

Using Seger's Standard Cones to Model Ceramic Melting Temperatures

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Abstract

This short paper presents a model of the melting temperature for clay bodies. Using Concepts developed by Herman Seger in 1886, Ceramicists are able to monitor kiln temperatures chemically rather than mechanically or electrically (This becomes useful at high temperatures since most electrical and mechanical devices cannot function under such intense heat). Using Seger's Pyrometric cones to monitor kiln temperatures, we can model the melting temperature of different clay bodies, as well as various glazes.

Keywords: Eutectics, Eutectic mixture, Alumina, Silica, Ceramics, Clay, Pyrometric Cones, Herman Seger, Melting Temperature, Kiln Temperature.

1 Pyrometric Cones

Pyrometric cones approximate the temperature in the kiln using a eutectic mixture of glass formers and fluxes. The glass formers of interest are Silica(SiO_2) and Alumina(Al_2O_3) and the fluxes are predominantly Potassium Oxide(K_2O) and Calcium Oxide(CaO). Each cone has a different molecular ratio of these glass formers and fluxes, and by letting the fluxes remain constant and varying the amount of glass formers we have cones that melt at different temperatures.

Cones, due to varying amounts of glass formers, will melt at different temperatures which signifies the temperature of the kiln and the rate of temperature increase. They are most often used in sets of 3-5 with the exception of bisque firings. Using sets of 3-5 help the ceramicist to see the range of temperature the kiln is at. A typical high-fire kiln will have at least two sets of 3-5 to assure the entirety of the kiln has reached the desired temperature, since temperatures differ in different regions of the kiln. The next page shows a figure of what cones look like before and after a firing.

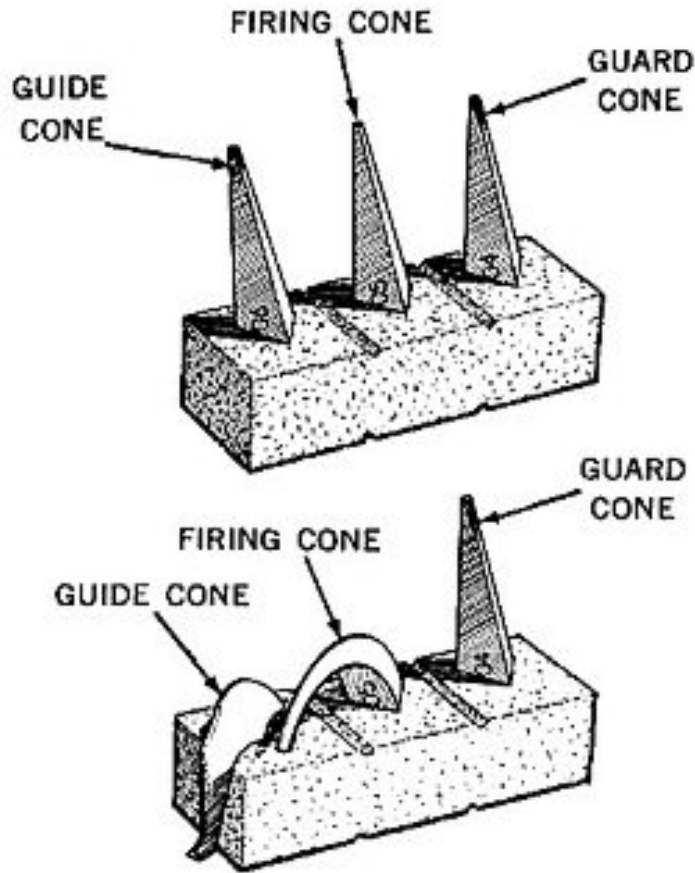


Figure 1: Cone packs before and after firing

1.1 Cone Composition and Heating

As stated previously, pyrometric cones have a varying amount of glass formers corresponding to certain temperatures. Cones are a simplification of clay and glazes. For example, low fire clay bodies may be much darker in color due to amounts of iron oxide in the clay. Iron oxide at low temperatures acts like a flux and can throw off our predicted melting point. Pyrometric cones only have 4 compounds in them, whereas clay and glazes are intricate mixtures of many complex compounds. Although it may seem straight forward, there are contaminants and residual amounts of unaccounted fluxes and glass formers that change the outcome slightly. Our model will be based off of cone composition and their respective melting temperatures, and hence we have already simplified a complex eutectic problem. This is good and bad, since this will help us construct a model but we lose some accuracy. Other forms of error will be discussed in the last section of this paper. The next page contains a table of relevant values for cone compositions and melting points. Note that the melting point changes with different heating rates, This will be a main point of discussion later.

