THE DECOMPOSITION KINETICS OF SOLIDS

THERMODYNAMIC EVIDENCE FOR THE ENTHALPY DRIVEN COOLING OF REACTION ENVIRONMENT PART 2

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ABSTRACT

The analysis of non-isothermal kinetic data for the decomposition of calcium carbonate, $CaCO_3$ (*s*) → CaO (*s*) + CO_2 (*g*) *in flowing nitrogen, shows that the decomposition of solids is accompanied by self-cooling/heating of the reaction environment depending on the sample mass and heating rate. The correctness of the kinetic model is established by the calculation of the enthalpy change of the reaction. This is the thermodynamic evidence of endothermic enthalpy driven cooling of the reaction environment. The enthalpy change* $\Delta H = 179.33$ *kJmol*$^{-1}$ ***estimated from this work for the*** *dissociation of* $CaCO_3$ ***is in*** *agreement with* $\Delta H = 179.17$ *kJmol*$^{-1}$ *derived from the enthalpies of formation of the reaction components. The results support the* ***mechanism suggesting*** *heat transport to be the rate-limiting step.*

Keywords: Solid-state decomposition, kinetic parameters, thermodynamics.

INTRODUCTION

The fundamental characteristic of an endothermic chemical reaction is the increase of the rate of reaction, $d\alpha/dt$, with the increase of the rate of heat supply. Solid-state decomposition reactions are supposed to obey this general rule and under a regulated heat supply, such a system should satisfy the Arrhenius equation,

$$k = A\exp(-E_a/RT) \qquad (1)$$

The equation allows the prediction of the rate constant, k, at any temperature, T. The homogeneous kinetic systems offer no difficulty in the application of the equation since they always yield non-variant kinetic parameters, namely, the frequency factor, A, and the activation energy, E_a. This is because there are no restrictions in the regulation of the heat that is supplied to the reactants. In solid state kinetics, variable values of the kinetic parameters are frequently obtained. In such kinetic systems, the regulation of heat-supply presents a difficult part in the interpretations of experimental data.

It has been established that solid state decompositions are interface chemical reactions localised at the reaction interface, accompanied by the self-cooling/heating of the reaction environment (Akwilapo and Kyobe, 2005). The cooling of the reaction environment was figured out to be the reason for the reduction of the kinetic parameters A and E_a to the apparent values A′ and E_a′, respectively.

Since the contraction of the reaction interface is in progress, a progressive decrease of the population of a solid reactant at the reaction interface occurs, causing a corresponding decrease of the heat demand of the interface chemical reaction. Because the pre-selected heating programme determines the heat supply, it therefore fails to regulate according to the decrease of the heat demand of the contracting reaction interface. The initial chemical reaction in this case tends to proceed with an undersupply of heat whereas the subsequent phase experiences an oversupply of the same. This is referred to as self-cooling/heating of the kinetic system (Maciejewski, 2000).

The frequently applied rate equation, in the form,

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

does not satisfy the requirement of a solid state chemical reaction, which is accompanied by self-cooling/heating of the kinetic system.

Under this circumstance, the experimental reaction rates $d\alpha/dt$ does not precisely match with the variation of the rate constant according to the Arrhenius rate equation (2). This suggests that the function $f(\alpha)$ of the remaining fraction $1 - \alpha$ of the reactant cannot alone be associated or identified with the real mechanism of the interface chemical reaction. The results of the recent Kinetics Project by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) (Maciejewski, 2000) and other previous investigations (Garn, 1978; Dollimore *et. al.*, 1984), support this view. Garn (1978) has made a remarkable suggestion indicating that the rate of a solid-state decomposition, $d\alpha/dt$, should not be a function of only $(1 - \alpha)$ and temperature, T, when variable kinetic values are obtained.

When the rate, $d\alpha/dt$, does not match with $f(\alpha)$, A and E_a (the kinetic triplet), one would fail to give an accurate account of the reaction mechanism. It is also difficult to make an accurate assessment of the impact of the experimental uncertainties for the measured rates on the quality of the kinetic analysis. In Akwilapo and Kyobe (2005), the solution to this problem was proposed by introducing the area, a, of the reaction interface besides, $f(\alpha)$ and temperature. The equation that was suggested will give, for the initial reaction that proceeds under the cooling of the reaction environment, apparent kinetic parameters A' and E_a' which are variables depending on the area a_o of the reaction interface.

