

***Research Question: Investigating the thermodynamic efficiency of an LHV hydrogen fuel cell (%) at standard conditions using a Van't Hoff plot.***

## **1. Introduction and Background Information**

In our current energy-driven society, the excessive use of hydrocarbons and our dependence on fossil fuels releases a polluting amount of carbon dioxide into the atmosphere. An area of innovation are fuel cells, that use chemical energy to cleanly and efficiently produce electricity. These have boundless applications in electrical appliances, electric vehicles, power generation, and beyond. A specific type of fuel cells are hydrogen fuel cells, and they could serve as a possible alternative to hydrocarbons, as they are pollution-free by only releasing water. In terms of energy production, operation at maximum efficiency is an important characteristic. Thermodynamically speaking, this efficiency is the amount of useful work the hydrogen fuel cell is able to output. Understanding this efficiency is a vital component to progressing the future of energy. This investigation will seek to use a chemical database analysis in order to produce a Van't Hoff plot, as a means of calculating thermodynamic efficiency of an LHV hydrogen fuel cell at 298 K.

### **1.1 Thermodynamics**

In thermodynamics, the fundamental underlying principle is the transfer of energy. Changes occur in two environments: system - the area of interest - and surroundings - the rest of the universe.<sup>1</sup> With respect to the conservation of energy, the total energy of a system and surroundings must remain constant.<sup>2</sup> Changes in enthalpy,  $\Delta H$ , is a numerical value that is used to describe the heat energy change of a system.<sup>3</sup> Moreover, the sign of enthalpy,  $\pm$ , is determined by the exothermic ( $\Delta H < 0$ ) or endothermic ( $\Delta H > 0$ ) nature of the system, surrounding, or reaction. In a reaction, the standard enthalpy of formation is a measure of the energy released or consumed when one mole of a substance is created under standard conditions ( $\ominus$ ) from its constituent elements, denoted by  $\Delta H_f^\ominus$ . The standard enthalpy change of formation is given by the difference between the sum of enthalpies of formation of reaction products and reaction reactants.<sup>4</sup>

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<sup>1</sup> Tsokos, K. A.. *Physics for the IB Diploma Sixth Edition*, Cambridge University Press, 2014

<sup>2</sup> Brown, Catrin, and Ford, Mike. *Higher Level Chemistry 2nd Edition*, Pearson Education Limited, 2014

<sup>3</sup> Harrison, K.W., Remick, R., and Martin, C.D. *Hydrogen Production: Fundamentals and Case Study Summaries*, National Renewable Energy Laboratory, 2018

<sup>4</sup> Nguyen, Jonathan, and Larimer, Garrett. "Standard Enthalpy of Formation." Chemistry LibreTexts, Last Updated: 5 Jun. 2019, Date Accessed: 27 Jan. 2022  
[https://chem.libretexts.org/Courses/Valley\\_City\\_State\\_University/Chem\\_121/Chapter\\_7%3A\\_Thermochemistry/7.4%3A\\_Standard\\_Enthalpy\\_of\\_Formation](https://chem.libretexts.org/Courses/Valley_City_State_University/Chem_121/Chapter_7%3A_Thermochemistry/7.4%3A_Standard_Enthalpy_of_Formation)

$$\Delta H_{\text{reaction}}^{\ominus} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$$

The second law of thermodynamics, that describes entropy, denoted by  $\Delta S$ , is the degree of disorder within a system. This is the distribution of available energy amongst particles.<sup>2</sup> Similar to enthalpy, entropy change of a reaction is given by the difference of the sum of entropies of reaction products and reaction reactants.

$$\Delta S_{\text{reaction}}^{\ominus} = \sum \Delta S_f^{\ominus}(\text{products}) - \sum \Delta S_f^{\ominus}(\text{reactants})$$

For a chemical reaction to be spontaneous, there must be a corresponding increase of entropy. However, as this is not always accurate, the combination of entropy and enthalpy formulate Gibbs Free Energy  $\Delta G$  of a system. This is specifically the measure of energy that is available to do useful work.<sup>2</sup> Gibbs Free Energy for a system can be calculated by the difference between the total energy of the system  $\Delta H$  and the so-called ‘unavailable’ energy to do useful work in entropy  $T\Delta S$ , where  $T$  is the temperature of the system.

