Entropy of Mixing Analysis for Ethanol and Water

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Ryan White
44990392

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Abstract

In an effort to investigate the first two laws of thermodynamics, three different mass fractions of ethanol and water were mixed together. With the initial and final temperature and volume values measured, the heat and work transfer, change in entropy, and change in gibbs free energy of the system was calculated, and compared with that which is expected should the first and second laws of thermodynamics hold. As expected, the volume of the mixtures were significantly less than that of the sum of their constituent volumes, with an observed heat transfer from the mixture to the environment. A broader range of mass fractions was suggested for future investigations, with a conclusion that it would provide a more accurate depiction of the nature of chemical mixing and particle interactions.

1   Introduction

One of the most prevalent chemical interactions in everyday life is the mixing of liquid compounds. Understandably, the physics and chemistry of these interactions are studied very closely, as said understanding underlies a multitude of essential aspects of our civilisation. One such chemical interaction is the mixing of liquid ethanol (C_2H_5OH) and water (H_2O). Flinn Scientific explains that the final volume of a mixture of alcohol and water is "*about 10% less*" than the volumes of its constituent parts as a result of hydrogen bonding. This analysis aimed to determine any entropic changes of the system as different volumes of water and ethanol were mixed with each other, and to observe the changes in the properties of the system as a result of the interaction between the liquids due to hydrogen bonding. After subsequent analysis, applications of the experiment were discussed with reference to underlying physical concepts.

2   Theory

The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. This is equivalent to stating that a system will spontaneously try to minimise its Gibbs free energy G, with the change in G being related to the change in enthalpy, the temperature, and the change in entropy from some process. This is formulated as

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

The mixing of two substances supports the second law, as the total microstates of a system of two species of particles is far greater than that of a system of the same number of homogeneous particles. Assuming that the intermolecular interactions between the particles are negligible, entropy must increase proportionally to the number of microstates that the system is characterised by. This increase in entropy is described by

$$\Delta S_{mixing} = -Rn_a \ln(n_a/n) - Rn_b \ln(n_b/n) \tag{2}$$

where the variable n denotes the total number of moles in the mixture, and n_a and n_b denotes the amount of moles of species a and b respectively so that $n = n_a + n_b$ (Source: PHYS2020 Laboratory Notes). In many cases, however, the moles of the substances are unknown and it is more practical to measure the masses instead. The mass fraction of a species i of molecules in a mixture of two genera is defined as $x_i \equiv m_i/(m_i + m_j)$. Now, denote the molar fraction as $w_i \equiv n_i/(n_i + n_j)$. By [2], the two fractions are related by

$$w_i = \frac{x_i}{M_i}\bar{M} \tag{3}$$

where the variables M_i and $\bar{M}$ are the molar mass of particle species i and the average molar mass of the whole mixture respectively. Also required is the fact that $n_i = m_i/M_i$. With equation (3), the entropy of mixing (equation (2)) may be expressed in terms of the mass fraction of the constituent particle species

$$\Delta S_{mixing} = -R\frac{m_a}{M_a}\ln\left(\frac{x_a}{M_a}\bar{M}\right) - R\frac{m_b}{M_b}\ln\left(\frac{x_b}{M_b}\bar{M}\right) \tag{4}$$

The physics in the experiment can be further investigated by analysing the change in enthalpy between the product (the mixture) and the 'reactants' (individual water and ethanol). Recall that the enthalpy of a system is defined as $H \equiv U + PV$. The change in enthalpy is given by $\Delta H = \Delta U + \Delta PV + P\Delta V$. At constant pressure (which is a reasonable assumption to make for mixing in an open atmosphere), the ΔP term is equal to 0, and the equation becomes $\Delta H = \Delta U + P\Delta V$, where ΔU here is calculated by

$$\Delta U = Q + W \tag{5}$$

Where W and Q is the work and heat being put *into* the system by the environment respectively. When no 'other' forms of work are being done, ΔH is simply $\Delta H = Q$. For the sake of calculating an approximate

