Development of a model to determine mass transfer coefficient and oxygen solubility in bioreactors

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Abstract

The objective of this paper is to present an experimentally validated mechanistic model to predict the oxygen transfer rate coefficient (Kla) in aeration tanks for different water temperatures. Using experimental data created by Hunter and Vogelaar, the formula precisely reproduces experimental results for the standardized Kla at 20 °C, comparatively better than the current model used by ASCE 2–06 based on the equation $K_{la20} = K_{la} (\theta^{20-T}$ where T is in °C. Currently, reported values for $\theta$ range from 1.008 to 1.047. Because it is a geometric function, large error can result if an incorrect value of $\theta$ is used. Establishment of such value for an aeration system can only be made by means of series of full scale testing over a range of temperatures required. The new model predicts oxygen transfer coefficients to within 1% error compared to observed measurements. This is a breakthrough since the correct prediction of the volumetric mass transfer coefficient (Kla) is a crucial step in the design, operation and scale up of bioreactors including wastewater treatment plant aeration tanks, and the equation developed allows doing so without resorting to multiple full scale testing for each individual tank under the same testing condition for different temperatures. The effect of temperature on the transfer rate coefficient Kla is explored in this paper, and it is recommended to replace the current model by this new model given by:
\[ K_{la20} = K_{la}(\frac{E}{E_T})^{20}(\frac{T}{T_0})^5 \]

where \( T \) is in degree Kelvin, and the subscripts refer to degree Celsius; \( E, \rho, \sigma \) are properties of water. Furthermore, using data from published data on oxygen solubility in water, it was found that solubility bears a linear and inverse relationship with the mass transfer coefficient.

Keywords: Physics methods, Physical chemistry, Energy, Chemical engineering, Civil engineering

1. Introduction

The main objective is to develop a mechanistic model (based on experimental results of two researchers, Hunter [1] and Vogelaar [2]) 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 [3]. 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 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) [4].

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 paper 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 Kla\textsubscript{20} than the current method.

2. Model

2.1. The temperature correction model for Kla

2.1.1. Basis for model development

Using the experimental data collected by two investigators [1, 2], data interpretation and analyses allowed the development of a mathematical model that related Kla to temperature, advanced in this paper as a temperature correction model for Kla. The new model is given as:

\[ Kla_T = K \times T^5 \times \frac{E \rho \sigma}{P_s} \]  

(1)

where \( Kla = \) overall mass transfer coefficient (min\(^{-1}\)); \( T = \) absolute temperature of liquid under testing (°K); the subscript \( T \) in the first term indicates Kla at the temperature of the liquid at testing; and \( K = \) proportionality constant. \( E = \) modulus of elasticity of water at temperature \( T \), (kNm\(^{-2}\)); \( \rho = \) density of water at temperature \( T \), (kg m\(^{-3}\)); \( \sigma = \) 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 3.

The model was based on the two film theory by Dr. Lewis and Dr. Whitman [5], and the subsequent experimental data by Professor Haslam [6], whose finding was that the transfer coefficient is proportional to the 4th power of temperature. Further studies by the subsequent predecessors [1, 2, 7] 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 [8], Benson and Krause’s stochastic model [9], 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 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. (1)) are excellent as can be seen in the following sections.

The paper 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 Kla, 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:

\[
\frac{K_{la 20}}{K_{la T}} = 1.024^{(20−T)}
\]  

(2)

In this equation, T is expressed in °C and not in °K defined in (Eq. (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 correction factor to adjust the test result for the mass transfer coefficient to a standard temperature and pressure. The ratio of \((K_{la})_T\) and \((K_{la})_{20}\) is known as the dimensionless water temperature correction factor N, so that

\[
N = \frac{K_{la 20}}{K_{la T}}
\]  

(3)

Current model is therefore given by:

\[
N = \theta^{20−T}
\]  

(4)

where \(\theta\) is the dimensionless temperature coefficient. This coefficient is based on historical testing, and is purely empirical. Furthermore, the above equations indicate that the Kla 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. (1)). Current wisdom is to assign different values of theta (θ) to suit different experimental testing. While adjusting the theta 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 the manuscript is to improve the temperature correction method for KLa (the mass transfer coefficient) used on ASCE Standard 2–06 [3] and to replace the current standard model by (Eq. (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 [10]. When the inverse of viscosity (fluidity) is plotted against the fourth power of temperature, the linear curve as shown in Fig. 1 below was obtained.

Therefore, viscosity happens to have a 4th order relationship with temperature, so that (Eq. (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 would influence the equilibrium state of oxygen saturation in the water system as well as its gas transfer rate. Although the above plot (Fig. 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.

![Water Fluidity and Temperature](image)

**Fig. 1.** Reciprocal of viscosity plotted against 4th power of temperature [10] [4].
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. 1 as:

\[
\frac{1}{\mu} = 0.2409 \times 10^3 \times \left( \frac{T}{1000} \right)^4 - 0.7815
\]

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

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

\[
T^4 = K' \times \left( \frac{1}{\mu} + 0.7815 \right)
\]

where \( K' \) is a proportionality constant.

Substitute (Eq. (6)) into (Eq. (1)), therefore,

\[
K_{\text{la}} T = K' \times \left( \frac{E \rho \sigma}{P_s} \right) T \times K' \times \left( \frac{1}{\mu} + 0.7815 \right) \times T
\]

Grouping the constants therefore,

\[
K_{\text{la}} T = K'' \times \left( \frac{E \rho \sigma}{P_s} \right) T \times \left( \frac{1}{\mu} + 0.7815 \right) \times T
\]

where \( K'' \) is another proportionality constant.

Therefore, \( K_{\text{la}} \) can be expressed as either (Eq. (8)) or as (Eq. (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 [5] and subsequent research postulated that the liquid film thickness is related to the fourth power of temperature in °K [6], it was not thought that this relationship could be applied on a macro scale. In a laboratory scale, Professor Haslam [6] 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 [5] 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 Cs is a function of depth, is based on a combination of seemingly unrelated events as follows:

i. Lee and Baillod [12, 13] derived by theoretical and mathematical development, the mass transfer coefficient (Kla) on a macro scale for a bulk liquid treating the saturation concentration Cs as a dependent variable;

ii. The derived Kla mathematically relates to the “apparent Kla” [3] as defined in ASCE 2-06 [3];

iii. 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;

iv. John Hunter [1] related Kla to viscosity via a turbulence index G;

v. 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;

vi. 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 function of temperature;

vii. It was then thought that Kla might be directly proportional to the 5th power of absolute temperature and indeed so, as verified by Hunter’s data described in Section 4 (Fig. 2); the relationship, however, was not exact because the data plot deviates from a straight line at the lower temperature region;

viii. 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 R² = 0.9991 (Fig. 3);

ix. The relationship is based on fixing all the extensive factors affecting the mass transfer mechanism. Specifically, Kla is dependent of the gas mass flow rate. Since Hunter’s data has slight variations in the gas mass flow rate over the tests, normalization to a fixed gas flow rate improves the accuracy to R² = 0.9994 (Fig. 4), with the straight line passing through the origin.
Fig. 2. Kla vs. 5th power of absolute temperature.

