

# Thermal Lens Calorimetry: A Novel Approach to the Study of Thermodynamics

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**Abstract:** There has been a great deal of interest in modernizing the physical chemistry curriculum from the perspectives of employing more modern instrumentation and new teaching methodology. This paper presents a physical chemistry experiment in which thermal lens calorimetry is used to teach some general thermodynamics principles; as well, it provides an interesting and unique experiment. The experiment addresses numerous thermodynamic concepts, which include enthalpy changes and the relationship of thermal conductivity, density, and heat capacity. In addition, other topics, such as data analysis and optics, may be addressed. Discussion topics and exercises are provided that lend themselves to more extensive dialogue and would be appropriate for cooperative teaching methods and classroom discussions.

## <sup>\*\*‡</sup> Introduction

Modernization of the Physical Chemistry curriculum has been a topic of interest for at least 10 years [1, 2]. The impetus for this interest has been a desire to provide students with a more realistic view of modern physical chemistry as well as to increase student enthusiasm for the topic. The process requires the development of student laboratory experiments along with a concomitant change in instructional methodology. Currently, an effort is being made, in connection with the National Science Foundation's systemic reform initiative, to improve instructional methodology. It is important to link both new teaching methodologies and laboratory techniques for successful reform to occur. This paper provides a description of a novel approach to the study of thermodynamics. The approach employs thermal lens calorimetry (TLC), a laser-based calorimetric measurement, and it provides a content-rich, conceptual approach to the subject that would be appropriate for group discussion and/or cooperative learning situations.

sample indirectly from a measurement of the refractive index change. The observed temperature changes can be less than 0.1 °C, yet the effect of this small temperature change, a refractive index gradient created in the sample, is easily measured. This requires that we know the spatial irradiance profile of the excitation source. To accomplish this we must use a laser beam operating in the TEM<sub>00</sub> mode. Such beams have a radially symmetric Gaussian intensity profile.

The temperature, and thus the refractive index, of the irradiated sample has a known spatial profile. The refractive index profile acts like a diverging lens, causing the laser beam to expand. The effect of the refractive index profile on a propagating Gaussian beam has been calculated [3] and is well understood.

Using the appropriate optical arrangement, the laser beam power change, detected through a pinhole placed far from the sample, is directly proportional to the excitation laser power,  $\Phi_e$  (W), the change in refractive index with temperature ( $dn/dT$ ) (K<sup>-1</sup>), and the sample absorbance,  $A$ . Mathematically, this is represented as

$$S = \frac{\Phi_0 - \Phi}{\Phi} = \ln(10) \left( \frac{dn}{dT} \right) \frac{\Phi_e A}{\lambda \kappa} \quad (1)$$

$$E = \left( \frac{dn}{dT} \right) \frac{P}{\lambda \kappa} \quad (2)$$

## Background

**The Basic Thermal Lens Measurement.** Thermal lens spectrophotometry (TLS) is a highly sensitive method for measuring the absorbance of light in a multitude of samples based on physical changes that occur in the sample during irradiation. When a molecule absorbs light energy that energy must eventually be given off to the surroundings. The molecule releases energy in the form of heat, causing the surroundings to increase in temperature. The temperature increase causes a change in the density and refractive index of the sample. In TLC we measure the temperature change in the

The laser is operating at wavelength  $\lambda$  (m) and the sample has a thermal conductivity of  $\kappa$  (W m<sup>-1</sup> s<sup>-1</sup>).  $S$ , which equals  $(\Phi_0 - \Phi)/\Phi$  is the TLS signal,  $\Phi_0$  (W) is the power transmitted through the pinhole at zero time,  $\Phi$  (W) is the laser transmitted power after equilibrium has been reached. We can combine the constants that describe the system into a single constant called the enhancement factor,  $E$ , which is given by the following equation.

**The Time-Dependent Signal.** Once students have a sufficient appreciation for the dynamics of the process, we introduce the formal time decay. The time decay of the TLC signal, assuming a thin-lens approximation, is given by the equation

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**Table 1.** Properties That May Be Determined Experimentally Using TLC

1. thermal conductivity
2. absorbance
3. temperature change
4. $dn/dT$
5. sample concentration
6. laser beam spot size
7. heat capacity
8. density

**Table 2.** Some Questions for Student Discussion

1. Calculate the energy transferred to a sample with an optical absorbance of 0.01 for one-second irradiation by a 20-mW laser.
2. Define *the system*. Is it the sample cell, the laser beam volume in the cell, or the absorbing molecules in the laser beam volume?
3. How does the experimental arrangement of the thermal lens signal define *your system*?
4. Is the *system* you defined in #2 closed or open, adiabatic or isothermal? Do these properties change with a change in how the *system* is defined?
5. Calculate the total temperature change in the sample cell given a 1-s laser irradiation, water solvent, and 3-mL cell volume.