change in enthalpy, this assumption that no 'other' forms of work are being done was taken as valid for this experiment performed at room temperature in atmospheric pressure. For other related calculations, such as the calculation of the change of internal energy given by equation (5), the work expended is significant and can be calculated by

$$W = -P\Delta V \tag{6}$$

The heat term in the change in internal energy may be calculated via the use of defined specific heat capacity values, and measured mass and temperature changes by

$$Q = mC_p\Delta T \tag{7}$$

In order to reliably and safely use liquid mixtures in the real world, physical characteristics of substances must be known with one such physical attribute being the specific heat capacity, denoted C_p, defined as the energy required to change the temperature of some mass of substance. The specific heat capacity of a substance is related to the heat capacity by $C_p = c/m$ where c is the heat capacity of some substance and m is the mass. The specific heat capacity of a mixture, given by [3], is calculated by

$$C_{p_{mix}} = \sum_{i=a}^{n} w_i C_{p_i} = \sum_{i=a}^{n} x_i C_{p_i} \tag{8}$$

where w_i, x_i and C_{p_i} represent the molar fraction, mass fraction and specific heat capacity of substance of genus i respectively. The summation is carried out over the number of species in the mixture, n. Equivalently, equation (8) may be expressed in terms of the heat capacity c and the mass m of each species,

$$C_{p_{mix}} = \sum_{i=a}^{n} w_i \frac{c_i}{m_i} = \sum_{i=a}^{n} x_i \frac{c_i}{m_i} \tag{9}$$

Unless otherwise stated, the above equations were referenced from Schroeder, *"An Introduction To Thermal Physics"*.

3 Experiment

3.1 Method

For the mixture of 25% ethanol to 75% distilled water, approximately 75 millilitres of distilled water was poured from a container into 1 of 2 graduated cylinders (designated cyl$_{\text{water}}$) through a funnel, where the cylinder was placed on top of electric scales, and the mass of the water was noted. Cyl$_{\text{water}}$ was then removed from the scales and set aside. This process was repeated with the second of the cylinders (designated cyl$_{\text{ethanol}}$), but with approximately 25mL of ethanol. Cyl$_{\text{ethanol}}$ was removed from the scales and set next to the water cylinder. The thermometer extension of the multimeter was submerged into the volume of ethanol and left until no temperature fluctuation was apparent on the multimeter screen. The temperature was then recorded, and the thermometer taken out and wiped clean. This was repeated again with the water. A beaker was placed on the scales, and tare weight was set. The smaller volume (in this case, ethanol), was poured into the beaker from its respective cylinder. The thermometer was submerged in the ethanol liquid, and the setup was left to rest until the thermometer remained at a steady temperature. The distilled water was then poured into the beaker steadily, and the resultant volume and temperature of the solution was recorded. A small pipette was then used to gently stir the solution to ensure that mixing of the two substances had occurred, and a temperature increase on the multimeter was observed. The peak temperature was recorded, and the mass of the solution was taken from the scales. The solution was then poured into a waste container after all records had been taken. This process was repeated 4 more times for this ratio of ethanol to water, and the entire method repeated for each of the other ratios tested (50-50 ethanol to water, and 75-25 ethanol to water) respectively.