Fig. 3. Kla vs. temperature, modulus of elasticity, density, surface tension.
Based on the above reasoning, data analysis as described in detail in the following sections confirmed the validity of (Eq. (1)), but only for the special case where Ps is at or close to atmospheric pressure (i.e. Ps = 1 atm). The experiments described in this Paper have not proved that Kla is inversely related to Ps. The author advances a hypothesis that Kla is inversely proportional to equilibrium concentration (Cs), 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 Kla must be inversely proportional to pressure, if the reciprocity relationship between Kla and Cs is true.

Furthermore, the concept of equilibrium pressure Ps and how to calculate Ps must be clarified for a bulk column of liquid (The details for the pressure adjustment are given in ASCE 2–06 Section 5 and ANNEX G) [3]. Insofar as the current temperature correction model has not accounted for any changes in Ps due to temperature, this manuscript has assumed that Ps is not a function of temperature for a fixed column height and therefore does not affect the application of (Eq. (1)) for temperature correction.

2.1.4. Theory

The Liquid Film Coefficient (kl) can be related to the Overall Mass Transfer Coefficient (Kt) for a slightly soluble gas such as oxygen. For any gas-liquid interphase, Lewis and Whitman’s two-film concept [5] proved to be adequate to derive a relationship between the total flux across the interface and the concentration gradient, given by:

![Fig. 4. Kla vs. temperature, modulus of elasticity, density, surface tension, gas flow rate.](image-url)
It can be proven mathematically that the bulk mass transfer coefficient is related to the respective film coefficients by the following equation:

$$K_L = \frac{k_g k_l}{H k_l + k_g}$$  \hspace{1cm} (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

$$K_L = k_l$$  \hspace{1cm} (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 [6] developed are given below:

$$k_g = 290 * MV^{0.8} T^{-1.4}$$  \hspace{1cm} (12)

$$k_g = 0.72 * MV^{0.8} \left(\frac{s}{\mu}\right)^{0.667}$$  \hspace{1cm} (13)

$$k_l = 5.1 * 10^{-7} * T^4$$  \hspace{1cm} (14)

$$k_l = 37.5 \left(\frac{s}{\mu}\right)^{0.667}$$  \hspace{1cm} (15)

Eqs. (12) and (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. Eq. (15) relates the liquid film to two physical properties of water, density ($s$) and viscosity ($\mu$). Eq. (14) is most useful since it relates the mass transfer coefficient directly to temperature, irrespective of the gas flow velocity ($V$) or the molecular weight ($M$), and appears to be independent of Eq. (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 Eq. (10), excellent agreement was found between the observed values of the overall coefficients and those calculated. Because of Eqs. (11) and (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:

$$K_L = k' T^4$$  \hspace{1cm} (16)

where $k'$ is a proportionality constant.
For spherical bubbles, the interfacial area (a) is given by:

\[ a = \frac{Q_a \cdot 6}{\pi d_b^2} \cdot \frac{\pi d_b^2}{V} \cdot t_c \]  \hspace{1cm} (17)

Where \( Q_a \) = average gas volumetric flow rate (\( \text{m}^3/\text{min} \)); \( d_b \) = average diameter of bubble (m, mm); \( t_c \) = contact time of bubble with liquid.

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 \( Z_d \):

\[ t_c = \frac{Z_d}{v_b} \]  \hspace{1cm} (18)

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

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

\[ a = 6 \cdot \frac{Q_a}{d_b v_b V} \cdot Z_d \]  \hspace{1cm} (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 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 as follows:

Combining Eq. A-1b in Section A.5.1 of the ASCE standard 2–06 [3] Annex A and Eq. A-2b where they were written as:

\[ Q_1 = Q_p \left( \frac{T_1 P_p}{T_p P_1} \right) \]  \hspace{1cm} (20)

\[ Q_s = Q_1 \frac{T_s P_1}{T_1 P_s} \]  \hspace{1cm} (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
Ts = standard air temperature (293 K for U.S. practice)

T1 = ambient (gas supply inlet) temperature, °K (= °C + 273)

Tp = gas temperature at the point of flow measurement

Substituting (Eq. (20)) into (Eq. (21)), we have

\[ Q_P = Q_S \left( \frac{P_S}{P_P} \right) \left( \frac{T_P}{T_S} \right) \tag{22} \]

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:

\[ Q_{top} = \left( \frac{P_P}{P_b} \right) Q_S \left( \frac{P_S}{P_P} \right) \left( \frac{T_P}{T_S} \right) \tag{23} \]

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 Eqs. (22) and (23) and is calculated by \( Q_a = 1/2(Q_{top} + Q_P) \) and so,

\[ Q_a = \frac{Q_S P_S T_P}{2 T_S} \left( \frac{1}{P_P} + \frac{1}{P_b} \right) \tag{24} \]

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. (24)) yields the average gas flow rate in terms of the standard gas flow rate as:

\[ Q_a = Q_S \times 172.82 \times T_P \times \left( \frac{1}{P_P} + \frac{1}{P_b} \right) \tag{25} \]

Combining Eqs. (16), (19) and (25) yield:

\[ K_L \alpha = k'T^4 \times 6 \times Q_S \times 172.82 \times T \times \left( \frac{1}{P_P} + \frac{1}{P_b} \right) \times \frac{Z_d}{d_b v_b V} \tag{26} \]

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

\[ K_L \alpha = k'' Q_S \times T^5 \times \left( \frac{1}{P_P} + \frac{1}{P_b} \right) \times \frac{Z_d}{d_b v_b V} \tag{27} \]

Where \( k'' \) is another proportionality constant. This equation (Eq. (27)) illustrates the 5th power temperature correction relationship as shown in (Eq. (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 Kla to temperature is affected by the behaviour of the water properties that are the other variables that affect the 5th order temperature relationship. As the temperature drops, the density of water ($\rho$) increases, and the maximum density is at about 4 °C. Similarly, the surface tension ($\sigma$) 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 4 below. These changes in water properties with respect to temperature are shown in Fig. 5, Fig. 6, and Fig. 7.

