

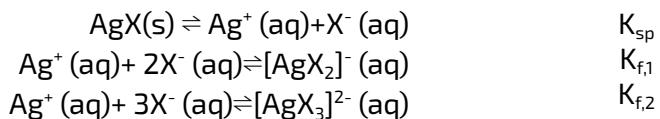
Problem x x% of total	Question	x.1	x.2	x.3	x.4	x.5	x.6	Total
	Points	2	4	2	4	2	4	33
Question	x.7	x.8	x.9	x.10	x.11	x.12		
Points	2	1	5	2	3	2		

## Problem x: Silver Chemistry

By Lim Dillion, Singapore

**Author's Note: Due to the propensity for propagation of errors when calculating exponentials, leading to extremely large errors in the final answer, the author recommends that all decimal places are used for subsequent calculations.**

In the spirit of the Silver tier of SChO, let us consider the solubility of the silver halides! There are three competing equilibria occurring (where X = Cl, Br).



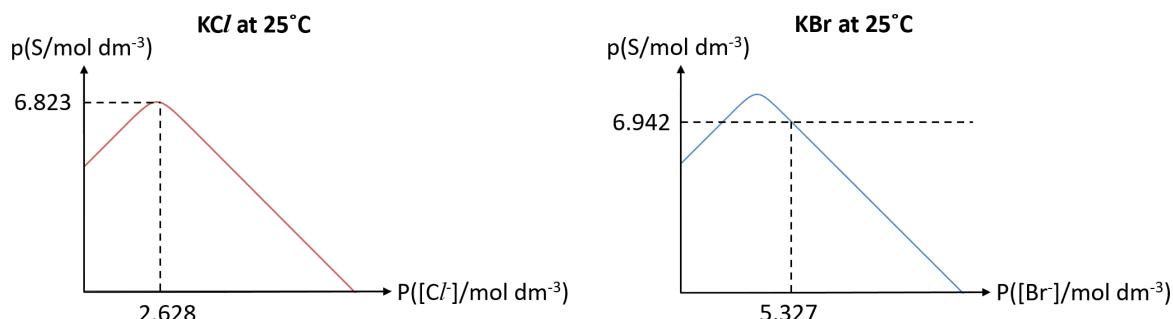
A student was looking at their data booklet for the values of  $K_{sp}$ ,  $K_{f,1}$  and  $K_{f,2}$  of both AgCl and AgBr. However, due to them being very careless, they accidentally knocked over a bottle of  $\text{AgNO}_3$  (aq) and now the values are covered by a black stain.

Hence, they have decided to conduct an investigation to determine this value.

- 1) By considering the equilibria above, write down an expression for S, the total concentration of silver in the solution just before  $\text{AgX}$  begins to precipitate.

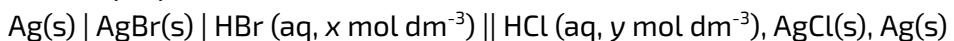
The student is told that  $K_{f,1} = K_{f,2}$  above. Hence, the student has decided to ignore the effects of  $K_{f,2}$  for all subsequent parts.

The student then prepared various aqueous KCl and KBr solutions. They then decided to conduct a very careful precipitation titration to plot a graph of how S varies with  $[\text{X}^-]$  at equilibrium. Denoting  $pA = -\lg A$ , the results are as follows:



- 2) Using the data above, compute the  $K_{sp}$  and  $K_f$  at 25°C for X = Cl.

Next, the student prepares an electrochemical cell:



A pH probe, when placed into the HBr solution gives a reading of 0.1549, while that of HCl gives a reading of 0.6021. When a high resistance voltmeter was placed across the electrochemical cell, the reading was +0.17537V.

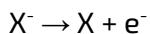
- 3) State the values of x and y. Hence, or otherwise, determine the  $\Delta_r G$  of the cell reaction at standard conditions.
- 4) Thus, calculate the value of  $K_{sp}$  and  $K_f$  for X = Br at 25°C.

