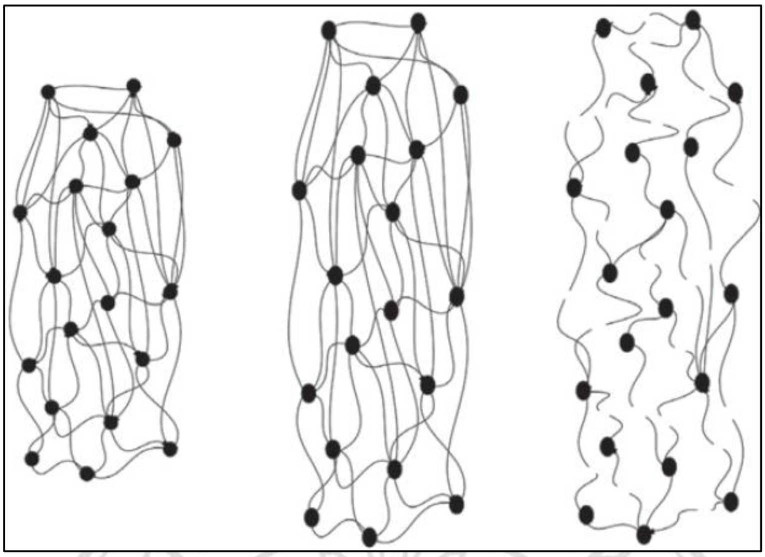
CHAPTER 4

Thermodynamics of Rubber Band

In this chapter, thermodynamics of rubber band demonstration was described in more detail. The objectives of this study to be 1) Determine an equation of state for system of rubber band 2) Investigate a change of entropy of a rubber band 3) Determine thermodynamic potential of rubber band such as such as Helmholtz free energy (ΔF), the internal energy (ΔU) and the change of entropy (ΔS) for different lengths of rubber band at different temperatures were determined using the Maxwell relations. In section 4.1, it reviews some theoretical aspects. A section 4.2 describes experimental design and equipment. Then, a section 4.3 reports the experimental results and discussion. Finally, section 4.4-4.5 includes conclusions and an implementation to teaching. Full details are described in the following sections.

4.1 Theoretical aspects

From previous research studies, there are many systems that characterize the thermodynamics behavior and display equation of state [79]. One interesting system is a rubber band. It is also interesting to study rubber band's elongation and contraction processes which result in changing of its internal structure. The rubber band is formed by long polymer chain which constructed from the monomer. The joining of structural monomer can form linear chains, branches and interconnected chains which indicate the degree of polymerization, as shown in the Figure 4.1(a). When the force is exerted on the rubber band, the deformation is created, as shown in the Figure 4.1(b). The breaking point of the rubber band is reached only when enough force is applied to break the chains that construct the rubber band. The breaking up of the polymer chains depend mostly on the load time regardless of their original length. Figure 4.1(c) shows the breaking up of the polymer chains.



(a) (b) (c)

Figure 4.1 The structural model of polymer chains deformation [80]

The theoretical equation of state for rubber band with variations to the rubber band's length given by

$$F = \frac{abT\left(L - L_0\right)}{L_0} \tag{8}$$

where F is tension of rubber band (N), a is a cross-section area of the rubber band (m^2), b is a constant of elasticity of material ($N/m^2.K$), T is rubber band temperature (K), L_0 is its original length (m) and L is a length at constant temperature (m). This equation can be recover by obtaining an approximation, valid when $L - L_0$ is small. However, it can not be concluded from thermodynamics because it is no hypothesis on the rubber band structure can be made in any precise thermodynamics study. While, it can also studied using the statistical mechanics by Gaussian models. It is based on a basic ideas and reach to the identical results [81]. For a small and moderate stretching, the equation of state for a rubber band is given by [82]

$$F = AT\left[\frac{L}{L_0} - \frac{L_0^2}{L^2}\right] \tag{9}$$

where A is a constant of rubber band to be determined (N/K), L_0 is a length of the rubber band at no hanging weight (m), F is force on the rubber band causing it to stretch to length (N), L is a length of the rubber band (m) when a force F is applied and T is an absolute temperature of the rubber band (K). From previous studies, the constant A was able to be determined in multiple ways. Savarino and Fish suggested four different analysis of constant A , as shown in the Table 4.1 [82].

