

# PHYS2712 Thermo 6 Laboratory Report

## Marcet Boiler

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**Abstract**—The vapour pressure indicates the pressure at which the transition between liquid and vapour is at equilibrium. Vapour pressure and temperature have an intimate relationship. Working through the Clausius-Clapeyron, Antoine, and further the Wagner equations, an expression for relating vapour pressure and temperature can be established. Water is heated in a pressure vessel. Measurements of the pressure and temperature are taken, and photographs of the bubbles formed are shown. The experimental p-T data are fitted to the Antoine and Wagner equations and empirical coefficients are calculated. The Antoine coefficients are compared to reference data, and the data shows good agreement.

**Keywords**—vapour pressure, Clausius-Clapeyron, Antoine, Wagner

## 1 Introduction

The pressure, temperature, and volume of a substance are all interdependent. Although water is known to boil at 100 °C at atmosphere pressure, the boiling temperature changes depending on the pressure. This pressure is termed the vapour pressure.

In order for a substance to change from a liquid to a vapour phase the molecules must have sufficient energy. The energies of molecules are

not all equal but vary, perhaps following a bell curve type distribution. Some molecules escape the liquid phase and enter the vapour phase, and some return. By increasing the temperature of the liquid, the overall energy of the molecules is increased and more will transition to the vapour. In a fixed volume system, as the molecules escape the liquid and enter the vapour, the pressure within system will increase, and more vapour molecules will return to the liquid state. When the number of molecules leaving and entering the liquid state are equal there is no net change and the system is in equilibrium. The pressure at which this occurs is the vapour pressure. [1]

A theoretical approach to investigating the thermodynamics of phase change is by using the Clapeyron equation. The Clapeyron equation states that the change in enthalpy during a state change is related to the slope of the saturation line (the line where liquid and vapour phases meet) in a p-T diagram, the change in specific volume, and the temperature at which the phase change occurs [2–4].

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v} \quad (1)$$

where  $p$  is the pressure,  $T$  is temperature,  $\Delta h = h_g - h_f$  is the change in specific enthalpy between the vapour ( $f$ ) and liquid ( $g$ ) phases, and  $\Delta v = v_g - v_f$  is the change in specific volume between the vapour and liquid phases.

Several assumptions can be made to simplify the equation. If the specific volume of the liquid phase is considerably less than that

of the vapour phase  $\Delta v$  can be set to  $\Delta v = v_g$  without introducing significant error [3]. Assume that vapour phase of the fluid behaves ideally (the pressure is sufficiently low) such that  $pv = RT$ . Substituting these assumptions and rearranging gives the Clausius-Clapeyron equation [2–4].

$$\frac{dp}{dT} = \frac{p\Delta h}{RT^2} \quad (2)$$

If  $\Delta h$  is independent of temperature, integration of the Clausius-Clapeyron equation produces:

$$\ln p = -\frac{\Delta h}{RT} + \text{constant} \quad (3)$$

The Antoine Equation shows a relationship between vapour pressure and temperature:

$$\log_{10} p = A - \frac{B}{C + T} \quad (4)$$

where  $p$  is the pressure,  $A$ ,  $B$ , and  $C$  are coefficients that depend on the substance and range of temperature, and  $T$  is the temperature.

A draw back to the Antoine equation is that it only accurately describes the pressure-temperature relationship under a range of temperatures [5]. Often coefficients are given for ranges such as 0°C to 100°C and another set of coefficients for 99°C to 300°C, for example.

The pressure and temperature can be expressed in any appropriate unit; so long as the coefficients are adjusted the relationship holds.

For example to change between pressure in units of mmHg to Pa apply the correction:  $A_{Pa} = A_{mmHg} + \log_{10}(133.32)$ , and from temperature in units of °C to K apply the correction:  $C_K = C_{°C} - 273.15$ . The  $B$  coefficient does not change with a unit change.

