

## Multiple Reactions at Equilibria

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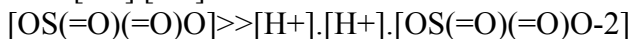
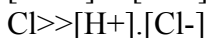
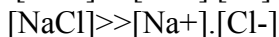
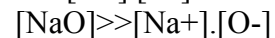
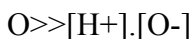
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It will be easier to work with absolute numbers of molecules, such as moles, and then convert later to concentrations. This approach also allows us to generalize the computation of pH to non-aqueous solutions.

Observe that I can be as “inconsistent” (and lazy and sloppy) as I like by drawing out as many significant digits as I like for all intermediate steps. For example, I enjoy obtaining as many significant digits as possible when I try to find the roots of the quintic by zooming-in with graphing. However, all final answers of each variable *must* have the same number of significant digits *and* this number of significant digits must not exceed the number of significant digits of any of the intermediate steps.

**Example 1.** Consider the set X of 5 “elements”  $\{H^+, Cl^-, Na^+, OH^-, SO_4^{2-}\}$ . This means that nowhere in our example will  $OH^-$  dissociate further into  $O^{2-}$  and  $H^+$ , for example. In SMILES (Simplified Molecular Input Line Entry Specification) notation, the hydronium cation is [H+], the chloride anion is [Cl-], the sodium cation is [Na+], the hydroxide anion is [O-], the sulfate anion  $SO_4^{2-}$  is [OS(=O)(=O)O-2], water is O, sodium hydroxide is [NaO],  $HSO_4^-$  is [OS(=O)(=O)O-], monosulfuric acid  $H_2SO_4$  is [OS(=O)(=O)O], hydrogen chloride (hydrochloric acid) is Cl (atomic chlorine is [Cl]), sodium chloride is [NaCl].

We have 6 reactions, each with its own equilibrium constant



Of the 11 species (multisets) present, only O, [NaO], [NaCl], Cl, [OS(=O)(=O)O-1], [OS(=O)(=O)O-2] appear in only 1 reaction. Hence, we will express the molar balances in terms of these 6 species.

$$\begin{bmatrix}
 1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & -1 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & -1 & 1 & 0 & -1 & 0 & 0 & 0 \\
 0 & -1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\
 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\
 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & -1
 \end{bmatrix}
 \begin{bmatrix}
 O \\
 [H^+] \\
 [O^-] \\
 [NaO] \\
 [Na^+] \\
 [NaCl] \\
 Cl \\
 Cl^- \\
 [OS(=O)(=O)O] \\
 [OS(=O)(=O)O^-] \\
 [OS(=O)(=O)O-2]
 \end{bmatrix}$$

$$\Delta [OS(=O)(=O)O] = - \Delta [OS(=O)(=O)O^-] - \Delta [OS(=O)(=O)O-2]$$

$$\Delta [Na^+] = - \Delta [NaO] - \Delta [NaCl]$$

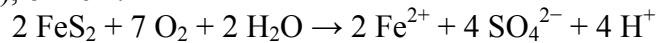
$$\Delta [Cl^-] = - \Delta Cl - \Delta [NaCl]$$

$$\Delta [O^-] = - \Delta O - \Delta [NaO]$$

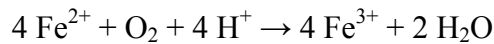
and the hardest one of all

$$\Delta [H^+] = - \Delta O - \Delta Cl + 2 \Delta [OS(=O)(=O)O-2] + \Delta [OS(=O)(=O)O-1]$$

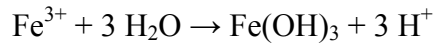
**Example 2.** The oxidation of iron sulfide [pyrite](#) ( $FeS_2$ ) by molecular oxygen produces iron(II), or  $Fe^{2+}$ :



The  $Fe^{2+}$  can be further oxidized to  $Fe^{3+}$ , according to:

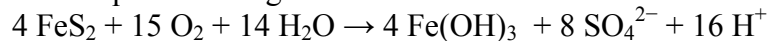


and the  $Fe^{3+}$  produced can be precipitated as the [hydroxide](#) or [hydrrous oxide](#). The equation for the formation of the hydroxide is