Table 4.1 The procedure of A constant analysis

No.	Procedure of analysis	Limitation
1	This technique is to perform a least square fit of the experiment data to an equation 2 $F = AT\left[\frac{L}{L_0} - \frac{L_0^2}{L^2}\right].$	The second term on the right hand side of equation is proportional to $1/L^2$ thus the normal fit programs cannot be used for this purpose. The least-squares-fitting program were written to fit the data directly to equation.
2	This technique consists of calculating the work done on the rubber band in stretching it from the length L_1 to L_2 by equation 3 $W = \int_{L_1}^{L_2} \bar{F}.d\bar{L} = AT\left[\frac{L_2^2 - L_1^2}{2L_0} + L_0^2\left(\frac{1}{L_2} - \frac{1}{L_1}\right)\right]$ The work can calculate by determining the area under the F versus L curve.	The L_0 value is critical to this calculation. A better estimate of L_0 can be obtained by using linear extrapolation back to $F = 0$ for which the first term on the right hand side of equation 2 $F = AT\left[\frac{L}{L_0} - \frac{L_0^2}{L^2}\right].$
3	This technique consists of calculating the $\left.\frac{\Delta F}{\Delta L}\right\|_T = \frac{F_i - F_j}{L_i - L_j} \approx \left.\frac{\partial F}{\partial L}\right\|_T$ where i and j refer to two neighboring data points then compared to the value calculated for the equation of state $\left.\frac{\partial F}{\partial L}\right\|_T = \frac{AT}{L_0} + \frac{2ATL_0^2}{L^3}$.	A good approximation the measurement is performed isothermal process so the uncertainty of this technique is quite large.

Table 4.1 (continued)

No.	Procedure of analysis	Limitation
4	This technique is followed the equation $\left(\frac{L}{L_0}\right)^2 F = AT\left[\left(\frac{L}{L_0}\right)^3 - 1\right]$. The data were used to draw a graph and the slope was to determine *A* constant.	It does not directly yield a value for L_0 , so L_0 must be determined directly.

The second procedure in Table 4.1 was used to analyze for the value of *A* constant in this study because it is convenient to set up for teaching with an active-learning approach. In this procedure, the limitation can be control by using the linear extrapolation to find the L_0 value. The work done on the rubber band in stretching it from the length L_1 to L_2 can be determined from the area under the F versus L curve, and then compared it to the right hand side of the equation (10), one can obtain the A constant [82].

$$W = \int_{L_1}^{L_2} \overline{F}.d\overline{L} = AT\left[\frac{L_2^2 - L_1^2}{2L_0} + L_0^2\left(\frac{1}{L_2} - \frac{1}{L_1}\right)\right] \tag{10}$$

For the first law of thermodynamics, Roundy and Rogers proposed the change of internal energy of rubber band to be

$$dU = TdS + \tau dL \tag{11}$$

where T is its temperature in K, τ is its tension in N, U is its internal energy in J, S is its entropy in J/K, and L is the length in m [83]. This relation is taken from the first law of thermodynamics, combined with the definition of work as the dot product between force and displacement. Since the system is at constant T , the Helmholtz free energy F is given by

$$dF = \tau dL - SdT \tag{12}$$

The corresponding Maxwell relation

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial \tau}{\partial T}\right)_L \tag{13}$$

This can be used to determine how entropy change with length at fixed temperature by measuring how the tension changes with temperature at a fixed length. Concurrently, a measurement of the tension tells how the free energy change isothermally with length to be given by

$$\tau = \left(\frac{\partial F}{\partial L}\right)_T \tag{14}$$

Therefore, the measurements of τ and $\left(\frac{\partial \tau}{\partial T}\right)_L$, as a function of length, can be used to find (ΔF), (ΔS) and (ΔU) by the equation (11).

4.2 Experimental design

In this experiment, the objective is to invent and develop the active learning approach to teaching thermodynamics by using rubber band. In addition, it was shown the equation of state and the work done on the rubber band. It also obtain the change of entropy and thermodynamic potential of rubber band. There are two parts of experiments. The detail of experimental design for each part are described in the following subsection.

4.2.1 Determination of a constant value of rubber band

The experimental setup for determining the A constant is shown in the Figure 4.2. The rubber band was hung from the top of a stand and a hook was fixed at the bottom end to allow additional mass to be suspended from the rubber band. Before additional mass was suspended to the hook, the distance between the hook to the base of stand was measured then recorded as H_0. Mass was added to the rubber band in an increment of 50g. The maximum load is 700g and any larger resulted in a permanent deformation and caused it to snap. The masses were attached and the distance between the mass to the base of the stand was measured then recorded as H for every load of mass. The distance H was also measured when the mass was unloaded. Thus, the elongation and the contraction of the rubber band were able to be calculated.