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

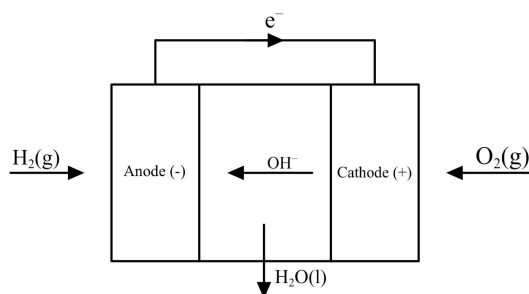
Alternatively, for equilibrium reactions, Gibbs Free Energy can be calculated in terms of the equilibrium constant  $k$  and the ideal gas constant  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>5</sup>

$$\Delta G = -RT \ln k$$

Both these definitions will be useful later on. Gibbs Free Energy, in terms of electrochemistry, will also be expanded upon in section 1.2.

## 1.2 Hydrogen Fuel Cells

In electrochemistry, redox reactions describe chemical reactions in which the transfer of electrons occurs between species, linking chemical reactivity and electricity. In a hydrogen fuel cell, heat energy is released upon the combination of one mole hydrogen and oxygen, and produces an electrical current when the reactants are physically separated. This fuel cell must operate under an acidic or alkaline electrolyte.<sup>2</sup>

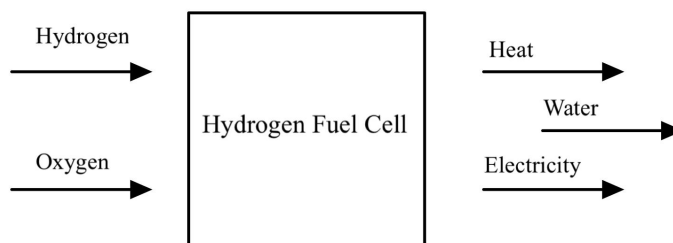


**Figure 1 - (Alkaline) Hydrogen Fuel Cell**

<sup>5</sup> Blaber, Mike, and Neils, Tom. "Gibbs Free Energy and Equilibrium." Chemistry LibreTexts, Last Updated 5 Jun. 2019, Date Accessed: 27 Jan. 2022

[https://chem.libretexts.org/Courses/Grand\\_Rapids\\_Community\\_College/CHM\\_120 - Survey of General Chemistry/7%3A\\_Equilibrium\\_and\\_Thermodynamics/7.11%3A\\_Gibbs\\_Free\\_Energy\\_and\\_Equilibrium](https://chem.libretexts.org/Courses/Grand_Rapids_Community_College/CHM_120_-_Survey_of_General_Chemistry/7%3A_Equilibrium_and_Thermodynamics/7.11%3A_Gibbs_Free_Energy_and_Equilibrium)

In the more common alkaline electrolyte hydrogen fuel cell, the half reaction at the anode is  $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$  where hydrogen gas is oxidized. At the cathode, oxygen gas is reduced. The reaction at this electrode is  $2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ . The net reaction for an alkaline hydrogen fuel cell, with halved coefficients, is  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ ,  $\Delta H_f^\theta = -285.8 \text{ kJ mol}^{-1}$ . However, the Gibbs Free Energy of the reaction is only  $237.2 \text{ kJ mol}^{-1}$  of electricity, implying that there is  $48.6 \text{ kJ mol}^{-1}$  of heat evolved. Thus, fuel cells simultaneously produce heat and electricity. However in practice, fuel cell devices incur losses from inefficiency by electrical and ionic resistances. Figure 2 shows a simplified diagram of a hydrogen fuel cell.<sup>2</sup>



**Figure 2 - Simplified Hydrogen Fuel Cell**

The forward reaction of this equilibrium is an exothermic combustion reaction. Furthermore, at sufficiently high temperatures above the boiling point of water, water vapour  $\text{H}_2\text{O}(\text{g})$  is released instead. The reaction  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$  releases less energy at  $\Delta H_f^\theta = -241.8 \text{ kJ mol}^{-1}$ . This is known as the LHV (lower hydrogen value), and describes the process for which hydrogen is combusted with excess oxygen and cooled down to standard temperature  $298 \text{ K}$ . The difference between the higher hydrogen value HHV of  $\Delta H_f^\theta = -285.8 \text{ kJ mol}^{-1}$  and the LHV is simply the molar latent heat of vapourization as it deals with gaseous products.<sup>6</sup>

As aforementioned in section 1.1, Gibbs Free Energy, though a thermodynamic concept, Gibbs Free Energy has applications in electrochemistry; the net work in an electrochemical cell is equal to its electrical work. Thermodynamic efficiency,  $\eta$ , is the fraction of heat that can become useful work.<sup>7</sup> In terms of Gibbs Free Energy  $\Delta G$  and enthalpy  $\Delta H$ , the thermodynamic efficiency of a cell is expressed as a percentage, which is:<sup>2</sup>

$$\eta = \frac{\Delta G}{\Delta H} \times 100\%$$

<sup>6</sup> Khotseng, Lindiwe. *Fuel Cell Thermodynamics*. University of Western Cape, 2019