Experimental

Samples of calcite were cut from large pieces of marble of 99.9% purity by mass supplied by May and Baker Dagenham, England. The kinetic studies were carried out using a Mettler TG 50 thermal balance that is supplied by Mettler Toledo, Switzerland. The balance has a weighing capacity of up to 150 mg and the reproducibility of ±1□g. The balance supplied is not equipped for studies under vacuum. Therefore dry flowing nitrogen gas, supplied by Tanzania Oxygen Limited (TOL), was employed to carry away CO_2 from the reaction environment. Before each experiment the temperature calibration was carried out using the Curie points of Isatherm (145°C), Nickel (357°C) and Trafoperm (748°C) as reference temperatures. The manufacturer supplied all the temperature calibration materials. For each temperature calibration, the calibration materials were placed in the alumina crucible. Sample masses cut to nearly spherical geometry ranging from 6 to 100 mg were decomposed between the heating rates of 1.5 to 4.5 K min^{-1}.

Results and Discussion

The kinetic data for the decomposition of 6 - 100 mg calcite at different heating rates between 1.5 and 4.5 $Kmin^{-1}$ are presented in Table 1 and a typical representative TG curve for the decomposition of $CaCO_3$, according to,

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (3)$$

is shown in Figure 1. For the 5.969 mg sample mass, the Arrhenius plot of $\ln k_m$ vs T^{-1} is shown in Figure 2 from which $\ln A' = 19.776$ and $E_a'/R = 26025$ were obtained as intercept and slope, respectively, for the range of alpha between 0.0063 and 0.60. It has already been shown (Akwilapo and Kyobe, 2005) that the linearity is arrested in mid-flight suggesting the break of the chemical reaction. This was described to be caused by the imbalance between the heat supplied to that which is demanded by the chemical reaction on the contracting reaction interface.

The kinetic break of the chemical reaction as shown in Figure 2 should not be expected if the preset heating rate would have been sensitive to the variation of the heat demand at the reaction interface. The kinetic break is therefore an indication that excess heat is supplied to the reacting species, a phenomenon that has been described in detail by Akwilapo and Kyobe (2005) making use of the expression,

$$k_m = k_T C_o \exp\{y(2 - aT/a_oT_o)^2\} \qquad (4)$$

in which k_m and k_T are the measured and Arrhenius rate constants, respectively, and C_o and y are the thermal transport parameters, which vary from one sample to another. The thermal transport parameters were determined from the plot of $\ln(k_m/k_T)$ vs $(2 - aT/a_oT_o)^2$ by making use of equation (5), derived earlier (Akwilapo and Kyobe (2005),

$$k' = \frac{d\alpha}{dt}\frac{a_o}{a}\left\{\frac{\exp\left(-a_o T_o/T\right)}{f(\alpha)}\right\} = A'\exp\left(\frac{-E_a}{RT}\right) \qquad (5)$$

For the 5.969 mg sample, the plot is presented in Figure 3 from which in $C_o = -1.4048$ and $y = 0.86155$ are obtained. On the basis of these parameters, the Arrhenius plot (Figure 2) is extended up to $\alpha = 0.9$ giving the same values of $\ln A'$ and E_a'/R as before (Akwilapo and Kyobe, 2005).

The Effect of Sample Mass and Heating Rate

The kinetics of a reaction that is dominated by heat transport should show great sensitivity to the sample mass and the heating rate, as shown by the shapes of α-T curves (Akwilapo and Kyobe, 2005). The curves indicated that the decomposition was accompanied by the cooling of the reaction environment. The effect increases with increasing sample mass and heating rate. When the heating rate is increased, the temperature gradients would increase such that for self-cooling the temperature error, ΔT, becomes increasingly negative. This will naturally be accompanied by the reduction of the apparent frequency factor A'. On the other hand, a large increase of the heating rate will increase the rate of heat supply, which increases the apparent frequency factor A'. Hence the reduction of A' is observed at moderate heating rate and large values of heating rates. However, as shown earlier (Akwilapo and Kyobe, 2005), the reduction of A' was observed between the heating rates of 2.5 and 4.5 $Kmin^{-1}$ for the sample mass of between 6 and 100 mg. For samples close to 8 mg, the decrease of A' was observed for the heating rates between 2.5 and 4.5 $Kmin^{-1}$ (Akwilapo and Kyobe, 2005; Elder and Reddy, 1986).