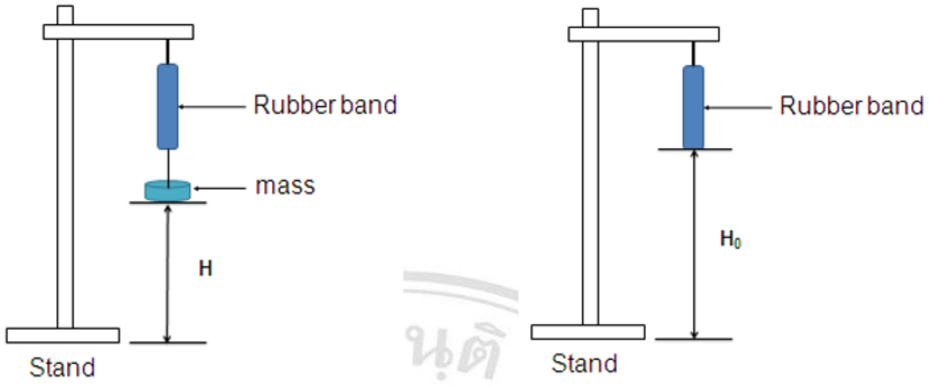


Figure 4.2 Experimental setup to determine the A constant of rubber band

The room temperature was also measured to be 28.0^{O}C (301.15K). The force exerted on the rubber band was calculated as $F = mg$, where g is the magnitude of the acceleration of gravity (≈ 9.784 m/s^2). The rubber bands were used for two difference cross-section areas and two different lengths. The experiment was repeated 3 times for each size of rubber band. The average of data was used to plot the curve between the forces versus length of the rubber band. Two graphs for loaded and unloaded for each rubber band were obtained. The area between two curves represents the work done on the rubber band. These values of work were used to calculate the constant A by using equation (10). The A constant of the rubber band at constant temperature was measured by the length of rubber band as a function of applied force. It is taking approximately 1 hour for collecting the data. The experiment is simple and convenient to perform by two students.

4.2.2 Thermodynamic potential change

The experiment setup for this part is shown in the Figure 4.3. A rubber band was stretch from a hook on the stopper of an acrylic tube to a chain connected to a force sensor at the top of the tube. This setup allows the rubber band to be completely submerged when the tube is filled with water at different temperature. During the experiment, the water temperature was adjusted by mixing boiling water, room temperature water and ice. Once the water is added to the tube, the temperature is monitored with a thermocouple inserted into the tube. It can be prepare several temperature of water by mixing the hot water and cold water. Six temperatures (5^{O}C, 15^{O}C, 25^{O}C, 35 ^{O}C, 45^{O}C and 55^{O}C) of water were used for each length of rubber band. There were five lengths (0.25m, 0.30 m, 0.35 m, 0.40 m, and 0.45 m) with a cross section area is 2.45×10^{-5} m^2. Several force measurements can be made for different lengths before the temperature dropped (or risen) by as much as 1^{O}C [83].

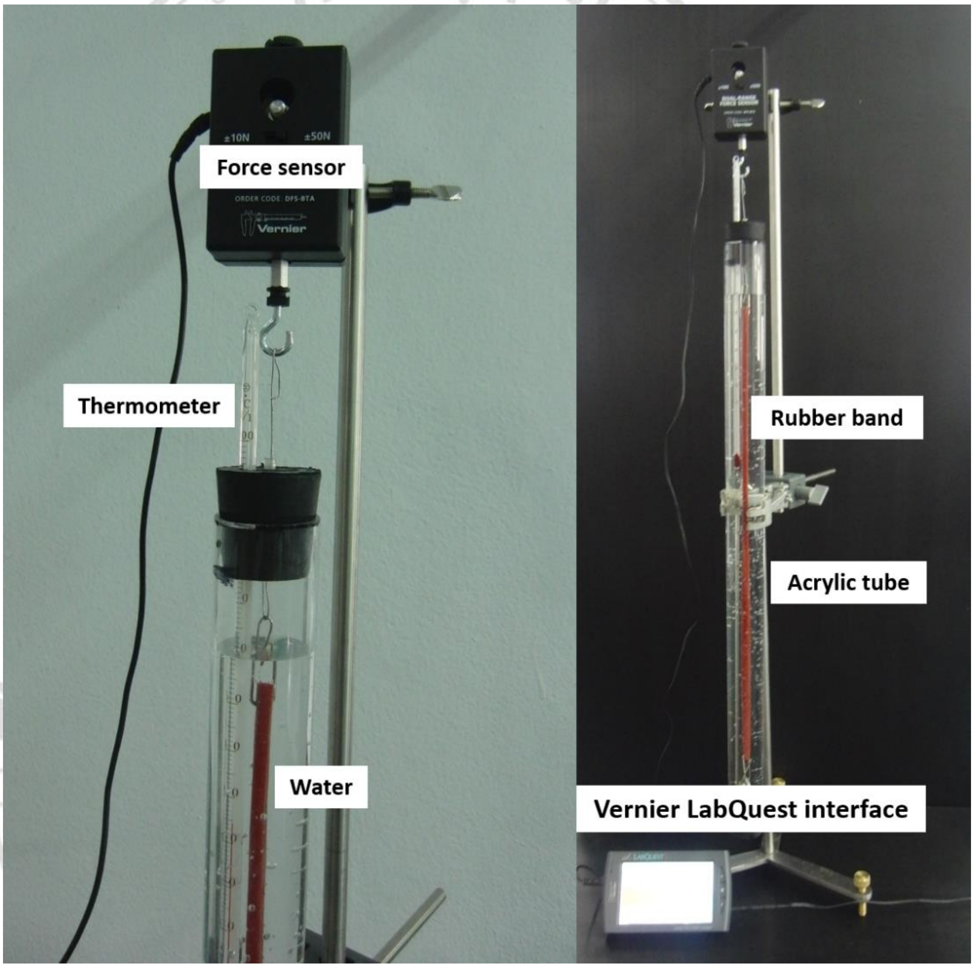


Figure 4.3 Photo of experimental setup for investigating thermodynamics potential change

