Thermochemical Relationships

Abstract

The goal of this study was to investigate the relationship between changes in enthalpy, free energy, and entropy in a precipitation reaction. By standardizing a solution of $AgNO_3$ $_{(aq)}$ and calculating its concentration, then titrating that standard solution with $PbCl_{2(aq)}$ at varying temperatures, we were able to determine the equilibrium constant for $PbCl_2$. Based on this data, ΔH°, the change in standard enthalpy, was found to be 20847.355 joules/n. ΔG°, the change in free energy, was determined to be 28813.949 joules/n and ΔS°, the change in entropy, was -27.88 joules/n· K. This experiment also verified the van't Hoff equation with only a 1.19% rate of error.

Introduction

The first law of themodynamics states that the total energy of the universe is constant. This means that energy can be converted from one form to another as a system gains energy from or loses energy to its surroundings. Changes in state functions, which are properties dependant on "current" states of a system, can often be measured to determine many different properties of chemical reactions including energy lost or gained, as well as spontaneity, the tendency of a reaction to proceed towards equilibrium. The state functions examined in this experiment include enthalpy, the sum of the internal energy of a system, and entropy, the number of ways energy can be dispersed within a system or its surroundings. The purpose of this experiment was to study the relationships between state functions and quantifiable data.

Equilibrium constants (K) are values obtained when equilibrium concentrations are substituted into a reaction quotient for a particular chemical reaction. The reaction chosen for this experiment was the dissolving of solid $PbCl_2$ to establish equilibrium with its ions:

$$PbCl_{2\,(s)} \leftrightarrow Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} \tag{1}$$

The equilibrium constant for this reaction, called a solubility product constant (K_{sp}), was determined at varying temperatures by determining the concentrations of chloride ion in a saturated solution of $PbCl_2$. K_{sp} was calculated using a rate law for the formation of $PbCl_{2\,(s)}$:

$$K_{sp} = [Pb^{2+}]\,[Cl^{-}]^{2} \tag{2}$$

By evaluating the rate law and equilibrium constant at differing temperatures, a graph of Ln K_{sp} values could be plotted against temperature in order to determine the enthalpy, $\Delta H°$, of the reaction in joules, using the equation:

$$\text{Slope} = m = -\Delta H°/R \tag{3}$$

Free energy ($\Delta G°$), a change in the thermodynamic quantity measuring the spontaneity of a process and the useful energy available from it, was then determined by substituting values from the graph of Ln K_{sp} versus 1/temperature into the equation:

$$\Delta G° = -R \cdot T \cdot \text{Ln } K \tag{4}$$

After calculating both the change in free energy and enthalpy, the change in entropy was established to complete the thermodynamic relationship via the equation:

$$\Delta S° = -(\Delta G° - \Delta H°)/ T \tag{5}$$

Another purpose of this experiment was to verify the van't Hoff equation:

$$\text{Ln } (K_1/K_2) = \Delta H°(1/T_2 - 1/T_1) / R \tag{6}$$

The van't Hoff equation shows how the equilibrium constant is affected by changes in temperature and was proven with the experimental data.

Experimental

This study involved two separate experiments; first the silver nitrate solution needed to be standardized then the second experiment involved titration of an unknown concentration of lead (II) chloride with the standardized silver nitrate for the ultimate purpose of calculating the K_{sp} of $PbCl_2$. To determine the precise molarity of the $AgNO_3$ solution used in the experiment, the solution was titrated with a KCl/K_2CrO_4 mixture. The final Cl^- concentrations were dependant on titrating the $AgNO_3$ using K_2CrO_4 as an indicator. Ag^+ reacts with CrO_4^{2-} to form an orange precipitate only after reacting with $Cl^-_{(aq)}$ to form $AgCl_{(s)}$. In both trials the dried KCl(s) was placed into an Erlenmeyer flask along with 20 mL of de-ionized water and 5 mL of K_2CrO_4 solution. The respective masses for each trial are shown in Table 1. The mixture was then titrated with the standardized $AgNO_3$ solution until an orange colored precipitate formed, indicating the formation of Ag_2CrO_4. The results are summarized in Table #1 (Standardization of $AgNO_3$).