3.2 Uncertainties

As with any experiment, there are a range of uncertainties in measurements as a result of several factors. Steps were taken to minimise such uncertainties where possible, however the scope of the experiment limited the effort expended in maximising measurement accuracy. Firstly, the graduated cylinders were calibrated. This was done by pouring in the respective substance up to the desired increment on the side of the cylinder. In the room at 27°C, the density of water is well defined, so the mass was taken at the room temperature, and using the density values in the calculation, the actual volume of liquid was determined. The results of the calibration are shown in Table 1

Cylinder	V (Measured - mL) ($\pm$1mL)	V (Calculated - mL) ($\pm$1mL)
Cylinder 1 (Mix)	25	24
	50	49.1
	75	73.4
Cylinder 2 (Ethanol)	25	25.1
	50	50.1
	75	74.3
Cylinder 3 (Water)	25	26.4
	50	49.6
	75	75.8

Table 1: Graduated Cylinder Volume Calibration Values

As can be seen, the calculated values of volume differ from those observed. To account for this, each subsequent measurement of volume was multiplied by some 'correction factor,' ϕ. To achieve this value, the average of the calculated vs measured values was taken, and this factor was multiplied to the raw data to show the corrected data. The correction factors follow, with the calculation of these parameters in Appendix 7.3.

$$\phi_1 = 0.974 \qquad \phi_2 \approx 1 \qquad \phi_3 = 1.02$$

The uncertainty for this correction factor was deemed negligible due to it being an order of magnitude smaller than the value of the lowest significant figure in the measurements taken. Both the apparent and calibrated values were shown in table 2.

As electronic equipment was used for the majority of the measurement-taking, the uncertainty remained quite low throughout the experiment. The uncertainty for each electronically measured variable (the temperature and mass) was taken as plus or minus the smallest decimal place of the readout. As a result, temperature measurements had an uncertainty of $\pm$0.1°C, and mass measurements had an uncertainty of $\pm$0.1g. Volume measurements were estimated to have an uncertainty of $\pm$1mL, as a result of the graduated cylinders having measurement increments of 1mL. Through uncertainty propagation using Appendix 7.1, uncertainty values for ΔT and ΔV were determined to be $\pm$0.2°C and $\pm$2mL respectively.

4 Results

The raw data taken from the experiment, coupled with the corrected values and Δ calculations are shown in Table 2.

Proportion	Trial	$T_{ethanol}$ ($\pm0.1\,°C$)	T_{water} ($\pm0.1\,°C$)	$T_{initial}$ ($\pm0.1\,°C$)	T_{final} ($\pm0.1\,°C$)	ΔT ($\pm0.2\,°C$)	$m_{cylinder+water}$ ($\pm0.1g$)	m_{final} ($\pm0.1g$)	$V_{apparent}$ ($\pm1mL$)	$V_{calibrated}$ ($\pm1mL$)	ΔV ($\pm2mL$)
	1	27.9	27.4	27.5	33.7	6.2	231.6	93.2	97	95	5
	2	27.4	27.6	27.6	34	6.4	231.9	93.5	98	96	4
25% Ethanol	3	27.5	27.9	27.8	34.5	6.7	232.1	93.7	98	96	4
	4	26.2	28.1	27.8	33.6	5.8	231.8	93.4	98	96	4
	5	26.8	28.2	28	33.9	5.9	233	94.6	100	98	2
	1	27.5	28.1	27.9	34.3	6.4	226.3	87.9	96	94	6
	2	27.4	28	27.8	31.2	3.4	227	88	99	97	3
50% Ethanol	3	27.5	27.8	27.7	30.4	2.7	227.5	89.1	99	97	3
	4	27.6	29.2	28.7	34.4	5.7	226.4	88.1	97	95	5
	5	27.6	28.8	28.4	34.7	6.3	227.3	88.9	98	95	5
	1	27.5	27.4	27.5	31.1	3.6	222.5	84.1	98	96	4
	2	27.6	28.8	28.1	31.6	3.5	221.7	83.3	97	95	5
75% Ethanol	3	27.5	28.4	27.9	31.7	3.8	221.5	83.1	97	95	5
	4	26.6	27.7	27.1	28.8	1.7	221.9	83.5	98	96	4
	5	26.4	27.5	26.9	30.4	3.5	221.5	83.1	98	95	5

Table 2: Temperature and Volume Raw/Corrected Data for Varying Proportions of Ethanol to Water

