

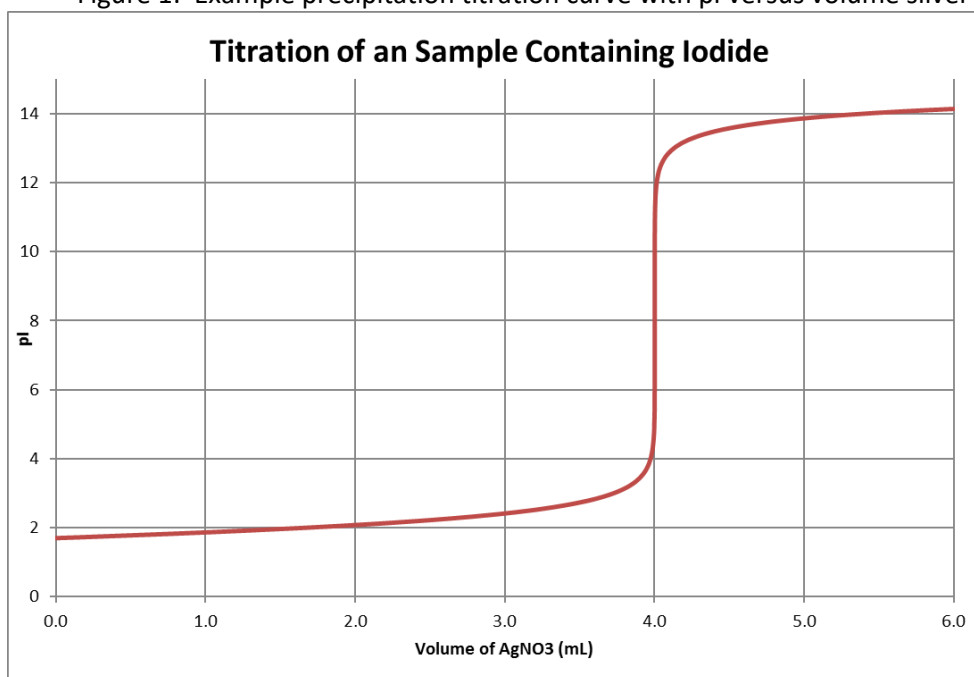
Precipitation Titrations:

Anatomy of a Precipitation Titration Curve:

A titration curve is a plot of a p-function (defined below) versus titrant volume. The shape is sigmoidal. Figure 1 shows a typical precipitation titration curve. **All** titration curves regardless of type, have four (4) distinct regions: initial, pre-equivalence, equivalence and post equivalence. Note the vertical portion of the curve at 10.00 mL of titrant added. The inflection point occurs here; the titrant volume corresponding to the inflection is called the *equivalence point volume*. If the titration curve is experimentally produced, we would call the inflection point the *end-point volume*. The difference between the *endpoint volume* and the *equivalence point volume* is a *bias* called *titration error*. The range of titrant volumes which define each region are based on a knowledge of the equivalence point volume, and because of this fact, this is one of the first things that is determined when calculating a titration curve.

It is imperative that the change in the p-function at the inflection point is sharp; basically, it should be instantaneous with an infinite slope ($\Delta\text{pH}/\Delta V$). Examination of theoretical titration curves give the analytical chemist a chance to determine if a titration is feasible by using an ion selective electrode and numerical methods to find the end-point or if a visual indicator is feasible.

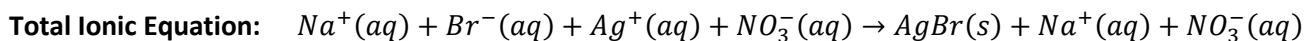
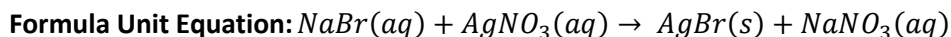
Figure 1: Example precipitation titration curve with pI versus volume silver nitrate added:



The solution chemistry in each region controls the concentration of the analyte, excess titrant and the solubility of the precipitate. The analyte concentration is usually written as a p-function; p-functions are based on the activity of the analyte species and are mathematically represented as the $-\log(\mathcal{A}_{\text{analyte}})$ or $-\log(\gamma_{\text{analyte}}[\text{Analyte}])$. In this example we will give the activity coefficients, γ_{analyte} , since we will keep the ionic strength constant. In this inquiry, you will be guided through the chemistry and calculations of a typical precipitation titration curve.

