

Practical 4: Solubility and Acid base Equilibria (Solutions)

Simple Acid-Base Problems

A common situation is to determine the pH of a solution of an acid or base. To this end, we first distinguish between strong acids (or bases) and weak acids (or bases). Important strong acids include HCl (hydrochloric), H₂SO₄ (sulphuric) and HNO₃ (nitric). Problems involving strong acids are easy. Since a strong acid dissociates completely, the proton concentration will simply equal the initial concentration of acid. Hence, for a 0.1 m solution of HCl (a strong acid), the concentration of H⁺ will be 0.1 m since the reaction



will go completely (99%) to the right since K for a strong acid > 10. As you know from lecture and reading, we express [H⁺] in a logarithmic scale as pH (= -log[H]).

1. What is the pH of a 0.01 m solution of HCl? *Solution = -log(0.01) = 2*
2. NaOH is a strong base. What is the pH of a solution that is 0.001 m in NaOH?

$$\text{Solution} = 14 - (-\log(0.001)) = 11$$

pC-pH plots of speciation

Suppose we have an acid-dissociation reaction



With

$$K = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

we can take the -log (=p) of both sides to get

$$\text{pK} = \text{pA} + \text{pH} - \text{pHA}$$

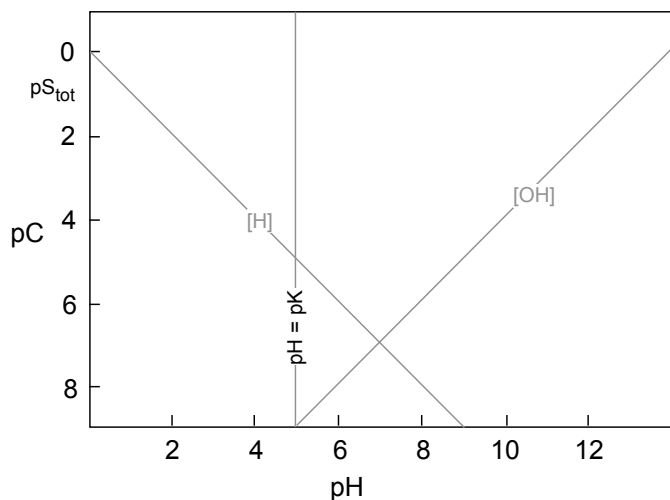
If we know the total concentration (Stot) of our dissolved acid (i.e., Stot = [A] + [HA]), then we can make a plot of pA vs pH and pHA vs pH. The reason we can do this in log space is because when pH < pK, we have that (to a really good approximation)

$$\text{pHA} = \text{pS}_{\text{tot}}$$

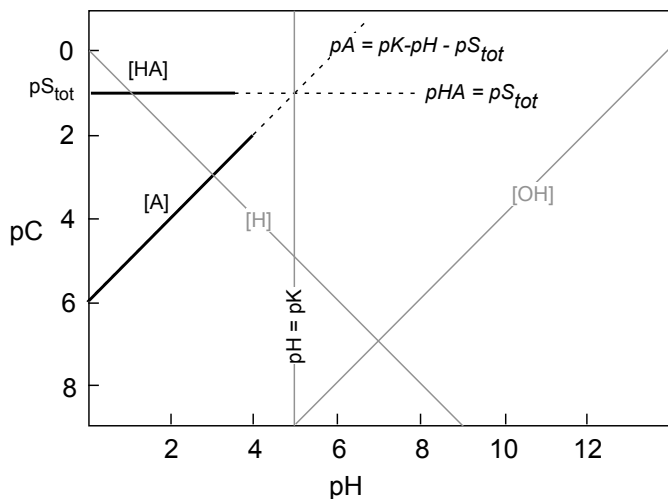
but with pHA = pS_{tot}, it follows that

$$pA = pK - pH + pS_{tot}$$

Let's plot this up using, for illustrative purposes, an acid with $pK = 5$ and $pS_{tot} = 1$. We set up a diagram with pC on the y-axis (here, C stands for concentration of either HA, A or H or OH) and pH on the x-axis.



