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Sublimating Paradichlorobenzene Spheres in a Natural Convection Environment

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SUBLIMATING PARADICHOLORBENZENE SPHERES IN A NATURAL CONVECTION ENVIRONMENT

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DEDICATION

This work is dedicated to those who have helped me throughout my academic career: my family for always pushing me to do my best, my friends for making sure I never overwhelmed myself, and Dr. Janna for showing me the way.

ABSTRACT

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Three sizes of paradichlorobenzene spheres were cast and allowed to sublimate in a natural convection environment. The mass loss over time was recorded, and a sublimation rate was calculated. The three sphere diameter sizes were: 0.04025 m (1.58 in), 0.0677 m (2.67 in), and 0.0846 m (3.33 in). The Schmidt number was shown to be a constant 3.64 from calculations. Results of experiments show that the range of Sherwood numbers varies from 1.19×10^4 up to 1.71×10^4, and the Rayleigh number climbs from 69.3 to 643.5. An equation was developed to relate these dimensionless numbers.

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CHAPTER 1 - INTRODUCTION

1.1 Objectives

The objective of this study was to develop a correlation for mass transfer using natural convection of paradichlorobenzene spheres. By utilizing three different sized spheres, a relationship was determined using dimensionless ratios.

1.2 Literature Survey

The subject of mass transfer has been extensively studied. A book by Geankoplis [1978] describes mass transfer as having multiple processes by which it occurs. These include distillation, absorption, and drying (evaporation) as examples; however, the process of interest for this study is sublimation, the direct conversion of a solid into a gas.

The majority of previous studies have focused on testing material, orientation of the sample, or forced versus natural convection. One such study conducted is by Bedingfield and Drew [1950]. Their primary focus was to study the analogy between heat and mass transfer. Their study regarding the mass transfer aspect is helpful as they studied cylinders evaporating into fluid streams. The materials used were paradichlorobenzene, naphthalene, paradibromobenzene and camphor, and the tests were performed in a wind tunnel to simulate forced convection environments. As a result of their experiments, they developed an equation for mass transfer:

$$J_m = 0.281(Re)^{-0.4}$$

Because the study concerned an analogy rather than one transfer process, Bedingfield and Drew ended with this equation which was designed to match that of their heat transfer equation.

Another set of studies were performed by Bautista [2010] and Snapp [2006]. Both works pertain to the sublimation rate of paradichlorobenzene in a natural convection environment. The difference between them is the orientation of the cylinders being tested. Snapp oriented his cylinders in a vertical direction, obtaining mass transfer rates from 7.56×10^{-7} kg/s to 8.5×10^{-7} kg/s for 1–nominal, 1.5-nominal, and 2-nominal cylinders. By utilizing the Sherwood and Rayleigh numbers, Snapp was able to minimize dependence upon the Schmidt number and produce the following:

$$Sh = 3 \times 10^{-5}(Ra) + 22.53$$

This correlated both dimensionless numbers together with maximum uncertainties of +1 to -1.1 for Sherwood and +3.04 to -2.96 for Rayleigh.

Bautista's cylinders were arranged in a horizontal direction, also using the 1-nominal, 1.5-nominal, and 2-nominal dimensions. The experiments provided mass transfer rates of 1.528×10^{-7} kg/s, 3.40×10^{-6} kg/s, and 6.90×10^{-6} kg/s. Bautista used the Grashof number, bypassing the Sherwood number altogether, in order to calculate the Rayleigh number and create comparisons between heat transfer and mass transfer.

Of particular interest to this experiment is a paper done by Garner and Grafton [1954]. They studied the effects of fluid flowing over solid spheres in a forced convection environment. By testing benzoic acid as well as naphthalene spheres submersed in water, the flow profile around the spheres was taken to determine mass transfer variations across the sphere's surface. Garner and Grafton were primarily concerned with the study of where mass transfer occurred on a sphere in a forced convection environment, rather than how much mass transfer occurred. In the course of their study, they used a dimensionless mass transfer unit, and created an equation for overall mass transfer from a sphere in a forced convection environment:

$$\frac{KD}{\mathscr{D}} = 44 + 0.48Re^{0.5}Sc^{0.33}$$

where K is the mass transfer film coefficient (m/s), the sphere's diameter D in meters, and $\mathscr{D}$ is the mass diffusivity (m^2/s).

