The PRECIPITATION TITRATION CURVE

Objectives

1. To learn the nature of the Mohr titration curve.
2. To be able to calculate analyte and titrant ion concentrations at any point during the Mohr titration.
3. To understand the role of K_{sp} in the feasibility of a titration.

Suppose that we have 50mL of 0.10F KBr in water in an Erlenmeyer flask and we add to it small amounts of 0.20F $AgNO_3$ solution. As we do this, we'll expect the reaction

$$Ag^+ + Br^- \rightarrow AgBr(s)$$

to take place. AgBr is quite insoluble in water, exhibiting a K_{sp} of 5.0×10^{-13}.

1. How many mL of $AgNO_3$ solution would need to be added to the KBr solution so that all of the Br^- would be consumed in a formal sense (of course there will always be a tiny amount of Br^- present due to equilibrium. Just pretend for the moment that this doesn't happen).

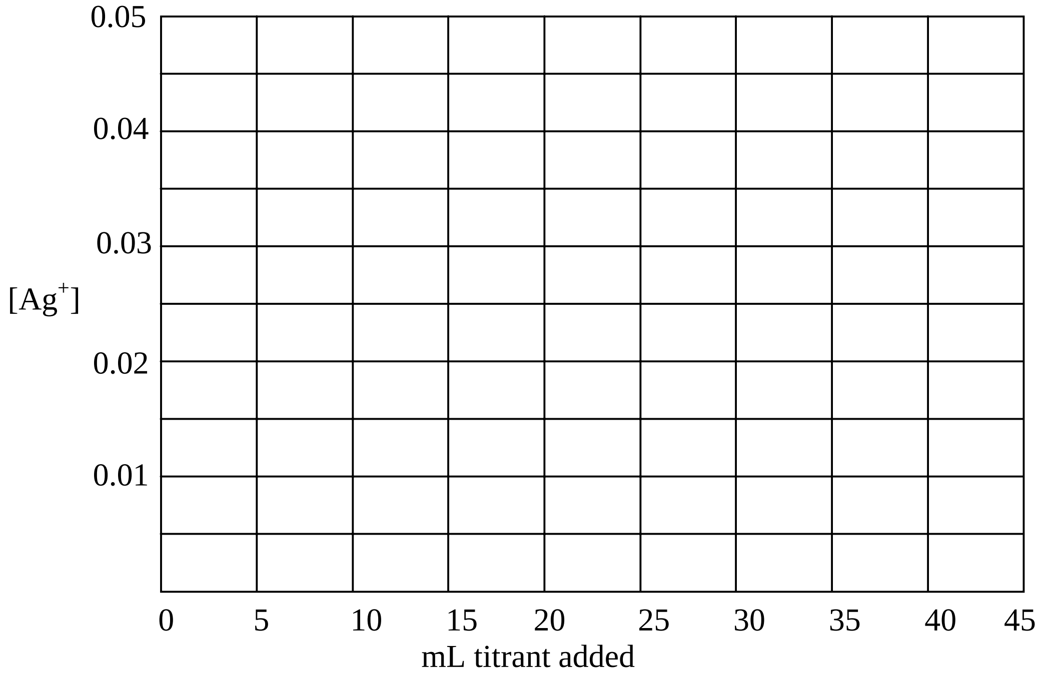
2. Once we add more than this amount of $AgNO_3$ solution, what happens to the extra Ag^+?

When this procedure is done for the express purpose of finding out what volume of $AgNO_3$ solution is needed to exactly consume a given amount of some anion it's called an *argentometric titration* (argentum is the Latin name for silver. Ever wonder why its symbol is Ag?). The volume where just the right amount of Ag^+ titrant has been added to consume all of the analyte is called the *equivalence point* of the titration. Finding the equivalence point of an argentometric titration can be a bit of a challenge and there are several ways to go about it, none of which gives exactly the correct volume in every case, but most of which are usually adequately close for some situation. The event which a given method provides to signal proximity of the equivalence point is called the *endpoint* of the titration.

