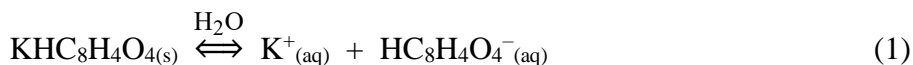

Experiment #8 – Solubility, K_{sp} , Common Ion Effect and ΔH_{soln}° of Potassium Hydrogen Phthalate

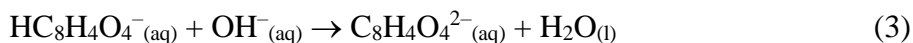
In this experiment you will determine the solubility and solubility product constant, K_{sp} , of Potassium Hydrogen Phthalate ($KHC_8H_4O_4$ abbreviated as KHP) at various temperatures. Equation 1 below shows the solubility product equation of KHP.



The K_{sp} expression associated with this reaction is given in equation 2 below.

$$K_{sp} = [K^+] [HC_8H_4O_4^-] \quad (2)$$

Because of the 1:1 mole ratio of $K^+ : HC_8H_4O_4^-$, we need only determine the concentration of one of these to calculate K_{sp} assuming that there is no source of these ions other than KHP. **Also, note that the solubility of KHP is equal to $[HC_8H_4O_4^-]$.** The acid dissociation of $HC_8H_4O_4^-$ can be treated as negligible as its K_a is around 4×10^{-6} . This K_a is four to five magnitudes smaller than the K_{sp} of KHP. KHP is a well known primary standard used in standardizing base solutions such as NaOH (aq). $HC_8H_4O_4^-$ reacts with OH^- (from NaOH) as described in equation 3 below.



In this experiment you will use saturated solutions of KHP at different temperatures. You will titrate an aliquot of the supernate (liquid above the solid) with a standard NaOH solution to determine $[HC_8H_4O_4^-]$ of each saturated solutions. You will then calculate K_{sp} at each temperature. Once K_{sp} at each temperature is obtained, you will use equation 4a to obtain the standard enthalpy of dissolution ΔH°_{soln} and the standard entropy of dissolution, ΔS°_{soln} .

$$\ln K_{sp} = \frac{-\Delta H^{\circ}_{soln}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^{\circ}_{soln}}{R} \quad (4a)$$

Note that equation 4a is in the form of an equation of a straight line ($y = mx + b$). Equation 4a is similar to the Arrhenius equation in the kinetics experiments that used specific rate constants (k) and temperature (T) to solve for activation energy (E_a). A plot of $\ln K_{sp}$ vs $1/T$ (in Kelvin) will allow you to solve for ΔH°_{soln} and ΔS°_{soln} . R is the gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. ΔH°_{soln} is the heat associated with reaction 1 at constant pressure. ΔS°_{soln} is the change in entropy of reaction 1. Entropy is a measure of energy dispersal (ways of being or randomness). A state in which a given amount of energy is more highly dispersed has more entropy than a state in which the same energy is more highly concentrated. If you only had two sets of K_{sp} and T , you could use equation 4b to calculate ΔH°_{soln} .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}_{soln}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4a)$$

Additionally, you will observe the common ion effect by comparing $[K^+]$ or $[HC_8H_4O_4^-]$ between a saturated solution of KHP and a solution that is also saturated with KHP but was prepared using 0.50 M KCl (both at room temperature). Note that common ion effect states that the solubility of a solid decreases when a common ion is present in the solution. Therefore, $[K^+]$ or $[HC_8H_4O_4^-]$ should be lower in a saturated solution where K^+ (a common ion from KCl) is present. You will be asked to calculate % decrease in solubility as given in equation 5 below.

$$\% \text{ decrease} = \left(\frac{[HC_8H_4O_4]_{\text{water}} - [HC_8H_4O_4]_{\text{sat'd KCl}}}{[HC_8H_4O_4]_{\text{water}}} \right) \times 100\% \quad (5)$$

You will calculate the room temperature K_{sp} in both water and with 0.50M KCl-saturated solutions. You will determine the consistency of your two room temperature K_{sp} values by calculating the % difference between them using equation 6. Ideally you will see that even when there is a common ion present, the value for K_{sp} should remain the same or constant (0% difference) between the two room temperature saturated solutions (water and with 0.50M KCl-saturated solution).

$$\% \text{ difference} = \left(\frac{K_{sp_{\text{water}}} - K_{sp_{\text{sat'd KCl}}}}{K_{sp_{\text{average}}}} \right) \times 100\% \quad (6)$$

