Spectroscopic and Theoretical Determination of Flame Temperature

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Note: There are lots of links to documents and URLs in this handout. Be prepared to have it up in the background of your computer throughout lab!

Abstract

In this lab, we will attempt to determine the temperature of an alcohol flame by using the UV-Vis spectra of the OH radicals formed in the flame. There are a variety of methods by which to determine the flame temperature from this data and two will be explored through Excel and Mathcad. In addition, a theoretical flame temperature will be determined through the use of heat capacities published on the NIST webbook and a Mathcad document. The temperatures determined by the various methods will then be compared.

Related Reading

Izarra et al., (J. Phys. D: Appl. Phys. **33** (2000) 1697-1704); McQuarrie and Simon, Ch 19-1 to 19-4 (with focus on 19-4).

Background

In this investigation we will consider the temperature of flames theoretically and compare our findings with our own experimental findings. The theoretical model is known as the adiabatic flame approximation. In this approximation all the heat generated through combustion is transferred to the gases occupying the flame volume in their stoichiometric ratios. The temperature rise and equilibrium temperature is computed by using temperature dependent heat capacities of each component (CO_2 , H_2O, and N_2) and the *assumption that no heat is transfered to the surroundings (adiabatic)*. We will experimentally determine the temperature of various flames by monitoring the spectrum (intensity vs. wavelength) of radiation emitted by a flame. In order to make this determination we need to assume certain theoretical models. In one method we can assume that the radiation emitted from a flame can be treated as ideal black-body radiation. A black-body is an object that is *capable* of emitting and absorbing all wavelengths of light equally well. The concept of an ideal black-body radiator is covered in Chapter 1 of McQuarrie and Simon. [*Interesting side note*: Experimental observation of black-body radiation was one observation that could not be explained by classical physics which predicted that the intensity of light from any heat object would increase without bounds in the ultraviolet portion of the electromagnetic spectrum. This was labeled the ultraviolet catastrophe and was the successful explanation of this phenomenon was one of the first successes of quantum theory emerging at the turn of the century.]

In our investigation, we will use a more accurate spectroscopic probe of temperature, high resolution spectroscopy of the emission of OH radicals formed in the flame. In the flame emission occurs from electronically excited OH radical in the $A\ ^2\Sigma$ to the ground state $X\ ^2\Pi$. At 306.4 nm the transition is between the zero-point vibrational level of the excited state (v'=0) to the zero-point vibrational level of the ground electronic state (v''=0). Rotational transitions are superimposed on these vibrational levels leading to a

highly structured spectrum. The structure corresponds to these rotational transitions with intensities corresponding to a number of factors including the number of molecules in the initial rotational state which in turn is related to temperature. We will use reference intensities for a 3000 K flame tabulated by Izarra (J. Phys. D: Appl. Phys. **33** (2000) 1697-1704). The spectrum will be recorded on various flames in the laser laboratory using a high resolution fiber optic coupled spectrograph with a LN_2 cooled CCD detector.

Pre-lab Exercises

As background for the experimental portion, read *UV OH spectrum used as a molecular pyrometer*, by Charles de Izarra (J. Phys. D: Appl. Phys. **33** (2000) 1697-1704). Write out the balanced equations for combustion of each of the following alcohols, and calculate the heat of combustion for each compound using WebMO and your favorite computational model chemistry (AM1 or PM3).

Compounds
Octanol
Ethanol
Methanol
Butanol

Procedure

Note: Implicit in all data analysis is the assumption that the area of the flame in which the combustion reactions are taking place is adiabatically separated (i.e., no heat transfer) from the area outside the flame for the instant at which we carry out a theoretical calculation.

1. We will take turns recording the OH radical emission spectrum of various alcohol flames using a spectrograph and a LN2 cooled CCD detector both interfaced to a computer. More detail on this procedure will be available in lab.

2. Experimental Flame Temperature Determination – Basic Method: A pre-developed Excel spreadsheet will allow for the determination of the flame temperature using a fairly simple method. The Excel spreadsheet is based on the work by Izarra and can downloaded here (Download Izarra Excel file). In this spreadsheet, you need only to adjust the intensity column (highlighted in yellow) by inputting the data from your experimental spectra. All other values will automatically adjust. Follow the directions in the text box at the bottom of the file to solve for the temperature.

3. Experimental Flame Temperature Determination - More Accurately: A Mathcad document designed by Dr. Smith allows for a more accurate determination of the flame temperature (Spectrum Fit.xcmd). This worksheet is designed such that user input is at

a minimum (i.e., the worksheet will automatically calculate the flame temperature once your experimental data and reference spectra are input). Before inputting your data, read through the Mathcad worksheet to gain an understanding of what is happening in the background. Then:

a. To input your spectra, first save both spectra as text files (.txt or .csv). You can download the reference spectra here (Download Ref Spectra).

b. In the Mathcad worksheet you'll see where the two spectra need to be input. To input your spectra, use the "File Input" command under Insert/Data menu. Browse for your spectra (or the reference spectra) and click "Finish". Name the file spec := or ref:= as appropriate (and delete the markers left for you in the document).

c. Once these files are uploaded, Mathcad will think and calculate for several minutes. When complete, the flame temperature will be printed at the bottom of the file. Record. (You'll probably need to force quit from Mathcad or it will continue to calculate in the background.)

4. It will be necessary to obtain temperature dependent heat capacities (from the NIST webbook). Note that in the Shomate equation given on the website, the temperature values in A, B, C, D, and E need to be divided by 1000 or your heat capacity will be incorrect (effectively you are multiplying A by 10^0, B by 10^{-3}, C by 10^{-6}, D by 10^{-9}, and E by 10^5). Note the Shomate equation and values of A-E for N_2, CO_2, and H_2O in your notebook. This information will be used in a theoretical calculation of the flame temperature.

5. Theoretical flame temperature determination: Read through the Mathcad worksheet, Flame.mcd, reprinted from *Physical Chemistry Using Mathcad* by Joseph Noggle, until you have an understanding of the steps and goals in this portion of the lab. Then use the second Mathcad worksheet, Flame-2.xmcd, to find the adiabatic temperature for the alcohol flame of your choice (from table above; same one chosen for the experimental section).

Analysis/Report

The following should be a part of your report for this lab. As always, this is a list of suggested discussion problems/questions. If you feel additional discussion is warranted, you should add that you your report as well.

- Compare and contrast the theoretical and experimental flame temperatures. Consider any error in the various calculations/determinations in your comparisons. How could the overall analysis be improved?
- Compare values with at least two other groups for different flames (e.g., compare trends in the calculations, real differences between the alcohols, etc).
- What seem to be the most important factors in determining flame temperature or is there a missing parameter?
- Can you think of a reason why the experimental value might deviate from the theoretical?
- Turn in a carefully formatted spectrum of your flames emission.