# 1 Introduction

As a child, I have always been passionate about the outdoors. During the Canadian winter, one of the most common sports is skiing, and I was obsessed from a very young age. It has become my family's tradition to visit a new ski resort every winter. However, I observed over the years that when I brought my phone along to take pictures of the landscapes, it would immediately shutdown as soon as I took it out of my coat pocket. It was not until high school when I read an article about how a battery stores electrical energy in the form of chemical energy and converts the stored energy into electrical energy through a chemical reaction (Schmidt-Rohr, 2018). During our thermodynamics unit, we learned about the concept of spontaneous and non-spontaneous reaction and how the spontaneity of a chemical reaction was dependent on the Gibbs Free Energy, which was in turn dependent on the absolute temperature. This led me to wonder how the absolute temperature of a chemical reaction affected the Gibbs Free Energy of reaction.

2 Investigation

2.1 Reaction Under Study

The reaction studied in this investigation is the dissolution of Ammonium Nitrate within water, which produces Ammonium cations and Nitrate anions. The reaction was chosen for this investigation as Ammonium Nitrate is rather affordable and the reaction is very endothermic as indicated by its Enthalpy of Solution value under SATP conditions, hence a small quantity can produce a noticeable temperature change. Furthermore, the dissolution process can be conducted in a simple Coffee Cup Calorimeter and does not produce harmful byproducts.

$$NH_4NO_3 \text{ (s)} \xrightarrow{H_2O \text{ (l)}} NH_4^+ \text{ (aq)} + NO_3^- \text{ (aq)} \tag{1}$$
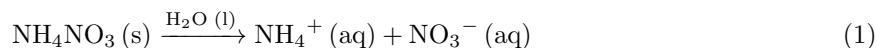
2.2 Research Question

The effect of absolute temperature on the Gibbs Free Energy of the dissolution of Ammonium Nitrate in Water at 298K, 303K, 308K, 313K and 318K by measuring the Enthalpy of Reaction at the respective absolute temperature values.

2.3 Background Information

The Gibbs Free Energy of a reaction (ΔG_{System}) combines the Enthalpy and Entropy values and is defined as the maximum amount of energy that is available from a chemical reaction to do useful work (Chen, 2019). The Gibbs Free Energy of a reaction is measured in units of (J/mol) and is as the Enthalpy of the System (ΔH_{System}) subtracted by the product between the Absolute Temperature (T) and the Entropy of the System (ΔS_{System}) (Brown and Ford, 2014).

$$\Delta G_{System} = \Delta H_{System} - \Delta S_{System} \tag{2}$$

The Gibbs Free Energy of a system can be used to predict the spontaneity of the reaction. If the amount of available energy in a reaction is a positive value ($\Delta G_{System} > 0$), then the reaction is non-spontaneous. However, if the available energy in a system is negative ($\Delta G_{System} < 0$), then the reaction is spontaneous (Greaves and Schlecht, 1992). Referencing equation (2), it can be seen that any changes to the Absolute Temperature will also alter the Gibbs Free Energy of the reaction. This mathematical relationship also results in the observation that a chemical reaction can be spontaneous at a given absolute temperature (T_1), but non-spontaneous at another absolute temperature (T_2). The absolute temperature at which the spontaneity of a reaction changes is known as the critical temperature (T_c) (Burovski et al., 2006). The absolute temperature of a reaction can be calculated by setting the Gibbs Free Energy value to be zero and evaluating for the absolute temperature value.

$$T_c = \frac{\Delta H_{System}}{T \Delta S_{System}} \tag{3}$$

Furthermore, both the Enthalpy and Entropy of a chemical reaction are also independently temperature dependent values. The enthalpy of reaction (ΔH) is given as the sum of the Internal Energy (ΔU) and the product between the Pressure (P) and Volume (ΔV) of the system (Keszei, 2016). In this investigation, the Ammonium Nitrate is dissolved in water, and due to liquid having constant pressure, only the volume changes and the pressure is constant.