The data from force sensor and temperature sensor for each length were used to calculate Helmholtz free energy (ΔF) ,the change of entropy (ΔS), and the change of internal energy (ΔU). The tension and length for each temperature of the rubber band were plotted on the graph. The trend of curve was fitted to a 3rd degree of polynomial equation. Then the equation (14) was integrated from the minimum length (0.25m) to the maximum length (0.45m), so the Helmholtz free energy (ΔF) was calculated. Using the same data, the tension and temperature for each length of the rubber band were plotted on the graph. The graph was used to fit for a straight line equation with the slope equal to $\left(\frac{\partial \tau}{\partial T}\right)_L$. The Maxwell relation was used to verify the slope to be $-\left(\frac{\partial S}{\partial L}\right)_T$ .The slope of each length was used to draw the graph between $\left(\frac{\partial S}{\partial L}\right)_T$ and length. A second degree polynomial equation was obtained from the best fit of the curve by using spread sheet program. The polynomial equation was integrated from the minimum length (0.25) to the maximum length (0.45m), so the change of entropy (ΔS) can be calculated by equation (13). Finally, the equation (11) was used to calculate the internal energy of the rubber band. The thermodynamic potential change were investigated by measuring the tension of rubber band as a function of length and temperature and use the Maxwell relation to calculate the entropy and internal energy for each isothermal stretch. This part takes about 2 hours for collecting and analyzing data.

4.3 Experimental results and discussion

The results of this experiment were divided for two parts. In the first part, after the force was applied, the rubber band was stretched. The data was collected and the average value was used to plot the graph between the force and extension. The results for each rubber band were shown in the Table 4.2, Table 4.3, and Table 4.4. For each graph, it plotted the load and unload curve in the same graph. The graph was hysteresis loop and used to calculate the area between the curves by using the spread sheet program. The graphs for each rubber band were shown in the Figure 4.4, Figure 4.5, and Figure 4.6.

Table 4.2 The elongation of rubber band No.1

No.	Mass: m(kg) $\times 10^{-3}$	Weight: F = mg (N)	Load (m)	Unload (m)
1	0	0.00	0.00	0.00
2	50	0.49	7.00×10^{-3}	8.00×10^{-3}
3	100	0.98	9.30×10^{-3}	1.00×10^{-2}
4	150	1.47	1.47×10^{-2}	1.50×10^{-2}
5	200	1.96	1.83×10^{-2}	2.07×10^{-2}
6	250	2.45	2.47×10^{-2}	2.77×10^{-2}
7	300	2.94	2.80×10^{-2}	3.20×10^{-2}
8	350	3.43	3.60×10^{-2}	4.10×10^{-2}
9	400	3.92	4.00×10^{-2}	4.73×10^{-2}
10	450	4.41	5.00×10^{-2}	5.67×10^{-2}
11	500	4.90	5.57×10^{-2}	6.30×10^{-2}
12	550	5.39	6.80×10^{-2}	7.27×10^{-2}
13	600	5.88	7.33×10^{-2}	7.90×10^{-2}
14	650	6.37	8.77×10^{-2}	8.87×10^{-2}
15	700	6.86	9.63×10^{-2}	9.93×10^{-2}

As shown in the Table 4.2, the graph for this data was shown in the Figure 4.4. The area between the curve was calculated and represented for the work done on the rubber band. The cross section area of rubber No.1 is 1.66×10^{-5} m^2 and the length is 15.0 cm. The work from the area between curves is 0.005J.

