

Kinetics, geochemical modeling: solution

1) Half lives

The table describe systems with two reactants, where the concentration of one reactant >> the concentration of the other reactant. The half-life is the time required for the reactant present at a lower concentration to decay (the second reactant remains approximately constant).

a) In table a), reactant B is present in small amounts, so the half-life calculation is done for reactant B. The concentration of A does not change much during the reaction and can be considered constant. The rate is first-order with respect to B:

We can simplify the rate law to: $-d[B]/dt = k'[B]$ with $k' = 0.5 * k * [A]^2 = \text{const.}$

For a (pseudo-)first order reaction, the half-life is independent of the initial concentration of B. It corresponds to:

$$t_{1/2} = \ln(2)/k'$$

We know that for $[A_0] = 300 \mu\text{M}$, $t_{1/2} = 62.2\text{s}$. We can therefore calculate:

$$k' = \ln(2)/62.2 \text{ s and then } k = 2k'/[A]^2 = 2.476 * 10^{-7} \mu\text{M}^{-2} \text{ s}^{-1}$$

Then use this k to re-calculate k' for the case where $[A_0] = 400 \mu\text{M}$

$$k' = 0.5 * k * [A]^2 = 1.238 * 10^{-7} \mu\text{M}^{-2} \text{ s}^{-1} * (400 \mu\text{M})^2 = 0.0198 \text{ s}^{-1}$$

And finally: $t_{1/2} = \ln(2)/k' = \underline{34.99 \text{ s}}$

b) In table b), reactant A is present at a lower concentration, so the half life calculation refers to A. B remains approximately constant.

The degradation rate of A is second order with respect to A:

$$-d[A]/dt = k[A]^2[B] = k''[A]^2, \text{ where } k'' = k[B] = \text{const.}$$

The half life of this second order reaction is:

$$t_{1/2} = 1/k''[A]_0$$

For second-order reactions, the half life does depend on the initial concentration of the reactant! So even though k'' is the same for both lines of the table, the half life of A will differ.

We can calculate k'' based on the values of A_0 and $t_{1/2}$ given in the first line of the table:

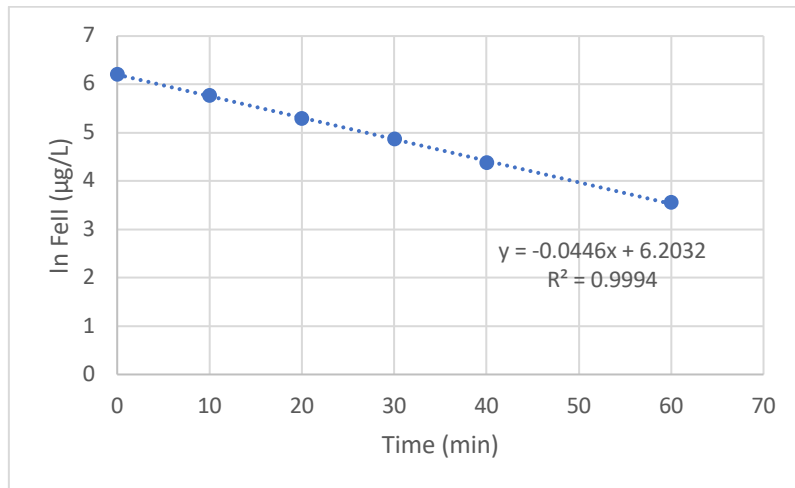
$$k'' = 1/(t_{1/2} * [A]_0) = 1/(625\text{s} * 5 \mu\text{M}) = 3.2 * 10^{-4} \mu\text{M}^{-1} \text{ s}^{-1}$$

With this k'' , we can now calculate the $t_{1/2}$ in the second row:

$$t_{1/2} = 1/k''[A]_0 = 1/(3.2 * 10^{-4} * 10 \mu\text{M}) = \underline{312.5 \text{ s}}$$

2) Rate constant for Fe^{II} oxidation

a) A first-order plot of the data, $\ln[\text{Fe}^{\text{II}}]$ versus time (graph below), yields a straight line with a slope of -0.0446 ; that is, $k' = 4.46 * 10^{-2} \text{ min}^{-1}$.



b) The half-life of Fe^{II} under the measurement conditions is $t_{1/2} = 0.693/k' = 0.693/(4.46 * 10^{-2} \text{ min}^{-1}) = \underline{15.54 \text{ min.}}$

c) The pseudo-first-order rate constant is related to the rate constant for the full rate equation as follows:

$$k' = kP_{\text{O}_2}[\text{OH}^-]^2$$

At pH 7.00 and $I = 0.001$, $\{\text{OH}^-\} = 10^{-7}$ and $[\text{OH}^-] = \{\text{OH}^-\} / 0.965 = 1.036 * 10^{-7} \text{ M}$.

