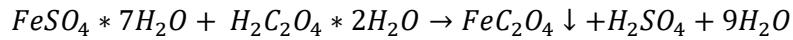


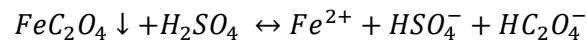
Concerning the preparation of H_2SO_4 via $FeSO_4 \cdot 7H_2O$ and $H_2C_2O_4 \cdot 2H_2O$

A possible route for sulfuric acid synthesis might emerge from the combination of iron(ii)sulfate combined with oxalic acid, as the resulting iron(ii)oxalate is rather insoluble in water:



A procedure calls for dissolution of both chemicals in water (oxalic acid in double the amount of boiling water, iron sulfate in twice its amount of 60°C water) and adding the 2 solutions, which results in a bright yellow-orange precipitate of iron oxalate. This precipitate can be filtered off, which leaves a solution of sulfuric acid.

However, the following equilibrium must be considered:



As the concentration of sulfuric acid rises, the precipitate will dissolve eventually. This can be understood easily by thinking the opposite way, namely dissolving iron oxalate via addition of sulfuric acid, resulting in the protonation of the oxalate. In the following calculation, the equilibrium of this reaction will be calculated.

Under the assumption that the reaction would simply go to completion, one would end up with a concentration of sulfuric acid as high as 1.25M.

The chosen approach considers mentioned reverse of the reaction described by the reaction above. For the equilibrium concentrations, a general formula is:

	FeC_2O_4	H_2SO_4	Fe^{2+}	HSO_4^-	$HC_2O_4^-$
Start	(solid)	1.25	-	-	-
Equilibrium	(solid)	1.25-x	x	x	x

Figure 1: general equilibrium considerations

Assuming that the concentration of hydrogen sulfate and oxalate are roughly identical (Reason will be given later) calculations can be made on the following basis:

Given the acid mixture of intermediate and weaker strength and using an appropriate formula to calculate the pH, considering HX, HSO_4^- as an intermediate strength acid and HY, $HC_2O_4^-$ as a weak acid, it follows:

$$c(H^+) = \frac{-K_{a,HX} + \sqrt{K_{a,HX}^2 + 4(K_{a,HX}c_{s,HX} + K_{a,HY}c_{s,HY})}}{2}$$

the concentration of the weaker base anion (oxalate) can simply be derived from its K_a value:

$$as K_s(HY) = \frac{[H^+][Y^-]}{[HY]}, c(Y^-) = \frac{K_{s,HY} * c(HY)}{c(H^+)}$$

in which calculations show that $c(HY) \approx c_0(HY)$ by the fact that $c(Y^-) \ll c(HY)$.

In turn, the starting concentration $c_0(HY)$ (which is equal to the iron(2+) concentration) times its corresponding anion concentration $c(Y^-)$ must be equal to the solubility product of the iron oxalate, due to $K_L(FeC_2O_4) = c(Fe^{2+}) * c(C_2O_4^{2-}) = c_0(HY) * c(C_2O_4^{2-})$.

By this, a more accurate starting concentration of HY can be calculated via $c_0(HY) = \frac{K_L(FeC_2O_4)}{c(C_2O_4^{2-})}$.

Using an Excel spreadsheet with a starting value of 1mol/L, the value converges in around 15 recursions to be approximately 0,179mol/L. Putting this back into the table above yields a maximum yield of 85,7%:

$$y = \frac{1,25 - x}{1,25} = \frac{1,25 - 0,179}{1,25} = 0,857$$

A practical run on a 0,2mol scale yielded an 85,0% yield, although some percent points were lost in the procedure. Therefore it can be argued that the theoretical yield must be higher, around 90%.

This can be justified because the distribution between hydrogen sulfate and hydrogen oxalate is not perfectly matched to a 1:1 ratio, but slightly on the side of sulfate/oxalic acid, lowering the essential hydrogen sulfate concentration for the calculations. A large shift is not to be assumed because practical results show that yields match the current calculation except for a small error, as well as that the protonation of hydrogen oxalate results in oxalic acid, an acid slightly stronger than hydrogen sulfate itself.

	A	B	C	D
1	K _a (HSO ₄ ⁻)	K _a (HC ₂ O ₄ ⁻)		
2	0,01258925	6,3096E-05		
3	c(HSO ₄ ⁻)	c(HC ₂ O ₄ ⁻)	c(H ⁺)	c(C ₂ O ₄ ²⁻)
4	1	1	0,106364026	0,000593206
5	0,08142203	0,08142203	0,026413205	0,000194501
6	0,24832837	0,24832837	0,050110689	0,000312677
7	0,1544725	0,1544725	0,038360299	0,000254079
8	0,19009817	0,19009817	0,043150402	0,000277967
9	0,17376169	0,17376169	0,041014104	0,000267313
10	0,18068676	0,18068676	0,041931241	0,000271887
11	0,17764727	0,17764727	0,041530865	0,00026989
12	0,17896149	0,17896149	0,04170439	0,000270756
13	0,17838952	0,17838952	0,041628946	0,00027038
14	0,17863774	0,17863774	0,041661703	0,000270543
15	0,17852988	0,17852988	0,041647472	0,000270472
16	0,17857673	0,17857673	0,041653653	0,000270503
17	0,17855638	0,17855638	0,041650968	0,000270489
18	0,17856522	0,17856522	0,041652134	0,000270495
19	0,17856138	0,17856138	0,041651628	0,000270493
20	0,17856304	0,17856304	0,041651848	0,000270494

Figure 2: recursion formula calculations

More accurate results could be achieved by analysing the solution itself for concentrations, which is yet to be done.

Closing remarks:

- For the proton concentration formula, the oxalic acid concentration is rather negligible, which is not very trivial, so I included it in the formula. It has very minor influence on actual pH changes.
- Also, considering either of the acids both intermediate or both weak strength results in theoretical yields of 98%+, which is far from the reality.
- As seen in the table, the concentration of oxalate is only 0,15% the concentration of hydrogen oxalate, which justifies assuming that $c(\text{HC}_2\text{O}_4^-) \approx c_0(\text{HC}_2\text{O}_4^-)$