William Murphy

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Contents

Page

Near-Field Processes and Variations
Scientific notebook in control of
William M. Murphy

William M Murphy is WMM

This book evolved to cover the
Evolution of the Near-Field Environment
KTI work.

WMM

WMM 3/15/96

Attached to the facing page is output from a mathematica verification of Eq. (10-10) in the semiannual report CNWRA 95-015. There are two errors in the equation as published.

The correct equation is

$$\ln K - \ln K^{\circ} =$$

$$\frac{A}{R} \ln \frac{T}{T^{\circ}}$$

$$+ \left(\frac{-A T^{\circ}}{R} + \frac{B (T^{\circ})^2}{2R} + \frac{\Delta H^{\circ}_{(T^{\circ})}}{R} \right) \left(\frac{1}{T^{\circ}} - \frac{1}{T} \right)$$

$$- \frac{B (T - T^{\circ})}{2R}$$

$$- \frac{C}{R} \left[\frac{T-D}{DT} \ln \left(\frac{T-D}{T^{\circ}-D} \right) + \frac{\ln T^{\circ}}{D} - \frac{\ln T}{D} \right]$$

Corrections are marked in blue.

CMM 3/15/96

First Cut

```
(D dHtO - A D TO + B D TO^2 - C TO Log[TO] - A D TO Log[TO] +
     C TO Log[-D + TO])/(D R TO) +
 (-2 D dHtO + 2 A D TO - B D TO^2 - B D T2^2 - 2 C D Log[-D + TO] +
   2 C T2 Log[T2] + 2 A D T2 Log[T2] + 2 C D Log[-D + T2] -
   2 C T2 Log[-D + T2])/(2 D R T2)
```

Simplify

```
(
+ 2 D dHtO
- 2 A D TO
+ 2 B D TO^2
- 2 C TO Log[TO]
- 2 A D TO Log[TO]
+ 2 C TO Log[-D + TO]
)/(2 D R TO)
+ (
- 2 D dHtO
+ 2 A D TO
- B D TO^2
- B D T2^2
- 2 C D Log[-D + TO]
+ 2 C T2 Log[T2]
+ 2 A D T2 Log[T2]
+ 2 C D Log[-D + T2]
- 2 C T2 Log[-D + T2]
)/(2 D R T2)
```

Simplify

```
+ Log[T/TO] (C/D + A)/R
+ Log[(T-D)/(TO-D)] (C/R)(D-T)/(T D)
+ (1/R)(dHtO - A TO) (1/TO - 1/T)
+ (B/R) (TO - (TO^2 + T^2)/2T)
```

Note:

```
(B/R) (TO - (TO^2 + T^2)/2T)
= (B/2R) ((TO^2)(1/TO - 1/T) + (TO - T))
```

CMM 3/15/96

Also note that there are also errors in the discussion concerning the publication by Nguyen et al. (1992) on page 10-21 of CNWRA 95-015.

These are corrected on the facing page.

MM 3/15/96

Above reaction (10-1)

Excess Si detected in the reactant material and deficit silica in solution were assumed to be a consequence of the presence and precipitation of amorphous silica, respectively.

Below equation (10-2)

$\Delta G_f^\circ = -3658 \pm 4.8$ kJ.mole^{-1}

These same errors occur in the report "Review of Empirical Thermodynamic Data for Uranyl Silicate Minerals and Experimental Plan", CNWRA 95-014, on page 2-4. In addition, in Table 2-2 of this report the Final Aqueous Solution entry for soddyite should be 1.00:0.27:0, and the second and third sentences of the bottom paragraph on page 2-3 should read:

In the soddyite experiment, the Si/U release ratio was considerably lower than either the nominal stoichiometric ratio or the ratio in the analyzed solid. Deficit aqueous silica could be a consequence of precipitation of amorphous silica following dissolution of soddyite.

I apologize to Nguyen et al.

MM 3/15/96

Blank page

CWM 4/5/96

Uranophane analytical data

Uran*syn x 3

Total mass of U + Si + Ca oxides dissolved
Data supplied by Prikryl

587.7 mg U/kg H_2O x 0.1 liter H_2O (kg/liter)

$$\times \frac{286.027 \text{ g } UO_3}{238.029 \text{ g U}} \frac{\text{g U}}{1000 \text{ mg U}} = \frac{0.06667 \text{ g } UO_3}{0.07062}$$

CWM 4/5/96

$$\frac{75.6 \text{ mg Si}}{\text{kg } H_2O} \times 0.1 \text{ liter} \times \frac{\text{kg}}{\text{liter}} \times \frac{60.0843 \text{ g } SiO_2}{28.0855 \text{ g Si}} \frac{\text{g}}{1000 \text{ mg}}$$

$= 0.01617$ g SiO_2

$$\frac{50.8 \text{ mg Ca}}{\text{kg } H_2O} \; 0.1 \text{ lit} \cdot \frac{\text{kg}}{\text{lit}} \cdot \frac{56.0794 \text{ g CaO}}{40.08 \text{ g C}} \frac{\text{g}}{1000 \text{ mg}}$$

$= 0.00711$ g CaO

$UO_3 + SiO_2 + CaO = 0.0939$ g

12.65% H_2O

$$\frac{0.0939 \text{ g}}{1 - 0.1265 \text{ g}} = 0.1075 \text{ g total mass}$$

(starting mass: 0.1034) 4% high

CWM 4/5/96

URAN*SYN*9

$513.3 \frac{mg}{kg}\ 0.1\ lit\ \frac{kg}{lit}\ \frac{286.027\ g\ UO_2}{238.029\ g\ U}\ \frac{g}{1000\ mg}$

$= 0.06168\ g\ UO_3$

$74.1 \frac{mg}{kg}\ 0.1\ lit\ \frac{kg}{lit}\ \frac{60.0843\ g\ SiO_2}{28.0855\ g\ Si}\ \frac{g}{1000\ mg}$

$= 0.01585\ g\ SiO_2$

$48.4 \frac{mg}{kg}\ 0.1\ lit\ \frac{kg}{lit}\ \frac{56.0794\ g\ CaO}{40.08\ g\ C}\ \frac{g}{1000\ mg}$

$= 0.00677\ g\ CaO$

Total mass $UO_3 + SiO_2 + CaO = 0.0843\ g$

12.78% H_2O

Total mass $= \frac{0.0843}{1-.1278} = 0.09665$

0.101 g starting material → 4% low

LWM 4/5/96

URAN*SYN*10

$(532.2)(0.1)\ \frac{286.027}{238.029}\ \frac{1}{1000} = 0.06395\ g\ UO_3$

$74.2(0.1)\ \frac{56.079}{28.0855}\ \frac{60.0843}{1000} = 0.01587\ g\ SiO_2$ cm 4/5/96

$49.6(0.1)\ \frac{56.0794}{40.08}\ \frac{1}{1000} = 0.00694\ g\ CaO$

oxide mass = 0.08676 g

H_2O: 13.14%

total mass $= \frac{0.08676}{1-.1314} = 0.09988\ g$

Starting mass: 0.1017 → 2% low

LWM 4/5/96

Molar quantities

URAN × SYN × 3

~~587.7~~ cwy 4/6/96

$\frac{0.07062\ g\ UO_3}{286.027\ g/mole} = 2.469 \times 10^{-4}$ mole

$\frac{0.01617\ g\ SiO_2}{60.0843\ g/mole} = 2.691 \times 10^{-4}$ mole

$\frac{0.00711\ g\ CaO}{56.0794\ g/mole} = 1.268 \times 10^{-4}$ mole

Nominal stoichiometry $Ca(UO_2)_2(SiO_3(OH))_2 \cdot 5H_2O$

Analytical, normalized to Ca

$Ca : U : Si : H_2O = 1 : 1.95 : 2.12 : 5.73$

Molar $H_2O = 0.1265 \times \frac{0.1034\ g}{18.0152\ g/mole} = 7.261 \times 10^{-4}$ mole

cwy 4/5/96

URAN × SYN × 9

$\frac{0.06168\ g}{286.027\ g/mole} = 2.156 \times 10^{-4}$ mole UO_3

$\frac{0.01585\ g}{60.0843\ g/mole} = 2.638 \times 10^{-4}$ mole SiO_2

$\frac{0.00677\ g}{56.0794\ g/mole} = 1.207 \times 10^{-4}$ mole CaO

$0.1278 \times \frac{0.101\ g}{18.0152\ g/mole} = 7.165 \times 10^{-4}$ mole H_2O

Normalized to Ca

$Ca : U : Si : H_2O = 1 : 1.79 : 2.19 : 5.94$

cwy 4/5/96

URAN*SYN*10

$\frac{0.06395\ g}{286.027\ g/mole} = 2.236 \times 10^{-4}$ mole UO_3

$\frac{0.01587\ g}{60.0843\ g/mole} = 2.641 \times 10^{-4}$ mole SiO_2

$\frac{0.00694\ g}{56.0794} = 1.238 \times 10^{-4}$ mole CaO

$0.1314 \times \frac{.1017\ g}{18.0152\ g/mole} = 7.418 \times 10^{-4}$ mole H_2O

$Ca : U : Si : H_2O = 1 : 1.81 : 2.13 : 5.99$

CWM 4/5/96

Mass fractions (using starting total mass

URAN*SYN*3

CaO	0.0688 %
SiO_2	0.1564 %
UO_3	68.298 %
H_2O	12.65 %
Total	103.5

ECP 8/11/2000

Concentration of Np in 1,000,000 year scenario of TSPA-'95

$$\left(\frac{\text{Dose}}{\text{Dose conversion factor}}\right)\frac{1}{\text{molecular weight}}$$

$$= 0.1\ \frac{\text{rem}}{\text{year}} \cdot \frac{\text{mole}}{237\ \text{g}} \cdot \frac{\text{m}^3}{1000\ \text{lit}} \cdot \frac{1}{2.25\times10^{3}\ \frac{\text{rem}}{\text{yr}}\ \frac{\text{m}^3}{\text{g}}}$$

$$= 1.87\times10^{-10}\ \frac{\text{moles}}{\text{lit}}$$

CWM 5/1/96

Q the possibility of acidification of groundwater by oxidation of siderite

Acid-intermediate pH, oxidizing

$$2FeCO_3 + 2H_2O + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2O_3 + 2HCO_3^- + 2H^+$$

$$2FeCO_3 + 3H_2O + \tfrac{1}{2}O_2 \rightleftharpoons 2FeO(OH) + 2HCO_3^- + 2H^+$$

$$2FeCO_3 + 2H_2O + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2O_3 + 2H_2CO_3$$

Alkaline pH, oxygenated:

$$2FeCO_3 + 2H_2O + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2O_3 + 2CO_3^{2-} + 4H^+$$

CWM 5/20/96

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ALL 5/22/96

Calculation of log K values for analcime at 0, 60, 100, 150, 200, 250, 300 °C at constant pressure of 1.0132 bar.

[Ana L. Unruh is ALL]

From Data0.com.R2

Analcime

$\Delta H_f^\circ = -3296.900\ ^{KJ}/_{mol} = -3.296900 \times 10^6\ ^{J}/_{mol}$

$C_p = 0.23763030 \times 10^3 - 0.47428400\,T + 0.16656600 \times 10^{-2} T^2 - 0.12360200 \times 10^{-5} T^3$ J

Source: Johnson, G.K et al 1982 Amer. Mineral., 67, 736-748

at 25 °C $\log K = 7.50$

conversion $\ln K = 17.2693882$

Source: Murphy, W.M. et al 1996 American Journal of Science, vol 296, p.128-186.

Temperature dependence of enthalpy

$\frac{d\Delta H}{dT} = \Delta C_p$

Fundamental Error ALL 5/17/96

ΔH at a given temperature is (from integrating above C_p equation)

$\Delta H_T = \Delta H^\circ + 0.23763030 \times 10^3\, T - \frac{0.47428400}{2} T^2 + \frac{0.16656600 \times 10^{-2}}{3} T^3 - \frac{0.12360200 \times 10^{-5}}{4} T^4$

* $T = (T_f - T_i)$

ALL 5/22/96

Assign

$a = 0.23763030 \times 10^{3}$ J

$b = -0.47428400$ J

$c = 0.16656600 \times 10^{-2}$ J

$d = -0.12360200 \times 10^{-5}$ J

Then

$$\Delta H_T = \Delta H^\circ + aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4$$

For an equilibrium reaction

$$\frac{d \ln K}{dT} = \frac{\Delta H_r^\circ}{RT^2}$$ fundamental Error AZU 5/27/96

We want to find $\ln K$ at 0, 60, 100, 150, 200, 250, 300°C using $\ln K^\circ$ (value at 25°C) and the heat capacity function.

$$\ln K - \ln K^\circ = \int_{25°C}^{T} \frac{\Delta H^\circ}{RT^2}\, dT$$

$$= \int_{25°C}^{T} \frac{\Delta H^\circ + aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4}{RT^2}\, dT$$

$$= \int_{25°C}^{T} \left\{ \frac{\Delta H^\circ}{RT^2} + \frac{a}{RT} + \frac{b}{2R} + \frac{cT}{3R} + \frac{dT^2}{4R} \right\} dT$$

$$= \frac{-\Delta H^\circ}{RT} + \frac{a}{R}\ln T + \frac{b}{2R}T + \frac{c}{6R}T^2 + \frac{d}{12R}T^3 \Big|_{25°C}^{T}$$

Therefore $\ln K$ for a given temperature is:

$$\ln K = \ln K^\circ - \frac{\Delta H^\circ}{RT} + \frac{a}{R}\ln T + \frac{b}{2R}T + \frac{c}{6R}T^2 + \frac{d}{12R}T^3 \Big|_{25°C}^{T}$$

AZU 5/22/96

$R = 8.314$ J/mol·K

For 0°C, ~~298 K~~ AZU 5/22/96 273 K

$$\ln K = \ln K^\circ - \frac{\Delta H^\circ}{R}\left(\frac{1}{273} - \frac{1}{298}\right) + \frac{a}{R}\ln(273-298) + \frac{b}{2R}(273-298) + \frac{c}{6R}(273^2 - 298^2) + \frac{d}{12R}(273^3 - 298^3)$$

Fundamental Error 5/27/96

For 60°C, 333 K

$$\ln K = \ln K^\circ - \frac{\Delta H^\circ}{R}\left(\frac{1}{333} - \frac{1}{298}\right) + \frac{a}{R}\ln(333-298) + \frac{b}{2R}(333-298) + \frac{c}{6R}(333^2 - 298^2) + \frac{d}{12R}(333^3 - 298^3)$$

AZU 5/22/96 AZU 5/22/96

$= -21.37$

For 100°C, 373 K

$$\ln K = \ln K^\circ - \frac{\Delta H}{R}\left(\frac{1}{373} - \frac{1}{298}\right) + \frac{a}{R}\ln(373-298) + \frac{b}{2R}(333-298) + \frac{c}{6R}(333^2 - 298^2) + \frac{d}{12R}(333^3 - 298^3$$

$= -127.67$

AZU 5/22/96

For 150°C, 423 K

$$\ln K = \ln K^\circ - \frac{\Delta H}{R}\left(\frac{1}{423}-\frac{1}{298}\right) + \frac{a}{R}\left(\ln(423-298)\right) +$$
$$\frac{b}{2R}(423-298) + \frac{c}{6R}(423^2-298^2) + \frac{d}{12R}(423^3-298^2)$$
$$= -239.13$$

For 200°C, 473 K

$$\ln K = \ln K^\circ - \frac{\Delta H}{R}\left(\frac{1}{473}-\frac{1}{298}\right) + \frac{a}{R}\ln(473-298) +$$
$$\frac{b}{2R}(473-298) + \frac{c}{6R}(473^2-298^2) + \frac{d}{12R}(473^3-298^3)$$
$$= -328.91$$

Fundamental Error AZL 5/27/96

For 250°C, 523 K

$$\ln K = \ln K^\circ - \frac{\Delta H}{R}\left(\frac{1}{523}-\frac{1}{298}\right) + \frac{a}{R}\ln(523-298)$$

AZL 5/22/96

$$+\frac{b}{2R}(523-298) + \frac{c}{6R}(523^2-298^2) + \frac{d}{12R}(523^3-298^3)$$
$$= -402.10$$

For 300°C, 573 K

$$\ln K = \ln K^\circ - \frac{\Delta H}{R}\left(\frac{1}{573}-\frac{1}{298}\right) + \frac{a}{R}\ln(573-298)$$
$$+\frac{b}{2R}(573-298) + \frac{c}{6R}(573^2-298^2) + \frac{d}{12R}(573^3-298^3)$$
$$= -462.68$$

Calculation of log K values for Analcime at 0, 60, 100, 150, 200, 250, and 300°C at constant pressure of 1.0132 bar.