Therefore,

$$k = k' / (P_{\text{O}_2}[\text{OH}^-]^2) = 4.46 * 10^{-2} \text{ min}^{-1} / (0.21 \text{ atm} * (1.036 * 10^{-7} \text{ M})^2)$$

$$\underline{k = 1.98 * 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}}$$

3) Acetoclastic methanogenesis

The basis panel in your Rxn window should look like this:

Rxn Community Edition - C:\Users\Public\Documents\GWB\Script

File Edit Run Config View Help

Basis Command Results

balance reaction for

CH3COO- -6.0 log activity

in terms of

HCO3- 3.0 log activity

H+ activity

CH4(aq) O2(aq) -6.0 log activity

H2O 1.0 activity

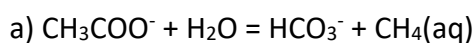
temperature 25.0 C

ionic strength true molal stoichiometric molal

add delete

factor reaction by 1.0 reverse

Go to the Results pane to see the modelling outcome. Note that the results can be extended by clicking the downward triangle left of the chemical reaction.

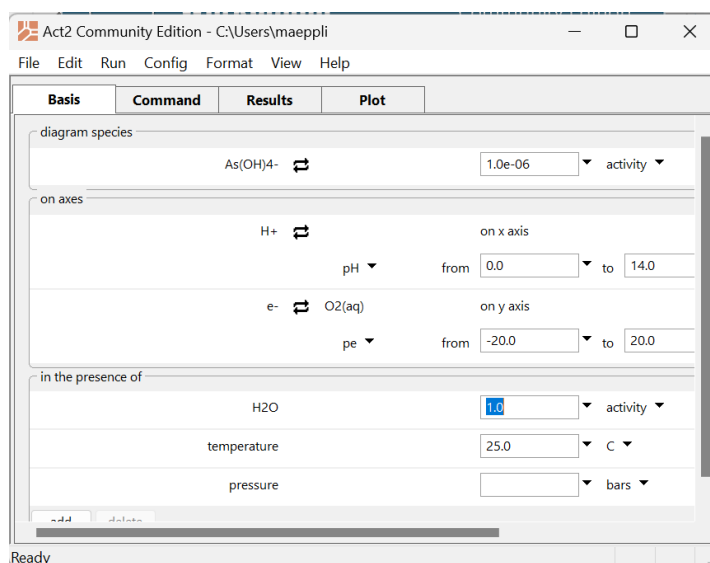


b) Yes, this is a redox reaction because C changes redox state from 0 in CH_3COO^- to +IV in HCO_3^- and -IV in CH_4 . Acetate serves both as electron acceptor and electron donor.

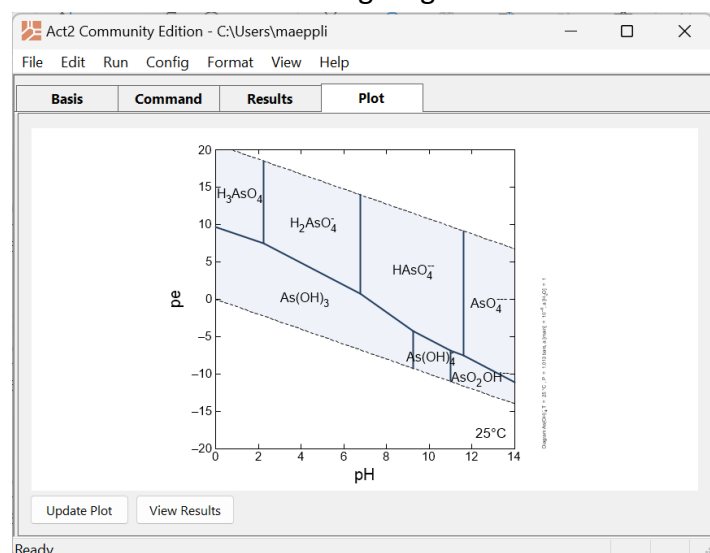
c) The log K of the reaction is 2.6407, delta G is -32.2 kJ/mol. The reaction therefore has a modest thermodynamic drive to proceed forward.

4) pe-pH diagram for As

- Open Act2.
- Select $\text{As}(\text{OH})_4^-$ as main species in the Basis tab. Set the activity to $1.0\text{e-}6$.
- Choose H^+ for the x axis and set units to pH.
- Choose $\text{O}_2(\text{aq})$ for the y axis, then swap in the e^- and set units to pe.
- Set temperature to 25°C . Your screen should look like this:



- Go to Run → Go to obtain the following diagram:



You can copy-paste the diagram into a Word or PowerPoint file by selecting Edit → Copy. Then, paste into the document as an Enhanced Metafile and ungroup the image to enable editing.

The results differ from the manual calculation because we simplified the system for the manual calculation by neglecting H_3AsO_4 , AsO_4^{2-} , $\text{As}(\text{OH})_4^-$ and $\text{AsO}_2\text{OH}^{2-}$. You could reproduce the exact manual diagram by changing the thermodynamic database used by Act2 in the TEdit app. This goes beyond the scope of the class, but if you are interested you can check p 167 ff in the [GWB Essentials guide](#) (release 12).