Occasionally a simplified Antoine equation is used whereby the coefficient  $C = 0$  is used to simplify analysis.

$$\log_{10} p = A - \frac{B}{T} \quad (5)$$

By plotting experimental data on log-linear axes the data will follow an approximately linear relationship, and a linear trend can be applied. The linear coefficients can then be applied directly to the simplified Antoine equation:

tion:

$$\log_{10} p = -B \frac{1000}{T} + A$$

$$y = mx + c$$

On the other end of complexity Wagner [6] describes a detailed process for developing more accurate vapour pressure equations. In particular is the focus on developing an equation that can work across a wider range of temperatures and be accurate at the critical point.

The conclusion of the work by Wagner is a new vapour pressure equation (numbered Equation 14 in the reference article):

$$\ln \pi = \frac{T_c}{T} \left( A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6 \right) \quad (6)$$

The equation makes use of the reduced pressure and temperature:

$$\pi = p_R = \frac{p}{p_c} \quad (7)$$

and

$$\tau = 1 - T_R = 1 - \frac{T}{T_c} \quad (8)$$

where  $p_c$  and  $T_c$  are the critical pressure and temperature for a substance.

## 1.1 Cavitation

Vapour pressure equations can be of use in industrial application as it applies to cavitation. Cavitation occurs when, due to the flow of a fluid or the geometry of a device, fluid encounters a region of low pressure. If the pressure is low enough for a given temperature the fluid may boil, or vaporise and form vapour bubbles, known as cavitation bubbles. The term cavitation bubbles refers to the cavity forming within the liquid filled with vapour. When these bubbles are moved back into a higher pressure region they condense back into a liquid and release high pressure shock waves. This produces damaging effects on turbines and pumps. [7]

A vapour pressure equation can be helpful in designing against cavitation.

## 1.2 Aim

The aim is to produce experimental data for vapour pressure vs temperature of water within

a constant volume vessel and attempt to fit this data to different equations that are used to represent vapour pressure as a function of temperature. The data is fit to linear, and thus simplified Antoine; Antoine; and Wagner functions. The Antoine coefficients are compared with reference data.

## 2 Methods

### 2.1 Apparatus

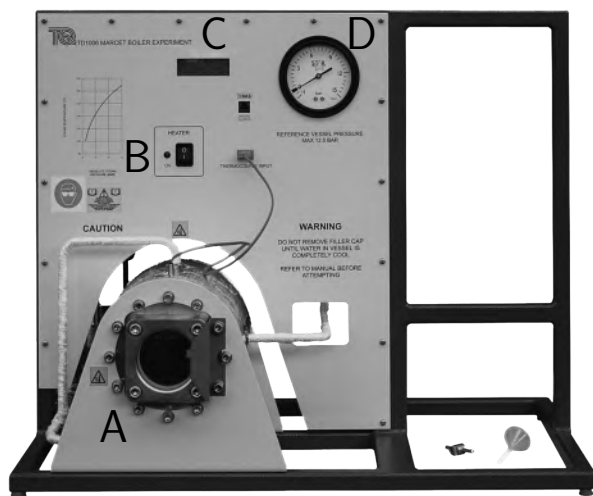


Figure 1: View of experimental pressure vessel apparatus. A – pressure vessel, showing sight glass; B – heater switch; C – digital pressure and temperature display; D – mechanical backup pressure gauge. Adapted from Tec-Quipment Ltd. [5].

The equipment consist of a cylindrical pressure vessel designed to contain working pressures up to  $1.25 \times 10^6$  Pa, of approximately 1.75 L volume. A electrical resistive heating element is mounted within the vessel that is rated up to  $180^\circ\text{C}$ . One end of cylinder vessel has a glass viewing port. On the reverse side there is a pass through for the heater element, and a port to connect a drain for any fluid contained within. On the top of the cylinder is a filler opening through which fluids can be poured into the vessel. The opening can then be subsequently closed with a special filler cap that achieves the pressure rating. A vent tube is connected to the top near the filler port.

The vent tube connects to a pressure relief/purge valve that is set to open around  $1.25 \times 10^6$  Pa. The valve also has provision

to be manually opened and allow the built up pressurised gas to escape to atmosphere via a standard drain. The drain tube is also plumbed into a drain. The entire vessel is covered in fibreglass insulation.

Pressure and temperature gauges are installed in the vessel and interface with a computer.