The variability of the compound parameter ($E\rho\sigma$) with temperature is also shown in Fig. 7 for the elasticity curve. Taking into account the changes in water properties in response to temperature, (Eq. (27)) can be simplified to:

$$Kla_T = K \times T^5 \times \frac{E\rho\sigma}{P_s} \quad (28)$$

where the symbols are as defined in (Eq. (1)). The inverse relationship between Kla$_T$ and $P_s$ is a hypothesis, based on the assumption that Kla$_T$ and $C_s$ the solubility are inversely related. (See Section 4.3 below.)
3. Materials and 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 4.3), and the knowledge that $K_{La}$ is inversely proportional to $C_s$, under a reasonable temperature boundary range. The other method is by use of examination and interpretation of
data performed by numerous investigators, such as Hunter’s data [1], on the relationship between Kla and temperature.

The new model for the correction number N as defined by (Eq. (3)), is based on the 5th power proportionality. Numerous investigators have performed experiments of Kla determination at different test water temperature, ranging from 0 °C to 55 °C. These data appear to support the hypothesis that Kla 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. This change from a liquid state to a solid state at this low temperature is unique to water. However, by incorporating these changes of the relevant properties into the Kla equation, as described previously, it becomes possible to find a high degree of correlation for the data interpretation.

The following paragraphs describe the derivation method to arrive at the proposed temperature correction model by use of experimental data. This derivation is purely based on data interpretation and data analysis using linear graphical verification, and is not derived theoretically.

3.1. Hunter’s experiment

Hunter [1] performed an experiment for the case of laboratory-scale submerged turbine aeration systems. Results shown in Table 1. He derived an equation that relates Kla to the various extensive properties of the system and to viscosity, and correlated his data for a temperature range of 0–40 °C. His method is described in the Paper cited in the manuscript and in his dissertation: Hunter, John S. “A Basis for Aeration Design”. Doctor of Philosophy Dissertation, Department of Civil Engineering, Colorado State University, Fort Collins CO, 1977.

3.2. Vogelaar et al.’s experiment

The experiments performed by J.C.T. Vogelaar et al. [2] consist of determining Kla using tapwater for a temperature range of 20–55 °C using a cylindrical bubble column with an effective volume of 3 litres and subject to aeration flow rates of 0.15, 0.3, 0.45, and 0.56 vvm (volume air volume liquid−1 min−1). The results for one particular volumetric air flow rate (0.3 vvm) among all the data are presented in Section 4.1.2 below.

The following section describes how the data from these two research workers have been used to develop the temperature correction equation for determining Kla20 for any clean water test carried out in accordance with ASCE 2–06, and it is proposed that this new equation is to be used to replace the current equation as stated in ASCE 2–06 Section 5 and the relevant sections concerning the use of (θ)
in the calculation of this important parameter $K_{la,20}$—the standardized $K_{la}$ at standard conditions as defined in the ASCE Standard.

### 4. Results and discussion

Hunter [1] has suggested that turbulence can be related to viscosity as well as the aeration intensity that created the turbulence. In surface aeration, aeration intensity can be the power input to the water being aerated, while in subsurface diffused aeration, it is likely to be the air bubbles flow rate. Therefore, for certain fixed power intensity, Hunter surmised that $K_{la}$ is only a function of viscosity which in turn is a function of temperature. He created a mathematical model that related $K_{la,T}$ to viscosity at different temperatures from 0 °C to 40 °C. His results are given in Table 1, where $K_{la}(G)$ are his modelled results. The model he used was expressed as:

$$K_{la}(G) = (4.04 + 0.00255G^2) \left(\frac{D}{T}\right)^{4}Q^{63}$$

(29)

where $D/T$ is a geometric function. [Note that $T$ in his equation is NOT temperature], $G^2 = P/V/\mu$ where $\mu$ is viscosity, $P$ is the power level (total power input into the water being aerated in ergs/s, and $V$ is the volume of tank in cm$^3$).

The term $G$ was defined as the turbulence index. However, just as in solubility, it is erroneous to consider $G$ as a function of viscosity because viscosity is an intensive property not extensive. Changing the viscosity would not increase turbulence, in the same way turbulence does not affect viscosity for a fixed temperature. However, in his paper’s attachment, he has theoretically derived a relationship between $r$, the rate of gas-liquid interfacial surface renewal, and the turbulence

### Table 1. Hunter’s experimental data (*Note: The air flow rate $Q$ is back calculated from Hunter’s equation at $D/T = 0.35$, $P/V = 2000$).

| $T$ (°C) | Viscosity (poise) | $T/(1000)^5 \times 10^4$ | $K_{la}(h^{-1})$ | $K_{la}(G)(h^{-1})$ | $Q$ (SCFH)* |
|--------|----------------|--------------------------|-----------------|-----------------|-----------|
| 0      | 0.01787        | 273.15                   | 15.21           | 7.99            | 8.8       | 1.093    |
| 5      | 0.01519        | 278.15                   | 16.65           | 9.12            | 9.64      | 1.1      |
| 10     | 0.01307        | 283.15                   | 18.2            | 10.26           | 10.55     | 1.107    |
| 15     | 0.01139        | 288.15                   | 19.87           | 11.39           | 11.51     | 1.113    |
| 20     | 0.01002        | 293.15                   | 21.65           | 12.53           | 12.53     | 1.118    |
| 25     | 0.008904       | 298.15                   | 23.56           | 13.66           | 13.6      | 1.124    |
| 30     | 0.007975       | 303.15                   | 25.6            | 14.79           | 14.71     | 1.128    |
| 35     | 0.007194       | 308.15                   | 27.79           | 15.93           | 15.87     | 1.132    |
| 40     | 0.006529       | 313.15                   | 30.11           | 17.06           | 17.08     | 1.136    |
index G, that they are equal. Since $K_L$, the liquid film coefficient is related to $r$, it can be concluded that turbulence affects the mass transfer coefficient, but this is not due to the apparent correlation between $G$ and $\mu$.

In this table, the observed Kla results are given in column 5. His modelled results are given in column 6. As one can see, his predicted results match up quite well with the true results for those tests carried out at 20 °C and above. At the lower temperature range, however, his errors increase progressively as the temperature drops to the water melting point (freezing point). His results can be seen from the following plot in Fig. 8.

Hunter did not explain why the errors in terms of percent difference become more pronounced toward the lower end of the temperature spectrum, since the turbulence index $G$ has already accounted for the increase of viscosity due to temperature, and so if turbulence was only a function of viscosity, the changes due to viscosity to the mass transfer coefficient should have been taken care of in his equation. However, in his attachment, he did derive an equation that relates Kla not only to $G$, but also to other system variables which he had not defined. (Note: Hunter’s formula did include the extensive properties as system variables in his experiment: geometry, power level, volume, gas flow rate. But while the extensive properties are important factors affecting Kla, it is found in this study that the relationship between Kla and the intensive properties is always linear, and this linear relationship is independent on the extensive properties. The intensive properties are all temperature dependent.) Hunter did not know of the 5th power model. Had he plotted his Kla($G$) values against the 5th power of absolute temperature, he would have been astonished to see a perfect straight line as shown in Fig. 2.