$$S(t) = \left[ 1 + \frac{\theta}{1+t_c/2t} \frac{1}{2} \left( \frac{\theta}{1+t_c/2t} \right)^2 \right]^{-1} \quad (3)$$

The magnitude of the TLC signal is a function of the thermal lens strength,  $\theta$ , where  $\theta = 2.303 \times E \times A$ . The thermal time constant is given by

$$t_c = \frac{w_0^2 \rho C_p}{4\kappa} \quad (4)$$

$\rho$  ( $\text{kg m}^{-3}$ ) is the density,  $C_p$  ( $\text{J kg}^{-1} \text{K}^{-1}$ ) is the specific heat capacity, and  $w_0$  is the laser spot size. To determine  $t_c$ , equation 3 may be fit to the signal decay, and the parameters  $t_c$  and  $\theta$  are determined. Typically, the data is normalized to the laser intensity. Equation 3 may be fit to the experimental data using a nonlinear fitting routine, (e.g., the Marquardt algorithm).

The thermal lens signal allows the direct or indirect measurement of a number of properties. One may choose which property is consistent with the goal of the laboratory. Table 1 provides a list of these properties.

### Introductory Exercise

At the outset of the experiment it is useful for students to examine the thermodynamics of the situation, perhaps after demonstrating the process, but before they perform any experiments. Ask the students to draw a diagram of the thermal lens system, relating the experimental details to the theoretical constructs of *system* and *surroundings*. In addition, they should consider the energy state of the system and relate the system properties measured in the TLC experiment to the state functions and variables. Some example questions are given in Table 2.

The purpose of this exercise is to require that the students first examine the TLS process from a conceptual view. For example,  $dn/dT$  is a property of the energy state of the system because it reflects the temperature, pressure, and volume of the system. The laser input power is given in watts, which can be converted to  $\text{J s}^{-1}$ . The thermal conductivity gives the rate at which energy is transferred out of the system or is dispersed within the system (depending on how the student chooses to define the system).

In answering these questions the student must consider the thermodynamics of the process rather than looking at the process as a black box. They see that the system and surroundings are defined by the experiment they perform and are not just an abstract concept. They gain an appreciation of the amount of energy input into the sample and the transformation of energy to different forms. Ideally, they will also recognize that the process is dynamic and will be time-dependant; therefore, dynamic parameters of the system, for example, thermal conductivity, are as important in describing the process as the static parameters. (It is called *thermodynamics*.)

The questions given above are best answered by following the treatment of Bialkowski [3]. We first recognize that the system, in this case, the volume of the sample irradiated by the laser, absorbs energy, and thus, it is raised to a higher potential energy. The potential is spontaneously converted to kinetic energy; this is observed as an increase in temperature. The enthalpy of the system is increased. The relationship between temperature and the enthalpy density,  $h$ , is

$$T = \frac{h}{\rho C_p} \quad (5)$$

where  $h$  is in ( $\text{J m}^{-3}$ ),  $\rho$  is the density ( $\text{kg m}^{-3}$ ), and  $C_p$  is in  $\text{J kg}^{-1} \text{K}^{-1}$ . We have assumed that the concentration of the absorbing sample is small and will not contribute to the thermal properties of the system. The term enthalpy density is unusual for students. Here, it should be stressed that the enthalpy varies with location in the sample. This illustrates that the enthalpy is more than bond energy (a common misconception among first-semester physical chemistry students).

**Study Question.** Ask students how to determine the heat capacity of a complex sample. Have students calculate the effect of a  $1 \times 10^{-5}$  M species on heat capacity.

The other property worth having students reflect on is  $dn/dT$ . While students at this level should be familiar with refractive index and know that it is dependent on temperature (based on their use of the refractometer in organic chemistry courses), they will be unfamiliar with the differential quantity, which is also dependent on temperature. The value of  $dn/dT$  has a significant impact on the sensitivity of the TLS measurement and results in the extremely sensitive measurement of temperature, because small changes in temperature can result in a significant change in  $dn/dT$ . Three other parameters that affect the signal also change with temperature. These are  $C_p$ ,  $\rho$ , and  $k$ . These latter terms also affect the time dependence of the TLS signal.

