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Boiling point of volatile liquids at various pressures

Punto de ebullición de sustancias volátiles a diferentes presiones

Ponto de ebulição das substâncias voláteis em diferentes pressões

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Abstract

Water, under normal conditions, tends to boil at a “normal boiling temperature” at which the atmospheric pressure fixes the average amount of kinetic energy needed to reach its boiling point. Yet, the normal boiling temperature of different substances varies depending on their nature, for which substances like alcohols, known as volatile, boil faster than water under same conditions. In response to this phenomenon, an investigation on the coexistence of both gas and liquid phases of a volatile substance in a closed system was made, establishing vapor pressure as the determining tendency of a substance to vaporize, which increases exponentially with temperature until a critical point is reached. Since atmospheric pressure is fixed, the internal pressure of the system was varied to determine its relationship with vapor pressure and thus with the boiling point of the substance, concluding that the internal pressure and boiling point of a volatile liquid in a closed system are negatively proportional.

Keywords: Enthalpy of vaporization, pressure, temperature.

Resumen

El agua, en condiciones normales, tiende a hervir a una “temperatura de ebullición normal”, en la que la presión atmosférica fija la cantidad media de energía cinética necesaria para alcanzar su punto de ebullición. Sin embargo, la temperatura de ebullición normal de las diferentes sustancias varía en función de su naturaleza, por lo que sustancias como los alcoholes, conocidos como volátiles, hierven más rápido que el agua en las mismas condiciones. En respuesta a este fenómeno, se realizó una investigación sobre la coexistencia tanto de fases gaseosa como líquida de una sustancia volátil en un sistema cerrado, estableciendo la presión de vapor como la tendencia determinante de una sustancia a la vaporización, que aumenta exponencialmente con la temperatura hasta que se alcanza un punto crítico. Dado que la presión atmosférica es fija, se varió la presión interna del sistema para determinar su relación con la presión de vapor y con el punto de ebullición de la sustancia, concluyendo que la presión interna y el punto de ebullición de un líquido volátil en un sistema cerrado son negativamente proporcionales.

Palabras clave: Presión, entalpía de vaporización, temperatura.

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RESUMO

A água, em condições normais, tende a ferver a uma «temperatura normal de ebulição» na qual a pressão atmosférica corrige a quantidade média de energia cinética necessária para atingir seu ponto de ebulição. No entanto, a temperatura normal de ebulição de diferentes substâncias varia dependendo da sua natureza, para as quais substâncias como álcoois, conhecidas como voláteis, ferver mais rapidamente do que a água nas mesmas condições. Em resposta a este fenômeno, foi feita uma investigação sobre a coexistência de fases gasosas e líquidas de uma substância volátil em um sistema fechado, estabelecendo pressão de vapor como a tendência determinante de uma substância a vaporizar, que aumenta exponencialmente com a temperatura até chegar a um ponto crítico. Uma vez que a pressão atmosférica é fixa, a pressão interna do sistema foi variada para determinar sua relação com a pressão de vapor e, portanto, com o ponto de ebulição da substância, concluindo que a pressão interna e o ponto de ebulição de um líquido volátil em um sistema fechado são negativamente proporcionais .

Palavras-chave: pressão, entalpia de vaporização, temperatura.

1. Introduction

The main aim of this investigation is to show the relationship between the vapor pressure and temperature (average kinetic energy of the molecules) of a fluid, more specifically a volatile liquid, by measuring the vapor pressure of the substance when it has balanced the atmospheric pressure at a certain temperature and total pressure inside the system. Unlike researches performed by other scientists on the subject, where the relationship between vapor pressure and temperature vapor pressure and temperature is analyzed in consideration of a substances' enthalpy of vaporization alone, this investigation will, in addition to the latter, alter the basic pressure conditions from which the experiment is carried on to understand how pressure changes determine the amount of energy needed to reach the boiling point in function to a set critical temperature and expand the already existing knowledge on the enthalpy of vaporization of a substance in vacuum. Hence, the question to be investigated in the experiment is: *What is the relationship between the vapor pressure and boiling point of a volatile liquid in a closed system as temperature is increased and internal pressure is modified?* This investigation will address the inquiry mentioned above by carrying on a detailed analysis on the fluctuations of the vapor pressure of a substance in a closed system when temperature is increased and the system is at different internal pressures, both theoretically and experimentally, and describe the rate of growth of vapor pressure in all cases by comparing the difference in initial pressure readings with the difference in boiling point readings for the samples obtained.

2. Hypothesis and theoretical background

In pursuance of properly and uniquely describing the state of a thermodynamic system, either it is open, closed or isolated, macroscopic state variables, both extensive and intensive, must necessarily be stated to fulfil said task always depending on the fundamental relation U = U (S, N, V…) from the first and second laws of thermodynamics, where U is the internal energy of the system and S, N and V are the main natural variables which can be set (entropy, number of particles and volume respectively). Thus, in a closed system where two different "phases" coexist, for instance a pure substance in both its liquid and vapor phase, each phase can be regarded as a partial system and its state can be defined

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through set macroscopic variables mentioned before by the postulation of the second law as demonstrated below (equation 1),

$$dU = Tds - pdV + \sum_{i=1}^{k} \mu_i dN_i \tag{1}$$

The equation (1), is the first law of thermodynamics for an open system (Euler's equation for internal energy U denoted as (1)), where quantities of the *i^th^* phase are denoted by $i = 1, 2\ldots P$ may be re-written as follows (2):

$$dU^{(i)} = T^{(i)} dS^{(i)} - p^{(i)} dV^{(i)} + \sum_{l=1}^{K} \mu_l^{(i)} dN_l^{(i)},\ i = 1, 2, \ldots P \tag{2}$$

