Sublimation of Two Dicarboxylic Acids Used in Solder Pastes

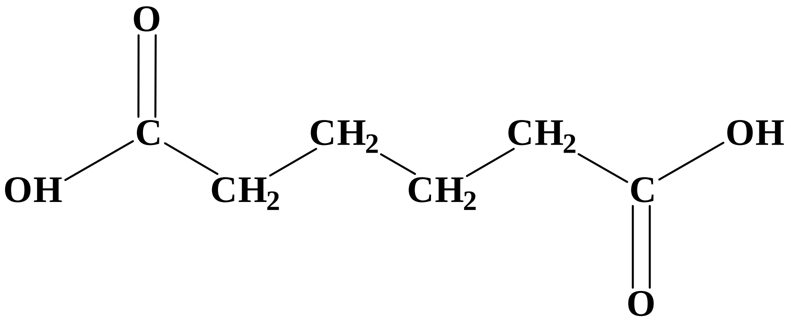
Bev Christian[a], Megan MacLean[b], Jason Thomas[b] and Andrew Michael[b]
Research In Motion
Waterloo, Ontario, CANADA

Abstract

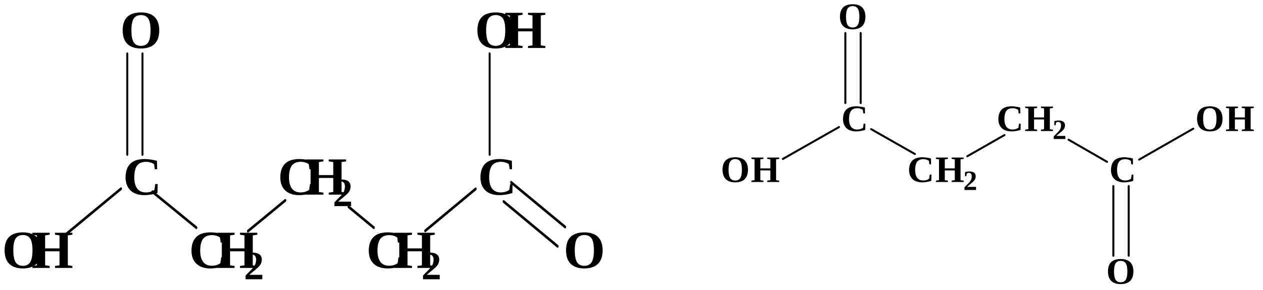
Our industry is slowly coming to the realization that many fluxes containing low molecular weight carboxylic acids cannot be adequately tested for surface insulation resistance and electrochemical migration at high temperatures. This paper describes the use of thermal gravimetric analysis (TGA) to look at the sublimation of succinic acid and glutaric acid from a paste flux formulation.

Introduction

Some of the activators used in most modern, weaker activity fluxes, solder pastes, paste fluxes, cored wires and preform fluxes are low molecular weight dicarboxylic acids. Examples of these include succinic acid, glutaric acid, adipic acid, and maleic acid. The acids are straight chain acids with the COOH moiety at either end. These materials are often man-made, although they also occur in nature. See **Figure 1** for the structure of the first three of the four listed above. Maleic acid is similar to succinic acid, except that there is a double bond between the two central carbons.



Adipic Acid m.p. 152°C



Glutaric Acid m.p. 97°C

Succinic Acid m.p. 88°C

Figure 1 - Molecular Structures of Some Dicarboxylic Acids Used in Fluxes

a) Author to whom correspondence should be addressed.
b) Co-op students from Dalhousie, Ryerson and Clarkson Universities, respectively

Ideally there would be no residue left on a printed circuit pack after reflow, however no solder paste has been produced to date with this property. Second choices include reduced levels of residues that are relatively benign, are “encased” or are washed away. One of the reasons the straight chain carboxylic acids are used is because of their ability to sublime at fairly low temperatures. This helps meet the first of the three second choice scenarios. The straight chain acids are often used in low residue solder pastes commonly referred to as “no-clean”. Each material needs to be carefully tested for the application to see if the latter descriptor is applicable.

Qualification testing of solder pastes is done by a variety of methods[1], with surface insulation resistance (SIR) and electrochemical migration (ECM) being two of the most rigorous. Much data has been collected, with a lot of data for ECM obtained at 85°C. The reasoning for that condition has been – the higher the temperature, the higher the activity and thus more data in a shorter period of time (more accelerated test). Because of the sublimating ability of the dicarboxylic acids, it has not been uncommon to find that the ECM resistance values of many fluxes increase with time[2]. Subsequently, work by other researchers[3] has shown that 65°C is still probably too high for, for example, pure adipic and succinic acids.

As a result of the above referenced work, the IPC test method for ECM had the soak temperature lowered to 65°C included in the last version of IPC-TM-650, Method 2.6.14.1[4]. The temperature chosen was a compromise to delay sublimation of the dicarboxylic acids and still keep a significant level of temperature related chemical activity.

Influenced by the above, recent, extensive work in Europe[5] has resulted in a new test to take into account this behavior, as well as contend with the closer spacings and lower voltages seen in much of the electronic equipment produced today.

The work in reference 3 examined the sublimation of succinic and adipic acids indirectly using “dynamic extractive ionic resistivity” to determine the amount of each acid left on either FR-4 or copper coupons after exposure to different temperatures for different lengths of time. The equipment to do this is relatively available, but it is not a direct method of obtaining the sublimation information.