<sup>7</sup> J.M.K.C. Donev et al. "Thermal efficiency", Energy Education, Last Updated: 18 May 2018, Date Accessed: 14 May 2021, [https://energyeducation.ca/encyclopedia/Thermal\\_efficiency](https://energyeducation.ca/encyclopedia/Thermal_efficiency)

### 1.3 Van't Hoff Equation

Since a hydrogen fuel cell reaction operates in equilibrium, the Van't Hoff Equation can be applied, relating the equilibrium constant  $k$  to the temperature  $T$  and standard enthalpy change  $\Delta H^\ominus$ . It can be modeled by the differential equation:

$$\frac{d}{dT} \ln k = \frac{\Delta H^\ominus}{RT^2}$$

Solving this differential equation and using the previously defined equation  $\Delta G = \Delta H - T\Delta S$ , the Van't Hoff Equation can express  $\ln k$  as a function of inverse temperature  $\frac{1}{T}$ .

$$\ln k = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$$

This linear function has a slope of  $-\frac{\Delta H^\ominus}{R}$  and a  $y$ -intercept of  $\frac{\Delta S^\ominus}{R}$ . For endothermic reactions, the Van't Hoff plot has a negative slope. For exothermic reactions, the Van't Hoff plot has a positive slope.<sup>8</sup>

## 2. Methodology

In this investigation, the focus is on the LHV hydrogen fuel cell reaction as shown in Section 1.2,  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ . The aim is to use a Van't Hoff plot as a method to calculate the thermodynamic efficiency of an LHV hydrogen fuel cell (%) at standard conditions. Recall that the Van't Hoff Equation of  $\ln k = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$ , implies  $\ln k$  is a function of  $\frac{1}{T}$ . Therefore, the independent variable used for the Van't Hoff plot will be  $\frac{1}{T}$ , and the dependent variable will be values of  $\ln k$  which will be calculated from database values of  $\Delta G$ . The controlled variable will be only the usage of data from the LHV hydrogen fuel cell reaction, to ensure consistency. This will be done with a Python 3 program and the matplotlib Python 3 graphing library. The code can be found in Section 7 - Appendix. Using graphical analysis from the Van't Hoff plot, the thermodynamic efficiency of the LHV hydrogen fuel cell reaction will be computed and compared to a theoretical straightforward thermodynamic efficiency based on chemical databases. In this investigation, the chosen databases are:

- (1) Lide, David R.. *CRC Handbook of Chemistry and Physics*, 87th edition. CRC Press, 2006
- (2) *Chemistry data booklet*. International Baccalaureate Organization, 2014
- (3) Khotseng, Lindiwe. *Fuel Cell Thermodynamics*. University of Western Cape, 2019
- (4) Cox, J.D, et al. *CODATA Key Values for Thermodynamics*. Hemisphere Publishing Corp., 1984
- (5) Chase, Malcolm W.. *NIST-JANAF Thermodynamic Tables*, 4th edition. American Institute of Physics, 1998

<sup>8</sup> Tuckerman, Mark. "The van't Hoff Equation." Chemistry LibreTexts, Last Updated 8 Sept. 2021, Date Accessed: 27 Jan. 2022,

[https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Physical\\_Chemistry\\_\(LibreTexts\)/26%3A\\_Chemical\\_Equilibrium/26.07%3A\\_The\\_Van\\_%27t\\_Hoff\\_Equation](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(LibreTexts)/26%3A_Chemical_Equilibrium/26.07%3A_The_Van_%27t_Hoff_Equation)

The *CRC Handbook of Chemistry and Physics*, the *Chemistry data booklet*, the *NIST-JANAF Thermodynamics Tables*, and the *CODATA Key Values for Thermodynamics* were chosen as a database due to their renowned history of authoritative and agreed peer-reviewed data. The *Fuel Cell Thermodynamics* research paper was chosen as a database as it contains the usage of rather obscure data.

### 3. Raw Data

The following data in Table 1 is adapted and averaged from database (1) and (5). This data follows the forward reaction of  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ . Temperature is presented to 5 significant figures. Gibbs Free Energy is presented to 6 significant figures. For example, for  $T = 1000 \text{ K}$ , the averaged Gibbs Free Energy is  $\Delta G = -\frac{192.603 + 192.59}{2} \text{ kJ mol}^{-1}$ , which is  $\Delta G \approx -192.597 \text{ kJ mol}^{-1}$ . Uncertainties are derived from largest half-range differences between the two databases, expanded upon in Section 3.1 - Uncertainty and Evaluation of Raw Data.