Suppose that following each addition of $AgNO_3$ we measure the concentration of Ag^+ in the solution. This is conveniently done using one of the so-called ion-sensitive electrodes or ISEs available on the market which are tailored to measure particular ion concentrations over several orders of magnitude, much as one would measure $[H^+]$ using a pH electrode. Here's some typical data obtained from such an experiment:

mL titrant added	$[Ag^+]$
5	6.88 x 10^{-12}
10	1.00 x 10^{-11}
15	1.62 x 10^{-11}
20	3.50 x 10^{-11}
22	6.00 x 10^{-11}
24	1.85 x 10^{-10}
26	2.63 x 10^{-3}
28	7.69 x 10^{-3}
30	1.25 x 10^{-2}
35	2.35 x 10^{-2}
40	3.33 x 10^{-2}

3. Draw a graph of $[Ag^+]$ as a function of mL titrant added and use it to locate the equivalence point. Be prepared to justify your choice of graph features for determining this.



4. It’s customary to graph titration curves as pAg as a function of mL titrant added. So calculate pAg for each of the additions and graph those, similarly noting where the equivalence point is:

mL titrant added	$[Ag^+]$	pAg
5	6.88×10^{-12}	
10	1.00×10^{-11}	
15	1.62×10^{-11}	
20	3.50×10^{-11}	
22	6.00×10^{-11}	
24	1.85×10^{-10}	
26	2.63×10^{-3}	
28	7.69×10^{-3}	
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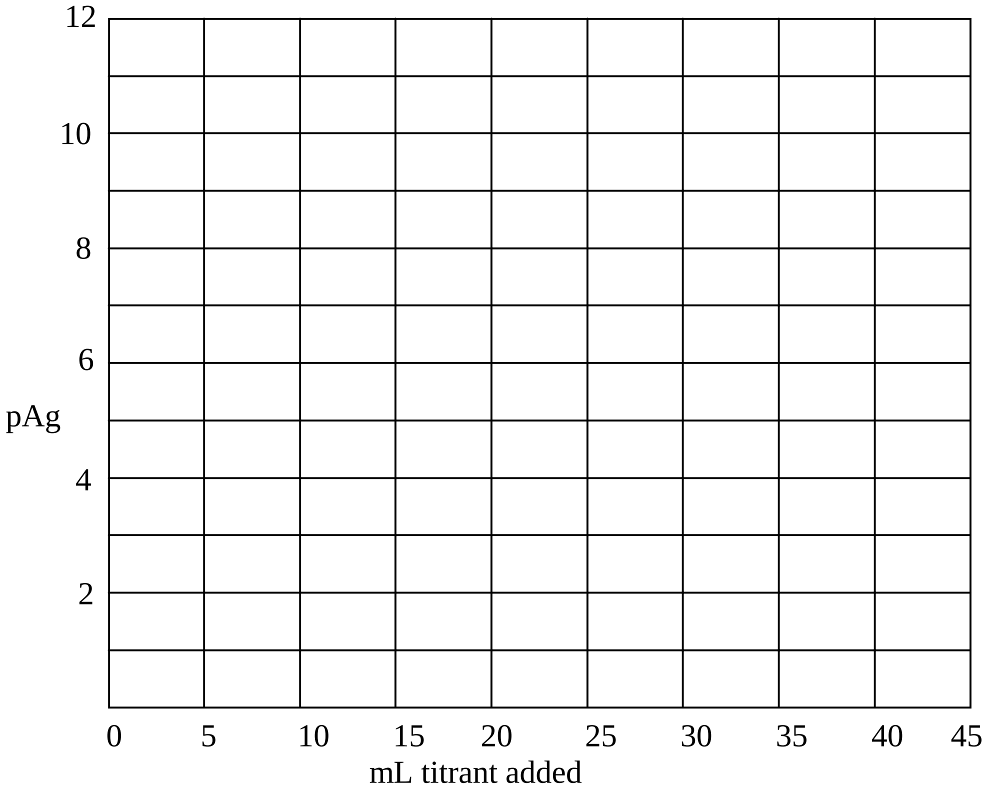
40	3.33×10^{-2}	



5. Of the two presentations, which do you think is easier to graph?

6. Which presentation makes the location of the equivalence point clearest?

7. Which presentation preserves the greatest amount of titrant concentration information both before and after the equivalence point?