The data shows consistent positive changes in temperature, ranging from an increase of 1.7°C at the 0.75 ethanol mass fraction, to 6.7°C at the 0.25 ethanol mass fraction, although the former example could reasonably be considered anomalous especially after observing figure 1. Figure 1 shows the relationship between the change in temperature to the ethanol mass fraction. There is a clear negative trend in temperature increase as ethanol mass fraction is increased. The inconsistencies in the data across each mass fraction can be attributed to human error, particularly in the measurement of volumes of water and ethanol.
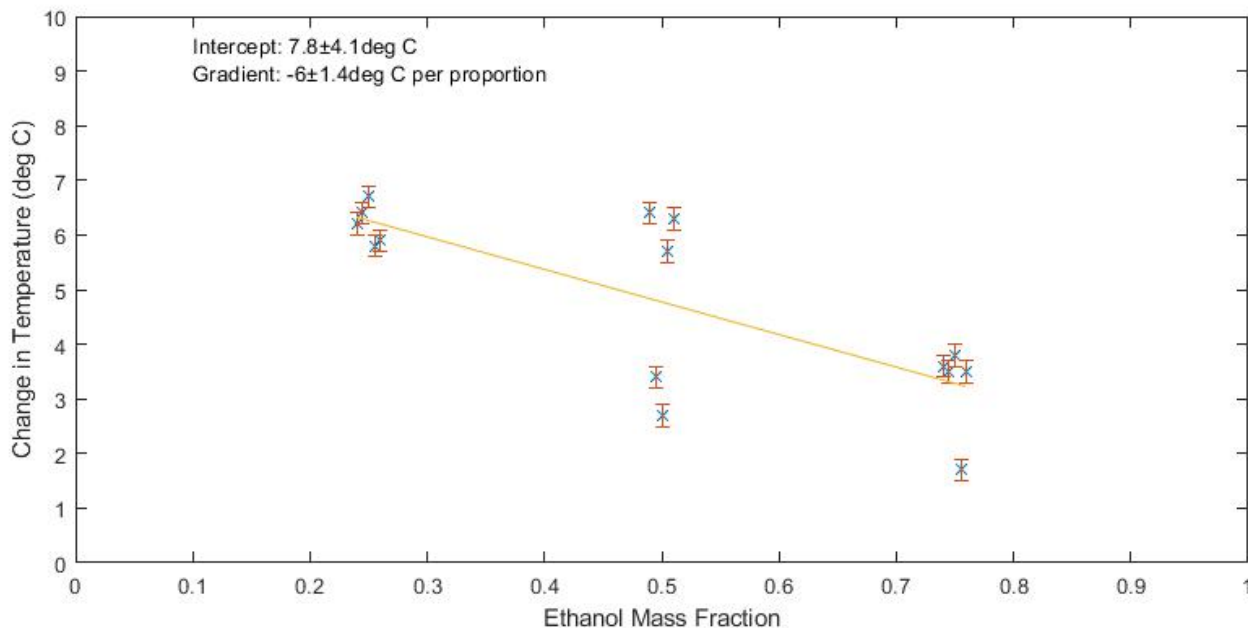