![Fig. 8. Hunter’s data of Kla plotted vs. temperature °C.](image-url)
His model is in fact correct if all the other system variables were fixed, so that Kla is only a function of viscosity. The other system variables are in fact the other properties of water, such as density, modulus of elasticity, and surface tension. As the liquid approaches its melting point (freezing point), it is subject to all the changes in these properties in precedence to the anticipated changes of physical states. These changes in water properties can be seen by plotting the handbook values for these parameters at different temperatures, as shown in Fig. 5, Fig. 6 and Fig. 7.

These changes in the other properties of water, explain why his data starts to deviate from a straight line when the temperature drops below 20 °C. Fig. 7 further shows what happens when Hunter’s data is successively corrected for these changes. The final curve showing the product $E \rho \sigma$ vs. $T$ represents the correction by the product of density, elasticity, as well as surface tension. The curve resembles the error structure in Hunter’s data [1] (comparing col.5 and col.6 in Table 2). And so, when the mass transfer coefficient data is plotted against $T^5$ multiplied by the correction factor $F$ which in this case is given by $\sigma \rho E$, a much better linear relationship is obtained, as is shown in Fig. 3.

4.1. Calculation

4.1.1. Hunter’s data

Data analyses based on Hunter’s experiments [1] has supported that Kla (the oxygen mass transfer coefficient) needs to be corrected for surface tension in addition to $E$ and $\rho$. The effect of surface tension on Kla is more pronounced toward the lower temperature region (below 20 °C and as it gets closer to the melting point (freezing point) of the solvent (Fig. 6).

From (Eq. (8)), it can be seen that Kla20 can be calculated based on a single test data on Kla. It is important to note that the temperature correction factor $N$ should not be calculated as the ratio $u_{20}/u_T$, but as $(K\lambda)_{20}/(K\lambda)_T$, therefore, at 20 °C.

$$K\lambda_{20} = K'' \left( \frac{E \rho \sigma}{Ps_{20}} \right) \left( \frac{1}{\mu_{20}} + 0.7815 \right)$$

(30)

By eliminating $K''$ and assuming $Ps = Ps_{20}$ therefore,

$$K\lambda_{20} = K\lambda \frac{[E \rho \sigma fn(u)]_{20}}{[E \rho \sigma fn(u)]_T}$$

(31)

or, $K\lambda_{20} = K'' \left( \frac{E \rho \sigma}{Ps_{20}} \right) \left( \frac{1}{\mu_{20}} + 0.7815 \right)$

$$N = \frac{[E \rho \sigma fn(u)]_{20}}{[E \rho \sigma fn(u)]_T}$$

(32)

where $fn(u)$ is given by $(1/u + 0.7815)$. 
Similarly, (Eq. (1)) for the 5th power model can be used to calculate $K_{la20}$ and result in the following Table 2 and the following Eq. (33):

$$K_{la20} = Kla \cdot \frac{[E\sigma \cdot T^5]_{20}}{[E\sigma T^5]_{T}}$$

and

$$N = \frac{[E\sigma \cdot T^5]_{20}}{[E\sigma T^5]_{T}}$$

The correction number values are given in column 10 of the following Table 2:

(It should be noted that even without including these additional variables $E$, $\rho$, $\sigma$, the 5th power model already gives a very good fit to the experimental data. In fact, the fifth power model gives a slightly better fit than the enhanced model for temperatures above 20 °C. The effects of these other physical properties seem to wane as the temperature increases toward the boiling point region. This is apparent from Hunter’s model as shown in Table 2 (comparing column 5 and column 6) where the prediction error of his model becomes negligibly small when compared with the observed data when temperature is above 20 °C.) The enhanced model plot that is inclusive of the factors $E$, $\rho$, $\sigma$, is given as Fig. 4 with a high degree of correlation ($R^2 = 0.9991$):

Using the predicted $K_{la20}$ based on the 5th power model, and plotting the simulated results with test temperatures, the following Fig. 9 is obtained:

Table 2. Simulated results for the prediction of $K_{la20}$ by the 5th power model.

| T       | T^5 | Kla | $\rho$ | E/10^6 | $\sigma$ | E.$\rho$.| *Corr. No. F | *Corr. No. N | Kla20 |
|---------|-----|-----|--------|--------|----------|---------|--------------|--------------|-------|
| [degC]  | [degK] | *  | [1/hr] | [kg/m3] | [kN/m2] | [N/m]   |              |              |       |
| 0       | 273.15 | 1.5206 | 7.99   | 999.8  | 1.98     | 0.0765  | 151.44       | 1.051        | 1.496 | 11.95 |
| 5       | 278.15 | 1.6649 | 9.12   | 1000.0 | 2.05     | 0.0749  | 153.55       | 1.036        | 1.348 | 12.29 |
| 10      | 283.15 | 1.8200 | 10.26  | 999.7  | 2.10     | 0.0742  | 155.77       | 1.022        | 1.215 | 12.47 |
| 15      | 288.15 | 1.9865 | 11.39  | 999.1  | 2.15     | 0.0735  | 157.88       | 1.008        | 1.099 | 12.51 |
| 20      | 293.15 | 2.1650 | 12.53  | 998.2  | 2.19     | 0.0728  | 159.15       | 1.000        | 1.000 | 12.53 |
| 25      | 298.15 | 2.3560 | 13.66  | 997.0  | 2.22     | 0.0720  | 159.36       | 0.999        | 0.918 | 12.54 |
| 30      | 303.15 | 2.5603 | 14.79  | 995.7  | 2.25     | 0.0712  | 159.51       | 0.998        | 0.844 | 12.48 |
| 35      | 308.15 | 2.7785 | 15.93  | 993.9  | 2.27     | 0.0704  | 158.48       | 1.004        | 0.782 | 12.46 |
| 40      | 313.15 | 3.0114 | 17.06  | 992.2  | 2.28     | 0.0696  | 157.45       | 1.011        | 0.727 | 12.40 |

* Note:

$F = \frac{(E\sigma)20/(E\sigma)T}$

$N = F \cdot (T20/T)^5$ or $K_{la20} = Kla \cdot N$

$T^5 = (T/1000)^5 \times 1000$
This shows that the variations in the prediction of $K_{la20}$ based on the various tests at different temperatures are very small and in fact are much smaller than would be obtained from using the current ASCE model. Fig. 10 and Fig. 11 show the discrepancies between the various models ($\theta = 1.024$, $\theta = 1.018$, and the 5th model) even further.