### 2.2 Procedure

Fill the vessel with clean water. Turn on the heater element and wait for the temperature to reach  $90^\circ\text{C}$ . Manually open the purge valve and keep it open while the temperature increases so that air within the vessel above the liquid water can be expelled. Close the relief valve. Let the heater boil the water and record the data until the pressure reaches  $1.25 \times 10^6$  Pa or the temperature reaches  $180^\circ\text{C}$ . Switch off the heater, save the data, and let the vessel cool.

### 2.3 Assumptions

The fluid under investigation is clean water. The Antoine equation requires the assumptions: the specific volume of liquid is significantly less than that of vapour; vapour follows ideal gas law, which implies that pressures are generally low; and enthalpy change between liquid and vapour is independent of temperature.

## 3 Results

The experimental data is shown in standard linear-linear (pressure vs temperature) form in Figure 2, and in log-linear ( $\log_{10}\text{Pressure}$  vs  $1000/\text{Temperature}$ ) form in Figure 3. Figure 4 shows the four function regressions against the experimental data. As the fits are generally very good it can be difficult to visualise the fit curve compared to the experimental data, and so underneath each plot the residuals are shown to give an easy comparison between each function fit.

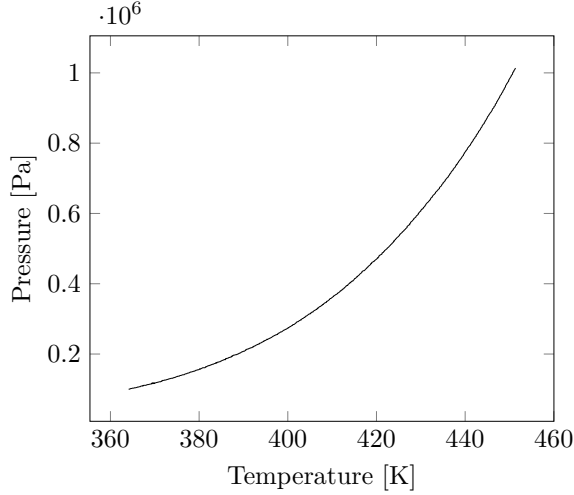


Figure 2: Plot of the experimental data obtained from the Marcet boiler apparatus on linear-linear axes.

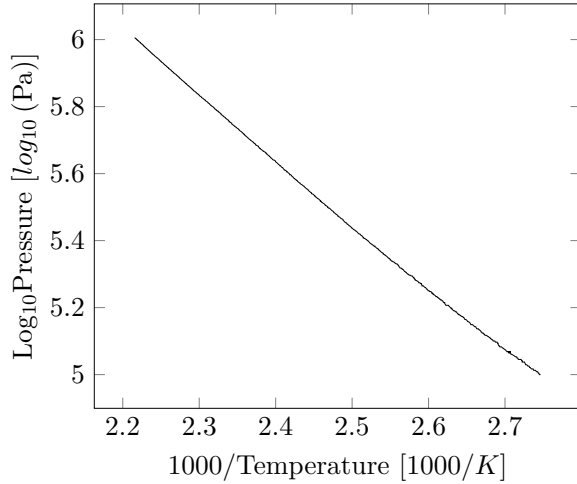


Figure 3: Plot of the experimental data obtained from the Marcet boiler apparatus on log-linear axes.

## 4 Analysis

The linear and simple Antoine regressions are in effect the same function. Referring to Figure 4, the residuals show that the simple Antoine function has the greatest deviation of all the functions, and this occurs at low temperatures. The Antoine function has the lowest deviation, with the greatest portion occurring at low temperatures. The Wagner fit has good agreement with the experimental data along most of the temperature range with the largest deviation occurring at the high temperatures.

The data shows that as temperature is increased, the pressure increases also, following

an exponential curve. This agrees with the theoretical expectation from Equation ??

Table 1: List of coefficients derived from regression analysis on four different functions to fit the experimental data. The coefficients listed are used to plot the comparisons shown in Figure 4.