For small samples and large heating rates, the entire reaction is dominated by self-heating, giving large values of A' and E_a'. However, it is unreasonable to assume that the reduction of the sample mass is sufficient to arrest the problem of heat transport. This is because by shifting from moderate to high heating rates, drastic changes of the conditions of heat transport occur even in very small sample sizes. This fact is substantiated using the results of Elder and Reddy (1986), while studying the decomposition kinetics of a 3.7 mg sample of $CaCO_3$ at the heating rates between 10 and 50 $Kmin^{-1}$. The authors obtained the apparent kinetic parameters, E_a', of between 246 and 256 $kJmol^{-1}$ and A' of between 1.6×10^9 and 10^{10} s^{-1} for the model of a first order reaction using the rate equation:

$$d\alpha/dt = AT\exp(-E_a/RT)f(\alpha) \qquad (6)$$

On the other hand, Gallagher and Johnson (1973) studied the decomposition kinetics of a 4 mg $CaCO_3$ sample at the heating rate of 5 $Kmin^{-1}$ in flowing nitrogen and obtained $E_a' = 217.5$ $kJmol^{-1}$, employing the Carrol-Freeman method. The difference between their results and those of Elder and Reddy (1986) can be associated with self-heating, which is amplified by high heating rates. The results according to Gallagher and Johnson (1973) are identical to the results of Elder and Reddy (1986) when the effect of self-heating on the kinetic measurement is taken into consideration by employing the rate equation (6) (Kyobe, 2001; Akwilapo and Kyobe, 2005).

The Effect of Sample mass

When the rate, $d\alpha/dt$, varies depending on the area of the reaction interface, samples of different masses cannot react identically. The reactivity of a solid reactant would always vary depending on the size of the sample mass as it has already been shown by the α-T curves (Akwilapo and Kyobe, 2005). This allows the apparent kinetic parameters to vary with the area a_o of the reaction interface according to equations (7) and (8),

$$\ln A' = \ln A + a_o x \qquad (7)$$

$$E_a' = E_a - a_o RT \qquad (8)$$

Analysis of the data show that the initial reaction is indolent when compared with the subsequent phase, which takes place at a greater rate due to the availability of excess heat (Akwilapo and Kyobe, 2005). In Figure 4, showing some plots of q_S vs a, the divergence of the data points explains the salient nature of the reaction profile. The divergence suggests that the initial reaction, which is indicated by a series of closed circles, (•), always proceeds at a reduced heat supply compared to the subsequent reaction, indicated by open circles, (o). A close examination on the slopes of the curves in Figure 4 suggests that the shift of the subsequent reaction to higher temperature coincides with the increase of the heat supply, q_S (Jcm^{-2}), which includes the heat component for the effect of the cooling of the reaction environment. Nucleation and growth of crystals is a thermodynamic perspective, which may involve a significant change in area of the reaction interface. This produces a room problem that induces strain energy into the kinetic system, thereby affecting the energy barrier. This happens because of the fluctuation of heat demand (thermal fluctuation) in the host phase (reaction interface) resulting into the formation of unstable clusters of atoms. The driving force for nucleation, like other rate processes, is the deviation of the kinetic system from equilibrium condition. Therefore the indolence nature of the initial reaction and subsequent reaction can be associated with the conditions of heat transport during the course of the decomposition.

It should be noted that the equation used to calculate the surface area, *a*, has assumed the sample to be a sphere with uniform radius. In actual situations, a grain of a sample will have pits and protrusions at the surface, emanating from sample preparation. With this regard the area of the reaction interface as calculated from the equation $a = Bm^{2/3}$ (Akwilapo and Kyobe, 2005) will be lower than the actual one by an amount Δa_o. During the progress of a decomposition these pits and protrusions are smoothened and the surface energy consumed in the smoothening process is given by the intercept, $b = \Delta a_o RT_o$, of Figure 4. The assumption is that the effect of the CO_2 partial pressure and the heat consumed by CaO(*s*) and CO_2(*g*), as reaction products, are both too small fit to be ignored. Table 2 shows the values of $\ln A'$ when the effect of pits and protrusions on the area of the reaction interface is taken into consideration. The values of ln A = 20.283 and x = 6.5429, which were determined earlier (Akwilapo and Kyobe, 2005), are used in equation (7). Figure 5 shows a typical plot of $\ln A'$ (Table 2) vs a_o. The pre-exponential term, lnA = 20.292 and the heat supply index, *x* = 6.7578 are obtained as intercept and slope, respectively.

