The Temperature Dependence of the Density of Methyl Alcohol

John Doe

Lab Partners:
       Karen Bolla
       John Fahey

Abstract

A Cassia volumetric flask is used to find the density of methyl alcohol for eight temperatures in the range t = 0 to 41 °C. The best fit to the data gives

$$\rho(t) = (0.80551 \pm 0.0015) \text{ g/cm}^3 - (8.07 \pm 0.61) \times 10^{-4} \text{ g/cm}^3\cdot°C)\, t$$

where the fitting parameters are given at 95% confidence limits. Based on this data we find that at 20. °C, $\rho = (0.7894 \pm 0.0019)$ g/cm^3, and $\alpha = (1.022 \pm 0.077) \times 10^{-3}$ °C^{-1}, also at 95% confidence limits.

Introduction

Unlike gases, the volume occupied by a given amount of a liquid is, to a first approximation, independent of temperature. However, careful measurements demonstrate that small changes in volume, and therefore density, do occur when the temperature of a liquid is changed. These changes can be important in experiments where the properties of a pure liquid or a solution are studied over a range of temperatures. These changes also provide information about the fundamental properties of liquids, such as α, the coefficient of thermal expansion. [1]

The purpose of the present experiment is to study the temperature dependence of the density of methyl alcohol (CH$_3$OH). The mass and volume of samples of methyl alcohol will be measured over a range of temperatures roughly between 0 °C and 40 °C. These data will be used to find the density of methyl alcohol at each experimental temperature, using the relationship

$$\rho = m/V \tag{1}$$

where m is the mass of methyl alcohol, V is the volume occupied by the methyl alcohol, and ρ is the density. The data will be fit to an empirical equation of the form

$$\rho(t) = \rho_0 + bt + ct^2 + ... \tag{2}$$

In the above expression $\rho(t)$ is density of methyl alcohol, expressed as a function of t, the temperature (in °C), ρ_0 is the density of methyl alcohol at 0 °C, and b, c, ... are fitting parameters. The 95% confidence limits on the fitting parameters will be used to determine the appropriate number of terms to include in the power series expansion in eq. 2.

Once an expression for is $\rho(t)$ is found, it will be used to find the corresponding expression for $\alpha(t)$, the coefficient of thermal expansion. α is defined by the relationship

$$\alpha = (1/V)\,(\partial V/\partial T)_p = (1/V)\,(\partial V/\partial t)_p \tag{3}$$

Using eq. 1 it can be shown that

$$V = m/\rho \tag{4}$$

Substitution of eq. 4 into eq. 3 leads to the result

$$\alpha(t) = \rho\,(\partial/\partial t)_p\,\rho^{-1} \tag{5}$$

$$= \rho\,(\partial(1/\rho)/\partial\rho)_p\,(\partial\rho/\partial t)_p \tag{6}$$

$$= -\,(1/\rho)\,(\partial\rho/\partial t)_p \tag{7}$$

from which $\alpha(t)$ can be found.

The final results from the experiment will be expressions for $\rho(t)$ and $\alpha(t)$. Values for ρ and α at 20. °C will be calculated from these expressions and compared to literature values. Finally, the major sources of error, their expected magnitude, and the effect of these errors on the results will be discussed.

Experimental Method

The experimental method used is a modification of that used in Experiment 9 of the lab manual ("Partial Molar Volume"). [2] Because there are significant differences between the procedure used in that experiment and the procedure used in the present experiment, a detailed outline of the experimental method is given below.

A 100 mL Cassia volumetric flask is thoroughly dried, and its mass measured twice on an analytical balance. The flask is then filled with slightly more than 100 mL of methyl alcohol. The filled flask is placed inside a water bath and held in place using a clamp and ringstand, with the stopper of the flask placed loosely on the top of the flask. The flask and liquid are given 15 minutes to equilibrate. At this time the stopper is fitted into the top of the flask, after which the temperature of the water bath is measured using a mercury thermometer, and the volume of the liquid in the flask is recorded. The flask is then removed from the water bath, dried on the outside, and allowed to cool. Finally, the mass of the filled flask is measured.

