

The Baseline Mass Transfer Coefficient

The Baseline Mass Transfer Coefficient:

*Water and Wastewater
Aeration Systems*

By

Johnny Lee

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This book is dedicated to the memory of Dr. C. R. Baillod who first introduced to the author the concept of a variable gas depletion rate. Dr. Baillod was a most sincere and diligent scholar who thought of nothing but contributing to society. The author also wishes to thank the reviewers for their painstaking review and their insights in this work.

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CHAPTER 1

PROLOGUE

The US EPA in the 70's poured in a substantial amount of money to fund fundamental research, as they recognized the importance of the connection between clean water tests and wastewater tests. Although they have made substantial progress, the fundamental question of relating clean water and wastewater tests remains unresolved. [Mahendrakar V., Mavinic, Donald S., and Rabinowitz, B. (2005a).] A new revolutionary finding may revive their interest.

In aeration systems, diffused air is a simple concept which entails pumping (injecting) air through a pipe or tubing and releasing this air through a diffuser below the water's surface. The submerged system has little visible pattern on the surface, and is able to operate in depths up to and exceeding 12 m (40 ft). The best aerators use quiet on-shore compressors that pump air to diffusers placed at a pond or tank bottom. From stone diffusers to self-cleaning dome diffusers, they release oxygen throughout the water column creating mass circulation that mixes bottom and top water layers, breaks up thermal stratification, and replenishes dissolved oxygen through molecular oxygen mass transfer by means of gas diffusion. Gas transfer is the exchange of gases between aqueous and gaseous phases. In a diffused aeration, gas exchange takes place at the interface between submerged air bubbles and their surrounding water. According to Lewis and Whitman (1924), these bubbles are each wrapped with two layers of films through which the gas must go through. The transfer rate is usually expressed by a mass transfer coefficient symbolized by K_{La} .

No one has seen the two films around a bubble, let alone measuring the thicknesses of these films based on which K_{La} can be quantified. The coefficient can only be determined by an indirect method, such as the one used by the current ASCE standard. The transfer rate can also be determined by mass balances---the gas depletion rate from the bubble must equal the oxygen uptake rate in the liquid. The amount of gas depleted from the bubble at any time not only depends on the films, but also on the path taken by the bubble that follows a gas depletion curve which is a function of many

variables. This curve would vary with different heights and depths. Also, this gas depletion curve in clean water is substantially different from that in wastewater. The loss rate of gas from the bubble is the amount rate transferred at any time and place inside an aeration tank.

Given that the mass transfer coefficient (K_{La}) is a function of many variables, in order to have a unified test result, it is necessary to create a *baseline* mass transfer coefficient, so that all tests will have the same measured baseline. K_{La} is found to be an exponential function of this new coefficient and is dependent on the height of the liquid column (Z_d) through which the gas flow stream passes. DeMoyer et al. (2003) and Schierholz et al. (2006) have conducted experiments to show the effect of free surface transfer on diffused aeration systems, and it was shown that high surface-transfer coefficients exist above the bubble plumes, especially when the air discharge (Q_a) is large. When coupled with large surface cross-sectional area and/or shallow depth, the oxygen transfer mechanism becomes more akin to surface aeration where water entrainment with air from the atmosphere becomes important. The water turbulence has a significant effect on oxygen transfer. The alternative to a judicious choice of tank geometry and/or gas discharge, is perhaps another mathematical model that could separate the effect of surface aeration from the actual aeration under testing in the estimation of the mass transfer coefficient. This separate modelling for surface aeration is not a topic in this book. Nevertheless, a simple graphical method to take this effect into account in the establishing of the *baseline* coefficient is proposed in Chapter 6 Section 6.5.4.

In engineering, the mass transfer coefficient is a diffusion rate constant that relates the mass transfer rate, mass transfer area, and concentration change as driving force, using the Standard Model, typically stated in the form given by eq. 4-1 in Chapter 4. This can be used to quantify the mass transfer between phases, immiscible and partially miscible fluid mixtures (or between a fluid and a porous solid). Quantifying mass transfer allows for design and manufacture of separation process equipment that can meet specified requirements and estimate what will happen in real life situations (chemical spill, wastewater treatment, fermentation, and so forth) if the effect of other factors, such as turbulence either due to the free surface exchange or due to mechanical mixing within the water body, can be isolated, or eliminated or modelled separately.

Mass transfer coefficients can be estimated from many different theoretical equations, correlations, and analogies that are functions of material properties, intensive properties and flow regime (laminar or turbulent flow),

all based on the Standard Model. Selection of the most applicable model is dependent on the materials and the system, or environment, being studied. This book is about the discovery of a new coefficient called the *baseline* mass transfer coefficient (K_{La_0}). The process of this discovery is described in Chapter 3. For open tank aeration, the author defines it as the ordinary mass transfer coefficient (K_{La}) measured at the **equilibrium** pressure of the standard sea-level atmospheric pressure (101.325 kPa). Since most testing is carried out in a vessel of some physical height, the equilibrium pressure must exceed this baseline pressure of 1 atmosphere. If water is used for an aeration test in accordance with current standards [ASCE 2007][CEN 2003][DWA 2007], the system would attain a “super-saturated” state at equilibrium. This super-saturated dissolved gas concentration (C^*_{∞}) would differ from the saturation concentration that can be readily found from published data or any chemistry handbook on gas solubility. The closest experiment that would yield a handbook solubility (C_s) value (and the corresponding baseline mass transfer coefficient) would be a laboratory-scale experiment.