It should be clear from these graphs that the 5th power model is superior to the current model that uses the theta correction factor, for temperatures between 10 °C and 30 °C, which is the temperature range stipulated in ASCE 2–06.

The plot in Fig. 3 can be further improved if the Kla data are normalized to the same gas flow rate (data given in Table 2 col. 7 for the flow rates). Hunter’s equation has stipulated that the predicted $K_{la}(G)$ is proportional to the value of
Q^{0.63} and so plotting Kla against the function $T^5\cdot E\cdot p\cdot \sigma$ as well as $Q^{0.63}$ further improves the correlation as shown in the following Fig. 4.

Based on Hunter’s experiment, and the good correlation results as shown in Fig. 3 ($R^2 = 0.9991$), and Fig. 4 ($R^2 = 0.9994$), it can be concluded that for a fixed mass gas flow rate, the mass transfer coefficient under different test temperatures can be calculated by (Eq. (1)). Therefore, the correction number $N$ can be calculated by simple proportion as given by (Eq. (34)). This equation has assumed that $P_s$ remains constant at different temperatures.

### 4.1.2. Vogelaar’s data

Similarly, Vogelaar’s Experiment [2] showed excellent correlation between Kla and Cs for temperatures above 20 °C, and Vogelaar’s experimental result is given in Table 3:

Fig. 12 shows a plot of Kla vs. $T^5\cdot (E\cdot p\cdot \sigma)$ and the correlation is excellent with $R^2 = 0.9975$, assuming $P_s = 1$ atm. However, it is not as good as Hunter’s data using the same model. At 55 °C, the deviation from the straight line is larger than the other data points. It is not clear why this is so. It could be that the distribution of the

| Table 3. Vogelaar’s experimental results. |
|------------------------------------------|
| $T$ (°C) | $T$ (°K) | $(T/1000)^5\cdot 10^4$ | Cs(mg/L) | I/Cs | Kla(h-1) |
|---------|---------|------------------------|--------|-----|---------|
| 0       | 0       | 0                      | 0      | 0   | 0       |
| 20      | 293.15  | 21.65                  | 9.19   | 0.1088 | 22.4 +/- 0.4 |
| 30      | 303.15  | 25.60                  | 7.43   | 0.1346 | 26.0 +/- 0.1 |
| 40      | 313.15  | 30.11                  | 6.5    | 0.1538 | 30.6 +/- 0.2 |
| 55      | 328.15  | 38.05                  | 5.15   | 0.1942 | 38.8 +/- 1.5 |
experimental errors is not even, or that the gas flow rate is not quite identical at this point. In any case, the prediction of $K_{la20}$ is still much better than using $\theta = 1.024$ or any other values except 1.016, as shown in Fig. 13.

At 55 °C, the discrepancy between the theta model and the 5th power model is greater than 30%. When plotting the predicted $K_{la20}$ values using the various models (5th power, $\theta = 1.024$, $\theta = 1.018$, $\theta = 1.016$), the following graph is obtained (Fig. 13).

As seen from this plot, the 5th power model predicts a series of consistent values of $K_{la20}$, whereas the ($\theta$) model using $\theta = 1.024$ gives very poor results. Although
using $\theta = 1.018$ improves the prediction, it is still not as good as the 5th power model. The difficulty of using the ($\theta$) model is that the value of $\theta$ must be determined by pre-testing which is the major disadvantage of this model.

4.2. Methodology

A new model to improve the temperature correction for Kla used in ASCE Standard 02 has been developed. Based on data analyses of two researchers’ work, it can be seen the new model gives excellent simulated results for Kla20 based on series of tests at increasing water temperatures, compared to the other models using the same data as seen in Fig. 9 and Fig. 13. The major function of this model is to predict Kla for any changes in temperature so that Kla20 can be predicted from any one single test at a specific temperature, and therefore would replace the current model in ASCE 2–06 with a higher degree of accuracy. For a certain equilibrium level (de) where the equilibrium pressure is at (Ps), the model is expressed by (Eq. (1)), in which the proportionality constant K is dependent on the extensive properties of the aeration system, such as gas flow rate, bubble size and other characteristics of the system. This equation is not complete because temperature also affects the volumetric gas flow rate $Q_a$. Therefore, as a result of the foregoing analysis, the formula for estimating Kla$_{20}$ based on any given test at a test temperature $T \, ^\circ C$ is given by:

$$Kla_{20} = \frac{Kla}{\rho E \sigma} \left( \frac{P_{30}}{P_s} \right)^{5} \left( \frac{T}{T + 273} \right)^{18} \left( \frac{Q_{a20}}{Q_{aT}} \right)$$

(Eq. 35)

where $T$ is expressed in $^\circ C$. For a series of tests under the same barometric pressure, as in Hunter's experiment, the change in (Ps) due to temperature is likely to be small, and so the ratio $P_{30}/P_{s20}$ can be cancelled. Temperature affects the gas volumetric flow rate, even for a fixed mass gas flow rate. Although Kla$_{20}$ should be normalized to the same average gas volumetric flow rate in order to be more precise, inasmuch as the current equation for correcting Kla in ASCE 2–06 has not accounted for changes in gas flow rate nor any other effects such as (Ps), it is recommended that, for the time being, it is sufficiently accurate to replace the current equation by a simplified equation as shown below, in the effort to standardize the mass transfer coefficient to a standard condition of 20 $^\circ$C and standard atmospheric pressure. For a fixed mass gas flow rate, the equation becomes:

$$Kla_{20} = \frac{Kla}{\rho E \sigma} \left( \frac{P_{30}}{P_s} \right)^{5} \left( \frac{T}{T + 273} \right)^{20} \left( \frac{Q_{a20}}{Q_{aT}} \right)$$

(Eq. 36)

where $T$ is again expressed in terms of degree Celsius.

Eq. (36) is the proposed model for temperature correction for Kla to be used on ASCE Standard 02. Since the values of E, $\rho$ and $\sigma$ for water are fixed, a Table of
correction factors can be compiled to make the application easy, as shown in Table 4, where \( F = \left( \frac{E\rho\sigma}{E\rho\sigma} \right)_{20}/\left( \frac{E\rho\sigma}{E\rho\sigma} \right)_{T} \) and the correction number \( N \) would be given by \( N = F \cdot (T_{20}/T)^{5} \):

In the application of the temperature correction model for \( K_{la20} \), therefore, \( K_{la20} \) is obtained by multiplying \( K_{laT} \) by the correction number \( N \) in column 8 at the test temperature \( T \).