This current study is a follow-up to previous work[6] that was carried out to look at the sublimation of the pure acids mentioned above. In that work it was apparent that lower testing temperatures for SIR and ECM were critical for enough of the acids to remain on the test coupons for the entire test periods to make the results valid. However, although all three referenced studies agree in their overall thrust, the principal author of this work was challenged as to whether the results were really applicable to solder pastes as well as liquid-based fluxes, which are a much simpler chemical system. The statement was made by a solder paste manufacturer[7] that the materials in the solder paste vehicle may inhibit the sublimation of the active fluxing agents (carboxylic acids) enough that the lower test temperatures that seem to be needed for fluxes may not be necessary for solder pastes. This would mean that the higher temperature tests – more acceleration, would still be appropriate for testing solder pastes.

In this present study, a TGA was again used, but this time to directly collect the weight changes of paste flux vehicles and paste flux vehicles to which had been added significant amounts of individual dicarboxylic acids. Glutaric and succinic acids were chosen for this study. Succinic acid was chosen as it is a straight chain dicarboxylic acid with a relatively high melting point (188°C), while glutaric acid is one with a relatively low melting point (99°C). The results obtained with these two acids should be fairly representative of the acids of this type used in paste fluxes.

Experimental

The acids were from Aldrich Chemical Company and were labeled as 99% pure. Confirmation of purity was discussed in reference 6 and will not be repeated here.

Samples were added to the aluminum TGA pans by means of a small, clean lab spatula. Before starting the TGA runs, a simple experiment was carried out. Using an analytical balance it was found that ~5 grams of the paste flux did not lose any weight but gained weight in the time the sample was monitored. This is shown in **Table 1**. This showed that no significant amounts would be lost/gained in the short time it took to prepare the TGA samples.

Table 1 - Weight Change of Paste Flux over Time at Room Temperature

Time	% Loss (-) or Gain (+)	Time	% Loss (-) or Gain (+)
Initial	0	60 minutes	+0.08
5 minutes	+0.04	2 hours	+0.21
15 minutes	+0.07	4 hours	+0.31
30 minutes	+0.07	6 hours	+0.37
45 minutes	+0.08		

The combination samples of paste flux and each acid were made by grinding up the acid of choice with a mortar and pestle and then slowly mixing the acid powder into the paste flux until a 15 weight percent of acid weight in paste flux (w/w) was achieved. This percentage amount was chosen to be large enough that any changes could hopefully be measured and yet not be totally unrealistic. The actual percentages of acids added to paste flux vehicles is not known by the authors. Conceivably this could be obtained by a simple acid/base titration. The mixture was manually stirred for about 5 minutes to produce a homogeneous mix.

A TA Associates, Model Q50 TGA was used for this study. Glutaric acid samples or samples containing this acid were run at 65°C to 95°C in five degree increments, with runs lasting up to three days, depending on the acid and the actual test temperature. Succinic acid-containing samples were run at 65, 85 130, 140 and 150°C. Higher temperature runs for succinic acid could be run in much less time than three days. Experimental run times varied with the samples. No sample runs were collected above the melting point of the acids being tested. In most cases samples were at least in triplicate. However, on occasion a data point was dropped for having considerably different results. Samples were pre-weighed using a four figure analytical balance to make sure samples were 30 +/- 3 milligrams to eliminate another cause of variability.

All experiments were of the ramp and hold type – ramp the TGA chamber from room temperature (all runs were ramped at 15 degrees per minute) to a specific temperature and held at that temperature for the duration of the particular run. The ramp rate was chosen to get the chamber to the temperature of interest quickly and yet try and keep overshooting to a minimum. An atmosphere of nitrogen (boil-off from a tank of liquid nitrogen) was used as the atmosphere in the TGA during the experiments.

Results and Discussion

From the weight loss/ temperature curves, it was immediately evident that an equilibrium situation did not exist at the beginning of each run. First, the equipment generally overshot the temperature plateau by about 5C° or less and it took 5 to 13 minutes to correct. However, it should be noted this was less than 2% of a 700 minute run time (a short run). Also, what was actually seen was an immediate weight gain of up to 2%, which persisted for less than ten minutes of the run. No reason for this has been determined. The first portion of the curve was not used in determining the weight change with time for each run.

In the previous related work of this lab (ref 6), the dicarboxylic acids were dissolved in isopropyl acid, put in the TGA vessel and the solvent evaporated before the test started. This left 0.38 to 1.2 mg of material in the pan. For this current work in the experiments run of just the pure acid, not in paste flux, weighed amounts of granulated acid (3.00 – 3.17 mg) were simply put into the TGA sample holder. Representative results are shown in **Figure 2**. The slopes of the lines after the sublimation stabilized after the first few minutes were measured. The natural log of the average values at each temperature were plotted as a function of the reciprocal of the absolute temperature of the test. See **Figure 3**. The average value obtained for the activation energy of the sublimation for succinic acid was 119 kJ/mole, which is quite close to the value of 122 kJ/mole obtained previously. Note that the correlation coefficients are very high. Previous experience has shown that very high coefficients (>99%) are expected for good kinetics data.