Table 1: Standardization of $AgNO_3$

	Trial #1	**Trial #2**
Grams of KCl	0.0710g	0.0755g
Volume of K_2CrO_4	5mL	5mL
Volume of H_2O	20mL	20mL
Volume of $AgNO_3$ used	19.9mL	20.2mL

By calculating the number of moles of KCl that were used, we were able to determine the number of moles of $AgNO_3$ used in the reaction. This calculation allowed us to determine the molarity of the $AgNO_3$ solution as given in the Results section.

In the second experiment, $PbCl_2$ solutions at differing temperatures were titrated using the standardized solution of $AgNO_3$. In general, 10 mL of $PbCl_2$ solution at 30°C was added to a 125 mL Erlenmeyer flask along with 5 mL of 0.2 M K_2CrO_4. The K_2CrO_4 was once again used to indicate the completion of the reaction by forming an orange precipitate. Using a burette, the volume of $AgNO_3$ solution needed to titrate the $PbCl_2$ was determined and presented in Table 2 for two trials.

Table #2: Titration of $PbCl_2$ solution at 30°C

	Trial #1A	**Trail #1B**
Volume of $PbCl_2$	10 mL	10 mL
Volume of K_2CrO_4	5 mL	5 mL
Volume of $AgNO_3$ used	16.51 mL	17.30 mL

There was less than 5% difference between the trials, which appears to be in the acceptable range so only 2 trials were done for this temperature. Time was limited and since multiple temperatures were analyzed, it was decided that below 5% difference would lead to acceptable results. The concentrations and K_{sp} values will be reported in the Results section.

Next, the same techniques were done on 10 mL of $PbCl_2$ solution but this time at 21.5°C. Again, the lead (II)chloride solution was added to a 125 mL Erlenmeyer flask along with 5 mL of 0.2 M K_2CrO_4 and 14.90 mL of $AgNO_3$ solution was used for the one titration, while 14.60 mL of $AgNO_3$ were used in trial #2B. Results are given in Table #3.

Table #3: Titration of $PbCl_2$ solution at 21.5°C

	Trial #2A	**Trial #2B**
Volume of $PbCl_2$	10 mL	10 mL
Volume of K_2CrO_4	5 mL	5 mL
Volume of $AgNO_3$ used	14.90 mL	14.90 mL

Lastly, the same experiment was done at 2.0°C keeping all other variable the same. Trial #3A used 10.18 mL of $AgNO_3$ solution while trial #3B used 9.94 mL of solution, as shown in Table 4.

Table #4: Titration of $PbCl_2$ solution at 2.0°C

	Trial #3A	**Trial #3B**
Volume of $PbCl_2$	10 ml	10 mL
Volume of K_2CrO_4	5 mL	5 mL
Volume of $AgNO_3$ used	10.18 mL	9.94 mL

Again, this is just the raw data collected and the calculated values and resulting analysis will be done in the Results section.

Results and Discussion

The experiment pertaining to the standardization of the titrant, the average concentration of the $AgNO_3$ was determined to be 0.049 M. Since Ag^+ reacts with Cl^- in a 1:1 mole ratio, the moles of Cl^- were easily calculated. Dividing by the volume of the solution, the concentrations of Cl^- and Pb^{2+} for all trials were determined. Since Pb^{2+} and Cl^- are combined in a 1:2 ratio, the concentration of Pb^{2+} was calculated by dividing the Cl^- concentration by 2, as demonstrated in Table # 5 given below.