For any mass transfer calculation, various properties and standard equations must be referenced. Çengel [2007] and Janna [2000] contain information regarding Fourier's Law, Fick's Law, various dimensionless groups, and provides information on mass convection. Paradichlorobenzene's molecular weight and vapor pressure were obtained from the Wolfram Alpha Computational Knowledge Engine while the mass diffusivity was obtained from Snapp [2006].

CHAPTER 2 - THEORY

2.1 Equations

In natural convection, the fluid surrounding the control volume moves on its own due to density or concentration gradients within the medium. These variations create slight differences causing the less dense molecules to rise.

The purpose of this study is to correlate the Rayleigh number, a ratio of buoyant force to mass diffusivity, and the Sherwood number, a ratio of mass transfer to mass diffusivity. To do this, we use the Grashof number, a dimensionless ratio of buoyant to viscous forces.

$$Gr = \frac{g\ (\rho_s - \rho_\infty)\ D^3\ \rho}{\mu^2} \tag{2.1}$$

Where *Gr* is the dimensionless Grashof number, g is gravity 9.81 m/s^2, and *D* is the diameter of the sphere in meters. The density in kg/m^3 of paradichlorobenzene at the sphere's surface is given as ρ_s and at a significant distance away as ρ_∞. Finally, there is the density (kg/m^3) and the dynamic viscosity (m^2/s) of air, ρ and μ.

From here, the Schmidt numbers and then the Rayleigh numbers can be obtained:

$$Sc = \frac{\upsilon}{\mathscr{D}} \tag{2.2}$$

$$Ra = Gr\ Sc \tag{2.3}$$

The kinematic viscosity is represented by υ, and $\mathscr{D}$ is the mass diffusivity. Both parameters have the units of m^2/s.

Now we use the original equation for mass transfer to obtain the Sherwood number. This initial equation is commonly known as Fick's Law:

$$J = -\mathscr{D}\frac{\delta C_a}{\delta r} \tag{2.4}$$

In this instance, J is the mass diffusion flux in m/s. C_a represents the concentration of paradichlorobenzene in the air along the radial direction, r, in meters. This equation can be written in a different format; introducing a new proportionality constant as the mass transfer coefficient, h_m. This provides us with another interpretation for the mass flux:

$$J = h_m(C_s - C_\infty) \tag{2.5}$$

In equation 2.7, C_s represents the concentration of paradichlorobenzene at the surface of the sphere while C_∞ is what is in the surrounding air.

In order to find h_m, we set equation 2.6 and 2.7 equal to each other and solve for the mass transfer coefficient:

$$h_m = \frac{-\mathscr{D}\frac{\delta C_a}{\delta r}}{(C_s - C_\infty)} \tag{2.6}$$

$$= \frac{\dot{m}}{A_s(\rho_s - \rho_\infty)}$$

This equation can be rewritten in terms of density which is easier to obtain than concentration:

$$h_m = \frac{\dot{m}}{A_s\,(\rho_s - \rho_\infty)} \tag{2.7}$$

$$\dot{m} = \frac{\Delta m}{\Delta t} \tag{2.8}$$

Where $\dot{m}$ is the change in mass with respect to a change in time; this value is obtained experimentally. Finally, we can calculate the Sherwood number using the following equation:

$$Sh = \frac{h_m D}{\mathscr{D}} \quad (2.9)$$

2.2 Assumptions

There are several assumptions for the experiment that must be made. One is that both air and the vaporized paradichlorobenzene gas will act as an ideal gas, and that there will be no form of chemical reaction occurring throughout the process. Another is that, because the geometry is a sphere, it can be said to be spherically symmetric meaning that we are only concerned with the radial direction, r. Lastly, it is assumed that the concentration of paradichlorobenzene in the ambient air will be zero due to the large size of the room the experiment will be performed in, and several days will be allowed to pass between each sample test.

CHAPTER 3 – EXPERIMENTAL PROCEDURE

3.1 Preparation

Paradichlorobenzene was chosen as the test material due to its low sublimation rate. In order to cast test samples, paradichlorobenzene was melted in a closed container and subsequently poured into rubber ball casting molds. A small amount of softened paraffin wax was placed over the opening to seal it and prevent loss during cooling. A second function of the wax cap was to hold a thin wooden skewer. The skewer was inserted prior to the benzene solidifying and used in hanging the test sample.