Problem

20.0 mL of 0.20F $AgNO_3$ is added to 50.0mL of 0.10F KBr. Calculate the pAg of the resulting solution, ignoring activity.

This is one point on the titration curve you plotted on a previous page, even though it's not couched directly in titration terms. It turns out that any mixture of 0.20F $AgNO_3$ and 0.10F KBr can be regarded as a point on the titration curve (although you might never expect to encounter most of those way beyond the equivalence point if you were awake). Consequently we'll typically state our arguments in titration terms, even though an actual titration might not be what the problem had in mind.

8. The reaction you're looking at is

$$Ag^{+} \quad + \quad Br^{-} \quad \rightarrow \quad AgBr(s)$$

Figure out the moles of Ag^{+} or Br^{-} left over in solution after the reaction takes place, ignoring equilibrium for the time being. Use this result to get the concentration of the leftover ion. This is called performing the formal reaction.

9. Now invoke the equilibrium

$$AgBr(s) \Leftrightarrow Ag^{+} + Br^{-} \qquad\qquad K_{sp} = 5.0 \times 10^{-13}$$

and calculate $[Ag^{+}]$ and pAg.

10. Calculate pAg at the equivalence point of a titration of 0.10F KBr with 0.20F $AgNO_3$.

11. Calculate pAg in a titration of 50.0mL of 0.10F KBr following the addition of 30.0mL of 0.20F $AgNO_3$.

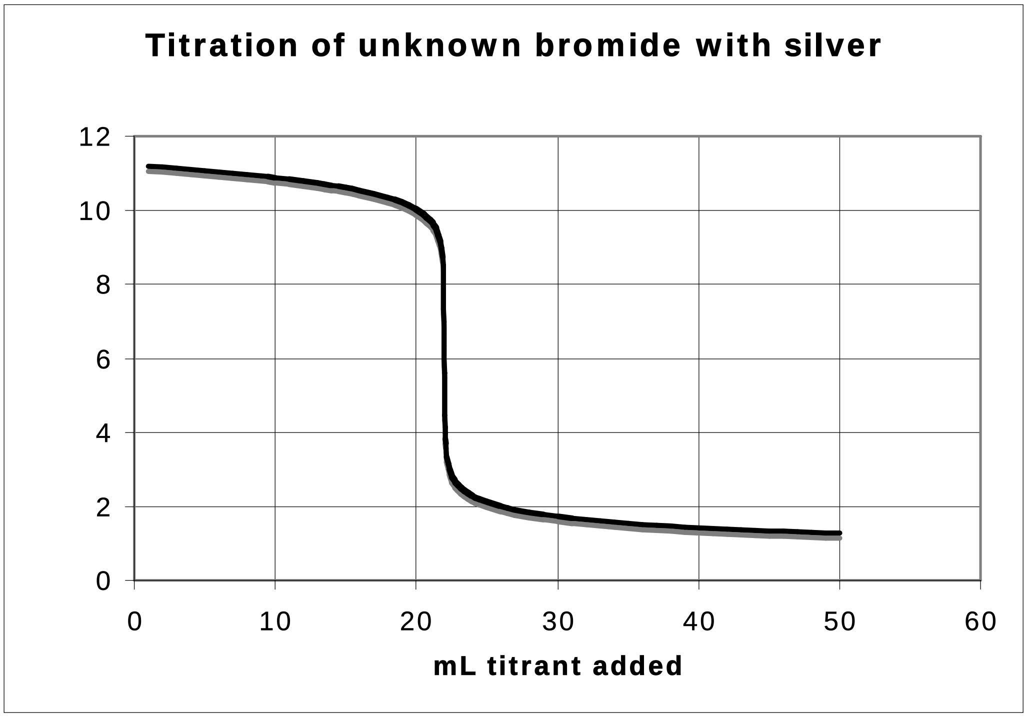
12. Does the Ag^+ released by the equilibrium dissolution of the AgBr(*s*) contribute significantly to the pAg in this case?