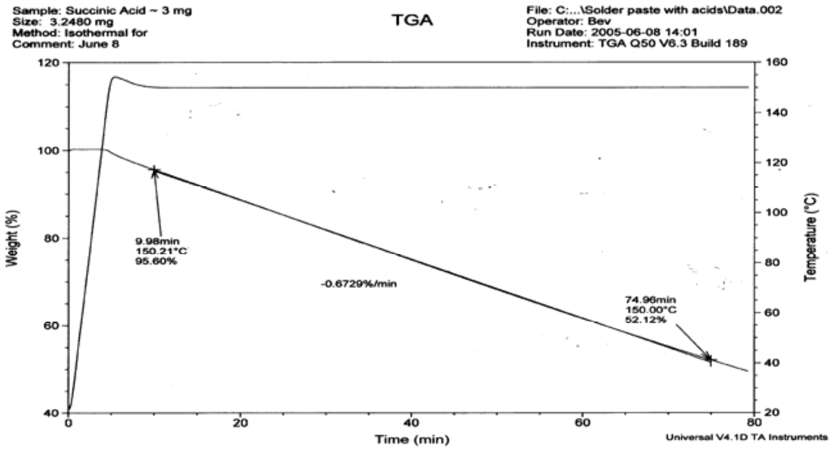


Figure 2 - Weight Change of Succinic Acid as a Function of Temperature and Time

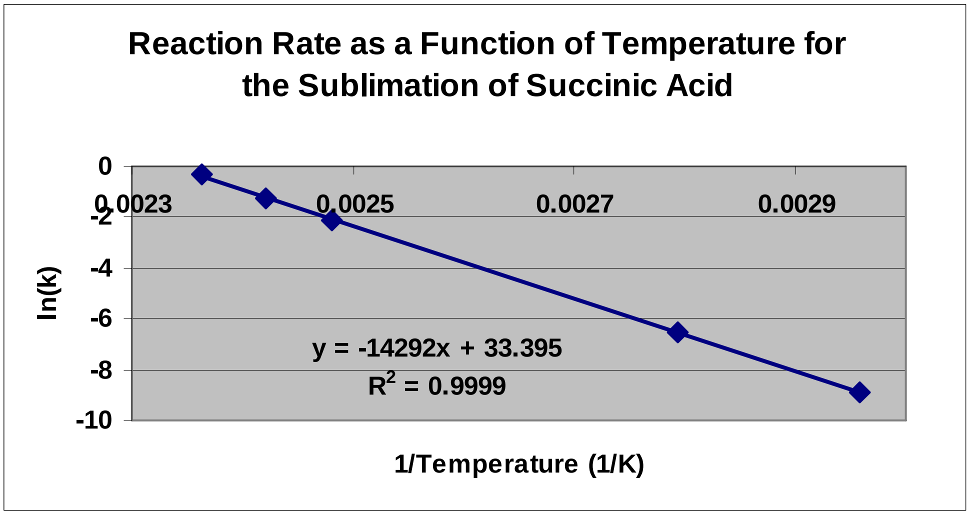


Figure 3 - Sublimation of Succinic Acid Kinetics

Similar work was performed to produce the graphs in **Figures 4 - 7** for the paste flux and the paste flux with the additionally added 15% of the individual dicarboxylic acids chosen for this study. As can be determined from the trend lines for all the succinic acid related data in **Figure 6**, there is little difference between the sublimation/evaporation of the paste flux and the paste flux with the added acid. The trend lines for these two data sets are almost parallel, meaning the rates of change are also similar. Since more negative ln(k) values mean slower weight loss, it can be seen that the paste flux/succinic acid combination actually has a lower rate of sublimation/evaporation than the paste flux itself. The lower rate could be due to more of the surface area of the combined acid/paste samples being taken up by the acid, which would mean 1) that the acid has a lower sublimation rate than the evaporation rate of the paste solvents and/or 2) in the paste flux/succinic acid mix more of the solvents are being held by hydrogen bonding to the carboxylic acid molecules.

Unfortunately one cannot conclusively say that the sublimation of the dicarboxylic acid is depressed by the paste flux. For most of the temperature range, the rate of weight loss is orders of magnitude higher for the paste flux/acid combination than that for the pure acid. And, as already stated, the paste flux/acid combination shows a lower weight loss rate than the rate for paste flux by itself. This leaves one without enough data to say how much of the weight loss in the mixture is due to the paste flux and how much is due to the acid itself.

The situation is somewhat different for the glutaric acid. Here the paste flux/glutaric acid mix is definitely losing weight slower than the acid by itself. One can be much more confident in saying that the sublimation of glutaric acid is retarded by the paste flux, although it is not proof. It is also interesting to note that the data for May and June test runs are essentially the same. The trend lines are $y = -4349.9x + 6.8879$, $R^2 = 0.995$ and $y = -4351.5x + 6.8922$, $R^2 = 0.9911$, respectively. However, the August data points that were obtained by using the same mixture used for the other data, although still giving a straight line ($R^2 = 0.9983$), are offset. It is interesting to speculate that material was lost from the mixture by sublimation during storage or more likely there has been reaction(s) in the mixture. The material was not stored at low temperature.