$$\Delta H = \Delta U + P\Delta V \tag{4}$$

The internal energy of a system is directly proportional to the absolute temperature, hence an increase in the temperature will also increase the internal energy of the reaction (Powers, 2018). Since the Enthalpy of reaction is also directly proportional to the internal energy, therefore the proportionality is maintained between absolute temperature and Enthalpy of reaction. The relationship between Enthalpy of reaction and absolute temperature is given by Kirchhoff's Law of Thermodynamics. If the Enthalpy of reaction at an initial temperature (T_1) and the function of the specific heat capacity $(c_p(T))$ is known, the Enthalpy of reaction at any other temperature value (T_2) can be calculated (Yagofarov et al., 2018).

$$\Delta H_{T_1} = \Delta H_{T_1} + \int_{T_1}^{T_1} c_p(T)dT \tag{5}$$

Kirchhoff's initial equation considered the specific heat capacity to be a function of temperature as the specific heat is also independently temperature dependent. However, the specific heat capacity of water remains measurably constant in the absolute temperature values investigated in this investigation $[298K, 318K]$ (Mallamace et al., 2020). Therefore, the specific heat capacity of water can be assumed to be a constant value instead of a function, hence equation (5) can be further simplified as shown in equation (6) below.

$$\Delta H_{T_2} = \Delta H_{T_1} + c_p(T_2 - T_1) \tag{6}$$

The Entropy of reaction is also temperature dependent, as molecules at higher absolute temperature possess more kinetic energy compared to molecules at lower absolute temperature. Therefore, they have greater disorder and hence a higher entropy of reaction value. Similar to the Enthalpy of reaction, if the Entropy of reaction at an initial temperature (T_1) and the function of the specific heat capacity $(c_p(T))$ is known, the Entropy of reaction at any other temperature value (T_2) can be calculated (Mauro et al., 2010).

$$\Delta S_{T_2} = \Delta S_{T_2} + \int_{T_1}^{T_2} \frac{c_p(T)}{T}dT \tag{7}$$

The equation can similarly be simplified by assuming the specific heat capacity to be a constant value rather than a function. The simplified equation is shown by equation (8) below.

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$
$$\Delta S_{T_2} = \Delta S_{T_1} + nC_p \ln \frac{T_2}{T_1} \tag{8}$$

By using equation (6) and (8), the Gibbs Free Energy value at any given temperature can be calculated. However, the Gibbs Free Energy can be directly calculated as a relationship to the Enthalpy of reaction using the Gibbs-Helmholtz Equation and does not involve the Entropy of reaction as a variable. The raw form of the Gibbs-Helmholtz equation can be derived directly from equation (2) assuming the pressure of the system remains constant (Keszei, 2016).

$$\Delta G = \Delta H - T\,\Delta S$$
$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$$
$$(\frac{\partial(\Delta G/T)}{\partial T})|_p = \frac{1}{T}\frac{\partial H}{\partial T}|_p - \frac{H}{T^2} - \frac{\partial S}{\partial T}|_p$$
$$= \frac{c_p}{T} - \frac{\Delta H}{T^2} - \frac{c_p}{T} \tag{9}$$
$$= -\frac{\Delta H}{T^2}$$
$$(\frac{\partial(\Delta G/T)}{\partial T})|_p = -\frac{\Delta H}{T^2}$$

If the Gibbs Free Energy at a given temperature $(\Delta G(T_1))$ is known, the Gibbs Free Energy at any other temperature $(\Delta G(T_2))$ can be calculated by integration equation (9) (Roósz et al., 2016). For the purpose of this investigation, the Gibbs Free Energy at any temperature can be determined based on the literature Gibbs Free Energy value under Standard Ambient Temperature and Pressure (SATP)

conditions.

$$\int_{\Delta G(T_1)/T_1}^{\Delta G(T_1)/T_1} (\frac{\partial(\Delta G/T)}{\partial T})|_p \, dT = \frac{\Delta G(T_1)}{T_1} + \frac{\Delta G(T_1)}{T_1}$$

$$= -\int_{T_1}^{T_1} \frac{\Delta H}{T^2} dT \qquad (10)$$

$$\Delta G_{T_2} = \Delta G_{T_1} - \int_{T_1}^{T_1} \frac{\Delta H}{T^2} dT$$

2.4 Calculation of SATP Values

To calculate the Enthalpy, Entropy and Gibbs Free Energy of the reaction at various temperatures, the value of these variables at SATP values must be determined.