Which depends on K + 2 extensive variables for each phase and P (K + 2) variables for the system noting K is the number of different particle species. This formula, however, is set to describe a system for reversible changes of state for which the process of vaporization (which will be considered next) is to be described for infinitesimal equilibrium points in a process that carries on by itself and is started when the total system is in thermodynamic equilibrium. In this way, since intensive variables T, p and μ are functions of extensive, natural variables S, V and N, and the system is in equilibrium, one variable can be eliminated to determine the state of the system, thus only K + 2 extensive variables are necessary [1]. From such, a parameter or degree of freedom can be solved from the Gibbs phase rule which will determine the number of intensive variables needed to describe the system following the formula F = (K + 2) – P where F is the number of intensive variables needed to describe the system and P represents the number of phases [2]. Following this rule, for instance, in a closed system containing a pure substance in both its vapor and liquid phase which exchanges heat with the outside will undergo an increase in temperature, causing surface molecules with a large amount of kinetic energy (regarding the average amount of KE) to vaporize [3]. As temperature is increased, vapor molecules will condense at the same rate liquid molecules are vaporizing until equilibrium is reached (saturated vapor pressure). Given that the system is now in its equilibrium state where $T_{liquid} = T_{vapor}$; $p_{liquid} = p_{vapor}$; $\mu_{liquid} = \mu_{vapor}$, applying the Gibbs phase rule fixes the number of intensive variables to be set, namely of one (Temperature), as K = 1, P = 2 and thus F= 1 + 2 – 2 = 1 such that the vapor pressure will automatically assume its equilibrium value [4]. Further, an expression for vapor pressure when a given temperature is set and the system is in thermodynamic equilibrium can be deduced regarding the Gibbs-Duhem relation, in which variables are not independent from each other. The follow expression, which is a total differentiation of the Euler equation for internal energy (Equation 1) describes the Gibbs-Duhem relation (3):

$$0 = SdT - V\, dp + \sum_{i} N_i\, d\mu_i \tag{3}$$

The latter equation, to make Euler's equation for internal energy valid, must be equal to zero. If equation 1 is known, and as T and p are dependent to each other and thus may assume a fixed value, the chemical potential may be calculated giving μ_{liquid} (p, T) = μ_{vapor} (p, T). If temperature is variated (dT) and thus pressure variates at an equivalent rate (dp), the chemical potential along a coexistence or bimodal curve is $d\mu_{liquid}$ (p, T) = $d\mu_{vapor}$ (p, T) [5]. This equation can be expressed through the Gibbs-Duhem relation (Equation 3) in the following way (4) and per Greiner et al:

$$\begin{gathered} d\mu_V\,(p,T) = -\frac{S_{li}}{N_{li}}\,dT + \frac{V_{li}}{N_{li}}dp \\ d\mu_V\,(p,T) = -\frac{S_v}{N_v}\,dT + \frac{V_v}{N_v}dp \end{gathered} \tag{4}$$

Where S/N for both equations is the specific entropy and V/N for both equations as well is the specific volume (in relation to the number of particles). After both equations (Equation 4) are equalized following that chemical potentials are equal the latest equation may be re-written as (5):

$$\frac{dp}{dT} = \frac{s_{li} - s_v}{v_{li} - v_v} \tag{5}$$

Where s_{li} is the specific entropy for the substance in its liquid phase, s_v is the specific entropy for the substance, v_{li} is the specific volume for the substance in its liquid phase and v_v is the specific volume for the substance in its vapor phase. This equation (5) is the Clausius-Clapeyron equation (named after Paul Émile Clapeyron and Rudolf Clausius in 1834), relating the rate of change of pressure over temperature when specific entropies and volumes are known. Noting that $s = \frac{\partial Q_{rev,li\to v}}{T} = S_{li} - S_v$, (amount of energy needed to evaporate all the substance), then $\frac{dp}{dT} = \frac{\partial Q_{rev,li\to v}5}{T\,(Vli - Vv)}$. These equations, still, must fulfill additional parameters to be true. As the latest re-evaluation of the Clausius Clapeyron equation deals with entropy differences, which determine the reasons why processes tend to happen, thermodynamic potentials as entropy and others equivalent to internal energy as enthalpy and free enthalpy should be considered. In fact, following that the process of vaporization is taken to be reversible, thermodynamic potentials will give information in function of the internal energy of the system relevant to equilibrium positions [6]. Additionally, as natural variable S is hardly measurable (considering it makes an account of the microscopic configuration of the system) given potentials, namely H for example, can transform U in such way entropy is stated in function of its correspondent intensive variable T, and so on via the Legendre Transformation [7]. For such purpose, given a function of internal energy U for two intensive variables, f(x), at a random point x a transformation to a new equation g(x) can be made by $g(x) = f(x) - \ x f'(x)$ or $g(x) = f(x) - p'$ when p' is the derivate of f(x). In this way, keeping a determinate variable in the process of vaporization controlled, the atmospheric pressure, and hence changing the function U (S, V) (Equation 1 without chemical potential) to a function H (S, p) the transformation reads as follows (6):

$$g \equiv f - wy \ = (U) - (P)(V) = U + PV \equiv H\ (S, P) \tag{6}$$

Where the potential *H*, the enthalpy in equation 6, is obtained following the assumption for g(x). Then, according to the differential of g(x), g(x), $dg = df - pdX - Xdp$, the change of enthalpy reads as (7):

$$dH \ = dU + pdV + Vdp \tag{7}$$

Enthalpy then, when viewing the experimental realization of the vaporization of a liquid, represents the energy needed to transform the substance into a gas [8]. The latter assumption is validated by the last transformation of the Clausius-Clapeyron equation, $\frac{dp}{dT} = \frac{\partial Q_{rev,li\to v}}{T\,(Vli - Vv)}$, as $H = Tds + Vdp$ given that when volume is constant in equation 7 $\partial W_{rev} = 0$, in such way $\frac{\Delta H}{T} = \frac{dp}{dT}$. Likewise, this assumption can be made from another potential, the free enthalpy, which is obtained by creating a function g(x) by means of the Legendre transformation of two extensive variables, S and V, and proves to be more convenient given that S is not easy to control [9]. This potential is also called the Gibbs potential for it was named after J.W. Gibbs as it closely resembles the Gibbs-Duhem relation (Equation 3), and is transformed as follows (8):