Suppose that I have this solution of roughly 0.1F Br^- for which I'd like to know the concentration with greater precision. One approach might be to prepare some $AgNO_3$ solution having accurately known concentration and perform an argentometric titration.

A titrant is prepared by dissolving 16.0g of pure, dry $AgNO_3$ (f.w. 169.88) in enough water to make 500.0mL of titrant.

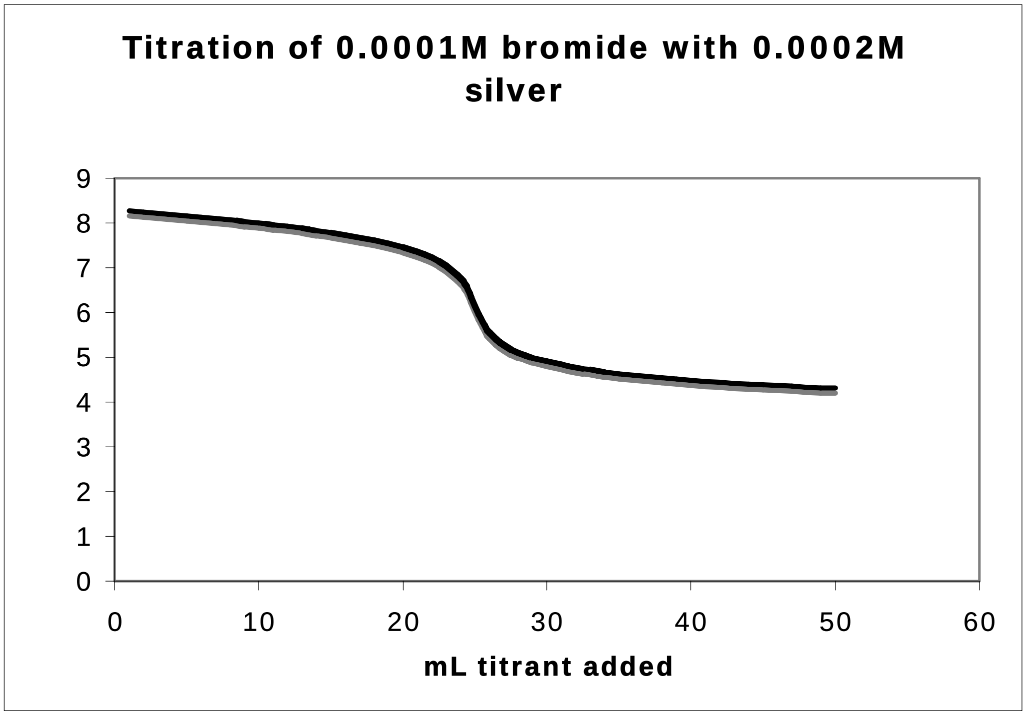
13. Calculate the formal concentration of $AgNO_3$ in the titrant.

Here's the titration curve I observe for 50.0 mL of the bromide solution



14. Calculate the concentration of bromide in the unknown solution.

Now, suppose that I'd like to determine bromide in this really dilute solution. It's probably like 10^{-4} M or so in Br^-. So I prepare this 2.0 x 10^{-4} F $AgNO_3$ solution and do a titration. Here's the curve that results:



