

Mohr's method challenge

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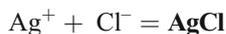
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In the present challenge, titration is the topic. And please note that there is a prize to be won (a Springer book of your choice up to a value of €100). Please read on...

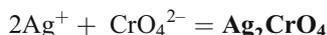
Meet the Mohr's method challenge

Among the various methods of volumetric analysis, precipitation titrations are based on the formation of compounds of limited solubility [1]. In particular, titrimetric methods based on the use of silver nitrate as precipitating reagent are termed as argentometric titrations. Named after German chemist and pharmacist Karl Friedrich Mohr (1806–1879), Mohr's method

determines the amount of chloride ions by titration with AgNO_3 . The endpoint of the titration is observed using potassium chromate as an indicator, which gives brown-red silver chromate precipitate when all chloride ions have reacted with the silver ions. Mohr's method remains one of the oldest titration methods and is still used in many laboratories. During the titration, the precipitation of silver chloride occurs



and the endpoint of this titration is observed by the appearance of silver chromate



as the new equilibrium solid phase, when all chloride ions have reacted with the silver ions. Mohr's method remains one of the oldest titration methods and is still used in many laboratories. This challenge examines the slight difference that exists between the observed endpoint and the actual chemical equivalence in titration along with the magnitude of errors that this discrepancy may cause.

The challenge

Consider a $V_0 = 100$ mL sample of sodium chloride solution, $C_0 = 0.01$ M, which is titrated with AgNO_3 solution, $C = 0.1$ M, in the presence of K_2CrO_4 indicator at concentration $C_{\text{ind}} = 0.002$ M. The oversimplified "textbook" model of this titration assumes that the titration of 100 mL 0.01 M NaCl sample "ends" after the addition of 10 mL 0.1 M AgNO_3 solution. This assumes that Ag_2CrO_4 will start forming only when all chloride ions are consumed by the silver ions. However, the solubility of AgCl and Ag_2CrO_4 and other chemical

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Table 1 Physicochemical equilibrium data relevant to Mohr's method ($pK = -\log K$)

Reactions	Definitions	Equilibrium data
$H_2CrO_4 = H^+ + HCrO_4^-$	$[H^+][HCrO_4^-] = K_{11}[H_2CrO_4]$	$pK_{11} = 0.8$
$HCrO_4^- = H^+ + CrO_4^{2-}$	$[H^+][CrO_4^{2-}] = K_{21}[HCrO_4^-]$	$pK_{21} = 6.5$
$HCr_2O_7^- = H^+ + Cr_2O_7^{2-}$	$[H^+][Cr_2O_7^{2-}] = K_{22}[HCr_2O_7^-]$	$\log K_{22} = 0.07$
$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	$[Cr_2O_7^{2-}] = K_1[HCrO_4^-]^2$	$\log K_1 = 1.52$
$H_2O = H^+ + OH^-$	$[H^+][OH^-] = K_w$	$pK_w = 14.0$
$Ag^+ + Cl^- = AgCl$	$[AgCl] = K_1^{Cl}[Ag^+][Cl^-]$	$\log K_1^{Cl} = 3.08$
$Ag^+ + 2Cl^- = AgCl_2^-$	$[AgCl_2^-] = K_2^{Cl}[Ag^+][Cl^-]^2$	$\log K_2^{Cl} = 5.08$
$Ag^+ + 3Cl^- = AgCl_3^{2-}$	$[AgCl_3^{2-}] = K_3^{Cl}[Ag^+][Cl^-]^3$	$\log K_3^{Cl} = 6.0$
$Ag^+ + OH^- = AgOH$	$[AgOH] = K_1^{OH}[Ag^+][OH^-]$	$\log K_1^{OH} = 2.3$
$Ag^+ + 2OH^- = Ag(OH)_2^-$	$[Ag(OH)_2^-] = K_2^{OH}[Ag^+][OH^-]^2$	$\log K_2^{OH} = 3.6$
$Ag^+ + 3OH^- = Ag(OH)_3^{2-}$	$[Ag(OH)_3^{2-}] = K_3^{OH}[Ag^+][OH^-]^3$	$\log K_3^{OH} = 4.8$
$AgCl = Ag^+ + Cl^-$	$[Ag^+][Cl^-] = K_{sp1}$	$pK_{sp1} = 9.75$
$Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-}$	$[Ag^+]^2[CrO_4^{2-}] = K_{sp2}$	$pK_{sp2} = 11.9$
$Ag_2Cr_2O_7 = 2Ag^+ + Cr_2O_7^{2-}$	$[Ag^+]^2[Cr_2O_7^{2-}] = K_{sp3}$	$pK_{sp3} = 6.7$
$AgOH = Ag^+ + OH^-$	$[Ag^+][OH^-] = K_{sp4}$	$pK_{sp4} = 7.84$