Figure 1: *Test sample recently sealed within tennis ball mold using a wax cap.*

Figure 2: *Sample being cut from mold to begin testing.*

No form of lubrication was required for the molds. Brief tests prior to full casting demonstrated that paradichlorobenzene does not stick to rubber. The benzene was given a minimum of 12 hours to re-solidify; however, before extraction of the test sample occurred, the mold was topped off with additional Paradichlorobenzene and allowed one hour to cool.

Because it would have been too expensive to have three different sized spherical molds either ordered or crafted, dog toy tennis balls were used as the casting molds. The initial hole from the toy's insert was widened slightly so that a funnel could be used for pouring, and the interior of the ball was washed out prior to casting with rubbing alcohol. To remove the test sample from the mold, a hobby knife was traced around the perimeter (being mindful not to cut too deeply and potentially create a distortion in the sample within) and then the halves of the tennis ball were forced open.

3.2 Testing

Before actual removal of the sample from its mold, the Metler Toledo MS-model digital scale was connected to a computer and the scale's accompanying software, LabX Direct Balance, was installed and opened on the computer. The scale was set to print readings into an Excel file every 60 seconds by means of this software. Once the scale set-up was completed, the sample was removed from its mold, and its diameter recorded. Then it was hung underneath the scale so that it would have an open area in which to sublimate. The interval between removal of sample from its mold and its subsequent hanging was considered small enough as to disregard any potential sublimation during that brief period.

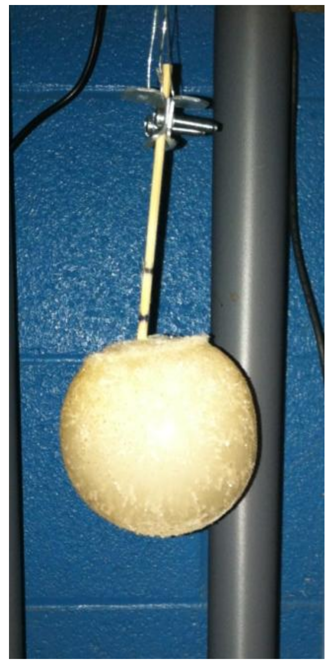

Figure 3: *Test sample hanging from digital scale.*

From this point in the procedure, the experiment was observed over time to confirm the continued spherical shape of the sample as well as to make sure environmental conditions had not been altered. Once the sample's shape became too distorted, the experiment was ended. Two to three days were allowed between samples in order to let the built-up paradichlorobenzene within the room to dissipate.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1 Experimental Results

A summary of all calculated results are provided as well as a list of all constants that were used for the calculations, Tables 1 and 2 below.

Table 1: *Summary of calculated results for each sphere size.*

	Small Sphere	**Medium Sphere**	**Large Sphere**
Diameter, D (m)	0.0403	0.0677	0.0846
Mass Transfer rate, $\dot{m}$ (kg/s)	5.12×10^{-8}	9.63×10^{-8}	1.54×10^{-7}
Grashof number (Eq 2.1)	19.05	90.67	176.87
Rayleigh number (Eq 2.3)	69.33	329.89	643.52
Mass Transfer Coefficient (m/s)	1.22	0.81	0.83
Sherwood number (Eq 2.9)	1.19×10^{4}	1.33×10^{4}	1.71×10^{4}

Table 2: *Constants and material properties used for calculations.*

Ambient Temperature	T_∞ = 72 °F = 295.37 K
Ambient Pressure	P = 1 atm = 101.325 kPa
Gravity	g = 9.81 m/s^2
Properties Used for Air: (Çengel [2007])	ρ_{air} = 1.22 kg/m^3 υ_{air} = 1.50×10^{-5} m^2/s μ_{air} = 1.84×10^{-5} kg/(m s) α_{air} = 2.11×10^{-5} m^2/s k_f = 0.025 W/(m K)
Properties Used for Paradichlorobenzene: (Wolfram Alpha, Snapp [2006])	p_A = 0.137 kPa ρ_s = 8.22×10^{-6} kg/m^3 $\mathscr{D}$ = 4.13×10^{-6} m^2/s M = 147 kg/kmol R = 56.561 J/(kg K)

The results of the recorded mass loss over time were graphed for each of the sphere sizes and can be found in the Appendix for reference. Using these, a graph of the Sherwood number as a function of the Rayleigh number was achieved, provided in Figure 4.