Figure 1: Change in Temperature after Mixing vs Ethanol Mass Fraction

The trendline in the above figure is intended as a basic model only. Considering the boundary conditions, one would expect values of $\Delta T = 0$ at both 0 and 1 ethanol mass fractions, as no mixing would occur at these points. The linear regression does not account for this, and a polynomial or exponential/logarithmic trendline could account for these boundary conditions. This suggestion also applies to the linear regression fit of the change of volume vs ethanol mass fraction shown in figure 2.
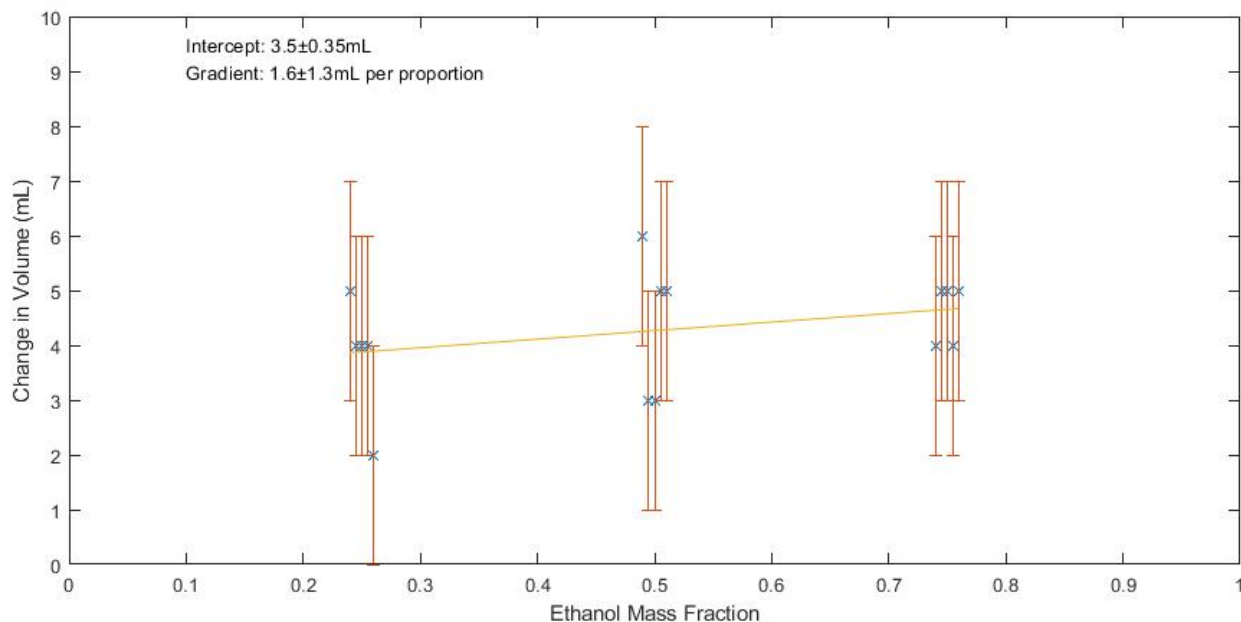

Figure 2: Change in Volume after Mixing vs Ethanol Mass Fraction

The ΔV associated with the mixing is undeniably less defined with varying ethanol mass fraction than the ΔT. Figure 2 shows this, with a 'shallower' trendline gradient in comparison with figure 1. Despite this, the trendline much better conforms to the uncertainties associated with the measurements taken, although it is worth noting that the uncertainties attributed to the volume measurements are relatively much greater than those linked to the temperature measurements. There is an evident positive trend in the decrease in volume after mixing with the increase in ethanol mass fraction. Once again, this does not take in to account the aforementioned boundary conditions.

5 Discussion

To thoroughly investigate how the mixing interactions follow the laws of thermodynamics, the heat and work expended in each mixing interaction were calculated. Firstly, the specific heat capacity of the mixtures were calculated according to equation (8) for each ethanol mass fraction. For water, the specific heat capacity is well defined at 4.184 J/(g°C) [5]. The specific heat capacity of ethanol (specifically at 300K) was found to be approximately 2.376 J/(g°C) [6]. Therefore, the specific heat capacity for each ethanol mass fraction is

$$C_{p_{0.25}} = 0.25 \cdot 2.376 + 0.75 \cdot 4.184 \approx 3.7 \,\text{J/(g°C)}$$
$$C_{p_{0.5}} = 0.50 \cdot 2.376 + 0.50 \cdot 4.184 \approx 3.3 \,\text{J/(g°C)}$$
$$C_{p_{0.75}} = 0.75 \cdot 2.376 + 0.25 \cdot 4.184 \approx 2.8 \,\text{J/(g°C)}$$

$$y = x^3 + \frac{3}{5x} \tag{10}$$

Using these specific heat capacities, and the measured data from Table 2, the calculated heat and work values including uncertainties are available in Table 3

