# Model Reality Check Dalton's Law of Evaporation

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#### **Abstract**

We present a differential equation that models the process of evaporation from a free-water surface, based on the principle of conservation of mass and Dalton's evaporation law. We collected experimental data to verify the accuracy of the analytic solution to the differential equation model. This verification process required the computation of the two vapor-pressure terms appearing in Dalton's equation:

- the saturation vapor pressure of the evaporating water, and
- the partial vapor pressure of the thin layer of moist air just above the evaporating water surface.

We explain these terms and others involved in the underlying physics. Finally, we calculate the proportionality constant in Dalton's equation, based on the slope coefficient of the least-squares linear fit to the experimental data.

The result is excellent agreement between the theoretical model and the experimental results, and it and serves to illustrate the exciting relevance of proper mathematical modeling.

# Background

Evaporation has been studied for hundreds of years, with one of the earliest experimental investigations conducted by Swedish physicist Nils Wallerius in the mid-18th century. Earlier, in the early 1800s, the renowned English physicist John Dalton had published results of his experimental work on evaporation [Dalton 1802], including his famous result known as Dalton's law of evaporation.

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We use Dalton's law of evaporation and the principle of conservation of mass to derive a first-order differential equation that models the evaporation of water from a free-water surface. A *free-water surface* means a water surface exposed to the air at atmospheric pressure, without disturbances that cause waves, with water being able to flow freely. Examples are a flat lake (no wind or waves), or a pan of water set on the ground.

#### Kinds of Evaporation

Evaporation can result from the effects of two different natural processes:

- forced evaporation, which occurs due to air moving across a free liquid surface, under the influence of advection. In this type of evaporation, the evaporative rate is determined primarily by the velocity of the air moving across the surface.
- free evaporation, which results from the process of diffusion. The effects of free evaporation are dependent primarily on the difference in the vapor pressure of the evaporating liquid and the vapor pressure in the thin layer of air just above the free liquid surface. This pressure difference causes the diffusive effects of heat and mass transfer. Free evaporation occurs when molecules in the liquid state experience a sufficient increase in kinetic energy (due to heat) to break their molecular bonds and escape from the liquid in the form of gas. As the liquid evaporates, there is a pressure increase in the thin layer of air just above the surface of the liquid. Evaporation will continue until the vapor pressure in this layer of air equalizes with the vapor pressure of the evaporating liquid.

The mathematical modeling and experimentation presented here focuses on the process of free evaporation.

## Why You Should Be Interested

Understanding both the process of evaporation and its effects is critical in many settings:

- Municipalities and irrigators must plan their water resources based on the effects of evaporation.
- Managers of nuclear power plants that use water for cooling purposes must fully understand the impact of the evaporative process in order to run their plants both safely and efficiently.
- Accurate weather forecasting entails an accurate incorporation of the impact of evaporation on the environment.

# Introduction

We begin by deriving a first-order differential equation that models free evaporation based on the fundamental principle of conservation of mass. This model incorporates Dalton's law of evaporation, and we provide a complete analytical solution of this equation. Then we present evaporation data that were collected experimentally over a period of 14 days. We determine the linear function that best fits the experimental data and then reconcile this function with the analytic solution to the differential equation model. Finally, we discuss our analysis and results.

# The Mathematical Model

The principle of conservation of mass dictates that in any physical or chemical reaction, the quantity of mass of the reactants is conserved. This law was first observed in 1789 by the father of modern chemistry, Antoine Lavoisier, and implies that in any system, mass can neither be created nor destroyed.

Consider a system comprised of water of mass M. The change of mass in this system over time equals the inflow of mass into the system minus the outflow of mass, as follows:

$$\frac{dM}{dt} = \text{mass}_{\text{in}} - \text{mass}_{\text{out}}.$$
 (1)

To determine the effect of evaporation on this system, the inflow of mass into the system is assumed to be 0 in (1) and the outflow of mass from the system is due to evaporation. Dalton's law of evaporation states that the evaporation rate from a free-water surface is directly proportional to the product of

- the area of the free-water surface, and
- the difference between the vapor pressure of the evaporating water and the vapor pressure in the thin layer of air just above the surface of the water [Ferguson 1952].

Dalton's evaporation rate is used to represent the change in mass on the right-hand side of (1) as follows:

$$\frac{dM}{dt} = -kA(p_w - p_a),\tag{2}$$

where

- *k* is Dalton's proportionality constant,
- *A* is the free-water surface area, and

•  $p_w$  and  $p_a$  are the vapor pressures of the evaporating water and of the moist air just above the surface of the water.