This is 8 species constrained by 3 reactions. Therefore, there exist 3 equilibrium conditions and 5 species molar balance equations. So  $\frac{1}{2} \Delta \{FeS_2\} = -\frac{1}{4} \Delta \{SO_4^{2-}\}$ . If we

add the three equations we get



So  $\Delta\{FeS_2\} = -\frac{1}{2}\Delta\{SO_4^{-2}\} = -\Delta\{Fe(OH)_3\}$ . This is 2 molar balance equations. We need

$$3 \text{ more. } \begin{bmatrix} 7 & 2 & -4 & -2 & 0 & -4 & 2 & 0 \\ 1 & -2 & 4 & 4 & -4 & 0 & 0 & 0 \\ 0 & 3 & -3 & 0 & 1 & 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} O_2 \\ H_2O \\ H^+ \\ Fe^{+2} \\ Fe^{+3} \\ SO_4^{-2} \\ FeS_2 \\ Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}. \text{ We may choose any}$$

one species that appears in a reaction. For example,

$$\begin{bmatrix} \Delta O_2 \\ \Delta H_2O \\ \Delta H^+ \\ \Delta Fe^{+2} \\ \Delta Fe^{+3} \\ \Delta SO_4^{-2} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} 7 & 1 & 0 \\ 2 & -2 & 3 \\ -4 & 4 & -3 \\ -2 & 4 & 0 \\ 0 & -4 & 1 \\ -4 & 0 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{7}n_{O_2,1} \\ \frac{1}{4}n_{H^+,2} \\ \frac{1}{1}n_{Fe^{+3},3} \end{bmatrix}. \text{ Reorder to get the simplest } R \times R \text{ invertible}$$

$$\text{matrix in the bottom} \begin{bmatrix} \Delta O_2 \\ \Delta H_2O \\ \Delta H^+ \\ \Delta Fe^{+2} \\ \Delta SO_4^{-2} \\ \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} 7 & 1 & 0 \\ 2 & -2 & 3 \\ -4 & 4 & -3 \\ -2 & 4 & 0 \\ -4 & 0 & 0 \\ 0 & -4 & 1 \\ 2 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{7}n_{O_2,1} \\ \frac{1}{4}n_{H^+,2} \\ \frac{1}{1}n_{Fe^{+3},3} \end{bmatrix}. \text{ So}$$

$$\begin{bmatrix} \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} 0 & -4 & 1 \\ 2 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{7}n_{O_2,1} \\ \frac{1}{4}n_{H^+,2} \\ \frac{1}{1}n_{Fe^{+3},3} \end{bmatrix}. \text{ Invert}$$

$$\begin{bmatrix} \frac{1}{7}n_{O_2,1} \\ \frac{1}{4}n_{H^+,2} \\ \frac{1}{1}n_{Fe^{+3},3} \\ 1 \end{bmatrix} = \begin{bmatrix} 0 & -4 & 1 \\ 2 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}^{-1} \cdot \begin{bmatrix} \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} 0 & \frac{1}{2} & 0 \\ -\frac{1}{4} & 0 & -\frac{1}{4} \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} \text{ So}$$

$$\begin{bmatrix} \Delta O_2 \\ \Delta H_2O \\ \Delta H^+ \\ \Delta Fe^{+2} \\ \Delta SO_4^{-2} \end{bmatrix} = \begin{bmatrix} 7 & 1 & 0 \\ 2 & -2 & 3 \\ -4 & 4 & -3 \\ -2 & 4 & 0 \\ -4 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \frac{1}{2} & 0 \\ -\frac{1}{4} & 0 & -\frac{1}{4} \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix} = \begin{bmatrix} -\frac{1}{4} & \frac{7}{2} & -\frac{1}{4} \\ \frac{1}{2} & 1 & -\frac{5}{2} \\ -1 & -2 & 2 \\ -1 & -1 & -1 \\ 0 & -2 & 0 \end{bmatrix} \cdot \begin{bmatrix} \Delta Fe^{+3} \\ \Delta FeS_2 \\ \Delta Fe(OH)_3 \end{bmatrix}$$

[Anhydrous](#) H<sub>2</sub>SO<sub>4</sub> is a very [polar](#) liquid, having a [dielectric constant](#) of around 100. It has a high electrical conductivity, caused by dissociation through [protonating](#) itself, a process known as [autoprotolysis](#), or [autoionization](#).<sup>[3]</sup>



The [equilibrium constant](#) for the autoprotolysis is<sup>[3]</sup>

$$K_{ap}(25^\circ\text{C}) = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 2.7 \times 10^{-4}.$$