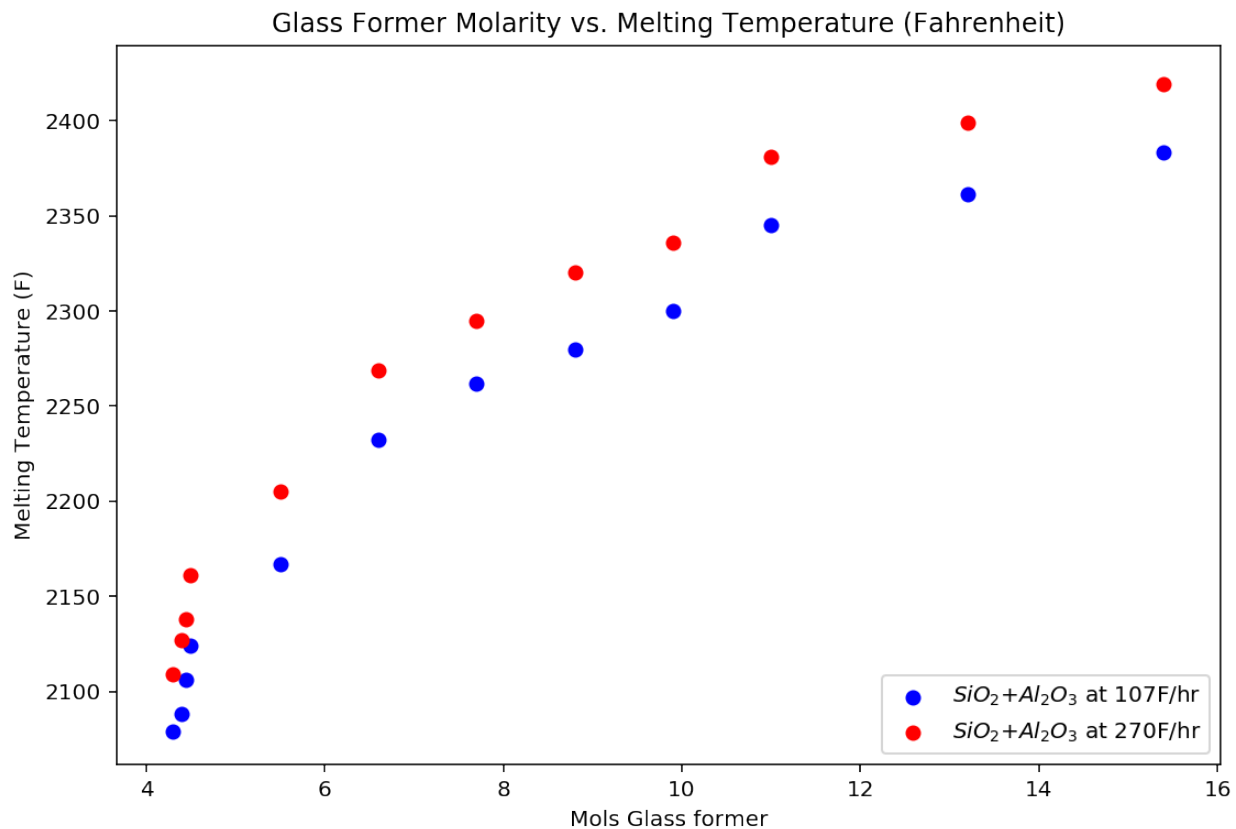
Cone #	K ₂ O	CaO	Al ₂ O ₃	SiO ₂	Melting Temp(F) (108F/hr)	Melting Temp(F) (270F/hr)
1	0.3	0.7	0.3	4.0	2079	2109
2	0.3	0.7	0.4	4.0	2088	2127
3	0.3	0.7	0.45	4.0	2106	2138
4	0.3	0.7	0.5	4.0	2124	2161
5	0.3	0.7	0.5	5.0	2167	2205
6	0.3	0.7	0.6	6.0	2232	2269
7	0.3	0.7	0.7	7.0	2262	2295
8	0.3	0.7	0.8	8.0	2280	2320
9	0.3	0.7	0.9	9.0	2300	2336
10	0.3	0.7	1.0	10.0	2345	2381
11	0.3	0.7	1.2	12.0	2361	2399
12	0.3	0.7	1.4	14.0	2383	2419

Figure 2: Cone Composition table

The melting point is determined by the rate at which the kiln is heated. This is apparent since the faster the kiln is heated, the faster the internal heat of the cone will increase, and hence will melt at a slightly lower temperature. The melting point of clay is therefore also determined by the rate at which the kiln is heated. Also note that there is always 1mol of flux and the molarity of glass formers vary. It was apparent to Herman Seger that fixing the fluxes to be constant would help standardize and predict cone melting properties. This also allows the ratio of flux to glass former to be its own ceramic metric, hence the name standard pyrometric cones. In the next section, we will scatter plot the moles glass former versus the outcome variable of interest, in this case its melting temperature.

1.2 Scatter Plot of the Data

From the previous table, we can add up the moles of glass formers, then scatter plot the resulting molarity versus temperature to see what kind of relations may be visible. We will compare the different melting points corresponding to 108F/hr and 270F/hr in the following scatter plot.



As we can see, there are some predictable trends in the data. We can see that the change in melting temperature for the two different heating rates is relatively constant. Consider $T1_n$, $T2_n$, and ΔT_n . Where $T1$ is the series of temperature data points for 108F/hr and $T2$ for 270F/hr. ΔT_n is the difference of $T1$ and $T2$, and n represents the cone number. consider the table below. Since the melting point of these mixtures are so high, we can consider the deviations of change to be 0 and accept the small resulting error.

