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# Thermal stability of $\text{LiPF}_6$ -EC:EMC electrolyte for lithium ion batteries

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## Abstract

A differential scanning calorimeter (DSC) was used to perform a thermal stability study of the  $\text{LiPF}_6$ -EC:EMC electrolyte. The effect of different variables on its thermal stability was evaluated: salt ( $\text{LiPF}_6$ ) concentration effect, solvents, EC:EMC ratios, and heating rates. Hermetically sealed and crimped DSC pans were used during the experiments. The results indicate that the salt concentration, solvent concentration, and heating rates play an important role in the thermal stability of the  $\text{LiPF}_6$ -EC:EMC electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Differential scanning calorimeter; Lithium ion batteries; Electrolyte; Thermal stability; Decomposition

## 1. Introduction

Despite the improvement and developments in safety of the lithium ion batteries (PTC, CID, shutdown separator [1,2], chemical shuttles [3,4], cathode additives [1,5], etc.) used in portable applications, there are still some safety concerns associated with scale up of these batteries to large-scale applications such as electric vehicles. For this reason, some researchers have carried out thermal stability studies on these batteries [6–15]. Most of the thermal studies have been focused on the anode and cathode materials in the presence and absence of electrolytes [6,7,9–12,14]. However, not much work has been done to study the thermal stability of the electrolytes per se. In this work a differential scanning calorimeter is used to perform a thermal stability study of  $\text{LiPF}_6$ -EC:EMC electrolyte in details. This is one of the electrolytes currently used in lithium ion batteries along with mixtures of other carbonates such as PC, DMC, and DEC [16]. Understating of the thermal stability of the electrolyte mixtures is essential in the design of safe and high-performance lithium ion batteries.

## 2. Experiment

The electrolyte mixture (1 M  $\text{LiPF}_6$ -EC:EMC 1:1), solvents (EC, EMC, DMC, and DEC) and salt ( $\text{LiPF}_6$ ) were

obtained from EM industries Inc. All of them were 99.9% pure with less than 30 ppm of water. Stainless steel hermetically sealed pans (15 ml of capacity) from Haake were used in the experiments. These pans can withstand 80 atm of pressure before rupturing [17]. The sample size was kept between 4.0 and 8.0 mg and the pans were hermetically sealed by crimping. The samples were prepared in a dry room at a temperature between 22 and 24°C and a dew point of -60°C. The measurements were carried out in a DSC 2910 from thermal analysis (TA) instruments. The weight of each sample (pan + electrolyte mixture) was taken before and after the experiment to verify that the system was hermetically sealed. In all cases, the weight was constant indicating that there were not leaks during the experiments (aluminum and silver hermetically sealed pans from Haake were also tried but they leaked during the experiments). The components of the electrolyte mixture were studied separately (salt and solvents) and combined (solvent combinations, salt-solvent combinations). Also, the salt ( $\text{LiPF}_6$ ) concentration, EC:EMC ratio, and the heating rate were varied. All of the DSC experiments were carried out at a heating rate of 10°C/min, except for the ones that involved the effect of the heating rate. The temperature range for all the experiments was from 50 to 350°C.

## 3. Results and conclusions

Fig. 1 shows the DSC curves of the salt ( $\text{LiPF}_6$ ) and the solvents. Fig. 1(a) presents the results of the experiment for a

