

Derivation of a working Manometric Temperature Measurement (MTM) Equation - Part I

Given a model for lyophilization consisting of vials of ice, there is a difference in the pressure of the chamber established by the vacuum pump, and the pressure at the surface of the ice, established by the Clausius-Clapeyron(C-C) equilibrium. If we knew, or could measure the equilibrium pressure then we could use the C-C equation to calculate the ice surface temperature. That would be good because we could then do away with thermocouples.

Now consider, if we were to suddenly isolate the chamber by closing a valve to the vacuum, then the pressure of the chamber would rise to be the same as the vapor pressure of the ice at the temperature of the ice interface. If we could simultaneously stop heating the ice by instantly making the shelf the same temperature as the bottom of the ice, then we could wait for equilibrium and from the newly established chamber pressure we would know the ice temperature. Although it would be challenging from an engineering perspective to do the experiment exactly, it is not so difficult to do it mathematically.

Let's start with an expression for the change in moles of ice with time. The change in mass per unit time is equal to total area of ice times pressure difference divided by resistance.

$$\frac{d}{dt} n = \frac{N \cdot A \cdot (P_i - P)}{R_p}$$

Equation 1

N = number of vials

A = Ice Area of one vial

P_i = pressure at the ice interface

P = Pressure in the chamber at any time t.

n = moles of water vapor.

This equation may not at first seem obvious, but will become more so once resistance is defined. In this case, we are referring to the resistance caused by molecular collisions with "stuff" as the molecules of water attempt to depart the ice surface. Let's define resistance using Ohm's law. First, E = I*R. Moving from electricity to water, Volage (E) becomes pressure (P). Amperage I, becomes throughput ((moles/s)/area). So

$$R = \frac{P}{\text{ThroughPut}} = \frac{\text{Pa}}{\frac{\frac{\text{mol}}{\text{s}}}{\text{m}^2}} . \text{ Of course this is expressed as } \frac{\text{Pa} \cdot \text{m}^2 \cdot \text{s}}{\text{mol}} . \text{ It can also be defined as } \frac{\text{Pa} \cdot \text{m}^2 \cdot \text{s}}{\text{kg}} . \text{ Be}$$

careful of the definition. The definition with kg is assuming that water is the departing molecule and dividing by .018 kg/mol to get kg in the denominator.

Now that we have defined resistance, one can see that the numerator of EQN #1 represents pressure x area, and that a unit analysis of equation one gives moles/sec on both sides.

$$\frac{d}{dt} n = \frac{\text{m}^2 \cdot \text{Pa}}{\left(\frac{\text{Pa} \cdot \text{m}^2 \cdot \text{s}}{\text{mol}} \right)} = \frac{\text{mol}}{\text{s}} \quad \Leftarrow \text{Unit analysis}$$

There is another, better known equation, that also involves pressure and moles. That would be the "ideal gas law". $P \cdot V = n \cdot R \cdot T$. If we solve for n and take the derivative of both sides with respect to time, taking volume and temperature to be constant, we get Equation 2.

$$\frac{d}{dt} n = \frac{d}{dt} P \cdot \frac{V}{R \cdot T} \quad \text{EQ \#2} \quad \text{Differential Form of the Ideal GAS LAW.}$$

$$\frac{N \cdot A \cdot (P_i - P)}{R_p} = \frac{d}{dt} P \cdot \frac{V}{R \cdot T} \quad \Leftarrow \text{Equate Equations 1 and 2}$$

$$\frac{d}{dt} P = \frac{N \cdot A \cdot (P_i - P) \cdot R \cdot T}{R_p \cdot V} \quad \Leftarrow \text{Solve for } dP/dt \quad \text{EQ \#3}$$

So why again are we doing all of this? It is to look at the change in chamber pressure with time that results from suddenly isolating the evacuated lyo chamber away from its vacuum pump. We know the pressure will rise to the equilibrium vapor pressure of the ice and we further know that using the Clausius-Clapeyron equation [to be introduced later], we will be able to predict the ice temperature from the equilibrium chamber pressure. Indeed, if we could actually do this experiment, then there would be little need for a kinetic analysis since it is the equilibrium pressure that is desired. However, as will be seen later, there are a few nuances (nuisances) that seem to require fitting of the kinetic data to predict the equilibrium pressure.