2.4.1 Molar Mass of Ammonium Nitrate

Because all of the literature values of the Enthalpy, Entropy and Gibbs Free Energy of the reaction is determined in units of kJ/mol or J/mol, the molar mass of Ammonium Nitrate must be determined to convert these values to units of kJ/g or J/g. The molar mass calculation of Ammonium Nitrate is using literature values provided by the National Institute of Standards and Technology (Dragoset et al., 1999) is shown by equation (11) below.

$$M_{NH_4NO_3} = 2 \times 14.01g/mol + 4 \times 1.01g/mol + 3 \times 16.00g/mol$$
$$= 80.06g/mol \qquad (11)$$

2.4.2 Enthalpy of Reaction

The Enthalpy of reaction is the Enthalpy of Solution of Ammonium Nitrate under SATP conditions (ΔH^θ), which is 25.69kJ/mol (Haynes, 2014).

2.4.3 Entropy of Reaction

The Entropy of reaction can be calculated as the difference between the Absolute Entropy of the products and the Absolute Entropy of the reactants provided in Lange's Handbook of Chemistry (Dean, 1990).

$$\Delta S^\theta = \sum \Delta S^\theta_{products} - \sum \Delta S^\theta_{reactants}$$
$$= (113.4J/molK + 146.4J/molK) - (151.1J/molK) \qquad (12)$$
$$= 108.7J/molK$$

2.4.4 Gibbs Free Energy of Reaction

From the calculated SATP Enthalpy and Entropy of reaction values, the Gibbs Free Energy under SATP conditions can be calculated by utilizing equation (2).

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$
$$= 25.69kJ/mol - 298.15K \times 108.7J/molK \qquad (13)$$
$$= -6.72kJ/mol$$

2.4.5 Critical temperature

To ensure that the reaction remains spontaneous throughout all the absolute temperature values investigated, the critical temperature of the reaction must be determined using equation (3).

$$T_c = \frac{\Delta H^\theta_{System}}{\Delta S^\theta_{System}}$$
$$= \frac{25.69kJ/mol}{108.7J/molK} \qquad (14)$$
$$= 236.34K$$

From the calculations above, the Critical Temperature of the reaction is determined to be 236.34K. As both the Enthalpy as well as Entropy of reaction are positive values, therefore any temperature above the

Critical Temperature will result in a spontaneous reaction. As all of the Absolute Temperature values investigated in this paper are all above 236.34K, the reaction will be spontaneous at all independent variable values.

2.5 Experimental Methodology

This paper investigates the effect of absolute temperature on the Gibbs Free Energy of reaction by measuring the Enthalpy of Reaction at the respective absolute temperature values. The theoretical Entropy of Reaction at the given temperature can also be calculated theoretically using equation (8). The experimental Enthalpy and theoretical Entropy values can be combined through equation (2) to determine the experimental Gibbs Free Energy value at the temperature.

2.5.1 Measurement of Experimental Enthalpy of Reaction

The enthalpy of reaction can be measured through the use of a coffee cup calorimeter, which measures the heat flow in a chemical reaction. The calorimeter is simply an insulated container, with the lid to act as the system for the chemical reaction to occur. When the chemical reaction occurs, the heat of the reaction is absorbed by or extracted from the water and the temperature of the water will change. The change in temperature is measured by a thermometer, which will be used to calculate the heat transfer of the reaction to the water (q) as shown by equation (15) below.

$$q = mc_p \Delta T \tag{15}$$

The enthalpy of reaction (ΔH) can be found to be the negative of the heat gained by the water (q), as all the heat lost by the reaction is absorbed by the water. This relationship is given by (16) below.