$$G = U - TS + pV \tag{8}$$

In fact, the latest equation (equation 8), when solved for a specific variable, gives one information about the equation for internal energy. The differential for G, following g(x), $dg \ = \ df - pdX - Xdp$, change of free enthalpy thus reads as (and should correspond to the transformation of the Clausius-Clapeyron) following equation (9):

$$G = dU - T\,ds - SdT + pdV + Vdp \tag{9}$$

Where Tds and pdV equal to zero as to satisfy Euler's equation. Further, when introducing μ in equation 9 and differentiating, a relation of proportionality is found, stating that G is directly proportional to N and "the free enthalpy per particle is identical to the chemical potential" [1]. In this way, for a system to be in thermodynamic equilibrium, the difference in Gibbs free energy must equal zero equivalent to $\mu_{liquid} = \mu_{vapor}$, and therefore, the Gibbs relation (Equation 3) can be applied. Consequently, dS in the differential may be solved for and introduced in the Clausius-Clapeyron, giving $S_v = \Delta H / T$ as stated before. Finally, assuming V follows the equation for ideal gases $V_v = RT/P$, the new equation for vapor pressure and its integration read as:

$$\frac{dp}{dT} = \frac{PL}{T^2 R} \tag{10}$$

$$\ln\frac{P_1}{P_2} = -\frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{11}$$

Where L is the specific latent heat of vaporization or ΔH, R is the gas constant, 8.3145 J mol^{-1} K^{-1}, and P, T are the vapor pressure and temperature respectively in both equation 10 and 11. In accordance to the information presented above, if a liquid is heated at different internal pressures in a closed system, then its temperature will increase as heat increases the average kinetic energy of the substance. Once vapor pressure equalizes the atmospheric pressure, the substance will reach its boiling point as liquid molecules are no longer being held by vapor pressure. As a result, a liquid heated in a closed system at room temperature and normal internal pressure will reach its boiling point at a temperature corresponding to 1atm. As noted in the equation for vapor pressure, as temperature is increased by 1°C, the molecules with sufficient energy to escape will grow exponentially [3]. Additionally, substances which tends to vaporize faster, as molecules have weaker bonds or a higher amount of internal kinetic energy, are known as volatile [10]. The vapor pressure of a volatile substance is greater than the vapor pressure a non-volatile substance like water. To change the boiling point of a substance, the internal pressure can be modified in such way that if it is decreased then the amount of energy required to boil the liquid from equilibrium with the vapor pressure in the same system, or enthalpy of vaporization, will be greater resulting in a higher boiling point. However, as the substance is the same, the rate of growth must be the same and the difference in initial pressure readings must equal the difference in boiling point.

3. Previous analysis

The graph for vapor pressure versus temperature must be exponential. According to the equation for vapor pressure stated before (equation 11), if the natural logarithm of the vapor pressure is graphed against the inverse temperature, the relationship must appear linear and its slope should be the enthalpy of vaporization, which is to be calculated in order to prove the equation and hypothesis valid. Various repetitions variating the internal pressure should be done, comparing every result at the end as well as boiling points and difference in initial pressure reading over difference in boiling points, which should be equal or close to one. Finally, free enthalpies are to be calculated and compared.

4. Variables

4.1 Controlled

Volume of the system (keeping the flask unaltered), Volume of the substance (measured in milliliters with a digital scale), approximated number of molecules (stays relatively constant as the same amount of substance is used per trial), atmospheric pressure (stays constant in the same altitude above the sea), Surface area (constant as the flask is the same).

4.2 Independent

Temperature as the substance reaches its boiling point (measured in °C and K with a Vernier logger pro temperature sensor inside a hot bath). The temperature results are different per trial, however, the rate of change of temperature per trial is the same and thus can be set independent. It is important to recognize that temperature, theoretically, does not behave as an independent variable. However, given every point in the infinitesimal set of data for the laboratory behaves as an equilibrium point it is correct to affirm that temperature is indeed an independent variable.

4.3 Dependent

Internal Pressure (initial pressure plus vapor pressure as temperature is increased) (Measured in kPa with a gas pressure Vernier logger pro sensor).

5. Materials

- A 50mL Erlenmeyer flask and a 1000mL beaker.
- A Vernier logger pro.
- A temperature sensor for the reader.
- A vapor pressure sensor for the reader. And a #5 rubber stopper fitting the tip of the flask and with holes for the sensor. Plus, the additional support parts of the sensors.
- A Bunsen burner.
- Approximately 1000mL of water.
- Approximately 25mL of Isopropyl alcohol.
- A 20mL plastic syringe.
- A tripod, a ring stand and a Wire Gauze.

6. Procedure

- Place the tripod and wire gauze over the Bunsen burner. Next, place the ring stand beside the Bunsen burner. Fill the beaker with water and put it over the tripod, as indicated in Figure 1.

Figure 1. Apparatus set up.

- Hold the tip of the Erlenmeyer flask with a ring from the stand tightly over the beaker. Close the Erlenmeyer flask and connect the gas pressure sensor to the flask. Lower the flask into the beaker, letting the water cover almost all the flask and hold tightly.
- Measure 3mL of alcohol with the pipette and put the liquid inside the syringe. Open the valve of the rubber stopper (an additional accessory) and insert the liquid into the flask. Close the valve and empty the syringe if liquid remains.
- Put the temperature sensor inside the water after calibrating it, turn the readings of the logger pro on and wait for it to equilibrate.
- After equilibrium is reached, turn on the Bunsen burner and start recording data for pressure and temperature.
- Record data until the rubber stopper pops out of the flask. Wait for the supplies to cool down and reach room temperature and repeat the processes, but instead, after adding the liquid and emptying the syringe, reopening the valve to take vapor

from the flask and closing it again. Variate the amount of vapor eliminated from the flask to obtain different results.

