Solution to Mohr's method challenge

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This challenge explores the precise endpoint location in Mohr's titration of sodium chloride with silver nitrate, in the presence of potassium chromate as indicator. First, we evaluate the pH of the titrand, i.e., NaCl (C_0) + K₂CrO₄ (C_{ind}) solution, and denote it as pH₀. This system is characterized by charge balance

$$[H^+] - [OH^-] + [K^+] - [HCrO_4^-] - 2[CrO_4^{2-}] - [HCr_2O_7^-] - 2[Cr_2O_7^{2-}] + [Na^+] - [Cl^-] = 0 \quad (1)$$

and concentration balances can be written as follows:

$$C_0 = [Na^+] \quad (2a)$$

$$C_0 = [Cl^-] \quad (2b)$$

$$2C_{ind} = [K^+] \quad (2c)$$

$$C_{ind} = [H_2CrO_4] + [HCrO_4^-] + [CrO_4^{2-}] + 2[HCr_2O_7^-] + 2[Cr_2O_7^{2-}] \quad (2d)$$

Addition of the sum of Eqs. 1, 2a, 2b, and 2c to Eq. 2d multiplied by 2 gives the proton balance

$$2[H_2CrO_4] + [HCrO_4^-] + 3[HCr_2O_7^-] + 2[Cr_2O_7^{2-}] + a = 0 \quad (3)$$

where

$$a = [H^+] - [OH^-] = 10^{-pH} - 10^{pH-14.0} \quad (4)$$

From Eqs. 3 and 4 we see that the starting solution of NaCl and K₂CrO₄ is alkaline because a has to be negative, i.e., $[H^+] < [OH^-]$. Hence, we can now simplify the titration problem by omitting two species that are present only in very acidic conditions, namely H₂CrO₄ and HCr₂O₇⁻. Equations 2d and 3 become

$$C_{ind} = [HCrO_4^-] + [CrO_4^{2-}] + 2[Cr_2O_7^{2-}] \quad (5)$$

$$[HCrO_4^-] + 2[Cr_2O_7^{2-}] + a = 0 \quad (6)$$

Combination of these equations gives

$$C_{ind} - [CrO_4^{2-}] = -a \quad (7)$$

This means $[CrO_4^{2-}] = C_{ind} + a = C_{ind} + 10^{-pH} - 10^{pH-14.0}$. The concentration of other chromium species can be obtained from the expressions $[H^+][CrO_4^{2-}] = K_{21}[HCrO_4^-]$ and $[Cr_2O_7^{2-}] = K_1[HCrO_4^-]^2$. We still do not know the pH and it can be obtained by calculating the values of $[CrO_4^{2-}]$, $[HCrO_4^-]$, and $[Cr_2O_7^{2-}]$ at any given pH (>7). Equation 5 will hold true only at the value of pH corresponding to the pH of titrand. For values of $C_{ind} = 0.002$, 0.005, and 0.010 mol/L, we obtain pH = 8.89, 9.09, and 9.24, respectively. We also can observe that $[CrO_4^{2-}]$ is the predominant chromium species (Fig. 1). The related

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Fig. 1 Logarithmic diagram for chromium species at $C_{\text{ind}} = 0.002$ mol/L

curves are plotted there on the basis of data presented in Table 1 of this Challenge [1] for different Cr species and without making simplifying assumptions as we did in the preceding paragraphs.

Now let us turn to the titration of $V_0 = 100$ mL of NaCl ($C_0 = 0.01$ mol/L) + K_2CrO_4 (C_{ind}). The addition of AgNO_3 solution results in the total volume of the mixture becoming $V_0 + V$, and the balances for Cl and Ag are as follows:

$$[\text{pr}] + [\text{Cl}^-] + \sum_{i=1}^3 i \cdot [\text{AgCl}_i^{1-i}] = \frac{C_0 V_0}{V_0 + V} \quad (8)$$

$$[\text{pr}] + [\text{Ag}^+] + \sum_{i=1}^3 [\text{Ag}(\text{OH})_i^{1-i}] + \sum_{i=1}^3 [\text{AgCl}_i^{1-i}] = \frac{CV}{V_0 + V} \quad (9)$$

where $[\text{pr}]$ is the concentration of AgCl in the system. Subtraction of Eq. 9 from Eq. 8 gives

$$[\text{Cl}^-] + \sum_{i=2}^3 (i-1) \cdot [\text{AgCl}_i^{1-i}] - [\text{Ag}^+] - \sum_{i=1}^3 [\text{Ag}(\text{OH})_i^{1-i}] = \frac{C_0 V_0 - CV}{V_0 + V} \quad (10)$$

Applying the relations $[\text{AgCl}_i^{1-i}] = K_i^{\text{Cl}} \cdot K_{\text{sp}1} [\text{Cl}^-]^{i-1}$ and $[\text{Ag}(\text{OH})_i^{1-i}] = K_i^{\text{OH}} [\text{Ag}^+] [\text{OH}^-]^i$, Eq. 10 becomes

$$z_1 [\text{Cl}^-] - z_2 [\text{Ag}^+] = \frac{C_0 V_0 - CV}{V_0 + V} \quad (11)$$

where

$$z_1 = 1 + K_2^{\text{Cl}} K_{\text{sp}1} + 2K_3^{\text{Cl}} K_{\text{sp}1} [\text{Cl}^-] \quad (12)$$

$$z_2 = 1 + K_1^{\text{OH}} [\text{OH}^-] + K_2^{\text{OH}} [\text{OH}^-]^2 + K_3^{\text{OH}} [\text{OH}^-]^3 \quad (13)$$