Example

To keep it simple, let's consider the titration of 10.00 mL of a 0.0500 M sodium bromide with 0.0500 M silver nitrate. All titrations require a *facile* reaction between the titrant and the analyte as well as a well-defined reaction stoichiometry. To find the relationship in this example, we must derive the net ionic equation for this system:

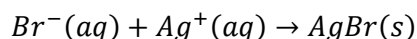


Q1. Write the net ionic equation in the space provided:

Net Ionic Equation:

Because the ionic strength will vary throughout the titration (this is a metathesis reaction after all), it will ultimately effect the activities of the analyte and titrant. To mitigate this effect, an ionic strength adjuster is added to the solution to keep the ionic strength constant at 0.100 M throughout the titration.

As mentioned, the equivalence point volume needs to be calculated and can be found from considering the net ionic reaction between the titrant and analyte:



Find the equivalence point volume for this titration.

Q2: Calculate the equivalence point volume for this titration.

Let's now examine the chemistry in the four regions so we can calculate the p-functions for the analyte and titrant as the titrant is added.

Region #1: Initial (0 mL titrant added)

Initially titrant has not been added to the analyte solution. Since starting analyte solution has a known concentration of bromide; the activity of the bromide ion can be determined from the activity coefficient we found previously and the actual molar concentration of the solution. There is really nothing complicated to work here except to find the p-function of the bromide ion concentration.

- Q3: *You have the initial solution of the analyte and you know the concentration of the bromide ion. Find the initial pBr. Find pBr (analyte) using the value of 0.755 for the activity coefficient of bromide, γ_{Br^-} .*

$$pBr = -\log(\mathcal{A}_{Br^-}) = -\log(\gamma_{Br^-} [Br^-]) =$$

We now need to find the pAg (titrant). We cannot get the value of pAg because there is not any silver ion present (that we know of!)

Region #2: Pre-Equivalence (0 < Volume Titrant Added < Equivalent Point Volume)

In this region, we have added a volume of titrant which is greater than 0, but less than the equivalence point volume. In this region, the titrant will ALWAYS be the limiting reagent. The analyte concentration is found based on the millimoles of bromide we started with minus the amount that went to form the precipitate. Unlike a gravimetric analysis where the precipitate will be filtered, here we want the precipitate to remain as a colloid so that the visual endpoint indicator or the ion selective electrode can work properly. Surfactants are added to the solution to keep the particles from coagulating.

- Q3: *What ion will be adsorbed onto the precipitate particles surface in this region?*
- Q4: *What will the charge of the particle be?*
- Q5: *Based on the ions present in the solution, which of those ions will be near the particle surface, but in solution?*

If we use dichlorofluorescein as a visual indicator for the titration, we are performing a Fajan's titration. The dichlorofluorescein is negatively charged in the analyte solution, and it is an eerie greenish-yellow fluorescent color. The indicator works by adsorbing onto the precipitate particles surface. This results in changes to the light absorbing characteristics of the indicator giving a pinkish color change. The solution will look like strawberry milk.

- Q6: *Do you think this indicator is absorbed onto the precipitate particles in this region? Explain.*

We can use an ICF chart to find the amount of each species left after the addition of a given volume of titrant. The “I” stands for initial. Here you find the initial millimoles for each reactant. “C” stands for change. From the initial quantities, you determine the limiting reagent and use that quantity and stoichiometry to calculate the change in the amounts of the other reactants and any products. “F” stands for final and represents the final amount for each reactant and product. This is calculated as the sum of the “Initial” and “Change” for each species.