- Repeat at least with five pressure readings per trial with initial pressure. The number of pressure variations may be seven or six.
- Get rid of the alcohol considering environmental and laboratory risks carefully and in such way alcohol is far from fire or hot surfaces.

7. Uncertainty evaluation

Variable measuring is bound to have a significant percentage of error which can be reduced if variables are carefully measured. First, it is important to acknowledge the fact that variables were properly chosen so that they match the first assumptions for the vapor pressure equation (equation 5), volume is constant, temperature is set and vapor pressure depends mainly on the internal energy and other extensive variables (excepting for volume) of the system. The system is set to only exchange reversible heat with the outside which is transferred through the heat bath and thus controlled. However, the heat bath, for not attempting to resemble an adiabatic system, may lose heat irreversibly and said change may be considered in the results. The uncertainty of the apparatus used to measure the two main variables, however, is minimal and results tend to be precise. Variables such as atmospheric pressure are always constant. The value for atmospheric pressure is 101.35 kPa. The amount of the substance, which is controlled, must be 3mL and more not only as it clearly affects the result but also as pressure will pop out the rubber stopper before the substance has reached its boiling point given that the gas occupies are larger volume than what its available. Other condition boundaries include room temperature which constantly variates but will only change the starting point of data. Lastly, the experiment may cause damages so the technological apparatus must stay far from the Bunsen burner and temperature cannot exceed 110°C or else the glass flasks may explode. Alcohol must also be disposed properly.

7.1 Data

After running the experiment five times per trial, seven trials, the best results were picked. The number of data taken was of 14486, over 900 each trial and a maximum run time of 53.25 minutes. A sample of the data for one of the runs is listed below in Table I.

Table I. Sample data obtained.

RUN 12												
TIME	PRESSURE	TEMPERATURE	TEMPERATURE	IT	NP	UNC P	UNC T	UNC C	%UNC P	%UNC T	% UNC LNP	% 1/T
T	P	T	T	1/T	LN(p)	KPa	K	C				
s	KPa	°C	K	T								
0	32,2	20,3	293,5	0,003407736	3,47197	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
1	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
2	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
3	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
4	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
5	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
6	32,21	20,4	293,6	0,003406575	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
7	32,27	20,3	293,5	0,003407736	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
8	32,27	21	294,2	0,003399626	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
9	32,27	21,1	294,3	0,003398471	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
10	32,27	21,1	294,3	0,003398471	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
11	32,21	18,9	292,1	0,003424071	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
12	32,27	20,3	293,5	0,003407736	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
13	32,21	20,3	293,5	0,003407736	3,47228	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
14	32,34	20,2	293,4	0,003408897	3,4763	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
15	32,27	20,2	293,4	0,003408897	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
16	32,27	20	293,2	0,003411223	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05
17	32,27	20,1	293,3	0,00341006	3,47414	0,6	54,63	0,2	0,1863	18,62	3,474	6,5E-05

For a trial starting at 32.2 kPa of pressure Table I. Values are aproximated to four significant values according to the uncertainties. As this run consisted of 2569 different data points, values seem to be unvaried. All variables are stated according to the information that was previously mentioned. Additionally, values for uncertainties were taken as well as propgated uncertainty for Ln (pressure) and 1/T. When considering the graph of Natural lograithm of pressure against the inverse of temperature, error propagation will be considred too. The first graph to be processed, the normal pressure graph, shows as following (Figure 2).

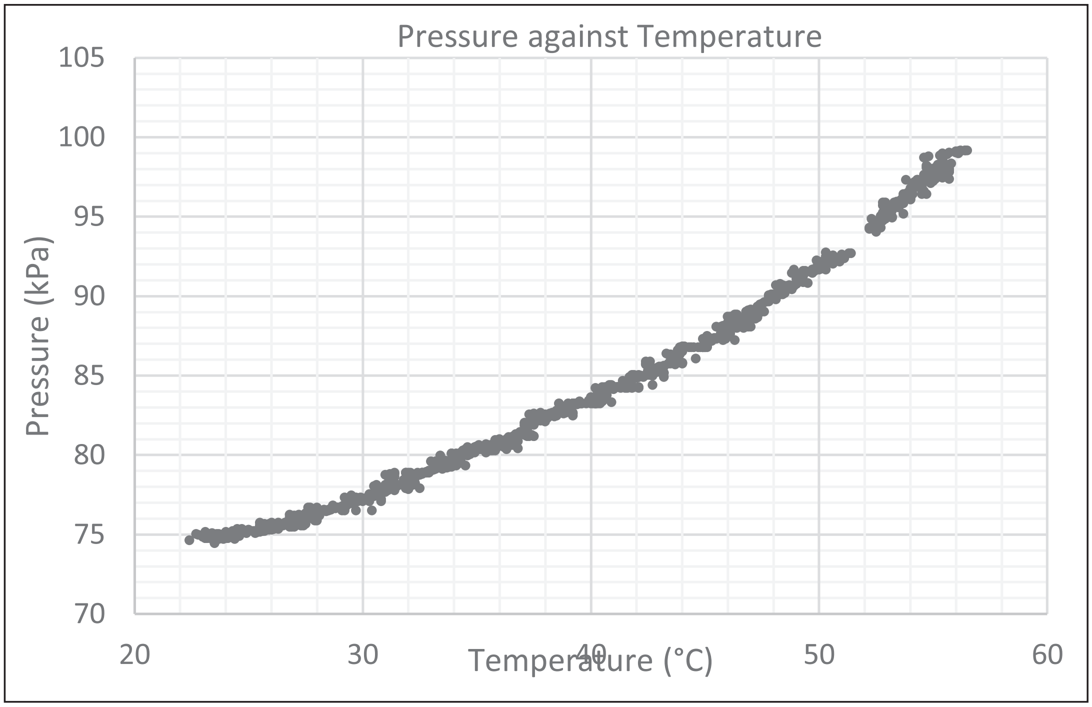

Figure 2. Pressure against Temperature.