$$\Delta H = -q \tag{16}$$

Due to the imperfect insulation of a coffee cup, the chemical system is not a perfectly isolated system. Furthermore, as the absolute temperature of the reaction is head to absolute temperatures in the range of $(298.00\text{K}, 318.00\text{K})$, which is the temperature of the surroundings, therefore heat will be lost from the system to the surroundings. This will result in the measured lowest temperature value to be lower than the final temperature value if the system was perfectly isolated. Therefore, the rate of heat loss can be determined graphically and the final temperature can be extrapolated to be the sum between the Lowest Measured Temperature and the product between the Time to Reach the Lowest Temperature and the Rate of Heat Loss.

Corrected Final Temperature (K) = Lowest Measured Temperature (K)
$$+ \text{Rate of Heat Loss (K/s)} \times \text{Time to Reach Lowest Temperature (s)} \tag{17}$$

2.6 Hypothesis

Based on the information provided in the background section of this paper, I would be inclined to hypothesize that an increase in the absolute temperature will result in an increase in the magnitude of the Gibbs Free Energy of reaction.

3 Variables

3.1 Independent Variable

The independent variable of this investigation was the absolute temperature of the water in which the ammonium nitrate was dissolved in $(298.00\text{K}, 303.00\text{K}, 308.00\text{K}, 313.00\text{K}, 318.00\text{K})$ with three repeats at each temperature value. These data values were chosen to ensure that the critical temperature of the reaction was not included in this temperature range. The temperature values were achieved through the use of a hotplate to heat up the water and a digital thermometer is used to verify the absolute temperature within the beaker.

3.2 Dependent Variable

The dependent variable of this investigation is the enthalpy of reaction as the Gibbs Free Energy cannot be directly measured experimentally. The enthalpy of reaction will be calculated based on the mass of the water, specific heat capacity of water and the temperature change measured through a calorimetric process. The calculated enthalpy of reaction can be used to determine the Gibbs Free Energy values at the respective absolute temperature values.

3.3 Controlled Variables

3.3.1 Coffee Cup Calorimeter

The same coffee cup calorimeter was used for all of the trials as different calorimeters have varying degrees of insulation and hence different rate of heat loss to environment. This controlled variable will alter the measured enthalpy of reaction as a calorimeter with greater insulation will result in a smaller magnitude of measured temperature change whereas a calorimeter with less insulation will produce a greater magnitude of temperature change.

3.3.2 Mass of Reactants

The mass of reactants must be kept constant between trials as the mass of the ammonium nitrate will determine the enthalpy of reaction. If the mass of ammonium nitrate dissolved was to be changed, then the temperature change will be different hence rendering the measured temperature change values useless.

3.3.3 Temperature of Surroundings

The temperature of the surroundings must be kept constant throughout the trials as different external temperature will result in a faster/slower rate of heat loss, causing a difference in the enthalpy of reaction. Therefore, the reaction must be conducted in the same location within a room as different parts of the room have different ambient room temperature. The room temperature can be verified between trails using the closest situated thermometer.

3.3.4 Even Distribution of Temperature within Water

The temperature of the water must be evenly distributed to ensure that the effect of temperature on the enthalpy of reaction is accurate. If only parts of the water is heated up to the specified temperature values, then only certain parts of the reactants come into contact with water at the desired temperature, which will make the measured enthalpy of reaction inconclusive.

3.3.5 Distilled Water

Distilled water is used in the calorimeter to ensure that the specific heat capacity of the water is exactly $4.18 \text{J/g}^\text{o}\text{C}$ and does not contain any impurities which might alter the specific heat capacity value. This will also ensure that the

4 Experimental Procedure

4.1 Apparatus

- 75.0 g of solid ammonium nitrate (NH_4NO_3 (s))
- 1500 mL of distilled water (H_2O (l))
- Insulated Styrofoam container with Lid
- Pasco-thermometer
- Laptop with SparkVue software and Bluetooth connection
- Paper weighing boat
- Glass stirring rod
- Scapula
- Electronic balance (two decimal place)
- Electronic hot plate
- Mortar and pestle
- Two 100 mL beaker
- 40 mL beaker
- Paper towel

5 Experimental Procedure

1. Measure 5.00g of ammonium nitrate using a paper weighing boat on a two digit electronic balance and then pour the ammonium nitrate into a mortar.