- Q7. How many millimoles of bromide ion were initially present? Enter this in the appropriate cell in the ICF chart.
- Q9. If we add 3.00 mL of silver nitrate to the bromide ion solution, how many millimoles of silver ion were added? Enter this in the appropriate cell in the ICF chart.
- Q8. Determine the limiting reagent based on stoichiometry and enter the change in the number of millimoles for all species. Enter these in the change row of the ICF chart.
- Q9. Find the final number of millimoles of each species, and of each species. Enter these in the Final row of the ICF chart.

	Ag⁺(aq)	Br⁻(aq)	⇌	AgBr(s)
Initial				
Change				
Final				

- Q10. If the molar mass of AgBr is 187.772 g/mol, what mass of precipitate formed?
- Q11. After precipitation, and equilibrium is achieved, describe the composition of the solution in terms of the ions present and their relative amounts.

Your answer to Q11 should have led to you think about the common ion effect and the law of mass action.

- Q12. Identify the common ion, and describe its effect does solubility of the precipitate.

To solve for the silver ion concentration (it represents the solubility), we fill in an ICE chart based on the final condition in the ICF chart above. Note that the initial molarity of silver ion is 0.

- Q13. What is the initial concentration of bromide ion before equilibrium is reached?

You can now fill in and complete the ICE chart for the solution

	Ag⁺(aq)	Br⁻(aq)	⇌	AgBr(s)
Initial				
Change				
Equilibrium				

'x' represents the number of moles of reaction that is gained or lost. Since 1 mol silver ion is equivalent to 1 mole AgBr, x represents the solubility of the solid in the solution.

The thermodynamic equilibrium constant expression is as follows:

$$K_{sp}^o = \gamma_{Ag^+}\gamma_{Br^-}[Ag^+][Br^-] = 5.35 \times 10^{-13}$$

Since the ionic strength of during the titration is maintained at 0.100 M, the activity coefficients will remain constant at $\gamma_{Ag^+} = 0.75$ and $\gamma_{Br^-} = 0.755$.

Q14: Substitute the activity coefficients and the equilibrium expressions for the ions (E row from ICE chart) into the solubility product expression:

Q14: Think about how you answered Q12. Can you make simplifying assumptions here?

Q15: Solve for silver ion using the assumptions and without. What do you think about the assumption? Remember that without the assumption you will have multiple roots. You have to decide which root make the most sense!

Q16: Find the pBr (analyte)

$$pBr = -\log(\mathcal{A}_{analyte}) = -\log(\gamma_{analyte}[Analyte])$$

Q17: Find the pAg (titrant)

$$pAg = -\log(\mathcal{A}_{Ag^+}) = -\log(\gamma_{Ag^+}[Ag^+]) =$$

Q18: What is the solubility at this point? Explain.

Q19: Other pre-equivalence point pBr and pAg can be found in a similar manner. Calculate pAg and pBr at 1.00 mL, 5.00 mL, 7.00 mL and 9.00 mL of titrant added.

Region #3: Equivalence (Volume Titrant Added = Equivalent Point Volume)

Here we have added a volume of titrant that has reacted with ALL of the analyte in the solution. Both analyte and titrant are limiting in this case. The precipitate particles in the colloid or solid will be of mixed charge. We use an ICF chart to confirm these facts:

Fill in the ICF chart after the addition of 10.00 mL of silver solution:

	Ag⁺(aq)	Br⁻(aq)	\rightleftharpoons	AgBr(s)
Initial	0.500 mmol	0.500 mmol		0 mmol
Change	-0.500 mmol	-0.500 mmol		+0.500 mmol
Final	0 mmol	0.000 mmol		0.500 mmol

Q20: Determine the charge of the precipitate particles.

Q21: What ion will be adsorbed onto the precipitate particles surface?

Q22: What ions will be near the particle surface, but in solution?