Analcime + $4H^+ \rightleftharpoons Al^{3+} + 2SiO_{2(aq)} + Na^+ + 3H_2O_{(l)}$

$NaAlSi_2O_6 \cdot H_2O$

$C_{p\,Analcime} = 237.6303 - 0.474284T + 0.166566\times10^{-2}T^2 - 0.123602\times10^{-5}T^3$

from Data0.com.R2

$C_{p\,H_2O} = \frac{4.19\ J}{g\cdot K} \times 18.015\ \frac{g}{mol} = 75.48285\ \frac{J}{mol\cdot K}$

$\Delta C_p = 3C_{p\,H_2O} - C_{p\,Analcime}$
$= 3(75.48285) - (237.6303 - 0.474284T + 0.166566\times10^{-2}T^2 - 0.123602\times10^{-5}T^3)$
$= -11.18175 + 0.474284T - 0.166566\times10^{-2}T^2 + 0.123602\times10^{-5}T^3$

Assign

$a = 11.18175$, $b = 0.474284$

$c = 0.166566\times10^{-2}$, $d = 0.123602\times10^{-5}$

$\Delta C_p = -a + bT - cT^2 + dT^3$

From Data0.com.R2

$\Delta H_{f,\,Analcime}^\circ = -3296.900$ KJ/mol

$\Delta H_{f,\,H_2O(l)}^\circ = -285.83$ KJ/mol

$\Delta H_{f,\,Al^{3+}}^\circ = -538.414$ KJ/mol

$\Delta H_{f,\,SiO_{2(aq)}}^\circ = -877.720$ KJ/mol

$\Delta H_{f,\,H^+}^\circ = 0$

$\Delta H_{f,\,Na^+}^\circ = -240.305$ KJ/mol

$\Delta H_r^\circ = (\Delta H_{f,Al^{3+}}^\circ) + 2(\Delta H_{f,SiO_2}) + \Delta H_{f,Na^+} + 3(\Delta H_{f,H_2O}) - \Delta H_{f,Analcime}$
$= -538.414 + 2(-877.720) - 240.305 + (3\times -285.83) - (-3296.9)$
$= -94,749$ KJ/mol $= -94749$ J/mol

AZL 5/27/96

From Murphy, et al, 1996

$\log K = 7.50$ at 25°C

$\ln K = 17.2693882$

$$\Delta H^\circ_{r(T)} - \Delta H^\circ_{r(T^\circ)} = \int_{T^\circ}^{T} \Delta C_p \, dT$$

$$= \int_{T^\circ}^{T} \{-a + bT - cT^2 + dT^3\} \, dT$$

$$= -a(T-T^\circ) + \frac{b}{2}(T^2 - T^{\circ 2}) - \frac{c}{3}(T^3 - T^{\circ 3}) + \frac{d}{4}(T^4 - T^{\circ 4})$$

$$\Delta H^\circ_{r(T)} = \Delta H^\circ_{r(T^\circ)} - a(T-T^\circ) + \frac{b}{2}(T^2 - T^{\circ 2}) - \frac{c}{3}(T^3 - T^{\circ 3}) + \frac{d}{4}(T^4 - T^{\circ 4})$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ_r}{RT^2}$$

$$\ln K_{(T)} - \ln K_{(T^\circ)} = \int_{T^\circ}^{T} \frac{\Delta H^\circ_r}{RT^2} \, dT$$

$$= \int_{T^\circ}^{T} \left\{ \frac{\Delta H^\circ_{r(T^\circ)}}{RT^2} - \frac{a(T-T^\circ)}{RT^2} + \frac{b(T^2-T^{\circ 2})}{2RT^2} - \frac{c(T^3-T^{\circ 3})}{3RT^2} + \frac{d(T^4-T^{\circ 4})}{4RT^2} \right\} dT$$

$$= \int_{T^\circ}^{T} \left\{ \frac{\Delta H^\circ_{r(T^\circ)}}{RT^2} - \frac{a}{RT} + \frac{aT^\circ}{RT^2} + \frac{b}{2R} - \frac{bT^{\circ 2}}{2RT^2} - \frac{cT}{3R} + \frac{cT^{\circ 3}}{3RT^2} + \frac{dT^2}{4R} - \frac{dT^{\circ 4}}{4RT^2} \right\} dT$$

$$= \frac{-\Delta H^\circ_{r(T^\circ)}}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) - \frac{a}{R}\ln\left(\frac{T}{T^\circ}\right) - \frac{aT^\circ}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) + \frac{b}{2R}(T - T^\circ) +$$

$$\frac{bT^{\circ 2}}{2R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) - \frac{c(T^2 - T^{\circ 2})}{6R} - \frac{cT^{\circ 3}}{3R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) + \frac{d(T^3 - T^{\circ 3})}{12R} + \frac{dT^{\circ 4}}{4R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right)$$

$$\ln K_{(T)} = \ln K_{(T^\circ)} + \left[\left(\frac{1}{T} - \frac{1}{T^\circ}\right)\left(\frac{-\Delta H^\circ_{r(T)}}{R} - \frac{aT^\circ}{R} + \frac{bT^{\circ 2}}{2R} - \frac{cT^{\circ 3}}{3R} + \frac{dT^{\circ 4}}{4R}\right)\right]$$

$$- \frac{a}{R}\ln\left(\frac{T}{T^\circ}\right) + \frac{b}{2R}(T - T^\circ) - \frac{c}{6R}(T^2 - T^{\circ 2}) + \frac{d}{12R}(T^3 - T^{\circ 3})$$

ALL 5/27/96

All initial temperatures are 25°C, 298.15 K

For Final temperature 0°C, 273.15°K
$\ln K = 20.7756$, $\log K = 9.0227$

For Final temperature 60°C, 333.15°K
$\ln K = 13.2627$, $\log K = 5.7599$

For Final temperature 100°C, 373.15°K
$\ln K = 9.6147$ $\log K = 4.1756$

For Final temperature 150°C, 423.15°K
$\ln K = 6.0201$, $\log K = 2.6145$

For Final temperature 200°C, 473.15°K
$\ln K = 3.1628$, $\log K = 1.3736$

For Final temperature 250°C, 523.15°K
$\ln K = 0.8170$, $\log K = 0.3548$

For Final temperature 300°C, 573.15°K
$\ln K = -1.1613$, $\log K = -0.5043$

T°C	log K
0	9.0227
25	7.50
60	5.7599
100	4.1754
150	2.6145
200	1.3736
250	0.3548
300	-0.5043

ALL 5/27/96

These values for log K were entered into a new Eq 3/6 data 0 file.

File name is: data0.alt1.R2

A data1.alt1.R2 file was successfully created by running EQPT.

The file data 0.alt1.R2 was renamed data 0.ana.R2 and data1.ana.R2 was successfully created by running EQPT.

ALL 5/27/94

Analyses of wremoplume and sodgrite provided by Trikryl converted to normalized moles:

$$ppm_i \left(\div \frac{mg_i}{g_T}\right) \frac{g_i}{1000\ mg_i} \frac{mole_i}{g_i} g_T = moles$$

$$\% \left(\div \frac{g_i}{100 g_T}\right) \frac{mole_i}{g_i} g_T$$

Analysis of Water using the ana database which includes the recalculated analcime thermodynamic data from pg 23.

EQ3 runs were performed for five Oasis Valley wells: 10s/47-14bab
11s/47-27cba
11s/46-26bcc
11s/47-3cdb
11s/47-10caa
From White 1979 USGS Professional Paper 712-E with additional data provided by McKinley, etal 1991 USGS open file report 90-355.

EQ3 runs were performed for six wells in the Yucca Mountain area: H1-4000
UE25b-1
UE29a-2
J-11
J-12
J-13

J wells data from Young, 1972, USGS Water supply paper 1938
Other wells data from McKinley, et al 1991 USGS open file report 90-355.

From the EQ3 outputs graphed $\log a_{SiO_2}$ vs. $\log(a_{Al^{3+}} a_{Na^+} / a^4_{H^+})$ and included the analcime solubility limit.

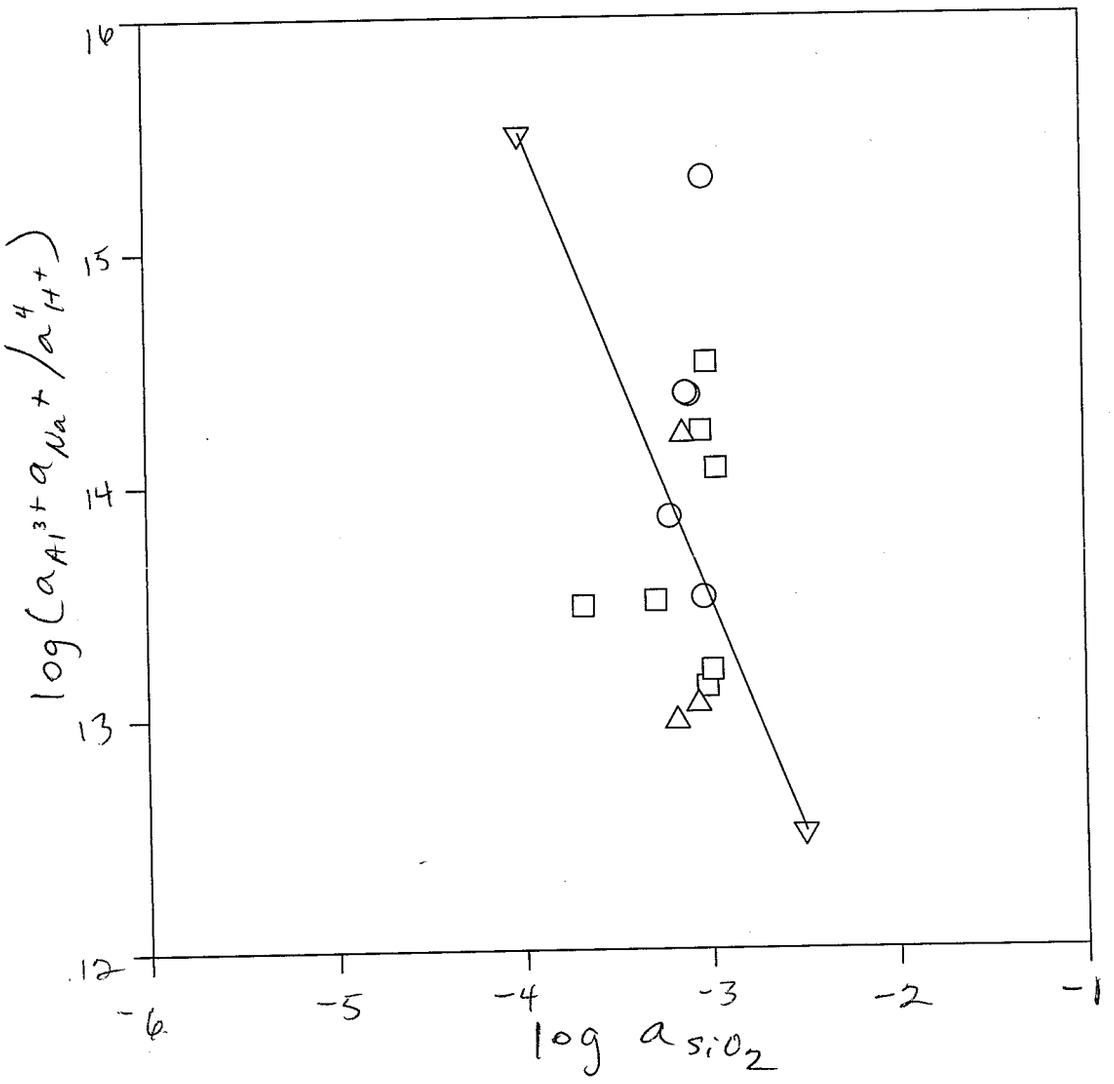
Most of the wells are buffered near $\log a_{SiO_2} = -3$

For those wells with $\log a_{SiO_2}$ values between -2.95 - 3.05 graphed them as $\log(a_{Na^+}/a_{H^+})$ vs. $\log(a_{Al^{3+}}/a^3_{H^+})$ and included the 25°C & 35°C analcime solubility limits and the 25°C Na-clinoptilolite solubility Limit.

AZH 6/21/96

AKU 4/21/96

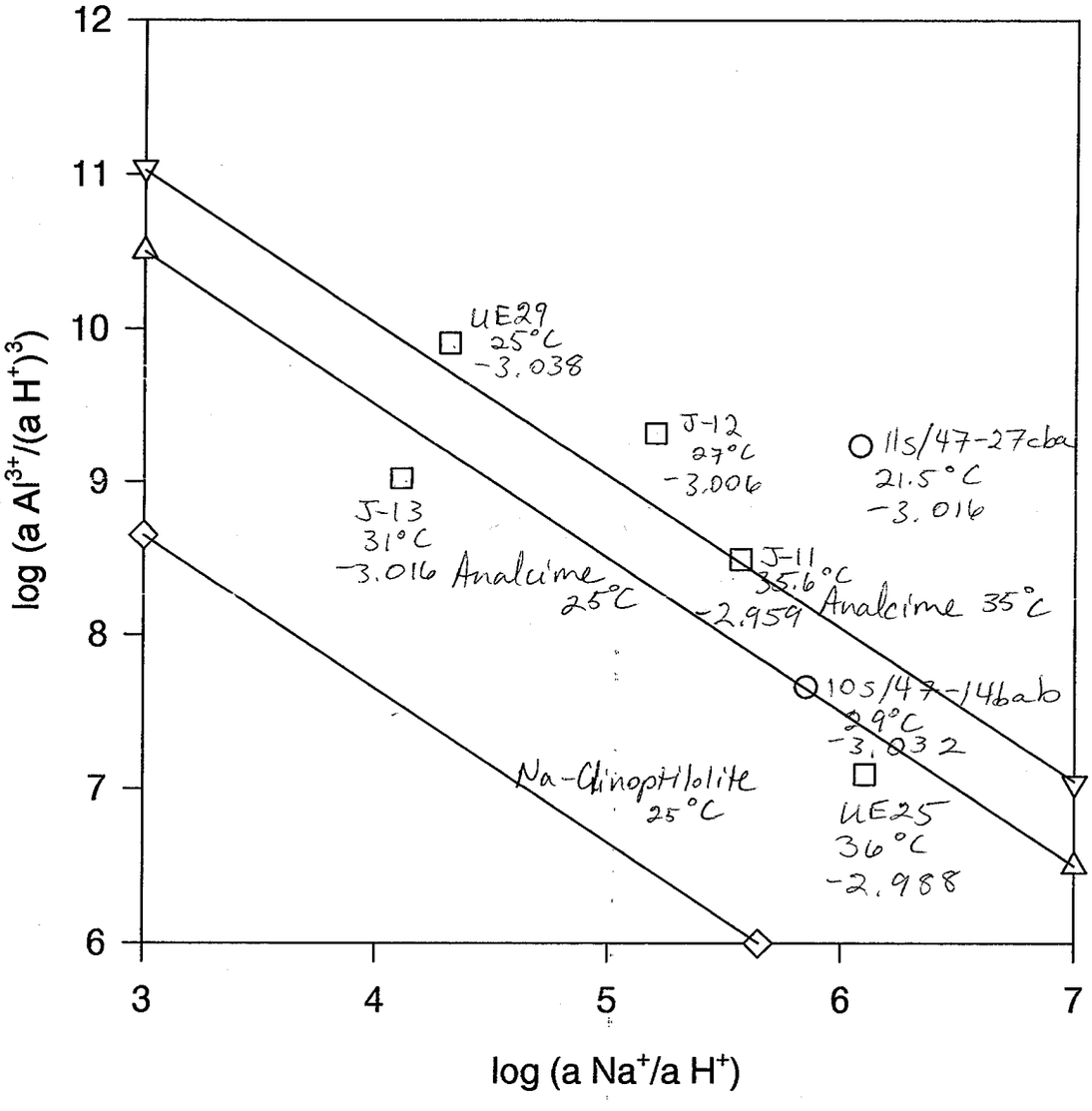
Analcime Solubility



○ Oasis Valley
□ Yucca Mtn
△ McKinley, et al
▽ Analcime solubility

AKU 4/21/96

2D Graph 1



○ Oasis Valley
□ Yucca Mtn

Data points amended with label, temperature and log activity of SiO_2

In the graph of constant log $a_{SiO_2} = -3$ all the data was well above the Na-clinoptilolite solubility limit. The rest of the data was scattered around the 25°C and 35°C solubility limits for analcime but did not correspond with their literature reported temperatures that were used in the EQ3 runs.

Unsaturated Zone Waters
from Yang, et al 1996 USGS WRIR 96-4058.

EQ3 runs using the data 0, ana, R2 were run for the Yang data for wells UZ 16 and UZ 14 for every depth that had measured Aluminum data.

The EQ3 outputs are saved on the three included disks.

A plot of a_{SiO_2} vs $\log(a_{Al^{3+}} a_{Na^+} / a^4_{H^+})$ including the analcime solubility limit. Again the data appeared to be buffered at log $a_{SiO_2} = -3$. Those data that had values between log $a_{SiO_2} = -2.95$ to -3.05 were plotted on a graph of $\log(a_{Na^+} / a_{H^+})$ vs. $\log(a_{Al^{3+}} / a^3_{H^+})$ which included the 25° & 35°C analcime solubility limit. All the data was well above these two limits.