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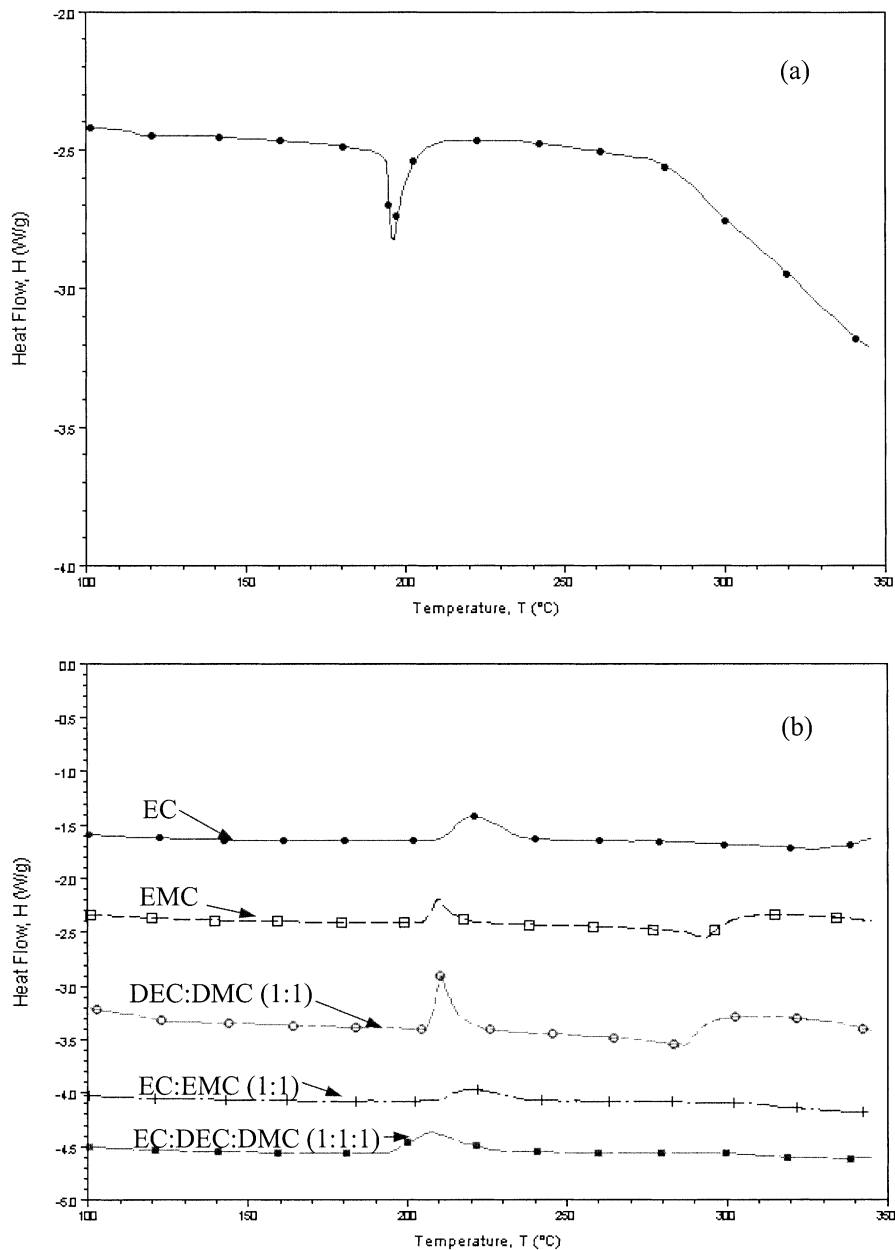


Fig. 1. DSC curves of the individual components of the electrolyte LiPF<sub>6</sub>-EC:EMC. (a) Pure salt (LiPF<sub>6</sub>); (b) pure solvents and combinations.

temperature range from 50 to 350 °C. The LiPF<sub>6</sub> was stable until about 180 °C. Two endothermic peaks are shown over the entire range, one goes from 180 to 210 °C and the other starts about 250 °C. It was found that the first peak is reversible and is due to the melting of the salt, this result agrees with what it has been reported by Du Pasquier et al. [9]. Notice that no exothermic decomposition peaks below 210 °C were observed because the amount of impurities present in the salt was insignificant (99.9% purity with maximum 30 ppm of water) and the DSC pans were hermetically sealed by crimping. Fig. 1(b) shows the DSC curves of the pure solvents and their combinations. The solvents were combined according to the volumetric ratios 1:1 (EC:EMC and DMC:DEC) or 1:1:1 (EC:DMC:DEC).