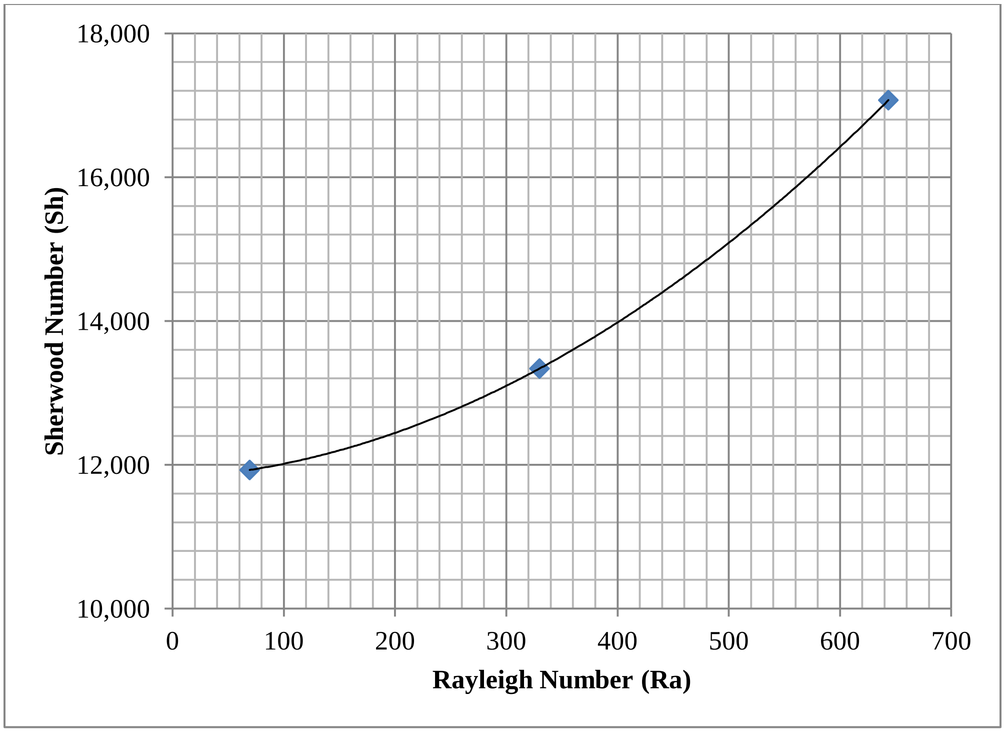

Figure 4: *The Sherwood number as a function of the Rayleigh number for each of the three spheres (with accompanying trend-line).*

We were then able to curve fit the Sherwood numbers and Rayleigh numbers, with an R^2 value of one:

$$Sh = 0.0113(Ra)^2 + 0.9004(Ra) + 11811$$

A summarization of the uncertainties (found in Table 3) was created based on equipment error.

Table 3: *Summary of uncertainties for Sherwood and Rayleigh numbers.*

Sphere Diameter	Sherwood Number	Rayleigh Number
0.0403 m (1.58 in)	± 491.7	± 0.069
0.0677 m (2.67 in)	± 51.4	± 0.195
0.0846 m (3.33 in)	± 17.4	± 0.304

4.2 Discussion and Conclusions

After the data were graphed, the mass transfer rate was determined by observing the sublimation over time of the recorded data.

Once the test sample's diameter changed by 0.5%, the experiment was terminated to maintain the associated geometry of the experimental data for calculation purposes. The spheres were allowed to continue sublimating after the 0.5% reduction in diameter so that their change in shape could be observed, but no more data was taken into account by that time. There was a slight "feathering" of the benzene developing in a ring about the top of the sphere after the termination of the sublimating samples (refer to Figure 3 in the Experimental Procedure section). This ring was assumed to be a build-up of evaporated paradichlorobenzene at the point of separation for the sublimation boundary layer. Because this ring fully developed only after the end of testing, it was ignored in terms of its alteration to the geometry of the sphere for the test itself.

The slight fluctuations in the sublimation graphs (Figures 5-7 in the Appendix) were attributed to uncontrollable fluctuations in temperature and air movement caused by the opening of doors and the ventilation system. Another possible source of error within the experiment could be attributed to potential imperfections during the casting, buried air pockets or even minor variations within the chemical mixture of the paradichlorobenzene used.

