

Running Head: CHEM LAB-THERMODYNAMICS

Chem Lab

Student Name

Institution Affiliations

Date

Pre-Lab Exercise

1. This laboratory experiment requires the simultaneous solving of two equations each containing two unknown variables. There are two mathematical methods to do this. One: rearrange one equation to isolate one variable (eg, $\Delta H = \dots$), then substitute that variable into the second equation. Method two: subtract the two equations from each other which cancels out one variable. Prepare by practicing with the data provided below and use equation 3 to solve for ΔH , and ΔS .

$$\text{Temperature 1} = 15 \text{ K} \quad \Delta G = -35.25 \text{ kJ/mol}$$

$$\text{Temperature 2} = 75 \text{ K} \quad \Delta G = -28.37 \text{ kJ/mol}$$

SOLUTION

$$\Delta G = \Delta H - T\Delta S$$

$$-35.25 = \Delta H - 15\Delta S \dots\dots\dots(\text{i})$$

$$-28.37 = \Delta H - 75\Delta S \dots\dots\dots(\text{ii})$$

Subtract (ii) from (i)

$$60\Delta S = -6.88$$

$$\Delta S = \frac{-6.88}{60} = -0.1147 \text{ kJ}$$

Substitute ΔS in (i) above

$$\Delta H = -35.25 + 15(-0.1147) = -36.97 \text{ kJ}$$

$$\text{Therefore, } \Delta G = (-36.97 + 0.1147T) \text{ kJ}$$

Relating Solubility Equilibrium and Thermodynamics

Purpose: This experiment allows students to measure the solubility of a salt by titration. By varying the temperature, the solubility data is used to determine the thermodynamic values Enthalpy, Entropy, and Gibbs free energy for the equilibrium process.

Safety: This lab involves the reaction of an acid with a base, and the filtering of a hot basic solution. Use caution in handling these materials. The neutralized titration solution can be disposed down the sink drain with water.

Introduction: The solubility equilibrium of a salt is a process that is based upon kinetics. The forward reaction being the dissolving of the salt, while the reverse reaction is the precipitation reaction. This dynamic process is constantly occurring in both directions once the salt solution has reached equilibrium, where the rates of both the forward and reverse reactions rates are equal.

In this experiment, the salt studied will be calcium hydroxide, $\text{Ca}(\text{OH})_2$.



Since the anion is a hydroxide, it can be measured via titration, a technique introduced in previous labs. From the molar solubility, (s), the solubility equilibrium constant, K_{sp} , can be calculated. Subsequently, the Gibbs free energy for the solubility of the salt, ΔG^0 , can be determined using equation 2.

$$\Delta G = - RT \ln K_{\text{sp}} \quad \text{(Equation 2)}$$

Relating Solubility Equilibrium and Thermodynamics

By measuring the solubility of the salt at two different temperatures, two **different** values for K_{sp} can be measured, resulting in two different values for ΔG , which will be used to determine the values for both Enthalpy, ΔH , and Entropy, ΔS for the solubility using equation 3. Since Enthalpy and Entropy changes are virtually constant over the temperature range investigated, only **one** ΔH and **one** ΔS will be determined.

$$\Delta G = \Delta H - T\Delta S \quad \text{(Equation 3)}$$

Entering the data from the two experiments at different temperatures generates two equations with two variables each, ΔH and ΔS . Using algebra, these two equations can be solved simultaneously for one variable. Knowing the values for two of the thermodynamic functions allows for the calculation of the third.

Safety: This lab involves the reaction of an acid with a base, and the filtering of a hot basic solution. Use caution in handling these materials. The neutralized titration solution can be disposed down the sink drain with water.

Procedure

A saturated solution of Ca(OH)_2 has been provided. It is heterogeneous and needs to be stirred to ensure equilibrium. Therefore, it is on a stirrer and should be sampled ensuring to obtain both the liquid and solid layers in each sample, every time you use some of it. Add approximately 100 mL of this saturated mixture directly to a beaker (its okay to use the markings on the beaker for this estimate).

In a small beaker, stir then add approximately 50 mL of the saturated calcium hydroxide mixture (its okay to use the markings on the beaker for this estimate) and heat it to a gentle boil. Set up a gravity filtration apparatus while you wait. Once the mixture is boiling, record the temperature, then gravity filter the mixture into an Erlenmeyer flask. Label and set the clear solution (filtrate) aside to cool. Discard the solids.

Repeat the filtration on approximately 50 mL of room temperature saturated calcium hydroxide mixture. Label and set the clear solution aside. Discard the solids.

Set up a titration apparatus with a 50 mL burette containing the provided HCl solution.

Pipet 10.0 mL of one of the clear filtered calcium hydroxide solutions into a clean 125 mL Erlenmeyer flask, add ~25 mL of distilled water and a drop of phenolphthalein indicator. Since the solution is basic, the indicator should turn pink immediately. Titrate the pink calcium hydroxide solution with the HCl solution until the indicator is barely visible. Repeat this titration until you have two good measurements for each of the calcium hydroxide solutions (low temperature and high temperature).

Analysis

Titration is measuring by reaction. Recall that at the equivalence point of a titration, the moles of the acid are equal to the moles of the base. Use your titration data to calculate the concentration of hydroxide based upon the amount of HCl it took to reach the equivalence point..

Calculate the concentration of Ca^{2+} using the hydroxide concentration (remember to take into account the stoichiometry).

Calculate the K_{sp} , using eqn 1.

Calculate ΔG using eqn 2.

Repeat this series of calculations for the second titration (the hot solution).