Proportion	Trial	Heat $(\times - 10^3\text{J})$ $(\pm 0.1 \times 10^3 \text{ J})$	Work (J) $(\pm 0.2 \text{ J})$	ΔS (J/K)	ΔG $(\times - 10^3 \text{ J})$ $(\pm 0.1 \times 10^3 \text{ J})$
	1	2.2	0.5		3.9
	2	2.3	0.4		4.0
25% Ethanol	3	2.4	0.4	5.7	4.1
	4	2.1	0.4		3.8
	5	2.1	0.2		3.8
	1	1.9	0.6		4.3
	2	1.0	0.3		3.4
50% Ethanol	3	0.80	0.3	7.9	3.2
	4	1.7	0.5		4.1
	5	1.9	0.5		4.3
	1	0.87	0.4		7.8
	2	0.84	0.5		7.8
75% Ethanol	3	0.92	0.5	23	7.8
	4	0.41	0.4		7.3
	5	0.84	0.5		7.8

Table 3: Calculated Heat and Work Values Acting Upon the System, with Entropy and Gibbs Free

Note: all propagated uncertainties for the heat were less than 0.1×10^3 J. As such, the uncertainty was rounded up to meet that value. The propagated uncertainties for the change in entropy were on the order of magnitude 10^{-3}, whereas the smallest significant figure calculated was on the order of magnitude 10^{-1}. As such, this uncertainty in ΔS was deemed negligible.

Table 3 shows a clear trend of decreasing heat transferred *from* the system as ethanol mass fraction is increased. The work done onto the system is comparatively very little, and is relatively consistent across mass fractions. Consequently, it is a valid approximation to negate the energy done to the system as work entirely, as it is roughly four orders of magnitude lesser than the heat expelled by the system. Considering this, the potential energy of the system (approximated as the internal energy given by equation (5)) is reduced consistently across the varying mass fractions, with the greatest reduction in potential energy being characteristic of lesser ethanol mass fractions. While the ΔU remains significant at high ethanol mass fractions, the impact of the uncertainty in values becomes more prevalent as it becomes a considerable fraction of the ΔU value. Extrapolating from the apparent trend in heat expended, this uncertainty would imply

values becoming relatively less accurate as mass fraction is further increased from 0.75.

The data also shows that the entropy increase with ethanol mass fraction increase is steeper than a linear correlation, with higher mass fractions being characterised by vastly larger entropies. The change in Gibbs free energy is reflected by this, with a similar non-linear relationship with ethanol mass fraction. While ΔG is reasonably similar when comparing the 0.25 and 0.50 ethanol mass fractions, the change in gibbs free energy is much larger for the 0.75 mass fraction, with some values being over double that in the 0.5 mass fraction. Even considering the impact of the uncertainties of the ΔG values, the non-linear increase with mass fraction change is undeniable. These results are in accordance with the second law of thermodynamics that suggests that an isolated system approaches a state of higher entropy, or conversely a state of lower gibbs free energy.

6   Conclusions

Through the mixing of varying ethanol mass fractions to water in controlled laboratory conditions, the first and second law of thermodynamics were further supported. As described by the first law, the potential energy of the mixture was seen to decrease compared to the potential energies of the two parts as separate systems. In accordance with the second law, the entropy of the mixture was seen to vastly increase with increasing ethanol mass fraction, with the change in gibbs free energy reflecting this with a similar, albeit negative, non-linear relationship. In future investigations, the data analysis would benefit from both more data points (in an effort to negate the impact of anomalous data), and a more broad range of tested ethanol mass fractions. Specifically, mass fractions at more extreme ends of the spectrum, such as 0.1 and 0.9, would ideally be tested to create a more accurate, non-linear trendline in graphs of ΔT or ΔV vs mass proportion. That said, the three mass fractions tested provided a wealth of data suitable for an in-depth analysis of the first two laws of thermodynamics.