4.3 Recommendations for Future Work

One recommendation would be to continue the investigation using paradichlorobenzene, extending the sphere size range. Also, the testing of different geometries such as square or triangular cross-sections could be done to determine their respective Sherwood versus Rayleigh equation types. Another potential investigation would lay in testing the impact of atmospheric pressure changes to paradichlorobenzene tests. Finally, paradichlorobenzene can be bought in varying degrees of purity (99.9%, 99.8%, 99.5%, 99.0etc.). This test was performed using a 99.8% purity of paradichlorobenzene. Perhaps, it could be tested as to what purity percentage will cause paradichlorobenzene to no longer be useful as a test material.

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APPENDICES

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APPENDIX A

Sample Calculations

All calculations were done using the data for the small sized sphere, diameter =0.0403 ± 2×10^{-5} meters.

First calculated using recorded data and its respective graph:

$$\dot{m} = \frac{\Delta m}{\Delta t} = slope\ of\ trend\text{-}line = 5.12 \times 10^{-8} \pm 2.11 \times 10^{-9}\, \frac{kg}{s}$$

The surface density of paradichlorobenzene vapor was needed for calculations:

$$\rho_s = \frac{p_A}{RT} = \frac{0.137\ kPa}{\left(56.56\ \frac{J}{kg\ K}\right)(295.4\ K)} = 8.22 \times 10^{-6}\, \frac{kg}{m^3}$$

where p_A is the vapor pressure of paradichlorobenzene (Wolfram Alpha) and T is the ambient temperature during observation.

Then, the Grashof number was determined:

$$Gr = \frac{g\ (\rho_s - \rho_\infty)\ D^3\ \rho}{\mu^2}$$

$$= \frac{9.81\frac{m}{s^2}\ (8.22 \times 10^{-6}\ \frac{kg}{m^3}\ - 0\frac{kg}{m^3})(0.0403\ \pm 2 \times 10^{-5} m)^3 (1.22\frac{kg}{m^3})}{\left(1.84 \times 10^{-5}\,\frac{kg}{m\ s}\right)^2}$$

$$= 19.05 \pm 1.89 \times 10^{-2}$$

From here, the Schmidt and Rayleigh numbers were calculated:

$$Sc = \frac{\upsilon}{\mathscr{D}} = \frac{1.5 \times 10^{-5}\,\frac{m^2}{s}}{4.13 \times 10^{-6}\,\frac{m^2}{s}} = 3.64$$

$$Ra = Gr\ Sc = (19.05 \pm 1.89 \times 10^{-2})(3.64) = 69.33 \pm 6.89 \times 10^{-2}$$

Now, the mass transfer coefficient can be calculated using:

$$h_m = \frac{\dot{m}}{A_s\,(\rho_s - \rho_\infty)}$$

$$= \frac{6.14 \times 10^{-8} \pm 2.11 \times 10^{-9}\,\frac{kg}{s}}{(1.86 \times 10^{-5} \pm 5.09 \times 10^{-3} m^2)\left(8.22 \times 10^{-6}\,\frac{kg}{m^3} - 0\right)}$$

$$= 401.9 \pm 5.0 \times 10^{-2}\,\frac{m}{s}$$

APPENDIX B

Sublimation Rate Graphs

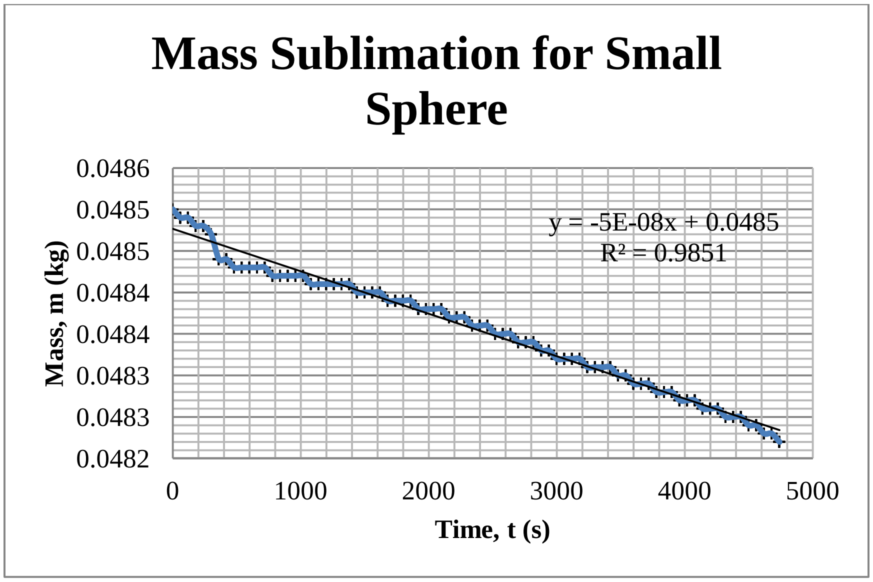

Figure 5: *Mass loss of small diameter sphere as measured in 60 second intervals.*