processes makes this trivial problem considerably more complex. Conceptually, the endpoint of titration corresponds to the point where the solubility product of Ag_2CrO_4 is crossed.

At what point will the endpoint of titration actually occur in this example?

All relevant data for detailed calculations are presented in Table 1 [2, 3]. For this system, the titrand (D) is NaCl solution, $V_0 = 100$ mL and $C_0 = 0.01$ M, with K_2CrO_4 (with concentration $C_{ind} = 0.002$ M), and the titrant (T) is $AgNO_3$ solution, $C = 0.1$ M. Volume of the titrant added up to a given point of titration is denoted as V . In order to calculate the precise endpoint of titration, it is instructive to follow the following steps:

- (I) Formulate the proton balance for D (i.e., at $V = 0$) and show that it is alkaline.
- (II) Formulate the relationship between $[CrO_4^{2-}]$ and pH for D.
- (III) Calculate the $pH = pH_0$ of D for $C_0 = 0.01$ M and $C_{ind} = 0.001, 0.002, 0.005,$ and 0.010 M.
- (IV) Plot the logarithmic concentration of the various chromium species as a function of pH at $C_{ind} = 0.002$ M and compare the value of $[CrO_4^{2-}]$ with C_{ind} at $pH = pH_0$.
- (V) For the titration stage ($V > 0$), formulate the concentration balances for Ag and Cl. Denote the concentration of $AgCl$ (precipitate) in the system as $[pr]$. Compare these two concentration balances in order to eliminate the $[pr]$ in the resulting equation and simplify this equation on the basis of quantitative knowledge in Table 1.
- (VI) Calculate the titration endpoint (V_{end}) where the solubility product K_{sp2} is crossed. Assume that pH does not change during the titration.

(VII) Calculate the C_{ind} value at which $V_{end} = V_{eq}$ (i.e., the bias in chloride determination vanishes).

(VIII) Check whether the solubility products for $Ag_2Cr_2O_7$ and $AgOH$ are crossed at $C_{ind} = 0.002$ M and $V = V_{end}$.

References

1. Kolthoff IM, Lauer WM, Sunde CJ. *J Am Chem Soc.* 1929;51(11): 3273–7.
2. Inczedy J. *Analytical Applications of Complex Equilibria.* Horwood: Chichester; 1976.
3. Kotrly S, Sucha L. *Handbook of Chemical Equilibria in Analytical Chemistry,* Ellis Horwood Series in Analytical Chemistry. New York: John Wiley and Sons; 1985.

We invite our readers to participate in the Analytical Challenge by solving the puzzle above. Please send the correct solution to abc-challenge@springer.com by April 1, 2016. Make sure you enter “Mohr's method challenge” in the subject line of your e-mail. The winner will be notified by e-mail and his/her name will be published on the “Analytical and Bioanalytical Chemistry” homepage at <http://www.springer.com/abc> and in the journal (volume 408/issue 17) where readers will find the solution and a short explanation.

The next Analytical Challenge will be published in 408/12, May 2016. If you have enjoyed solving this Analytical Challenge you are invited to try the previous puzzles on the ABC homepage.