Q23: The visual indicator used in the titration works by adsorbing onto the surface of the particle and it has a negative charge. This results in changes to the light absorbing characteristics of the indicator giving a color change. The indicator is in solution in its anionic form, In^- . Do you think it will absorb and change color in this region?

After the reaction, the silver ion, bromide ion and the solid AgBr will come to equilibrium. At that point, we will have a saturated solution of silver bromide. Deducing the concentrations of the ions in this solution is 'similar' to finding the solubility of a precipitate in pure water (except that other spectator ions are present). We again use the final conditions of the ICF chart as the starting concentration in the ICE chart.

Q24: Fill in the ICE chart for this solution.

	Ag⁺(aq)	Br⁻(aq)	\rightleftharpoons	AgBr(s)
Initial				
Change				
Equilibrium				

Q25: Do you expect the solubility of the AgBr to be greater than or less than the pre-equivalence region.

Q26: As before, the thermodynamic equilibrium constant expression is as follows:

$$K_{sp}^o = \gamma_{Ag^+} \gamma_{Br^-} [Ag^+] [Br^-] = 5.35 \times 10^{-13}$$

Since the ionic strength of during the titration is maintained at 0.100 M, the activity coefficients will remain constant at $\gamma_{Ag^+} = 0.75$ and $\gamma_{Br^-} = 0.755$.

Find the concentration of the ions in solution.

$$[Br^-] = [Ag^+] =$$

Q27: Compare this answer to the prediction of Q25 and explain why you were right or incorrect.

Q28: Find the pAg and pBr at this point.

For pBr (analyte)

$$pBr = -\log(\mathcal{A}_{Br^-}) = -\log(\gamma_{Br^-} [Br^-]) =$$

For pAg (titrant)

$$pAg = -\log(\mathcal{A}_{Ag^+}) = -\log(\gamma_{Ag^+} [Ag^+]) =$$

Q29: What is the solubility of AgBr, s

$$s =$$

Region #4: Post-Equivalence (Volume Titrant Added > Equivalent Point Volume)

In this region, we have added a volume which is greater than the equivalence point volume (10.00 mL). By definition, the titrant is in excess and the analyte is now the limiting reagent. We basically have to figure out how much excess titrant we have, and this is easy to do since we know the starting quantity of bromide and the quantity of silver we have added. The precipitate particles will take on the charge of the excess titrant in the solution. Again, we will use an ICF chart to find the concentration of the excess titrant.

For instance, after the addition of 15.00 mL of silver solution:

	Ag⁺(aq)	Br⁻(aq)	\rightleftharpoons	AgBr(s)
Initial	0.750 mmol	0.500 mmol		0 mmol
Change	-0.500 mmol	-0.500 mmol (LR)		+0.500 mmol
Final	0.250 mmol	0 mmol		0.500 mmol

Q30. What will the charge of the particle be?

Q31. Do you think it will absorb and change color in this region?

After the reaction, the silver and bromide ion are in equilibrium with solid silver bromide. We once again have the common ion effect at work as the excess silver ion will drive down the solubility of the solid. We use the Final conditions of the ICF chart as the starting concentration in the ICE chart.

We need the concentration of silver from the F row of the ICF chart:

$$\frac{\text{mmol Ag}^+ \text{ left}}{V_{\text{total}}} = \frac{0.250 \text{ mmol Ag}^+}{10.00 \text{ mL} + 15.00 \text{ mL}} = 0.0100 \text{ M Ag}^+$$

	Ag⁺(aq)	Br⁻(aq)	\rightleftharpoons	AgBr(s)
Initial	0.0100 M	0 M		---
Change	+x	+x		---
Equilibrium	0.0100 M + x	x		---

Q32: As before, the thermodynamic equilibrium constant expression is as follows:

$$K_{sp}^o = \gamma_{\text{Ag}^+} \gamma_{\text{Br}^-} [\text{Ag}^+][\text{Br}^-] = 5.35 \times 10^{-13}$$

Since the ionic strength of during the titration is maintained at 0.100 M, the activity coefficients will remain constant at $\gamma_{\text{Ag}^+} = 0.75$ and $\gamma_{\text{Br}^-} = 0.755$.