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EQ3 unsaturated zone waters outputs

(10)

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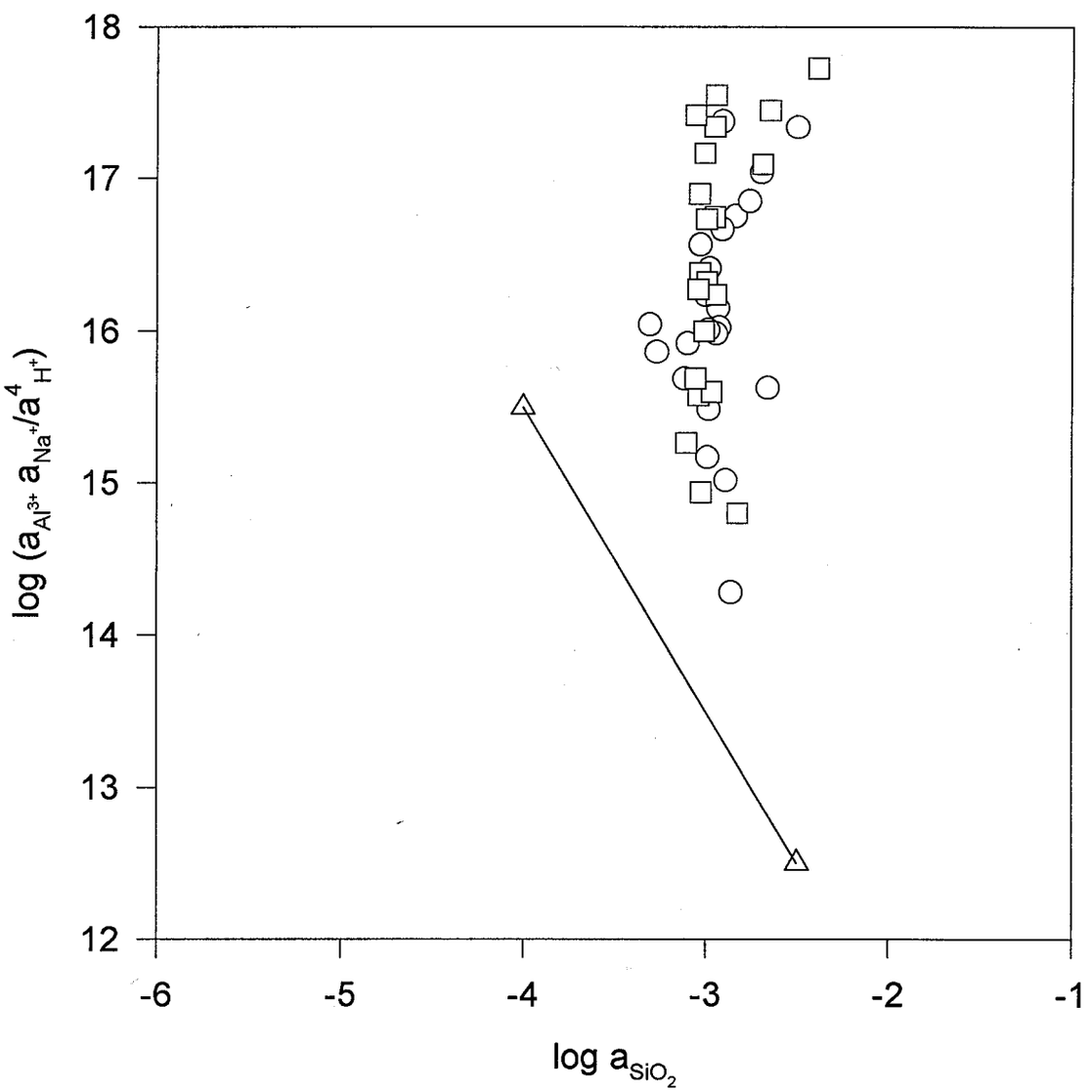
Pore waters from UZ-16 and UZ-14



- UZ-16
- UZ-14
- Analcime Solubility Limit

-2.95 - -3.05

AZU 6/21/94

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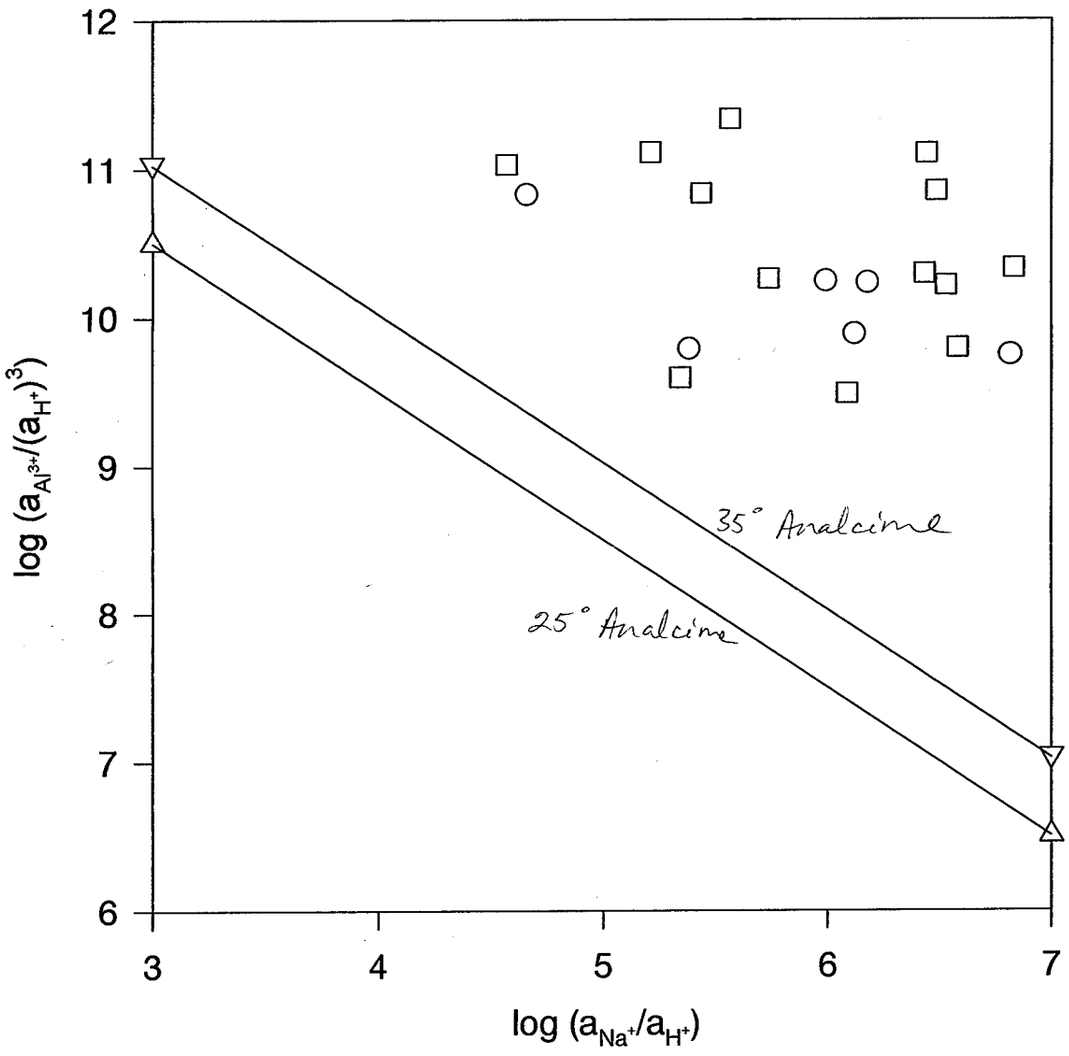
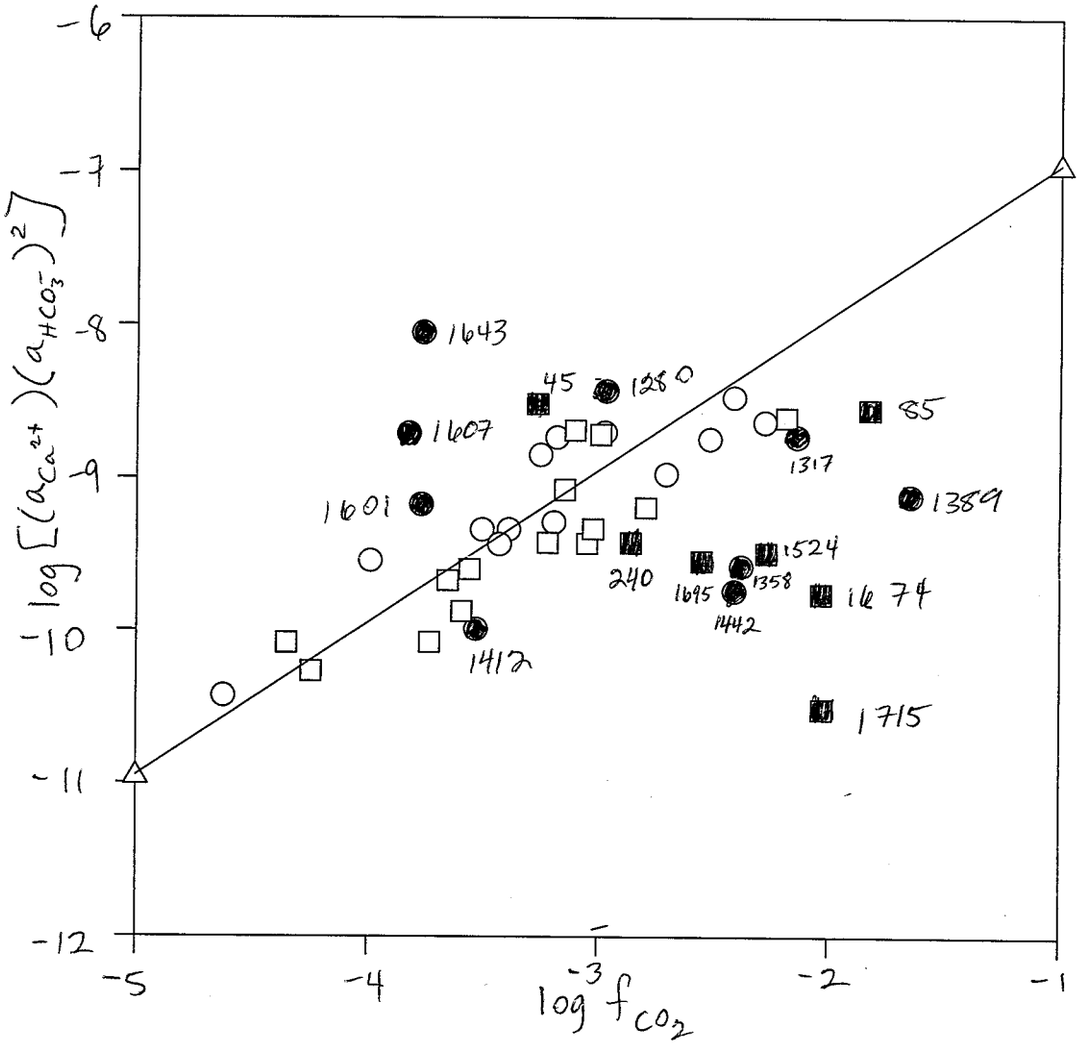


○ UZ-16
□ UZ-14
△ Analcime Limit 25°C
▽ Analcime Limit 35°C



○ UZ-16
□ UZ-14
△ Calcite solubility Limit

colored points are outliers

The unsaturated zone water data was then plotted as $\log f_{CO_2}$ v. $\log (a_{Ca^{2+}} a^2_{HCO_3^-})$ with the calcite solubility limit at 25°C included. The data scattered around the solubility limit. The outliers were selected and a series of graphs were plotted showing the outliers versus the data in equilibrium with calcite.

The Graphs were as follows:

Ca^{2+} vs. Mg^{2+}
Cl^- v. SO_4^{2-}
Na^+ v HCO_3^-
Na^+ v Cl^-
pH v. HCO_3^-
pH v. adjustment in HCO_3^- that EQ3 made
HCO_3^- v. adjustment in HCO_3^-

EQ3 inputs and outputs for both groundwater runs and unsaturated zone runs can be found in /home/dopey/bmurphy/eq3_6v7.2b/import/Ana

Copies of graphs and spreadsheets used can be found on the disk:
Analcime and Wells
Groundwater and
Unsaturated zone
Ana Unruh June 1996

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Uranophane and Soddyite Analysis

Two sets of standards were used for the ICP analysis.

Group 1: 20A2, 20A6, 20AA
Group 2: 20AE, 20AG, 20AI

Each standard was analysized for Ca, Si, U.

For each group I plotted the expected value (ppm) of the standard versus the measured value (ppm). I picked a linear fit and ~~and~~ forced the line to go through the origin. If the analysis was perfect, the slope of the line should be 1.

Slopes are as follows:
Group 1 Standards
Ca: 0.9997
Si: 1.0358
U: 0.9792

Group 2 Standards
Ca: 1.0300
Si: 1.0312
U: 0.9498

D Those samples that were analyzed for water content were looked at separately.

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The averages and standard deviations of the normalized mole value for each element were calculated. The first group included analyses of Uran 9, Uran 10, and Uran 3.

	Avg	standard deviation
Ca	0.193	± 0.002
Si	0.421	± 0.003
U	0.386	± 0.001

These values were adjusted by dividing each average by the slope of the respective standard line from group 1 leading to adjusted averages of:

Ca : 0.193
Si : 0.406
U : 0.394

These values correspond to a Ca:Si:U mole ratio of 1 : 2.10 : 2.04 were the moles of Si and U were divided by the moles of Ca.

The same procedure was done for the Uran 12 synthesis that did not have water measured. except the Group2 Stnds were used.

	Avg	Stnd deviation	Adjusted Avg	Mole ratio
Ca	0.205	0.001	0.199	1
Si	0.415	0.001	0.402	2.02
U	0.379	0.001	0.399	2.01

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The samples of Uran 9, Uran 10, and Uran 3 that were analysized for water were also statistically analysized as the previous using Group I Standards.

	Avg	Stnd deviation	Adjusted Avg	Mole ratio
Ca	0.089	0.001	0.089	1
Si	0.191	0.002	0.184	2.07
U	0.178	0.002	0.182	2.04
H_2O	0.542	0.005	~~0.445~~	~~4.66~~ 5.75

28 8/11/00 AZU

(No adjusted avg for H_2O because I have no standard data for it)

The two soddyite samples were treated the same way and adjusted using Group I Standards.

	Avg	Stnd deviation	Adjusted Avg	Mole ratio
Si	0.166	0.001	0.160	1
U	0.353	0.005	0.360	2.25
H_2O	0.481	0.006		3.01

Nominal formulas are
Uranophane : $Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5H_2O$
Soddyite : $(UO_2)_2SiO_4 \cdot 2H_2O$

With the exception of the waters of hydration being slightly high for uranophane, the synthetic minerals appear to be in close agreement with the nominal stoichiometry of the minerals.

Standard graphs are stored on the disk:
Uranophane and Soddyite/Ana Uranb June 1996.

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^{36}Cl Analysis

I calculated the Shapiro-Wilk Test statistic and corresponding p-value for the ^{36}Cl data based on Conover, W.J. Practical Nonparametric Statistics. John Wiley & Sons: New York, 1980.

I calculated for the data

less than 700
< 800
< 900
< 915
< 950
< 958
< 975
< 1000
< 1100
< 1200
< 1400
< 1700
< 1900
< 2100

~~on~~ I plotted the highest ^{36}Cl value for the set on the x axis versus the p value on the y and amended the graph with the x coordinate and number of samples in the set.

The ^{36}Cl data appears to be closest to a normal data set~~s~~ for values less than ~~14~~ 915 or 941.

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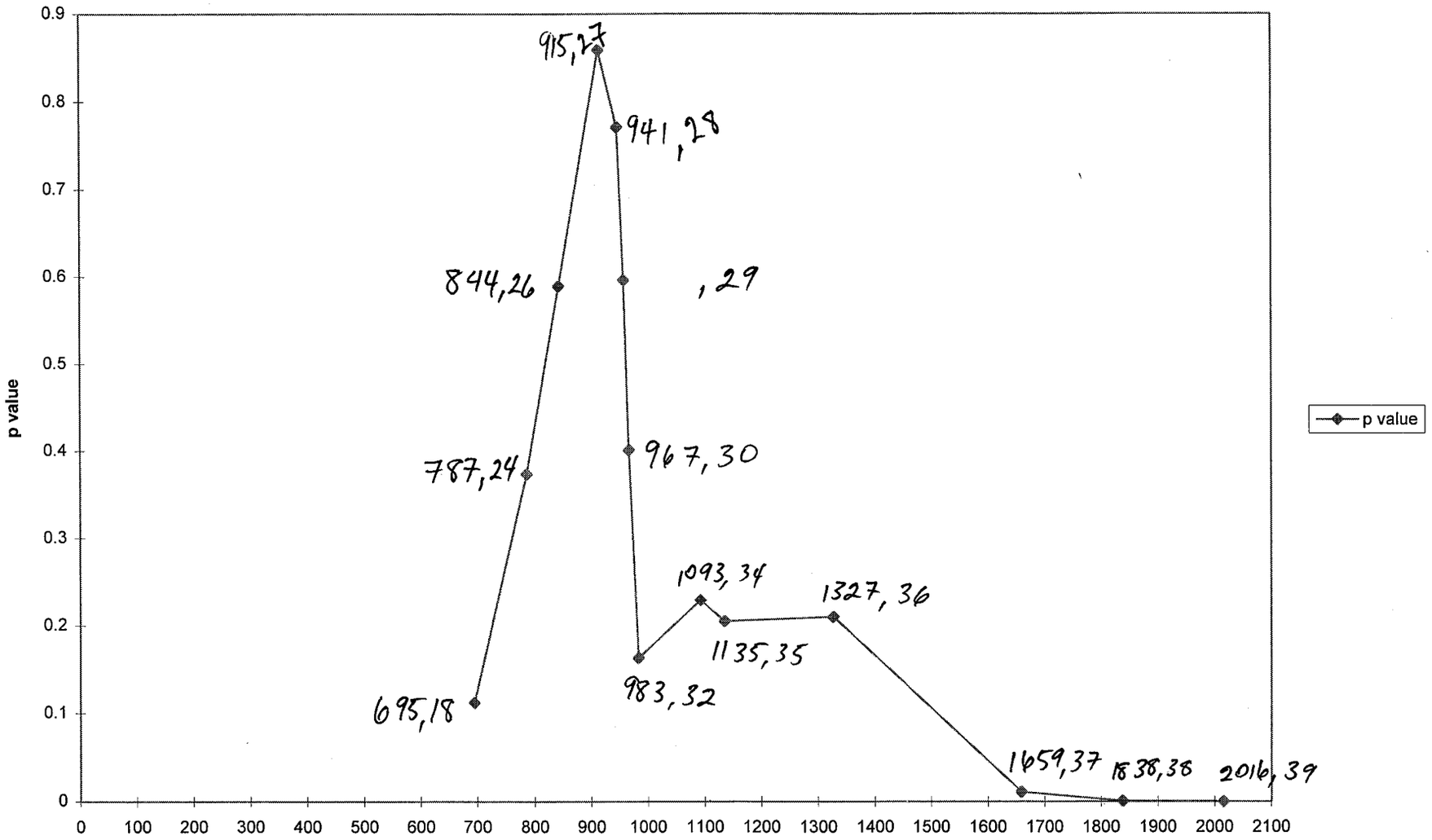
Graph Chart 2

Shapiro Wilks Test for 36-CI



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I took the 915 and 941 data sets and calculated the mean and standard deviation. Using sigmaplot ~~a~~ I created a random set of normally distributed numbers with a mean and standard deviation like the ^{36}Cl data sets. I created a histogram of the random numbers with 10 evenly spaced bins and fit a Gaussian curve to it. On top I plotted a histogram of the ^{36}Cl data with 10 equally spaced bins and fitted a Gaussian curve to it.

Both graphs show a normal distribution.

I used this same technique to make a plot of the distribution of the geomagnetic data for the past 100,000 years. This also showed a normal distribution.