In any other situations, K_{La_0} is not directly measurable. This book is about how the baseline can be determined using the Standard Model for gas transfer, despite the many variables affecting such transfer and K_{La} . Based on the various literature data cited, the baseline has proven to be a valuable parameter (perhaps even more useful than K_{La} itself) that can be used to predict gas transfer under different test conditions, such as different heights or liquid depths. This is a *revolutionary change* as, up to now, it has not been possible to correlate K_{La} from one test to another, even under ordinary testing circumstances. The baseline, however, is a “true” constant for every test. In the context of the meaning of “baseline”, the book is expected to be a baseline itself for future upgrading when more data becomes available. People interested in this book would certainly be scientists, engineers, researchers, treatment plant operators, and manufacturers of aeration systems.

As mentioned, the mass transfer coefficient K_{La} is related to the air discharge and is found to be dependent on the gas average flow rate (Q_a) passing through the liquid column. Q_a is estimated from the gas *mass* flow rate (Q_s), and is expressed in terms of *actual* volume of gas per unit time, as distinct from Q_s that is expressed as *mass* per unit time. For a uniform liquid temperature (T) throughout the liquid column, Q_a is calculated by Boyle’s Law, and taking the arithmetic mean of the volumetric flow rates over the tank column. (Although the mass flow rate Q_s is sometimes also expressed as volume per unit time, it is not true volume because it is expressed as

standard conditions, which is equivalent to mass per unit time.) As such, Q_a is a variable dependent on temperature, pressure and volume, even when the gas supply Q_s is fixed and non-variant.

When an intensive property such as temperature is varied, $K_L a_0$ is directly proportional to this mean gas flow rate (Q_a) to a power q , where q is usually less than unity for water in a fixed column height and a fixed gas supply rate at standard conditions (Q_s). However, $K_L a_0$ is not proportional to Q_s as the case studies presented in this book would show. When temperature is fixed, the same relationship holds for different values of Q_a , regardless of column height. This book provides theoretical development and case studies that verify this baseline which can be standardized specifically to the average gas flow rate as a new function $(K_L a_0)/Q_a^q$ that is applicable to submerged bubble aeration testing. This function is termed the *specific baseline* in this document, and is a constant quantity for any test temperature T . This relationship between the baseline and gas flow can be determined by experiments, as the case studies in Chapter 5 demonstrate, in which it was shown that the overhead (or headspace) pressure is also an intensive property that, when varied, would give the same baseline versus gas flowrate relationship. When the function is determined at standard conditions, it is termed the *standard specific baseline* expressed as $(K_L a_0)_{20}/Q_{a20}^q$ and is a constant independent of tank height Z_d and gas flow Q_a .

Lastly, the suggested replacement of the temperature correction model for the mass transfer coefficient that is based on the Arrhenius equation as stipulated by ASCE Standard 2-06 [ASCE 2007], with the new 5th power model, (see Chapter 2), may be controversial, because the former equation is well known and has been used by the standard for a long time. This controversy is not too important in this manuscript, as all the tests cited were conducted in the neighborhood of 20 °C (within the range of 10 °C to 30 °C), and so there are only small differences in the calculations of $K_L a_{20}$ or $(K_L a_0)_{20}$ between the two models. Nevertheless, a discussion is in order since the new model gives a slightly better correlation between the standard baseline and the gas flow rates in all cases. As Dr. Stenstrom explained for the background: “In the first version of the standard, we debated the value of theta (Θ) ... and found that most of the literature data supported 1.020 to 1.028 with the diffused systems clustering toward the bottom of the range and the surface [aeration systems] clustering toward the top of the range.” [Stenstrom and Lee, 2014].

From this, it can be inferred that there may be two different ranges of the temperature correction factor Θ for the two aeration systems referred to by Stenstrom. Based on analyzing literature data on diffused systems, the author found that the 5th power model fits more closely with a theta (Θ) value in the range of 1.016~1.018 [Lee 2017][Chapter 2] which is closer to the range for diffused systems. Furthermore, the ‘standard-recommended’ theta value of 1.024 is probably based on tests on conventional treatment plants or shop tests of similar height that is usually around 3 m (10 ft) to 4.5 m (15 ft). The 5th power model is suitable for ‘zero’ height since most laboratory tests were carried out on a bench scale of very little height. Since the baseline pertains to a mass transfer coefficient of an infinitesimally shallow tank, it would appear that this new 5th power model is more suitable for correcting the *baseline* to the standard temperature. It should be noted in passing that, temperature is an intensive property (i.e., independent of scale), whereas $K_{L,a}$ is a function of height and other variables, and it is dependent on scale; and so, it cannot be accurately corrected by a single factor that summarily ignores changes in height and other factors.