The student has instead decided to prepare an electrochemical cell with a glassy carbon electrode, a saturated calomel electrode (SCE), and a Pt wire as working, reference, and counter-electrodes, respectively. The student wants to conduct a cyclic voltammetry on a sample containing aqueous NaCl, but he notices that the sample has been unfortunately contaminated with aqueous KBr.

- 5) The student noticed this with the addition of a common qualitative test. Explain what test the student conducted.

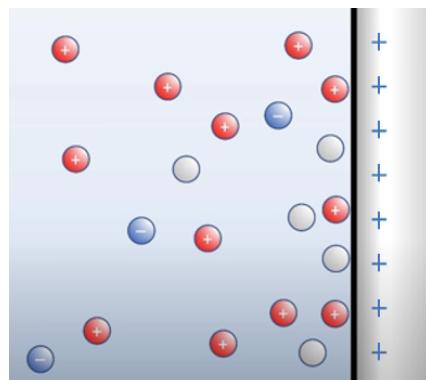
Cyclic voltammetry is an electrochemical technique for measuring the current response of a redox active solution to a linearly cycled potential sweep between two or more set values. The principles of cyclic voltammetry are founded on two basic principles: the rate of diffusion, which is independent of the potential difference across electrodes, and the ion-drift speed, which is affected by the potential difference and current.

Let us consider an anodic process:



It is known that the ion-drift speed,  $s = u|E|$ , where  $u$  is the ion mobility, which can be treated as a constant for the same ion, and  $E$  is the electric field the ion experiences.

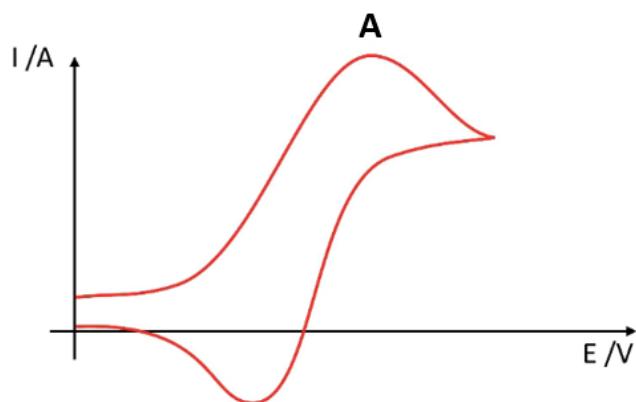
The shape of a cyclic voltammetric graph is very peculiar, but analysing what occurs at the electrode surface will help to clear up a lot of the confusion.



- 6) Using the above information, give a possible reason why increasing (a) the current of the electrolytic setup and (b) the potential difference across electrodes may increase the rate at which this oxidation occurs.
- 7) By further considering what occurs at the electrode surface, give a possible reason why increasing the electrode potential further may cause the rate of the oxidation to slow down instead.

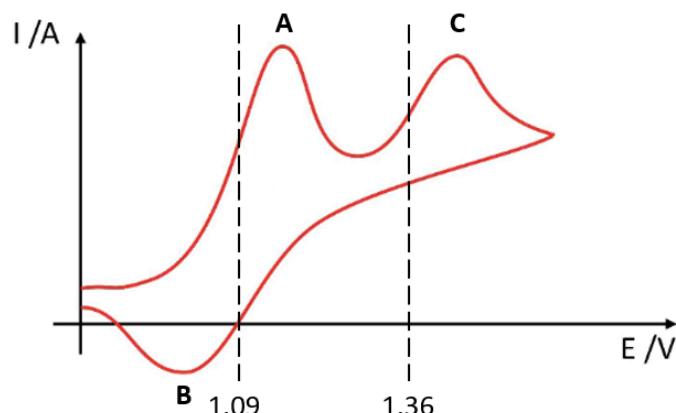
The reverse curve of a cyclic voltammetry curve is obtained when the redox reaction reverses, and a similar analysis can be used. The midpoint of the two peaks of a cyclic voltammetry curve represents the standard reduction potential of the reaction.