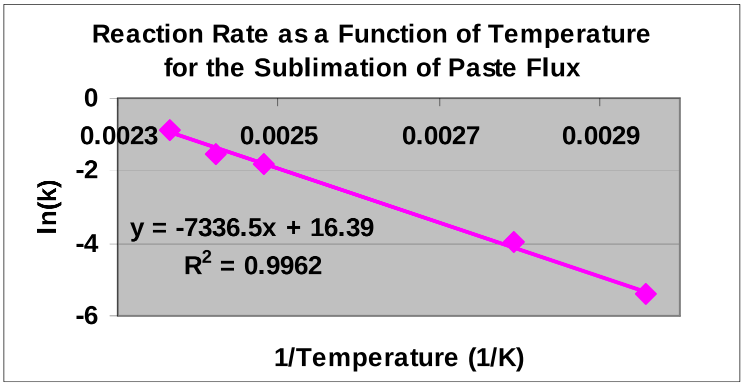


Figure 4 - Sublimation/Evaporation of Paste Flux Kinetics

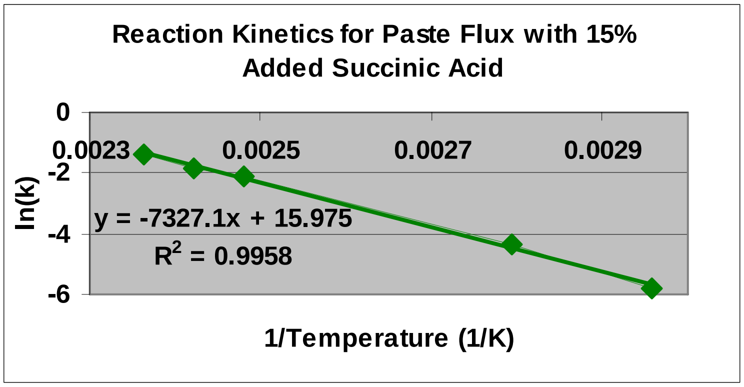


Figure 5 - Sublimation/Evaporation of Paste Flux/Succinic Acid Kinetics

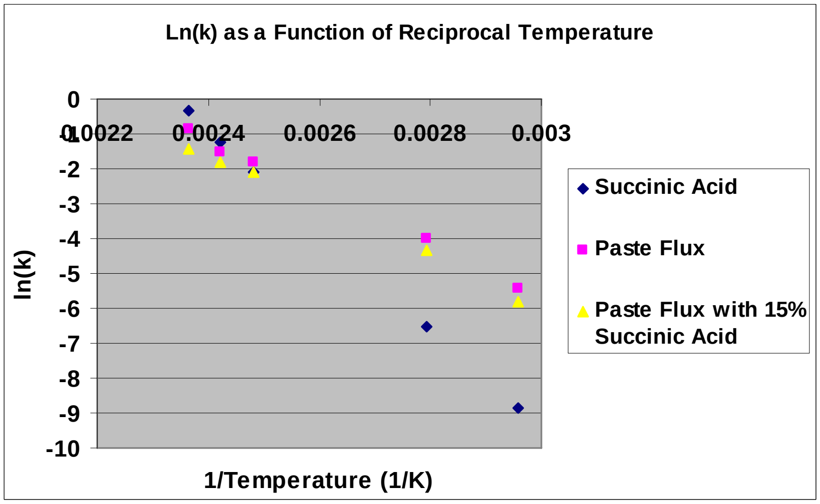


Figure 6 - Comparison of All Succinic Acid Sublimation Data

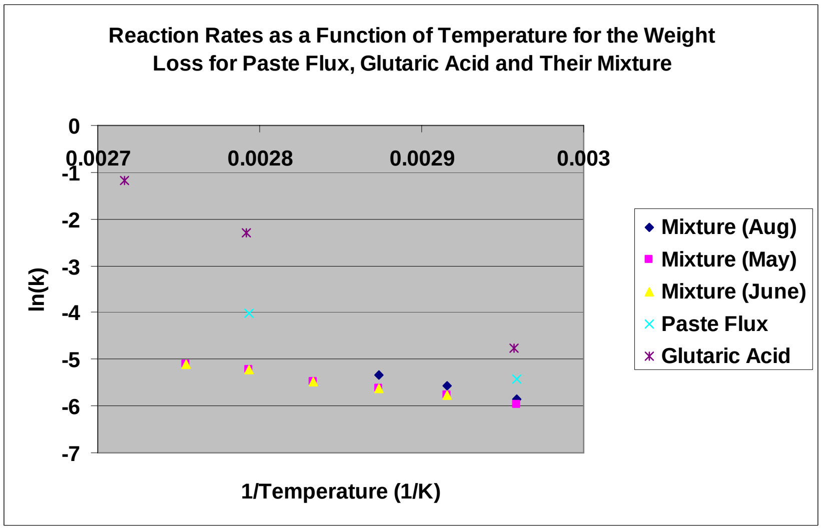


Figure 7 - Comparison of All Glutaric Acid Sublimation Data

Conclusions

The data obtained shows that the sublimation rates of glutaric acid in paste flux is probably much less than that of the same acid not encased in the other constituents of solder paste. Even less assurance of this can be given for the succinic acid. Thus a definitive statement cannot be made that solder paste qualification temperatures of 65°C or 85°C for solder pastes tested by SIR or ECM are still most likely to produce real, useable results. Further clarification of this will require more experimental work using ion chromatography studies of the solder pastes before and after typical SIR and ECM experiments or by gas chromatography/mass spectrometry experiments.

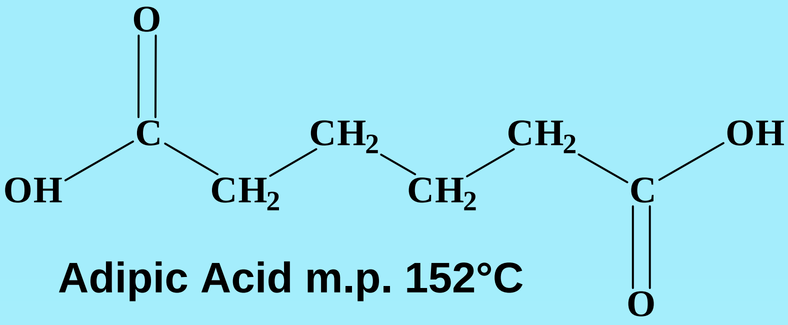
References

1. IPC J-STD-005 Requirements for Soldering Pastes, IPC, January, 1995.
2. J. Sohn, “Evaluation of No-Clean Fluxes Using Surface Insulation Resistance Testing”, Proc. NEPCON West ’93, pp 1325-1331, 1993.
3. K. Tellefsen and K. Stromgren, “The Disappearance of Dicarboxylic Acid No-Clean Flux Activators with Time and Temperature”, IPC Printed Circuits Expo ’97 Technical Proceedings, San Jose, CA, 1997.
4. IPC-TM-650, Method 2.6.14.1 Electrochemical Migration Resistance Test, 2000.
5. C. Hunt, “Development of Surface Insulation Resistance Measurements for Electronic Assemblies”, National Physics Laboratory (NPL), UK, October 2001. Issued as part of an NPL CD entitled “NPL – Electronics Interconnection Reports 1996 – 2002.
6. Bev Christian, David Turner and Leonard Zgrablic, “The Effect of Temperature and Atmosphere on the Sublimation of Some Dicarboxylic Acids Used in Fluxes”, Proceedings of ECWC 10 Conference, Anaheim, California, 2005.
7. Private communication with Brian Deram, Kester Solder