The book is divided into seven chapters. Chapter 2 below deals with the derivation of the 5th power model for temperature correction. Chapter 3 deals with the development of the model to determine the baseline mass transfer coefficients in aeration tanks. Chapter 4 is dedicated to the derivation and theoretical development of the Lee-Bailod model on which the subsequent depth correction model is based. Chapter 5 illustrates the functionality of the Baseline Mass Transfer Coefficient and Interpretation of Non-steady State Submerged Bubble Oxygen Transfer Data. Chapter 6 asks the question: (Is Oxygen Transfer Rate (OTR) in Submerged Bubble Aeration affected by the Oxygen Uptake Rate (OUR)?), concerning the use of the baseline for in-process field working conditions, and Chapter 7 is the Epilogue that summarizes all the core findings. It is expected that this book would serve practitioners in the designing of aeration systems, as well as serve as Standard Guidelines for water and wastewater (both In-Process and non-In-Process) oxygen transfer testing, enhancing the current standards and guidelines, ASCE 2-06 [ASCE 2007] and ASCE-18-96 [ASCE 1997].

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CHAPTER 2

MASS TRANSFER COEFFICIENT AND GAS SOLUBILITY

2.0 Introduction

The main objective of this chapter is to develop a mechanistic model (based on experimental results of two researchers, Hunter [1979] and Vogelaar et al. [2000]), to replace the current empirical model in the evaluation of the standardized mass transfer coefficient (K_{La20}) being used by the ASCE Standard 2-06 [ASCE 2007]. The topic is about gas transfer in water, (how much and how fast), in response to changes in water temperature. This topic is important in wastewater treatment, fermentation, and other types of bioreactors. The capacity to absorb gas into liquid is usually expressed as solubility, C_s ; whereas the mass transfer coefficient represents the speed of transfer, K_{La} , (in addition to the concentration gradient between the gas phase and the liquid phase which is not discussed here). These two factors, capacity, and speed, are related and the manuscript advocates the hypothesis that they are inversely proportional to each other, i.e., the higher the water temperature, the faster the transfer rate, but at the same time less gas will be transferred.

This hypothesis was difficult to prove because there is not enough literature or experimental data to support it. Some data [ASCE 1997], do support it, but they are approximate, because some other factors skew the relationship, for example, concentration gradient; and the hypothesis is only correct if these other factors are normalized or held constant.

This hypothesis may or may not be proved by theoretical principles, such as by means of thermodynamic principles to find a relationship between equilibrium-concentration and mass transfer coefficient, but such proof is beyond the expertise of the author. However, the hypothesis can in fact be verified indirectly by means of experimental data that were originally used to find the effects of temperature on these two parameters, solubility (C_s) and mass transfer coefficient (K_{La}). Temperature affects both equilibrium

values for oxygen concentration and the rate at which transfer occurs. Equilibrium concentration values (C_s) have been established for water over a range of temperature and salinity values, but similar work for the rate coefficient is less abundant.

This chapter uses the limited data available in the literature to formulate a practical model for calculating the standardized mass transfer coefficient at 20 °C. The work proceeds with general formulation of the model and its model validation using the reported experimental data. It is hoped that this new model can give a better estimate of K_{La20} than the current method.

2.1. The temperature correction model for K_{La}

2.1.1. Basis for model development

Using the experimental data collected by two investigators Hunter [1979] [Vogelaar et al. 2000], data interpretation and analyses allowed the development of a mathematical model that related K_{La} to temperature, advanced in this paper as a temperature correction model for K_{La} . The new model is given as:

$$K_{LaT} = K \times T^5 \times \frac{E\rho\sigma}{P_s} \quad (2 - 1)$$

where K_{La} = overall mass transfer coefficient (min^{-1}); T = absolute temperature of liquid under testing in Kelvin; the subscript T in the first term indicates K_{La} at the temperature of the liquid at testing; and K = proportionality constant; E = modulus of elasticity of water at temperature T , (kNm^{-2}); ρ = density of water at temperature T , (kg m^{-3}); σ = interfacial surface tension of water at temperature T , (N m^{-1}); P_s is the saturation pressure at the equilibrium position (atm). The derivation is based on the following findings as described in Section 2-3.

The model was based on the two-film theory by Lewis and Whitman [1924], and the subsequent experimental data by Haslam et al. [1924], whose finding was that the transfer coefficient is proportional to the 4th power of temperature. Further studies by the subsequent predecessors [Hunter 1979, Boogerd et al. 1990, Vogelaar et al. 2000] unveiled more relationships, which when further analyzed by the author, resulted in a logical mathematical model that related the transfer coefficient (how fast the gas is transferring when air is injected into the water) to the 5th order of

temperature. Perhaps this is also a hypothesis, but it matches all the published data sourced from literature.

Similarly, using the experimental data already published for saturation dissolved oxygen concentrations, such as the USGS (United States Geological Survey) tables [Stewart Rounds 2011], Benson and Krause's stochastic model [Benson and Krause 1984], etc., it was found that solubility also bears a 5th order relationship with temperature.