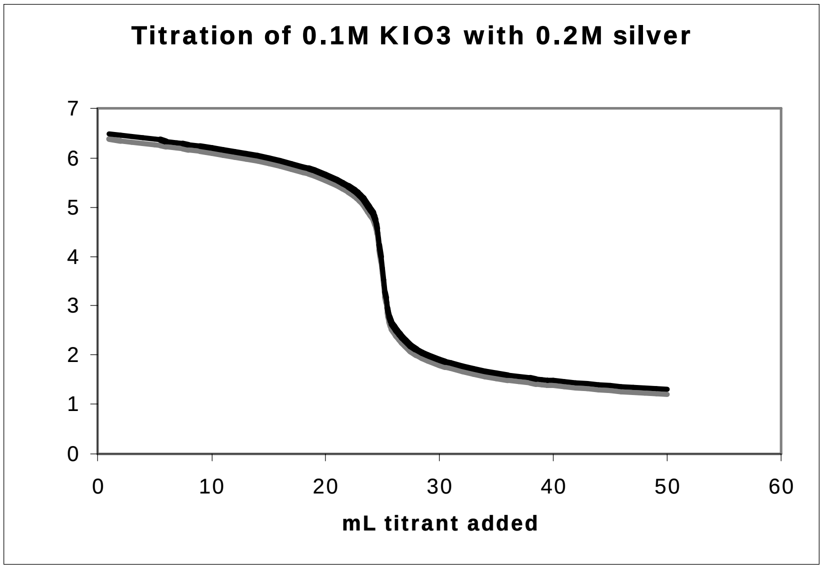
15. What happens to the precision with which the equivalence point can be determined in an argentometric titration as the concentrations of the reagents decrease?

16. See if you can give an explanation for this behavior.

As you might well imagine, bromide isn't the only anion that one might attempt to determine argentometrically. Iodate forms a nice insoluble adduct with silver thus:

$$Ag^+ + IO_3^- \rightarrow AgIO_3(s) \qquad K_{sp} = 3.1\times10^{-8}$$

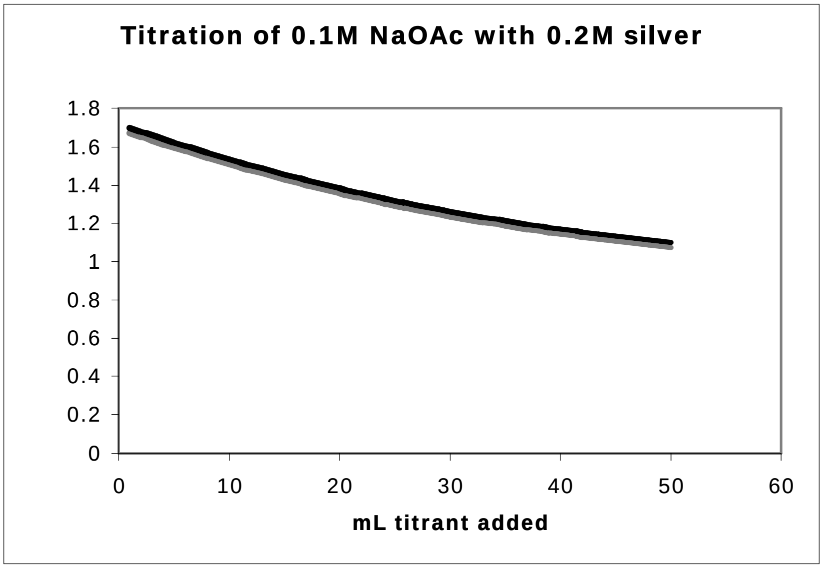
Here's the titration curve for 50.0mL of 0.10F KIO_3 with 0.20M Ag^+:



Even acetate forms an insoluble adduct with silver:

$$Ag^+ + OAc^- \rightarrow AgOAc(s) \qquad K_{sp} = 2.3\times10^{-3}$$

Here's the titration curve you get for 50.0mL of 0.10F sodium acetate with 0.20M Ag^+:



17. Does it look as though silver titrations of acetate will yield useful results?

18. Compare this curve with those obtained for 0.1 M Br^- and IO_3^-. What might be responsible for this fairly radical difference in appearance?

Exercise

25mL of 0.20*F* $La(NO_3)_3$ is titrated with 0.5*F* oxalic acid, $H_2C_2O_4$ resulting in the precipitation of $La_2(C_2O_4)_3(s)$. The oxalate ion, $C_2O_4^{-2}$ is too weak a base to affect the precipitation equilibrium significantly in neutral solution. Calculate the pLa following addition of 10mL, 15mL and 20mL of titrant.