The plots are unable to be printed at this time but are located on the disk ^{36}Cl files / Ana Unruh June 1996 as files 915.spw, 941.spw, and geomag.spw

The Shapiro Wilks calculation and graph are on the same disk in file alldata.xls.

AUU 6/26/96

I have reviewed this notebook and find it in general compliance with QAP-001 and there is sufficient information so that another qualified person could repeat the activity.

E.C. Rea
1/7/97

1/3/97

What is the retardation factor for Pu in fractures?

Pu sorbs strongly on smectite. Smectite is a common fracture lining mineral in the Topopah Spring Tuff.

TSPA-93 gives fracture apertures of 180 μm.

Shibutani et al. (1994) MRS proceedings gives K_D for Pu on bentonite of 1 to 10 m^3/kg for relevant pH of 7 to 9.

$(1\ m^3/kg)(kg/1000g)(10^3\ cm^3/m^3)(ml/cm^3)$

$= 10^3\ ml/g$

The LANL group (e.g., Transport Synthesis Report, 1996, and Mineralogy-Petrology Report, 1996) note that smectite is a common fracture lining mineral and that smectites are commonly about 10 μm plates.

Hypothetical K_D for Pu in fractures:

Suppose 5% of 180 μm wide fractures are coated with 10 μm thick smectite with a diameter of 10^2 μm.

5/13/97

In $1\ m^2$ of fracture plane the mass of smectite is

$.05 \times 1\ m^2 \times 2\ \text{sides} \times 10\ \mu m \times \rho_{smectite}$

$\rho_{smectite} \approx 2.5\ g/cm^3$

$.05 \times 1\ m^2 \times \frac{100^2\ cm^2}{m^2} \times 2 \times 10\ \mu m \times \frac{cm}{10^4\ \mu m} \times 2.5\ \frac{g}{cm^3}$

$= 2.5\ g$

The volume of water in the saturated fracture is

~~$1\ m^2 \times 180\ \mu m \times \frac{m^3}{10^{\cdot}}$~~ clw 5/13/97

$1\ m^2 \times 180\ \mu m \times \frac{100^2\ cm^2}{m^2} \times \frac{cm}{10^4\ \mu m}$

$= 180\ cm^3$

For a K_D of 1000 ml/g, the fraction of Pu on clay is

$\frac{2.5\ g}{180\ cm^3} \times 1000\ \frac{ml}{g} \times \frac{cm^3}{ml} = 13.88$

That's not the fraction, its the ratio clw 5/13/97

of the amount on clay to the amount in solution, which is the retardation factor + 1.

The last step is derived

$K_d = \frac{\text{moles sorbed}}{\text{mass of solid}} \quad \frac{\text{volume of liquid}}{\text{moles dissolved}}$

$\frac{\text{moles sorbed}}{\text{moles dissolved}} = K_d \frac{\text{mass of solid}}{\text{volume of liquid}}$

Retardation factor is defined

$R_d = 1 + \frac{\rho_{bd}}{\phi S_w} K_d$

$= 1 + \frac{\text{dry bulk density}}{\text{porosity} \cdot \text{saturation}} K_D$

For the example just worked

$R_d = 1 + \frac{(2.5\ g/181\ cm^3)}{(180\ cm^3/181\ cm^3) \cdot 1} \times 10^3 = 14.88$

$R_d = 1 + 13.88 = 14.88$

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WWL 6/11/97

What is the bin size for ^{36}Cl data histogram?

From M.P. Wand "Data-Based Choice of Histogram Bin Width" The American Statistician, v. 51, p. 59-64, 1997.

Sturge's proposal

$$\hat{h} = \frac{\text{range of data}}{1 + \log_2(\text{number of data})}$$

For ^{36}Cl data base from Levy et al. 1997 (LANL Milestone SP2301M4; LA-EES-1-TIP-97-004, draft)

$$\hat{h} = \frac{(4105 - 140)}{1 + \log_2(189)} = 463$$

This value is far too large because of the long tail to high values. Applying this formula to the roughly normal part of the main data set yields

$$\hat{h} = \frac{(1093 - 140)}{1 + \log_2(153)} = 115$$

WWL 6/11/97

PCL 1/23/98

Evolution of the near-field environment
- Multiflow - coupled geochemical flow model of the near field repository environment.

Peter C. LaFemina is P.G. - CNWRA scientist working w/ Dr. Bill Murphy

Determination of volume fraction of calcite in the unsaturated zone to be used in Multiflow modeling.

The calculated estimate of the volume fraction of calcite in the unsaturated zone was determined using the following reference:

Ack. file 11/23/98 Paces, J.B.; Neymark, L.A., Marshall, B.D., Whelan, J.F., and Peterman, Z.E. U.S. Geological Survey, Ages and Origins of subsurface secondary minerals in the exploratory studies facility (ESF). U.S. Geological Survey - Yucca Mtn. Project Branch 1996 Milestone Report 3GQH450M. pp 38-39.

To calculate the spatial distribution of secondary minerals (that is calcite & opal), the above reference authors measured the length & thickness of secondary fracture & lithophysal cavity coatings every 100m in a 30m x 60cm area. "An ultraviolet lamp was used to determine the presence of fluorescent opal." (p 38). The area covered by the secondary fracture and lithophysal cavity coatings ranged from "absent to 0.48% of the total area of rock for each 30m survey" (p 38).

The total volume of secondary minerals present in the mountain can be estimated using the following assumptions:

(1) "line surveys are assumed to be representative of the potential repository horizon

(2) "this horizon is typical of the rest of the unsaturated zone.

The authors state that these assumptions are "probably not true," however they provide a "first attempt". The authors' goal was to determine a past flux of water through the potential repository based on mineral data

PCL. 1/23/98

Determination of volume fraction of calcite (cont.)

area of potential repository = 5.2 Km^2 (5,200,000 m^2)

avg. depth to water table = 630m (0.630Km)

volume of unsaturated zone (UZ) rock in potential repository

$5.2\ Km^2 \times 0.630 Km = 3.276\ Km^3$

$\approx 3.3\ Km^3$

the average fraction of secondary mineral filling is 0.11%

therefore, the volume of secondary calcite & opal within the potential repository block is = 0.0036 Km^3

calcite constitutes 90% of the volume of secondary coatings

therefore; calcite = 0.0032 Km^3

opal = 0.00036 Km^3

$$\text{Volume fraction} = \frac{\text{volume of mineral}}{\text{volume of rock}} \times 100$$

$$\text{calcite} = \frac{0.0032\ Km^3}{3.276\ Km^3} \times 100$$

$$= 0.097\%$$

$$\text{opal} = \frac{0.00036\ Km^3}{3.276\ Km^3}$$

$$= 0.01\%$$

CLh. 1/23/98

Calculation of volume fraction of minerals in the proposed repository horizon, calculated from weight fraction data from Bish & Chipera, 1989.

Full Reference: Bish, D.L. and Chipera, S.J., 1989. Revised Mineralogic Summary of Yucca Mountain, Nevada. Los Alamos National Laboratory -LA-11497-MS. 68pp.

$$\text{volume fraction} = \frac{\text{mineral volume}}{\text{total volume}}$$

$$= \frac{\text{mineral volume}}{\text{total mineral volume + pore volume}}$$

$$\text{mass fraction} = \frac{\text{mineral mass}}{\text{total mineral mass}}$$

$$\text{mineral density} = \frac{\text{mineral mass}}{\text{mineral volume}}$$

$$\text{dry rock density} = \frac{\text{total mineral mass}}{\text{total volume}}$$

$$\text{volume fraction} = \frac{\frac{\text{mineral mass}}{\text{mineral density}}}{\frac{\text{total mineral mass}}{\text{dry rock density}}}$$

$$\text{volume fraction} = \frac{\text{mass fraction} * \text{dry rock density}}{\text{mineral density}}$$

Calculation/equation for dry rock density:

$$\text{dry rock density} = \frac{\text{total mineral mass}}{\text{total volume}}$$

(continued on next page)

CLh 2/3/98

Dry rock density equation (cont.)

$$\text{rock density} = \frac{\text{total mineral mass} + \text{water mass}}{\text{total volume}}$$

$$\text{rock density} = \text{dry rock density} + \frac{\text{water mass}}{\text{total volume}}$$

$$\text{rock density} = \text{dry rock density} + \left(\frac{\text{porosity} * \text{saturation} * \text{total vol.} * \text{water density}}{\text{total volume}}\right)$$

$$\text{rock density} = \text{dry rock density} + (\text{porosity} * \text{saturation} * \text{water density})$$

$$\text{dry rock density} = \text{rock density} - (\text{porosity} * \text{saturation} * \text{water density})$$

Porosity & density data can be taken from:

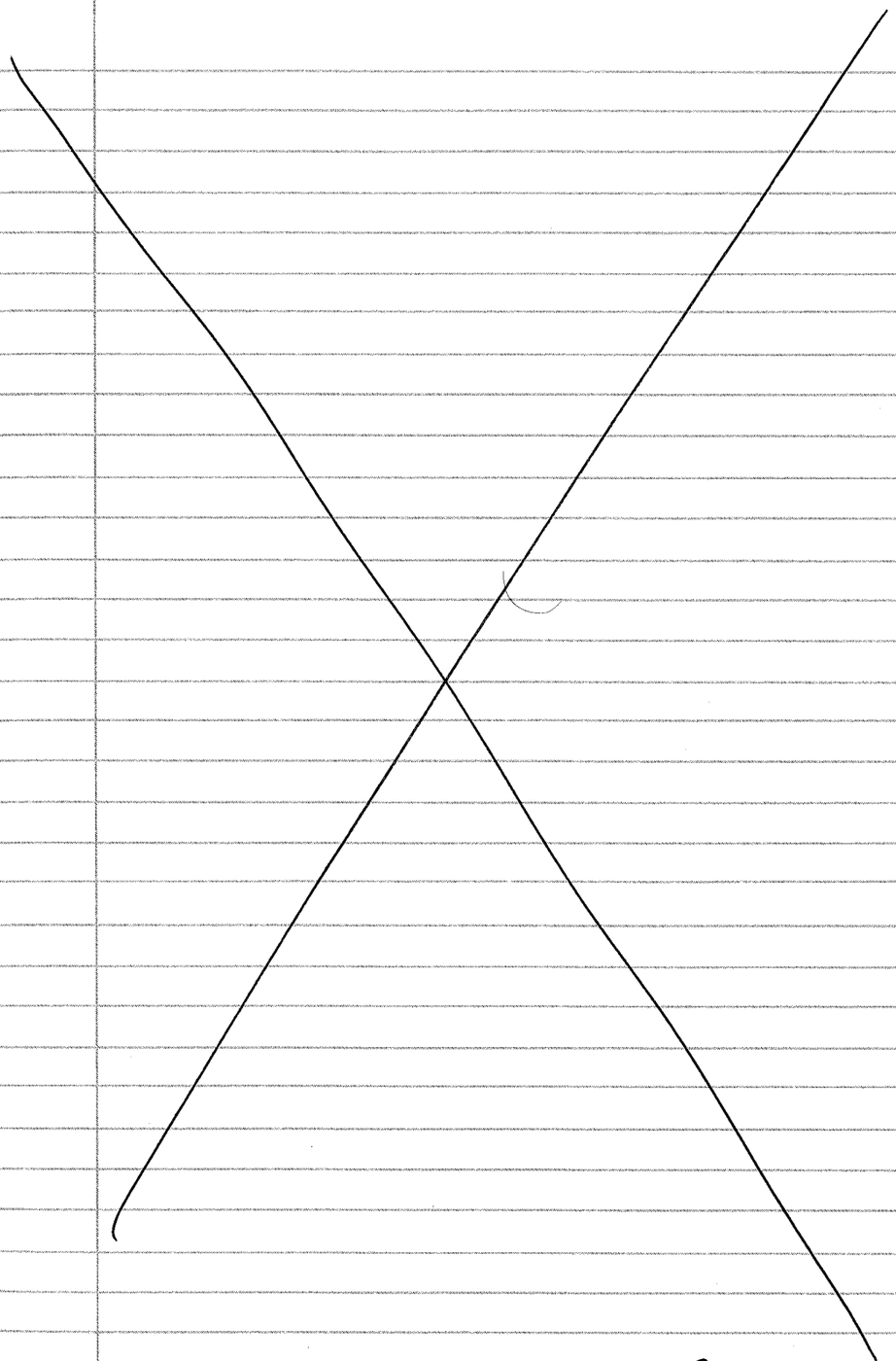
Anderson, L.A., 1984. Rock property measurements on large-volume core samples from Yucca Mountain USW GU-3/G-3 and USW G-4 boreholes, Nevada Test Site, Nevada. United States Department of the Interior Geological Survey Open-File Report 84-552. Denver, Colorado. 39 pp.

$$\text{Mineral density} = \frac{\text{mineral mass}}{\text{mineral volume}}$$

Mineral mass and mineral volume may be taken from:

Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1979. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. Geological Survey Bulletin 1452, U.S. Government Printing Office, Washington D.C. 456 pp.

PCh. 2/3/98



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Mass balance of oxygen (O_2) in the proposed geologic repository block at Yucca Mountain, Nevada

Prepared by:

Peter C. La Femina
CNWRA - SwRI
Scientist

Step 1. Repository block volume above the static water level (SWL)[1]

- thickness (H) = 630 m avg. depth to the SWL
- area (A) = 5.2 km^2

V = H * A
V = 0.63 km * 5.2 km^2
V = **3.276** km^3

1 = Paces et al., 1996. Ages and origins of subsurface secondary minerals in the exploratory studies facility (ESF)

Step 2. Pore volume of the repository block

- Porosity of the unsaturated zone = pore volume/total volume

- average porosity of the unsaturated zone = 0.285 or 28.5%
  - *porosity was averaged for each unit in the spreadsheet calculations*
- pore volume (pv) = total volume * porosity
- pv = 3.276*10^9 m^3 * 0.285
- pv = **9.3366*10^8** m^3

Step 3. Volume of pores saturated within the unsaturated zone

- Saturation = saturated pore volume / total pore volume

- average saturation value of the unsaturated zone = 0.722 or 72.2%
  - saturation was averaged for each unit in the spreadsheet calculations
- saturated pore volume (spv) = total pore volume * saturation
- spv = 9.3366*10^8 m^3 * 0.722
- spv = **6.741 * 10^8** m^3

Step 4. Pore volume of air

- pore volume of air (pva) = total pore volume - saturated pore volume
- pva = 9.3366*10^8 m^3 - 6.741 * 10^8 m^3
- pva = **2.5956 * 10^8** m^3

Rec'd 4/29/98

Step 5. Oxygen (O_2) volume in air pore volume

- O_2 volume = pva * percent O_2 in air
- O_2 volume = $2.5956 * 10^8$ m^3 * 0.21
- O_2 volume = $5.4508 * 10^7$ m^3

Step 6. Number of moles of Oxygen (O_2) in unsaturated pores

- PV = nRT
- P = pressure at 1km altitude (88494.01 PA)
- V = volume of O_2 ($5.4508 * 10^7$ m^3)
- n = number of moles
- R = molar gas constant (8.31451 m^3 *PA/mol * K)
- T = temperature (298 K)

- n = PV/RT
- n = $2.2291 * 10^9$ moles of O_2 in unsaturated pores

Rev. 4/29/98

zeolite

Zeolite Abundances by Lithologic Unit - Average Volume Fractions												
Tiva Canyon Tuff - (84.1 m)[1]		**Paintbrush Bedded Tuff - (17.88 m)**		**Topopah Spring Tuff - (332.96 m)**		**Calico Hills Formation - (62 m)**		**pre-Ta bedded tuffs[2] - (19.7 m)**		**Prow Pass Tuff[2] - (62.4 m)**		**Bullfrog Tuff[3] - (140.82 m)**	
Smectite	0.043	Smectite	0.087	Smectite	0.014	Smectite	0.011	Smectite	0.010	Smectite	0.024	Smectite	0.011
Mica	0.001	Mica	0.009	Mica	0.005	Mica	0.003	Mica	0.015	Mica	0.002	Mica	0.011
Clinoptilolite	0.000	Clinoptilolite	0.000	Clinoptilolite	0.037	Clinoptilolite	0.291	Clinoptilolite	0.146	Clinoptilolite	0.272	Clinoptilolite	0.111
Mordenite	0.000	Mordenite	0.000	Mordenite	0.002	Mordenite	0.041	Mordenite	0.052	Mordenite	0.000	Mordenite	0.013
lithologic volume	4.37E+08		9.30E+07		1.73E+09		3.22E+08		1.02E+08		3.24E+08		7.32E+08
1= Average unit thickness.													
2= Average calculated from wells USW GU-3 & G-4.													
3= Values from USW GU-3.													
Ideal Mineral Compositions													
Clinoptilolite: $(Ca, Na, K)_{3.6}[Al_6Si_{30}O_{72}]*24H_2O$													
Mordenite: $Na_8KCa_2[Al_6Si_{40}O_{96}]*28H_2O$													
Smectite - Na-Montmorillonite: $(0.5Ca, Na)_{0.7}(Al, Mg, Fe)_4[(Si,Al)_8O_{20}](OH)_4*nH_2O$													
Mica - Muscovite: $K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$													

BCG. 4/29/98

minvf-avg.