So, there are actually three hypotheses. But are they hypotheses or are they in fact physical laws that are beyond proof? For example, how does one prove Newton's law? How does one prove Boyle's law, Charles' law, or the Gay-Lussac's law? They can be verified of course, but do not lend themselves easily to mathematical derivation using basic principles. As mentioned, Prof. Haslam found that the liquid film transfer coefficient varies with the 4th power of temperature, but how does one prove it by first principles? The model just fits all the data that one can find although it would be great if it can be proven theoretically. However, the correlation coefficients for (eq. 2-1) are excellent as can be seen in the following sections.

The paper for this chapter is not a theory/modelling paper in the sense that a theory was not derived based on first principles. Nor in fact is it an experimental/empirical paper since the author did not perform any experiments. However, the research workers who did the experiments did not recognize the correlation, and so they have missed the connection. This paper revealed that these data can in fact support a new model that relates gas transfer rate to temperature that they missed. They used their data for other purposes, and drew conclusions for their purposes.

Further tests may therefore be required to justify these hypotheses. Although other people's data are accurate since they come from reputable sources, they are different from experiments specifically designed for this model development purpose only. The novelty of the proposed model is that it does not depend on a pre-determined value of theta (Θ) to apply a temperature correction to a test data for K_{La} , if all other conditions affecting its value are held constant or convertible to standard conditions.

The current model adopted by ASCE 2-06 is based on historical data and is given by the following expression:

$$\frac{K_L a_{20}}{K_L a_T} = 1.024^{(20-T)} \quad (2 - 2)$$

In this equation, T is expressed in °C and not in K (Kelvin) defined for (eq. 2-1). It has been widely reported that this equation is not accurate, especially for temperatures above 20 °C. Current ASCE 2-06 employs the use of a theta (Θ) correction factor to adjust the test result for the mass transfer coefficient to a standard temperature and pressure. The ratio of $(K_L a)_T$ and $(K_L a)_{20}$ is known as the dimensionless water temperature correction factor N, so that

$$N = \frac{K_L a_{20}}{K_L a_T} \quad (2 - 3)$$

Current model is therefore given by:

$$N = \theta^{(20-T)} \quad (2 - 4)$$

where Θ is the dimensionless temperature coefficient. This coefficient is based on historical testing, and is purely empirical. Furthermore, the above equations indicate that the $K_L a$ water temperature correction factor N is exclusively dependent on water temperature. This is definitely not the case, as the correction factor is also dependent on turbulence, as well as the other properties as shown in (eq. 2-1). Current wisdom is to assign different values of theta (θ) to suit different experimental testing. While adjusting the theta (Θ) value for different temperatures may eventually fit all the data, this may lead to controversies. Furthermore, it is necessarily limited to a prescribed small range of testing temperatures.

2.1.2. Description of proposed model

The purpose of this chapter manuscript is to improve the temperature correction method for $K_L a$ (the mass transfer coefficient) used on ASCE Standard 2-06 and to replace the current standard model by (eq. 2-1).

The proposed model can also be expressed in terms of viscosity as described below. Viscosity can be correlated to solubility. When a plot of oxygen solubility in water is made against viscosity of water, a straight-line plot through the origin is obtained [IAPWS 2008]. When the inverse of viscosity (fluidity) is plotted against the fourth power of temperature, the linear curve as shown in Figure 2-1 below was obtained.

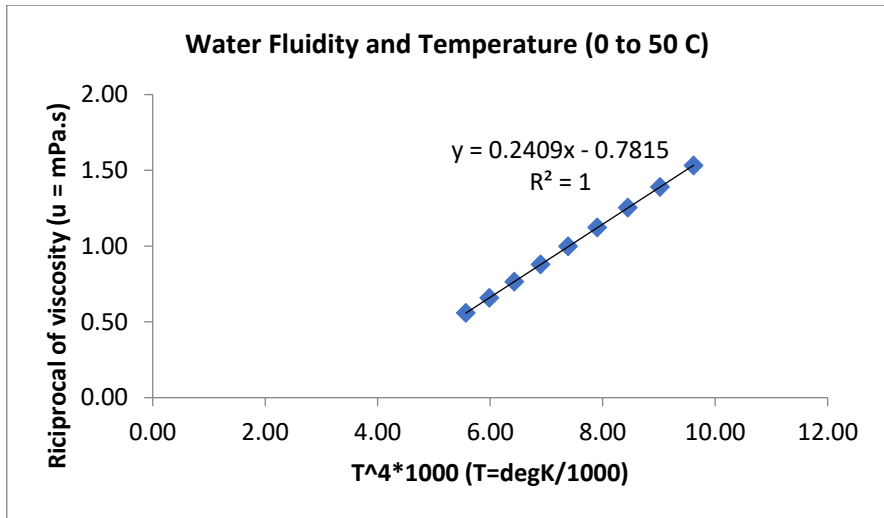


Figure 2-1. Reciprocal of Viscosity plotted against 4th power of temperature

Therefore, viscosity happens to have a 4th order relationship with temperature, so that (Eq. 2-1) can be expressed in terms of viscosity and a first order of temperature, instead of using the 5th order term. The concept of molecular attraction between molecules of water and the oxygen molecule is important since changes in the degree of attraction system would influence the equilibrium state of oxygen saturation in the water system as well as its gas transfer rate. Although the above plot (Figure 2-1) shows that the reciprocal of viscosity (fluidity) is linearly proportional to the 4th order of absolute temperature, the line does not pass through the origin.