Since the mass of the water in the system is equal to its density times its volume, we can write (2) as follows:

$$\frac{d(\rho V)}{dt} = -kA(p_w - p_a),\tag{3}$$

where

- $\rho$  is the density of water (1 g/ml) and
- V is the volume of the water of mass M,

both at standard temperature  $0^{\circ}$  C and pressure of 1 atmosphere. Assuming a constant area A for the free-water surface, the volume can be expressed as

$$V = Ah,$$
 (4)

where h is the height of the water in the system, and (3) can be written as

$$A\frac{dh}{dt} = -kA(p_w - p_a). {(5)}$$

Dividing each side of (5) by A, we arrive at a first-order ordinary differential equation that models the evaporative effects on the height of the water in the system as a function of time, as follows:

$$\frac{dh}{dt} = -k(p_w - p_a).$$
(6)

Equation (6) is a separable differential equation whose integration yields the following integral equation:

$$\int dh = \int -k(p_w - p_a) dt. \tag{7}$$

Performing the indicated integration on both sides of (7) gives the general solution for h as follows:

$$h(t) = -k(p_w - p_a)t + h(0), (8)$$

where h(0) is the height of the water in the system initially. Based on experimental data, we provide in the next section details on the estimated values for both  $p_w$  and  $p_a$ , along with the resulting estimate of Dalton's proportionality constant k.

# The Experiment

To validate Dalton's law as it relates to evaporation of water from a free surface, in addition to computing an estimated value for his proportionality constant, we collected and analyzed experimental data.

A group of students in my Mathematical Modeling course used a cylindrical glass vase of height 228.6 mm and diameter 94 mm and initially filled it with water to a height of 190.5 mm. Over a 14-day period, they took water height measurements (**Table 1**).

**Table 1**. Height of water in vase.

Day	Height $h$ (mm)
0	190.5
3	182.9
10	162.6
14	152.4

A scatterplot of the experimental data from **Table 1** is shown in **Figure 1**, together with the least-squares line of best fit:

$$h = -2.76(\text{Day}) + 190.71.$$
 (9)

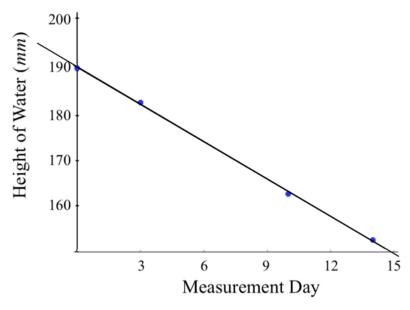


Figure 1. Height of water in the vase vs. days elapsed.

The strength and direction of the linear relationship between measurement day and water height is measured by the correlation coefficient r. Its

value, -.9997, indicates a very strong negative relationship. Close bunching of the data about the negatively-sloped line that models the data provides support for the computed value of r. The value of the coefficient of determination, which measures the proportion of variability in the height of the water that can be explained by a linear fit based on measurement day, is  $r^2 = .9993$ —almost perfect. The graph too shows that a linear fit is almost perfect.

# Data vs. Model

In order to reconcile the experimental data with the solution in (8) to the differential equation, we first need to estimate values for both  $p_w$  and  $p_a$ . Water vapor becomes saturated when it is in equilibrium with a free-water surface at the same pressure and temperature.

#### The Parameter $p_w$

This saturation vapor pressure  $p_w$  of the evaporating water depends only on the surface water temperature. As Alduchov and Eskridge [1996, 603] point out, the various formulas for saturation vapor pressure derived from experiments are "complex and inconvenient to use in calculations" and have led to the use of much simpler (though not as accurate) formulas. In particular, a much simpler approximating form due to Magnus [1844] is

$$p_w = c \exp\left(\frac{aT}{b+T}\right),\tag{10}$$

where a, b, and c are constants and T is the temperature in degrees Celsius. "The main reason to derive approximations ... is to simplify the equations, so that ... it is easy to calculate the saturation vapor pressure using only the temperature [and not powers of it, the logarithm of it, and further exponentials involving it]. ... It is difficult to suggest a more convenient equation for the saturation vapor pressure than the Magnus form." [Alduchov and Eskridge 1996, 604]

Alduchov and Eskridge [1996, 608] recommend the formulation

$$p_w = 6.1094 \exp\left(\frac{17.625T}{243.04 + T}\right),\tag{11}$$

where T is the temperature in degrees Celsius and  $p_w$  is in hectopascals (hPa), as having a maximum relative error of less than 0.4% with respect to three basic (but more-complicated) formulas.

#### The Parameter $p_a$

The estimation of  $p_a$  requires an estimation of the partial pressure of the moisture in the air just above the free-water surface. Relative humidity RH is a measure of the amount of water vapor in air as a percentage of the amount of water vapor required for the air to be saturated at a given temperature. In terms of  $p_w$  and  $p_a$ , RH may be computed as

$$RH = \frac{p_a}{p_w}.$$
 (12)

Using (12), we can estimate  $p_a$  from a calculated value of  $p_w$  from (11) and an estimated value for RH.

The students who collected the experimental data reported a surface water temperature of 19° C. Using this value in (11) yields the estimate  $p_w=21.93~\mathrm{hPa}$ . The experimental data were collected at the home of one of my students in a winter month, and homes typically have RH values in the range of 30% to 40% during winter months [Cormick and Kumaran 2008]. Using an estimate of 0.35 for RH and 21.93 hPa for  $p_w$  in (12), we estimate  $p_a=7.68~\mathrm{hPa}$ .