The EC results include an exothermic decomposition peak that goes from 205 to 250 °C, with a heat generation of -23 J/g. The EMC shows a lower temperature of decomposition than EC, the peak goes from 195 to 230 °C for a heat generation of -10 J/g. The decomposition of the EMC is also exothermic. The DSC curve for the combination of both solvents, EC and EMC at the 1:1 volumetric ratio shows an exothermic peak that goes from 205 to 250 °C with a heat generation of -11 J/g. The DEC:DMC (1:1) results show the same reactivity performance that the EMC, as well as the EC:DEC:DMC (1:1:1) shows the same reactivity performance that the mixture of EC:EMC (1:1). The total heat generation of the DEC:DMC (1:1) mixture is -22 J/g while for the EC:DEC:DMC (1:1:1) mixture is the -20 J/g. The

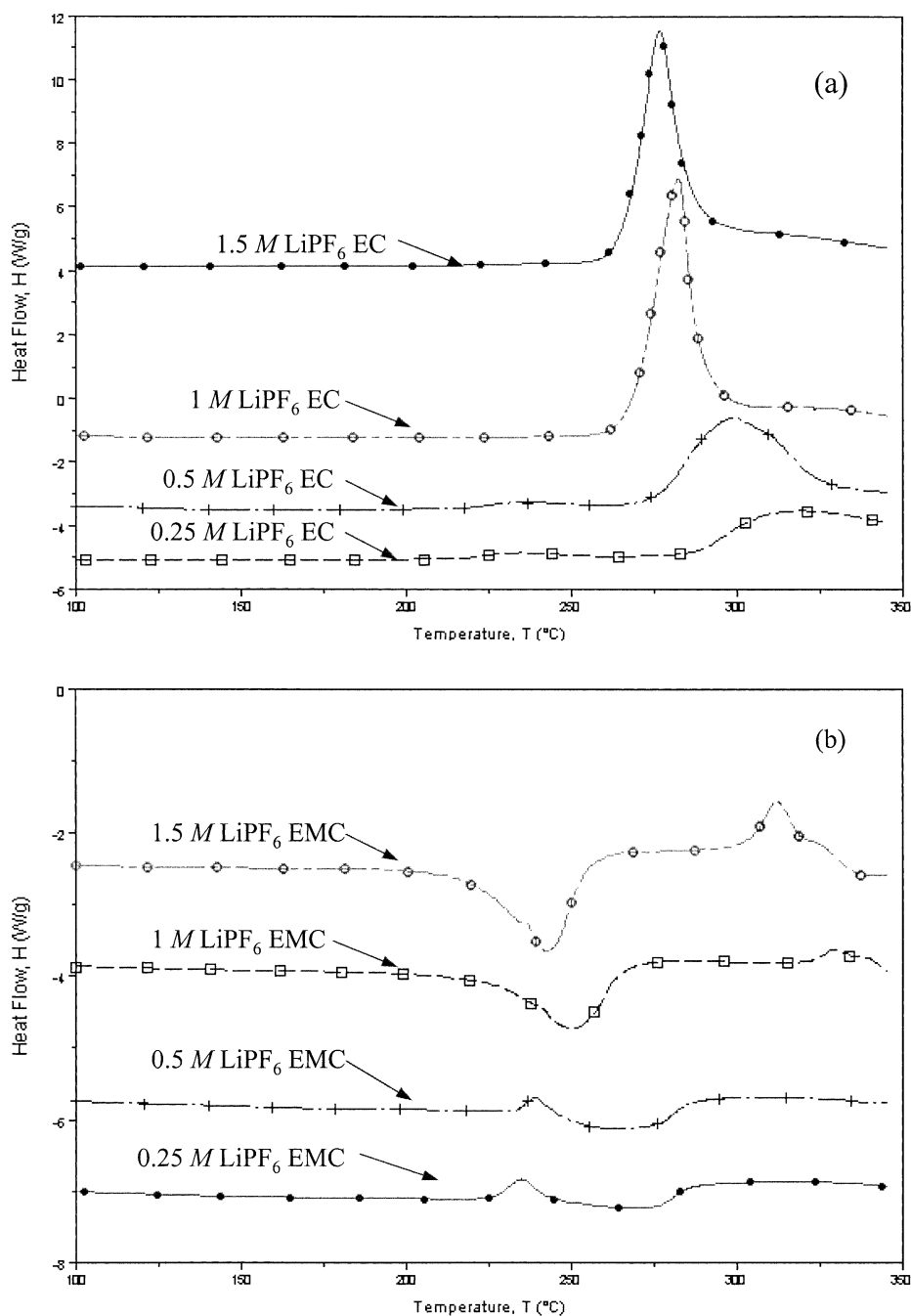


Fig. 2. DSC curves of the salt plus individual solvents with different concentrations of the salt. (a)  $\text{LiPF}_6$  with EC; (b)  $\text{LiPF}_6$  with EMC.