Next, using the **Kelvin** temperature and the experimental values for ΔG , solve for both ΔH and ΔS for the dissolution of calcium hydroxide (like in the prelab exercise.) Since you have two unknown values, you will need to simultaneously solve two equations. Using the two different temperatures in the Gibbs free energy equation makes it possible to solve for ΔH and ΔS .

Show all of your calculations below.

Data Table

Concentration of HCl solution: 0.0100M

Low Temperature: <u>22 °C</u>		High Temperature: 90.10 <u>°C</u>	
Vol. Ca(OH) ₂ (mL)	Vol. HCl (mL)	Vol. Ca(OH) ₂ (mL)	Vol. HCl (mL)
10 mL	40.40 mL	10 mL	22.80 mL

Calculations- show your work for full credit

(NEED TO CALCULATE EACH STEP UNDERNEATH THE QUESTION) (IT IS REALLY CONFUSING ALL TOGETHER) (I PUT ALL THE CHANGES IN RED PLEASE LOOK OVER AND CORRECT IT) (MOST PROBABLY IT IS WRONG SO RECALCULATE EVERYTHING)

- i. Calculate $[\text{OH}^-]$ in the 10.0 mL sample based on $[\text{HCl}]$ required to reach the EP

EX:- ANSWER

- ii. Calculate $[\text{Ca}^{2+}]$ using $[\text{OH}^-]$
- iii. Calculate K_{sp} (eqn 1)
- iv. Calculate ΔG at lower temp (eqn 2)

Repeat the four calculations for the higher temp solution:

- i. Calculate $[\text{OH}^-]$ based on $[\text{HCl}]$ required to reach EP
- ii. Calculate $[\text{Ca}^{2+}]$ using $[\text{OH}^-]$
- iii. Calculate K_{sp} (eqn 1)
- iv. Calculate ΔG at higher temp (eqn 2)

SOLUTION**Equations needed**

- a) $\text{Ca}(\text{OH})_{2(l)} + 2\text{HCl}_{(aq)} \longrightarrow \text{CaCl}_{2(aq)} + 2\text{H}_2\text{O}_{(l)}$
- b) $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$
- c) $\text{Ca}(\text{OH})_{2(s)} \rightleftharpoons \text{Ca}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)}$

Calculations

Quantity	Lower Temperature	Higher Temperature
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Calculations- show your work for full credit

Volume of HCl	40.4ml	22.8ml
Volume of Ca(OH) ₂	10ml	10ml
Molarity of HCl	0.1M	0.1M
Moles of HCl Reacted	$\frac{40.4 \times 0.1}{1000} = 0.00404 \text{ mol}$	$\frac{22.8 \times 0.1}{1000} = 0.00228 \text{ mol}$
Moles of H ⁺ ions	0.00404 mol	0.00228 mol
Moles of (OH ⁻) ions reacted	0.00404 mol	0.00228 mol
Moles of Ca ²⁺ ions	$\frac{0.00404}{2} = 0.00202 \text{ mol}$	$\frac{0.00228}{2} = 0.00114 \text{ mol}$
Molarity of (OH ⁻) ions	$\frac{0.00404 \times 1000}{10} = 0.404 \text{ M}$	$\frac{0.00228 \times 1000}{10} = 0.228 \text{ M}$
Molarity of Ca ²⁺ ions	$\frac{0.00202 \times 1000}{10} = 0.202 \text{ M}$	$\frac{0.00114 \times 1000}{10} = 0.114 \text{ M}$
K _{sp} value=[Ca ²⁺][OH ⁻] ²	K _{sp} = [0.202][0.404] ² =0.0003297	K _{sp} = [0.114][0.228] ² =0.0000593
ΔG=-RT(ln K _{sp})	R=8.314 JK ⁻¹ mol ⁻¹ T=273+22=295K ΔG=-8.314 X 295 X (ln 0.0003297) =25310.93 J/mol =25.31093 kJ/mol	R=8.314 JK ⁻¹ mol ⁻¹ T=273+90.1=363.1K ΔG=-8.314 X 363.1 X (ln 0.0000593) =36332.89 J/mol =36.33289 J/mol

$$\Delta G = \Delta H - T\Delta S$$

$$36.33289 = \Delta H - 363.1\Delta S \dots\dots\dots(i) \text{ for higher temp}$$

$$25.31093 = \Delta H - 295.0\Delta S \dots\dots\dots(ii) \text{ for lower temp}$$

Subtract (ii) from (i)

$$-68.1\Delta S = -11.02196$$

$$\Delta S = \frac{-11.02196}{-68.1} = 0.1618496 \text{ kJ/mol}$$

Calculations- show your work for full credit

Substitute ΔS in (i) above

$$\Delta H = 36.33289 + 363.1(0.1618496) = 95.10048 \text{ kJ/mol}$$

Post Lab Questions

1. What does the data obtained, particularly, ΔG , indicate about the dissolution process for calcium hydroxide?

Since $\Delta G > 0$, then the dissolution of calcium hydroxide is non-spontaneous.

2. Examining the results of your titrations at the two different temperatures, is calcium hydroxide more or less soluble as the temperature is increased?

The solubility of calcium hydroxide decreases as temperature increases

3. A negative ΔH and ΔS value for a process indicates that the spontaneity will change at a certain temperature (crossover temp.) Calculate the temperature for when ΔG changes from negative to positive for the dissolution of calcium hydroxide.

At crossover temperature, $\Delta G = 0$, therefore

$$\Delta G = (-22.444 + 0.1045T) \text{ kJ}$$

$$0 = -22.444 + 0.1045T$$

$$0.1045T = 22.444$$

$$T = 214.88\text{K}$$