Figure 2 shows the relationship between pressure and temperature, appearing to be exponential as hypothesized. Error bars were added but are minimal and do not show in Figure 2. In order to find the factor of growth of the exponential vapor pressure curve, and following equation 11, the relationship pressure-Temperature will be linearized by graphing ln(pressure) against the inverse temperature as shown below in Figure 3:

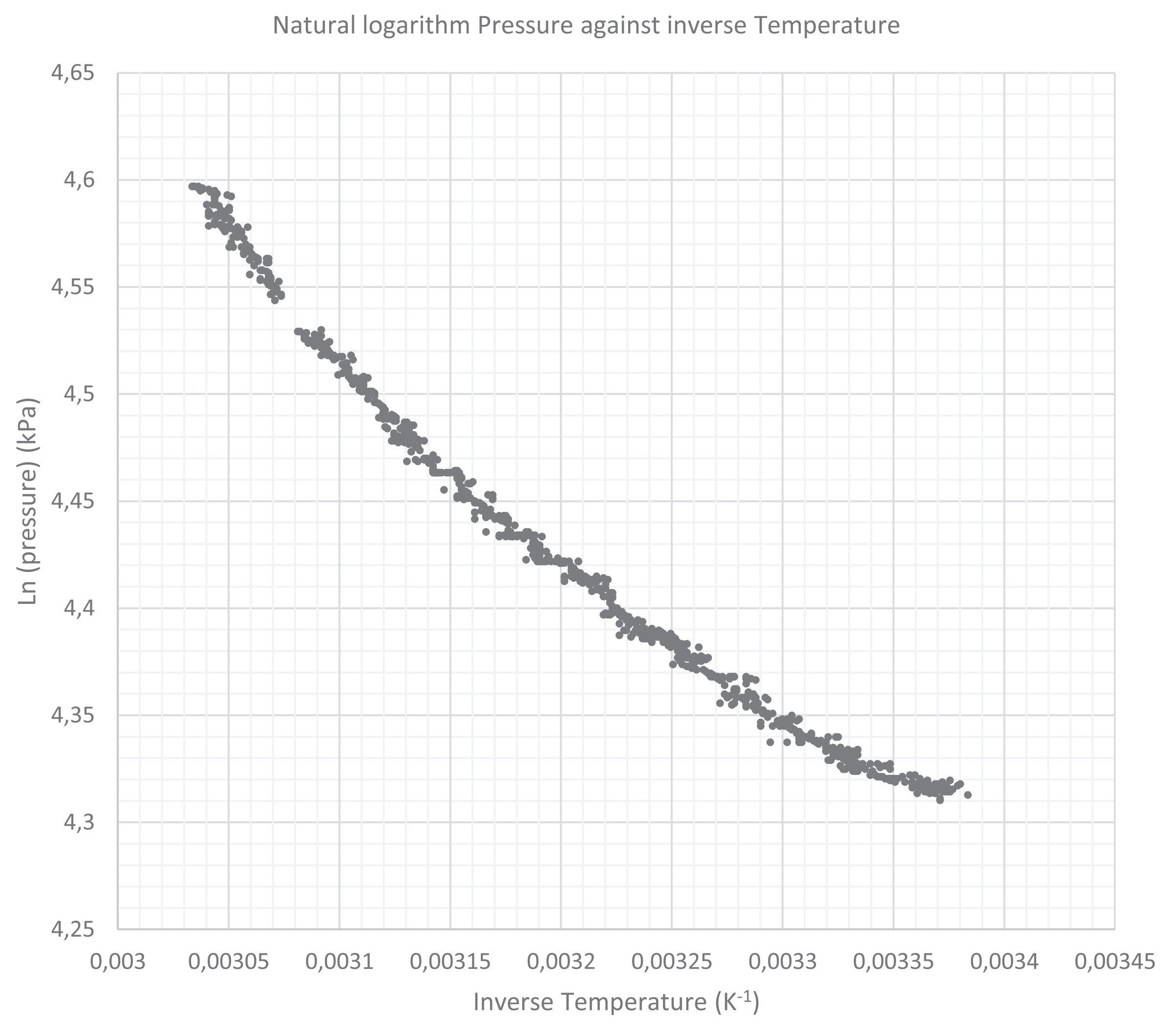

Figure 3: Natural logarithm pressure against inverse Temperature.

Figure 3 shows the relationship between the natural logarithm of the pressure against the inverse temperature, relationship which should hypothetically be linear and its slope should be the enthalpy of vaporization of such process. Now that error is propagated, error bars were added but again proved to be insignificant as error in this experiment is not relevant. However, the latest graph (Figure 3) is not linear. In fact, the graph is linear until some certain approximated point and then proceeds to be curved. This happened because the process was forced to perform work when popping the rubber stopper out of the flask changing the initial formulae that set dV as zero and thus $\partial W_{rev} = 0$. This error will be discussed later. The enthalpy of vaporization will be calculated partially assuming the Figure 3 is linear. The linearization appears as following,