differences in the heat generated between the EMC and the DEC:DMC (1:1) mixture and the EC:EMC (1:1) mixture and the EC:DEC:DMC (1:1:1) mixture are due to heat generated between DEC:DMC to produce EMC according to the reaction [18]



None of the peaks shown in Fig. 1(b) were reversible, which means that they did not take place after cooling down and heating up the sample again.

Fig. 2 shows the DSC curves of the salt plus individual solvents with different concentrations of the salt. Fig. 2(a) indicates that the reactivity of the EC increases with increasing the concentration of the salt. At small concentrations of the salt (0.25 and 0.5 M), two exothermic peaks are shown in Fig. 2(a): a small peak and a large peak. The small peak corresponds to the decomposition of the EC and could be due to a combustion reaction (see Fig. 1(b)), while the large peak may be due to the decomposition of the salt (see Table 1), this hypothesis would be tested in the future.

Table 1  
Summary of the onset temperatures and heat of reactions of the results shown in Figs. 1–3<sup>a</sup>

Material	$T_i \pm 1^\circ\text{C}$	$T_f \pm 1^\circ\text{C}$	$T_{\text{onset}} \pm 1^\circ\text{C}$	$H_R$ (J/g) <sup>b</sup>
LiPF <sub>6</sub>	180	210	194	20 ± 2
EC	205	250	211	−23 ± 2
EMC	195	230	205	−10 ± 1
DEC:DMC (1:1)	200	245	208	−22 ± 2
EC:EMC (1:1)	205	250	209	−11 ± 1
EC:DEC:DMC (1:1:1)	195	235	205	−20 ± 2
1 M LiPF <sub>6</sub> –EC	250	>350	270	>−620 ± 60
1 M LiPF <sub>6</sub> –EMC	195	280	233	160 ± 20
	320	340	324	−22 ± 2
1 M LiPF <sub>6</sub> –DEC:DMC (1:1)	195	280	231	150 ± 20
1 M LiPF <sub>6</sub> –EC:EMC (1:1)	200	250	228	30 ± 3
	250	>350	253	>−330 ± 30
1 M LiPF <sub>6</sub> –EC:DEC:DMC (1:1:1)	200	250	225	76 ± 8
	250	>350	256	>210 ± 20
0.25 M LiPF <sub>6</sub> –EC	200	261	219	−21 ± 2
	280	>350	290	>−170 ± 20
0.5 M LiPF <sub>6</sub> –EC	207	260	219	−21 ± 2
	263	>350	277	>−500 ± 50
1.5 M LiPF <sub>6</sub> –EC	244	>350	267	>−740 ± 70
0.25 M LiPF <sub>6</sub> –EMC	213	244	227	−15 ± 1
	244	290	No define	38 ± 4
0.5 M LiPF <sub>6</sub> –EMC	226	246	234	−9 ± 1
	246	288	No define	44 ± 4
1.5 M LiPF <sub>6</sub> –EMC	186	267	228	180 ± 20
	285	330	304	−43 ± 4
0.25 M LiPF <sub>6</sub> –EC:EMC (1:1)	275	>350	312	>−84 ± 8
0.5 M LiPF <sub>6</sub> –EC:EMC (1:1)	240	>350	261	>−260 ± 30
1.5 M LiPF <sub>6</sub> –EC:EMC (1:1)	200	250	225	40 ± 4
	250	>350	248	>−320 ± 30
2 M LiPF <sub>6</sub> –EC:EMC (1:1)	200	250	219	41 ± 4
	250	>350	240	>−340 ± 30
1 M LiPF <sub>6</sub> –EC:EMC (1:2)	180	250	225	51 ± 5
	250	>350	255	>−260 ± 30
1 M LiPF <sub>6</sub> –EC:EMC (2:1)	180	250	225	15 ± 2
	250	>350	250	>−340 ± 30

<sup>a</sup>  $T_i$ ,  $T_f$ ,  $T_{\text{onset}}$ , and  $H_R$  represent the initial decomposition temperature, the final decomposition temperature, the onset temperature and the heat of reaction, respectively.