The Enthalpy Change of the Reaction

The statements according to equations (7) and (8) can be used to establish the thermodynamic evidence of an endothermic enthalpy driven cooling of the reaction environment on the dissociation equilibrium of equation 3. When the dissociation equilibrium is to the extreme right, the rate constant at the threshold temperature, i.e. the temperature when the decomposition was first detected, T_o, for the dissociation reaction is;

$$k_o = A\exp(-E_a/RT_o) \qquad (9)$$

However, the rate constant k_o would apply for the temperature T_o if the chemical reaction would have proceeded free of the cooling of the reaction environment. Since this is not the case, the cooling of the reaction interface reduces the kinetic parameters A and E_a to the apparent ones A' and E_a', respectively. The rate constant for the forward reaction is reduced to,

$$\underset{\rightarrow}{k} = A'\exp\left(\frac{-E_a'}{RT_o}\right) \qquad (10)$$

The shift of the dissociation equilibrium to the left is the result of the backward association reaction CaO(*s*) + CO_2(*g*) □ $CaCO_3$(*s*), which proceeds giving the rate constant;

$$\underset{\leftarrow}{k} = k_o - \underset{\rightarrow}{k} \qquad (11)$$

The activation energy of the association reaction is derived from,

$$E_a(a) = -RT_o \ln\left(\frac{\underset{\rightarrow}{k}}{\underset{\leftarrow}{k}}\right) \qquad (12)$$

For 1 cm^2 area of the reaction interface, $\ln A' = 13.5345$ is obtained using lnA = 20.292 and x = 6.7578 of Figure 5 and $E_a/R = 26162.25$ (Akwilapo and Kyobe, 2005). This information gives $k_o = 379.086 \times 10^{-8}\ s^{-1}$ and $\underset{\rightarrow}{k} = 1.1972 \times 10^{-8}\ s^{-1}$. The rate constant for the reverse reaction is $\underset{\leftarrow}{k} = 377.889 \times 10^{-8}\ s^{-1}$. The activation energy for the association reaction is E(a) = 38192.30 $Jmol^{-1}$. The enthalpy change for the decomposition reaction of $CaCO_3(s)$ to products $CaO(s)$ and $CO_2(g)$ is $\Delta H = 179.33\ kJmol^{-1}$. The enthalpies of formation of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$ as listed in Lide (1992) give $\Delta H = 179.17\ kJmol^{-1}$ which is in excellent agreement with the values derived in this study.

If in equation 9 we assumed that $k_o >> \underset{\rightarrow}{k}$, appropriate substitutions for $\ln k_o = \ln A - {E_a}/{RT_o}$ and $\ln \underset{\rightarrow}{k} = \ln A - x - {E_a}/{RT_o} + 1$ will modify equation (12) to,

$$E_a(a) = RT_o(x-1) \tag{13}$$

For x = 6.7578 and T_o = 798.24 K (Akwilapo and Kyobe, 2005) the activation energy $E_a(a)$ = 38213.41 Joules for the association reaction is derived, which compares favourably well with $E_a(a)$ = 38192.30 Joules according to equation (12). These results vindicate the significance of the term "x" in relation to the dissociation equilibrium.