A total of 6-10 measurements of temperature, mass, and volume are made by repeating the above procedure, with the temperature of the water bath changed by ~ 5 °C between measurements. Small amounts of methyl alcohol can be added or removed from the flask to keep the volume of liquid slightly larger than 100 mL. After all of the measurements have been completed the flask is emptied and dried, and two additional measurements of the mass of the dry flask are made.

Results

The data for the mass of the Cassia flask when empty are given in Table 1.

TABLE 1 - Mass of dry flask (m_e)

Trial 1 23.4128 g	Trial 3 23.4127 g
Trial 2 23.4131 g	Trial 4 23.4128 g

Average value: 23.41285 g $s_{n-1} = 0.000173$ g $t_{.95,3} = 3.18$

Final result: $m_e = 23.4128 \pm 0.0003$ g, at 95% confidence limits.

The experimental data and calculation of the density of methyl alcohol are given in Table 2.


TABLE 2 - Data and calculation of ρ

t (°C)	V (cm^3)	m (g)	m - m_e (g)	ρ (g/cm^3)
0.2	100.47	104.2791	80.8663	0.80488
6.5	100.56	103.9836	80.5708	0.80122
11.8	100.85	103.7485	80.3357	0.79659
17.1	100.41	102.7773	79.3645	0.79040
21.5	100.56	102.7041	79.2913	0.78849
26.4	100.70	103.1672	79.7544	0.79200 (not used)
31.2	100.38	101.7208	78.3080	0.78012
35.7	100.65	101.4866	78.0738	0.77570

| 40.9 | 100.61 | 101.2402 | 77.8274 | 0.77356 |

NOTE: m_e = 23.4128 g (Table 1). Data at 26.4 °C are not used in the subsequent analysis.

The data are plotted on the next page. Note that the data point at 26.4 °C (shown as an x in the plot) was not used in the analysis of the data, as it is clearly not consistent with the other data obtained in the experiment.

Plot of density vs temperature for methyl alcohol
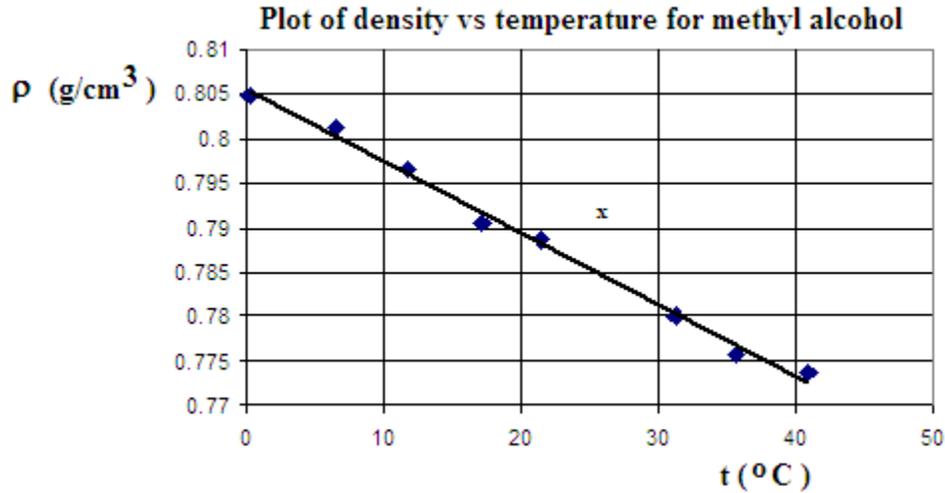
Data were fit to eq. 2 by a first order polynomial (linear fit) and a second order polynomial (quadratic fit) using the POLY program. The results are given in Table 3.

TABLE 3 - Fit of density vs temperature data to eq. 2

	ρ_0 (g/cm^3)	b (g/cm^3•°C)	c (g/cm^3•°C^2)
linear	0.80551 $\pm$ 0.0015	(- 8.07 $\pm$ 0.61) x 10^{-4}	
quadratic	0.80581 $\pm$ 0.0023	(- 8.55 $\pm$ 2.6) x 10^{-4}	(1.16 $\pm$ 6.1) x 10^{-6}

Since the second order term (c) in the quadratic fit is not significantly different from zero at 95% confidence limits, a linear fit to the data is used. Therefore, the final expression for the density of methyl alcohol in the range 0 - 40 °C is

$$\rho(t) = (0.80551 \pm 0.0015) \text{ g/cm}^3 - (8.07 \pm 0.61) \text{ x } 10^{-4} \text{ g/cm}^3\text{•°C}) \text{ t} \qquad (8)$$

Values for $\alpha(t)$ can be found using eq. 7. Note that $(\partial\rho/\partial t)p$ = b when a linear fit to the density data is used, and so

$$\alpha(t) = - \text{ b}/\rho(t) \qquad (9)$$

where b is given in Table 3 and $\rho(t)$ is given in eq. 8.