<sup>b</sup> Negative values indicate exothermic reaction.

Fig. 2(b) indicates that the reactivity of the EMC increases with increasing the concentration of the salt. The small exothermic peaks for 0.25 and 0.5 M LiPF<sub>6</sub>–EMC correspond to the decomposition of the EMC (see Fig. 1(b)). The large endothermic peak may be related to the decomposition of the salt or cracking of the EMC (see Fig. 1(a)), this hypothesis would be tested in the future. In both, Fig. 2(a) and (b), the presence of the salt enhances the heat generation of large peaks and the temperature at which the large peaks

are shown is shifted to lower values with increasing the salt concentration. At large concentrations of the salt, the small peaks (with total heat generation lower than −25 J/g) are not observed because they get overlap (included) with the large peaks.

Fig. 3 presents the effect of the salt and solvent concentrations on the reactivity of the electrolyte system. Fig. 3(a) shows the DSC curves of the salt plus the solvents for different concentrations of the salt. The salt concentrations

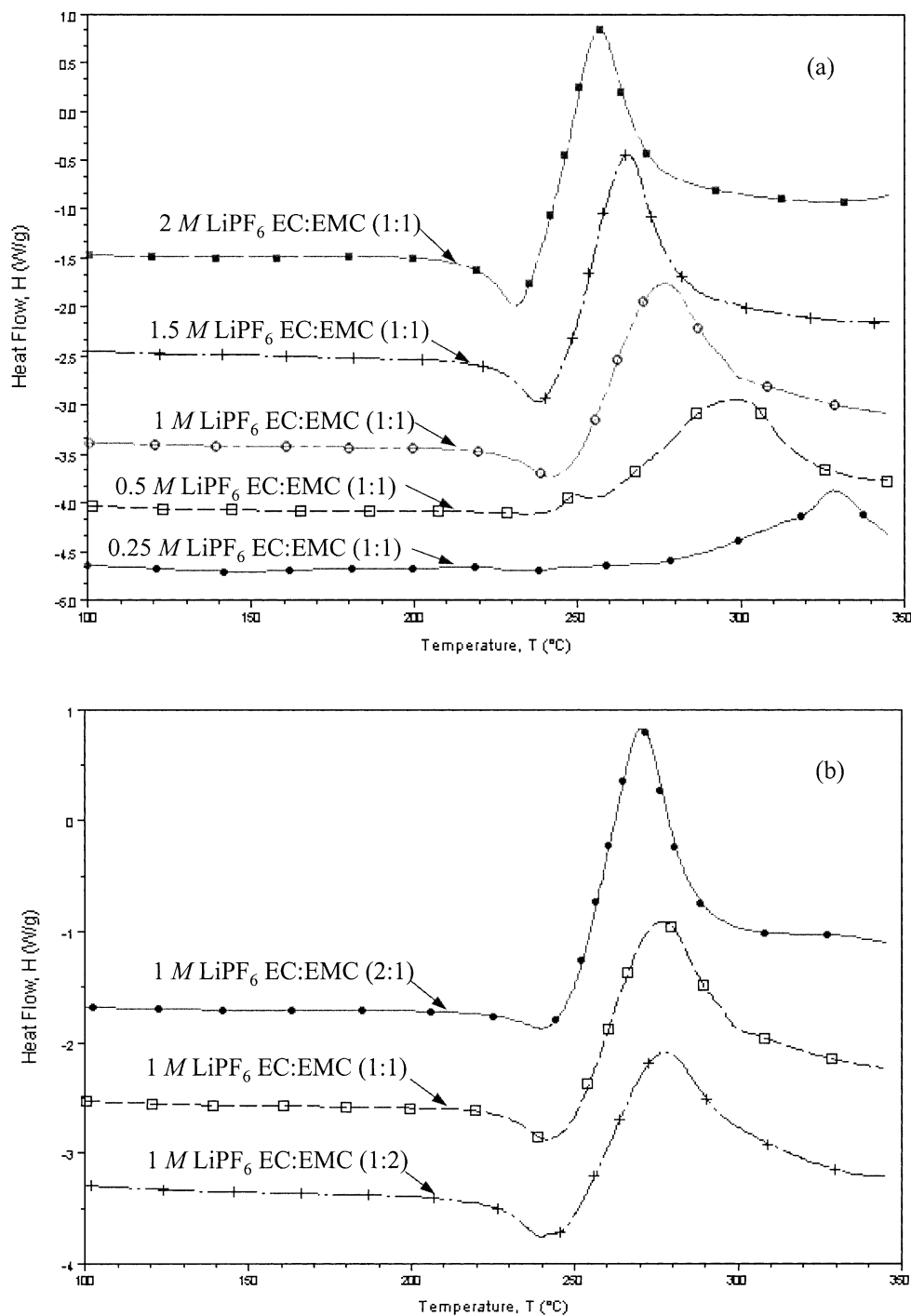


Fig. 3. Effect of the salt and solvent concentrations on the reactivity of LiPF<sub>6</sub>-EC:EMC. (a) DSC curves of the salt plus combinations of the solvents with different concentrations of the salt; (b) DSC curves of the salt plus the solvents with different volume ratios of the solvents.

analyzed during the experiment were 0.25, 0.5, 1, 1.5, and 2.0 M LiPF<sub>6</sub>. In all the cases, the ratio of the solvents was kept constant at 1:1 (EC:EMC). These results indicate that the reactivity of the electrolyte increases with increasing the salt concentration.

At small salt concentrations (0.25 and 0.5 M) the endothermic peak related to the reaction between the salt

and the EMC is not observed. This indicates that the salt concentration is not large enough to make this reaction takes place. Fig. 3(b) shows curves of the salt plus the solvents with different volume ratios of the solvents. All of the samples contained 1 M LiPF<sub>6</sub>. The results indicate that the reaction rates are a function of the solvent concentrations. Large EMC concentrations enhance the reaction rate