Temperature $T$ (K)	CRC Handbook of Chemistry and Physics $\Delta G$ (kJ mol <sup>-1</sup> )	NIST-JANAF Thermodynamic Tables, 4th edition $\Delta G$ (kJ mol <sup>-1</sup> )	Averaged Gibbs Free Energy $\Delta G$ (kJ mol <sup>-1</sup> )
298.15	- 228.582	- 228.582	- 228.582 $\pm$ 0.017
300.00	- 228.500	- 228.500	- 228.500 $\pm$ 0.017
400.00	- 223.900	- 223.901	- 223.901 $\pm$ 0.017
500.00	- 219.050	- 219.051	- 219.051 $\pm$ 0.017
600.00	- 214.008	- 214.007	- 214.008 $\pm$ 0.017
700.00	- 208.814	- 208.812	- 208.813 $\pm$ 0.017
800.00	- 203.501	- 203.496	- 203.498 $\pm$ 0.017
900.00	- 198.091	- 198.083	- 198.087 $\pm$ 0.017
1000.00	- 192.603	- 192.590	- 192.597 $\pm$ 0.017
1100.00	- 187.052	- 187.033	- 187.042 $\pm$ 0.017
1200.00	- 181.450	- 181.425	- 181.437 $\pm$ 0.017
1300.00	- 175.807	- 175.774	- 175.791 $\pm$ 0.017

**Table 1 - Gibbs Free Energy of Water Vapour Formation at Different Temperatures**

The following data in Table 2 is adapted from database (1), (2), (3), and (4). These values assume standard conditions. Data is presented to 5 significant figures.

Substance	$\Delta H_f^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta S^\ominus$ (J K <sup>-1</sup> mol <sup>-1</sup> )
H <sub>2</sub> (g)	0	0	+ 131.00 ± 0.00
O <sub>2</sub> (g)	0	0	+ 205.00 ± 0.01
H <sub>2</sub> O(g)	- 241.80 ± 0.04	- 228.58 ± 0.017	+ 189.00 ± 0.01

**Table 2 - Enthalpy of Formation, Gibbs Free Energy, and Entropy of H<sub>2</sub>(g), O<sub>2</sub>(g), and H<sub>2</sub>O(g)**

### 3.1 Uncertainty and Evaluation of Raw Data

In Table 1, the usage of two datasets, which can be found in the Section 7 - Appendix, uncertainties of averaged Gibbs Free Energy  $\Delta G$  are evaluated by half-ranges. This is the maximum value between the maximum difference and minimum difference of Gibbs Free Energy at some temperature  $T$ , divided by two, from the two datasets. Using the convention  $\Delta$  to denote uncertainty values, the half-range uncertainty  $\Delta(\Delta G)$  is therefore the value of the differences at 1300 K and 298.15 K, divided by two.

$$\Delta(\Delta G) = \frac{(0.807 - 0.774) \text{ kJ mol}^{-1} - (228.582 - 228.582) \text{ kJ mol}^{-1}}{2} \approx 0.017 \text{ kJ mol}^{-1} \text{ (3 decimal points)}$$

Therefore, the maximum uncertainty between the two datasets applied is  $\pm 0.017 \text{ kJ mol}^{-1}$ .

In Table 2, uncertainty is retrieved and adapted directly from chosen databases, corrected to satisfy significant figures. The uncertainty of the standard entropy of hydrogen gas is likely accurate with  $\pm 0.00 \text{ J K}^{-1} \text{ mol}^{-1}$ , since hydrogen is an extremely well-studied and commonly accessible gas. This evaluation could also be applied for oxygen and water vapour.

## 4. Analysis and Discussion

To graph a Van't Hoff plot, values of  $\ln k$  and  $\frac{1}{T}$  can be calculated from Table 1. In an LHV hydrogen fuel cell reaction  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ , the equilibrium satisfies the equation  $\Delta G = -RT \ln k$ . If this is rearranged in terms of  $\ln k$ ,

$$\ln k = -\frac{\Delta G}{RT}$$

for any given temperature  $T$  if  $\Delta G$  is known. Consider from Table 1 that  $T = 1300 \text{ K}$  and  $\Delta G = 175.791 \text{ kJ mol}^{-1}$ . This yields that  $\ln k = -\frac{(-175791 \pm 17 \text{ J mol}^{-1})}{8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 1300 \text{ K}} \approx 16.3 \pm 1.0\%$ .