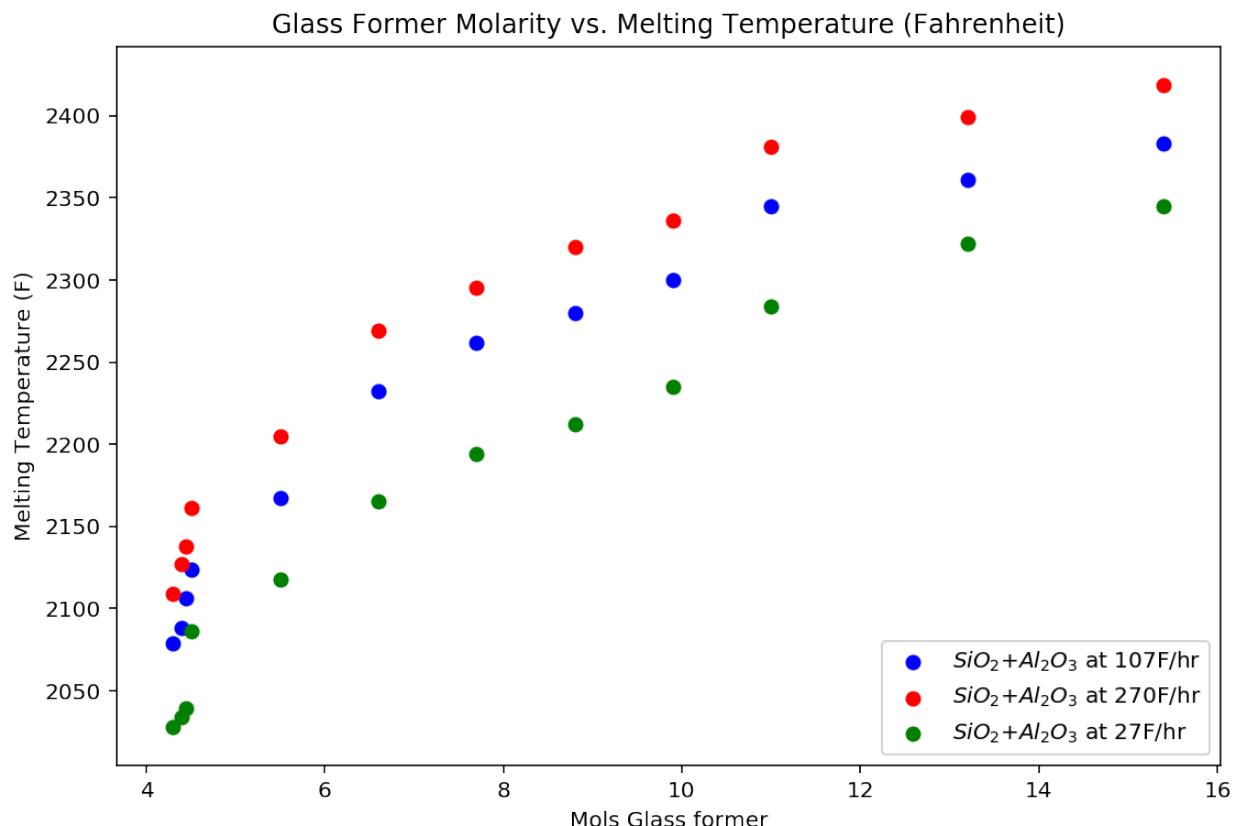
n	1	2	3	4	5	6	7	8	9	10	11	12
ΔT_n	30	39	32	37	38	37	33	40	36	36	38	36

We see that the difference in temperature is relatively constant. To verify that the difference of each melting temperature is relatively constant, we should collect data for another heating rate, see the table below

n	T1 at 27F/hr	Δ_{1-2}	T2 at 108F/hr	Δ_{2-3}	T3 at 270F/hr
1	2028	51	2079	30	2109
2	2034	54	2088	39	2127
3	2039	67	2106	32	2138
4	2086	38	2124	37	2161
5	2118	49	2167	38	2205
6	2165	67	2232	37	2269
7	2194	68	2262	33	2295
8	2212	68	2280	40	22320
9	2235	65	2300	36	2336
10	2284	61	2345	36	2381
11	2322	39	2361	38	2399
12	2345	36	2383	36	2419

This data is important to us since the rate at which the mixture is heated changes the melting temperature noticeably. This variable will have to be included in the model or we will have to make the model under the assumption that the user of the model uses a specific heating rate, which would be overly constraining and we lose model versatility.

Let us reconsider a scatter plot of the data in the above table, and see if our prediction of constant melting temperature change is reasonable. The next page contains said scatter plot, this is the main data we wish to model.



We can see that each melting temperature scatter seems to have the same shape, but has a shift in the y-axis. We can construct a model for the rate of 27 F/hr and create a second model that approximates the how much heat to add if the user uses a different heating rate. We can therefore expect our model to pass in two inputs, moles glass former relative to one mole flux and the rate at which the mixture is heated.