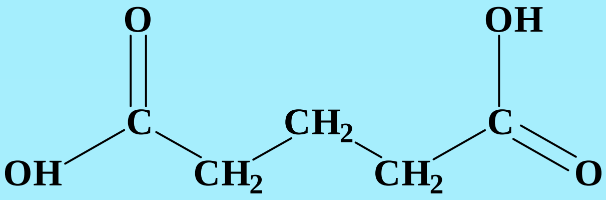
Sublimation of Two Dicarboxylic Acids Used in Solder Pastes

Bev Christian, Megan MacLean, Jason Thomas and Andrew Michael
Research In Motion
Waterloo, Ontario, CANADA

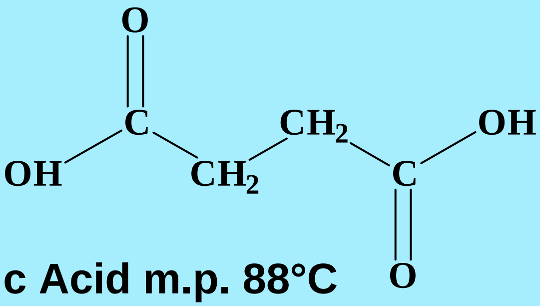
Three of the Common Dicarboxylic Acids



Adipic Acid m.p. 152°C



Glutaric Acid m.p. 97°C



Succinic Acid m.p. 88°C

Previous Work

- **SIR & ECM done using 85°C/85%RH in many cases**
- **Sohn found ECM values increased with time for 85°C measurements**
- **Tellefsen and Stromgren showed 65°C too high for adipic and succinic acids**
- **Work by EU consortium showed 40°C worked well**
- **Subsequent work in author's lab for the 3 acids showed zero order kinetics for the sublimation and confirmed extensive losses for the higher temperatures**

Result?

- IPC TM-650, Test Method 2.6.3.7 (draft)
- Very similar method required by HP

Is this all?

- What about solder pastes?
- Acids imbedded in other materials.
- Do the same “rules” apply?
- Present work done to look at this.

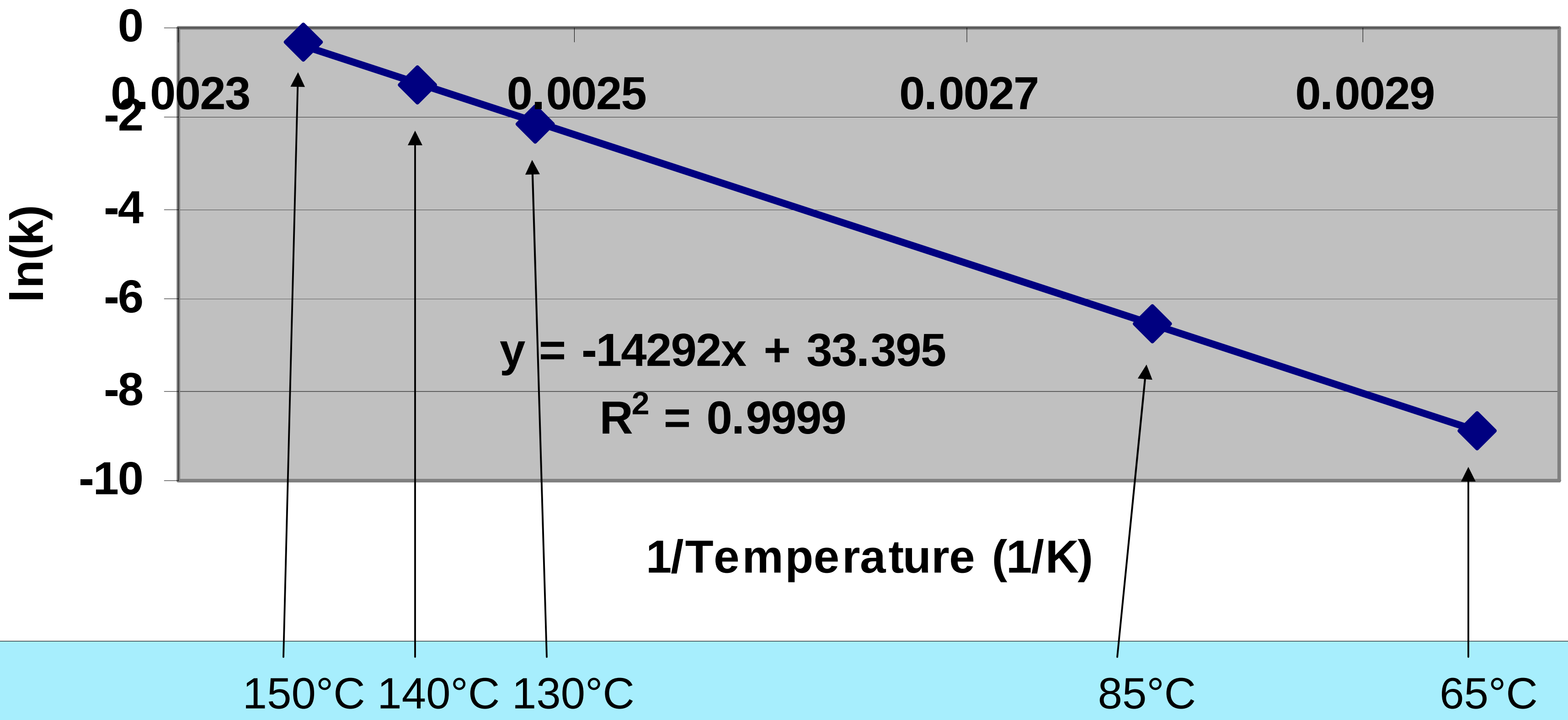
Procedure

- Mixed fine powder of acid into paste flux (15% w/w)
- Put 29 +/- 1 mg of material into Al TGA pan
- Ramped at 15°C/min to hold temperature
- Measured weight loss as a function of time

