
3. Hydrazine salts

Hydrazine (N_2H_4) is a weak diprotic base ($K_{b1} = 8.5 \cdot 10^{-7}$; $K_{b2} = 8.9 \cdot 10^{-16}$). It can form various anhydrous salts with sulfuric acid. The second acid dissociation constant of sulfuric acid is $K_{a2} = 1.02 \cdot 10^{-2}$.

- 3.1. **Provide** the theoretically conceivable empirical formulas of anhydrous salts.
- 3.2. Starting from aqueous solutions, two of these salts can be expected to form. **Identify** these two salts? **Why** doesn't the aqueous procedure work for the other salts?
- 3.3. **Calculate** the pH of the 0.1 M solutions of these salts?

Solution

3.1.

In theory, salts with the following compositions, containing two types of ions, can exist:

$(\text{N}_2\text{H}_5)(\text{HSO}_4)$, empirical formula $\text{N}_2\text{H}_6\text{SO}_4$

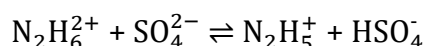
$(\text{N}_2\text{H}_5)_2(\text{SO}_4)$, empirical formula $\text{N}_4\text{H}_{10}\text{SO}_4$

$(\text{N}_2\text{H}_6)(\text{HSO}_4)_2$, empirical formula $\text{N}_2\text{H}_8\text{S}_2\text{O}_8$

$(\text{N}_2\text{H}_6)(\text{SO}_4)$, empirical formula $\text{N}_2\text{H}_6\text{SO}_4$

3.2.

The salt with the empirical formula $\text{N}_2\text{H}_6\text{SO}_4$ can be described as $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ in solution. It is easily shown that the equilibrium:



is strongly shifted to the right due to the high equilibrium constant of the process.

$$K = \frac{K_w}{K_{a2} \cdot K_{b2}} = 1.1 \cdot 10^3$$

The preparation of $\text{N}_2\text{H}_6(\text{HSO}_4)_2$ would also be problematic because the concentration of $\text{N}_2\text{H}_6^{2+}$ ions is very low compared to N_2H_5^+ ions. Their concentration ratio is low even at pH 1.

$$\frac{[\text{N}_2\text{H}_6^{2+}]}{[\text{N}_2\text{H}_5^+]} = \frac{K_{b2}}{K_w} [\text{H}^+] = 8.9 \cdot 10^{-3}$$

That is because the diprotonated hydrazine is a rather strong acid.

$$K_a = \frac{K_w}{K_{b2}} = 11.2$$

We only expect $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ and $(\text{N}_2\text{H}_5)_2(\text{SO}_4)$ as feasible in solution. [Actually, in the solid $(\text{N}_2\text{H}_6)(\text{SO}_4)$ was detected.]

3.3.

Let us first calculate the pH of the 0.1 mol/dm^3 $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ solution. In the first approximation, neglect the hydrolysis of the N_2H_5^+ ion. This seems justified because it is very weak both as an acid and as a base. In this case, the pH is practically determined only by the hydrolysis of the HSO_4^- ion.

$$K_{a2} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]}, \text{ giving } [\text{H}^+] = 2.72 \cdot 10^{-2}, \text{ and pH} = 1.56$$

If we consider the hydrolysis of the N_2H_5^+ ion, it suffices to account for the presence of $\text{N}_2\text{H}_6^{2+}$. The N_2H_4 concentration is still negligible, because $\frac{[\text{N}_2\text{H}_5^+]}{[\text{N}_2\text{H}_4]} = \frac{K_{b1}}{K_w} \cdot [\text{H}^+] = 2.3 \cdot 10^6$ at the estimated pH.

Writing down the usual system of equations (equilibrium constants, charge and mass balance), we arrive at the following third-order equation:

$$\frac{K_{b2}}{K_w \cdot K_{a2}} \cdot [\text{H}^+]^3 + \left(\frac{K_{b2}}{K_w} + \frac{K_{b2} \cdot c}{K_w \cdot K_{a2}} + \frac{1}{K_{a2}} \right) \cdot [\text{H}^+]^2 + [\text{H}^+] - c = 0$$

From this $[\text{H}^+] = 2.71 \cdot 10^{-2} \text{ mol/dm}^3$, and $\text{pH} = 1.57$. So, the neglect of the hydrolysis was justified.

Some simplifications can be made when calculating the pH of $0.1 \text{ mol/dm}^3 (\text{N}_2\text{H}_5)_2(\text{SO}_4)$ solution. The protonation of N_2H_5^+ is certainly negligible, because the $\frac{[\text{N}_2\text{H}_6^{2+}]}{[\text{N}_2\text{H}_5^+]}$ ratio was already very small at pH 1.

If we consider the low basicity of sulfate ions and disregard their protonation, then the system simplifies to the pH of a 0.2 mol/dm^3 weak acid. ($K_a = \frac{K_w}{K_{b1}} = 1.18 \cdot 10^{-8}$)

$$[\text{H}^+] = \sqrt{K_a \cdot c} = 4.86 \cdot 10^{-5}, \text{pH} = 4.3$$

If we do not neglect the protonation of sulfate and the deprotonation of N_2H_5^+ ions, then the system of equations gives another third-order equation.

$$\frac{K_{b1}}{K_w \cdot K_{a2}} \cdot [\text{H}^+]^3 + \left(\frac{K_{b1} \cdot c}{K_w \cdot K_{a2}} + \frac{1}{K_{a2}} + \frac{K_{b1}}{K_w} \right) \cdot [\text{H}^+]^2 + \left(1 - \frac{c}{K_{a2}} \right) [\text{H}^+] - 2c = 0$$

Here $[\text{H}^+] = 1.48 \cdot 10^{-5} \text{ mol/dm}^3$, and $\text{pH} = 4.83$. Here the simplifications caused a sizable difference. Although only a small portion of the sulfate ions gets protonated, the resulting shift in the hydrazonium deprotonation yields a noticeable pH shift.