### 4.3. The solubility model

As mentioned in the introduction, the author advocates the hypothesis that solubility is inversely proportional to \( K_{la} \). The foregoing sections have established that \( K_{la} \) is related directly to the 5th order of temperature. If this hypothesis is true, then one would expect the solubility also bears a 5th order relationship with temperature, but in an inverse manner. The following sections illustrate that solubility is indeed related to the 5th order of temperature using published scientific data. This section is significant for 2 reasons:

First, a new physical law is discovered. By definition according to Oxford English dictionary, a physical law “is a theoretical principle deduced from particular facts, applicable to a defined group or class of phenomena, and expressible by the statement that a particular phenomenon always occurs if certain conditions be present.” The rationale behind the solubility law is similar to the Universal Gas Law which is in fact an extension of Boyle's Law or Charles' Law. As Boyle's Law states that for a fixed temperature, volume is inversely proportional to pressure; so

| Table 4. Table of correction factors for the temperature correction model (F, N). |
|-------------------|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| T | T(°K) | \( \rho \) | E/10^6 | \( \sigma \) | E\( \cdot \rho\sigma \) | F | N = F \cdot (T_{20}/T)^{5} |
| °C | (kg/m³) | (kN/m²) | (N/m) |
|---|---|---|---|---|---|---|---|
| 0 | 273.15 | 999.8 | 1.98 | 0.0765 | 151.44 | 1.051 | 1.496 |
| 5 | 278.15 | 1000 | 2.05 | 0.0749 | 153.55 | 1.036 | 1.348 |
| 10 | 283.15 | 999.7 | 2.10 | 0.0742 | 155.77 | 1.022 | 1.215 |
| 15 | 288.15 | 999.1 | 2.15 | 0.0735 | 157.88 | 1.008 | 1.099 |
| 20 | 293.15 | 998.2 | 2.19 | 0.0728 | 159.15 | 1.000 | 1.000 |
| 25 | 298.15 | 997 | 2.22 | 0.072 | 159.36 | 0.999 | 0.918 |
| 30 | 303.15 | 995.7 | 2.25 | 0.0712 | 159.51 | 0.998 | 0.844 |
| 40 | 313.15 | 992.2 | 2.28 | 0.0696 | 157.45 | 1.011 | 0.727 |
| 50 | 323.15 | 988 | 2.29 | 0.0679 | 153.63 | 1.036 | 0.636 |
| 60 | 333.15 | 983.2 | 2.28 | 0.0662 | 148.40 | 1.072 | 0.566 |

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the Universal Gas Law states that, for any pressure and temperature, volume is inversely proportional to pressure, but directly proportional to temperature.

The solubility law relates oxygen solubility in water to the 5th power of temperature, and also to certain properties of water. (Eq. (37) below). This relationship has not appeared in any literature until now and it is therefore accurate to claim that the 5th power inverse relationship is hitherto unknown prior to this manuscript. The author believes that the reason this solubility law has not been discovered earlier like the gas law is that, in the gas law all the parameters are first order and can easily be verified experimentally. In the solubility law, the inverse 5th power phenomenon is not directly observable. Furthermore, the solubility law deals with the interaction of two phases and two species—solute gas and solvent liquid, whereas the gas law deals with only a single gas phase. It is one thing to test a model once it has been discovered, but quite another to find the physical law in the first place.

Second, the law can be applied to real situations in wastewater treatment, and in many bioreactor processes. One of the major applications is the prediction of oxygen transfer in water. The topic discussed in this manuscript is about gas transfer in water, how much and how fast, in response to changes in water temperature. The hypothesis is that Kla and Cs are in fact inversely proportional to each other. This paper demonstrates how the discovered physical law can be compared with the temperature correction model for Kla based on experimental data [1, 2] that will prove the hypothesis that Kla is inversely and linearly proportional to Cs.

4.4. Description of the oxygen solubility model

Oxygen solubility in water is affected by both temperature and pressure. The influence of temperature on the solubility of gases is predictable. The Benson and Krause (1980, 1984) oxygen solubility model is well known and is adopted by the USGS and ASCE 2–06. This model however is only applicable for a special case where the atmospheric pressure is at the standard pressure of 101.3 kN/m². The model is empirical and based on data collected for that pressure only.

Apart from temperature, pressure has a strong effect on the solubility of a gas. For a fixed temperature, the relationship between solubility and pressure is governed by Henry’s Law. Hitherto, however, equation has not existed that combines both effects into one single formula.

Henry’s Law, which states that the solubility (or saturation concentration) of a gas in a liquid is directly proportional to the partial pressure of the gas if the temperature is constant, can be explained by Le Chatelier’s principle in a body of water. The principle states that when a system at equilibrium is placed under stress,
the equilibrium shifts to relieve the stress. In the case of saturated solution of a gas in a liquid, equilibrium exists whereby gas molecules enter and leave the solution at the same rate. When the system is stressed by increasing the pressure of the gas, more gas molecules go into solution to relieve that increase. This happens at the lower regions of a body of water such as an aeration tank or a lake well-mixed. Conversely, when the pressure of the gas is decreased, more gas molecules come out of solution to relieve the decrease and this happens at the upper regions.

The solubility law proposed herewith is an extension of Henry's Law. The proposed solubility law states that for any temperature and pressure, solubility is directly proportional to pressure, and inversely proportional to the fifth power of temperature in absolute, and inversely proportional to density and modulus of elasticity of the solution, expressed as:

\[
Cs = K \frac{Ps}{T^5E\rho}
\]

where,

\(K = \text{proportionality constant. For water of zero salinity, } K \text{ has a value of approximately } 43.4 \text{ kg}^{-2}.N.\text{degK.m}^{-8}.\text{atm}^{-1} \text{ when the units of the parameters are defined as } Cs = \text{mg/L; } Ps = \text{atm; } T = 9K*10^{-3}; E = (kN/m}^2) *10^{-6}; \rho = \text{kg/m}^3\)

Justification of this model, its derivation and verification, and the evaluation of the importance of temperature-dependent properties of water including the bulk modulus of elasticity of water and the density of water in the relationship will be presented later in Section 4.5 below. Since this solubility law is newly discovered in the scientific community, it should be given a name such as the Law of Oxygen Solubility in Pure Water, and the constant K should be called the Oxygen-Water Solubility Law Constant.

4.5. Analysis

There are many ways to confirm a physical law, once it has been discovered. For example, thermodynamic data could be used such as enthalpy and entropy, and the Gibbs free energy may be sufficient to verify the model. This method was used by Desmond Tromans [14] in his derivation of his model of oxygen solubility in pure water. In this manuscript, graphical methods using linear proportions are used. Solubility data for other gases and other liquids are available, so that it should be possible to test the law on other media in order to determine whether the law can be applied to some other liquids. For example, solubilities of oxygen in water of different chlorinities (salinities) are given by USGS, as well as in ASCE 2–06.