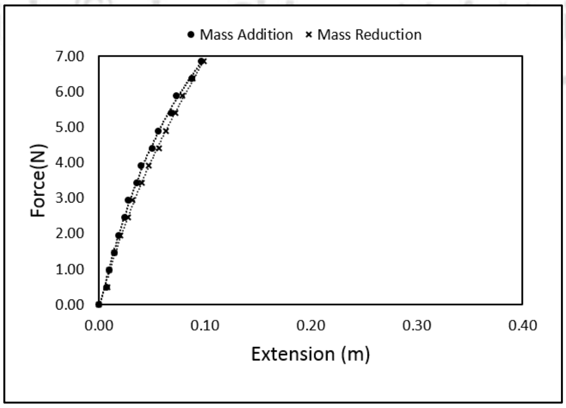


Figure 4.4 The relation between force and extension of the rubber band No.1

Table 4.3 The elongation of rubber band No.2

No.	Mass: m(kg) $\times 10^{-3}$	Weight: F = mg (N)	Load (m)	Unload (m)
1	0	0.00	0.00	0.00
2	50	0.49	1.07×10^{-2}	1.37×10^{-2}
3	100	0.98	1.73×10^{-2}	2.50×10^{-2}
4	150	1.47	3.13×10^{-2}	4.23×10^{-2}
5	200	1.96	4.00×10^{-2}	5.30×10^{-2}
6	250	2.45	5.53×10^{-2}	7.27×10^{-2}
7	300	2.94	6.73×10^{-2}	8.77×10^{-2}
8	350	3.43	8.80×10^{-2}	1.09×10^{-1}
9	400	3.92	1.03×10^{-1}	1.26×10^{-1}
10	450	4.41	1.29×10^{-1}	1.53×10^{-1}
11	500	4.90	1.47×10^{-1}	1.72×10^{-1}
12	550	5.39	1.79×10^{-1}	1.99×10^{-1}
13	600	5.88	2.02×10^{-1}	2.13×10^{-1}
14	650	6.37	2.38×10^{-1}	2.43×10^{-1}
15	700	6.86	2.54×10^{-1}	2.567×10^{-1}

As shown in the Table 4.3, the graph for this data was shown in the Figure 4.5. The area between the curve was calculated and represented for the work done on the rubber band. The cross section area of rubber No.2 is 1.66×10^{-5} m^2 and the length is 35.0 cm. The work from the area between curves is 0.114J.

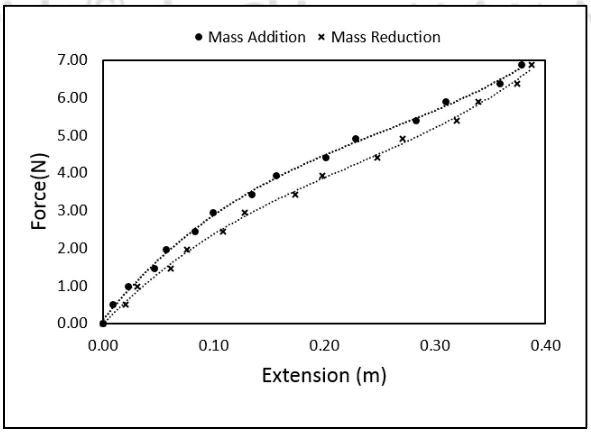


Figure 4.5 The relation between force and extension of the rubber band No.2

Table 4.4 The elongation of rubber band No.3

No.	Mass: m(kg) $\times 10^{-3}$	Weight: F = mg (N)	Load (m)	Unload (m)
1	0	0.00	0.00	0.00
2	50	0.49	9.30×10^{-3}	2.07×10^{-2}
3	100	0.98	2.33×10^{-2}	3.13×10^{-2}
4	150	1.47	4.63×10^{-2}	6.10×10^{-2}
5	200	1.96	5.70×10^{-2}	7.60×10^{-2}
6	250	2.45	8.37×10^{-2}	1.08×10^{-1}
7	300	2.94	9.97×10^{-2}	1.28×10^{-1}
8	350	3.43	1.35×10^{-1}	1.74×10^{-1}
9	400	3.92	1.57×10^{-1}	1.98×10^{-1}
10	450	4.41	2.02×10^{-1}	2.48×10^{-1}
11	500	4.90	2.29×10^{-1}	2.71×10^{-1}
12	550	5.39	2.83×10^{-1}	3.19×10^{-1}
13	600	5.88	3.09×10^{-1}	3.39×10^{-1}
14	650	6.37	3.59×10^{-1}	3.76×10^{-1}
15	700	6.86	3.78×10^{-1}	3.87×10^{-1}

As shown in the Table 4.4, the graph for this data was shown in the Figure 4.6. The area between the curve was calculated and represented for the work done on the rubber band. The cross section area of rubber No.3 is 1.09×10^{-5} m^2 and the length is 35.0 cm. The work from the area between curves is 0.078J.

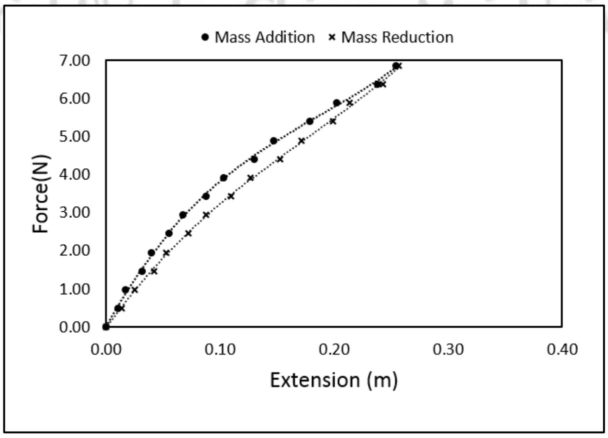


Figure 4.6 The relation between force and extension of the rubber band No.3

The hysteresis loop suggests that the polymer chain is broke up during a cycle of elongation and contraction. This energy is converted into heat as a result of internal friction, breaking bonds and forming the new polymer chains [84]. It was found that the work done on the rubber band with a larger cross section area is more than that with a smaller one if the length are the same. Moreover, the work done on the longer rubber band is more than that of a shorter one if the cross section area are the same. The work done on the rubber band is proportional with the size of the rubber band because larger one has more molecules of polymer chain and required more energy to rearrange the molecules when it was stretched. From the second procedure in the Table 4.1, data of force and extension length were obtained and used to calculate the A constant by using equation (10). The results of A constant and margins of error were shown in the Table 4.5.