As viscosity is closely correlated to solubility, it is obvious that the molecular attraction between water molecules that influences viscosity and the molecular attraction between water and oxygen molecules are interrelated. This correlation does not establish that an alteration of water viscosity, such as changes in the characteristics of the liquid, will have an impact on oxygen solubility. However, it will certainly affect the mass transfer coefficient. Viscosity due to changes in temperature is therefore an intensive property of the system, whereas viscosity due to changes in the quality of water characteristics is an extensive property. The equation relating viscosity to temperature is given by Fig. 2-1 as:

$$\frac{1}{\mu} = 0.2409 \times 10^3 \times \left(\frac{T}{1000}\right)^4 - 0.7815 \quad (2-5)$$

where μ = viscosity of water at temperature T, (mPa.s)

Rearranging the above equation, T^4 can be expressed in terms of viscosity and therefore,

$$T^4 = K' \times \left(\frac{1}{\mu} + 0.7815\right) \quad (2-6)$$

where K' is a proportionality constant.

Substitute (eq. 2-6) into (eq. 2-1), therefore,

$$K_L a_T = K \times \frac{(E\rho\sigma)_T}{P_S} \times K' \times \left(\frac{1}{\mu} + 0.7815\right) \times T \quad (2-7)$$

Grouping the constants therefore,

$$K_L a_T = K'' \times \frac{(E\rho\sigma)_T}{P_S} \left(\frac{1}{\mu} + 0.7815\right) \times T \quad (2-8)$$

where K'' is another proportionality constant.

Therefore, $K_L a$ can be expressed as either (eq. 2-8) or as (eq. 2-1). For the sake of easy referencing to this model, this model shall be called the 5th power model.

2.1.3. Background

The universal understanding is that the mass transfer coefficient is more related to diffusivity and its temperature dependence at a fundamental level on a microscopic scale. Although Lewis and Whitman long ago advanced the two-film theory [Lewis and Whitman 1924] and subsequent research postulated that the liquid film thickness is related to the fourth power of temperature in K [Haslam et al. 1924], it was not thought that this relationship could be applied on a macro scale. In a laboratory scale, Professor Haslam conducted an experiment to examine the transfer coefficients in an apparatus, using sulphur dioxide and ammonia as the test solute. Based on Lewis and Whitman's finding that the molecular diffusivities of all solutes are identical, he derived four general equations that link the various parameters affecting the transfer coefficients which are dependent upon gas velocity, temperature, and the solute gas. He found that

the absolute temperature has a vastly different effect upon the two individual film coefficients. The gas film coefficient decreases as the 1.4th power of absolute temperature, whereas the liquid film coefficient increases as the fourth power of temperature. The discovery that the power relationship between the liquid film coefficient and temperature can be applied to an even higher macroscopic level where C_s is a function of depth, is based on a combination of seemingly unrelated events as follows:

- Lee and Baillo [Lee 1978] [Baillo 1979] derived by theoretical and mathematical development, a formula for the mass transfer coefficient (K_{La}) on a macro scale for a bulk liquid treating the saturation concentration C_s as a dependent variable;
- The derived K_{La} mathematically relates to the “apparent K_{La} ” [ASCE 2007] that is defined in ASCE 2-06 standard;
- It was thought that K_L (the overall liquid film coefficient) might perhaps be related to the fourth power of temperature on a bulk scale similar to the same finding by Professor Haslam on a laboratory scale, as described above;
- John Hunter [Hunter 1979] related K_{La} to viscosity via a turbulence index G ;
- It was then thought that viscosity might be related to the fourth power temperature and a plot of the inverse of absolute viscosity against the fourth power of temperature up to near the boiling point of water gives a straight line;
- the interfacial area of bubbles per unit volume of bulk liquid under aeration is a function of the gas supply volumetric flow rate which is in turn a first-order function of temperature;
- It was then thought that K_{La} might be directly proportional to the 5th power of absolute temperature and indeed so, as verified by Hunter’s data described in the following Section 2.4.1 (Fig. 2-2); the relationship, however, was not exact because the data plot deviates from a straight line at the lower temperature region;
- Adjustment of the initial equation based on observations of the behavior of certain other intensive properties of water in relation to temperature improved the linear correlation with a correlation coefficient of $R^2 = 0.9991$ (Fig. 2-3);
- The relationship is based on fixing (holding constant) all the extensive factors affecting the mass transfer mechanism. Specifically, K_{La} is dependent on the gas mass flow rate. However, since Hunter’s data has slight variations in the gas mass flow rate over the temperature tests, normalization to a fixed gas flow rate

improves the accuracy for the straight line passing through the origin with $R^2 = 0.9994$ (Fig. 2-4).