Consider this general cyclic voltammetry curve.



- 8) Compare the rate of migration of anions and the rate of diffusion of the oxidised species at point **A**.

Now, the student conducts the cyclic voltammetry on the sample he has. He then obtains the following graph.

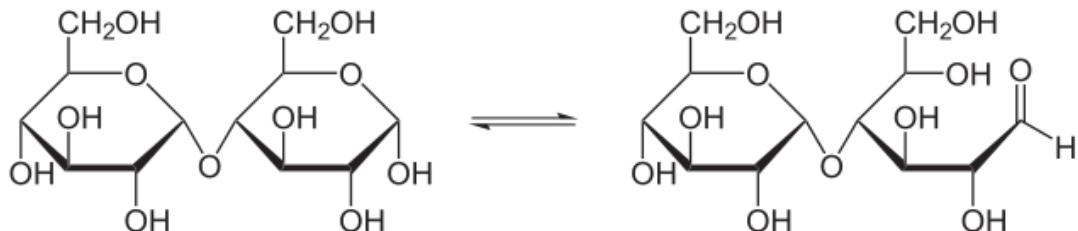


The following thermodynamics data are also given:

	Enthalpy change of atomisation / kJ mol <sup>-1</sup>	Electron affinity / kJ mol <sup>-1</sup>	Enthalpy change of hydration / kJ mol <sup>-1</sup>
Cl	+121	-349	-364
Br	+112	-324	-335

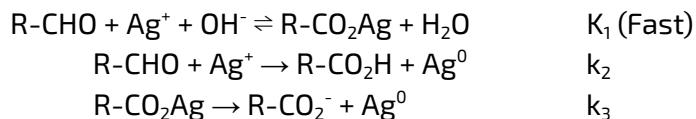
- 9) By considering the enthalpy change of the oxidation of chlorine and bromine respectively, explain which peaks, **A** or **C** correspond to which species, and hence state the standard reduction potential of the corresponding species, assuming that the cyclic voltammetry was conducted at standard conditions.
- 10) Assuming that the respective aqueous solutions are saturated with gas and any gas that forms is liberated, explain why only one peak, **B** is obtained in the reverse sweep. Hence, deduce, with reasoning, which sweep, the forward sweep or the reverse sweep is the sweep which oxidises the halides.

Silver nanoparticles are a promising area of study for medicinal or antibacterial purposes. A common method of synthesising silver nanoparticles is through the reduction of  $\text{Ag}^+$  with maltose. Maltose, when undergoing a conversion between its  $\alpha$ - and  $\beta$ - forms, passes through a ring opening which reveals an aldehyde.



For this question, we will be considering the aldehydelic form of maltose, denoting it as R-CHO.

The kinetics of the formation of silver nanoparticles has been investigated and determined as follows:



- 11) By making use of a steady-state approximation, show that the rate of reaction is first order with respect to both  $[\text{Ag}^+]$  and  $[\text{R-CHO}]$ .
- 12) Hence, how does the rate of formation of silver nanoparticles change when the reaction mixture is buffered at  $\text{pH} = 9$  instead of  $\text{pH} = 11$ ? Justify your answer using the rate equation obtained in part 5.

## Problem x: Solution

- 1) By considering the equilibria above, write down an expression for S, the total concentration of silver in the solution just before AgX begins to precipitate.

We can consider the fact that  $S = [Ag^+] + [AgX_2^-] + [AgX_3^{2-}]$ .

By rearranging the  $K_{f,1}$  equation, we obtain  $[AgX_2^-] = [Ag^+][X^-]^2 K_{f,1}$ .

Similarly, we obtain  $[AgX_3^{2-}] = [Ag^+][X^-]^3 K_{f,2}$ .

Hence, we can write  $S = [Ag^+](1 + K_{f,1}[X^-]^2 + K_{f,2}[X^-]^3)$ .

From here, it is not hard to see that we can simply apply  $[Ag^+] = \frac{K_{sp}}{[X^-]}$ .