In the next section, we discuss the proposed model. Before we do so, it may be worth while to discuss some assumptions we have already made. We have a few problems that our model simply cannot handle. We've made an assumption that whatever mixture we are modeling only contains the four fluxes and glass formers we've discussed, however it has been mentioned that clay and glaze alike contain a fair amount of other materials that can act on the clay and glaze. However the four we have discussed contribute the most to the melting point. The second assumption is that the ratio of fluxes will always be 3:7. But since each flux has its own unique melting point and effect on the glass formers, it is not the safest assumption to make that we only need consider the combined effect; Likewise for the glass formers. However, these assumptions are necessary since it is clear that a couple of best fit curves cannot explain eutectic chemistry as a whole. These simplifications are necessary for minimizing the complexity of our model. The number of variables as a whole in firing can be overwhelming, ranging from the atmosphere of the kiln to how the kiln was loaded. We do not want to bite off more than we can chew.

2 The Model

The model should be function that is dependent on two things, the rate of temperature increase and the moles of glass former with respect to one mol of flux. finding the molarity of glass former is the responsibility of the user of the model; One may use Seger's Unity Molecular Formula which adds up the total molarities of flux and glass formers, and finds their ratio with respect to one mol flux. Once the total molarities of both glass former and flux are found, one can divide the moles glass former by the moles flux to obtain the ratio of one mol flux to moles glass former, an example is shown below.

$$\frac{15 \text{ moles glass former}}{5 \text{ moles flux}} = \frac{3 \text{ moles glass former}}{1 \text{ moles flux}}$$

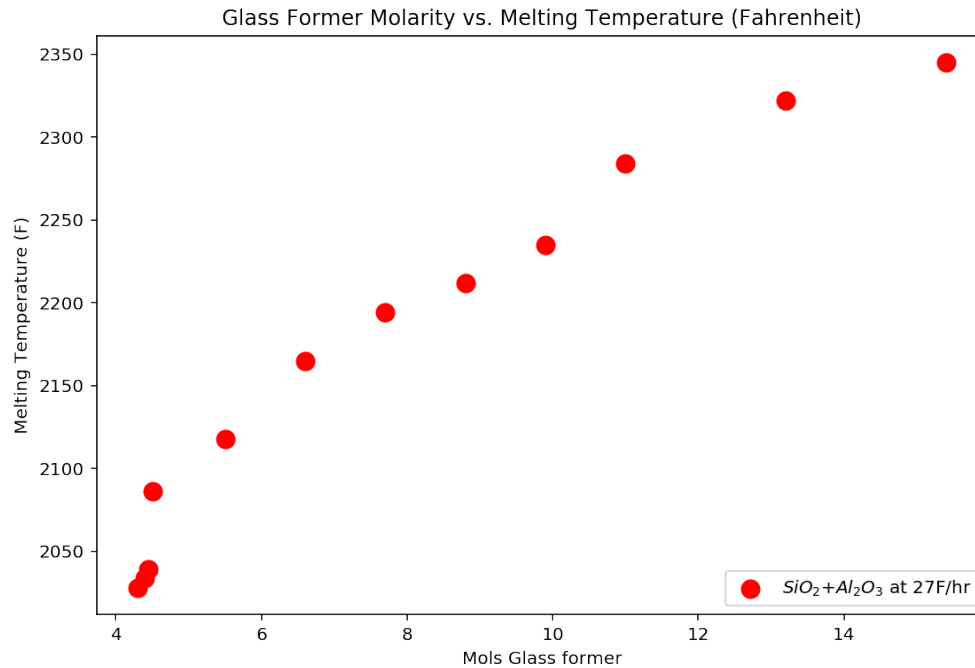
Where 3 moles of glass former is one of our inputs to the model. In general our model should look something like

$$f(x, r) = m(x) + g(r)$$

Where x is our moles glass former relative to one mole flux, and r is the rate at which its heated; and $m(x)$ is our model without the rate adjustment, $g(r)$ is the rate adjuster, and $f(x, r)$ is our final melting temperature of the eutectic mixture. $g(r)$ is an important adjuster to $m(x)$ because if we don't include it, we make the assumption that the user of the model is using the rate of heating that we modeled for, the model becomes more versatile and usable when we take this factor into account. However we make a dangerous assumption about $g(r)$. The first assumption is that with different heating rates, we have a constant change in melting points for each cone. We saw that the change in melting temperature was not completely constant and varies slightly. We also made an assumption that the relative amount of silica and alumina is irrelevant, its only their sum that matters, however this is not true. For example, a clay body with 10 mols of alumina acts differently than a clay body with 5 mols silica and 5 mols alumina, but our model treats them the same since only their sum is taken into account.

To start the model, we will take $m(x)$ to be the melting temperature at 27 F/hr and let $g(27) = 0$. As the rate of heating changes, $m(x)$ will not be affected, and the change in melting temperature will be adjusted by $g(r)$.