Introduce the collective variable k to ease an upcoming integration.

$$\frac{d}{dt} P = \frac{N \cdot A \cdot (P_i - P) \cdot R \cdot T}{R_p \cdot V} = k \cdot (P_i - P) \quad k = k' \cdot \frac{T_v}{R_p} \quad k' = \frac{N \cdot A \cdot R}{V} \quad \text{Eq \#3a}$$

aside: If R_p had been defined as $\text{Pa} \cdot \text{m}^2 \cdot \frac{\text{s}}{\text{kg}}$ instead of $\text{Pa} \cdot \text{m}^2 \cdot \frac{\text{s}}{\text{mol}}$ then

$$k' = \frac{N \cdot A \cdot R}{V \cdot 0.018 \frac{\text{kg}}{\text{mol}}}$$

k' is a constant for any given run. i.e. in a given lyo at a fixed number of vials, fixed vial, fixed starting volume, fixed product, while k is only a constant for one particular execution of the experiment. Remember that the experiment is to isolate the chamber and watch the pressure rise. Each time that is done, the resistance may be different and the ice temperature may be different.

One might ask, what temperature is being held constant in the ideal gas law. We know that temperature, pressure and volume are related by the gas law. In this case we are talking about the temperature of the gas in the open volume of the chamber. Roughly that temperature is constant and pressure rises as a consequence of the mass rising. Most of the time, we do experiments with fixed mass and it is common to say that with fixed volume Pressure and Temperature vary together. Not so, if the mass is allowed to change.

$$\frac{d}{dt}P = k \cdot (P_i - P) \quad \Leftarrow \text{Equation 3a, simplified form.}$$

From here to the first answer is just algebra and calculus. Our goal is to solve the differential equation for Pressure, P .

$$\frac{dP}{P - P_i} = -k \cdot t \quad \text{Change the sign and separate the variables.}$$

$$\int_{P_0}^P \frac{1}{P - P_i} dP = \int_0^t -k dt \quad \text{Integrate both sides. } P_0 \text{ is the chamber pressure at time 0.}$$

$$\ln\left(\frac{P - P_i}{P_0 - P_i}\right) = -k \cdot t \quad \text{Show the integral result}$$

$$\frac{P - P_i}{P_0 - P_i} = e^{-k \cdot t} \quad \text{Algebra}$$

$$P - P_i = (P_0 - P_i) \cdot e^{-k \cdot t} \quad \text{More Algebra}$$

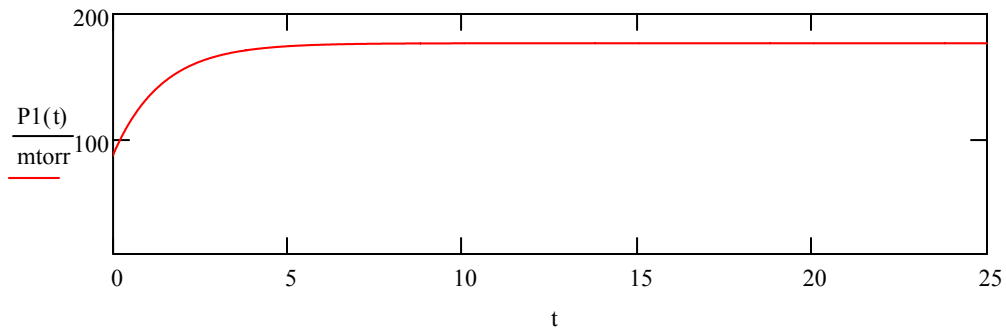
$$P(t) = P_i + (P_0 - P_i) \cdot e^{-k \cdot t} \quad \text{Final answer. EQ \#4}$$

Notice how rapidly this equilibrium is established, and under these ideal conditions how flat the equilibrium pressure line is.

$$P_1(t) := P_i - (P_i - P_0) \cdot e^{-k \cdot t}$$

$$k = 0.726 \frac{1}{s} \quad P_i = 23.598 \text{ Pa} \quad P_0 = 11.866 \text{ Pa}$$

The idea is to fit this equation (or an even more complex one) to actual data in order to find P_i , and then convert P_i to T_i using Clausius Clapeyron



Although one could hardly hope to fit this equation to data, let's suppose for an instant that you could. Then we could obtain then ice interface temperature by a simple transformation, using the Clausius-Clapeyron Equation.

$$P_i = \xi \cdot e^{\frac{-\Delta H_{\text{sub}}}{R \cdot T_i}} \quad \Leftrightarrow \text{Clausius Clapeyron Equation} \quad \xi = 3.493 \times 10^{12} \text{ Pa}$$

$$T_i := \frac{-\Delta H_{\text{sub}}}{\ln\left(\frac{P_i}{\xi}\right) \cdot R} \quad T_i = 238.607 \text{ K} \quad T_i = -34.543 \text{ }^\circ\text{C}$$

In the next section, we will add in a term for the change in temperature that results from heating of the interface during the time that the valve is closed and look at the additional pressure rise that results.