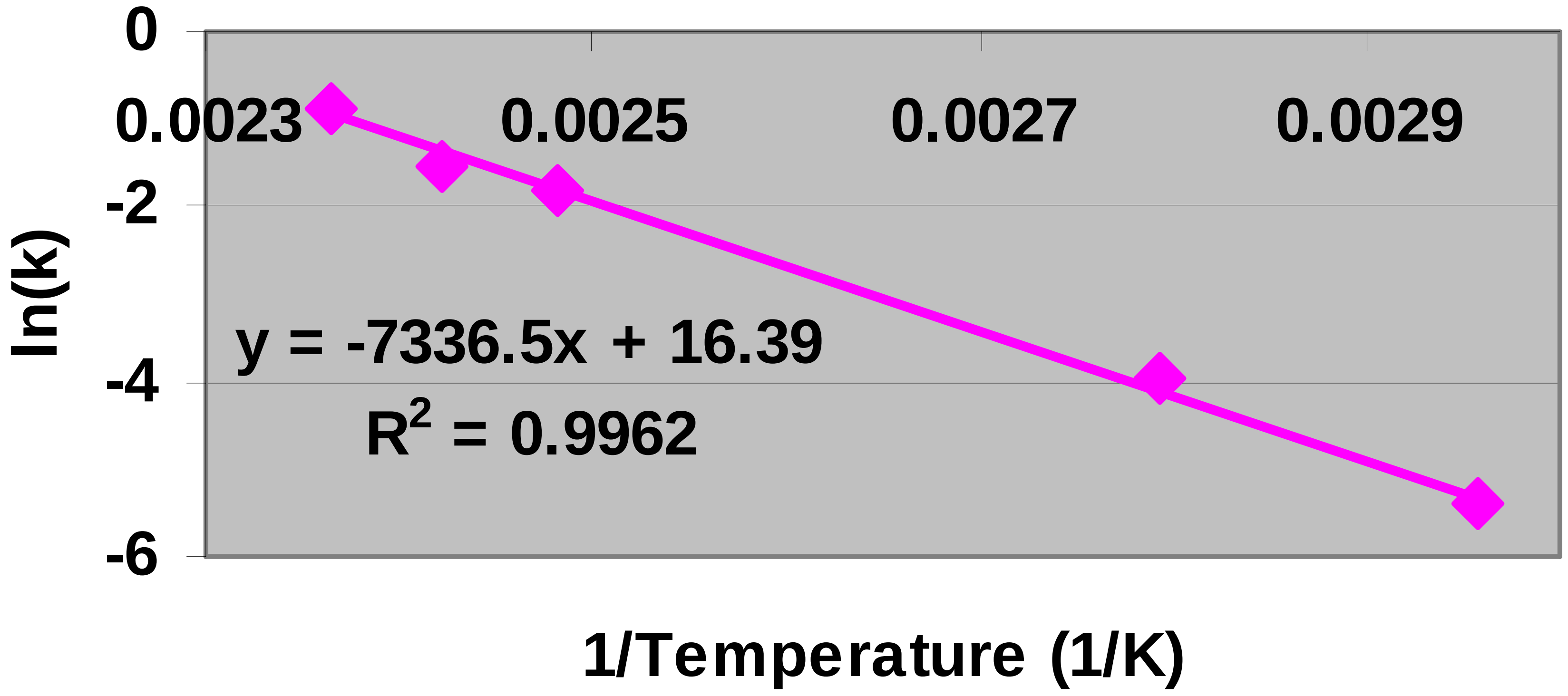
Procedure

- Plotted natural log of reaction rate as a function of the reciprocal of temperature (°K)
- Because dealing with a logarithmic function, need a correlation coefficient close to one to have confidence in the data