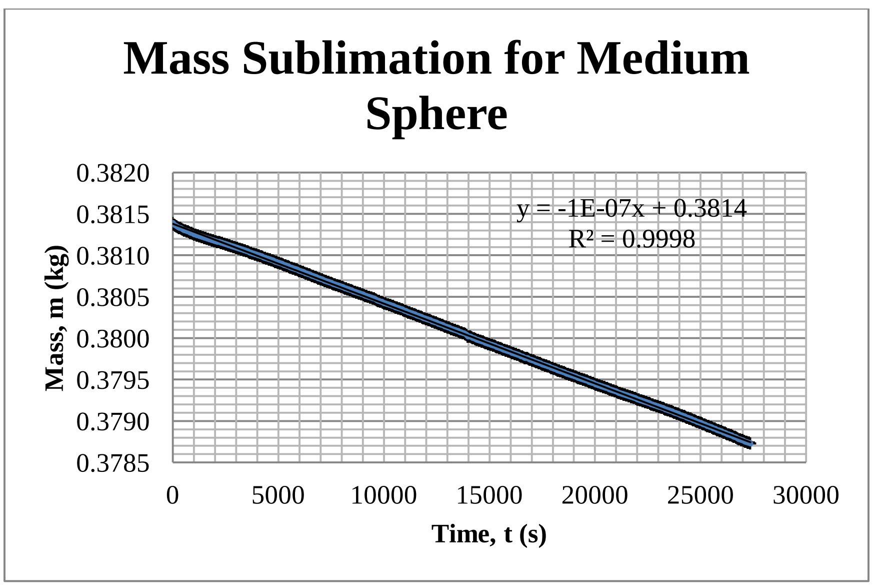

Figure 6: *Mass loss of medium diameter sphere as measured in 60 second intervals.*

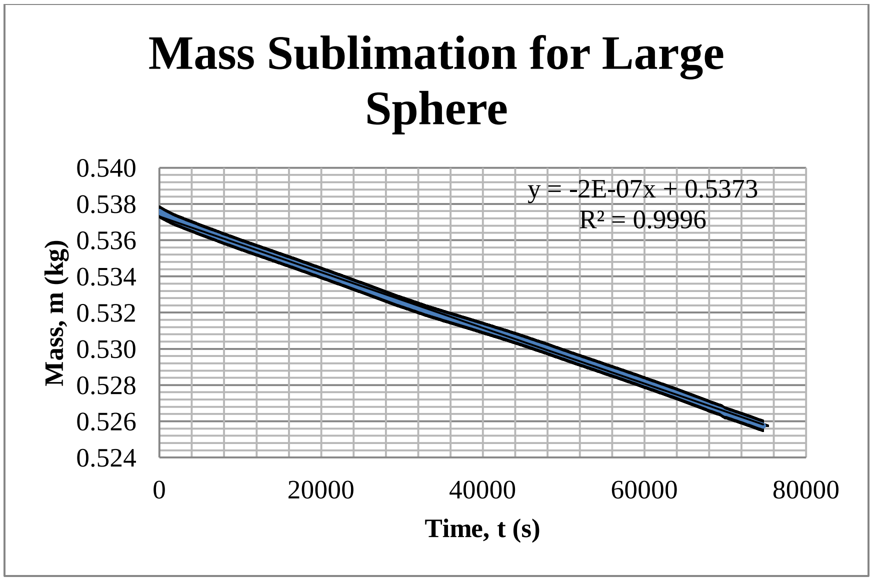

Figure 7: *Mass loss of medium diameter sphere as measured in 60 second intervals.*