2.1 Modeling $m(x)$ Using Least Square Criterion



We see that the scatter plot for which we wish to model $m(x)$ after is increasing but decreasing in the rate of growth. It seems that it may be a good fit to use a function of the form

$$m(x) = ax^2 + bx + c$$

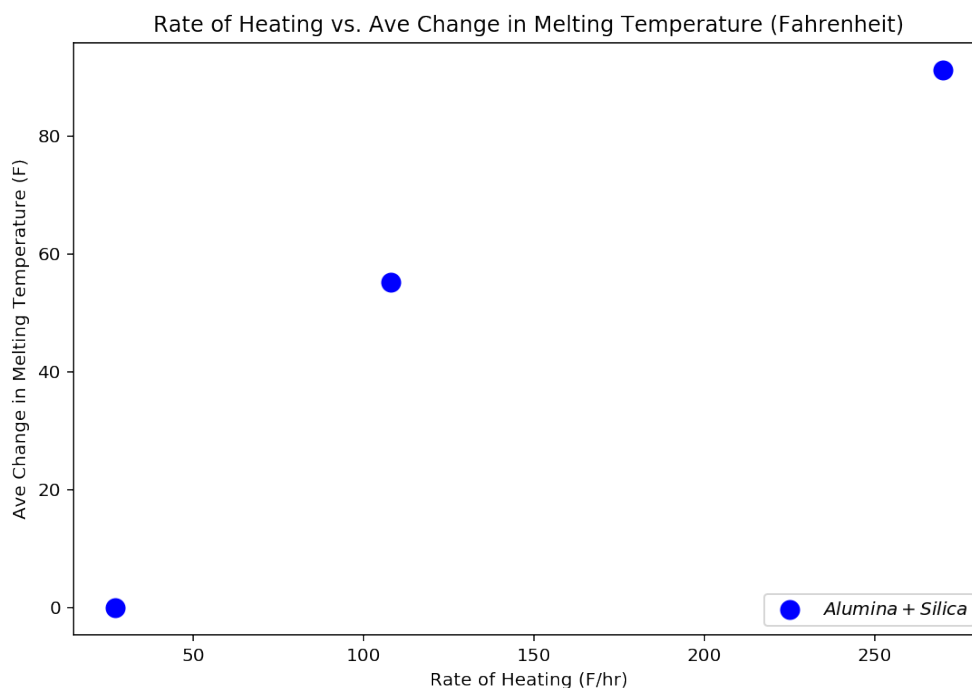
Using least square criteria for the parabolic curve, we have

$$m(x) = -1.9x^2 + 64.1x + 1806.2$$

2.2 Modeling $g(r)$ Using Least Square Criterion

From a previous table where T1 is the melting point for 27 (F/hr), T2 is 108 (F/hr), and T3 is 270(F/hr), we can construct the below table and plot the average difference. We should also take careful note of the average deviation from the midpoint since this will be a good reference point for the error of our function. For now, it seems that our $g(r)$ can have an error of roughly 16 F. The scatter plot below is the average melting temperature change versus the rate of heating. Our points are (27, 0), (108, 55.25), and (270, 91.17).

cone	1	2	3	4	5	6	7	8	9	10	11	12	ave.	dev.
T2-T1	51	54	67	38	49	67	68	68	65	61	39	36	55.25	16
T3-T1	81	93	99	75	87	104	101	107	101	97	77	72	91.17	17.5



The three points on the scatter plot indicate that $g(r)$ can be modeled by a quadratic function,

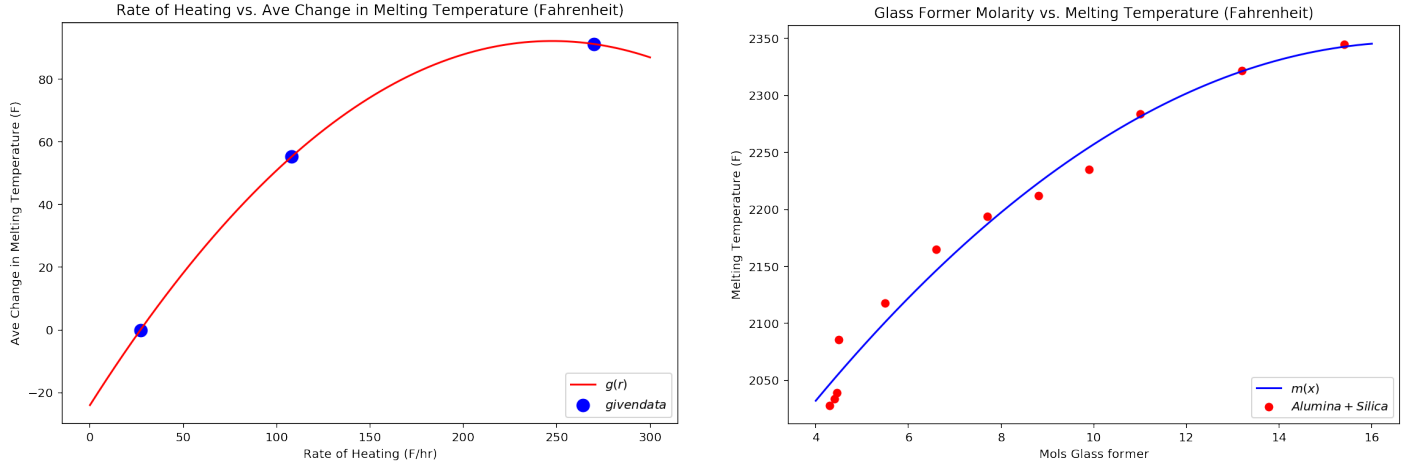
$$g(r) = ar^2 + br + c$$

Let it be known that three points is not enough data to create a reliable model, however this is not our main model, and $g(r)$ is only meant to bump our resulting melting point in the right direction. This said, we do wish to have as much accuracy as we can with $m(x)$. Using the least square criteria, we find that

$$g(r) = -.00189461r^2 + .937871r - 23.9413577$$

2.3 Analysis and Adjustment of the Model

From our $g(r)$ and $m(x)$ models, we have the following plots.