The linear regression of Figure 4 gives the heat supply q_S per cm^2 area of the reaction interface. The heats are in excess compared with the heat demand RT_o = 6636.81 J (Akwilapo and Kyobe, 2005) because of self-heating. This will raise the heat supply index from x to x_o according to

$$x_o = x + 1 - \frac{RT_o}{q_s} \tag{14}$$

where x = 6.5429 (Akwilapo and Kyobe, 2005). Table 3 presents the values of x_o calculated for various conditions of heat transport. The values of x_o are seen to increase with either sample mass or heating rate. Figure 6 shows the plot of q_s vs x_o, indicating the linear relationship between the two quantities. The following relationship is, thus, developed:

$$q_s = C + cx_o \tag{15}$$

where C = -58209 Joules is the thermodynamic constant obtained as the intercept and the constant c = 9863 Jcm^2 is the slope of the graph. Inspection of the result indicates that, more heat was consumed than the necessary required for the reaction. The heat consumed by the reaction products can create a deficit of heat supply because the fraction of it is used to raise the internal energy of the same. Similarly, the heat consumed by $CaCO_3$ in order to raise its internal energy facilitates the accumulation of energy required in bond cleavage. Therefore, during the rise of temperature from room temperature to the temperature T_o of the decomposition, the enthalpy change decreases. At the temperature T_o, the enthalpy change will decrease by an amount $\Delta H = \Delta C_p dT$ and heat supply would decrease by the same amount. If, however, $C_p(CaCO_3)$, $C_p(CaO)$, and $C_p(CO_2)$, are the respective heat capacities of $CaCO_3(s)$ $CaO(s)$ and $CO_2(g)$, respectively, the value of the heat capacity, C, can be derived from

$$C = \int_{298.15}^{798.24} \Delta C_p dT + \left(C_p(CaO) - C_p(CaCO_3)\right)T_o$$

The heat capacities of each component are deduced from the following equations (Kubaschewski and Alcork, 1979),

$C_p(CaCO_3\ \{s\}) = 24.98 + 5.24 \times 10^{-3}T - 6.2 \times 10^5 T^{-2}$

$C_p(CaO\ \{s\}) = 11.86 + 1.08 \times 10^{-3}T - 1.66 \times 10^5 T^{-2}$ and

$C_p(CO_2\ \{g\}) = 10.55 + 2.16 \times 10^{-3}T - 2.04 \times 10^5 T^{-2}$

By making use of these expressions in equation (16), C = 58224.31 J is obtained, which is in good agreement with 58209 J obtained according to Figure 6. The assumption is that during the experiment efficient removal of CO_2 from the reaction environment prevails. The observed discrepancy between the thermodynamic constant C according to equation (16) and that of Figure 4 indicates that the effect of $CO_2(g)$ on the dissociation reaction of $CaCO_3$ is somehow significant. It is obvious that the heat supply includes a component, which is used to raise the internal energy of $CaO(s)$ formed around the solid reactant. If, however, the removal of CO_2 gas from the reaction environment was arrested, the chemical reaction would consume more energy making the value of the heat capacity, C, to increase. The energy consumption is further reduced by the decrease of the enthalpy change of the reaction interface. This suggests that the reaction would consume more heat at low temperatures.

CONCLUSIONS

The mechanism of the reaction is considered well established when the experimental results are in accordance with known physical properties of the kinetic system. The studies of the decomposition of $CaCO_3$ according to the present investigation show that the results are consistent with the thermodynamic properties of the chemical reaction. On the basis of the present results, the enthalpy change ΔH = 179.33 kJmol^{-1} is derived in excellent agreement with literature thermochemical value, i.e. ΔH = 179.17 kJmol^{-1} (Lide, 1992).

Besides the ICTAC Kinetics Project (Maciejewski, 2000), there is no other method of kinetic analysis, which allows satisfactory comparison of the experimental result of kinetic studies of solid state decomposition reaction under variable conditions of heating rates and for different sample masses. This study had made it possible to identify and justify the mechanism of the reaction regardless of the heating rate and sample mass. The decomposition is identified to be a first order reaction. Therefore, the statement that the kinetic triplet (i.e. $f(\alpha)$, E_a and A) are not intrinsic properties of a decomposing solid according to ICTAC Kinetics Project (Maciejewski, 2000), is of questionable doubts since no attempts have been made to contain the limitations associated with the self-cooling/heating of the reaction environment.