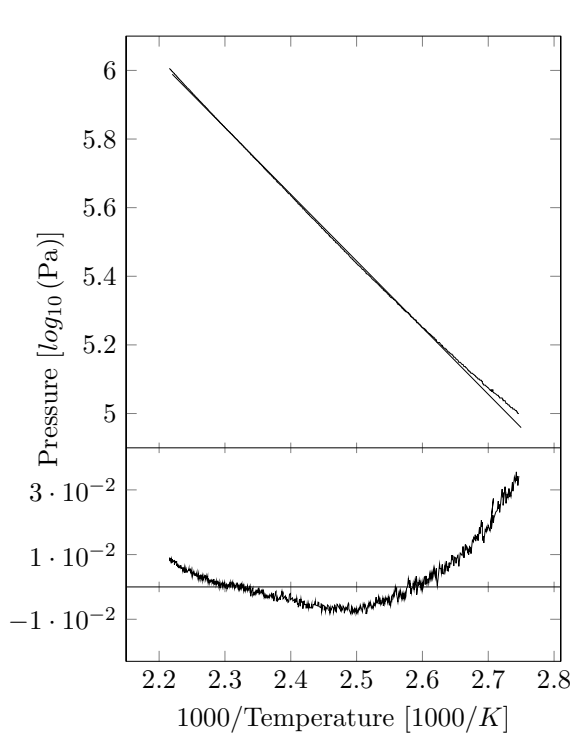
Model	Coefficients			
	A	B	C	D
Linear	$m = -1.943, c = 10.303$			
Simple Antoine	10.40	1986.83		
Antoine	12.52	4196.60	192.47	
Wagner	-10.99	10.26	-21.68	87.93

Table 2: List of coefficients for the Antoine equation, as used in Figure 6. Set 1 are the coefficients derived for the regression analysis on the experimental data set. Sets 2 and 3 are obtained from reference sets as listed in *Refs.*

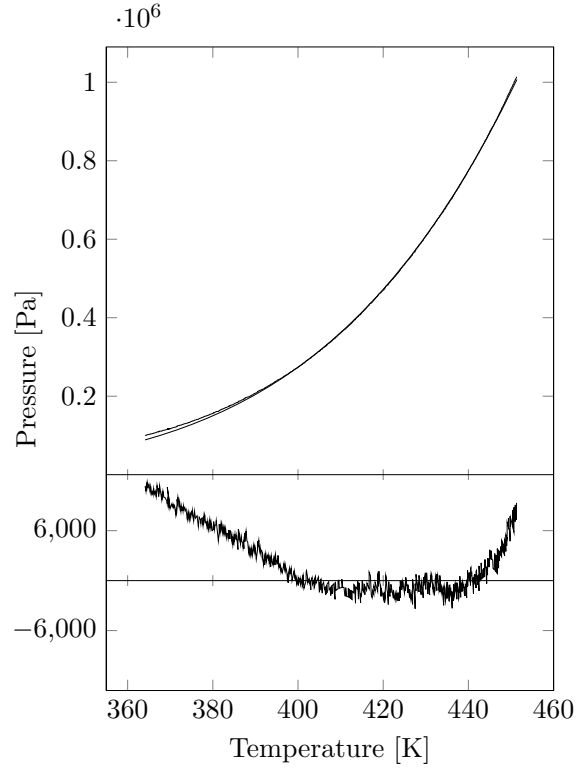
Set	Coefficients			Refs.
	A	B	C	
1	12.52	4196.60	192.47	Experimental Fit
2	8.56	643.75	-198.04	[8]
3	10.27	1810.94	-28.67	[9]

The function coefficients as found by regression analysis are shown listed in Table 1. Note that although the linear and simple Antoine functions are mathematically equivalent, the converted coefficients are not exactly equal. For example see that from the linear function the equivalent coefficients for the simple Antoine function are  $A = 10.30$  and  $B = 1943.24$ , which are very close (within 2%) to those listed for the simple Antoine function ( $A = 10.40$  and  $B = 1986.83$ ). This is due to the regression analysis algorithm behaving slightly differently between the two different expressions of the functions, perhaps as a result of floating point accuracy.