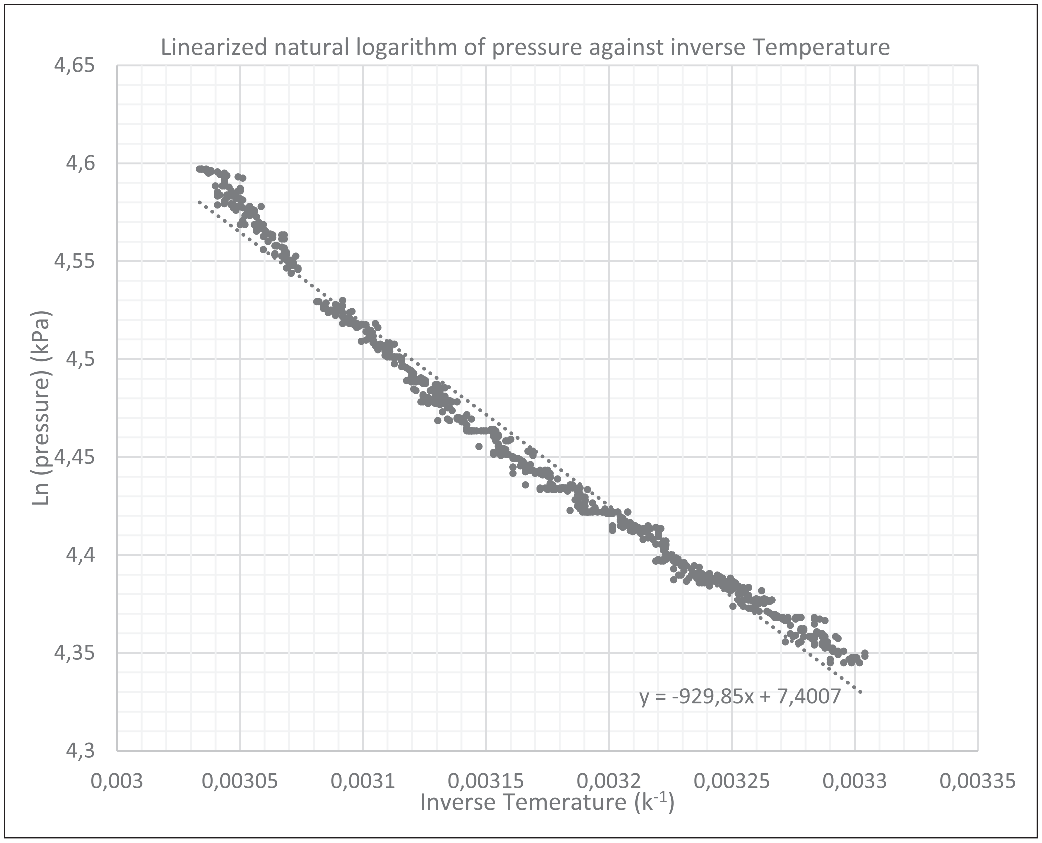

Figure 4. Linearized natural logarithm pressure against inverse Temperature.

Proving the enthalpy of vaporization, which is the slope of the Figure 4, to be 929.85 kJ kg-^{1} and having its corresponding negative sign as when enthalpy is obtained from the Legendre Transformation it holds the sign for -pdV. Additionally, the value for the squared correlation is of 0.9815 proving data to be strictly related. Given that this trial corresponds to "normal pressure" then the theoretical value for the enthalpy of vaporization should correspond to this result. For such, relative error in comparison to the fixed value, 732.2 kJ kg-^{1} will be calculated following /Equation 12):

$$\%Diff = \frac{|Theor.Value - Exp.Value|}{Theor.Vaue} x100\% \qquad \textbf{(12)}$$

Giving 27% of relative error. The reasons behind the high percentage of error will be explained later. Yet, values appear to be accurate regarding the boiling point. Moving on, the remaining data was similarly processed and its graphs were analyzed as well. The results for the remaining data read as follows (Table II):

Table II. Processed results for remaining selected trials.

TRIAL	H(p) SAT	INITIAL PRESSURE ±0,06	BOILING POINT (°C)+-0,2	% UNC H(p) SAT
1	-579,07	79,46	51	7,367
2	-929,9	79,46	58,5	7,558
3	-803,02	74,2	55	7,492
4	-1117,9	66,04	64,2	7,337
5	-1577,8	53,01	70,0	6,974
6	-2025,6	41,51	77,4	6,717
7	-2030,9	32,21	80,0	6,1
8	2505	24,39	85,2	7,035

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Where H (p)sat is Enthalpy of vaporization of the linearized graphs (Figure 3 and Figure 4) measured in (kJ kg-1) and %Unc H(p) sat is measured in (kJ kg-1), proving the hypothesis true, as the enthalpy of vaporization is greater for lower initial values of pressure because the amount of energy for it to vaporize will be greater and thus its boiling point, which is just a reading for temperature will be greater as well. This can be elaborated noting that H and T are related in the Clausius Clapeyron equation (equation 10) in such way data is presented. Still, the amount of error present in the first processed data will equivalent be one of the next data (or greater) for error must be explained. The percentage uncertainty noted accounts for systematic errors in the measurement, which will also be discussed in the error section. Lastly, graphs for data are depicted below (Figure 5),