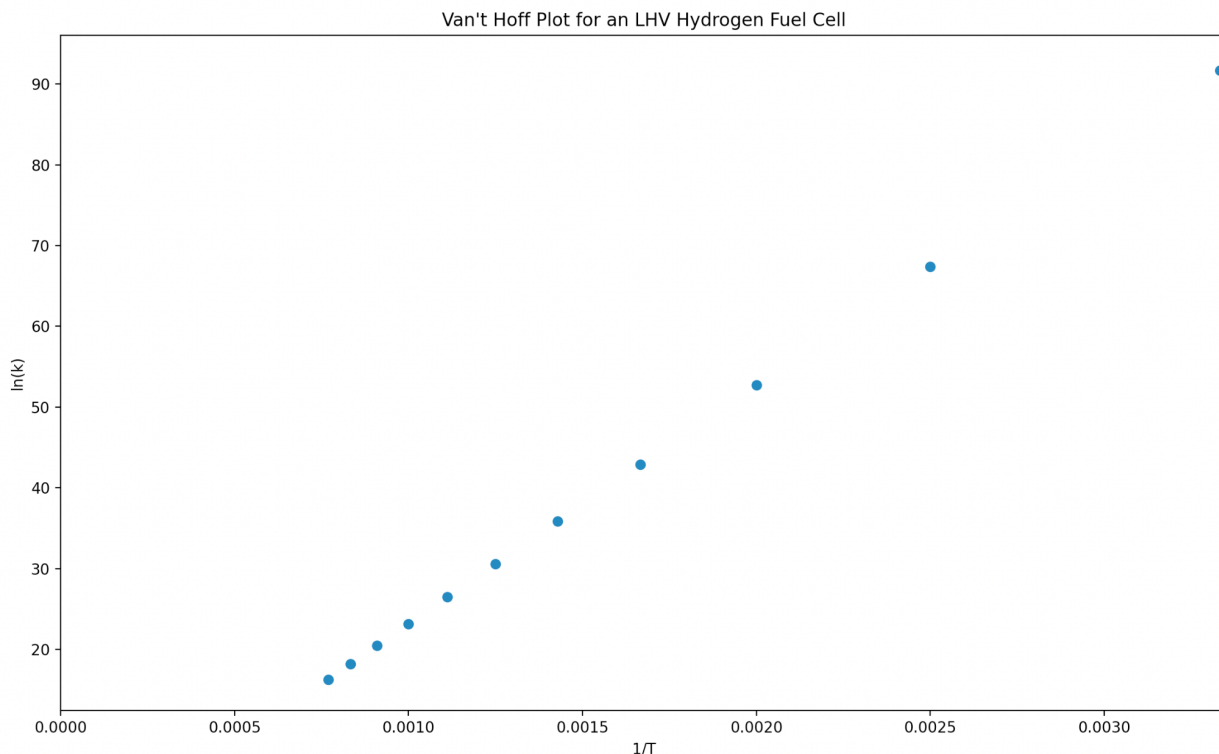
Moreover, the  $\frac{1}{T}$  value for this data point would be  $\frac{1}{T} = \frac{1}{1300 \text{ K}} \approx 0.000769 \text{ K}^{-1}$ . Repeating this calculation process using a Python 3 program produces a set of processed data in Table 3. Data is shown to 3 significant figures. The  $\pm 1.0\%$  uncertainty is applied for all points as it is

the greatest plausible percentage uncertainty value that can be mathematically deduced from this calculation.

Inverse Temperature $\frac{1}{T}$ (K <sup>-1</sup> )	Natural log of Equilibrium Constant $\ln k$
0.00335	92.3 $\pm$ 1.0%
0.00333	91.7 $\pm$ 1.0%
0.00250	67.4 $\pm$ 1.0%
0.00200	52.7 $\pm$ 1.0%
0.00167	42.9 $\pm$ 1.0%
0.00143	35.9 $\pm$ 1.0%
0.00125	30.6 $\pm$ 1.0%
0.00111	26.5 $\pm$ 1.0%
0.00100	23.2 $\pm$ 1.0%
0.000909	20.5 $\pm$ 1.0%
0.000833	18.2 $\pm$ 1.0%
0.000769	16.3 $\pm$ 1.0%