Reaction Rate as a Function of Temperature for the Sublimation of Succinic Acid

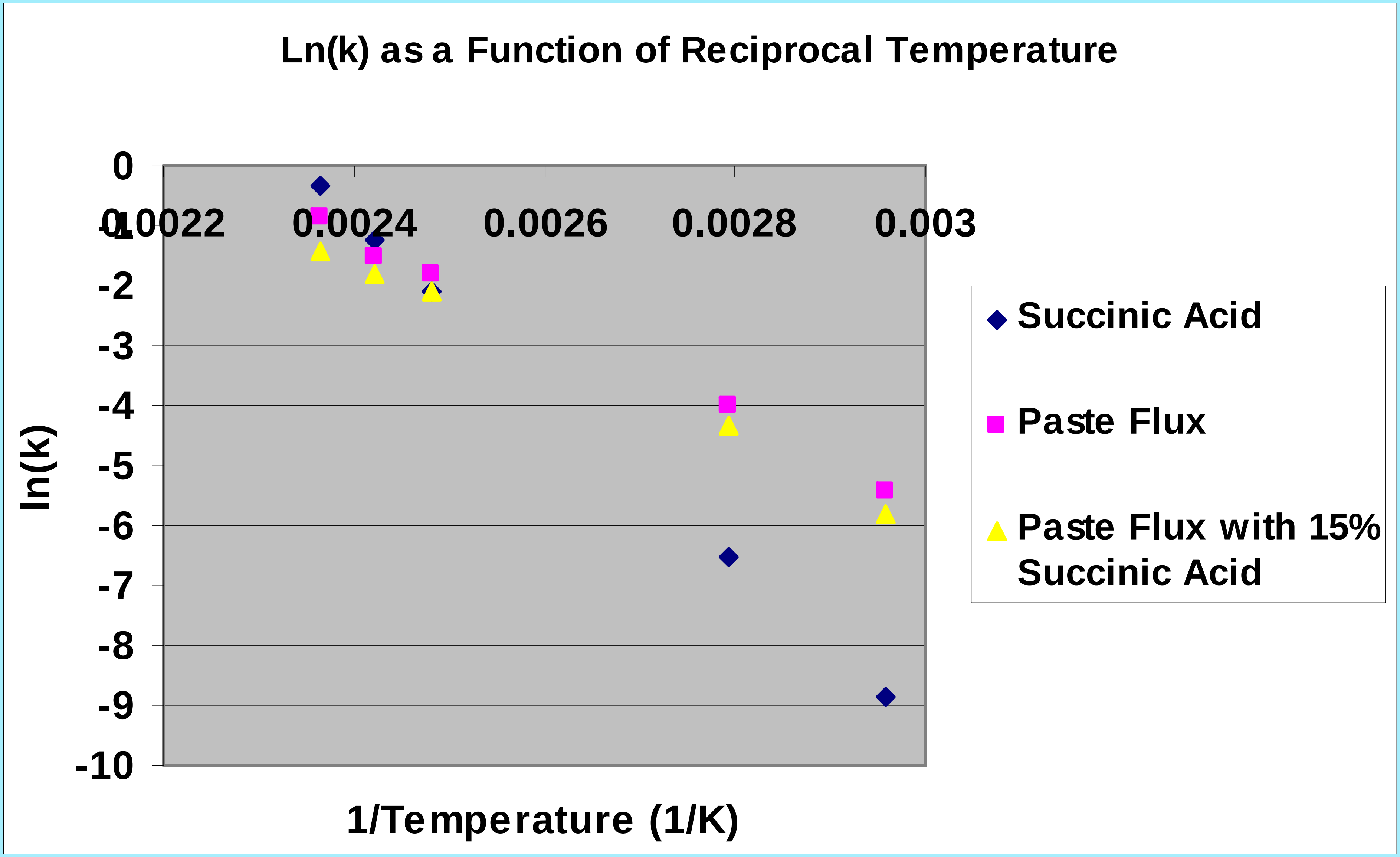


Reaction Rate as a Function of Temperature for the Sublimation of Paste Flux



$y = -7336.5x + 16.39$

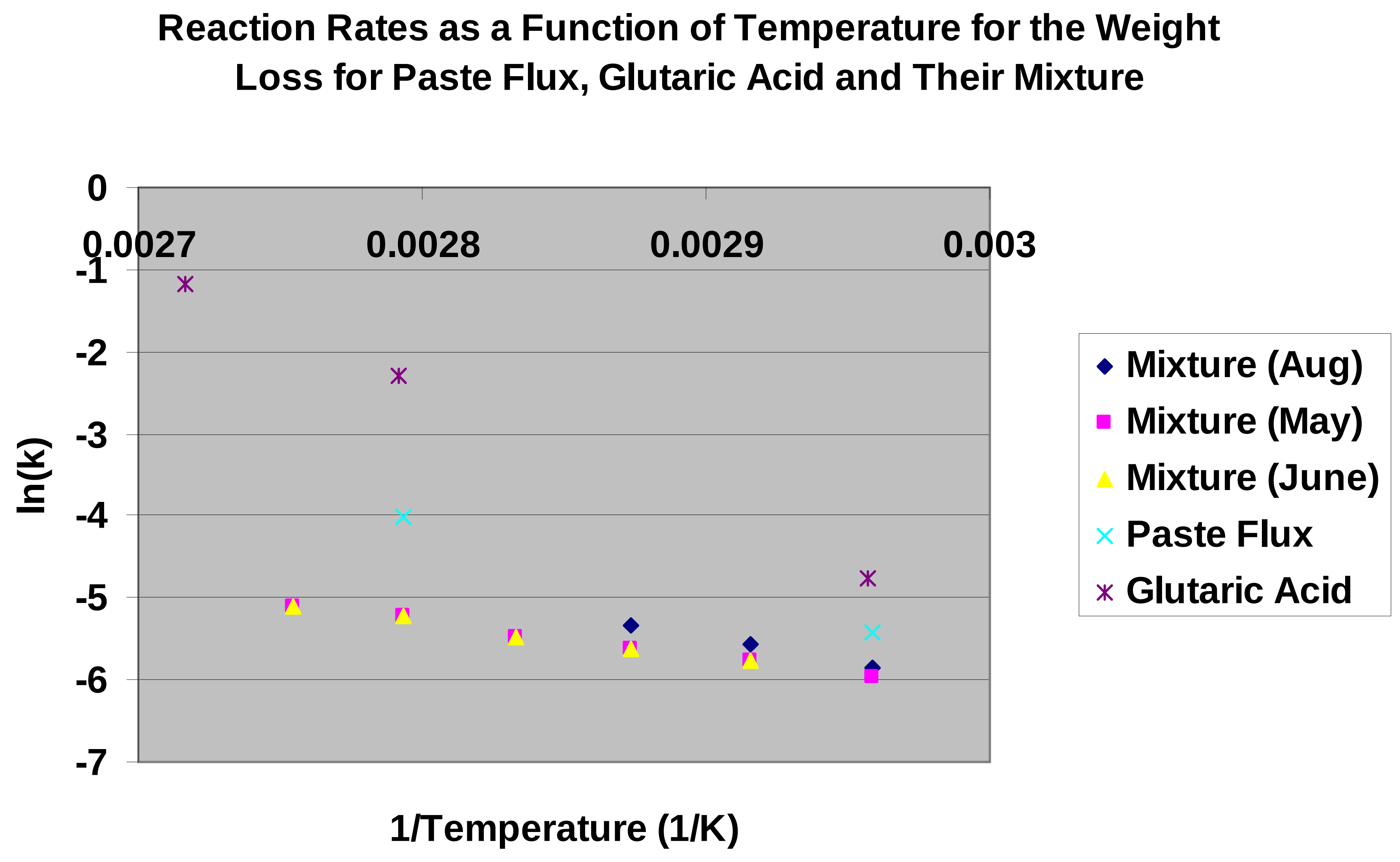
$R^2 = 0.9962$


Ln(k) as a Function of Reciprocal Temperature
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
ln(k)
0.0022
0.0024
0.0026
0.0028
0.003
1/Temperature (1/K)
◆ Succinic Acid
■ Paste Flux
▲ Paste Flux with 15% Succinic Acid

What does this mean?

- Unfortunately, not very much
- For the temperatures where ECM, etc, would be conducted the sublimation rate of the succinic acid is much less than the paste flux
- The mixture has intermediate rates, so cannot tell if the decrease is due to the decrease in acid sublimation OR (more likely) a decrease in the evaporation of the paste flux solvents
- The latter would most likely be due to acid molecules occluding the surface of the material and/or hydrogen bonding to the solvents, holding them.

Different Story for Glutaric Acid



Glutaric Acid

- **One can be more confident that that the sublimation of glutaric acid is retarded by the paste flux, although <u>it is not proof</u>.**

Conclusions

- Did not definitively prove that the paste flux inhibits the sublimation of the dicarboxylic acids studied
- Further clarification of this will require more experimental work using ion chromatography studies of the solder pastes before and after typical SIR and ECM experiments or by gas chromatography/mass spectrometry experiments.

Acknowledgment

- The authors would like to thank Mr. Benson Tendler, VP of Hardware Quality, RIM, for his support of this work.

Appendix 1- Succinic Acid

Weight (mg)	Slope (%/min)	% @Time	Run Time (min)	Temp (°C)
34.32	-0.422	72.3	59.9	150
34.60	-0.414	72.1	59.9	150
32.26	-0.424	71.6	59.9	150
33.73	**-0.420**	**72.0**	**59.9**	**150**
30.22	-0.2188	68.53	102.06	140
29.76	-0.2197	68.37	120.06	140
29.76	-0.2202	68.13	120.06	140
29.91	**-0.2196**	**68.34**	**114.06**	**140**
30.14	-0.1640	70.07	160.04	130
30.03	-0.1637	70.13	160.04	130