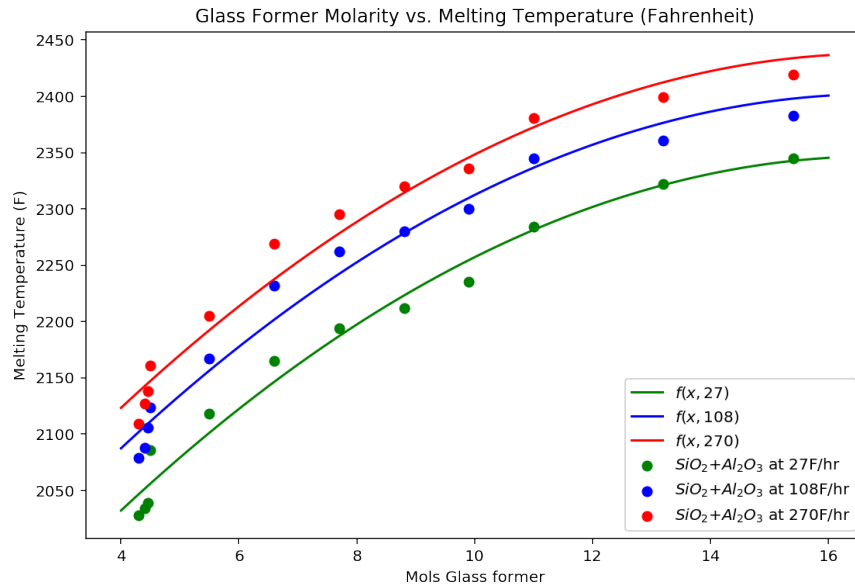
Now let's consider the combined effect of $g(r)$ and $m(x)$. If we have that

$$m(x) = -1.9x^2 + 64.1x + 1806.2 \text{ and } g(r) = -.00189461r^2 + .937871r - 23.9413577$$

then,

$$\begin{aligned} f(x, r) &= m(x) + g(r) \\ &= (-1.9x^2 + 64.1x + 1806.2) + (-.00189461r^2 + .937871r - 23.9413577) \end{aligned} \quad (1)$$

Let us consider $f(x, 27)$, $f(x, 108)$, and $f(x, 270)$ compared to our scatter plot to see the goodness of fit. The graph below will help to see this visually.



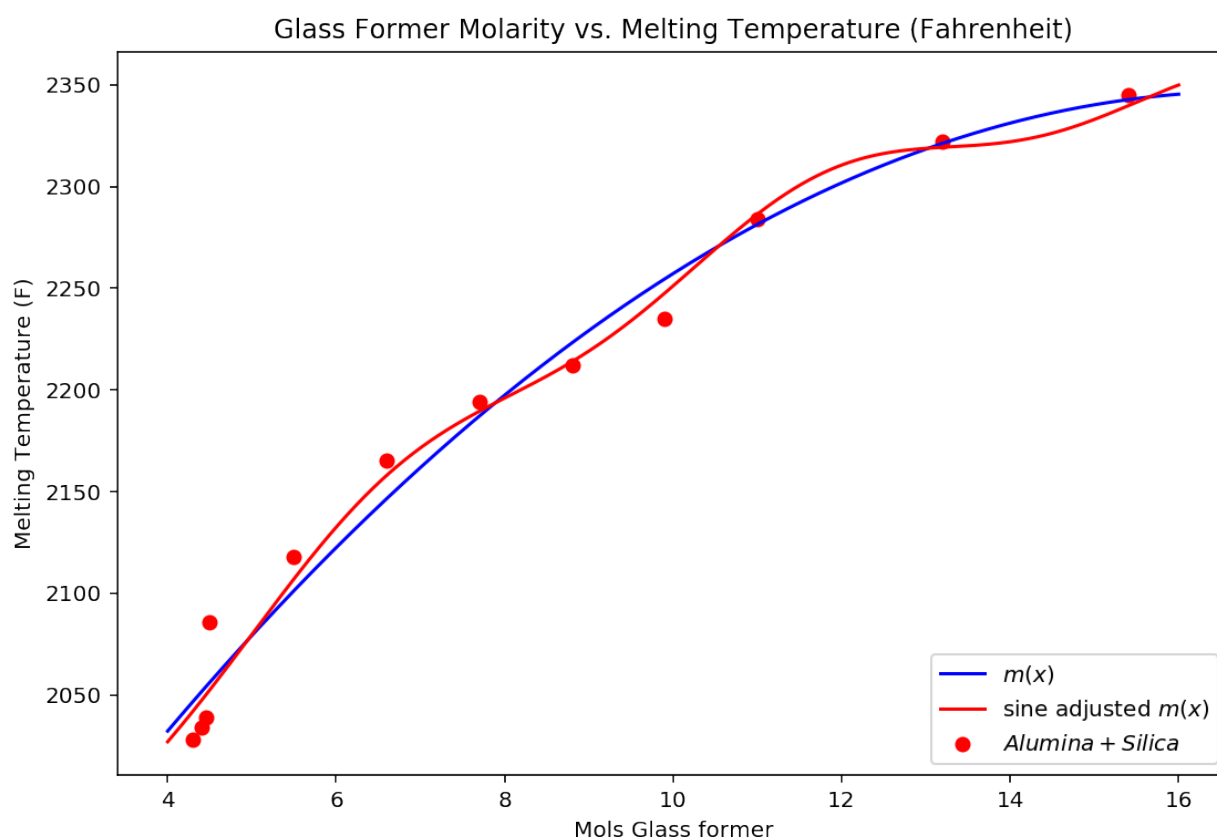
We can see that there are definitely some outliers to the plot. A closer inspection shows that the points seem to oscillate predictably around the parabolic fit. We could remodel the curve in the form