**Table 3 - Processed Data of  $\frac{1}{T}$  and  $\ln k$**

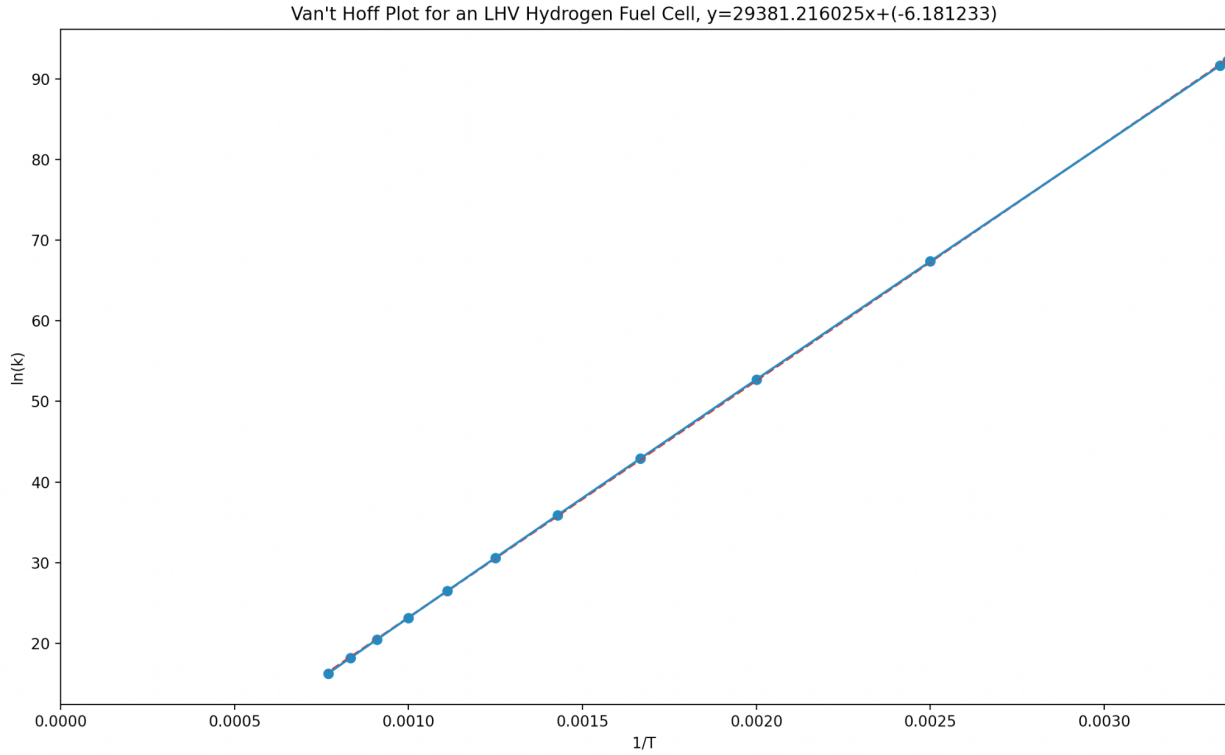
With this data, a Van't Hoff plot for each data point can be produced by graphing  $\ln k$  as a function of  $\frac{1}{T}$  in Figure 3. This was produced using matplotlib Python 3 graphing library.



**Figure 3 - Van't Hoff plot of  $\ln k$  as a function of  $\frac{1}{T}$**

From Figure 3, two significant observations can be made. Firstly, it is justified that the data points increase in a positive fashion. Theoretically, exothermic reactions produce positive slopes in Van't Hoff plots because  $\Delta H < 0$ . This is correct for the forward reaction of an LHV hydrogen fuel cell  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$  where energy is released to do work. Secondly, the consistent pattern between each data point allows for the use of a trendline to find the function that defines  $\ln k = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$ . This is produced in Figure 4 with the addition of an error bar and error line.





**Figure 4 - Van't Hoff Plot of  $\ln k$  as a function of  $\frac{1}{T}$  with a trendline and error line**

From Figure 4, the trendline with equation  $y = 29381.216025x + (-6.181233)$  can be rewritten in terms of  $\ln k$  and  $\frac{1}{T}$ . Visually, the error line is negligible. Mathematically speaking, the uncertainty of the slope and  $\ln k$  intercept will remain at  $\pm 1.0\%$ .

$$\ln k = 29381.216025 \frac{1}{T} + (-6.181233)$$

Therefore, this linear function shows that the slope  $m$  is  $m = -\frac{\Delta H^\ominus}{R}$  and the  $\ln k$  intercept  $b$  is  $b = \frac{\Delta S^\ominus}{R}$ . With this, the enthalpy and entropy can be calculated, to determine the thermodynamic efficiency of an LHV hydrogen fuel cell. Given the slope of  $m = 29381.216025 \pm 1.0\% \text{ K}$ ,  $\Delta H^\ominus = -Rm = -8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times (29381.216025 \pm 1.0\% \text{ K})$ ,

$$\therefore \Delta H^\ominus = -244158 \pm 1.0\% \text{ J mol}^{-1}$$

Given the  $\ln k$  intercept of  $b = -6.181233 \pm 1.0\%$ ,

$$\Delta S^\ominus = Rb = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times (-6.181233 \pm 1.0\%),$$

$$\therefore \Delta S^\ominus = -51.366 \pm 1.0\% \text{ J mol}^{-1} \text{ K}^{-1}$$

