

Clarifications re phase rule:

H^+ is also a component

$CO_2(g)$ is considered a phase IF its activity is fixed

Phase rule: $F = C - P + 2 =$ degrees of freedom. If P is fixed, lose 1 degree of freedom; if T is also fixed, lose another degree of freedom; etc.

Recap of examples given in class:

1) Ca^+ , CO_3^- , H^+ , $H_2O = 4$ components

Calcite, aqueous solution, $CO_2(g)$ at fixed partial pressure = 3 phases

$F = 4 - 3 + 2 = 3$. With T and P fixed, have 1 degree of freedom. This is shown in Figure 5.2 where P, T, P_{CO_2} are fixed, aqueous solution is present, and calcite is saturated. These 3 phases are at equilibrium along the line, or there is one degree of freedom where if pH is known, then $[Ca]_{Total}$ or $[CO_3]_{total}$ is known. Similarly if $[Ca]_{Total}$ is known or given, then pH is known.

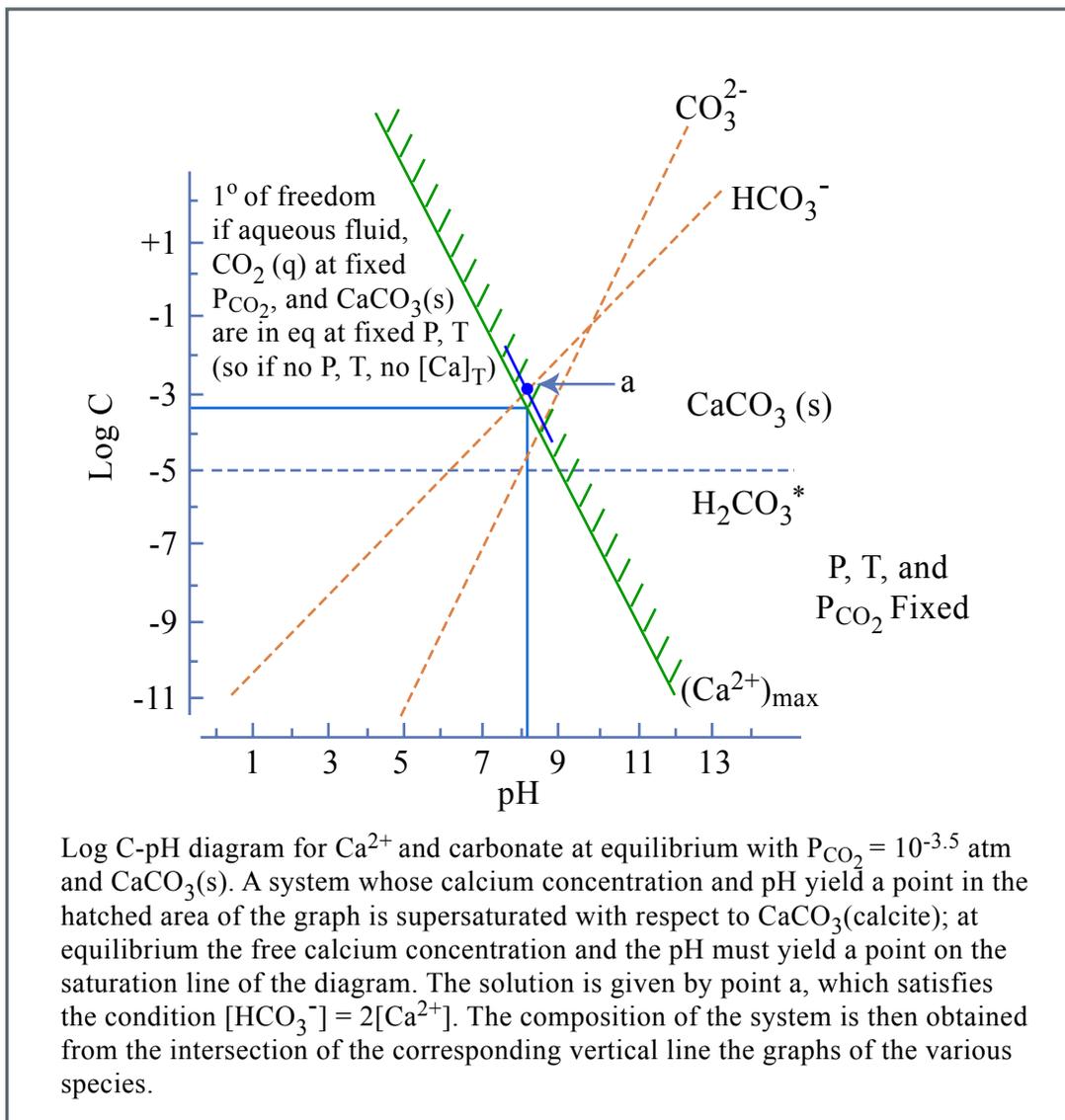


Figure by MIT OCW.