$$m(x) = ax^2 + bx + c + d\sin(nx)$$

Using least square criteria, we can solve for all but n . So we will let $n = 1$ and solve a , b , c , and d , then guess-checking to solve n . n is an important variable to include since it will "stretch" out the sine curve, where d only amplifies it. This model would not be reasonable without n . Using least square criteria, and guess-checking n , we arrive at

$$m(x) = -1.8x^2 + 61.8x + 10\sin(1.2x) + 1818.5$$

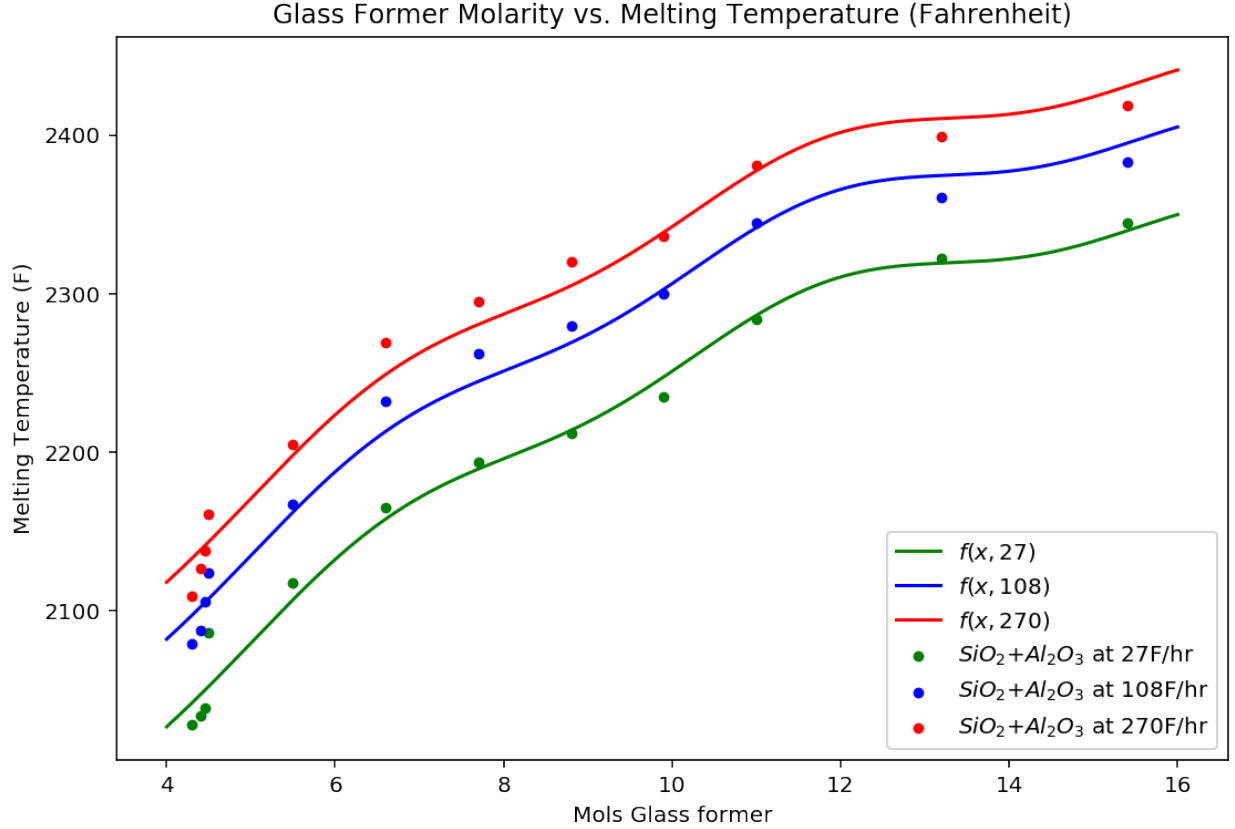
graphing our original model, and our sine adjusted model, we have



We can see clearly that the sine adjusted $m(x)$ is able to hug the points closer than our original $m(x)$. These oscillations can possibly be explained by different ratios of alumina and silica for each cone.