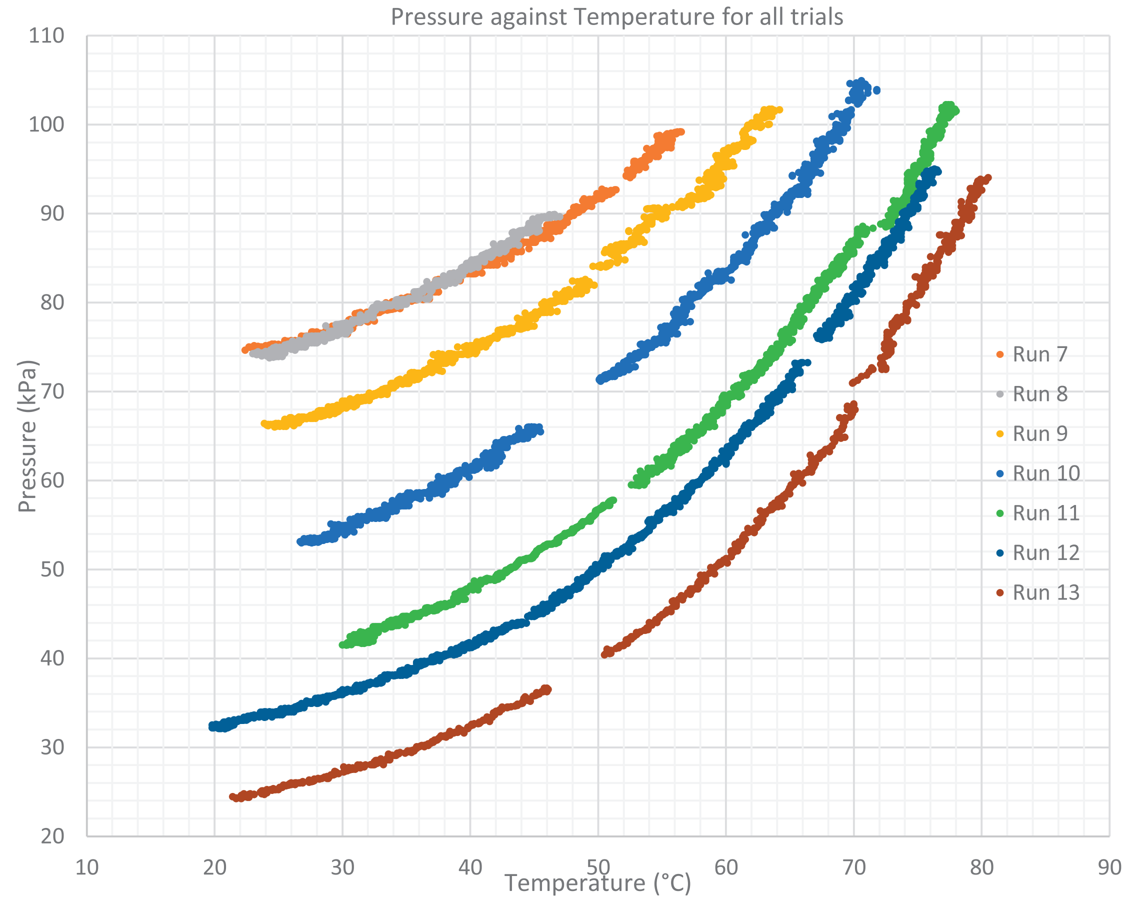

Figure 5. Pressure against Temperature for all selected trials.

Figure 5 shows the comparison of the vapor pressure curves obtained from which several conclusions can be drawn, reinforced by the information provided by the boiling point against internal pressure of the obtained samples shown below (Figure 6):

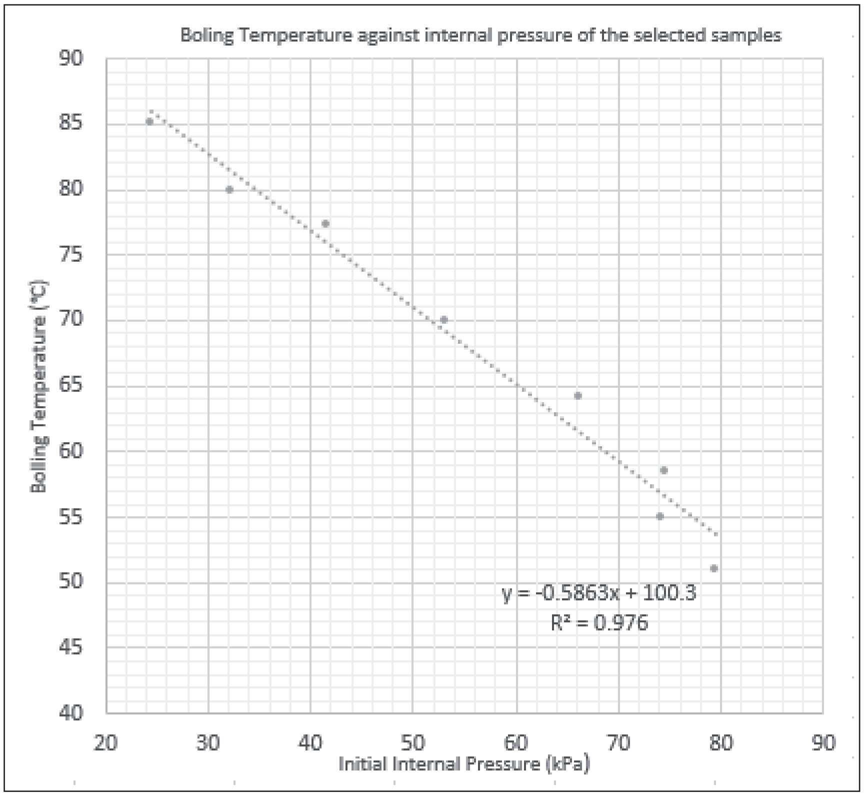

Figure 6. Boiling Temperature against internal pressure of the selected samples.

Where, as hypothesized, the relationship between internal pressure and boiling point of a volatile liquid is negatively proportional. Firstly, as mentioned before, that rate of growth of graphs which start at lower pressures in Figure 5 (Run 11, 12, 13) is significantly greater for which the process will need more energy (added by the change of temperature) to reach a given value in both the x and y axis, given the boiling point (note curves are steeper). After calculating the difference on initial pressure over the difference on final temperature per each pair of graphs one gets results close to one as of 2, 1.8, 1,5, etc., indicating that graphs in Figure 5 are merely displaced and their slopes will be the only indicators of their difference. Another conclusion that can be drawn and is clearly evidenced in Figure 5 is the fact that as the processes proceed exponentially, the processes starting at lower internal pressures will reach its critical point in temperature at lower temperatures as heat cannot longer be added to neither the liquid (because its evaporated) nor its vapor (because its overly saturated). In fact, noting that isopropyl alcohol reaches its critical point at approximately 234.3 °C (508.7 K) only “normal” graphs (under normal pressure conditions as in Figure 2) will fulfil this parameter, displaced graphs as those in Figure 5 will reach it before, at lower temperatures. This happens because the heat needed to vaporize the liquid is greater at lower pressures noting the liquid must additionally overcome fixed, lower pressures, a conclusion that fulfills the notation for enthalpy given it is a function of the internal energy plus an additional value which is the increased one. Further, if the equation of the total differential of U was known, one could determine the amount of extra energy added in order to successfully vaporize the liquid. Additionally, after enthalpy is obtained, Gibbs free energies can be obtained and compared, which, should be the same because they ultimately depend on the substance and are always constant and equal (between vapor and liquid).