On this diagram, I have plotted three lines: $pH = pK$, $pOH = 14 - pH$ and $pH = pH$. I can plot the equations for pA and pHA in the region where $pH < pK$:



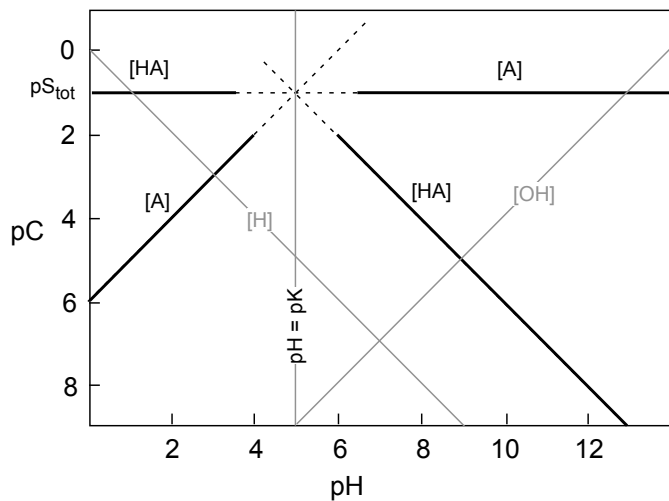
Now we can plot the speciation under the conditions when $pH > pK$. Under those conditions, we have $[A^-] \gg [HA]$ so that, to a very good approximation,

$$pA = pS_{tot}$$

If $pA = pS_{tot}$, then it follows that

$$pHA = pS_{tot} + pH - pK$$

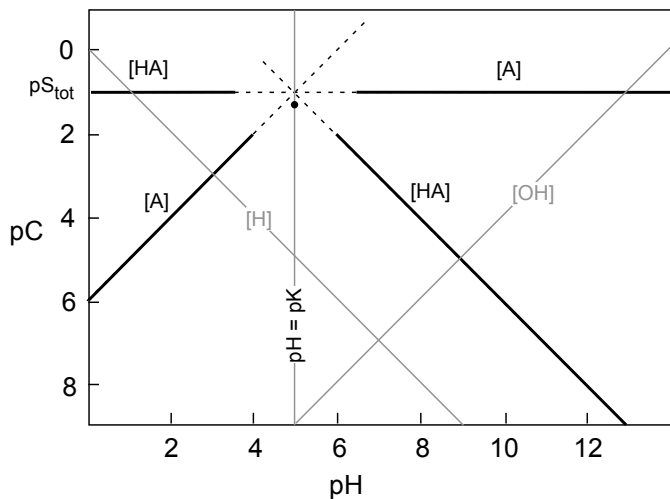
We can now plot pA and pHA in the region $pH > pK$:



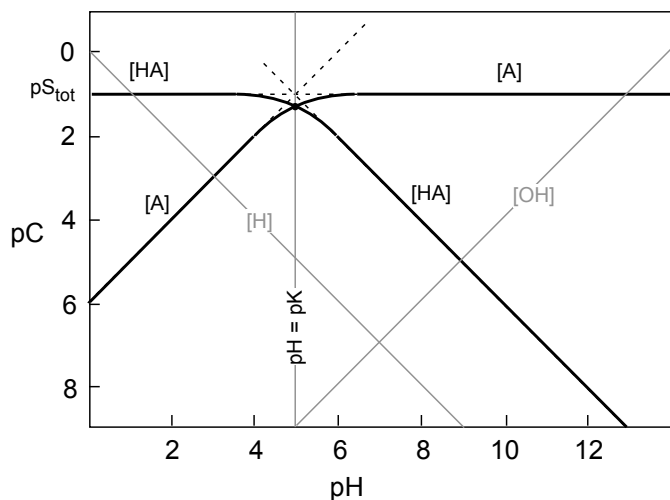
What about the region where $pH = pK$? When $pH = pK$, we have

$$[HA] = [A] = S_{tot}/2$$

Therefore, $pHA = pA = S_{tot} + 0.301$ (why is this?). We can plot this special point:



We can now connect our lines through the special (buffer) point and get our final pC-pH diagram:

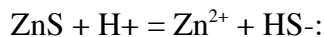


You should now, hopefully, realize that these diagrams can be constructed with almost no effort: all you have to know is the pK for the acid. You don't even have to know S_{tot} as you can simply plot $pC-pS_{tot}$ on the y-axis (you are just plotting relative concentrations).