Results according to the present study have shown that the modern commercial thermobalance gives rates, $d\alpha/dt$, of reasonably high accuracy and that, the poor correlation coefficients frequently obtained in Arrhenius analyses are not the result of errors in the rate measurements, but rather due to the self-cooling/heating processes. This is a fact, which was demonstrated by the experimental results of Elder and Reddy (1986), and supported by the current study (Akwilapo and Kyobe, 2005). The enthalpy driven cooling of the reaction interface (environment) is shown to occur during the initial state of reaction, this is proved by the calculation of the enthalpy change. By the correction of the effects of self-cooling/heating the kinetic parameters, E_a = 217.5 kJmol^{-1} and A = 7.0 x 10^{8} s^{-1}, are obtained, consistent with the derived enthalpy change. At the same time it is concluded that heat transport plays a dominant role in the kinetics of the decomposition reactions of solids. It has also been demonstrated quantitatively that the heat supply to the reactant at the reaction interface is reduced by the heat consumed in raising the internal energy of the solid reaction product, which is progressively formed around the reactant.

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Nomenclature

k = Reaction Rate Constant
A = Frequency Factor
E_a = Activation energy
R = Universal gas constant
T = Kelvin Temperature
a = Area of the reaction interface
B = $(36\pi/d^2)^{1/3}$
TOL = Tanzania Oxygen Limited
ICTAC = International Confederation for Thermal Analysis and Calorimetry

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Table 1. The kinetic measurements for the decompositions of 6 - 100 mg $CaCO_3$ decomposed at different heating rates.

T (K)	**5.969 mg (2.5) Kmin^{-1}**			**29.875 mg (2.5 Kmin^{-1})**			**7.991 mg (3.5 Kmin^{-1})**		
	α	$d\alpha/dt$ $\times 10^5$ s^{-1}	a cm^2	α	$d\alpha/dt$ $\times 10^5$ s^{-1}	a cm^2	α	$d\alpha/dt$ $\times 10^5$ s^{-1}	a cm^2
843.15	0.00639	1.48787	0.08152						
848.75									
853.15	0.01150	2.17202	0.08124						
863.15	0.01917	3.11100	0.08082	0.00641	1.11350	0.23851			
873.15	0.02556	4.46362	0.08047	0.09615	1.55052	0.23800	0.00962	2.68203	0.09880
883.15	0.03834	5.95149	0.07976	0.01282	2.07160	0.23749	0.01604	3.71357	0.09838
888.15									
893.15	0.05431	7.70988	0.07887	0.01923	2.88510	0.23646	0.02244	4.99270	0.09795
903.15	0.07692	9.46828	0.07761	0.02885	4.08733	0.23491	0.03526	7.01454	0.09709
913.15	0.10224	14.6082	0.07619	0.03846	5.19380	0.23336	0.05128	9.30234	0.09601
923.15	0.13419	17.7192	0.07437	0.05128	6.79190	0.23128	0.07051	11.93126	0.09471
933.15	0.17308	20.8302	0.07212	0.07372	8.92270	0.22762	0.09295	14.96463	0.09318
943.15	0.21725	25.1586	0.06953	0.09615	10.7870	0.22393	0.12179	19.07105	0.09119
953.15	0.27796	29.2164	0.06589	0.12821	13.5840	0.21860	0.16026	23.66028	0.08851
963.15	0.33865	33.5448	0.06214	0.16026	16.7800	0.21321	0.20513	29.41216	0.08533
973.15	0.41534	37.6026	0.05724	0.21154	20.2430	0.20444	0.25641	35.88810	0.08162
978.15									
983.15	0.49840	40.4431	0.05168	0.25641	27.5900	0.19661	0.32051	41.69552	0.07686
988.15									
993.15	0.59425	41.5252	0.04487	0.32051	29.8240	0.18514	0.39103	48.39254	0.07144
998.15	0.64462	41.7355	0.04107						
1003.15	0.69010	41.7694	0.03749	0.38462	31.8290	0.17330	0.47436	52.68798	0.06477
1008.15	0.74380	40.7024	0.03302						
1013.15	0.78594	39.0905	0.02929	0.46795	35.8240	0.15728	0.58333	59.53894	0.05548
1018.15	0.83058	37.3967	0.02507						
1023.15	0.88174	31.5827	0.01972	0.55055	39.9886	0.13771	0.68910	62.36452	0.04564
1033.15				0.63842	40.88499	0.11368	0.79487	60.54808	0.03459
1037.15				0.69231	41.2842	0.10917			
1043.15				0.74359	40.3520	0.09668	0.89103	52.55573	0.02269
1053.15				0.852564	37.82166	0.06685	0.96795	33.70510	0.01003
1063.15				0.935897	31.1629	0.03837			