Further, by assuming that the pH remains unchanged during titration, i.e., $\text{pH} \approx \text{pH}_0$, we can evaluate the numerical values of z_1 and z_2 , both of which are close to 1. Hence, Eq. 11 can be written as follows:

$$[\text{Cl}^-] - [\text{Ag}^+] = \frac{C_0 V_0 - CV}{V_0 + V} \quad (14)$$

At the titration endpoint (end), $V = V_{\text{end}}$, we have

$$[\text{Cl}^-]_{\text{end}} - [\text{Ag}^+]_{\text{end}} = \frac{C_0 V_0 - CV_{\text{end}}}{V_0 + V_{\text{end}}} \quad (15)$$

At the equivalence point (eq) we have the relation $C_0 V_0 = CV_{\text{eq}}$. Hence,

$$V_{\text{eq}} = \frac{C_0 V_0}{C} = 10 \text{ mL} \quad (16)$$

At the titration endpoint, $V = V_{\text{end}}$, the solubility product $K_{\text{sp}2}$ is crossed, i.e., $[\text{Ag}^+]_{\text{end}}^2 \cdot [\text{CrO}_4^{2-}]_{\text{end}} = K_{\text{sp}2}$. At $\text{pH} = \text{pH}_{\text{end}} = \text{pH}_0$, CrO_4^{2-} predominates significantly over all other chromium species (Fig. 1) and it is still not consumed by silver nitrate, which acts mainly as a diluent at $V \leq V_{\text{end}}$. Hence,

$$[\text{CrO}_4^{2-}]_{\text{end}} = \frac{C_{\text{ind}} V_0}{V_0 + V_{\text{end}}} \quad (17)$$

$$[\text{Ag}^+]_{\text{end}} = \sqrt{K_{\text{sp}2} \frac{V_0 + V_{\text{end}}}{C_{\text{ind}} V_0}} \quad (18)$$

Since AgCl is also the equilibrium solid phase in this system, $[\text{Cl}^-]_{\text{end}} = K_{\text{sp}1} / [\text{Ag}^+]_{\text{end}}$. Gathering these expressions, we can rewrite Eq. 15:

$$\frac{K_{\text{sp}1}}{\sqrt{K_{\text{sp}2} \frac{V_0 + V_{\text{end}}}{C_{\text{ind}} V_0}}} - \sqrt{K_{\text{sp}2} \frac{V_0 + V_{\text{end}}}{C_{\text{ind}} V_0}} = \frac{C_0 V_0 - CV_{\text{end}}}{V_0 + V_{\text{end}}} \quad (19)$$

Equation 19 can be solved for V_{end} iteratively by inserting all known numerical values (C , C_{ind} , C_0 , V_0 , $K_{\text{sp}1}$, $K_{\text{sp}2}$). For the value $C_{\text{ind}} = 0.002$ mol/L, we find that $V_{\text{end}} = 10.022$ mL satisfies Eq. 19. Given that simple chemical stoichiometry suggests the equivalence point at $V_{\text{eq}} = 10$ mL, ignoring the corrections due to solubility and other chemical processes leads to a 0.22% error. Results for other values of C_{ind} are summarized in Table 1.

Table 1 Titration endpoints for Mohr's method

$C_{\text{ind}} / (\text{mol/L})$	Approx. pH_0	Titration endpoint, $V_{\text{end}} / \text{mL}$	Relative difference between the endpoint and equivalence point, $V_{\text{end}} / V_{\text{eq}} - 1$
0.001	8.74	10.036	+0.36 %
0.002	8.99	10.022	+0.22 %
0.005	9.09	10.007	+0.07 %
0.010	9.24	9.996	-0.04 %

As we can see from Table 1, errors in chloride determination are affected by the initial concentration of K_2CrO_4 , C_{ind} . With the increase of C_{ind} , the systematic error decreases, assumes zero at $C_{ind}=0.0078$ mol/L, and then increases gradually.

On the basis of the data obtained from calculations, one can also check whether the solubility products K_{sp3} for $Ag_2Cr_2O_7$ and K_{sp4} for Ag_2O are crossed. At $C_{ind}=0.002$ mol/L, we calculate $[Ag^+]_{end}=2.632 \times 10^{-5}$ mol/L from Eq. 18. At pH=8.99 we have $[Cr_2O_7^{2-}]=3.46 \times 10^{-8}$ mol/L and $[Ag^+]^2[Cr_2O_7^{2-}]=2.4 \times 10^{-17} < 10^{-6.7}$, $[Ag^+][OH^-]=2.6 \times 10^{-10} < 10^{-7.84}$. Hence, these solubility products are not crossed.

Conclusion

Titration is still considered as a primary method of chemical analysis. From this example it is evident that the accuracy of the titration results can be significantly improved by better understanding of the physicochemical conditions of the system.

References

1. Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Mohr's method challenge. *Anal Bioanal Chem.* 2016;408:1721–22.