3. Construct a pC-pH diagram for H_2S system, with $[S]_{tot} = [H_2S] + [HS^-] + [S^{2-}] = 0.001$ m, given the following equilibria:

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 10^{-7.03}$$

4. Now plot the concentration of dissolved Zn (as pZn) on the same diagram, given the equilibrium constant for the reaction



$$K_2 = \frac{[Zn^{2+}][HS^-]}{[H^+]} = 10^{-11.4}$$

and the condition that $[S]_{\text{tot}} = 0.001 \text{ m}$.

5. Finally plot pZn on a new diagram for the case where there is no other source of sulfur (i.e. $[Zn] = [H_2S] + [HS] + [S]$).

Solution:

$$pK_1 = pH + pHS - pH_2S = 7.03$$

Under acidic conditions ($pH < 7.03$), $pH_2S = pS_{\text{tot}} = 3$. When $pH_2S = pHS = p(S_{\text{tot}}/2)$, $pH = 7.03$. When H_2S is dominant, $pHS = 7.03 + pS_{\text{tot}} - pH$. When HS is dominant, $pH_2S = pH + pHS - 7.03$.

4. For the ZnS dissolution when $S_{\text{tot}} = 0.001$,

$pZn + pHS - pH = 11.4$ or $pZn = 11.4 - pHS + pH$. At $pH = 0$, $pHS = 10.03$ and $pZn = 1.43$. At $pH = 4$, $pHS = 5.97$ so $pZn = 11.4 + 4 - 5.97 = 9.43$. When HS is dominant, $pHS = 3$, so $pZn = 8.4 + pH$

c) For the ZnS dissolution when $[Zn] = [H_2S] + [HS] + [S]$

$pZn + pHS - pH = 11.4$. When HS is dominant, $pZn = pHS$ so that

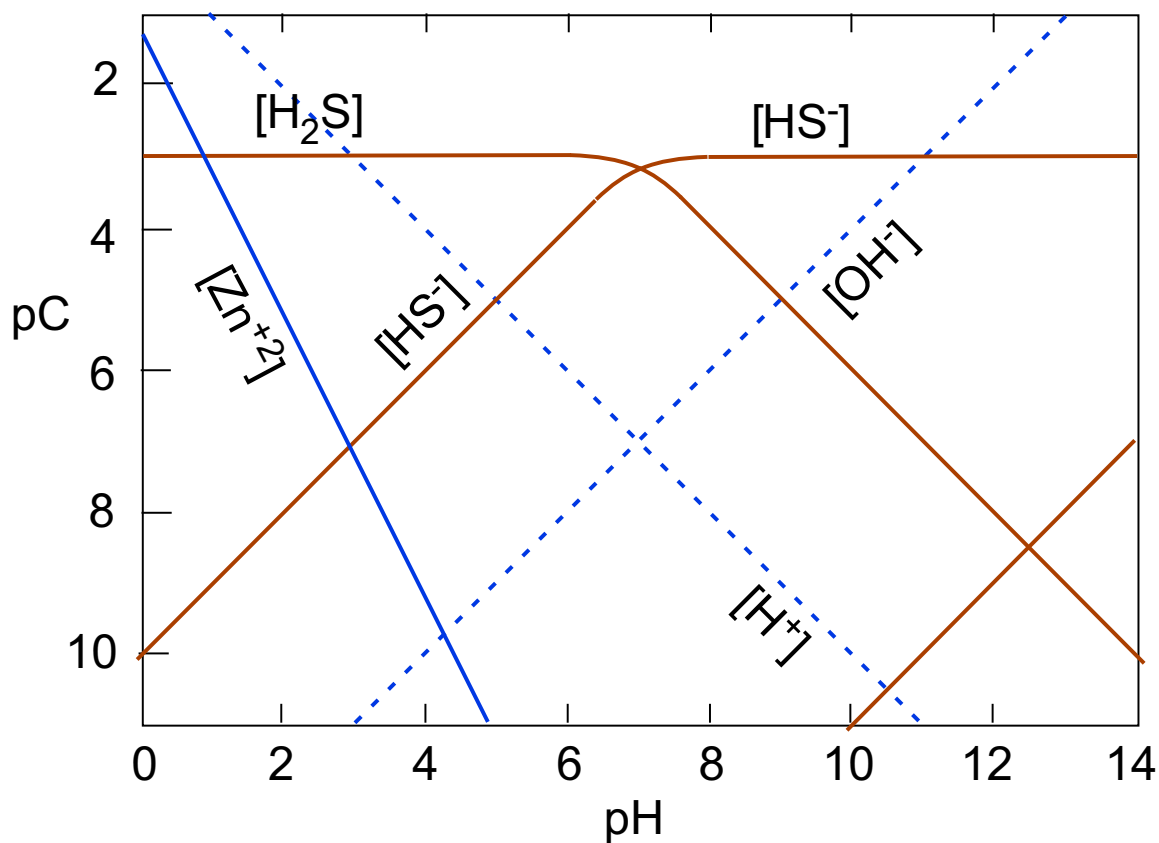
$$2pZn - pH = 11.4 \text{ or } pZn = (11.4 + pH)/2$$