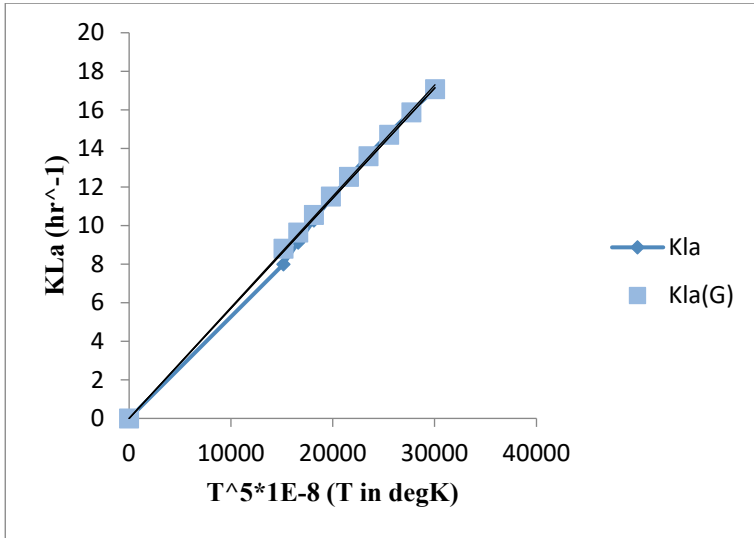


Figure 2-2. K_{La} vs. 5th power of absolute Temperature

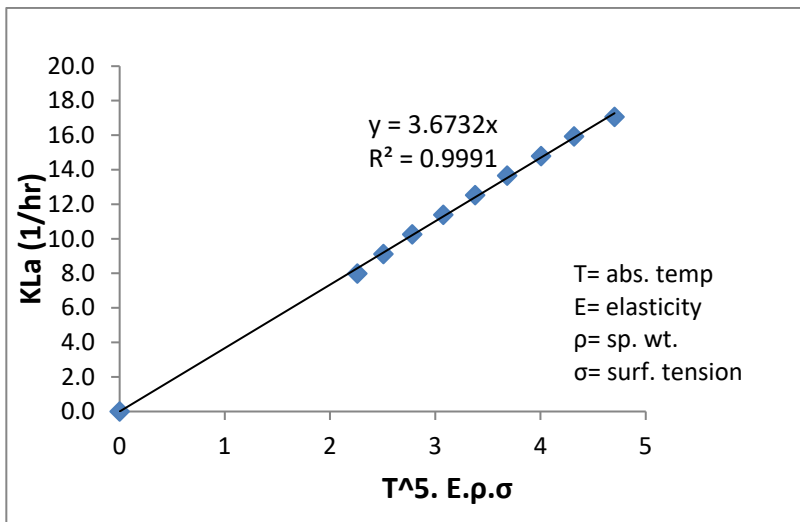


Figure 2-3. K_{La} vs. temperature, modulus of elasticity, density and surface tension

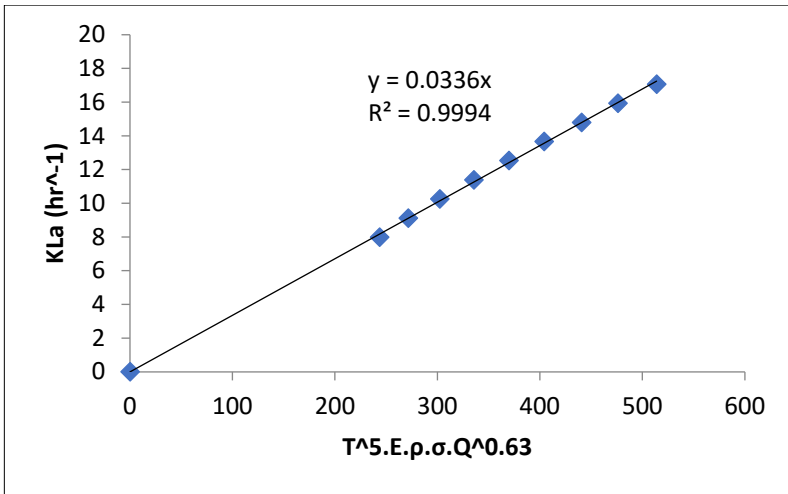


Figure 2-4. K_{La} vs. temperature, modulus of elasticity, density, surface tension, gas flow rate

Based on the above reasoning, data analysis as described in detail in the following sections confirmed the validity of (eq. 2-1), but only for the special case where P_s is at or close to atmospheric pressure (i.e. $P_s = 1$ atm), assuming Hunter's tests were carried out at 1 atm. The experiments described in this paper have not proved that K_{La} is inversely related to P_s . The author advances a hypothesis that K_{La} is inversely proportional to equilibrium concentration (C_s), which can be related to pressure which therefore in turn is related to the depth of a column of water. Since saturation concentration is directly proportional to pressure (Henry's Law), therefore K_{La} must be inversely proportional to pressure, if the reciprocity relationship between K_{La} and C_s is true. This is discussed in another paper published by the author [Lee 2018] and in the following chapters where relevant.