Furthermore, thermodynamic efficiency, the fraction of heat that can become useful work is  $\eta = \frac{\Delta G}{\Delta H} \times 100\%$ . Since  $\Delta G = \Delta H - T\Delta S$ ,  $\eta = \frac{\Delta H - T\Delta S}{\Delta H} \times 100\%$ . Simplifying this algebraically:

$$\eta = \left(1 - \frac{T\Delta S}{\Delta H}\right) \times 100\%$$

Hence, using the values of  $\Delta H^\ominus$  and  $\Delta S^\ominus$  calculated from the Van't Hoff plot, the thermodynamic efficiency of an LHV hydrogen fuel cell at 298 K is

$$\eta = \left(1 - \frac{298 \text{ K} \times (-51.366 \pm 1.0 \% \text{ J mol}^{-1} \text{ K}^{-1})}{-244158 \pm 1.0 \% \text{ J mol}^{-1}}\right) \times 100\%$$

$$\therefore \eta = (93.73 \pm 2.0 \%) \%$$

Using the Van't Hoff plot, the thermodynamic efficiency of an LHV hydrogen fuel cell was found to be  $(93.73 \pm 2.0 \%) \%$ .<sup>9</sup> Comparing this to theoretical values, again,  $\eta$  must be calculated from literature values in Table 2 containing enthalpy, Gibbs Free Energy, and entropy data. For the reaction of  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ ,  $\eta$  can be rewritten to show changes in enthalpy, Gibbs Free energy, and entropy for the forward reaction. Recall the following two equations as defined in Section 1.1.

$$\Delta S_{\text{reaction}}^\ominus = \sum \Delta S_f^\ominus(\text{products}) - \sum \Delta S_f^\ominus(\text{reactants})$$

$$\Delta H_{\text{reaction}}^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$

For the forward reaction of an LHV hydrogen fuel cell that produces  $\text{H}_2\text{O}(\text{g})$ , data from Table 2 can be used to calculate  $\Delta S_{\text{reaction}}^\ominus$  and  $\Delta H_{\text{reaction}}^\ominus$ .

$$\Delta S_{\text{reaction}}^\ominus = 0.189 \text{ kJ mol}^{-1} \text{ K}^{-1} - (0.131 \text{ kJ mol}^{-1} \text{ K}^{-1} + \frac{1}{2} (0.205 \text{ kJ mol}^{-1} \text{ K}^{-1}))$$

$$\therefore \Delta S_{\text{reaction}}^\ominus = -0.0445 \pm 2 \times 10^{-5} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta H_{\text{reaction}}^\ominus = \Delta H_f^\ominus(\text{H}_2\text{O}(\text{g})) = -241.8 \pm 0.04 \text{ kJ mol}^{-1}$$

$\Delta H_{\text{reaction}}^\ominus$  is simply the enthalpy of formation of water vapour because  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  are water's constituent elements. Substituting these into  $\eta = \left(1 - \frac{T\Delta S}{\Delta H}\right) \times 100\%$  for standard condition temperature 298 K,

$$\eta = \left(1 - \frac{298 \text{ K} \times (-0.0445 \pm 2 \times 10^{-5} \text{ kJ mol}^{-1} \text{ K}^{-1})}{-241.8 \pm 0.04 \text{ kJ mol}^{-1}}\right) \times 100\%$$

$$\therefore \eta = (94.52 \pm 0.06 \%) \%$$

The theoretical thermodynamic efficiency of an LHV hydrogen fuel cell was found to be  $(94.52 \pm 0.06 \%) \%$ . In comparison to the thermodynamic efficiency deduced from the Van't Hoff plot, the percent error deviation  $\delta$  is:

$$\delta = \frac{|93.73\% - 94.52\%|}{94.52\%} \times 100\% = 0.84\%$$

<sup>9</sup> To clarify,  $\eta = (93.73 \pm 2.0 \%) \%$  indicates that there is a 2.0 % percentage uncertainty and the thermodynamic efficiency is about 93.73 %.

## **5. Conclusion**

Subsequent to data collection and processing, it can be deduced that using a Van't Hoff plot was an accurate approach to determine the thermodynamic efficiency of an LHV hydrogen fuel cell. In this investigation, graphical inspection of the visually linear pattern from processed datasets allowed for the use of a trendline that produced a Van't Hoff equation. Considering the forward reaction of the LHV hydrogen fuel cell reaction, the exothermic nature satisfied the theoretical and mathematical predictions given by the Van't Hoff equation. Despite the low percent error deviation of 0.84% when compared to literature calculations, several factors may be the result of this error, which will be expanded upon in Section 5.1 - Evaluation and Error. Mathematically speaking, using a Van't Hoff plot should have produced the same result as simply using entropy and enthalpy data. When analyzing the final uncertainties of thermodynamic efficiencies, the result propagated from the Van't Hoff plot overlapped with the set of uncertainty values of literature calculations. This was shown as