Table 4.5 The A constant of rubber band

Cross section Area (m^2)	Length (m)	$A \pm \sigma_A$	
		Mass Addition ($\times 10^{-2}$ kg)	Mass reduction($\times 10^{-2}$ kg)
1.09×10^{-5}	0.15	2.80 ± 0.24	2.21 ± 0.12
	0.25	1.39 ± 0.19	1.23 ± 0.14
	0.35	1.27 ± 0.15	1.09 ± 0.08
1.66×10^{-5}	0.15	1.74 ± 0.18	1.55 ± 0.13
	0.25	1.18 ± 0.94	0.86 ± 1.00
	0.35	0.32 ± 0.03	0.18 ± 0.07

There found that, with the same length, the A constant of a rubber band with a larger cross section area is less than that of a smaller one. With the same cross section area, the A constant of a longer rubber band is less than that of a shorter one.

In the second part, a graph between tensions versus length with several temperatures were plotted, as shown in the Figure 4.7.

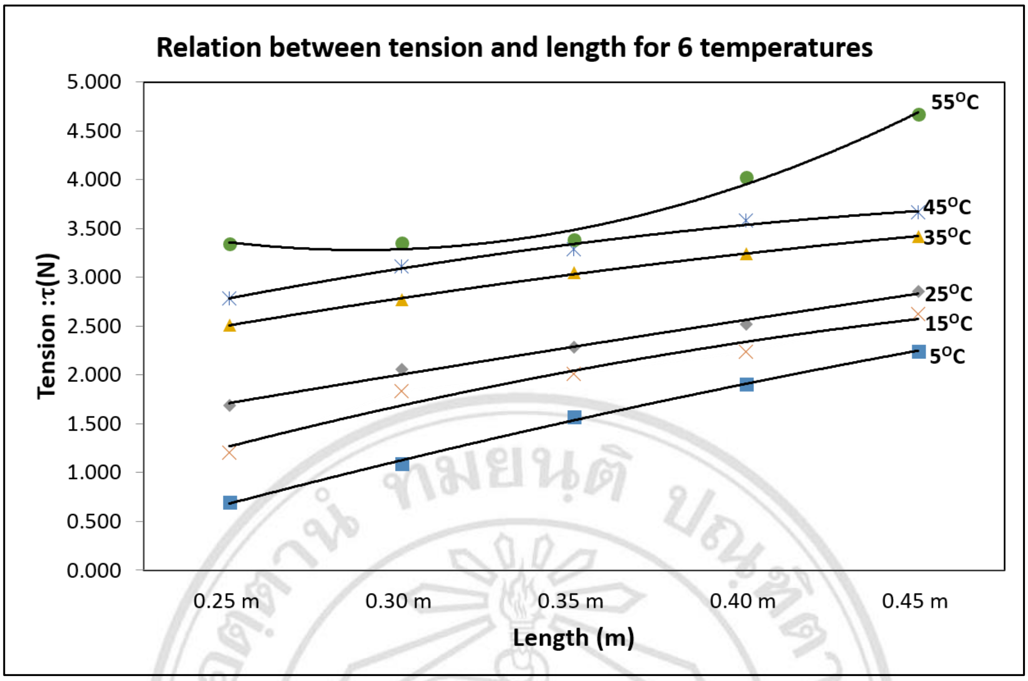


Figure 4.7 Relation between tension (τ) and length (L) for six different temperatures.

The graph between tension (τ) and temperatures (T) at several lengths were also plotted as shown in the Figure 4.8.