2. Using a pestle, crush the ammonium nitrate into a fine powder and place the finer ammonium nitrate into a 40 mL beaker.

3. Measure 100.0mL of distilled water and pour the liquid into a 100 mL beaker.

4. Place the beaker of distilled water on to a electronic hot plate and insert the temperature probe inside. Turn on the hot plate and wait until the water is heated up to 298K.

5. Pour the heated distilled water into the coffee cup calorimeter and add the previously weighed ammonium nitrate. Immediately close the lid and insert the stirring rod and Pasco-thermometer through the opening in the lid.

6. As soon as the temperature probe has been inserted, start recording the temperature change over time in the Sparkvue software and begin to stir the ammonium nitrate using the glass stirring rod.

7. Record the reaction for 14 seconds and record the absolute temperature of the water in the calorimeter in 2s intervals.

8. After the data value has been recorded, stop recording the temperature change in the Sparkvue software and pour the ammonium nitrate solution down the drain.

9. Dry the inside of the calorimeter with a piece of paper towel and repeat steps (1-8) for three trials at each absolute temperature value and for all five independent variable values.

6 Data Collection

6.1 Raw Data

The collected experimental data is shown in a tabular format below.

6.2 Qualitative Observations

The coffee cup calorimeter was visibly colder to the touch after the reaction compared to before. Furthermore, after certain trials, there were still small pieces of ammonium nitrate visibly left in the container.

7 Data Processing

The data processing procedure is demonstrated through the use of a sample calculation. The data used in the following calculations are the trial one raw data collected for the temperature at 303K. Based on the experimental value for the enthalpy of reaction and using the theoretical entropy of reaction value, the Gibbs Free Energy of the reaction can be determined.

7.1 Corrected Final Temperature (T_{final})

7.2 Calculation of Temperature Change (ΔT)

The temperature change (ΔT) can be determined by finding the difference between the final temperature (T_{final}) and the initial temperature ($T_{initial}$).

$$\begin{aligned}
\Delta T &= T_{final} - T_{initial} \\
&= 299.67 \pm 0.01K - 303.02 \pm 0.01K \\
&= -3.35 \pm 0.02K
\end{aligned} \tag{18}$$

7.3 Calculation of Enthalpy of Reaction ($\Delta H_{\text{experimental}}$)

Based on the calculated temperature change, the enthalpy of reaction ($\Delta H_{\text{theoretical}}$) can be calculated through the calorimetric process based on the quantity of heat transferred (q) between the reaction to the distilled water. The heat transfer is calculated as the product between the mass of the water (m), specific heat capacity of water (c_p) and temperature change (ΔT).

$$
\begin{aligned}
q &= mc_p\Delta T \\
&= 100.0\text{mL} \times 1\text{g/mL} \times 4.18\text{J/gK} \times (-3.35\text{K} \pm 0.6\%) \\
&= -1.4\text{kJ} \pm 0.6\% \\
\Delta H_{\text{experimental}} &= -q \\
&= (-1.4\text{kJ} \pm 0.6\%) \\
&= 1.4\text{kJ} \pm 0.6\%
\end{aligned}
\tag{19}
$$

7.4 Calculation of Theoretical Entropy of Reaction ($\Delta S_{\text{theoretical}}$)

In order to determine the Gibbs Free Energy of the reaction, the entropy of reaction at 303K must be determined. The entropy of reaction can be determined based on the the literature value for the specific heat capacity (c_p) of ammonium nitrate, which is (139.30J/molK) (**stephenson1955heat**) and the number of moles (n). The final temperature (T_2) and the temperature of the literature value under standard conditions (T_1) are also required

$$
\begin{aligned}
\Delta S_{\text{change}} &= nc_p \ln \frac{T_2}{T_1} \\
\Delta S_{\text{theoretical}_{T_2}} &= \Delta S_{\text{theoretical}_{T_1}} + nc_p \ln \frac{T_2}{T_1} \\
&= 108.7\text{J/molK} + 139.30\text{J/molK} \times \ln \frac{303.02\text{K}}{298.15\text{K}} \\
&= 110.96\text{J/molK}
\end{aligned}
\tag{20}
$$