Lithologic Units of the Unsaturated Zone in wells USW G-4, GU-3, & UE-25a#1

USW G-4

Lithologic Units of the Unsaturated Zone - Mineral Volume Fraction - Averages

Tiva Canyon Tuff (9.1 - 45.1 m)		**Pah Canyon Tuff (51.3 - 69.5 m)**		**Topopah Spring Tuff (69.5 - 428.7 m)**		**Calico Hills Formation (428.7 - 519.8 m)**		**pre-Ta bedded tuffs (519.8 - 537.3 m)**		**Prow Pass Tuff (537.3 - 681.7 m)**	
Smectite	0.106	Smectite	0.081	Smectite	0.025	Smectite	0.012	Smectite	0.004	Smectite	0.041
Mica	0.000	Mica	0.016	Mica	0.006	Mica	0.005	Mica	0.018	Mica	0.000
Clinoptilolite	0.000	Clinoptilolite	0.000	Clinoptilolite	0.054	Clinoptilolite	0.420	Clinoptilolite	0.286	Clinoptilolite	0.371
Mordenite	0.000	Mordenite	0.000	Mordenite	0.000	Mordenite	0.041	Mordenite	0.104	Mordenite	0.000
Tridymite	0.000	Tridymite	0.000	Tridymite	0.047	Tridymite	0.000	Tridymite	0.000	Tridymite	0.000
Cristobalite	0.234	Cristobalite	0.025	Cristobalite	0.119	Cristobalite	0.044	Cristobalite	0.124	Cristobalite	0.219
Quartz	0.011	Quartz	0.026	Quartz	0.064	Quartz	0.033	Quartz	0.056	Quartz	0.000
Feldspar	0.449	Feldspar	0.227	Feldspar	0.483	Feldspar	0.082	Feldspar	0.261	Feldspar	0.081
Glass	0.146	Glass	0.105	Glass	0.086	Glass	0.000	Glass	0.000	Glass	0.000
Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000
Calcite	0.000	Calcite	0.000	Calcite	0.000	Calcite	0.000	Calcite	0.000	Calcite	0.000
subtotal	0.946	subtotal	0.480	subtotal	0.884	subtotal	0.637	subtotal	0.853	subtotal	0.712
porosity	0.073	porosity	0.519	porosity	0.115	porosity	0.342	porosity	0.204	porosity	0.341
Total	1.019	Total	0.999	Total	0.999	Total	0.979	Total	1.057	Total	1.053

UE-25a#1

Lithologic Units of the Unsaturated Zone - Mineral Volume Fraction - Averages

Tiva Canyon Tuff (9.1-66.4 m)		**Paintbrush Bedded Tuff (66.4-82.3 m)**		**Topopah Spring Tuff (82.3-415.7 m)**		**Calico Hills Tuff (415.7-545.4 m)**	
Smectite	0.011	Smectite	0.138	Smectite	0.011	Smectite	0.018
Mica	0.000	Mica	0.008	Mica	0.003	Mica	0.000
Clinoptilolite	0.000	Clinoptilolite	0.000	Clinoptilolite	0.056	Clinoptilolite	0.449
Mordenite	0.000	Mordenite	0.000	Mordenite	0.005	Mordenite	0.081
Tridymite	0.000	Tridymite	0.000	Tridymite	0.016	Tridymite	0.000
Cristobalite	0.227	Cristobalite	0.002	Cristobalite	0.072	Cristobalite	0.000
Quartz	0.216	Quartz	0.001	Quartz	0.162	Quartz	0.019
Feldspar	0.614	Feldspar	0.074	Feldspar	0.476	Feldspar	0.050
Glass	0.000	Glass	0.247	Glass	0.056	Glass	0.000
Hematite	0.002	Hematite	0.000	Hematite	0.002	Hematite	0.000
Calcite	0.000	Calcite	0.000	Calcite	0.000	Calcite	0.000
subtotal	1.070	subtotal	0.470	subtotal	0.860	subtotal	0.618
porosity	0.119	porosity	0.537	porosity	0.157	porosity	0.302
Total	1.189	Total	1.007	Total	1.017	Total	0.920

USW GU-3

Lithologic Units of the Unsaturated Zone - Mineral Volume Fraction, Averages

Tiva Canyon Tuff (0 - 113.9 m)		**Paintbrush Bedded Tuffs (113.9 - 129.2 m)**		**Topopah Spring Tuff (129.2 - 430.7 m)**		**Calico Hills Formation (430.7 - 459.3 m)**		**pre-Ta bedded tuffs (459.3 - 473.6 m)**		**Prow Pass Tuff (473.6 - 611.1 m)**		**Bullfrog Tuff (611.1 - 803.8 m)**	
Smectite	0.012	Smectite	0.041	Smectite	0.006	Smectite	0.002	Smectite	0.016	Smectite	0.007	Smectite	0.011
Mica	0.002	Mica	0.003	Mica	0.005	Mica	0.004	Mica	0.012	Mica	0.003	Mica	0.011
Clinoptilolite	0.000	Clinoptilolite	0.000	Clinoptilolite	0.000	Clinoptilolite	0.004	Clinoptilolite	0.006	Clinoptilolite	0.173	Clinoptilolite	0.111
Mordenite	0.000	Mordenite	0.000	Mordenite	0.000	Mordenite	0.000	Mordenite	0.000	Mordenite	0.000	Mordenite	0.013
Tridymite	0.039	Tridymite	0.000	Tridymite	0.037	Tridymite	0.000	Tridymite	0.000	Tridymite	0.013	Tridymite	0.007
Cristobalite	0.181	Cristobalite	0.083	Cristobalite	0.126	Cristobalite	0.028	Cristobalite	0.028	Cristobalite	0.058	Cristobalite	0.089
Quartz	0.005	Quartz	0.015	Quartz	0.050	Quartz	0.039	Quartz	0.098	Quartz	0.043	Quartz	0.103
Feldspar	0.588	Feldspar	0.270	Feldspar	0.496	Feldspar	0.146	Feldspar	0.262	Feldspar	0.293	Feldspar	0.470
Glass	0.039	Glass	0.052	Glass	0.173	Glass	0.412	Glass	0.425	Glass	0.078	Glass	0.000
Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000	Hematite	0.000
Calcite	0.126	Calcite	0.000	Calcite	0.042	Calcite	0.000	Calcite	0.007	Calcite	0.001	Calcite	0.000
subtotal	0.991	subtotal	0.464	subtotal	0.934	subtotal	0.634	subtotal	0.854	subtotal	0.668	subtotal	0.814
porosity	0.127	porosity	0.523	porosity	0.104	porosity	0.356	porosity	0.204	porosity	0.348	porosity	0.168
Total	1.117	Total	0.987	Total	1.037	Total	0.990	Total	1.058	Total	1.016	Total	0.981

BCA. 4/29/98

Thick.

Average lithologic unit thicknesses								
	Paintbrush Group				Calico Hills Formation		Crater Flat Group	
Well[1]		Paintbrush Bedded						
	Tiva Canyon	Yucca Mtn.	Pah Canyon	Topopah Spring	Calico Hills	pre-Ta Bedded	Prow Pass	Bullfrog
USW G-1	0.00	0.00	0.00	362.80	95.00	19.00	**23.40**	0.00
USW H-5	149.30	15.90		356.00	51.80	19.80	97.00	**114.00**
USW G-4	36.00	6.20	18.20	359.20	91.10	17.50	**4.00**	0.00
UE-25a#1[3]	57.30	15.90		333.40	**54.60**	0.00	0.00	0.00
USW H-4	0.00	0.00	0.00	334.70	80.20	15.80	**22.80**	0.00
USW WT-2	64.00	0.00	0.00	314.90	66.10	22.60	**85.10**	0.00
USW H-3	0.00	0.00	0.00	301.20	28.90		128.10	**169.60**
USW G-3	113.90	15.30		301.50	28.60	14.30	137.50	**139.20**
avg.[2]	84.10	7.44	10.44	332.96	62.00	19.70	62.24	140.82
max.	149.30	7.95	18.20	362.80	95.00	38.90	193.90	169.60
min.	36.00	6.20	7.65	301.20	28.60	13.00	97.00	114.00
lith. volume (m^3)	4.37E+08	3.87E+07	5.43E+07	1.73E+09	3.22E+08	1.02E+08	3.24E+08	7.32E+08
avg. mean porosity[4]	0.227	0.333	0.494	0.144	0.314	0.266	0.293	0.187
avg. mean saturation[4]	0.666	0.61	0.375	0.743	0.823	1	0.845	0.99
pore volume (m^3)	9.93E+07	1.29E+07	2.68E+07	2.49E+08	1.01E+08	2.72E+07	9.48E+07	1.37E+08
saturated pore vol. (m^3)	6.61E+07	7.86E+06	1.01E+07	1.85E+08	8.33E+07	2.72E+07	8.01E+07	1.36E+08
pore air volume (m^3)	3.32E+07	5.02E+06	1.68E+07	6.41E+07	1.79E+07	0.00E+00	1.47E+07	1.37E+06
oxygen volume	6.96E+06	1.05E+06	3.52E+06	1.35E+07	3.76E+06	0.00E+00	3.09E+06	2.88E+05
moles of O_2 in pore air[5]	2.58E+08	3.91E+07	1.30E+08	4.99E+08	1.40E+08	0.00E+00	1.14E+08	1.07E+07
moles of H_20 in pores	1.54E+12	1.84E+11	2.35E+11	4.33E+12	1.95E+12	6.37E+11	1.87E+12	3.17E+12
total moles of O_2 in pores	**1.19E+09**							
total moles of H_2O in pores	**1.39E+13**							
1= Wells are in order from north to south.								
2= Average calculated using wells with an exposure of the unit.								
3= Well located outside the proposed repository footprint.								
4= porosity and saturation measurements from Flint, 1996; Matrix Properties of Hydrogeologic Units at Yucca Mtn., Nevada - USGS								
5= PV=nRT; P= 89876.01 PA (1000m altitude); R=8.31451 m^3*PA/mol*K; T=298 K.								
Note: Values for avg. mean porosity and saturation for the pre-Ta bedded unit are the measured values.								
Note: Thicknesses in **bold** are the depth to the SWL.								
molar volume of H_2O = 42.8 cm^3/mol								
USW G-2	74.7	77.1	79.7	304	249.8	38.9	176.1	89.1
USW WT-1	135.1	0	0	277.6	53.7	0	4.6	

BCG. 4/29/98

Por.&Sat.

porosity and saturation from Flint, 1996. Matrix properties of Hydrogeologic Units at Yucca Mtn., Nevada								
							avg. values for the unsaturated zone	
Geologic Unit	Hydrogeologic Unit	Mean Porosity	sd	Mean Saturation	sd		avg. Porosity	avg. saturation
Tiva Canyon	CCR	0.062	0.02	0.75	0.13		0.227	0.666
	CUC	0.253	0.06	0.4	0.17		0.333	0.61
	CUL	0.164	0.062	0.61	0.15		0.494	0.375
	CW	0.082	0.03	0.8	0.14		0.144	0.743
	CMW	0.203	0.054	0.9	0.13		0.314	0.823
	CNW	0.387	0.07	0.69	0.24		0.298	0.845
	BT4	0.439	0.123	0.51	0.19		0.187	0.99
	avg.	**0.227**		**0.666**			**0.285**	**0.722**
Yucca Mtn.	TPY	0.254	0.082	0.68	0.2			
	BT3	0.411	0.079	0.54	0.16			
	avg.	**0.333**		**0.61**				
Pah Canyon	TPP	0.499	0.041	0.36	0.13			
	BT2	0.489	0.105	0.39	0.15			
	avg.	**0.494**		**0.375**				
Topopah Canyon	TC	0.054	0.036	0.62	0.17			
	TR	0.157	0.03	0.51	0.13			
	TUL	0.154	0.031	0.72	0.15			
	TMN	0.11	0.02	0.85	0.12			
	TLL	0.13	0.031	0.78	0.14			
	TM2	0.112	0.031	0.85	0.1			
	TM1	0.094	0.019	0.87	0.09			
	PV3	0.036	0.039	0.88	0.14			
	PV2	0.173	0.106	0.84	0.16			
	BT1a	0.288	0.072	0.93	0.16			
	BT1	0.273	0.067	0.32	0.1			
	avg.	**0.144**		**0.743**				
Calico Hills	CHV	0.345	0.034	0.5	0.24			
	CHZ	0.331	0.039	0.97	0.07			
	BT	0.266	0.041	1	0.03			
	avg.	**0.314**		**0.823**				
Prow Pass	PP4	0.325	0.045	0.94	0.08			
	PP3	0.303	0.043	0.55	0.29			
	PP2	0.263	0.072	0.93	0.1			
	PP1	0.28	0.053	0.96	0.08			
	avg.	**0.293**		**0.845**				
Bull Frog	BF3	0.115	0.04	0.98	0.07			
	BF2	0.259	0.084	1	0.08			
	avg.	**0.187**		**0.99**				

Rec. 4/29/98

Approximation of total U concentration for oxidizing conditions for TPA 3.? :

$$U(\text{total}) = UO_2^{2+} + UO_2(CO_3)_2^{2-} + UO_2(CO_3)_3^{4-} + UO_2CO_3 + UO_2(OH)_2$$

2 $$UO_2(CO_3)_2^{2-} + 2H^+ \rightleftharpoons UO_2^{2+} + 2HCO_3^-$$

$$K_2 = \frac{[UO_2^{2+}][HCO_3^-]^2}{[aUO_2(CO_3)_2^{2-}][H^+]^2}$$

$$[UO_2(CO_3)_2^{2-}] = \frac{[UO_2^{2+}][HCO_3^-]^2}{K_2[H^+]^2}$$

3 $$UO_2(CO_3)_3^{4-} + 3H^+ \rightleftharpoons UO_2^{2+} + 3HCO_3^-$$

$$K_3 = \frac{[UO_2^{2+}][HCO_3^-]^3}{[UO_2(CO_3)_3^{4-}][H^+]^3}$$

$$[UO_2(CO_3)_3^{4-}] = \frac{[UO_2^{2+}][HCO_3^-]^3}{K_3[H^+]^3}$$

1 $$UO_2CO_3 + H^+ \rightleftharpoons UO_2^{2+} + HCO_3^-$$

$$K_1 = \frac{[UO_2^{2+}][HCO_3^-]}{[UO_2CO_3][H^+]}$$

$$[UO_2CO_3] = \frac{[UO_2^{2+}][HCO_3^-]}{K_1[H^+]}$$

5/18/98

o $UO_2(OH)_2 + 2H^+ \rightleftharpoons UO_2^{2+} + 2H_2O$

$$K_0 = \frac{[UO_2^{2+}][H_2O]^2}{[UO_2(OH)_2][H^+]^2}$$

$$[UO_2(OH)_2] = \frac{[UO_2^{2+}][H_2O]^2}{K_0 [H^+]^2}$$

$$\ln K = \ln K_\phi + \frac{\Delta H^\phi}{R}\left[\frac{1}{T^\phi} - \frac{1}{T}\right]$$

use enthalpy in kJ/mole on page 52

$\log K_{\phi 2}$	3.7136	ΔH_2^ϕ	-2350.96 kJ/mole
$\log K_{\phi 3}$	9.3804	ΔH_3^ϕ	-3083.89 kJ/mole
$\log K_{\phi 1}$	0.6468	ΔH_1^ϕ	-1689.23 kJ/mole
$\log K_{\phi o}$	10.3002	ΔH_o^ϕ	?

WM 5/18/98

Data consistent with NEA Uranium Thermodynamics Book - Grenthe et al. 1992.

WM 5/18/98

Uranyl from schoepite solubility

$UO_3 \cdot 2H_2O + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O$

$$K_s = \frac{[UO_2^{2+}][H_2O]^3}{[UO_3 \cdot 2H_2O][H^+]^2} \approx \frac{[UO_2^{2+}]}{[H^+]^2}$$

$$[UO_2^{2+}] = K_s [H^+]^2$$

$\log K = 4.8117$ $\quad \Delta H_r^\circ = -50.39 \frac{kJ}{mole}$

From Grenthe et al.

$\Delta G_f^\circ = -952.551 + 3(-237.14)$

$-(-1636.506) = -27.465$ kJ/mole

$\Delta G_r^\circ = -RT \ln K_r$

$$K = \exp\left(\frac{-\Delta G_r^\circ}{RT}\right) = \exp\left\{\frac{27.465 \text{ kJ/mole}}{0.0083144 \frac{kJ}{K\,mole}\ 298.15 K}\right\}$$

$= 64,818.$

$\log K = 4.8117$

WM 5/18/98

$\Delta H^\circ_r = -1019. + 3(-285.83)$ ~~-241.826~~ LWC 5/18/98

$-(-1826.1)$

$= -50.39$

Enthalpies of reaction reported on page 56 were really enthalpies of formation for the complexes. Correct values are calculated below using data from Grenthe et al,

$\Delta H^\phi_2 = 2(-586.895) + (-1019.)$ ~~-689.93~~

LWC 5/18/98

$-(-2350.96) =$ ~~-7990.1~~ -47.9 kJ/mole

LWC 5/18/96

$\Delta H^\phi_3 = 3(-689.93) + (-1019.)$

$-(-3083.89) = -4.9$ kJ/mole

$\Delta H^\phi_1 = -689.93 - 1019. + 1689.23$

$= -19.7$

$\Delta H^\phi_0 = -1019. + (-285.83)2 - ?$

See page 61 for estimation of ΔH^ϕ_0

LWC 5/12/98

Bicarbonate as a function of total carbonate:

$C_T = HCO_3^- + CO_3^{2-} + CO_{2(aq)}$

C_T is given by sampling in the TPA 3 code.

$HCO_3^- = C_T - CO_3^{2-} - CO_{2(aq)}$

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

$K_2 = \dfrac{[HCO_3^-]}{[CO_3^{2-}][H^+]}$

$CO_{2(aq)} + H_2O \rightleftharpoons HCO_3^- + H^+$

$K_0 = \dfrac{[HCO_3^-][H^+]}{[CO_{2aq}][H_2O]}$

$HCO_3^- \cong [HCO_3^-]$, etc.

$HCO_3^- = C_T - \dfrac{[HCO_3^-]}{K_2[H^+]} - \dfrac{[HCO_3^-][H^+]}{K_0[H_2O]}$

LWC (5/22/98)

$$HCO_3^- = C_T - \frac{[HCO_3^-]}{K_2[H^+]} - \frac{[HCO_3^-][H^+]}{K_0[H_2O]}$$

$$HCO_3^- + \frac{[HCO_3^-]}{K_2[H^+]} + \frac{[HCO_3^-][H^+]}{K_0[H_2O]} = C_T$$

$$HCO_3^- \left[1 + \frac{1}{K_2[H^+]} + \frac{[H^+]}{K_0[H_2O]}\right] = C_T$$

$$HCO_3^- = C_T \left[1 + \frac{1}{K_2[H^+]} + \frac{[H^+]}{K_0[H_2O]}\right]^{-1}$$

$$\ln K = \ln K_\phi + \frac{\Delta H^\phi}{R}\left[\frac{1}{T^\phi} - \frac{1}{T}\right]$$

	ΔH°_{298}
$\log K_{\phi\,0}{}_{298} = -6.3447$	9.51 kJ/mole
$\log K_{\phi\,2}{}_{298} = 10.3288$	-14.708 kJ/mole

Data from EQ3/6 Data base data0.com.R2
except ΔH°_f H_2O from Grauthe et al.