Table #5: Concentrations of Cl^- and Pb^{2+}

	[Cl^-] in mol/L	**[Pb^{2+}] in mol/L**
Trial #1A	.02567	.01284
Trial #1B	.02624	.01312
Trial #2A	.02441	.01221
Trial #2B	.02417	.01208
Trial #3A	.01981	.009905
Trial #3B	.01953	.009765

By substituting these concentrations in the rate law for $PbCl_2$, equation (2), the solubility product constant, (K_{sp}), was determined. Table 6 below summarizes the K_{sp} results independently at different temperatures as well as giving the average value for K_{sp} for $PbCl_2$ at that specific temperature.

Table 6: $K_{(sp)}$ values for $PbCl_2$

	Trial A	**Trial B**	**Average**
K_{sp} values at 30°C	8.462×10^{-6}	9.0383×10^{-6}	**8.750×10^{-6}**
K_{sp} values at 21.5°C	7.280×10^{-6}	7.0589×10^{-6}	**7.169×10^{-6}**
K_{sp} values at 2.0°C	3.887×10^{-6}	3.724×10^{-6}	**3.806×10^{-6}**

These numbers prove that as the temperature of the reaction rose, the $K_{(sp)}$ values got larger and larger thus there is a direct relationship between the equilibrium constant and temperature (equation 6). A 10°C increase in temperature resulted in a 22% increase in the equilibrium value and a 20°C decrease in temperature lowered the equilibrium constant by 46%. This demonstrates the mathematical relationship of temperature to K_{sp}. Next by plotting a graph of ln $K_{(sp)}$ values versus 1/Temperature in Kelvin, we were able to determine the slope of the curve which was –2507.5. The graph is given below in figure 1.

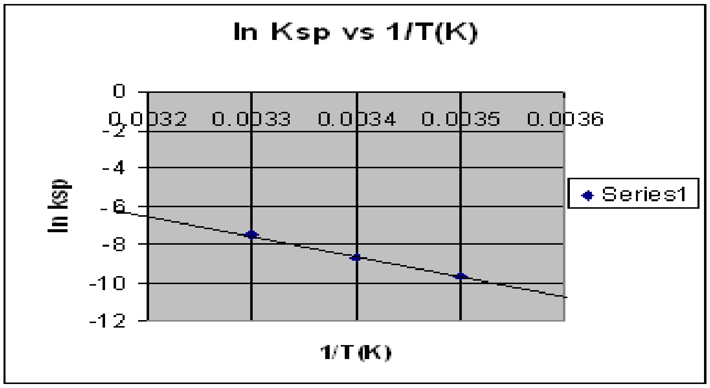

Fig. 1: Graph of ln Ksp vs. 1/T (in kelvin). The slope represents ΔH°/R, where R is the ideal gas constant 8.314 J/mol K

Using equation (3), ΔH°, for the formation of $PbCl_2$, was determined to be +20.847 kJ/mole, an endothermic reaction. By then using a point in the middle of the graph, point (.0035, -12.13), in equation number (4), the free energy, ΔG°, was calculated to be +28.813 kJ/mol, a nonspontaneous reaction. Substituting the ΔG and ΔH values into equation (5), allowed us to determine the standard entropy of the reaction, ΔS, which was -27.88 J/mol K.

Finally, substituting the experimental data into the van't Hoff equation, equation (6), yielded only a 1.9% discrepancy between the calculated $K_{(sp)}$ values and temperature. The calculations are given in the appendix, handwritten.

Conclusion

This experiment successfully demonstrated the relationships between state functions, including entropy and enthalpy, free energy, spontaneity, and equilibrium constants. Since ΔH was 20.847 kJmol, a positive number, and ΔS was –27.88 J/mol K, a negative number, the reaction, equation (1), is nonspontaneous at all temperatures. This means that the $PbCl_2$ needed energy from its surroundings in order to dissolve. However, the reverse reaction, $Pb^{2+} + 2Cl^- \rightarrow PbCl_2$, is spontaneous. ΔG equaling 28.813.949 kJ/mol also proved that the reaction was nonspontaneous. Overall, the calculation of equilibrium constants with respect to temperature allowed for specific determination of these different state functions and proved that all of the equations and theories learned in class concerning thermodynamics and thermochemical relationships are correct and true.