7.5 Calculation of Gibbs Free Energy ($\Delta G_{\text{experimental}}$)

From the previously calculated enthalpy of reaction (ΔH) and entropy of reaction (ΔS) values, and the absolute temperature of the reaction is known (T), the Gibbs Free Energy (ΔG) of the reaction can be calculated.

$$
\begin{aligned}
\Delta G &= \Delta H_{\text{experimental}} - T\Delta S_{\text{theoretical}} \\
&= 1.4 \pm 0.6\%\text{kJ} - 303.02\text{K} \times \frac{5.00\text{g}}{80.06\text{g/mol}} \times 110.96\text{J/molK} \\
&= -0.70 \pm 0.6\%\text{kJ/mol}
\end{aligned}
\tag{21}
$$

7.6 Calculation of Theoretical Enthalpy of Reaction ($\Delta H_{\text{theoretical}}$)

In order to determine the theoretical Gibbs Free Energy ($\Delta G_{\text{theoretical}}$) at the specific temperature value, the theoretical enthalpy of reaction ($\Delta H_{\text{theoretical}}$) must first be determined.

$$
\begin{aligned}
\Delta H_{\text{theoretical}_{T_2}} &= \Delta H_{\text{theoretical}_{T_1}} + c_p(T_2 - T_1) \\
&= 25.69\text{kJ/mol} + 139.30\text{J/molK}(303.02\text{K} - 298.15\text{K}) \\
&= 26.37\text{kJ/mol}
\end{aligned}
\tag{22}
$$

7.7 Calculation of Theoretical Gibbs Free Energy ($\Delta G_{\text{theoretical}}$)

Utilizing the previously calculated theoretical enthalpy of reaction ($\Delta H_{\text{theoretical}}$), the theoretical Gibbs Free Energy ($\Delta H_{\text{theoretical}}$) can be calculated using the Gibbs-Helmholtz equation.

$$
\begin{aligned}
\Delta G_{\text{theoretical}_{T_2}} &= \Delta G_{\text{theoretical}_{T_1}} - \int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT \\
&= \Delta G_{\text{theoretical}_{T_1}} - \int_{T_1}^{T_2} \frac{\Delta H_{\text{theoretical}_{T_2}} - \Delta H_{\text{theoretical}_{T_1}}}{(T_2 - T_1)^2} dT \\
&= -6.72\text{kJ/mol} - \int_{298.15\text{K}}^{303.02\text{K}} \frac{26.37\text{kJ} - 25.69\text{kJ}}{(303.02\text{K} - 298.15\text{K})^2} \times \frac{5.00\text{g}}{80.06\text{g/mol}} \\
&= -7.4\text{kJ/mol} \times \frac{5.00\text{g}}{80.06\text{g/mol}} \\
&= -0.46\text{kJ/mol}
\end{aligned}
\tag{23}
$$

7.8 Calculation of Percentage Error ($\%$Error)

$$
\begin{aligned}
\%\text{Error} &= \frac{|\Delta G_{\text{experimental}} - \Delta G_{\text{theoretical}}|}{|\Delta G_{\text{theoretical}}|} \times 100\% \\
&= \frac{|-0.70\text{kJ} - 0.46\text{kJ}|}{|-0.46\text{kJ}|} \\
&= 52.2\%
\end{aligned}
\tag{24}
$$

8 Processed Data

The raw data can be processed using the procedure demonstrated in the previous section and the correlation between absolute temperature and the Gibbs Free Energy of reaction can be shown as follows.

8.1 Tabular Representation of Processed Data

9 Evaluation of Data

The experimental data can be compared to the theoretical Gibbs Free Energy at the respective data values.

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