Table 2  
Effect of the heating rate on the onset temperature and heat of reaction of the thermal decomposition of 1 M LiPF<sub>6</sub>-EC:EMC (1:1)<sup>a</sup>

Heating rate (°C/min)	$T_i \pm 1^\circ\text{C}$	$T_f \pm 1^\circ\text{C}$	$T_{\text{onset}} \pm 1^\circ\text{C}$	$H_R$ (J/g) <sup>b</sup>
1	185	210	194	14 ± 1
	210	300	212	-270 ± 30
5	190	235	216	23 ± 2
	235	>300	240	>-290 ± 30
10	200	250	228	30 ± 3
	250	>350	253	>-330 ± 30
15	220	260	235	40 ± 4
	260	>350	264	>-300 ± 30
30	240	280	252	67 ± 7
	280	>350	283	>-260 ± 30

<sup>a</sup>  $T_i$ ,  $T_f$ ,  $T_{\text{onset}}$ , and  $H_R$  represent the initial decomposition temperature, the final decomposition temperature, the onset temperature and the heat of reaction, respectively.

<sup>b</sup> Negative values indicate exothermic reaction.

for the LiPF<sub>6</sub>-EMC, while large EC concentrations enhance the reaction rate for the LiPF<sub>6</sub>-EC.

A summary of the onset temperatures, initial and final decomposition temperatures, and heat of reactions associated with the results shown in Figs. 1–3 are summarized on Table 1.

Table 2 shows the effect of the heating rate on the onset temperature and heat of reaction of the thermal decomposition of 1 M LiPF<sub>6</sub>-EC:EMC (1:1). The results indicate that increasing the heating rate increases the heat production or consumption of the reactions. However, the higher the heating rates, the higher the start up temperature of the reactions. At high heating rates, the temperature of the system is forced to rise fast with time, so it will take a high temperature to generate the sensitive heat (heat associated with the mass of the system) necessary to start up the reaction. Nevertheless, once the reaction starts it will be much faster than at a lower temperature because the reaction

rate increases with increasing the temperature, increasing the total heat generated or consumed by the reaction.

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