Find the concentration of the ions in solution.

$$[\text{Br}^-] =$$

$$[\text{Ag}^+] =$$

Q33: Find pBr (analyte)

$$pBr = -\log(\mathcal{A}_{Br^-}) = -\log(\gamma_{Br^-}[Br^-]) =$$

Find pAg (titrant)

$$pAg = -\log(\mathcal{A}_{Ag^+}) = -\log(\gamma_{Ag^+}[Ag^+]) =$$

Q34: Find the solubility and comment on this value compared to the pre-equivalence point volumes and the equivalence point volumes pAg and pBr.

$$s =$$

Other post-equivalence point pBr and pAg values can be found in a similar manner. Calculate pAg and pBr at 11.00 mL, 12.00 mL, 13.00 mL and 14.00 mL of titrant added. Each group should one of the volumes.

Q35: Plot the data on the graph paper.

Post Questions:

Q36: How would the plot change if we titrated chloride with silver or iodide with silver?

Q37: How would changing the concentration of the titrant change the curve?

Q38: How would changing the concentration of the analyte change the curve?

Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α , pm)	Ionic strength (μ , M)				
		0.001	0.005	0.01	0.05	0.1
<i>Charge = ± 1</i>		<i>Activity coefficient (γ)</i>				
H ⁺	900	0.967	0.933	0.914	0.86	0.83
(C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻	700	0.965	0.930	0.909	0.845	0.81
Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻	450	0.964	0.928	0.902	0.82	0.775
⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₃ ⁺	400	0.964	0.927	0.901	0.815	0.77
OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH ₂ ⁺	350	0.964	0.926	0.900	0.81	0.76
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻	300	0.964	0.925	0.899	0.805	0.755
Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺	250	0.964	0.924	0.898	0.80	0.75
<i>Charge = ± 2</i>		<i>Activity coefficient (γ)</i>				
Mg ²⁺ , Be ²⁺	800	0.872	0.755	0.69	0.52	0.45
CH ₂ (CH ₂ CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂ ⁻) ₂	700	0.872	0.755	0.685	0.50	0.425
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂ ⁻) ₂ , H ₂ C(CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CO ₂ ⁻) ₂	600	0.870	0.749	0.675	0.485	0.405
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂ ⁻) ₂ , (CH ₂ CO ₂ ⁻) ₂ , (CHOHCO ₂ ⁻) ₂	500	0.868	0.744	0.67	0.465	0.38
Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , Co(NH ₃) ₅ Cl ²⁺ , Fe(CN) ₅ NO ²⁻ , C ₂ O ₄ ²⁻ , Hcitrate ²⁻	450	0.867	0.742	0.665	0.455	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻	400	0.867	0.740	0.660	0.445	0.355
<i>Charge = ± 3</i>		<i>Activity coefficient (γ)</i>				
Al ³⁺ , Fe ³⁺ , Cr ³⁺ , Sc ³⁺ , Y ³⁺ , In ³⁺ , lanthanides ^a	900	0.738	0.54	0.445	0.245	0.18
citrate ³⁻	500	0.728	0.51	0.405	0.18	0.115
PO ₄ ³⁻ , Fe(CN) ₆ ³⁻ , Cr(NH ₃) ₆ ³⁺ , Co(NH ₃) ₆ ³⁺ , Co(NH ₃) ₅ H ₂ O ³⁺	400	0.725	0.505	0.395	0.16	0.095
<i>Charge = ± 4</i>		<i>Activity coefficient (γ)</i>				
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	1 100	0.588	0.35	0.255	0.10	0.065
Fe(CN) ₆ ⁴⁻	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: J. Kielland, J. Am. Chem. Soc. 1937, 59, 1675.