Furthermore, the concept of equilibrium pressure P_s and how to calculate P_s must be clarified for a bulk column of liquid. (The details for the pressure adjustment are given in ASCE 2-06 Section 8.1 and ANNEX G) [ASCE 2007].) Insofar as the current temperature correction model has not accounted for any changes in P_s due to temperature, this manuscript has assumed that P_s is not a function of temperature for a fixed column height and therefore does not affect the application of (eq. 2-1) for temperature correction.

2.2. Theory

The Liquid Film Coefficient (k_l) can be related to the Overall Mass Transfer Coefficient (K_L) for a slightly soluble gas such as oxygen. For any gas-liquid interphase, Lewis and Whitman's two-film concept proved to be adequate to derive a relationship between the total flux across the interface and the concentration gradient, given by:

$$N_0 = K_L \times (C_S - C) \quad (2 - 9)$$

It can be proven mathematically that the bulk mass transfer coefficient is related to the respective film coefficients by the following equation:

$$K_L = \frac{k_g k_l}{H k_l + k_g} \quad (2 - 10)$$

where k_l and k_g are mass transfer coefficients for the respective films that correspond directly to their diffusivities and film thicknesses. H is the Henry's Law constant.

When the liquid film controls, such as for the case of oxygen transfer or other gas transfer that has low solubility in the liquid, the above equation is simplified to

$$K_L = k_l \quad (2 - 11)$$

This means that the gas transfer rate on a macro scale is the same as in a micro scale when the liquid film is controlling the rate of transfer due to the fact that the liquid film resistance is considerably greater than the gas film resistance. The four equations Prof Haslam developed are given below:

$$k_g = 290 \times MU^{0.8} T^{-1.4} \quad (2 - 12)$$

$$k_g = 0.72 \times MU^{0.8} \left(\frac{S}{\mu}\right)^{0.667} \quad (2 - 13)$$

$$k_l = 5.1 \times 10^{-7} \times T^4 \quad (2 - 14)$$

$$k_l = 37.5 \left(\frac{S}{\mu}\right)^{0.667} \quad (2 - 15)$$

Equations (2-12) and (2-13) are not important, since any changes in the rate of transfer in the gas film are insignificant compared to the changes in the

liquid film for a slightly soluble gas such as oxygen. Equation (2-15) relates the liquid film to two physical properties of water, density (ρ) and viscosity (μ). Equation (2-14) is most useful since it relates the mass transfer coefficient directly to temperature, irrespective of the gas flow velocity (U) or the molecular weight (M), and appears to be independent of Equation (2-15). Because the interphase concentrations are impossible to determine experimentally, only the overall mass transfer coefficient K_L can be observed in his apparatus. However, by substituting the values of the film coefficients calculated using the above equations into Equation (2-10), excellent agreement was found between the observed values of the overall coefficients and those calculated. Because of Equation (2-14), it can be concluded that the overall mass transfer coefficient in a bulk liquid is proportional to the fourth power of temperature, given by:

$$K_L = k' \times T^4 \quad (2 - 16)$$

where k' is a proportionality constant.

For spherical bubbles, the interfacial area (a) is given by:

$$a = \frac{Q_a \times 6}{d_b^3} \times \frac{\pi d_b^2}{V} \times t_c \quad (2 - 17)$$

where Q_a = average gas volumetric flow rate (m^3/min); d_b = average diameter of bubble (m, mm); t_c = contact time of bubble with liquid; V = tank volume.

The contact time is dependent upon the path of the bubble through the liquid and can be expressed in terms of the average bubble velocity v_b and the liquid depth Z_d :

$$t_c = \frac{Z_d}{v_b} \quad (2 - 18)$$

where, v_b = average bubble velocity, (m s^{-1})

The area of bubble interface per unit of tank volume V is then

$$a = 6 \times \frac{Q_a}{d_b v_b V} \times Z_d \quad (2 - 19)$$

This shows that for a given tank depth, and a fixed aeration system, 'a' is proportional to the gas flow rate Q_a . The mass transfer coefficient is

dependent on the volumetric gas flow rate which changes with temperature and pressure---the higher the gas flow rate the faster is the transfer rate. The average gas flow rate is dependent on the test temperature of the bulk liquid. With this in mind, Q_a can be determined using the ASCE standard 2-06 [ASCE 2007] as follows:

Combining Eq. A-1b and Eq. A-2b in Section A.5.1 of Annex A where they were written as:

$$Q_1 = Q_P \left(\frac{T_1 P_P}{T_P P_1} \right) \quad (2 - 20)$$

$$Q_S = \frac{Q_1 T_S P_1}{T_1 P_S} \quad (2 - 21)$$

where,

Q_S = gas flow rate given at standard conditions (i.e. the feed gas mass flow rate), (Nm^3/min)