In the Office of Water Quality Technical Memorandum 2011.03[8], it was announced the equations that traditionally had been used by the U.S. Geological
Survey (USGS) to predict the solubility of dissolved oxygen (DO) in water resulted in slight discrepancies between values predicted for DO solubility by USGS tables and tables and computer programs compared with values computed by following the methods listed in Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 2005) (Standard Methods). Subsequent analysis resulted in a well-documented recommendation to replace the Weiss (1970) equations with the equations developed by Benson and Krause (1980, 1984).

The Benson and Krause (1980, 1984) oxygen-solubility formulations (now adopted by USGS) are documented in Eqs. (1) and (7) through 11 of the Attachment to the Technical Memorandum. The equations adopted by the USGS and now in line with the Standard Methods are summarized in the following form:

\[
DO = DO_0 \times F_S \times F_P
\]

where the dissolved oxygen (DO) concentration in mg/L is represented as a baseline concentration in freshwater (DOo) multiplied by a salinity correction factor (FS) and a pressure correction factor (FP). All three terms are a function of water temperature. In addition, the salinity correction factor is a function of salinity and the pressure correction factor is a function of barometric pressure. For freshwater (salinity = 0‰) and standard pressure (1 atm), the salinity and pressure factors are equal to 1.0.

\[
DO_0 = \exp \left( -139.34411 + \frac{1.575701 \times 10^4}{T} - \frac{6.642308 \times 10^7}{T^2} + \frac{1.243800 \times 10^{10}}{T^3} - \frac{8.631949 \times 10^{11}}{T^4} \right)
\]  

The salinity correction factor and the pressure correction factor are given by:

\[
F_S = \exp \left[ -S \left( \frac{10.754}{T} + \frac{2140.7}{T^2} \right) \right]
\]

\[
F_P = \frac{P - Pvt}{1 - \theta_0} \left[ \frac{1 - \theta_0}{P - Pvt} \right]
\]

where S is salinity in parts per thousand (‰) and T is temperature in Kelvin. P is the barometric pressure in atmospheres, Pvt is the vapor pressure of water in atmospheres, and θ0 is related to the second virial coefficient of oxygen. Using the above equations it was possible to construct a solubility Table similar to the published Table CG-1 as given in ASCE 2–06. Such a constructed Table for zero salinity is given in Table 5 col. 2:

The other data pertaining to the physical properties of water as shown in Table 5 is from the standard handbook and textbook [11], which enabled calculating:
• a temperature correction function: \( T^{5.5} \cdot \frac{\rho}{P_s} \), and
• the reciprocal of solubility, or Insolubility

When the insolubility \((1/C_s)\) is plotted against the temperature function at \( P_s = 1 \) atm, a straight line passing through the origin is obtained with the correlation \( R^2 = 0.9998 \) (Graph not shown). The significance of this plot is that the extension of the linear plot passes through the point of origin at zero °K. This does not mean the absolute temperature could reach the zero point, but such linear relationship offers a simple means of calculating solubility at any physical parameters of the solvent, by simple ratios. Since water changes from a liquid state to a solid state as the temperature approaches its melting point (freezing point), once the temperature drops past the melting point (normally 0 °C at standard pressure), the law no longer holds and any projection past the solid state is therefore purely hypothetical. If the data of solubility is plotted against the inverse of the temperature correction function affecting solubility, the straight line linear plot would be as shown in Fig. 14. Therefore, the solubility law can be expressed either by the equation derived from plotting the insolubility, or expressed by the equation from plotting the data as in Fig. 14. In the former method, the equation gives the insolubility of oxygen expressed by:

\[
\frac{1}{C_s} = 0.02302 \cdot T^{5.5} \cdot \frac{\rho}{P_s} \tag{41}
\]

where \( T \) is in °K to the power 10^-3.

**Table 5. Physical Properties of water at various temperatures** [11] [3].

| T (°C) | Cs(T) (mg/L) | \( \rho \) (kg/m³) | \( E/10^6 \) (kN/m²) | \( \sigma \) (N/m) | \( \mu \times 10^3 \) (N.s/m²) | \( \gamma \times 10^6 \) (N/m) | \( p_c \) (m²/s) | \( \text{kN/m}^2 \) |
|-------|-------------|---------------------|----------------------|------------------|-------------------|------------------|-----------------|-----------------|
| 0     | 14.62       | 999.8               | 1.98                 | 0.0765           | 1.787             | 1.785            | 0.61            |
| 5     | 12.77       | 1000                | 2.05                 | 0.0749           | 1.518             | 1.519            | 0.87            |
| 10    | 11.29       | 999.7               | 2.1                  | 0.0742           | 1.307             | 1.306            | 1.23            |
| 15    | 10.08       | 999.1               | 2.15                 | 0.0735           | 1.139             | 1.139            | 1.7             |
| 20    | 9.09        | 998.2               | 2.19                 | 0.0728           | 1.002             | 1.003            | 2.34            |
| 25    | 8.26        | 997                 | 2.22                 | 0.072            | 0.89              | 0.893            | 1.17            |
| 30    | 7.56        | 995.7               | 2.25                 | 0.0712           | 0.798             | 0.8              | 4.24            |
| 40    | 6.41        | 992.2               | 2.28                 | 0.0696           | 0.653             | 0.658            | 7.38            |
| 50    | 5.49        | 988                 | 2.29                 | 0.0679           | 0.547             | 0.553            | 12.33           |
| 60    | 4.71        | 983.2               | 2.28                 | 0.0662           | 0.466             | 0.474            | 19.92           |
In the latter case, the equation gives the solubility directly and is expressed by:

\[ Cs = 43.457 \frac{Ps}{T^5E/p} \]  

(42)

Henry's Law is applicable only to ideal solutions [15] [16]; and for an imperfect liquid subject to state changes at extreme temperatures, it is only approximate and limited to gases of slight solubility in a dilute aqueous solution with any other dissolved solute concentrations not more than 1 percent. Similar plots (see Fig. 15) for solubility at different pressures can be made using the following data [15] obtained from downloading from the internet at www.EngineeringToolBox.com to get Table 6:

Fig. 14. Solubility plot for water dissolving oxygen at Ps = 1 atm (1.013 bar).