Substituting this into the previous equation and simplifying, we obtain the final expression:

$$S = \frac{K_{sp}}{[X^-]} + K_{f,1}K_{sp}[X^-] + K_{f,2}K_{sp}[X^-]^2$$

**0.5 points for writing down a correct expression for S in terms of sums of silver ion species.**

**1 point for correct substitution of  $K_f$  equations to give the expression of S in terms of  $[X^-]$  and the relevant equilibrium constants.**

**0.5 points for correct substitution of  $K_{sp}$  to give the final expression.**

- 2) Using the data above, compute the  $K_{sp}$  and  $K_{f,1}$  at 25°C for X = Cl.

Let  $K_{f,1} = K_f$  for brevity below.

Differentiating the above equation, one discovers that

$$\frac{dS}{d[X^-]} = K_f K_{sp} - \frac{K_{sp}}{[X^-]^2}$$

Notice that at the point given in the graph, it is a turning point and hence the derivative is 0. Setting the derivative to 0, and substituting in  $[X^-] = 10^{-2.628}$ , one obtains:

$$K_f(10^{-2.628})^2 - 1 = 0$$

Solving, one obtains  $K_{f,1} = 1.80 \cdot 10^5$ .

Now, substituting in  $[X^-] = 10^{-2.628}$ , the value of  $K_{f,1}$  obtained above, and  $S = 10^{-6.823}$  into the above equation in part 1, we obtain:

$$10^{-6.823}(10^{-2.628})^2 = K_{sp} + K_{f,1}K_{sp}(10^{-2.628})^2$$

Isolating  $K_{sp}$  and solving, one obtains  $K_{sp} = 1.77 \cdot 10^{-10}$ .

**1 point for correct differentiation. (0.5 points for an attempt to differentiate the above equation, but incorrectly)**

**1 point for solving and obtaining the correct value of  $K_{f,1}$ .**

**1 point for evidence of substituting in values from the graph to calculate  $K_{f,1}$ .**

**1 point for solving and obtaining the correct value of  $K_{sp}$  using the above value of  $K_{f,1}$ .**

- 3) State the values of  $x$  and  $y$ . Hence, or otherwise, determine the  $\Delta_rG$  of the cell reaction at standard conditions.

Since HBr and HCl are strong acids, it is trivial to see that:

$$x = 10^{-0.1549} = 0.700 \text{ and } y = 10^{-0.6021} = 0.250.$$

The overall cell equation is:  $\text{AgCl}(\text{s}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s}) + \text{Cl}^-(\text{aq})$ .

$$E_{\text{cell}}^\circ = E_{\text{cell}} + \frac{RT}{zF} \ln Q, z = 1.$$

Hence, substituting in  $E_{\text{cell}} = +0.1754\text{V}$  and  $Q = \frac{y}{x}$ , one obtains  $E_{\text{cell}}^\circ = +0.14892\text{V}$ .

$$\text{Thus, } \Delta_rG = -0.14892(1)(96485) = -14400 \text{ J mol}^{-1}$$

**0.25 points for each correct value of  $x$  or  $y$ . (Total 0.5 points)**

**1 point for the correct use of Nernst Equation to obtain standard cell potential.**

**0.5 points for the correct value of  $\Delta_rG$  using  $\Delta_rG = -nFE$ . (0.25 points for correct magnitude of  $\Delta_rG$ , but wrong sign)**

- 4) Thus, calculate the value of  $K_{\text{sp}}$  and  $K_{f,1}$  for  $X = \text{Br}$  at  $25^\circ\text{C}$ .