Q_1 = gas flow at the gas supply system

Q_P = gas flow at the point of flow measurement (at the diffuser depth)

P_S = standard air pressure, 1.00 atm (101.3 kPa)

P_1 = ambient (gas supply inlet) atmospheric pressure

P_P = gas pressure at the point of flow measurement

T_S = standard air temperature (293 K for U.S. practice)

T_1 = ambient (gas supply inlet) temperature, K ($= ^\circ\text{C} + 273$)

T_P = gas temperature at the point of flow measurement

By substituting (eq. 2-20) into (eq. 2-21), we have

$$Q_P = Q_S \left(\frac{P_S}{P_P} \right) \left(\frac{T_P}{T_S} \right) \quad (2 - 22)$$

Assuming the mass amount of gas is conserved, as the bubbles rise to the surface, Boyle's Law states that the volume is increased as the liquid pressure decreases, giving the following:

$$Q_{top} = \left(\frac{P_p}{P_b}\right) Q_s \left(\frac{P_s}{P_p}\right) \left(\frac{T_p}{T_s}\right) \quad (2-23)$$

where P_b is the barometric pressure over the tank and Q_{top} is the volumetric flow rate at the top of the tank. The average gas flow rate over the entire column is therefore obtained by averaging of the gas flow rates given by eq. (2-22) and eq. (2-23) and is calculated by $Q_a = 1/2(Q_{top} + Q_p)$ and so,

$$Q_a = \frac{Q_s P_s T_p}{2 T_s} \times \left(\frac{1}{P_p} + \frac{1}{P_b}\right) \quad (2-24)$$

Since $P_s = 1.01325 \times 10^5 \text{ N/m}^2$ and $T_s = 293.15 \text{ K}$ (20°C),

Therefore, substituting the standard values into (eq. 2-24) yields the average gas flow rate in terms of the standard gas flow rate as:

$$Q_a = Q_s \times 172.82 \times T_p \left(\frac{1}{P_p} + \frac{1}{P_b}\right) \quad (2-25)$$

Combining eq. (2-16), eq. (2-19) and eq. (2-25) yield:

$$K_L a = k' T^4 \times 6 Q_s \times 172.82 \times T \times \left(\frac{1}{P_p} + \frac{1}{P_b}\right) \frac{Z_d}{d_b v_b V} \quad (2-26)$$

Grouping all the numerical constants together into one single term, we have

$$K_L a = k'' Q_s \times T^5 \times \left(\frac{1}{P_p} + \frac{1}{P_b}\right) \frac{Z_d}{d_b v_b V} \quad (2-27)$$

where k'' is another proportionality constant. This equation (eq. 2-27) illustrates the 5th power temperature correction relationship as shown in (eq. 2-1) for a fixed height Z_d , volume V , and assuming the pressures and the average bubble diameter (d_b) and velocity (v_b) do not change substantially over the temperature range tested.

As stated above, the response of $K_L a$ to temperature is affected by the behavior of the water properties that are the other variables that also affect the 5th order temperature relationship. As the temperature drops, the density of water (ρ) increases, and the maximum density is at about 4°C . Similarly, the surface tension (σ) also increases with the decrease of temperature. However, the modulus of elasticity (E) decreases as the temperature decreases. This is because the modulus of elasticity is proportional to the

inverse of compressibility, which increases as the water approaches the solid state. Compressibility of water is at a minimum at around 50 °C. Combining all the three variables in response to temperature with the 5th order relationship would result in a curve that resembles the error structure in Hunter's experiment as described in Section 2-4 below. These changes in water properties with respect to temperature are shown in Figs. 2-5, 2-6, and 2-7. The variability of the compound parameter ($E\rho\sigma$) with temperature is also shown in Fig. 2-7 for the elasticity curve. Taking into account the changes in water properties in response to temperature, (eq. 2-27) can be simplified to:

$$K_L a_T = K \times T^5 \times \frac{E\rho\sigma}{P_S} \quad (2 - 28)$$

where the symbols are as defined in (eq. 2-1). The inverse relationship between $K_L a_T$ and P_S is a hypothesis, based on the assumption that $K_L a_T$ and C_{sT} the solubility are inversely related.

2.3. Materials & Methods

To derive a temperature correction model, there are two ways. One is to use the solubility law derived from the solubility table for water, (section 2.5), and the knowledge that $K_L a$ is inversely proportional to C_s , under a reasonable temperature boundary range. The other method is by use of examination and interpretation of actual data performed by numerous investigators, such as Hunter's data [Hunter 1979], on the relationship between $K_L a$ and temperature.

The new model for the correction number N as defined by (eq. 2-3), is based on the 5th order proportionality. Numerous investigators have performed experiments of $K_L a$ determination at different test water temperature, ranging from 0 °C to 55 °C. These data appear to support the hypothesis that $K_L a$ is proportional to the 5th power of absolute temperature for a range of temperatures close to 20 °C and higher. For temperatures close to 0 °C, however, the water properties begin to change in anticipation of a change of physical state. (See Figs. 2-5, 2-6, 2-7 below).