**Table 3.** Mean Values for the TLS Signal and Their Respective Enhancement Factors

	TLS signal	Enhancement factor
1 (24 °C)	0.217 ± 0.00372	1.013 ± 0.037
2 (24 °C)	0.212 ± 0.00528	0.99 ± 0.04
3 (19 °C)	0.176 ± 0.00380	0.822 ± 0.032
4 (14 °C)	0.135 ± 0.00466	0.63 ± 0.03
5 (6 °C)	0.0724 ± 0.00707	0.338 ± 0.035

**Table 4.** Thermal Conductivity and Calculated  $dn/dT$  of Water

	Thermal conductivity of water	$dn/dT$ (1/K)
1 (24 °C)	6.046 mW cm <sup>-1</sup> × K	157.4 ± 5.807
2 (24 °C)	6.046 mW cm <sup>-1</sup> × K	153.8 ± 6.317
3 (19 °C)	5.962 mW cm <sup>-1</sup> × K	125.9 ± 4.929
4 (14 °C)	5.883 mW cm <sup>-1</sup> × K	95.29 ± 4.529
5 (6 °C)	5.745 mW cm <sup>-1</sup> × K	49.91 ± 5.139

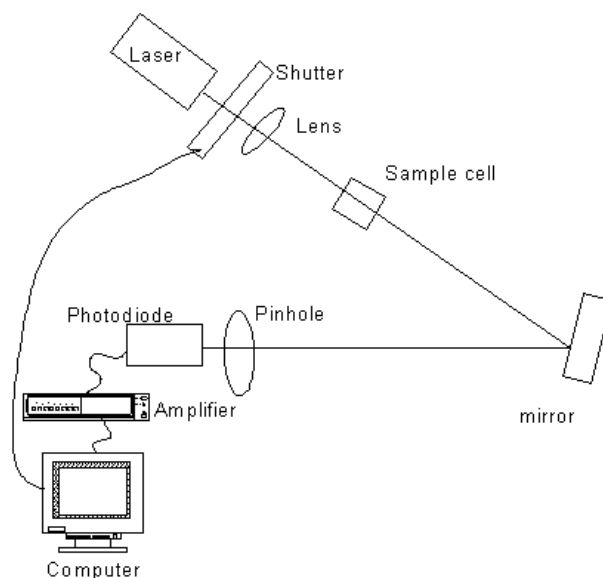
**Table 5.** Student Values for the TLC Time Constants and Laser Spot Size Values at Various Temperatures

Temperature (°C)	Time constant	Laser spot size (w)
1 (24 °C)	0.149 s	0297 cm
2 (24 °C)	0.179 s	0326 cm
3 (19 °C)	0.128 s	0274 cm
4 (14 °C)	0.128 s	0271 cm
5 (6 °C)	0.0975 s	0233 cm

## Experimental

Most experiments involving TLS measurements have addressed the determination of thermodynamic parameters of solvents based on a TLS enhancement factor and/or the decay time. These experiments suffer from the fact that other parameters are not measured directly in the experiment, but are obtained from the literature. This gives the experiment something of an unrealistic flavor. This is particularly true when we consider that the measured parameter is in the same handbook as the parameters used in the calculation. Also, because of the difficulties in measuring the diameter of the laser-beam spot, the experimental results will typically have errors greater than 50%. We chose to have students calculate  $dn/dT$  as a function of temperature and the laser spot size. The  $dn/dT$  parameter is perhaps an unusual choice (compared to  $C_p$ ); however, it is more accurately determined, because it comes from determination of the enhancement factor. The laser spot size is chosen specifically because it requires a determination of the time dependence of the TLS signal. It is also interesting, because Harris and Dovichi [4] in their early work suggest that the time constant should not be used to measure the spot size of the laser beam. Their results are born out in this experiment, and it becomes quite evident to the student when they obtain vastly different spot sizes for different experiments. For those interested in data analysis, tracing the source of the inaccuracy to the determination of the time constant by a fitting method is a useful process, and it teaches much about treatment of decay data.

**Apparatus.** A typical arrangement for the thermal lens calorimetric (TLC) equipment is shown in Figure 1. In our particular experiment, the laser was a 20-mW argon ion laser operating at 514.5 nm. The shutter operated at 1 shot per second. Data collection was performed by a Markenrich Corporation, model WAAG II, data-acquisition board operating at 2 kHz. The data-acquisition board was triggered by the shutter controller so that data collection was synchronized with the opening of the shutter. More details of this arrangement can be found in previous publications [5]. It should be noted that other laser sources and configurations might be used for this particular experiment. General experimental considerations for using TLS with students can be found in the text by Schewnz and Moore (reference 2, p 232).