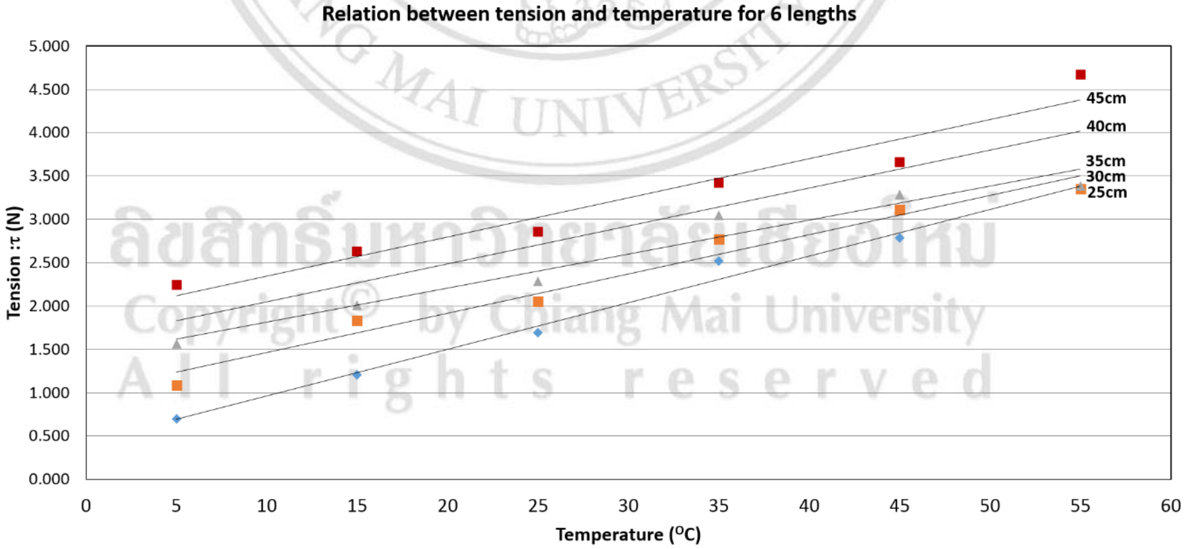


Figure 4.8 Relation between tension (τ) and temperature (T) for five different lengths.

From the Figure 4.8, the linear equation between tension (τ) and temperature (T) of the rubber bands was came up. Then, there were calculated slope of the equation that was equal to $\left(\partial S/\partial L\right)_T$ by the Maxwell relations. The slope of the graph was matched to find the relation between $\left(\partial S/\partial L\right)_T$ and the length of rubber band as shown in the Figure 4.9. A second order polynomial equation was obtained from the graph. The equation is $y = 0.851x^2 - 0.636x + 0.1583$ with R-square value equal to 0.9297.

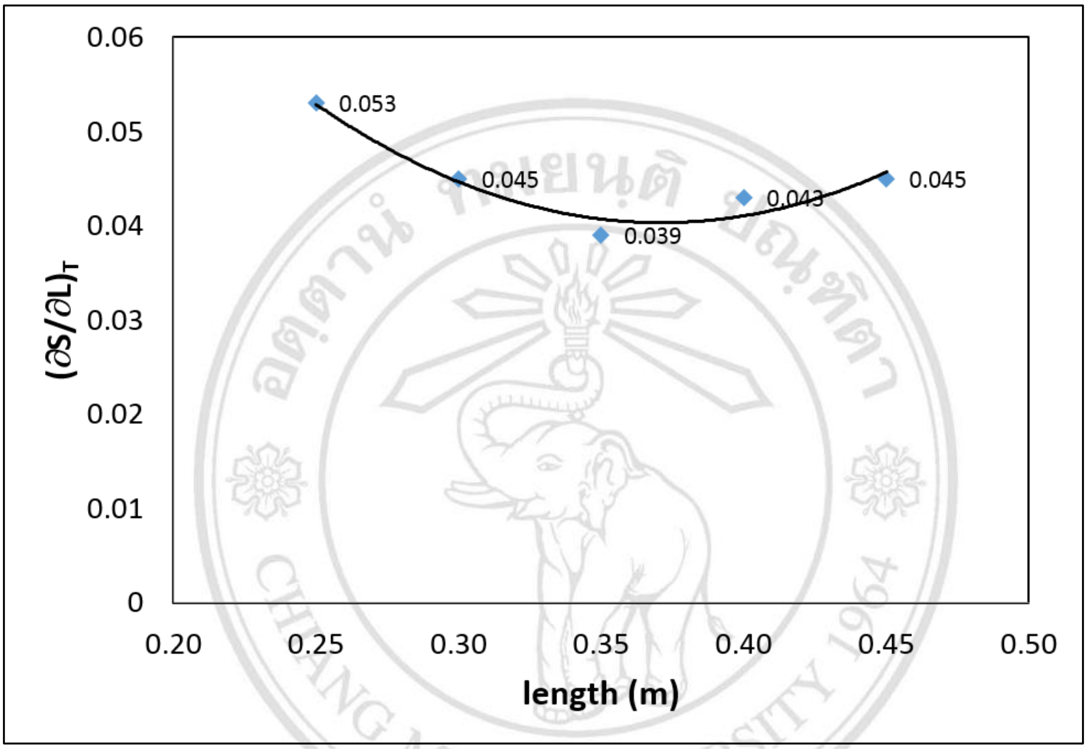


Figure 4.9 Relation between tension $\left(\partial S / \partial L\right)_T$ and length (L) of rubber band.