By considering the equilibrium expressions for  $K_{\text{sp}}$  of AgBr and AgCl, denoting the reaction in part 3 as reaction 1 with equilibrium constant  $K_1$ ,

$$K_{\text{sp}}(\text{AgBr}) K_1 = K_{\text{sp}}(\text{AgCl})$$

$$\text{Since } K_1 = e^{\frac{14368.148069}{298.15 \cdot 8.3145}} = 328.99176,$$

$$\text{Hence, } K_{\text{sp}}(\text{AgBr}) = 5.38 \cdot 10^{-13}.$$

Substitute the value in the second graph,  $S = 10^{-6.942}$ ,  $[X^-] = 10^{-5.327}$  into the equation in part 1, obtaining

$$10^{-6.942}(10^{-5.327}) = K_{\text{sp}} + K_{\text{sp}} K_{f,1} (10^{-5.327})^2$$

Solving for  $K_{f,1}$ , one obtains the value  $K_{f,1} = 2.23 \cdot 10^7$ .

**1 point for correct computation of the value of  $K_1$ .**

**1 point for the correct value of  $K_{\text{sp}}$  of AgBr.**

**1 point for evidence of substitution of values to attempt to calculate  $K_{f,1}$ .**

**1 point for the correct value of  $K_{f,1}$  of AgBr. A 10% tolerance is accepted for this question due to the propagation of errors. [2.01·10<sup>7</sup> to 2.46·10<sup>7</sup>]**

- 5) The student noticed this with the addition of a common qualitative test. Explain what test the student conducted.

Addition of  $\text{AgNO}_3$  followed by addition of dilute aqueous  $\text{NH}_3$ .

A precipitate formed which was insoluble in dilute aqueous  $\text{NH}_3$ , corresponding to a bromide salt.

**0.5 points for stating the addition of  $\text{AgNO}_3$ .**

**0.5 points for stating the addition of dilute  $\text{NH}_3$  (aq).**

**1 point for stating that an insoluble precipitate formed, corresponding to the bromide salt.**

- 6) Using the above information, give a possible reason why increasing (a) the current of the electrolytic setup and (b) the potential difference across electrodes may increase the rate at which this oxidation occurs.

(a) Increasing the current increases the rate at which electrons arrive at the electrode, thus a higher rate of oxidation occurs at the anode.

Alternative explanation:

Increasing the current will increase the number of charges per unit time by  $Q = It$ , increasing the number of moles of anions oxidised per unit time by  $Q = nF$ .

(b) Increasing the potential difference across the electrodes increases the magnitude of the electric field strength at the ion. This increased electric field strength causes the ion drift speed to increase. Hence, the rate at which the anions arrive at the anode increases, causing the rate of oxidation to increase.

**1 point for stating increasing current increases the rate at which electrons move to the electrode, or giving a quantitative explanation using  $Q = nF = It$ .**

**1 point for stating increasing potential difference increasing the magnitude of electric field strength.**

**1 point for relating this to ion drift speed.**

**1 point for relating this to the rate of anions arriving at anode.**

- 7) By further considering what occurs at the electrode surface, give a possible reason why increasing the electrode potential further may cause the rate of the oxidation to slow down instead.

At high electrode potentials, the cations formed are immediately reduced *but* the uncharged species formed at the electrode surface block active sites, preventing the oxidation from occurring.

Rate of diffusion is not affected by the electrode potential.

Alternative explanation (Not required but accepted):

Fick's First Law of Diffusion states that  $\mathbf{J} = -D\nabla\varphi$ . Electrode potential does not affect the diffusion flux vector.

**1 point for stating that the rate of diffusion is not affected by electrode potentials, or by quoting Fick's Law.**

**1 point for stating that the cations formed block active sites.**

- 8) Compare the rate of migration of anions and the rate of diffusion of the oxidised species at point A.

Rate of migration of anions = rate of diffusion of oxidised species.

**1 point for stating that the rates are equal.**

- 9) By considering the enthalpy change of the oxidation of chlorine and bromine respectively, explain which peaks, **A** or **C** correspond to which species, and hence state the standard reduction potential of the corresponding species, assuming that the cyclic voltammetry was conducted at standard conditions.