Equations 8 and 9 can be used to find the values for ρ and α at t = 20. °C. The results, with the 95% confidence limits found using the rules for propagation of error in addition/subtraction and for multiplication/division in calculations, are ρ(20. °C) = (0.7894 ± 0.0019) g/cm^3, and α(20. °C) = (1.022 ± 0.077) x 10^{-3} °C^{-1}.

Discussion

The major sources of error in this experiment are as follows:

Measurement of mass. The precision of the analytical balance used in the experiment is estimated to be ± 0.0003 g. This would lead to an error in in m and m_e, and therefore a corresponding error in ρ of ~ ± 4 x 10^{-6} g/cm^3, a negligible error.

Measurement of volume. The volume of liquid in the Cassia volumetric flask can be read to a precision of approximately ± 0.03 mL. This would lead to an error in V, and therefore a corresponding error in ρ of ~ ± 0.0002 g/cm^3. Since the same flask is used in all of the measurements, there is also the potential of systematic error. The uncertainty in the volume of the Cassia flask (not the reading uncertainty) is ~ 0.08 mL [2], leading to a corresponding systematic error in ρ of ~ ± 0.0006 g/cm^3.

Measurement of temperature. The reading error for the thermometer used in the experiments is ~ 0.2 °C. The systematic error in the thermometer is estimated to be approximately the same magnitude as the reading error. Using the experimental value for b, this would lead to random error in ρ of ~ $|b\Delta t|$ = 0.0002 g/cm^3, and a systematic error of approximately the same magnitude.

The combination of the above three sources of random error would lead to a combined random error due to the measurement process used in the experiment of ~ 0.0003 g/cm^3, about six times smaller than the reported error in the value for density at t = 20. °C, ± 0.0019 g/cm^3.

There are additional errors expected to be present due to the difficulty in drying the outside of the volumetric flask before weighing and the volatility of methyl alcohol (which increases as t increases). These are the most likely sources of the additional random error observed in the experimental results. Note that the dependence of the volatility of methyl alcohol on temperature might also be a possible source of systematic error.

Literature values for the density and coefficient of thermal expansion for methyl alcohol are given at t = 20. °C in the CRC Handbook of Chemistry and Physics. [3] The literature value for ρ(20. °C) is 0.7909 g/cm^3, within the 95% confidence limits of the experimental value. The literature value for α(20. °C) is 1.49 x 10^{-3} °C^{-1}, approximately 45% larger than the value found experimentally and well outside the 95% confidence limits. The reason for the difference is not known, though it should be noted that a temperature dependent systematic error, such as might be caused by the increasing volatility of methyl alcohol with temperature, could account for the difference. The experimental value for α is also sensitive to the curvature in the plot of ρ vs t, and so the difference might indicate that the use of a second order polynomial fit for ρ is justified. The values for α reported in ref. [3] also show a stronger dependence on temperature than those found in the present experiment. The reason for this is not known.

In summary, we were able to obtain high precision values for the density of methyl alcohol that were in good agreement with the literature. There was a significant difference (at 95% confidence limits) between the literature value for α and the value found in this experiment, with the reason for the difference not clearly identified.

References

1. Atkins, P. W. and J. de Paula, Physical Chemistry, 10th Edition. W. H. Freeman: New York, 2014. The coefficient of thermal expansion is defined and briefly discussed on page 93.

2. Garland, C. W., J. W. Nibler, and D. P. Shoemaker, Experiments in Physical Chemistry, 8th Edition. McGraw-Hill: New York, 2003, pp. 172-178.

3. CRC Handbook of Chemistry and Physics, 94th Edition, 2013-2014. Retrieved online 1/19/2014. ρ is taken from a data table on p 15-25, and α from a data table from page 6-156.