8. Error evaluation

- The first error to be considered is the rubber stopper error, which would not fit in neither the definition of systematic and random error and is an unavoidable error in the experiment if Vernier products are used for the experiment. The volume of the fluid inside the flask was measured in such way its expansion would not pop out the stopper before pressure reached and equalized one atm of pressure, however it is set to pop out and popping out the stopper requires an additional effort. In fact, popping out the stopper would mean that the volume of vapor must increase breaking the thermodynamic partial equilibrium of the two phases inside the flask. A considerable solution would be, for instance, to choose a bigger Erlenmeyer flask and thus a bigger heat bath as the gas could have expanded without popping the stopper out, and the curve for the graph which as hypothesized to be linear (Figure 3) would be corrected. Still, the stopper that is part of the kit for the gas pressure Vernier sensor solely fits the tip of a 50mL Erlenmeyer flask and gas sensors are not widely available for school researched. Similarly, reducing the liquid would have proven to be a failure as the liquid would vaporize faster and noting that heat cannot be transferred to the liquid if there is no liquid, glass would break or the stopper would pop out faster.

- The second error to be considered is the relative error in function to the theorized value for the enthalpy of vaporization of a liquid starting a normal pressure. The concentration of the liquid studied in this experiment, for safety and legal reasons, has a concentration lower than 80%, which means the substance closely resembles a pure substance (specially at such small volumes) but still isn't a pure substance. Equations for pure substances can still be applied as in this experiment because, again, difference is minimal. The percentage of error, in fact, corresponds to the percentage of concentration which isn't part of the pure substance. As the substance used was dissolved with water and water vaporizes at higher temperatures, the amount of substance vaporized is smaller. Observing that the concentration of the substance used was of 70%, the remaining percentage, 30%, is equivalent to the error which is of 27%. This error can either be ignored or fixed via the application of Raoul's law for pressure of fugacity and repeat the entire experiment.

- The third error to be discussed is the error proper of the measuring apparatus. Although it was stated in Table 1 and its propagation was calculated, it did not appear relevant for both the original graph (Figure 2) and the fit line (Figure 3 and 4). For said reason, a sample of the calculations will be made. The uncertainty for p and T was previously given and using a rule of three, the absolute uncertainty for T in Kelvin was calculated. For the percentage uncertainties, the absolute value for the uncertainty corresponding to each data point of each variable was divided by the corresponding experimental data point and multiplied by one hundred. As uncertainties for one or a pair of variables when operated mathematically will be calculated by adding its percentages unless the operation is a sum or a difference, the uncertainty for the inverse temperature was obtained simply operating for the fractional uncertainty of each point as being a divisor of 1 any other calculation is canceled. For the natural logarithm, the fractional uncertainty for each point was added to the value for natural logarithm of pressure. The propagation of error was minimal, changing 1 kPa for the natural logarithm and 0.000001 K for the inverse temperature.

- The fourth error to be considered is a human error regarding data processing. Graphs appear to have gaps (appear to be functions by parts) when they are perfectly continuous functions, as in the case of Run 7, 9, 10, 11, 12 and 13 from Figure 5. This error took place because the Vernier logger pro data reader and collector was set to collect data until 900s, but many processes in fact lasted twice or thrice as long. When I realized, the sensor had stopped taking data, the continued data taking was appended and the function appears to have holes in them. Let it be clear that being more careful would have avoided the error and that it is not a fallacy of the experiment or the background. Nevertheless, graphs (Figure 2, 3, 4 and 5) could still be studied and results were not affected beyond this discontinuity issue.

- The last error to be considered encompasses every approximation to a value for boiling point. After doing an extensive research it was effectively found that the proper amount of alcohol to be used to determine the temperature at which the substance boils as being the same temperature at which the rubber stopper jumps out was used in this laboratory based on several calculations on the expansion of the gas, the volume of the flask and the heat source. This approximation, however, has a large potential amount of error. Still, by indicating the uncertainty of the measurements and of the final processed results as demonstrated in table 2.0, one can give an approximated range of values in which the boiling point took place. Nevertheless, the results of this experiment are still coherent and necessary for the relationship between the variables was obtained properly. The understanding of this error, as well as the understanding of the error regarding the work done to pop the rubber stopper out, aids the comprehension of the drastic change in data towards the end of their recordings for which the experiment changed from doing no work into doing an additional effort to pop the rubber stopper off and thus making an account of the boiling point before gas accumulated to make the additional effort.

9. Additional conclusions and improvements

- In general, the experiment worked as expected. How discussed before in the error section, the first and most important improvement would be to change the volume of the system that contains the substance into one that is significantly larger.

- Another improvement would be to use a substance with a hundred percent of concentration. Although error can be explained and justified, a perfect experiment can be effectively done with a perfectly volatile and pure substance. Still, these tend to be flammable and dangerous for people inside school laboratories (ex. gasoline, ethanol, etc.)

- Another improvement would be to get a scientific heat bath so that the amount of reversible heat lost when heating water inside the beaker is minimal, as discussed in the uncertainty section. Although almost impossible to measure, this variation of the increase in temperature can be seen in the graph (Figure 2) given that for very short intervals of time temperature decreases and increases. The latter, whilst can make the analysis of specific points of the process hard, is, however, insignificant for equilibrium thermodynamics as only equilibrium states are studied and necessary. Even if the process is said to be a reversible process with infinitesimal equilibrium points, the main purpose was to evaluate the first and last data of the process for which boiling pressure and initial pressure reading where the data compared.

10. Proposals

- To process the data further into extracting the enthalpy at ending of the process as well as the free enthalpy and reaching far more interesting conclusions.

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