

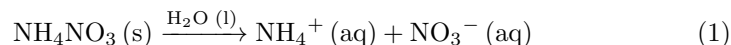
# 1 Introduction

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.



### 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 ( $\Delta G_{\text{System}}$ ) 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 ( $\Delta H_{\text{System}}$ ) subtracted by the product between the Absolute Temperature (T) and the Entropy of the System ( $\Delta S_{\text{System}}$ ) (Brown and Ford, 2014).

$$\Delta G_{\text{System}} = \Delta H_{\text{System}} - T\Delta S_{\text{System}} \quad (2)$$

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 ( $\Delta G_{\text{System}} > 0$ ), then the reaction is non-spontaneous. However, if the available energy in a system is negative ( $\Delta G_{\text{System}} < 0$ ), 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.

$$T_c = \frac{\Delta H_{\text{System}}}{T\Delta S_{\text{System}}} \quad (3)$$

Furthermore, both the Enthalpy and Entropy of a chemical reaction are also independently temperature dependent values. The enthalpy of reaction ( $\Delta H$ ) is given as the sum of the Internal Energy ( $\Delta U$ ) and the product between the Pressure ( $P$ ) and Volume ( $\Delta V$ ) 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.

$$\Delta H = \Delta U + P\Delta V \quad (4)$$

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).

$$\Delta H_{T_f} = \Delta H_{T_i} + \int_{T_i}^{T_f} c_p(T) dT \quad (5)$$

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.

$$\Delta H_{T_f} = \Delta H_{T_i} + c_p(T_f - T_i) \quad (6)$$

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).

$$\Delta S_{T_f} = \Delta S_{T_i} + \int_{T_i}^{T_f} \frac{c_p(T)}{T} dT \quad (7)$$

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.

$$\Delta S = nC_p \ln \frac{T_2}{T_1} \quad (8)$$

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).

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S \\ \frac{\Delta G}{T} &= \frac{\Delta H}{T} - \Delta S \\ \left( \frac{\partial(\Delta G/T)}{\partial T} \right) \Big|_p &= \frac{1}{T} \frac{\partial \Delta H}{\partial T} \Big|_p - \frac{\Delta H}{T^2} - \frac{\partial \Delta S}{\partial T} \Big|_p \\ &= \frac{c_p}{T} - \frac{\Delta H}{T^2} - \frac{c_p}{T} \\ &= -\frac{\Delta H}{T^2} \\ \left( \frac{\partial(\Delta G/T)}{\partial T} \right) \Big|_p &= -\frac{\Delta H}{T^2} \end{aligned} \quad (9)$$

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.

$$\begin{aligned} \int_{\Delta G(T_i)/T_i}^{\Delta G(T_f)/T_f} \left( \frac{\partial(\Delta G/T)}{\partial T} \right) |_p dT &= \frac{\Delta G(T_f)}{T_f} + \frac{\Delta G(T_i)}{T_i} \\ &= - \int_{T_i}^{T_f} \frac{\Delta H}{T^2} dT \end{aligned} \quad (10)$$

## 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.

$$\begin{aligned} M_{\text{NH}_4\text{NO}_3} &= 2 \times 14.01\text{g/mol} + 4 \times 1.01\text{g/mol} + 3 \times 16.00\text{g/mol} \\ &= 80.06\text{g/mol} \end{aligned} \quad (11)$$

### 2.4.2 Enthalpy of Reaction

The Enthalpy of reaction is the Enthalpy of Solution of Ammonium Nitrate under SATP conditions ( $\Delta H^\theta$ ), 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).

$$\begin{aligned} \Delta S^\theta &= \sum \Delta S^\theta_{\text{products}} - \sum \Delta S^\theta_{\text{reactants}} \\ &= (113.4\text{J/molK} + 146.4\text{J/molK}) - (151.1\text{J/molK}) \\ &= 108.7\text{J/molK} \end{aligned} \quad (12)$$

#### 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).

$$\begin{aligned}\Delta G^\theta &= \Delta H^\theta - T\Delta S^\theta \\ &= 25.69\text{kJ/mol} - 298.15\text{K} \times 108.7\text{J/molK} \\ &= -6.72\text{kJ/mol}\end{aligned}\tag{13}$$

#### 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).

$$\begin{aligned}T_c &= \frac{\Delta H_{\text{System}}^\theta}{\Delta S_{\text{System}}^\theta} \\ &= \frac{25.69\text{kJ/mol}}{108.7\text{J/molK}} \\ &= 236.34\text{K}\end{aligned}\tag{14}$$

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.

$$q = mc_p \Delta T \quad (15)$$

The enthalpy of reaction ( $\Delta H$ ) 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.

$$\Delta H = -q \quad (16)$$

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 (298.00K, 318.00K), 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.

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

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