**Example.**  $A + B \leftrightarrow X$  and  $2A + 3B \leftrightarrow Y$ . Let  $n_{A,1}$  denote the number of moles of  $A$  which go into reaction 1. Let  $n_{A,2}$  denote the number of moles of  $A$  which go into reaction 2. Let  $n_A, N_A, n_B, N_B, n_X, n_Y$  denote the final (resp. initial) number of moles of  $A$  (resp.  $B$ ) in equilibrium. Define  $\Delta A \equiv n_A - N_A$  and  $\Delta B \equiv n_B - N_B$ . So  $-\Delta A = n_{A,1} + n_{A,2}$  and  $-\Delta B = n_{B,1} + n_{B,2}$ . We also have from the stoichiometric coefficients of the reactions  $n_{A,1} = n_{B,1} = n_X$  and  $\frac{1}{2}n_{A,2} = \frac{1}{3}n_{B,2} = n_Y$ . From this we can derive

$$-\begin{bmatrix} \Delta A \\ \Delta B \end{bmatrix} = \begin{bmatrix} 1 & 2 \\ 1 & 3 \end{bmatrix} \cdot \begin{bmatrix} n_X \\ n_Y \end{bmatrix}. \text{ Suppose the equilibria conditions are } n_X = 5 \cdot n_A \cdot n_B \text{ and}$$

$n_Y = 4 \cdot n_A^2 \cdot n_B^3$ . (Yes, yes –in general concentrations, not absolute numbers of molecules, appear in equilibrium equations. I am doing it this way for computational simplicity.) Let  $N_A = 17$  and  $N_B = 18$ . Then  $-108 \cdot n_A^3 + 1495 \cdot n_A^2 - 8225 \cdot n_A + 13500 = 0$  and

$900 \cdot n_B^3 - 25 \cdot n_B^2 - 105 \cdot n_B - 54 = 0$ . The only real-valued solutions are  $n_A = 2.7261371548305$  and  $n_B = 0.50045820500410$ . Thus  $n_X = 7.82250492$  and  $n_Y = 3.22567896$ .

If we use concentrations instead of absolute mole numbers in our equilibria conditions, define  $T \equiv n_A + n_B + n_X + n_Y$ . Then  $n_X \cdot T = 5 \cdot n_A \cdot n_B$ ,  $n_Y \cdot T^4 = 4 \cdot n_A^2 \cdot n_B^3$ , and  $T = N_A - n_X - 2n_Y + N_B - n_X - 3n_Y + n_X + n_Y = N_A + N_B - n_X - 4n_Y$ . So  $n_X \cdot (N_A + N_B - n_X - 4n_Y) = 5 \cdot (N_A - n_X - 2n_Y) \cdot (N_B - n_X - 3n_Y)$   
 $n_Y \cdot (N_A + N_B - n_X - 4n_Y)^4 = 4 \cdot (N_A - n_X - 2n_Y)^2 \cdot (N_B - n_X - 3n_Y)^3$   
 Again let  $N_A = 17$  and  $N_B = 18$ . After 151.47 seconds of computation, a realistic solution was found  $n_X = 10.021796702210$ ,  $n_Y = 0.20277861861646$ ,  $n_A = 6.572646063$ ,  $n_B = 7.369867444$ ,  $T = 24.16708883$ . [A]=0.2719668103 [B]=0.3049547050 [X]=0.4146877918 [Y]=0.008390692815

**Example.**  $A + B \leftrightarrow C + D$  and  $2A + 3B \leftrightarrow 4C + 5D$ . As in the previous example, define intermediate variables  $\Delta A = -n_{A,1} - n_{A,2}$ ,  $\Delta B = -n_{B,1} - n_{B,2}$ ,  $\Delta C = n_{C,1} + n_{C,2}$ ,

$\Delta D = n_{D,1} + n_{D,2}$ . Stoichiometry forces  $n_{A,1} = n_{B,1} = n_{C,1} = n_{D,1}$  and

$$\frac{1}{2}n_{A,2} = \frac{1}{3}n_{B,2} = \frac{1}{4}n_{C,2} = \frac{1}{5}n_{D,2}. \text{ Hence, } \begin{bmatrix} \Delta A \\ \Delta B \\ \Delta C \\ \Delta D \end{bmatrix} = \begin{bmatrix} -1 & -2 \\ -1 & -3 \\ 1 & 4 \\ 1 & 5 \end{bmatrix} \cdot \begin{bmatrix} n_{A,1} \\ \frac{1}{2}n_{A,2} \end{bmatrix}. \text{ From this we can}$$

derive the relations  $\begin{bmatrix} \Delta C \\ \Delta D \end{bmatrix} = \begin{bmatrix} 1 & -2 \\ 2 & -3 \end{bmatrix} \cdot \begin{bmatrix} \Delta A \\ \Delta B \end{bmatrix}$ .