When H_2S is dominant, $pZn = pH_2S$. Since $pHS + pH - pH_2S = 7.03$ we get

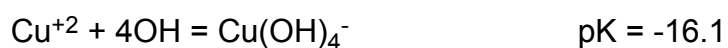
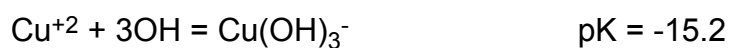
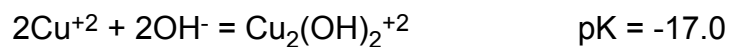
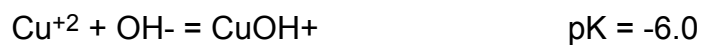
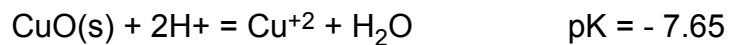
$pHS = 7.03 - pH + pH_2S$. If we combine this with $pZn + pHS - pH = 11.4$, we get

$pZn + 7.03 - pH + pH_2S - pH = 11.4$ or (since, $pZn = pH_2S$),

$$2pZn - 2pH = 4.37 \text{ or } pZn = (4.37 + 2pH)/2$$



5. Given the following equilibria, draw a pC-pH diagram showing the solubility of CuO.:



Would mobilization of CuO require acid or basic conditions? CuO forms by the oxidation of CuFeS₂. What does this tell us about supergene ore-deposits?

Solution:

Write out the equilibrium expressions, take the “p-function” and get

i) $p\text{Cu} = 2p\text{H} - 7.65$

ii) $-6.0 = p\text{CuOH} - p\text{Cu} - p\text{OH}$

or, since $p\text{OH} = 14 - p\text{H}$ and $p\text{Cu} = 2p\text{H} - 7.65$, we get $p\text{CuOH} = p\text{H} + 0.35$

iii) $p\text{Cu}_2(\text{OH})_2 - 2p\text{OH} - 2p\text{Cu} = -17.0$

gives $p\text{Cu}_2(\text{OH})_2 - 2(14 - p\text{H}) - 2(2p\text{H} - 7.65) = -17.0$ or

$$p\text{Cu}_2(\text{OH})_2 = 2p\text{H} - 4.3$$

iv) $p\text{Cu}(\text{OH})_2 = p\text{Cu} + 2p\text{OH} - 12.8 = 2p\text{H} - 7.65 + 28 - 2p\text{H} - 12.8 = 7.55$

v) $p\text{Cu}(\text{OH})_3^- - 3p\text{OH} - p\text{Cu} = -15.2$ gives $p\text{Cu}(\text{OH})_3^- = 19.15 - p\text{H}$

vi) $p\text{Cu}(\text{OH})_4^- - 4p\text{OH} - p\text{Cu} = -16.1$ gives $p\text{Cu}(\text{OH})_4^- = 32.25 - 2p\text{H}$