5/22/98

Reaction 0

$$UO_2(OH)_2 + 2H^+ \rightleftharpoons UO_2^{2+} + 2H_2O$$

$$\Delta H^\phi_0 = \Delta H^\circ_f(UO_2^{2+}) + 2\Delta H^\circ_f(H_2O) - (+\Delta H^\circ_f(UO_2(OH)_2))$$

$$= -1019. + 2(-285.83) + 1540.20 \text{ kJ/mole}$$

$$= -50.46 \text{ kJ/mole}$$

↑ See page 62

$\Delta H^\circ_f(UO_2(OH)_2)$ taken from
Shock et al. 1997
Geochimica Cosmochimica Acta
v. 61, p. 4247

(By unconvention Shock's $UO_3(aq)$ is equivalent to $UO_2(OH)_2(aq)$.
Thermodynamic properties of reactions such as $UO_2(OH)_2 \rightleftharpoons UO_3 + H_2O$ are defined to be zero.

9/23/98

Elaboration on $UO_2(OH)_2$ data

From Grenthe et al. '92:

$UO_2(OH)_2$ $\quad \Delta G^\circ_f \geq -1368.038$ kJ/mole

H_2O $\quad \Delta G^\circ_f = -237.140$ kJ/mole

From Shock et al. 1997:

UO_3 $\quad \Delta G^\circ_f = -270300$ cal/mole

$\quad \Delta H^\circ_f = -299600$ cal/mole

$\Delta G^\circ_f(UO_3) = \Delta G^\circ_f(UO_2(OH)_2) - \Delta G^\circ_f(H_2O)$

$= -1368.038 - (-237.140)$

$= -1130.898$ kJ/mole

$\div 4.1868 = -270.110$ kcal/mole

Shock's ΔG°_f is based on Grenthe's limit: confirmed as attested.

$\Delta H^\circ_f(UO_2(OH)_2) = \Delta H^\circ_f(UO_3) + \Delta H^\circ_f(H_2O)$

$= -299.600 \times 4.1868$ kJ/mole ~~-237.140~~ WW 9/24/98

-285.830 kJ/mole (from Grenthe)

$=$

-1540.195 kJ/mole

WW 9/24/98

Grenthe's value for $\Delta G^\circ_f(UO_2(OH)_2)$ is ~~an upper~~ a lower limit. The species is therefore less stable than this limit predicts. Use of this value in speciation/solubility calculations gives an upper limit for its concentration. WW 9/24/98

$\Delta H^\circ_f(UO_2(OH)_2)$ from Shock is based on the Grenthe value and is also a lower limit. So ΔH°_0 calculated on page 61 (= -50.46 kJ/mole) is an upper limit on the reaction enthalpy.

$$\ln K_{(T)} = \ln K_{(T_0)} + \frac{\Delta H^\circ}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

for ΔH° = negative and $\left(\frac{1}{T_0} - \frac{1}{T}\right)$ = positive

$\ln K_{(T)}$ gets smaller with increasing T:

$UO_2(OH)_2$ increases stability with increasing T.

WW 9/24/98

If ΔH° for the reaction

$UO_2(OH)_2 + 2H^+ \rightleftharpoons UO_2^{2+} + 2H_2O$

is more negative than the upper limit of -50.46 kJ/mole the $UO_2(OH)_2$, then the stability of the species would increase more with increasing temperature. Therefore use of the limiting values of ΔG° and ΔH° gives a maximum limit for $UO_2(OH)_2$ at 25°C, but underestimates the increase in its stability with increasing T.

WM 9/24/98

Theoretical waters for uranophane solubility experiments

EQ3 runs are attached to pages 67 + 69, without and with carbonate, respectively.

Stoichiometric uranophane dissolution reaction is

$$Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5H_2O + 6H^+ \rightleftharpoons$$

$$Ca^{2+} + 2UO_2^{2+} + 2SiO_2 + 9H_2O$$

$$\log Q_0 \equiv \frac{a_{Ca^{2+}} a_{UO_2^{2+}}^2 a_{SiO_2}^2}{a_{H^+}^6}$$

WM 4/20/99

for unit activity of uranophane and H_2O

from carbonate-free EQ3 run

$$\log Q_0 = \frac{10^{-2.2723}\ 10^{(-5.8036)2}\ 10^{-4.0\times2}}{10^{-4.0\times6}}$$

WM 4/20/99

$$\log Q_0 = 2.1205$$

log K from data0.com.R2 from Langmuir 78 = 17.285

WM 4/20/99

EQ6 files attached to the following pages 67 and 69 are models to test water compositions for forthcoming urenophane experiments.

4/20/99

```
EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-UNIX)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-SPARC)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-SPARC)

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California, Lawrence Livermore National Laboratory. All rights
reserved.

This work is subject to additional statements and
disclaimers which may be found in the README.txt file
included in the EQ3/6 software transmittal package.


Run  14:17:04  13Nov95


--- Reading the input file ---

Input file name = Uranophane solubility experiments

Computations by William M. Murphy November 1995
endit.
     tempc=  0.25000E+02
       rho=  0.10000E+01    tdspkg=  0.00000E+00     tdspl=  0.00000E+00
       fep= -0.70000E+00    uredox=
    tolbt=  0.00000E+00     toldl=  0.00000E+00    tolsat=  0.00000E+00
   itermx=  0
              1    2    3    4    5    6    7    8    9   10
  iopt1-10=   0    0    0    1    0    0    0    0    0    0
  iopg1-10=   0    0    0    0    1    0    0    0    0    0
  iopr1-10=   0    0    0   -2    0    0    0    0    0    0
 iopr11-20=   0    0    0    0    0    0    0    0    0    0
  iodb1-10=   0    0    0    0    0    0    0    0    0    0
     uebal= Cl-
     nxmod=  0
data file master species= Cl-
   switch with species=
   jflag=  0   csp=  0.10000E-01
data file master species= Ca++
   switch with species=
   jflag=  0   csp=  0.10000E-01
data file master species= SiO2(aq)
   switch with species=
   jflag=  0   csp=  0.10000E-03
data file master species= H+
   switch with species=
   jflag= 16   csp= -0.40000E+01
data file master species= UO2++
   switch with species=
   jflag= 19   csp=  0.10000E-05
  uphas1= Soddyite                  uphas2=
endit.

--- The input file has been successfully read ---

--- Reading the data1 file ---

--- The data1 file has been successfully read ---

* note - (eqlib/inbdot) The following aqueous species
       have been assigned a default hard core diameter of
         4.000 Angstroms-
         CaCl2(aq)
```

```
eeee   qqq   33333  n   n  rrrr
e     q   q      3  nn  n  r   r
eeee  q   q    33   n n n  rrrr
e     q q q      3  n  nn  r  r
eeee   qqq   3333   n   n  r   r
          q
```

EQ3NR, version 7.2b (R139)
supported by EQLIB, version 7.2b (R168)

Input file name = Uranophane solubility experiments

Computations by William M. Murphy November 1995

data0.com.R2
CII: GEMBOCHS.V2-EQ8-DATA0.COM.R2
THERMODYNAMIC DATABASE
generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06
Output package: eq3
Data set: com

The activity coefficients of aqueous solute species
and the activity of water are calculated according to the
B-dot equation plus others

Temperature= 25.00 degrees Celsius
pressure= 1.0132 bars

79 elements are in the data base
100 elements can be loaded into memory
6 elements are active in this problem

972 aqueous species are in the data base
206 aqueous species were loaded into memory
800 aqueous species can be loaded into memory
43 aqueous species are active in this problem

892 aqueous reactions are in the data base
126 aqueous reactions were loaded into memory
699 aqueous reactions can be loaded into memory

942 minerals are in the data base
71 minerals were loaded into memory
850 minerals can be loaded into memory
71 minerals are active in this problem

12 solid solutions are in the data base
50 solid solutions can be loaded into memory

88 gases are in the data base
20 gases were loaded into memory
80 gases can be loaded into memory
20 gases are active in this problem

iopt1 = 0 (redox option switch)
iopt2 = 0 (automatic basis switching switch)
iopt3 = 0 (interfacing output control switch)
iopt4 = 1 (turn-on solid solutions switch)
iopt5 = 0 (not used)

```
iopt6  =  0 (conv. test criteria switch)
iopt7  =  0 (0/1 version 7/post-version 7 pickup file)
iopt8  =  0 (not used)
iopt9  =  0 (not used)
iopt10 =  0 (not used)


      iopg1  =  0 (act. coeff. choice)
      iopg2  =  0 (pH scale convention switch)
      iopg3  =  0 (not used)
      iopg4  =  0 (not used)
      iopg5  =  1 (not used)
      iopg6  =  0 (not used)
      iopg7  =  0 (not used)
      iopg8  =  0 (not used)
      iopg9  =  0 (not used)
      iopg10 =  0 (not used)


           iopr1  =  0 (list loading of species)
           iopr2  =  0 (list reactions and log K values)
           iopr3  =  0 (aqueous species print order control)
           iopr4  = -2 (aqueous species print cut-off control)
           iopr5  =  0 (mass balance percentages print control)
           iopr6  =  0 (mean ionic act coeff print control)
           iopr7  =  0 (mineral affinity print control)
           iopr8  =  0 (ion size and hydr. no. print control)
           iopr9  =  0 (Pitzer coefficients tabulation)
           iopr10 =  0 (print concbs array)
           iopr11 =  0 (not used)
           iopr12 =  0 (not used)
           iopr13 =  0 (not used)
           iopr14 =  0 (not used)
           iopr15 =  0 (not used)
           iopr16 =  0 (not used)
           iopr17 =  0 (not used)
           iopr18 =  0 (not used)
           iopr19 =  0 (not used)
           iopr20 =  0 (not used)


                iodb1  =  0 (print info. messages switch)
                iodb2  =  0 (print pre-Newton-Raphson optimizations switch)
                iodb3  =  0 (request iteration variables to kill)
                iodb4  =  0 (print Newton-Raphson iterations switch)
                iodb5  =  0 (list stoichiometric equivalences)
                iodb6  =  0 (controls iodb5 level of detail)
                iodb7  =  0 (write reactions on file rlist switch)
                iodb8  =  0 (not used)
                iodb9  =  0 (not used)
                iodb10 =  0 (not used)

The default redox state is constrained by log fO2 =   -0.7000 (log bars)

           Solution density =  1.00000 g/mL

           Total dissolved salts =       0.00 mg/kg solution
           Total dissolved salts =       0.00 mg/L


      Tolbt  =  0.10000E-05 (convergence tolerance on residual functions)
      Toldl  =  0.10000E-05 (convergence tolerance on correction terms)
      Tolsat =  0.50000E+00 (phase saturation tolerance, does not affect
                             convergence)


                --- Input Constraints ---
```

Species	Csp	Jflag	Input Type/Co-species
Cl-	1.0000E-02	0	Total conc, molal
Ca++	1.0000E-02	0	Total conc, molal
SiO2(aq)	1.0000E-04	0	Total conc, molal
H+	-4.0000E+00	16	Log activity
UO2++	1.0000E-06	19	Mineral equilibrium Soddyite

	1.000	Soddyite
+	4.000	H+
	==	
	4.000	H2O
+	1.000	SiO2(aq)
+	2.000	UO2++

Electrical balance will be achieved by adjusting
the concentration of "Cl- ". Any other specified
constraint will be overridden.

--- Inactive Aqueous Species ---

--- Modified Input Constraints ---

Species	Csp	Jflag	Input Type/Co-species
Ca++	1.0000E-02	0	Total conc, molal
Cl-	1.0000E-02	0	Total conc, molal
H+	-4.0000E+00	16	Log activity
SiO2(aq)	1.0000E-04	0	Total conc, molal
UO2++	1.0000E-06	19	Mineral equilibrium Soddyite

	1.000	Soddyite
+	4.000	H+
	==	
	4.000	H2O
+	1.000	SiO2(aq)
+	2.000	UO2++

ClO-	0.0000E+00	30	Eliminated species
ClO2-	0.0000E+00	30	Eliminated species
ClO3-	0.0000E+00	30	Eliminated species
ClO4-	0.0000E+00	30	Eliminated species
H2(aq)	0.0000E+00	27	Dependent species
O2(aq)	0.0000E+00	27	Dependent species
U+++	0.0000E+00	30	Eliminated species
U++++	0.0000E+00	30	Eliminated species
UO2+	0.0000E+00	30	Eliminated species

--- Optimization ended within requested limits ---

iter= 0
del( )= 0.00000E+00, delfnc= 0.00000E+00
beta(conc Cl-)= 3.36244E-01, betfnc= 0.00000E+00
bbig= 3.36244E-01, ubbig= Cl-
bneg= 0.00000E+00, ubneg= none
bgamx= 9.71722E-06, ubgamx= H4(H2SiO4)4----
bsigmm= -1.88365E-05
bxi= -2.25241E-05
btfcnr= 0.00000E+00

```
iter=   1
       del(conc     Cl-      )=  4.38499E-01, delfnc=  0.00000E+00
      beta(conc     Cl-      )= -1.54449E-01, betfnc=  5.40662E-01
        bbig=  6.63815E-04, ubbig= Ca++
        bneg= -1.54449E-01, ubneg= Cl-
        bgamx= -1.34462E-01, ubgamx= H4(H2SiO4)4----
        bsigmm=  8.51822E-01
        bxi=  3.46544E-01
        btfcnr=  5.40811E-01

iter=   2
       del(conc     Cl-      )= -1.16248E-01, delfnc=  7.34896E-01
      beta(conc     Cl-      )= -2.18859E-02, betfnc=  8.58297E-01
        bbig=  1.57401E-04, ubbig= Ca++
        bneg= -2.18859E-02, ubneg= Cl-
        bgamx=  4.67190E-02, ubgamx= H4(H2SiO4)4----
        bsigmm= -1.70133E-01
        bxi= -9.54800E-02
        btfcnr=  8.58211E-01

iter=   3
       del(conc     Cl-      )= -1.86619E-02, delfnc=  8.39465E-01
      beta(conc     UO2++    )= -1.09717E-03, betfnc=  9.49869E-01
        bbig=  9.80055E-06, ubbig= Ca++
        bneg= -4.72816E-04, ubneg= Cl-
        bgamx=  6.69459E-03, ubgamx= H4(H2SiO4)4----
        bsigmm= -2.81144E-02
        bxi= -1.45241E-02
        btfcnr=  9.78312E-01

iter=   4
       del(conc     UO2++    )= -1.72162E-03, delfnc=  9.07746E-01
      beta(conc     UO2++    )= -2.44480E-05, betfnc=  9.77717E-01
        bbig=  1.70347E-07, ubbig= Ca++
        bneg= -1.86626E-07, ubneg= Cl-
        bgamx=  1.49255E-04, ubgamx= H4(H2SiO4)4----
        bsigmm= -6.33531E-04
        bxi= -3.26875E-04
        btfcnr=  9.99792E-01

iter=   5
       del(conc     UO2++    )= -3.83827E-05, delfnc=  9.77706E-01
      beta(conc     UO2++    )= -2.65165E-08, betfnc=  9.98915E-01
        bbig=  1.83573E-10, ubbig= Ca++
        bneg= -4.86536E-14, ubneg= SiO2(aq)
        bgamx=  1.61886E-07, ubgamx= H4(H2SiO4)4----
        bsigmm= -4.84931E-07
        bxi= -3.54612E-07
        btfcnr=  1.00000E+00

iter=   6
       del(conc     UO2++    )= -4.16308E-08, delfnc=  9.98915E-01
      beta(conc     UO2++    )= -1.63336E-11, betfnc=  9.99384E-01
        bbig=  1.13451E-13, ubbig= Ca++
        bneg=  0.00000E+00, ubneg= none
        bgamx=  9.97171E-11, ubgamx= H4(H2SiO4)4----
        bsigmm= -1.98950E-10
        bxi= -2.18431E-10
        btfcnr=  1.00000E+00


Hybrid Newton-Raphson iteration converged in   6 steps.


                --- Summary of the Aqueous Solution ---

          --- Elemental Composition of the Aqueous Solution ---
```

Element	mg/L	mg/kg	Moles/kg
O	0.88811E+06	0.88811E+06	0.5550914235E+02
Ca	400.78	400.78	0.1000000000E-01
Cl	713.38	713.38	0.2012190899E-01
H	0.11190E+06	0.11190E+06	0.1110169858E+03
Si	2.8086	2.8086	0.1000000000E-03
U	0.76940	0.76940	0.3232384775E-05

--- Elemental Composition as Strict Basis Species ---

Species	mg/L	mg/kg	Moles/kg
H2O	0.10000E+07	0.10000E+07	0.5550914235E+02
Ca++	400.78	400.78	0.1000000000E-01
Cl-	713.38	713.38	0.2012190899E-01
H+	0.11190E+06	0.11190E+06	0.1110169858E+03
SiO2(aq)	6.0084	6.0084	0.1000000000E-03
UO2++	0.87283	0.87283	0.3232384775E-05

--- Equivalent Composition of the Aqueous Solution ---

--- Original Basis ---

Species	Moles/kg H2O
H2O	0.5550914235E+02
Ca++	0.1000000000E-01
Cl-	0.2012190899E-01
H+	0.1110169858E+03
SiO2(aq)	0.1000000000E-03
UO2++	0.3232384775E-05

--- Current Basis (cte) ---

Species	Moles/kg H2O
H2O	0.5550914235E+02
Ca++	0.1000000000E-01
Cl-	0.2012190899E-01
H+	0.1110169858E+03
SiO2(aq)	0.1000000000E-03
UO2++	0.3232384775E-05

