

Thermochemical Relationships

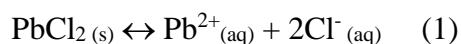
Abstract

The purpose of the “Thermochemical Relationships” experiment was to investigate the relationships 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 it with PbCl_2 solutions at varying temperatures, equilibrium constants for PbCl_2 were determined. Based on the 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 thermodynamics 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:



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 $\text{PbCl}_2(s)$:

$$K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^{-}]^2 \quad (2)$$

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

$$\text{Slope} = m = -\Delta H^\circ/R \quad (3)$$

Free energy (ΔG°), 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 $\text{Ln } K_{\text{sp}}$ versus $1/\text{temperature}$ into the equation:

$$\Delta G^\circ = -R \cdot T \cdot \text{Ln } K \quad (4)$$

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

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T \quad (5)$$

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

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

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 experiment 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 $\text{KCl}/\text{K}_2\text{CrO}_4$ 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 $\text{Cl}^-_{(\text{aq})}$ to form $\text{AgCl}_{(\text{s})}$. In the first trial 0.0710 grams of dry KCl were placed into an Erlenmeyer flask along with 20 mL of de-ionized water and 5 mL of K_2CrO_4 solution. The mixture was titrated with the 19.9 mL of AgNO_3 solution until an orange colored precipitate formed, indicating the formation of

Ag_2CrO_4 . In trial #2, 0.0755 grams of KCl were used, along with 20 mL of water and 5 mL of K_2CrO_4 solution. This trial was standardized using 20.2 mL of the AgNO_3 solution. 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.

In second half of the experiment, PbCl_2 solutions at differing temperatures were titrated using the solution of AgNO_3 . In trial #1A, 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, 16.51 mL of AgNO_3 solution was used to titrate the PbCl_2 . In trial #1B, all components of the experiment remained the same, but this time 17.3 mL of AgNO_3 was used. See Table #2 given below.

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

In trial #2A, 10 mL of PbCl_2 solution at 21.5°C 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

In trial #3A and #B, 10 mL of PbCl_2 solution at 2.0°C was added to a 125 mL Erlenmeyer flask along with 5 mL of 0.2 M K_2CrO_4 . Trial #3A used 10.18 mL of AgNO_3 solution while trial #3B used 9.94 mL of solution. See 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

Results and Discussion

In part one, 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 Pb²⁺

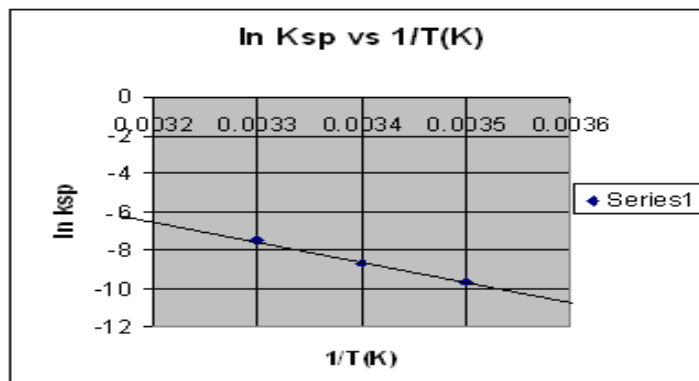
	[Cl ⁻]	[Pb ²⁺]
Trial #1A	.025674071	.012837035
Trial #1B	.026244582	.013122291
Trial #2A	.02441806	.01220903
Trial #2B	.024168918	.012084459
Trial #3A	.019810166	.0099050834
Trial #3B	.01952927	.009764635

By substituting these concentrations in the rate law for PbCl₂, 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 PbCl₂ at that specific temperature.

Table 6: K_(sp) values for PbCl₂

	Trial A	Trial B	Average
K_{sp} values at 30°C	8.4616 x 10 ⁻⁶	9.0383 x 10 ⁻⁶	8.74997 x 10⁻⁶
K_{sp} values at 21.5°C	7.27953 x 10 ⁻⁶	7.058975 x 10 ⁻⁶	7.169252 x 10⁻⁶
K_{sp} values at 20°C	3.88717 x 10 ⁻⁶	3.724157 x 10 ⁻⁶	3.805663 x 10⁻⁶

These numbers prove that as the temperature of the reaction rose, the K_(sp) values got larger and larger. By then 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.

Graph 1: Ln K_{sp} vs. 1/Temperature

Using equation (3), ΔH° , for the formation of PbCl_2 , was determined to be 20847.355 joules/mole. 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 28813.949 joules/n·K. Substituting the ΔG and ΔH values into equation (5), allowed us to determine the standard entropy of the reaction, ΔS , which was -27.88 joules/n.

Finally, substituting the experimental data into the van't Hoff equation, equation (6), yielded only a 1.9% discrepancy between the calculated $K_{(\text{sp})}$ 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 20847.355 joules/n, a positive number, and ΔS was -27.88 joules/n, 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, $\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2$, is spontaneous. ΔG equaling 28813.949 joules/nK 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.