2) If add a phase, $\text{Ca}(\text{OH})_2(\text{s})$, have 0 degrees of freedom ($4-4+2$ but P and T are fixed so $F=0$). Have to be at a specific P_{CO_2} , NOT an arbitrary P_{CO_2} . This is why Morel and Hering state that these 4 phase cannot be in equilibrium while Stumm and Morgan note that they can be at equilibrium with one another.

3) Example of aqueous solution concentrated by isothermal evaporation with K^+ , Mg^+ , Na^+ , Cl^- , SO_4^{2-} , H_2O and H^+ . Minimal components = H_2O , H^+ , Na_2SO_4 , KCl , MgCl_2 = 5; At specified P,T, there can be 5 phases in equil, = 4 solids and aqueous solution.

4) Last example shown in class of apatite, calcite, $\text{CaHPO}_4(\text{s})$, H_2O , $\text{CO}_2(\text{g})$ at $T=10\text{C}$: $P = 5$ only if P_{CO_2} is fixed. $C=5$ (CO_2 , H_2O , P_2O_5 , CaO , and H^+) so $F=2$, but T is given and, if are writing a reaction using $\log K$, P is also given so 0 degrees of freedom.

This leaves the last 2 examples in Morel and Hering on p. 276:

5) silica(s), gibbsite(s), kaolinite(s), H_2O CANNOT coexist at equil under a fixed (arbitrary) pressure of CO_2 :

$C=5$ (H_2O , H^+ , CO_2 , SiO_2 , Al_2O_3); $P=5$; $F=2$ and $F=0$ if P and T are fixed. Note that these CAN be in equilibrium at some SPECIFIC P_{CO_2} , but not at an ARBITRARY P_{CO_2} .

6) I cannot make this last example work: $C=6$ (H_2O , CO_2 , CaO , Al_2O_3 , SiO_2 , H^+); $P = 5$ (anorthite, fixed P_{CO_2} , H_2O , kaolinite, calcite); $F=3$ so even if P and T are given, still have $F=1$. Bonus points for anyone finding out what Morel and Hering are trying to get at here.

7) Finally, the example given in the Stumm and Morgan reading is a good one that illustrates things well:

$C=5$ (HCO_3^- , Fe^{2+} , HS^- , H^+ , H_2O)

a) For $P=1$ = aqueous solution only, or any of the solids only (FeS(s) or $\text{FeCO}_3(\text{s})$ or $\text{Fe(OH)}_2(\text{s})$, $F=5-1+2=6$

On figure 7.16 (below), $[\text{Fe}]_{\text{total}}$ is fixed, $[\text{Alk}]$ is fixed, and P and T are fixed, so for a) there are 2 degrees of freedom.

b) For $P=2$ = aqueous solution and FeS(s) OR aqueous solution and $\text{FeCO}_3(\text{s})$, or on bounds between any two solids, $F=5-2+2=5$, and on fig 7.16 4 variables are fixed, so $F=1$ and there is one degree of freedom (on lines – if choose pH , then will know $\log S_T$).

c) For $P=3$ (aqueous solution and $\text{FeCO}_3(\text{s})$ and FeS(s) OR $\text{FeCO}_3(\text{s})$, FeS(s) , $\text{Fe(OH)}_2(\text{s})$, $F=5-3+2=4$, but 4 fixed on figure 7.16, so $F=0$ and can only be at one pH and $\log S_T$ for each group of 3 that are in equilibrium.

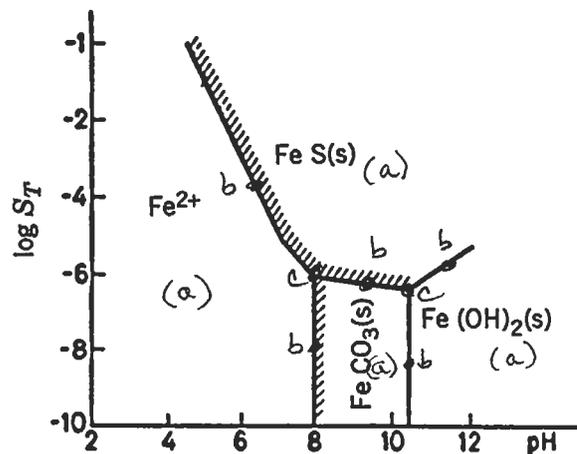


Figure 7.18. Concentration conditions for the existence of the solid phases FeS(s) , $\text{FeCO}_3(\text{s})$, and $\text{Fe(OH)}_2(\text{s})$. Conditions $[\text{Fe}^{2+}] = 10^{-6} \text{ M}$, $\text{Alk} = 5 \times 10^{-3} \text{ eq liter}^{-1}$. (Adapted from Sigg and Stumm, 1994.)