delta G_{f, e^-}^0 - \Delta G_{f, \text{Fe}^{2+}}^0$$

$$\Delta G_r^0 = -4.6 + 0.0 - (-78.87) = 74.27$$

$$\Delta G_r^0 = nFE^0 \text{ or } E^0 = \frac{74.27}{1 \times 23.06 \times 4.184} = 0.77 \text{ V}$$

$$Eh = E^o + 0.059 \log \left(\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \right) = 0.77 + 0.059 \times (-4 - (-6)) = 0.89V$$

Alternatively,

$$\Delta G_r^0 = 74.27 \frac{kJ}{mol} \text{ and } \log K = -\frac{\Delta G_r^0}{5.708} = -13.01$$

$$\log K = -13.01 = \log \left(\frac{a_{Fe^{3+}} a_{e^-}}{a_{Fe^{2+}}} \right) = \log a_{Fe^{3+}} - pe - \log a_{Fe^{2+}}$$

$$pe = 13.01 + (-4) - (-6) = 15.01$$

$$pe = 16.9Eh \text{ or } Eh = 0.89V.$$

The initial solution is defined to have the specified amounts of the two valence states of iron. A data block in the output gives the corresponding pe and Eh for this redox couple.

```
#
# Problem 20
#
TITLE Problem 20
SOLUTION 1
    pH 2
    -units mmol/kgw
    Fe(3) .1
    Fe(2) .001
END
```

20.

Data Summary	
Rain	Spoils
Fe ²⁺	0 2.0
Ca ²⁺	0 1.0
SO ₄ ²⁻	0 4.0

$$\text{CO}_{2,\text{Total}} \quad 0 \quad 0.0$$

$$\text{Redox State} \quad 028.0 \quad (2\text{Fe}^{2+} + 6\text{SO}_4^{2-} = 2 \times 2 + 6 \times 4)$$

$$\Delta Fe = 2.0 = \Delta FeS_2$$

$$\Delta Ca = 1.0 = \Delta CaCO_3 + \Delta CaSO_4 \cdot 2H_2O$$

$$\Delta S = 4.0 = 2\Delta FeS_2 + \Delta CaSO_4 \cdot 2H_2O$$

$$\Delta C = 0.0 = \Delta CaCO_3 + \Delta CO_{2(g)}$$

$$\Delta RS = 28.0 = 0\Delta FeS_2 + 6\Delta CaSO_4 \cdot 2H_2O + 4\Delta CaCO_3 + 4\Delta CO_{2(g)} + 4\Delta O_{2(g)}$$

$$\Delta FeS_2 = 2.0 \frac{\text{mmol}}{L}$$

$$\Delta CaSO_4 \cdot 2H_2O = 4.0 - 2\Delta FeS_2 = 4 - 2(2) = 0.0 \frac{\text{mmol}}{L}$$

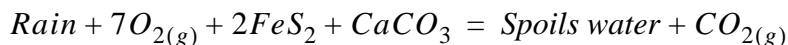
$$\Delta CaCO_3 = 1.0 - \Delta CaSO_4 \cdot 2H_2O = 1.0 - 0.0 = 1.0 \frac{\text{mmol}}{L}$$

$$\Delta CO_{2(g)} = 0.0 - \Delta CaCO_3 = 0.0 - 1.0 = -1.0 \frac{\text{mmol}}{L}$$

$$\Delta O_{2(g)} = \frac{28.0 - (0\Delta FeS_2 + 6\Delta CaSO_4 \cdot 2H_2O + 4\Delta CaCO_3 + 4\Delta CO_{2(g)})}{4.0}$$

$$\Delta O_{2(g)} = \frac{28.0 - (0 + 6(0) + 4(1) + 4(-1.0))}{4.0} = \frac{28.0}{4.0} = 7.0 \frac{\text{mmol}}{L}$$

The net reaction is



The system consumes oxygen gas and produces carbon dioxide gas. The oxygen presumably enters from the atmosphere because far more oxygen is consumed than is soluble in water (only about 0.25 mmol/L). Because the total carbon in the spoils is zero, carbon dioxide must be leaving the solution. Therefore the system must be open to both oxygen and carbon dioxide.

Inverse modeling with PHREEQC requires a SOLUTION keyword data block for each solution that is to be used and the INVERSE_MODELING data block. SOLUTION 1 defines pure water and SOLUTION 2 defines the composition of the water given in the problem definition. In the INVERSE_MODELING keyword data block, “-solutions” indicates that solution 1 evolves to the composition of solution 2. The “-phases” identifier indicates that calcite, gypsum, pyrite, oxygen, and carbon dioxide are potential reactants. Results are identical to the hand calculation.

```
#
# Problem 21
#
TITLE Problem 21
SOLUTION 1
SOLUTION 2
    -units mmol/kgw
    pH      7      charge
    Fe(2)    2.0
    Ca       1.
    S(6)     4
Inverse_modeling
    -solution 1 2
    -phases
        Calcite
        Gypsum
        Pyrite
        O2(g)
        CO2(g)
END
```

$$21. \quad \delta^2 H = \left[\frac{(\ ^2H/\ ^1H)_{sample}}{(\ ^2H/\ ^1H)_{VSMOW}} - 1 \right] 1000$$

$$\delta^2 H = \left[\frac{\left(\frac{0.0081}{100 - 0.0081} \right)}{\left(\frac{0.015574}{99.984426} \right)} - 1 \right] 1000 = -479.94 \text{ o/oo}$$