From Figure 4.7, the Helmholtz free energy (ΔF) for rubber bands at each temperature was calculated by integration the equation (14). From Figure 4.8, the change of entropy (ΔS) was calculated by integration the Maxwell relation with the equation (13). It was found that $T\Delta S$ equal to -0.009J. The Helmholtz free energy (ΔF) and $T\Delta S$ were then used to calculate the change of internal energy (ΔU) by equation (11) and the results are shown in the Table 4.6.

Table 4.6 Result for thermodynamics potential change

Temperature (^{O}C)	Potential change		
	$T\Delta S$ (J)	ΔF (J)	ΔU (J)
5.0	-0.009	0.075	0.066
15.0	-0.009	0.192	0.183
25.0	-0.009	0.302	0.293
35.0	-0.009	0.460	0.451
45.0	-0.009	0.509	0.500
55.0	-0.009	0.706	0.697

The change of internal energy (ΔU) was proportional to the temperature change of the rubber band. The relation is shown in the Figure 4.10.

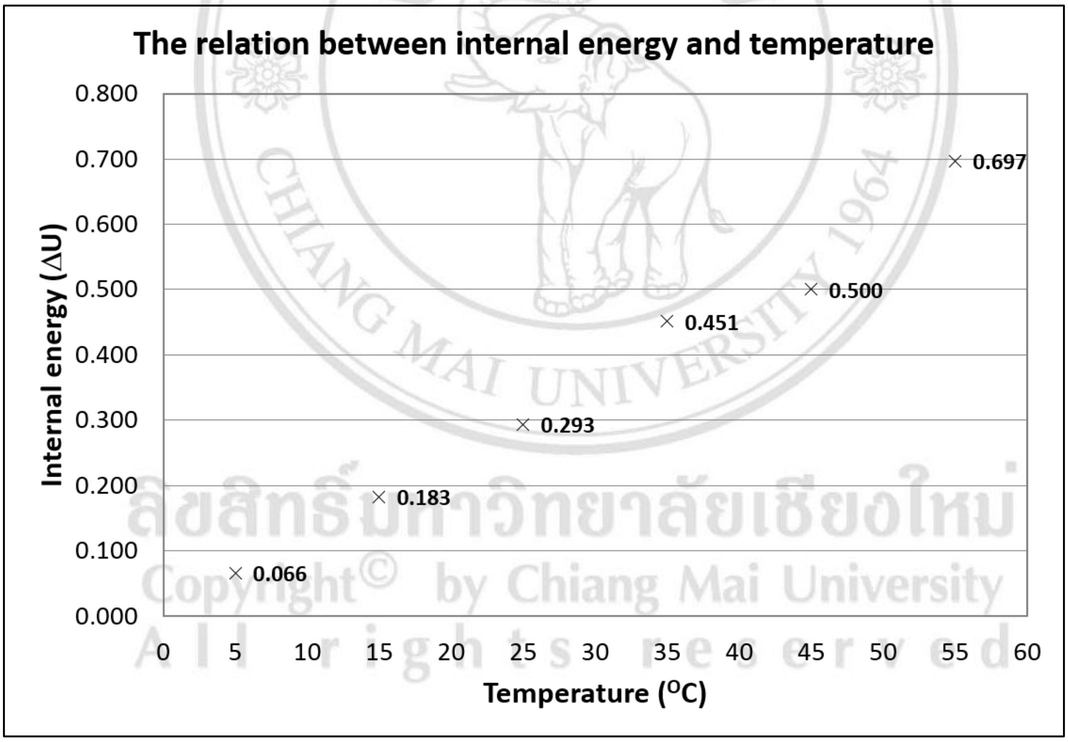


Figure 4.10 Relation between the change of internal energy (ΔU) and the change of temperature (ΔT)

4.4 Conclusion

In the first experiment, it presents the simple and usefulness of rubber band as an equipment to use for determines the equation of state for a common material. This method obtained the parameters which verify the rubber band equation of state. As discussed in a previous section, the rubber band is a good approximation to follow the theoretical equation of state in the equation (9).

For the second experiment, it presents the utility of rubber band as a system for thermodynamics study. It can determine the change of entropy by using the measurable parameter. It also used Maxwell relation to verify the relation between the entropy changes with length at fixed temperature to the tension change with temperature at fixed length. For this reason, it was precious material to determine thermodynamics potentials.

4.5 Implementation for teaching

This experiment was suitable for thermodynamics demonstration. It can presented the parameter in a real measurement which make students feel like visual experiment. It can be used to explain parameters in thermodynamics and appropriated to use Maxwell relations. This is a simple yet powerful experiment in demonstrating a concept of an equation of state, change in entropy and thermodynamic potential. Whereas, it complicated to setup and calculate the thermodynamics potentials, so it suitable for teaching in advance laboratory and small group of student. Before demonstrating with rubber band, the students have to use the spread sheet program for creating the graph and fitting the equation of graph because it allows an analysis many thermodynamics parameters. The students were obtained the techniques of data analysis and explore the thermodynamics of the simple object as rubber bands. Finally, it is an inexpensive material that can easy to find and set up for the experiment.