Fig. 15. Comparison of oxygen solubility plots for various pressures.
Table 6. Solubility of oxygen in fresh water (salinity ~ 0) at different pressures and temperatures [14].

| T(degC) | T(degK) | 1 bar | 2 bar | 4 bar |
|---------|---------|-------|-------|-------|
| 0       | 273.15  | 14.6  | 29.2  | 58.4  |
| 5       | 278.15  | 12.8  | 25.5  | 51.1  |
| 10      | 283.15  | 11.3  | 22.6  | 45.1  |
| 15      | 288.15  | 10.1  | 20.2  | 40.3  |
| 20      | 293.15  | 9.1   | 18.2  | 36.4  |
| 25      | 298.15  | 8.3   | 16.5  | 33.1  |
| 30      | 303.15  | 7.6   | 15.2  | 30.3  |
| 35      | 308.15  | 7     | 14    | 27.9  |
| 40      | 313.15  | 6.5   | 12.9  | 25.9  |
| 45      | 318.15  | 6     | 12    | 24    |
| 50      | 323.15  | 5.6   | 11.3  | 22.7  |

From Fig. 15, the solubility is inversely proportional to the temperature function expressed in terms of $T$, $E$ and $\rho$, so that

$$\frac{1}{Cs} = K(T^5E\rho)$$  \hspace{1cm} (43)

where $K$ is a constant.

Plotting the $K$ values (0.023 at 1 bar; 0.0115 at 2 bar; 0.0057 at 4 bar) from Fig. 15 against the reciprocals of pressures, the following graph shown in Fig. 16 is obtained:

**Fig. 16.** Proportionality constant $K$ plotted against reciprocal of pressure.
Therefore,

\[ K = 0.023 \left( \frac{1}{P_s} \right) \]  

(44)

Combining (Eq. (43)) and (Eq. (44)) we have

\[ \frac{1}{C_s} = 0.023 \left( \frac{1}{P_s} \right) \cdot (T^3 \cdot E \cdot \rho) \]  

or

\[ C_s = 43.478 \frac{P_s}{T^3 \cdot E \cdot \rho} \]  

(46)

(Eq. (46)) is equivalent to (Eq. (42)) showing that solubility is indeed proportional to pressure, in accordance with Henry’s Law. The slight discrepancy in the \( K \) value arises from the two different sources of data, one from Bensen and Krause, and the other from www.engineeringtoolbox.com. But it is likely that the former is more accurate since the solubility data has two decimal places.

5. Conclusions

The primary intent of this manuscript is to replace the geometric technique as used in ASCE 2-06 [3]. The current method that uses an assigned theta (\( \theta \)) value for correcting the effects of temperature on oxygen transfer coefficient (\( \text{Kla}_{20} \)) is empirical and attempts to lump all possible factors, such as changes in viscosity, surface tension, diffusivity of oxygen, geometry, rotating speed, type of aerators, etc. This empirical approach has produced a great variety of correction factors for theta. Therefore, a wide range of temperature correction factors is reported in the literature which has ranged from 1.008 to 1.047 [3]. ASCE 2-06 Commentary CG-3 recommends \( \theta \) to be 1.024 and clean water testing should be at temperatures close to 20 °C. When a value different from 1.024 is proposed, it usually requires justification by an extensive array of testing [7], and preferably full scale for the range of testing temperatures as required, under the same conditions from test to test. This may not be possible at all.

The 5th power model developed is mechanistic in nature. Unlike the conventional empirical model, it does not require the selection of an uncertain parameter (a priori) value, such as theta (\( \theta \)). The correction number \( N \), is independent on the extensive properties of an aeration system in the estimation of \( \text{Kla}_{20} \); whereas the correction number for the \( \theta \) model cannot be applied universally and pertains to the system that was used to obtain the parameter only. The new model should prove to be valid for other similar testing especially in full-scale, because the resultant \( \text{Kla}_{20} \) is dependent only on temperature and the other intensive properties of the fluid, if the extensive properties are fixed.
For the temperature correction model, a formula is derived as defined by (Eq. (36)):

\[
K_{\text{la}20} = K_{\text{la}T} \left( \frac{\rho E \sigma}{\rho E \sigma}_{T} \right)^{5} \left( \frac{T_{20} + 273}{T_{T} + 273} \right)^{5} \tag{47}
\]

The improvement of this model relative to the old model as given by (Eq. (2)) is readily apparent when plotting the simulated Kla20 for both models on a same plot, as shown in Fig. 9, Fig. 10, Fig. 11, and Fig. 13. The prediction error is within 1% for the temperature range between 10 °C and 55 °C. This is assuming that the measured Kla20 in the literature is correct, but there will be experimental error associated with that measurement as well. The improvement over the existing model can be as much as 30% since the error of the old model can be as much. It is recommended that this equation replaces the current ASCE 2–06 model.

Although some extensive properties may change in response to a change in temperature in the new model, such as the volumetric gas flow rate, bubble size, barometric pressure, etc., small changes in these extensive properties can be easily normalized within a reasonable temperature range, such as in the treatment of Hunter’s data, where the gas flow rates are normalized, resulting in an improved correlation. However, this should be verified with testing before changing the Standard. It may be difficult to normalize some extensive variables, such as the rotating speed of an impeller-sparger type of aeration system. The effect of such extensive variables has not been discussed in this manuscript, and if normalization is impractical, testing is required in the same way that the theta model would require.

Hunter’s assertion [1] that “equations do not exist . . . for full scale aeration systems that express Kla as a function of G [the temporal velocity gradient which is dependent on viscosity]” is incorrect. This is because even though turbulence affects Kla substantially, the new model has excluded the turbulence effect due to temperature. Therefore, as long as such extensive variables are fixed, any one test result can be extrapolated to estimate Kla20.

The discovery of a 5th order relationship between solubility and temperature leads to the hypothesis that solubility (Cs) is related to (Kla), but in an inverse manner. Since solubility is related to pressure as given by Henry’s Law, therefore Kla must be related to pressure as well. Therefore, in a clean water test with a deep tank, the effect of pressure at the equilibrium level may need to be considered in the use of (Eq. (1)) for the temperature correction model on Kla.

Apart from the advantage of a more accurate prediction of Kla20, the model has advantages in design. In a treatment process, the best design is usually when the oxygen consumption balances the oxygen supply. This balance is needed not only to save energy but also beneficial from the standpoint of the welfare of the
microorganisms which are very sensitive to water temperature. It is seldom practical to conduct full scale testing for a range of water temperatures under process conditions. Therefore, a more accurate prediction of $K_{LaT}$ would enhance designing the treatment process. This is certainly an enormous advantage in the application of equation CG-1 in ASCE 2–06 for designing the oxygen transfer rate in process condition. However, wastewater characteristics do need to be individually measured in the application of the proposed model, since $E$, $\rho$ and $\sigma$ may all be different from that of pure water.

Declarations

Author contribution statement

Johnny Lee: Conceived and designed the analysis; Analyzed and interpreted the data; Wrote the paper.

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