7 Appendices

7.1 Uncertainty Calculations/Propagations for Table 2

All uncertainties were propagated according to the rules shown in Table 4

Relationship	Uncertainty obtained from
General expression	
$p = f(x,y,z,...)$	$(\Delta p)^2 = \left(\frac{\partial f}{\partial x}\Delta x\right)^2 + \left(\frac{\partial f}{\partial y}\Delta y\right)^2 + \left(\frac{\partial f}{\partial z}\Delta z\right)^2 + ...$
Specific cases	
$p = x + y$	$\Delta p = \sqrt{(\Delta x)^2 + (\Delta y)^2}$
$p = x - y$	$\Delta p = \sqrt{(\Delta x)^2 + (\Delta y)^2}$
$p = x\,y$	$\frac{\Delta p}{|p|} = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$
$p = \frac{x}{y}$	$\frac{\Delta p}{|p|} = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$
$p = Bx$	$\Delta p = B\,\Delta x$
$p = Ax^n$	$\frac{\Delta p}{p} = n\frac{\Delta x}{x}$
$p = \log x$	$\Delta p = \frac{1}{2.3x}\Delta x$
$p = \sin\theta$	$\Delta p = |\cos\theta|\,\Delta\theta$

Table 4: Uncertainty Propagation Formulae

Source: PHYS2020 Linear Regression Document

To avoid confusion in variables, uncertainties were calculated with δ symbolising uncertainty as opposed to Δ.

7.2 Example Uncertainty Propagations

7.2.1 Calculation of ΔV Uncertainty

$$\delta p = \sqrt{(\delta x)^2 + (\delta y)^2}$$
$$\Rightarrow \delta\Delta V = \sqrt{(1)^2 + (1)^2}$$
$$= 1.41 \Rightarrow 2\text{mL}$$

This value was rounded up to the appropriate significant figure value.

7.2.2 Calculation of Q Uncertainty

$$\frac{\delta p}{|p|} = \sqrt{\left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2}$$

$$\Rightarrow \delta Q = Q\sqrt{\left(\frac{\delta m}{m}\right)^2 + \left(\frac{\delta \Delta T}{\Delta T}\right)^2}$$

$$= 2200\sqrt{\left(\frac{0.2}{96}\right)^2 + \left(\frac{0.2}{6.2}\right)^2}$$

$$= 71.11 \Rightarrow 0.1 \times 10^3 \, \text{J}$$

Once again, this value was rounded up to match the lowest significant figure of Q.

7.3 Correction Factor Calculations

For mixing cylinder (Cyl 1):

$$\phi_1 = \frac{1}{3}\left(\frac{24}{25} + \frac{49.1}{50} + \frac{73.4}{75}\right)$$

$$= 0.974$$

For ethanol cylinder (Cyl 2):

$$\phi_2 = \frac{1}{3}\left(\frac{25.1}{25} + \frac{50.1}{50} + \frac{74.3}{75}\right)$$

$$= 0.999$$

$$\approx 1$$

For water cylinder (Cyl 3):

$$\phi_3 = \frac{1}{3}\left(\frac{26.4}{25} + \frac{49.6}{50} + \frac{75.8}{75}\right)$$

$$= 1.02$$

7.4 Volume to Mass Relationships for Ethanol and Water

Ethanol Mass Fraction	Ethanol Mass (g) (± 0.1g)	Water Mass (g) (± 0.1g)	Total Mass (g) (± 0.2g)
0.25	19.7	76.3	96
0.5	39.5	50.5	90
0.75	59.2	26.8	86

Table 5: Ethanol Mass Fractions vs Equivalent Masses

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