Single ion activities and activity coefficients are here defined
with respect to the modified NBS pH scale

	pH	Eh	pe
modified NBS pH scale	4.0000	0.9821	1.6601E+01
rational pH scale	3.9385	0.9857	1.6663E+01

pHCl = 5.7672

Activity of water = 0.99950
Log activity of water = -0.00022

True osmotic coefficient= 0.90466
Stoichiometric osmotic coefficient= 0.90398

Sum of true molalities= 0.0305680639170
Sum of stoichiometric molalities= 0.0305910625085

True ionic strength= 0.0300797424341
Stoichiometric ionic strength= 0.0301252082788

--- Electrical Balance Totals ---

	equiv/kg H2O
Sigma(mz) cations =	0.2009891186E-01
Sigma(mz) anions =	-0.2009891186E-01
Total charge =	0.4019782371E-01
Mean charge =	0.2009891186E-01
Charge imbalance =	0.1117161919E-14

Total charge = sigma(mz) cations + abs (sigma(mz) anions)
Mean charge = 1/2 total charge

The electrical imbalance is

0.278E-11 per cent of the total charge
0.556E-11 per cent of the mean charge
0.556E-11 per cent of sigma(mz) cations
0.556E-11 per cent of abs (sigma(mz) anions)

--- Electrical Balancing on Cl- ---

	mg/L	mg/kg	Moles/kg
input	354.53	354.53	0.1000000000E-01
final	713.38	713.38	0.2012190899E-01
adj	358.85	358.85	0.1012190899E-01

--- Activity Ratios of Ions -----

Log (act(Ca++	) / act(H+)xx 2) =	5.7277
Log (act(Cl-	) x act(H+)xx 1) =	-5.7672
Log (act(SiO2(aq)	) =	-4.0000
Log (act(UO2++	) / act(H+)xx 2) =	2.1964
Log (act(ClO-	) x act(H+)xx 1) =	-22.6678
Log (act(ClO2-	) x act(H+)xx 1) =	-32.4735
Log (act(ClO3-	) x act(H+)xx 1) =	-28.4255
Log (act(ClO4-	) x act(H+)xx 1) =	-28.6729
Log (act(H2(aq)	) =	-44.3077
Log (act(O2(aq)	) =	-3.5983
Log (act(U+++	) / act(H+)xx 3) =	-59.9076
Log (act(U++++	) / act(H+)xx 4) =	-29.9533
Log (act(UO2+	) / act(H+)xx 1) =	-16.9210

--- Distribution of Aqueous Species ---

(Species with concentrations .lt. 1.e-12 are not listed)

Species	Molality	Log molality	Log gamma	Log activity
Cl-	2.0099E-02	-1.6968	-0.0704	-1.7672
Ca++	9.9778E-03	-2.0010	-0.2713	-2.2723
O2(aq)	2.5034E-04	-3.6015	0.0032	-3.5983
H+	1.1521E-04	-3.9385	-0.0615	-4.0000
SiO2(aq)	1.0000E-04	-4.0000	0.0000	-4.0000
CaCl+	2.1877E-05	-4.6600	-0.0751	-4.7351
UO2++	3.0603E-06	-5.5142	-0.2893	-5.8036
HCl(aq)	3.6542E-07	-6.4372	0.0000	-6.4372
CaCl2(aq)	3.5454E-07	-6.4503	0.0000	-6.4503
UO2OH+	1.1588E-07	-6.9360	-0.0751	-7.0111
UO2Cl+	4.5870E-08	-7.3385	-0.0751	-7.4136
UO2(OH)2(aq)	7.6103E-09	-8.1186	0.0000	-8.1186

(UO2)2(OH)2++	1.1147E-09	-8.9528	-0.2893	-9.2422
(UO2)2OH+++	2.0784E-10	-9.6823	-0.6323	-10.3146
HSiO3-	1.3006E-10	-9.8858	-0.0669	-9.9527
OH-	1.1887E-10	-9.9249	-0.0704	-9.9953
UO2Cl2(aq)	3.4412E-11	-10.4633	0.0000	-10.4633
CaOH+	8.9657E-12	-11.0474	-0.0751	-11.1225

--- Major Aqueous Species Contributing to Mass Balances ---

Aqueous species accounting for 99% or more of Ca++

Species	Factor	Molality	Per Cent
Ca++	1.00	9.9778E-03	99.78
Total		1.0000E-02	99.78

Aqueous species accounting for 99% or more of Cl-

Species	Factor	Molality	Per Cent
Cl-	1.00	2.0099E-02	99.89
Total		2.0122E-02	99.89

Aqueous species accounting for 99% or more of SiO2(aq)

Species	Factor	Molality	Per Cent
SiO2(aq)	1.00	1.0000E-04	100.00
Total		1.0000E-04	100.00

Aqueous species accounting for 99% or more of UO2++

Species	Factor	Molality	Per Cent
UO2++	1.00	3.0603E-06	94.68
UO2OH+	1.00	1.1588E-07	3.59
UO2Cl+	1.00	4.5870E-08	1.42
Total		3.2324E-06	99.68

--- Summary of Aqueous Redox Reactions ---

Couple		Eh, volts	pe-	Log fO2	Ah, kcal
DEFAULT		0.982	0.1660E+02	-0.700	22.649
ClO-	/Cl-	0.982	0.1660E+02	-0.700	22.649
ClO2-	/Cl-	0.982	0.1660E+02	-0.700	22.649
ClO3-	/Cl-	0.982	0.1660E+02	-0.700	22.649
ClO4-	/Cl-	0.982	0.1660E+02	-0.700	22.649
H2(aq)	/H2O	0.982	0.1660E+02	-0.700	22.649
O2(aq)	/H2O	0.982	0.1660E+02	-0.700	22.649
U+++	/UO2++	0.982	0.1660E+02	-0.700	22.649
U++++	/UO2++	0.982	0.1660E+02	-0.700	22.649
UO2+	/UO2++	0.982	0.1660E+02	-0.700	22.649

--- Summary of Aqueous Non-equilibrium Non-redox Neactions ---

Reaction	Log Q/K	Aff, kcal	State
None			

--- Summary of Pure Mineral Saturation States ---

(Minerals with affinities .lt. -10 kcal are not listed)

Mineral	Log Q/K	Aff, kcal	State
Chalcedony	-0.272	-0.371	satd
Coesite	-0.811	-1.106	
Cristobalite(alpha)	-0.551	-0.752	
Cristobalite(beta)	-0.995	-1.357	
Haiweeite	-6.840	-9.332	
Ice	-0.139	-0.190	satd
Quartz	-0.001	-0.001	satd
Schoepite	-2.638	-3.598	
Schoepite-dehy(.393)	-4.528	-6.178	
Schoepite-dehy(.648)	-4.010	-5.471	
Schoepite-dehy(.85)	-2.901	-3.958	
Schoepite-dehy(.9)	-2.821	-3.848	
Schoepite-dehy(1.0)	-2.907	-3.966	
SiO2(am)	-1.286	-1.755	
Soddyite	0.000	0.000	satd
Tridymite	-0.172	-0.235	satd
UO2(OH)2(beta)	-2.750	-3.751	
UO2ClOH:2H2O	-5.878	-8.019	
UO3(alpha)	-6.443	-8.790	
UO3(beta)	-6.113	-8.340	
UO3(gamma)	-5.511	-7.519	
UO3:.9H2O(alpha)	-2.821	-3.848	
UO3:2H2O	-2.638	-3.598	

--- Summary of Hypothetical Solid Solutions ---

5 approx. saturated pure minerals
0 approx. saturated input solid solutions
0 saturated hypothetical solid solutions

0 supersaturated pure minerals
0 supersatd. input solid solutions
0 supersatd. hypothetical solid solutions

--- Summary of Gases ---

Gas	Fugacity	Log fugacity
Ca(g)	2.8104-158	-157.5512
Chlorine	4.6365E-17	-16.3338
H2(g)	6.2702E-42	-41.2027
H2O(g)	2.5965E-02	-1.5856
HCl(g)	8.4584E-13	-12.0727
O2(g)	1.9953E-01	-0.7000
Si(g)	4.4402-221	-220.3526
U(g)	1.7767-291	-290.7504
U2Cl10(g)	5.3052-175	-174.2753
U2Cl8(g)	3.5474-189	-188.4501
UCl(g)	1.3226-241	-240.8786
UCl2(g)	2.9452-190	-189.5309
UCl3(g)	1.4365-136	-135.8427
UCl4(g)	3.7941-100	-99.4209
UCl5(g)	5.1558-101	-100.2877
UCl6(g)	1.3017E-96	-95.8855
UO(g)	1.3678-206	-205.8640

```
UO2(g)                          2.4701-122    -121.6073
UO2Cl2(g)                       5.0005E-58     -57.3010
UO3(g)                          1.7710E-69     -68.7518

--- Reading the input file ---

--- No further input found ---

         Start time = 14:17:04  13Nov95
           End time = 14:17:07  13Nov95

          Run time =    3.00     seconds
         User time =    2.62     seconds
          Cpu time =   0.483     seconds

Normal exit
```

Dronedarone solubility calculations
attached to following page

4/20/99

```
EQ3/6, Version 7.2b (EQ3/6-V7-REL-V7.2b-UNIX)
EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R139-SPARC)
Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R168-SPARC)

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reserved.

This work is subject to additional statements and
disclaimers which may be found in the README.txt file
included in the EQ3/6 software transmittal package.


Run  08:16:14  20Apr99


--- Reading the input file ---

Input file name = Uranophane solubility experiments

Computations by William M. Murphy November 1995 and April 1999
endit.
     tempc=  0.25000E+02
       rho=  0.10000E+01    tdspkg=  0.00000E+00     tdspl=  0.00000E+00
       fep= -0.70000E+00    uredox=
     tolbt=  0.00000E+00     toldl=  0.00000E+00    tolsat=  0.00000E+00
    itermx=  0
                1    2    3    4    5    6    7    8    9   10
  iopt1-10=     0    0    0    1    0    0    0    0    0    0
  iopg1-10=     0    0    0    0    1    0    0    0    0    0
  iopr1-10=     0    0    0   -2    0    0    0    0    0    0
 iopr11-20=     0    0    0    0    0    0    0    0    0    0
  iodb1-10=     0    0    0    0    0    0    0    0    0    0
     uebal= Cl-
     nxmod=  0
data file master species= Cl-
   switch with species=
   jflag=  0   csp=  0.10000E-01
data file master species= Ca++
   switch with species=
   jflag=  0   csp=  0.10000E-01
data file master species= SiO2(aq)
   switch with species=
   jflag=  0   csp=  0.10000E-03
data file master species= H+
   switch with species=
   jflag= 16   csp= -0.40000E+01
data file master species= UO2++
   switch with species=
   jflag= 19   csp=  0.10000E-05
  uphas1= Soddyite                  uphas2=
data file master species= HCO3-
   switch with species=
   jflag= 21   csp= -0.35000E+01
  uphas1= CO2(g)                    uphas2=
endit.

 --- The input file has been successfully read ---

 --- Reading the data1 file ---

 --- The data1 file has been successfully read ---

 * note - (eqlib/inbdot) The following aqueous species
        have been assigned a default hard core diameter of
          4.000 Angstroms-
          CO(aq)
          Ca(CH3COO)2(aq)
          CaCO3(aq)
          CaCl2(aq)




 eeee   qqq   33333  n   n  rrrr
 e     q   q      3  nn  n  r   r
 eeee  q   q    33   n n n  rrrr
```

```
e     q q q      3  n  nn  r  r
eeee   qqq   3333   n   n  r   r
         q
```

EQ3NR, version 7.2b (R139)
supported by EQLIB, version 7.2b (R168)

Input file name = Uranophane solubility experiments

Computations by William M. Murphy November 1995 and April 1999

data0.com.R2
CII: GEMBOCHS.V2-EQ8-DATA0.COM.R2
THERMODYNAMIC DATABASE
generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06
Output package: eq3
Data set: com
+---

The activity coefficients of aqueous solute species
and the activity of water are calculated according to the
B-dot equation plus others

Temperature= 25.00 degrees Celsius
pressure= 1.0132 bars

79 elements are in the data base
100 elements can be loaded into memory
7 elements are active in this problem

972 aqueous species are in the data base
286 aqueous species were loaded into memory
800 aqueous species can be loaded into memory
139 aqueous species are active in this problem

892 aqueous reactions are in the data base
206 aqueous reactions were loaded into memory
699 aqueous reactions can be loaded into memory

942 minerals are in the data base
82 minerals were loaded into memory
850 minerals can be loaded into memory
82 minerals are active in this problem

12 solid solutions are in the data base
50 solid solutions can be loaded into memory

88 gases are in the data base
25 gases were loaded into memory
80 gases can be loaded into memory
25 gases are active in this problem

iopt1 = 0 (redox option switch)
iopt2 = 0 (automatic basis switching switch)
iopt3 = 0 (interfacing output control switch)
iopt4 = 1 (turn-on solid solutions switch)
iopt5 = 0 (not used)
iopt6 = 0 (conv. test criteria switch)
iopt7 = 0 (0/1 version 7/post-version 7 pickup file)
iopt8 = 0 (not used)
iopt9 = 0 (not used)
iopt10 = 0 (not used)

iopg1 = 0 (act. coeff. choice)
iopg2 = 0 (pH scale convention switch)
iopg3 = 0 (not used)
iopg4 = 0 (not used)
iopg5 = 1 (not used)

```
iopg6  =  0 (not used)
iopg7  =  0 (not used)
iopg8  =  0 (not used)
iopg9  =  0 (not used)
iopg10 =  0 (not used)
```

```
iopr1  =  0 (list loading of species)
iopr2  =  0 (list reactions and log K values)
iopr3  =  0 (aqueous species print order control)
iopr4  = -2 (aqueous species print cut-off control)
iopr5  =  0 (mass balance percentages print control)
iopr6  =  0 (mean ionic act coeff print control)
iopr7  =  0 (mineral affinity print control)
iopr8  =  0 (ion size and hydr. no. print control)
iopr9  =  0 (Pitzer coefficients tabulation)
iopr10 =  0 (print concbs array)
iopr11 =  0 (not used)
iopr12 =  0 (not used)
iopr13 =  0 (not used)
iopr14 =  0 (not used)
iopr15 =  0 (not used)
iopr16 =  0 (not used)
iopr17 =  0 (not used)
iopr18 =  0 (not used)
iopr19 =  0 (not used)
iopr20 =  0 (not used)
```

```
iodb1  =  0 (print info. messages switch)
iodb2  =  0 (print pre-Newton-Raphson optimizations switch)
iodb3  =  0 (request iteration variables to kill)
iodb4  =  0 (print Newton-Raphson iterations switch)
iodb5  =  0 (list stoichiometric equivalences)
iodb6  =  0 (controls iodb5 level of detail)
iodb7  =  0 (write reactions on file rlist switch)
iodb8  =  0 (not used)
iodb9  =  0 (not used)
iodb10 =  0 (not used)
```

The default redox state is constrained by log fO2 = -0.7000 (log bars)

```
Solution density =  1.00000 g/mL

Total dissolved salts =       0.00 mg/kg solution
Total dissolved salts =       0.00 mg/L
```

```
Tolbt  =  0.10000E-05 (convergence tolerance on residual functions)
Toldl  =  0.10000E-05 (convergence tolerance on correction terms)
Tolsat =  0.50000E+00 (phase saturation tolerance, does not affect
                       convergence)
```