# Data Inform the Analytic Solution

In order to reconcile the experimental data with the analytic solution to the differential equation model given in (6), we need to estimate the proportionality constant k in (8). We set the slope coefficient from the least-squares equation in (9) to the slope coefficient in (8):

$$-2.76 = -k(p_w - p_a). (13)$$

Using the values for  $p_w$  and  $p_a$  given above, we estimate k = 0.1937. Finally, the initial condition h(0) shown in (8) is set equal to the initial height of the water in the vase, 190.5 mm.

# Discussion

#### The Model Is Not Perfect

The derivation of the differential equation model incorporates some simplifying assumptions about the evaporation process:

In Dalton's equation, we assume that the difference between the saturation vapor pressure of the evaporating water and the partial vapor pressure in the thin layer of air above the surface, known as the vapor pressure deficit, is a constant value during the entire evaporation process.

That is not the case. A modification of Dalton's equation, introduced by Robert Horton and discussed in Vimal and Singh [2022], includes a multiplier term  $\Psi$  on the saturation vapor pressure of the evaporating water. This multiplier is not a constant; it ranges in value from 1 to 2 and accounts for vapor removed by wind action and convection from the vapor blanket. Even if we assume zero wind conditions during data collection, convective vapor removal may be non-negligible, due to varying surface water temperature values.

- A more-rigorous calculation of the saturation vapor pressure of the evaporating water requires the second law of thermodynamics and the Clausius-Clapeyron equation, including the varying latent heat of vaporization [Brown 1951]. In order to maintain liquid-vapor equilibrium at the free-water surface, the Clausius-Clapeyron equation dictates that there is a unique saturation vapor pressure for any given temperature and that this unique vapor pressure increases exponentially with temperature increases.
- A more precise calculation of the partial vapor pressure in the thin layer of moist air above the free-water surface would require the ideal gas law. This more-complicated computation would involve the specific humidity in the thin air blanket, along with the fact that the moist air is composed of multiple gases.

### The Experiment Was Not Perfect

- The experiment was conducted with tap water, which evaporates more slowly than distilled water, since "dissolved salt ions lower the free energy of the water molecules" [Mor et al. 2018].
- The temperature of the water, initially 19° C, may have varied over the course of the experiment (e.g., if the heat in the room was turned down overnight).
- The observations were conducted in Glassboro, NJ, whose altitude is 148 ft / 45 m. Higher altitude has lower air pressure, which increases the rate of water molecules escaping from the surface. So an experiment at a different altitude would likely give different values for  $p_w$ ,  $p_a$ , and k. At a particular location, "atmospheric pressure doesn't fluctuate by more than few percent" [Infoplease 2022] (apart from storms, hurricanes, and tornadoes). The normal small daily variation in atmospheric pressure over the course of the experiment would tend to average out over the course of the experiment.
- The measurements with the precisions presented contain natural measurement uncertainties: temperature ( $\pm 0.5^{\circ}$  C), heights ( $\pm 0.05$  mm), and relative humidity ( $\pm 5\%$ ). The uncertainties could be carried through

to calculate corresponding uncertainties in  $p_w$ ,  $p_a$ , and k (whose values are not as precise as the number of decimal places that we report).

- Despite the high value of the coefficient of determination, the slope -2.76 of the line of best fit contains some uncertainty; it has a standard error of 0.05. Ideally, the experiment would be replicated, to reduce chance variation and uncertainty in the slope.
- We assume that the data were taken at the same time each day. Additional data on other days might have resulted in less uncertainty in the slope of the line of best fit. However, if the experiment had been longer, perhaps there would not have been so strong a linear relationship.
- The density of water at standard temperature and pressure is 1 g/ml. However, the difference from that value in the density of the water during the course of the experiment—due to differences and changes in temperature, pressure, and salinity—can be considered negligible.

## The Result

So the values of the parameters  $p_w$ ,  $p_a$ , and k in the resulting equation are subject to variability in light of the considerations above.

On the positive side, however, the graph of the data suggests a very strong negative linear relationship between time elapsed and the height of the water in the vase. The negative association is intuitively expected, since the evaporative process naturally results in lesser amounts of water in the vase with each passing day. The linear relationship exhibited in the experimental data is consistent with the work of Dalton, whose law is based on the simplifying assumption that the vapor pressure difference is constant during evaporation.

In short, the experimental data confirm our model spectacularly, and we have provided a validated underpinning model for Dalton's law of evaporation.

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# **About the Author**



Paul Laumakis earned an M.A. in Mathematics from Villanova University and a Ph.D. in Applied Mathematics from Lehigh University. He is a professor of mathematics at Rowan University, where he has developed and teaches a mathematical modeling course for undergraduate mathematics majors. Paul has created various capstone projects for the course that give students the opportunity to research, develop, and solve a mathematical model, collect and analyze experimental data, and report their results through formal classroom presentations.

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