**Figure 1.** Diagram of the thermal lens apparatus used for these experiments.

**Procedure.** In the example experiment methylene blue is used as the absorber. Methylene blue has only a small molar absorptivity at 514.5 nm, the laser wavelength of choice for this experiment. Thus, sample sizes are easily handled, allowing students to prepare a reasonably accurate sample. (If alternate laser sources are used, the sample and sample concentration should be adjusted appropriately.) Students will need to decide on a concentration. The solution should be dilute enough to, essentially, have the thermodynamic properties of water, yet concentrated enough to have a reasonable absorbance at 514.5 nm. Solutions between  $10^{-4}$  and  $10^{-5}$  M should be sufficient. The example student data used  $3.145 \times 10^{-5}$  M methylene blue. The TLS signal as a function of temperature for a series of different temperatures is measured. Students are required to decide on the temperatures to use. The temperature range is limited by the equipment used to control the temperature of the sample cell and, of course, should not go below 0 °C. In the example, a total of five trials were made; two trials at 24 °C and single trials at 19 °C, and 6 °C.

**Note:** Be sure to employ all appropriate precautions to insure laser safety.

## Data Collection and Calculations

**Enhancement Factor.** The mean value for the TLS signal was obtained using a boxcar integration routine, and is taken as  $1 - \Phi_0/\Phi$ . The signal from 100 laser shots is used to determine a mean value for the TLS signal as well as the standard deviations. The enhancement factor is calculated from the TLS signal and the measured absorbance of the sample. Student results from this experiment are shown in Table 3. The absorbance of the solution was  $0.093 \pm 0.003$  (measured by a Bausch and Lomb Spectronic 601). The thermal conductivity of water is determined by interpolation of values from the CRC Handbook [6]. Plotting the published thermal conductivity values and fitting these values to a polynomial is the best way to perform the interpolation. The  $dn/dT$  for each temperature was calculated. The results are shown in Table 4.

**Thermal Lens Time Constant.** Students calculate the  $t_c$  values for each system by fitting the equation for the time dependent thermal lens signal to the experimental data.

From the calculated value of  $t_c$ , they may calculate the laser spot size from eq. 4, provided they use the corresponding

literature values for  $C_p$ ,  $\rho$ , and  $k$ . These results are shown in Table 5. It is possible to show that the change in density is the primary factor responsible for the change in time constant.

Once the students calculate the spot size, it will become clear that there is significant error in the measurement. Obviously, the spot sizes should be the same, but there will be significant differences. This stems from the difficulty in fitting a decay function that has a high amount of noise. While averaging the TLS signal yields good results for the signal magnitude, the  $t_c$  term is extremely sensitive to the inherent errors in the TLS signal.

**Student Discussion.** The student uses literature data for the relevant temperature dependent properties and attempts to calculate an experimental parameter. The students come to their own conclusion concerning the error in the experiment, though the data provide a good illustration of the difficulty of determining an exact value for the spot size,  $w$ , and the time constant  $t_c$ . A useful exercise is to have students use an application like MathCad to vary the value of  $t_c$ , and to calculate the deviation between the resulting line and the data. This will show that  $t_c$  can be varied significantly. Alternatively, students that are well versed in statistics may simply calculate the error in the fitting parameters [7].

Each of the thermodynamic parameters must be determined for various temperatures. This provides a good opportunity to have students discuss the reasons for the temperature dependence of heat capacity, density, and thermal conductivity. In fact, one useful exercise is to have students predict the relative changes in  $t_c$ , based on changes of the thermodynamic parameters. Students can use Mathcad or a similar tool to plot the theoretical temperature dependence for the TLS signal. Students may study the temperature dependence of both  $t_c$  and the signal magnitude depending on the available data, the instructor's needs, and time constraints. Both calculations are good ways to let students increase the depth of their understanding concerning the thermodynamic

properties, even at a molecular level. Students might discuss why the thermal conductivity of liquid water decreases with temperature, or even why texts indicate that the  $C_p$  of water is independent of temperature at these ranges, while the CRC gives temperature-dependent values here.

### Conclusion

Thermal lens calorimetry is a useful technique to introduce into the undergraduate physical chemistry laboratory, and it may be a good alternative to the traditional thermal lens experiments, such as bomb calorimetry. Several previous works have discussed the use of TLC in the physical chemistry laboratory. Here we have expanded this discussion to detail how TLC might be used to illustrate several thermodynamic principles, and to focus student discussion on the underlying concepts of the experiment. Clearly, the complexity of the TLC experiment provides many avenues for addressing a wide range of important thermodynamic concepts.

### References and Notes

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