30.05	-0.1634	70.17	160.04	130
30.07	**-0.1637**	**70.12**	**160.04**	**130**
30.35	-0.01869	79.47	1020.04	85
30.74	-0.01874	79.65	1020.04	85
28.80	-0.01698	81.26	1023.05	85
29.96	**-0.01814**	**80.13**	**1021.043**	**85**
29.69	-0.00445	81.47	3899.94	65
30.28	-0.00445	81.51	3899.94	65
28.90	-0.00382	83.87	3901.36	65
29.62	**-0.00424**	**82.28**	**3900.413**	**65**

Appendix 2- Succinic Acid and Paste Flux

Weight (mg)	Slope (%/min)	% @Time	Run Time (min)	Temp (°C)
29.6	-0.244	75.32	81.22	150
29.1	-0.2436	75.58	80.97	150
30.2	-0.243	75.60	80.59	150
29.6	**-0.24353**	**75.50**	**80.93**	**150**
30.3	-0.1602	75.35	125.82	140
30.6	-0.1608	75.47	125.66	140
30.1	-0.1598	75.36	125.71	140
30.3	**-0.1603**	**75.39**	**125.73**	**140**
30.1	-0.1229	76.37	165.26	130
30.4	-0.1222	76.39	165.32	130
30.7	-0.1194	77.08	165.24	130
30.4	**-0.1215**	**76.61**	**165.27**	**130**
31.3	-0.01319	84.94	1021.53	85
31.2	-0.0132	84.83	1023.04	85
30.9	-0.0131	84.83	1023.04	85
31.1	**-0.01316**	**84.87**	**1022.54**	**85**
31.7	-0.00293	87.04	3894.49	65
				65
				65
31.0	**-0.00293**	**87.04**	**3894.49**	**65**

Appendix 3- Glutaric Acid

Temp	1/T(1/K)	k	Mixture (Aug)	Mixture (May)	Mixture (June)	Paste Flux	Glutaric Acid	Data Set	Weights
(°C)	(1/K)								(mg)
65	0.002959	0.002866	-5.8548379					August	29.9
70	0.002915	0.003774	-5.5796198					August	30.2
75	0.002874	0.004758	-5.3479279					August	30.1
65	0.002959	0.002525		-5.9815142				May	27.9
70	0.002915	0.003098		-5.7769985				May	29.6
75	0.002874	0.003627		-5.6193494				May	29.4
80	0.002833	0.004195		-5.4738619				May	29.3
85	0.002793	0.005337		-5.2330916				May	29.1
90	0.002755	0.006122		-5.0958664				May	28.9
70	0.002915	0.003098			-5.7769985			June	29.6
75	0.002874	0.003627			-5.6193494			June	29.4
80	0.002833	0.004195			-5.4738619			June	29.3
85	0.002793	0.005337			-5.2330916			June	29.1
90	0.002755	0.006122			-5.0958664			June	28.9
85	0.002793					-4.0096		Paste Flux	
65	0.002959					-5.4149		Paste Flux	
65	0.002957	0.00863					-4.752511	Glutaric Acid	
85	0.002792	0.1014					-2.288682	Glutaric Acid	
95	0.002716	0.3074					-1.179605	Glutaric Acid	