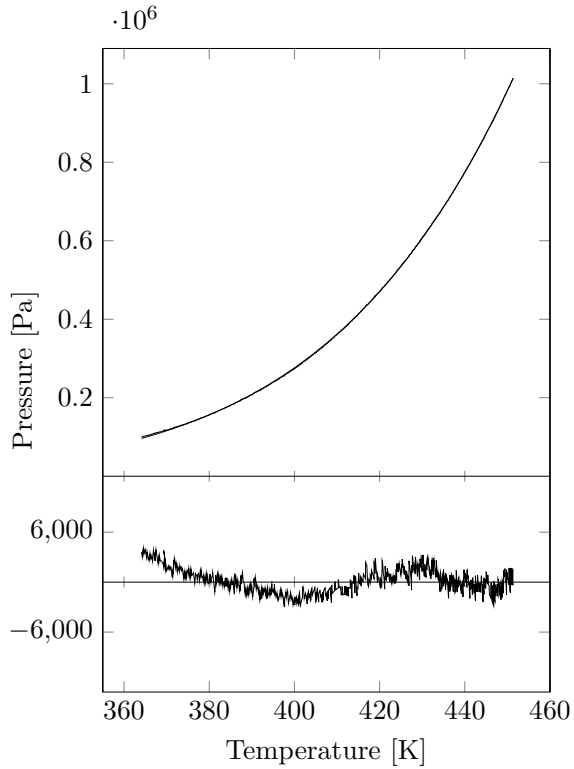
A list of coefficients for the Antoine Equation are shown listed in Table 2. Set 1 are the coefficients derived from the regression analysis on the experimental data set. Sets 2 and 3 are obtained from reference sets. The references listed have several sets of coefficients listed for different ranges of temperature. Those listed in Table 2 and compared in Figure 6 match, or include the range of temperatures used within the experimental data.