*Thought process (Not required for answer):*

*Consider that for reduction of a halide to occur, that is,*



*The following must occur:*

1. *The breaking of the X-X bond.*
2. *The gaining of an electron to become the respective gaseous anions.*
3. *The hydration of these gaseous anions.*

*Hence, (1) corresponds to the enthalpy change of atomisation, (2) corresponds to the first electron affinity and (3) corresponds to the enthalpy change of hydration.*

*By Hess' Law, one can compute the enthalpy change of the oxidation of the halide, noting that the oxidation is simply the reverse of the reduction process, and hence the negative of the enthalpy change of reduction.*

For Cl: Enthalpy change of oxidation =  $-[121 - 349 - 364] = +592 \text{ kJ mol}^{-1}$

For Br: Enthalpy change of oxidation =  $-[121 - 324 - 335] = +547 \text{ kJ mol}^{-1}$

Since the enthalpy change of oxidation of Cl is more positive, it is more readily oxidised, assuming a similar entropy change, then Cl has a more negative standard reduction potential (and a more positive corresponding standard oxidation potential). Thus, Cl corresponds to peak **C** and Br corresponds to peak **A**.

The standard reduction potential of Cl is +1.36V.

The standard reduction potential of Br is +1.09V.

**1 point each for calculating enthalpy change of oxidation for each Cl/Br. (Total 2 points)**

**1 point for arguing that Cl has more negative standard reduction potential / more positive standard oxidation potential.**

**0.5 points each for correct peak assignment. (Total 1 point)**

**0.5 points each for correct standard reduction potential read from graph. (Total 1 point)**

- 10) Assuming that the respective aqueous solutions are saturated with gas and any gas that forms is liberated, explain why only one peak, **B** is obtained in the reverse sweep. Hence, deduce, with reasoning, which sweep, the forward sweep or the reverse sweep is the sweep which oxidises the halides.

Only one peak is formed in the reverse sweep since  $\text{Cl}_2$  gas formed in the forward sweep is liberated and is removed from the solution. The  $\text{Cl}_2$  gas formed cannot be reduced afterwards.

The forward sweep is the sweep which oxidises the halides.

**0.5 points for stating  $\text{Cl}_2$  gas is liberated from solution.**

**0.5 points for stating that as a result,  $\text{Cl}_2$  gas cannot be reduced in the reverse sweep.**

**1 point for stating that the oxidation sweep is the forward sweep.**

- 11) By making use of a steady-state approximation, show that the rate of reaction is first order with respect to both  $[Ag^+]$  and  $[R-CHO]$ .

From the above mechanism, the rate equation is:

$$v = k_2[R-CHO][Ag^+] + k_3[R-CO_2Ag]$$

From the equilibrium, we obtain:

$$[R-CO_2Ag] = K_1[R-CHO][Ag^+][OH^-]$$

Substituting this above, we obtain:

$$v = k_2[R-CHO][Ag^+] + k_3K_1[R-CHO][Ag^+][OH^-]$$

Factorising, we can determine that:

$$v = [R-CHO][Ag^+](k_2 + k_3K_1[OH^-])$$

Letting  $k_{obs} = k_2 + k_3K_1[OH^-]$ , we can write  $v = k_{obs}[R-CHO][Ag^+]$

Hence, the rate of reaction is first order with respect to both  $[Ag^+]$  and  $[R-CHO]$ . (Shown)

**0.5 points for writing out the rate equation using  $k_2$  and  $k_3$ .**

**0.5 points for writing out the equilibrium equation.**

**0.5 points for substituting to obtain the correct rate equation.**

**0.5 points for showing that it is first order with respect to both  $[Ag^+]$  and  $[R-CHO]$ , either by using  $k_{obs}$ , or by simply factorising it out.**

- 12) Hence, how does the rate of formation of silver nanoparticles change when the reaction mixture is buffered at pH = 9 instead of pH = 11? Justify your answer using the rate equation obtained in part 5.

The rate of formation of silver nanoparticles decreases.

At pH = 9, the  $[OH^-]$  is lower. Hence,  $k_{obs} = k_2 + k_3K_1[OH^-]$  decreases, hence the rate of reaction decreases.

**1 point for stating that the rate of formation decreases.**

**1 point for correct justification using the rate law.**