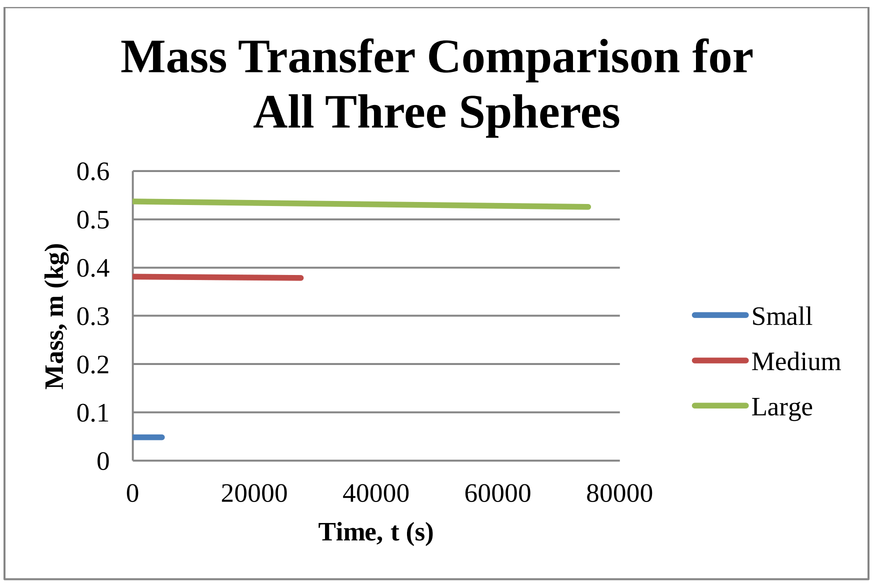

Figure 8: *Comparison of mass sublimation rates for all three spheres to determine if they are parallel over longest time frame.*

APPENDIX C

Mass Transfer Differential Equation Derivation

Density, ρ_A, is interchangeable with concentration, C_A, in the mass derivation due to them both being a measure of the amount of paradichlorobenzene per volume at a particular location from the sphere.

$$\frac{d}{dr}\left[r^2 \frac{dC_A}{dr}\right] = 0$$

Introducing a dimensionless ratio, φ, and boundary conditions at the surface, R, of the sphere and ambient condition's at a distance, ∞:

$$\varphi = \frac{C - C_\infty}{C_R - C_\infty}$$

$$r = R \quad C = C_R$$

$$\varphi = 1$$

$$r = \infty \quad C = C_\infty$$

$$\varphi = 0$$

$$C = \varphi(C_R - C_\infty) + C_\infty$$

$$\frac{dC}{dr} = \frac{dC}{d\varphi}\frac{d\varphi}{dr} = (C_R - C_\infty)\,\varphi'$$

By adding in the solved derivative:

$$\frac{d}{dr}(r^2\,\Delta C\,\varphi') = 0$$

$$r^2\,\cancel{\Delta C}\,\varphi' = B_1$$

$$\varphi' = B_1\,r^{-2}$$

The concentration difference, *ΔC*, was removed because it is a constant. Integrating *φ'* and applying boundary conditions gives:

$$\varphi = B_2 - \frac{B_1}{r}$$

$$r = \infty \quad \varphi = 0$$

$$\therefore \; B_2 = 0$$

$$r = R \quad \varphi = 1$$

$$\therefore \; B_1 = -R$$

$$\varphi = \frac{R}{r}$$

$$\varphi' = -\frac{R}{r^2}$$

Solving the initial mass transfer equation for *J*:

$$J = -\mathscr{D}\,\frac{dC}{dr}$$

$$J = -\mathscr{D}\,(C_R - C_\infty)\,\frac{d\varphi}{dr}\bigg|_{r=R}$$

$$J = -\mathscr{D}\,(C_R - C_\infty)\left(-\frac{R}{R^2}\right)$$

$$J = \frac{\mathscr{D}}{R}\,(C_R - C_\infty)$$

$$R = \frac{D}{2}$$

$$J = \frac{2\mathscr{D}}{D}\,(C_R - C_\infty)$$

Taking the alternate formula for mass transfer:

$$J = h_m(C_R - C_\infty)$$

Then setting them equal to each other:

$$h_m \cancel{(C_R - C_\infty)} = \frac{2\mathscr{D}}{D} \cancel{(C_R - C_\infty)}$$

The concentration differences cancel out leaving:

$$Sh = \frac{h_m\, D}{\mathscr{D}} = 2$$

Because this would be for a mass transfer without convection, a correction amount would be added to the two based upon the geometry of the object in question.