--- Input Constraints ---

Species	Csp	Jflag	Input Type/Co-species
Cl-	1.0000E-02	0	Total conc, molal
Ca++	1.0000E-02	0	Total conc, molal
SiO2(aq)	1.0000E-04	0	Total conc, molal
H+	-4.0000E+00	16	Log activity
UO2++	1.0000E-06	19	Mineral equilibrium Soddyite
	1.000 Soddyite + 4.000 H+ == 4.000 H2O + 1.000 SiO2(aq) + 2.000 UO2++		
HCO3-	-3.5000E+00	21	Gas equilibrium CO2(g)
	1.000 CO2(g) + 1.000 H2O == 1.000 H+		

```
                  +  1.000  HCO3-

Electrical balance will be achieved by adjusting
  the concentration of "Cl-                    ". Any other specified
  constraint will be overridden.

          --- Inactive Aqueous Species ---


                        --- Modified Input Constraints ---

   Species                      Csp       Jflag   Input Type/Co-species

Ca++                      1.0000E-02     0     Total conc, molal
Cl-                       1.0000E-02     0     Total conc, molal
H+                       -4.0000E+00    16     Log activity
HCO3-                    -3.5000E+00    21     Gas equilibrium
                                                 CO2(g)

                     1.000  CO2(g)
                  +  1.000  H2O
                        ==
                     1.000  H+
                  +  1.000  HCO3-
HCO3-                    -3.5000E+00    21     Gas equilibrium
SiO2(aq)                  1.0000E-04     0     Total conc, molal
UO2++                     1.0000E-06    19     Mineral equilibrium
                                                 Soddyite

                     1.000  Soddyite
                  +  4.000  H+
                        ==
                     4.000  H2O
                  +  1.000  SiO2(aq)
                  +  2.000  UO2++
Acetic acid(aq)           0.0000E+00    30     Eliminated species
Acetone(aq)               0.0000E+00    30     Eliminated species
Benzene(aq)               0.0000E+00    30     Eliminated species
Butanoic acid(aq)         0.0000E+00    30     Eliminated species
ClO-                      0.0000E+00    30     Eliminated species
ClO2-                     0.0000E+00    30     Eliminated species
ClO3-                     0.0000E+00    30     Eliminated species
ClO4-                     0.0000E+00    30     Eliminated species
Ethane(aq)                0.0000E+00    30     Eliminated species
Ethanol(aq)               0.0000E+00    30     Eliminated species
Ethylene(aq)              0.0000E+00    30     Eliminated species
Ethyne(aq)                0.0000E+00    30     Eliminated species
Formic acid(aq)           0.0000E+00    30     Eliminated species
H2(aq)                    0.0000E+00    27     Dependent species
Methane(aq)               0.0000E+00    30     Eliminated species
O2(aq)                    0.0000E+00    27     Dependent species
Pentanoic acid(aq)        0.0000E+00    30     Eliminated species
Phenol(aq)                0.0000E+00    30     Eliminated species
Propanoic acid(aq)        0.0000E+00    30     Eliminated species
Toluene(aq)               0.0000E+00    30     Eliminated species
U+++                      0.0000E+00    30     Eliminated species
U++++                     0.0000E+00    30     Eliminated species
UO2+                      0.0000E+00    30     Eliminated species
o-Phthalate               0.0000E+00    30     Eliminated species


--- Optimization ended within requested limits ---


iter=   0
       del(                 )=  0.00000E+00, delfnc=  0.00000E+00
      beta(conc    Cl-      )=  3.36241E-01, betfnc=  0.00000E+00
        bbig=  3.36241E-01, ubbig= Cl-
        bneg=  0.00000E+00, ubneg= none
        bgamx=  2.20925E-05, ubgamx= (UO2)3(CO3)6(6-)
        bsigmm= -1.82110E-05
        bxi= -2.25334E-05
        btfcnr=  0.00000E+00

iter=   1
```

```
      del(conc    Cl-     )=  4.38497E-01, delfnc=  0.00000E+00
     beta(conc    Cl-     )= -1.54448E-01, betfnc=  5.40664E-01
       bbig=  6.63783E-04, ubbig= Ca++
       bneg= -1.54448E-01, ubneg= Cl-
       bgamx= -3.05761E-01, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm=  8.51367E-01
       bxi=  3.46540E-01
       btfcnr=  5.40813E-01

iter=   2
      del(conc    Cl-     )= -1.16247E-01, delfnc=  7.34896E-01
     beta(conc    Cl-     )= -2.18855E-02, betfnc=  8.58299E-01
       bbig=  1.57406E-04, ubbig= Ca++
       bneg= -2.18855E-02, ubneg= Cl-
       bgamx=  1.06278E-01, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm= -1.70084E-01
       bxi= -9.54789E-02
       btfcnr=  8.58213E-01

iter=   3
      del(conc    Cl-     )= -1.86615E-02, delfnc=  8.39467E-01
     beta(conc    UO2++   )= -1.09715E-03, betfnc=  9.49869E-01
       bbig=  9.80142E-06, ubbig= Ca++
       bneg= -4.72797E-04, ubneg= Cl-
       bgamx=  1.52254E-02, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm= -2.81041E-02
       bxi= -1.45238E-02
       btfcnr=  9.78312E-01

iter=   4
      del(conc    UO2++   )= -1.72160E-03, delfnc=  9.07746E-01
     beta(conc    UO2++   )= -2.44471E-05, betfnc=  9.77718E-01
       bbig=  1.70365E-07, ubbig= Ca++
       bneg= -1.86604E-07, ubneg= Cl-
       bgamx=  3.39432E-04, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm= -6.33249E-04
       bxi= -3.26863E-04
       btfcnr=  9.99792E-01

iter=   5
      del(conc    UO2++   )= -3.83826E-05, delfnc=  9.77705E-01
     beta(conc    UO2++   )= -2.65161E-08, betfnc=  9.98915E-01
       bbig=  1.83598E-10, ubbig= Ca++
       bneg= -5.05509E-14, ubneg= SiO2(aq)
       bgamx=  3.68164E-07, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm= -4.83911E-07
       bxi= -3.54606E-07
       btfcnr=  9.99999E-01

iter=   6
      del(conc    UO2++   )= -4.16557E-08, delfnc=  9.98915E-01
     beta(conc    UO2++   )= -1.63345E-11, betfnc=  9.99384E-01
       bbig=  1.13104E-13, ubbig= Ca++
       bneg=  0.00000E+00, ubneg= none
       bgamx=  2.26812E-10, ubgamx= (UO2)3(CO3)6(6-)
       bsigmm= -1.98006E-10
       bxi= -2.18460E-10
       btfcnr=  9.99999E-01


Hybrid Newton-Raphson iteration converged in   6 steps.


                    --- Summary of the Aqueous Solution ---

          --- Elemental Composition of the Aqueous Solution ---

  Element          mg/L          mg/kg          Moles/kg

    O          0.88811E+06    0.88811E+06    0.5550916386E+02
    Ca          400.78          400.78        0.1000000000E-01
    Cl          713.37          713.37        0.2012184893E-01
    H          0.11190E+06    0.11190E+06    0.1110169859E+03
    C          0.12881         0.12881        0.1072461017E-04
    Si          2.8086          2.8086        0.1000000000E-03
    U          0.76944         0.76944        0.3232551344E-05
```

--- Elemental Composition as Strict Basis Species ---

Species	mg/L	mg/kg	Moles/kg
H2O	0.10000E+07	0.10000E+07	0.5550916386E+02
Ca++	400.78	400.78	0.1000000000E-01
Cl-	713.37	713.37	0.2012184893E-01
H+	0.11190E+06	0.11190E+06	0.1110169859E+03
HCO3-	0.65439	0.65439	0.1072461017E-04
SiO2(aq)	6.0084	6.0084	0.1000000000E-03
UO2++	0.87288	0.87288	0.3232551344E-05

--- Equivalent Composition of the Aqueous Solution ---

--- Original Basis ---

Species	Moles/kg H2O
H2O	0.5550916386E+02
Ca++	0.1000000000E-01
Cl-	0.2012184893E-01
H+	0.1110169859E+03
HCO3-	0.1072461017E-04
SiO2(aq)	0.1000000000E-03
UO2++	0.3232551344E-05

--- Current Basis (cte) ---

Species	Moles/kg H2O
H2O	0.5550916386E+02
Ca++	0.1000000000E-01
Cl-	0.2012184893E-01
H+	0.1110169859E+03
HCO3-	0.1072461017E-04
SiO2(aq)	0.1000000000E-03
UO2++	0.3232551344E-05

Single ion activities and activity coefficients are here defined
with respect to the modified NBS pH scale

	pH	Eh	pe
modified NBS pH scale	4.0000	0.9821	1.6601E+01
rational pH scale	3.9385	0.9857	1.6663E+01

pHCl = 5.7672

Activity of water = 0.99950
Log activity of water = -0.00022

True osmotic coefficient= 0.90470
Stoichiometric osmotic coefficient= 0.90370

Sum of true molalities= 0.0305787251052
Sum of stoichiometric molalities= 0.0306123915990

True ionic strength= 0.0300797357185
Stoichiometric ionic strength= 0.0301358730738

--- Electrical Balance Totals ---

	equiv/kg H2O
Sigma(mz) cations =	0.2009890850E-01
Sigma(mz) anions =	-0.2009890850E-01
Total charge =	0.4019781700E-01
Mean charge =	0.2009890850E-01
Charge imbalance =	0.1106753578E-14

Total charge = sigma(mz) cations + abs (sigma(mz) anions)
Mean charge = 1/2 total charge

The electrical imbalance is

0.275E-11 per cent of the total charge
0.551E-11 per cent of the mean charge
0.551E-11 per cent of sigma(mz) cations
0.551E-11 per cent of abs (sigma(mz) anions)

--- Electrical Balancing on Cl- ---

	mg/L	mg/kg	Moles/kg
input	354.53	354.53	0.1000000000E-01
final	713.37	713.37	0.2012184893E-01
adj	358.85	358.85	0.1012184893E-01

--- Activity Ratios of Ions -----

Log (act(Ca++	) / act(H+)xx 2) =	5.7277
Log (act(Cl-	) x act(H+)xx 1) =	-5.7672
Log (act(HCO3-	) x act(H+)xx 1) =	-11.3138
Log (act(SiO2(aq)	) =	-4.0000
Log (act(UO2++	) / act(H+)xx 2) =	2.1964
Log (act(Acetic acid(aq)	) =	-157.4232
Log (act(Acetone(aq)	) =	-311.4036
Log (act(Benzene(aq)	) =	-578.3969
Log (act(Butanoic acid(aq)	) =	-386.2230
Log (act(ClO-	) x act(H+)xx 1) =	-22.6678
Log (act(ClO2-	) x act(H+)xx 1) =	-32.4735
Log (act(ClO3-	) x act(H+)xx 1) =	-28.4255
Log (act(ClO4-	) x act(H+)xx 1) =	-28.6729
Log (act(Ethane(aq)	) =	-264.5371
Log (act(Ethanol(aq)	) =	-235.9744
Log (act(Ethylene(aq)	) =	-240.4399
Log (act(Ethyne(aq)	) =	-223.0160
Log (act(Formic acid(aq)	) =	-48.5671
Log (act(H2(aq)	) =	-44.3077
Log (act(Methane(aq)	) =	-148.2586
Log (act(O2(aq)	) =	-3.5983
Log (act(Pentanoic acid(aq)	) =	-500.7659
Log (act(Phenol(aq)	) =	-546.0658
Log (act(Propanoic acid(aq)	) =	-271.4896
Log (act(Toluene(aq)	) =	-690.2130
Log (act(U+++	) / act(H+)xx 3) =	-59.9076
Log (act(U++++	) / act(H+)xx 4) =	-29.9533
Log (act(UO2+	) / act(H+)xx 1) =	-16.9210
Log (act(o-Phthalate	) x act(H+)xx 2) =	-606.3557

--- Distribution of Aqueous Species ---

(Species with concentrations .lt. 1.e-12 are not listed)

Species	Molality	Log molality	Log gamma	Log activity
Cl-	2.0099E-02	-1.6968	-0.0704	-1.7672
Ca++	9.9778E-03	-2.0010	-0.2713	-2.2723
O2(aq)	2.5034E-04	-3.6015	0.0032	-3.5983
H+	1.1521E-04	-3.9385	-0.0615	-4.0000
SiO2(aq)	1.0000E-04	-4.0000	0.0000	-4.0000
CaCl+	2.1877E-05	-4.6600	-0.0751	-4.7351
CO2(aq)	1.0664E-05	-4.9721	0.0032	-4.9689
UO2++	3.0603E-06	-5.5142	-0.2893	-5.8036
HCl(aq)	3.6542E-07	-6.4372	0.0000	-6.4372
CaCl2(aq)	3.5454E-07	-6.4503	0.0000	-6.4503
UO2OH+	1.1588E-07	-6.9360	-0.0751	-7.0111
HCO3-	5.6631E-08	-7.2469	-0.0669	-7.3138
UO2Cl+	4.5870E-08	-7.3385	-0.0751	-7.4136
UO2(OH)2(aq)	7.6103E-09	-8.1186	0.0000	-8.1186
CaHCO3+	3.4331E-09	-8.4643	-0.0751	-8.5394
(UO2)2(OH)2++	1.1147E-09	-8.9528	-0.2893	-9.2422
(UO2)2OH+++	2.0784E-10	-9.6823	-0.6323	-10.3146
UO2CO3(aq)	1.6566E-10	-9.7808	0.0000	-9.7808
HSiO3-	1.3006E-10	-9.8858	-0.0669	-9.9527
OH-	1.1887E-10	-9.9249	-0.0704	-9.9953
UO2Cl2(aq)	3.4412E-11	-10.4633	0.0000	-10.4633
CaOH+	8.9656E-12	-11.0474	-0.0751	-11.1225

--- Major Aqueous Species Contributing to Mass Balances ---

Aqueous species accounting for 99% or more of Ca++

Species	Factor	Molality	Per Cent
Ca++	1.00	9.9778E-03	99.78
Total		1.0000E-02	99.78

Aqueous species accounting for 99% or more of Cl-

Species	Factor	Molality	Per Cent
Cl-	1.00	2.0099E-02	99.89
Total		2.0122E-02	99.89

Aqueous species accounting for 99% or more of HCO3-

Species	Factor	Molality	Per Cent
CO2(aq)	1.00	1.0664E-05	99.44
Total		1.0725E-05	99.44

Aqueous species accounting for 99% or more of SiO2(aq)

Species	Factor	Molality	Per Cent
SiO2(aq)	1.00	1.0000E-04	100.00
Total		1.0000E-04	100.00

Aqueous species accounting for 99% or more of UO2++

Species	Factor	Molality	Per Cent
UO2++	1.00	3.0603E-06	94.67
UO2OH+	1.00	1.1588E-07	3.58
UO2Cl+	1.00	4.5870E-08	1.42
Total		3.2326E-06	99.68

--- Summary of Aqueous Redox Reactions ---

Couple	Eh, volts	pe-	Log fO2	Ah, kcal
DEFAULT	0.982	0.1660E+02	-0.700	22.649
Acetic acid(/HCO3-	0.982	0.1660E+02	-0.700	22.649
Acetone(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Benzene(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Butanoic aci/HCO3-	0.982	0.1660E+02	-0.700	22.649
ClO- /Cl-	0.982	0.1660E+02	-0.700	22.649
ClO2- /Cl-	0.982	0.1660E+02	-0.700	22.649
ClO3- /Cl-	0.982	0.1660E+02	-0.700	22.649
ClO4- /Cl-	0.982	0.1660E+02	-0.700	22.649
Ethane(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Ethanol(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Ethylene(aq)/HCO3-	0.982	0.1660E+02	-0.700	22.649
Ethyne(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Formic acid(/HCO3-	0.982	0.1660E+02	-0.700	22.649
H2(aq) /H2O	0.982	0.1660E+02	-0.700	22.649
Methane(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
O2(aq) /H2O	0.982	0.1660E+02	-0.700	22.649
Pentanoic ac/HCO3-	0.982	0.1660E+02	-0.700	22.649
Phenol(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
Propanoic ac/HCO3-	0.982	0.1660E+02	-0.700	22.649
Toluene(aq) /HCO3-	0.982	0.1660E+02	-0.700	22.649
U+++ /UO2++	0.982	0.1660E+02	-0.700	22.649
U++++ /UO2++	0.982	0.1660E+02	-0.700	22.649
UO2+ /UO2++	0.982	0.1660E+02	-0.700	22.649
o-Phthalate /HCO3-	0.982	0.1660E+02	-0.700	22.649

--- Summary of Aqueous Non-equilibrium Non-redox Neactions ---

Reaction	Log Q/K	Aff, kcal	State

None

--- Summary of Pure Mineral Saturation States ---

(Minerals with affinities .lt. -10 kcal are not listed)

Mineral	Log Q/K	Aff, kcal	State
Chalcedony	-0.272	-0.371	satd
Coesite	-0.811	-1.106	
Cristobalite(alpha)	-0.551	-0.752	
Cristobalite(beta)	-0.995	-1.357	
Haiweeite	-6.840	-9.332	
Ice	-0.139	-0.190	satd
Quartz	-0.001	-0.001	satd
Rutherfordine	-5.011	-6.836	
Schoepite	-2.638	-3.598	
Schoepite-dehy(.393)	-4.528	-6.178	
Schoepite-dehy(.648)	-4.010	-5.471	
Schoepite-dehy(.85)	-2.901	-3.958	
Schoepite-dehy(.9)	-2.821	-3.848	
Schoepite-dehy(1.0)	-2.907	-3.966	
SiO2(am)	-1.286	-1.755	
Soddyite	0.000	0.000	satd
Tridymite	-0.172	-0.235	satd
UO2(OH)2(beta)	-2.750	-3.751	
UO2CO3	-4.991	-6.809	
UO2ClOH:2H2O	-5.878	-8.019	
UO3(alpha)	-6.443	-8.790	
UO3(beta)	-6.113	-8.340	
UO3(gamma)	-5.511	-7.519	
UO3:.9H2O(alpha)	-2.821	-3.848	
UO3:2H2O	-2.638	-3.598	

--- Summary of Hypothetical Solid Solutions ---

5 approx. saturated pure minerals
0 approx. saturated input solid solutions
0 saturated hypothetical solid solutions

0 supersaturated pure minerals
0 supersatd. input solid solutions
0 supersatd. hypothetical solid solutions

--- Summary of Gases ---

Gas	Fugacity	Log fugacity
C(g)	3.2539-190	-189.4876
C2H4(g)	7.6501-239	-238.1163
CH4(g)	3.9054-146	-145.4083
CO(g)	6.1958E-49	-48.2079
CO2(g)	3.1623E-04	-3.5000
Ca(g)	2.8104-158	-157.5512
Chlorine	4.6365E-17	-16.3338
H2(g)	6.2702E-42	-41.2027
H2O(g)	2.5965E-02	-1.5856
HCl(g)	8.4584E-13	-12.0727
O2(g)	1.9953E-01	-0.7000
Si(g)	4.4402-221	-220.3526
U(g)	1.7767-291	-290.7504
U2Cl10(g)	5.3050-175	-174.2753
U2Cl8(g)	3.5473-189	-188.4501
UCl(g)	1.3225-241	-240.8786
UCl2(g)	2.9452-190	-189.5309
UCl3(g)	1.4365-136	-135.8427

```
UCl4(g)                         3.7940-100    -99.4209
UCl5(g)                         5.1558-101   -100.2877
UCl6(g)                         1.3016E-96    -95.8855
UO(g)                           1.3678-206   -205.8640
UO2(g)                          2.4701-122   -121.6073
UO2Cl2(g)                       5.0004E-58    -57.3010
UO3(g)                          1.7710E-69    -68.7518

--- Reading the input file ---

--- No further input found ---

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           End time = 08:16:18  20Apr99

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         User time =   3.45     seconds
          Cpu time =  0.810     seconds

Normal exit
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Estimation of water chemistry in uranophane synthesis procedures.

Effort discontinued in this book

7/28/00

This Notebook is in compliance with QAP-001.

E.C.P.

8/11/2000

E.C.P.

8/11/2000

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK #: 140

Document Date:	03/15/1996
Availability:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
Contact:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
Data Sensitivity:	■"Non-Sensitive" □ Sensitive □"Non-Sensitive - Copyright" □ Sensitive - Copyright
Date Generated:	06/18/1996
Operating System: (including version number)	Macintosh
Application Used: (including version number)	EQ3
Media Type: (CDs, 3 1/2, 5 1/4 disks, etc.)	3-3 ½ disks
File Types: (.exe, .bat, .zip, etc.)	Proprietary data files
Remarks: (computer runs, etc.)	Media contains: Outputs for unsaturated zone numbers 1, 2, and 3.