Procedure

1. Transfer the indicated amount of the saturated KHP solution into an Erlenmeyer flask. Make sure that you withdraw from the top portion of the flask and take care not to agitate the solid that has settled on the bottom of the flask. If you see any KHP crystals floating on the surface, dip a small piece of clean dry paper towel into the liquid to remove the crystals.
2. Add about 20 mL deionized water and 2 drops of phenolphthalein indicator to the flask. Titrate the saturated KHP solution with standardized NaOH of known molarity until a persistent pink color is established.
3. Repeat steps above for the saturated solutions (in water) at two other temperatures and the one at room temperature with 0.50 M KCl.

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Pre-Lab Questions

1. A student withdraws 3.00 mL of supernate from a saturated solution of $\text{KHC}_8\text{H}_4\text{O}_4$ at room temperature ($\sim 22\text{ }^\circ\text{C}$). This sample was titrated to the phenolphthalein endpoint and 12.85 mL of 0.0997 M NaOH was required.
 - a. Calculate moles of $\text{HC}_8\text{H}_4\text{O}_4^-$ in the 3.00 mL aliquot.
 - b. Calculate the $[\text{HC}_8\text{H}_4\text{O}_4^-]_{\text{equil}}$ (a.k.a. solubility).
 - c. What is the value for $[\text{K}^+]_{\text{equil}}$?
 - d. Calculate K_{sp} at $22\text{ }^\circ\text{C}$.
2. A similar titration as in #1 above was done for a saturated solution of KHP in 0.500 M KCl also at room temperature. The withdrawn supernate was 5.00 mL (instead of 3.00 mL). The volume of titrant (0.0997 M NaOH) used was 8.35 mL.
 - a. Calculate the new solubility in 0.500 M KCl.

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b. Calculate the % decrease in solubility by using equation 5.

3. Two more titrations like the one in #1 above were done at two other temperatures and a plot of $\ln K_{sp}$ vs $1/T$ (in Kelvin) was constructed and yielded the trendline equation below. Calculate ΔH°_{soln} (**kJ/mol**) and ΔS°_{soln} (**kJ/K·mol**).

$$y = -4480x + 13.8$$

$$\Delta H^\circ_{soln} = \underline{\hspace{2cm}} \text{ kJ/mol} \quad \Delta S^\circ_{soln} = \underline{\hspace{2cm}} \text{ kJ/K}\cdot\text{mol}$$

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Data and Calculations**Concentration of standard NaOH: _____ M**

Sample of sat'd KHP	Temperature (Kelvin)	Vol KHP acid (mL)	Vol NaOH base (mL)	$[\text{HC}_8\text{H}_4\text{O}_4^-]_{\text{eq}}$ (<i>solubility</i>) (M)	$[\text{K}^+]_{\text{eq}}$ (M)	K_{sp}
At room temp						
warmer						
colder						
At room temp with 0.50M KCl						

Show sample calculations for $[\text{HC}_8\text{H}_4\text{O}_4^-]_{\text{eq}}$, $[\text{K}^+]_{\text{eq}}$ and K_{sp} below:

Prepare an Excel[®] chart filling in K_{sp} and T values. Have the computer program calculate $\ln(K_{\text{sp}})$ and $1/T$ for the 4 sets of data.

Plot a scatter graph with $y = \ln(K_{\text{sp}})$ values and $x = 1/T$ (Kelvin) and display the linear trendline equation of your plot. Attach your graph.

Write out the linear trendline equation _____

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4. Calculate the % difference in K_{sp} at room temperature, equation 6. Based on a 10% acceptable difference, are your K_{sp} values in water and in KCl the same? If they are not within 10% of each other, propose a specific error that might have caused this significant difference in K_{sp} .

5. Plot $\ln K_{sp}$ vs $1 / T$ (Kelvin) and determine the linear trendline equation of your plot. Attach your graph.

Linear Trendline Equation: _____

6. Calculate the ΔH°_{soln} and ΔS°_{soln} for the dissolution of solid KHP from the trendline equation of your scatter graph; $\ln(K_{sp})$ vs $1 / T$ (Kelvin). R is the gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$\Delta H^{\circ}_{soln} =$ _____ **kJ / mol** $\Delta S^{\circ}_{soln} =$ _____ **kJ / K·mol**