Let us now focus our attention on $f(x, r)$ using our new $m(x)$ and see if the goodness of fit is also visible in other heating rates. Again, let us consider $f(x, 27)$, $f(x, 108)$, and $f(x, 270)$.

$f(x, 27)$, $f(x, 108)$, and $f(x, 270)$ are graphed below.



3 Conclusion

So, our final $f(x, r)$ is

$$f(x, r) = m(x) + g(r) \\ = (-1.8x^2 + 61.8x + 10\sin(1.2x) + 1818.5) + (-.00189461r^2 + .937871r - 23.9413577)$$

Note that for glazes, we heat them far beyond their melting temperature to let them become a vitreous liquid and homogeneously cover the pot. Hence, we expect our melting temperature from our model to not be cone 10, but more near cone 2-5. Conversely, for clay bodies, we expect their melting temperature to be far above the cone number they are meant to be used for. For example, a cone 10 clay body shouldn't melt at cone 10. This makes sense since we only want our clay to form a crystalline structure but never melt. Let us take an example formula for a cone 8 porcelain clay body and analyze the resulting U.M.F.

formulas for glazes and clay alike come to us in ratios of materials, so that we can scale up to any size batch we desire. the following table demonstrates the calculation for finding the ratio of moles glass former to 1 mole flux using the U.M.F. The following formula calls

for 27 percent Kaolin, Ball clay, Potash Feldspar, and 19 percent silica. To calculate the U.M.F. we need to find how much fluxes and glass formers are in each material and divide by the molecular weight to find the molarity. Consider the table below,

Material	Formula ratio	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	TiO ₂
glass/flux		glass	glass	flux	flux	flux	flux		
Molecular weight		60.09	101.96	61.98	94.2	40.31	56.08	159.7	80.9
Ball clay	27	59.83	25.02	.40	.90	.30	.30	1.02	1.00
Finding percentages (times .27)		16.15	6.755	.108	.243	.081	.081	.2754	.27
Kaolin	27	47.29	40.21						
Finding percentages (times .27)		12.76	10.85						
Feldspar	27	64.76	18.32		16.92				
Finding percentages (times .27)		17.485	4.94		4.568				
Silica	19	100.0							
Finding percentages (times .19)		19							
SUM columns		65.395	22.545	.108	4.811	.081	.081	.2754	.27
Sum/M.W. = Moles		1.088	.2211	.001	.051	.002	.001	.0017	.0033
Sum fluxes	0.055								
U.M.F. (i.e. moles/sumflux)		19.78	4.02	.018	.927	.036	.018	.031	.06
Sum glass moles		23.8							

So, our ratio glass formers to 1 mole flux is 23.8, this will be the input into our model, and the rate of temperature increase can be arbitrarily set to 108 F/hr.

Calculating the melting temperature using our model we get

$$f(23.8, 108) = m(23.8) + g(108) = 2322.18$$

At a rate of 108 F/hr, our clay body begins to vitrify at 2322.18 F, which lies right between cone 9 and 10. This is what we expect for a cone 8 clay body. We don't want the clay to be liquid and melt everywhere, however we do want the molecules to become loose and reform into a semi-glass crystalline structure to give the clay strength post firing. Hence, we expect the true melting temperature to be a couple hundred degrees higher than the cone of the clay body itself.

It's important to realize that the given cone of a glaze or clay isn't precisely the melting temperature, rather it's the temperature it should be heated to in order to achieve the desired result. With glazes, the desired result is for the glaze to be completely melted over the pot; for clay, the desired result is for it to be slightly vitrified but never melted. Thus, our function doesn't tell us the desired temperature to bring a clay or glaze to, but only what temperature the mixture begins to melt. This model may be helpful as a precautionary result to the user. For example, if one is creating a new glaze formula or clay body formula, and you want to make sure that when you heat it that the clay doesn't melt or that the glaze will melt.

As a final note to the user, realize that this model is inherently a rough estimate. As you can see from the previous table, we don't take into account the ratios of the different fluxes or glass formers. Furthermore, we left out the residual effects of tin oxide and iron oxide which effects the melting temperature, opacity, color and texture of result. However, there are other graphical models that based off the ratios of flux and glass former will tell you the resulting texture, and vitrification level of your mixture.

The data used for the model was derived from glazy.org, and the basic Orton cone chart. It would have been ideal to have more data for the cones, since there are more than 12 cones. The data presented by the Orton cone chart only contains melting temperature for the three different heating rates discussed, Our model would be more accurate with more heating rates. It would also have been ideal to find a relationship between different amounts of fluxes and different amounts of glass formers. Our model would have more accuracy if it took each flux and glass former as separate input. These are the trade offs when using pyrometric cones to model the melting temperature of clays and glazes.