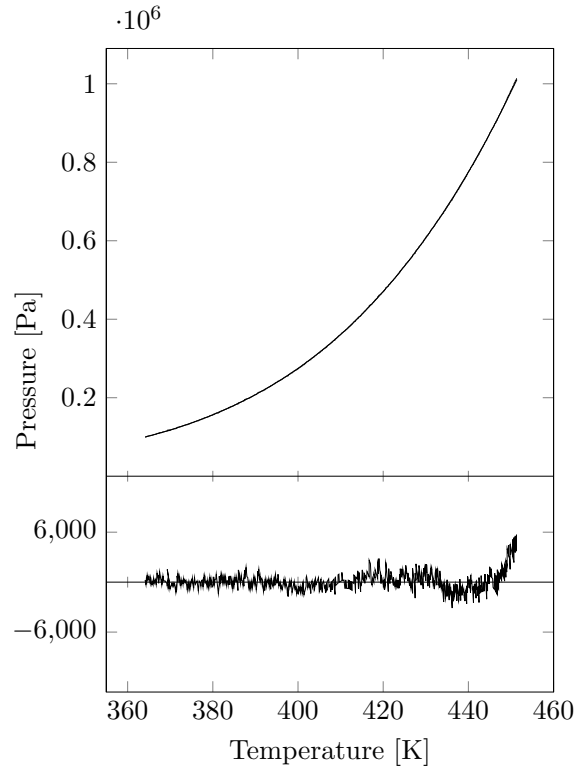
(a) Linear



(b) Simple Antoine



(c) Antoine

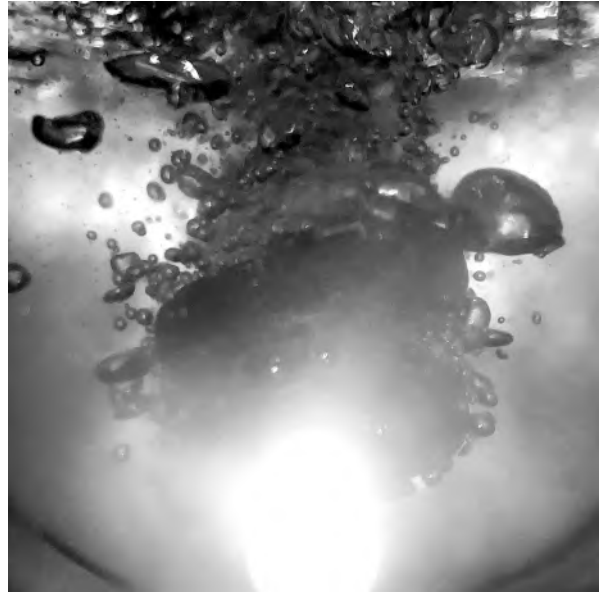


(d) Wagner

Figure 4: Plots of the regression functions compared to the experimental data. Figure 4a is plotted on log-linear axes to show a linear trend. Figures 4b, 4c, and 4d are plotted on linear-linear (pressure vs temperature) axes. Below each plot is a subplot showing the residuals between the function and experimental data. The non-linear functions and residuals are all plotted on the same scales to allow for direct comparison.



(a)



(b)



(c)



(d)

Figure 5: Series of images taken as the experiment progressed showing a view through the sight glass on the front of the apparatus. The images show the water vapour gas bubbles as they are formed on the heating element and subsequently rise towards the top of the liquid water. Note how the bubbles change size as the pressure within the vessel increases from (a) through to (d). The large white area towards the bottom centre of each image is a flash reflection from the camera, and coincides with the location of the heater element.

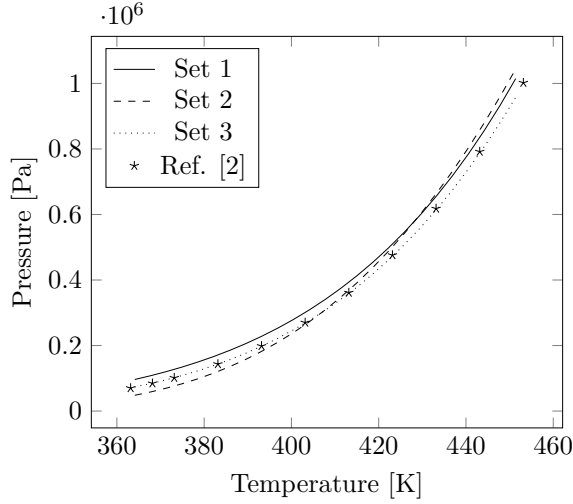


Figure 6: Plot of Antoine functions with coefficients as listed in Table 2. Set 1 are the coefficients as derived from the regression analysis on the experimental data, and Sets 2 and 3 use reference data as listed in Table 2. The points labelled Ref. [2] are pressure/temperature values listed in the cited resource.

Figure 6 shows a comparison between several sets of Antoine equations using reference coefficients compared to the coefficients generated from the regression fit to the experimental data. Several stand-alone points of pressure-Temperature from a reference are also plotted for comparison.

Figure 5 shows a comparison between four different time points as the experiment progressed showing the bubble size as the pressure and temperature increase. The average bubble size can be seen to decrease, as would be expected if the pressure were increasing.

It was observed that as the pressure of the boiler increased the vapour gas bubbles reduced in size, increased in velocity and decreased in quantity. This is consistent with the theory, as the pressure increases less water will boil into vapour reducing the size of the bubbles [10]. With the pressure increase, the boiling temperature also increases. Consequently, the bubbles that form from liquid that boils are at a higher temperature, with more energy. This explains the increase in the velocity at which the bubbles rise in the boiler.

The assumptions made are validated by the consistency of the experimental and reference data. As the temperature increases, the relative temperature to the critical temperature

will increase. As the pressure increases relative to the critical pressure, the vapour is no longer considered an ideal gas and the Antoine equation would become inaccurate. Testing at higher pressures would create larger discrepancies for Antoinnes equation than Wagners.

## 5 Conclusion

The data was consistent with the reference data for all four equations used. The Antoine and Wagner equations particularly showed few inconsistencies with the reference data. The simplified Antoine and linear equations reflected minor comparisons at lower temperatures between the experimental and reference data. This difference could be attributed to sensors used in the apparatus being more accurate for higher pressures and temperatures. This could be improved by having multiple sensors for both higher and lower specifications.

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