$$\eta = (93.73 \pm 2.0 \%) \% \in (94.52 \pm 0.06 \%) \%$$

Therefore, using a Van't Hoff plot produced a result within the range of literature calculations. If this is true, it begs the question of the optimal way to test thermodynamic efficiency in hydrogen fuel cells. It can be suggested that Van't Hoff plots may help support the accurate calculations for a wider range of hydrogen fuel cells. In real-world applications, hydrogen fuel cells do not operate at chemistry's idealistic assumptions of standard conditions, rather, around the range of 433 K to 493 K. In this investigation, utilizing values of temperatures from 298.15 K to 1300 K may have been a better representation of the thermodynamic efficiencies of real LHV hydrogen fuel cells. Research into hydrogen fuel cells will continue to serve as an imperative focus in the fields of energy production, in a world where environmental concerns have become more relevant than ever — and only with sufficient efficiency, is clean energy able to compete with the world's dependence on fossil fuels.

### **5.1 Evaluation and Error**

Systematic Errors	Significance
<i>Range of Temperature Values:</i> In this investigation, temperatures ranged from 298.15 K to 1300 K. It may have been more suitable to only use values above 373 K, the boiling point of water, since this investigation dealt with an LHV hydrogen fuel cell reaction.	Real world hydrogen fuel cells operate above the boiling point of water, which may have also contributed to error. However, the many other data points used would nearly consider this small difference negligible.
<i>Gay-Lussac's Law:</i> In this investigation, it was assumed all Gibbs Free Energy data was at constant pressure. However, Gay-Lussac's Law states there exists a proportional change of pressure at varied temperatures.	It is unrealistic to assume ideal gases and constant pressures when discussing varied temperatures. However, given the reliability of databases used, this factor may have been considered for results.

Random Errors	Significance
No random error given the non-experimental approach.	No significance given the non-experimental approach.

### **5.2 Extensions**

In this investigation, using database data was, overall, a successful outcome. Nonetheless, there are several improvements or methodologies to continue this study. Most notably, the non-experimental database approach would be extended upon with experiments or studies. For example, creating an LHV hydrogen fuel cell reaction and measuring the equilibrium constant at different temperatures, or alternatively measuring enthalpy change, Gibbs Free Energy, entropy, etc., depending on equations. Other methods such as computational chemistry simulations would help verify the result produced in this investigation. In addition, considering that hydrogen fuel cells have already been applied in real-world appliances, it may be useful to measure their energy output and thermodynamic efficiency in comparison to literature values, or the calculated Van't Hoff plot outcome.

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## **7. Appendix**

In the appendix, there is the Python 3.8.3 (64-bit) program used to process and graph databases throughout this investigation.

```
#CHEMISTRY IA - Investigating the thermodynamic efficiency of an LHV hydrogen fuel
cell (%) at standard conditions using a Van't Hoff Plot
import matplotlib.pyplot as plt
import numpy as np
#Define datasets
temperatures = [298.15,300,400,500,600,700,800,900,1000,1100,1200,1300]
G1 =
[228.582,228.5,223.9,219.05,214.008,208.814,203.501,198.091,192.603,187.052,181.45,175
.807] #kJ/mol * -1
G2 =
[228.582,228.5,223.901,219.051,214.007,208.812,203.496,198.083,192.59,187.033,181.425,
175.774]
G = []
for i in range(len(G1)):
    G.append(((G1[i]+G2[i])/2)*1000) #Average and convert to J/mol
inverse_temperatures = [1/i for i in temperatures] #inverse temperatures
lnk = []
R = 8.31

#Calculate all k values
for i in range(len(temperatures)):
    lnk.append(G[i]/(R * temperatures[i]))

print(G)
print(lnk)
print(inverse_temperatures)

#Calculate Trendline
z = np.polyfit(inverse_temperatures, lnk, 1)
p = np.poly1d(z)
plt.plot(inverse_temperatures, p(inverse_temperatures), "r--")
equation = "y=%.6fx+(%.6f) "%(z[0],z[1])
print(equation)

#Create Van't Hoff Plot
plt.scatter(inverse_temperatures, lnk)
plt.errorbar(inverse_temperatures, lnk, yerr=0.017,elinewidth=0.01,ecolor="green")
plt.xlim([0,1/min(temperatures)]) #Range of Values
```

```
plt.xlabel("1/T")  
plt.ylabel("ln(k) ")  
plt.title(f"Van't Hoff Plot for an LHV Hydrogen Fuel Cell, {equation}")  
plt.show()
```