

1 **New insights on the kinetic analysis of isothermal data: the independence of**
2 **the activation energy from the assumed kinetic model.**

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6

7 **Abstract**

8 Isothermal experiments are widely employed to study the kinetics of solid state reactions or
9 processes in order to extract essential kinetic information needed for modeling the processes at
10 an industrial scale. The kinetic analysis of isothermal data requires finding or assuming a
11 kinetic function that can properly fit the evolution of reaction rate with time so that the
12 resulting parameters, i.e. the activation energy and the preexponential factor, can be considered
13 reliable. In the present work, we demonstrate using both simulated and experimental data that
14 the kinetic analysis of a set of isothermal plots obtained at different temperatures, considering a
15 single step solid state reaction, necessarily leads to the real activation energy, regardless the
16 mathematical function selected for performing the kinetic analysis. This makes irrelevant the
17 election of the kinetic function used to fit the experimental data and greatly facilitates the
18 estimation of the activation energy for any single process.

19 **Keywords:** Kinetic Analysis, Isothermal; Kinetic Model; Activation Energy; Process
20 Modeling

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22 **1. Introduction**

23 Kinetic analysis is widely employed as a tool for obtaining the essential knowledge needed for
24 modeling processes on an industrial scale. This is also true in the field of energy conversion
25 and production, with an important number of papers published every year in which the main
26 objective is determining the kinetics governing processes such as pyrolysis, gasification,
27 combustion or thermal decomposition in order to optimize operating conditions¹⁻¹⁴. The
28 experimental data are usually collected under isothermal or linear heating conditions. While
29 linear heating rate experiments provide quickness and simplicity, in many studies such as those
30 involving long-term aging at operation temperatures¹⁵⁻¹⁷, oxidation processes¹⁸⁻²⁰, reaction
31 progress followed by spectral or DRX peak intensity measurements²¹⁻²³, chemical looping
32 processes^{1, 3, 11, 24} or those set-ups that try to replicate industrial operation conditions^{9, 12, 13},
33 isothermal experiments are still the most convenient or even feasible option. Moreover,
34 isothermal experiments present the distinct advantage of a higher capability for kinetic
35 mechanism discrimination due to the fact that the shape of the integral α -time curve is directly
36 related to the obeyed model^{25, 26}. Thus, the α -time traces of phase boundary controlled reaction
37 (so called “n order” reactions) are convex, the diffusion controlled reactions are concave and
38 those whose rate is controlled by the formation and growth of nuclei (Avrami-Erofeev models)
39 have sigmoidal shape. On the other hand, the α -temperature plots recorded under rising
40 temperature are always sigmoidal-shaped, whatever the reaction kinetic model^{27, 28}

41 A former review²⁹ on the kinetic dehydroxylation of kaolinite found that similar activation
42 energies had been reported by different authors despite the proposal of different kinetic models.
43 An analysis of those experimental data assuming a set of different kinetic models revealed that
44 the activation energies obtained were independent of the kinetic model previously assumed,
45 although no explanation was given. If such behavior was generalized, it would constitute an
46 extraordinary advantage since it is generally assumed that the activation energy obtained by a

47 kinetic analysis is dependent on the kinetic law used to fit the experimental data^{27,30,31}. Thus,
48 authors must spend a great deal of effort to determine the kinetic function most adequate to the
49 process under study in order to assure a reliable set of kinetic parameters²⁷. In the present work
50 we explore the influence the kinetic law selected to fit the experimental data has on the
51 activation energy yielded by the kinetic analysis of a set of isothermal curves recorded at
52 different temperatures. It is demonstrated first theoretically and then analyzing sets of both
53 simulated and experimental data, that the activation energy obtained by this kind of analysis
54 would always be the correct one, regardless the mathematical function selected for fitting the
55 data.

56 **2. Experimental**

57 Thermal degradation experiments were carried out using polytetrafluoroethylene (Aldrich,
58 product number 182478) at temperatures of 480, 490 and 500 °C in a Q5000IR TA Instruments
59 TGA (TA Instruments, Crawley, UK) connected to a gas flow system to work in inert
60 atmosphere equipment under 100 mL min⁻¹. Samples sizes of ~20 mg were placed in a
61 platinum crucible and heated at 300 °C min⁻¹ to the final temperature in order to avoid mass
62 loss before the steady state is attained.

63

64 **3. Theory**

65 It is well known that the kinetics of a solid state reaction, in conditions far from the
66 equilibrium, can be described by the general equation:

$$67 \quad \frac{d\alpha}{dt} = kf(\alpha) \quad (1),$$

68 where t represents the time, α is the extent of reaction and k is the rate constant, which depends
69 on the temperature according to the Arrhenius equation, $k=A\exp(-E_a/RT)$. The kinetic model,
70 $f(\alpha)$, is a function describing the relationship between the reaction rate and the reacted fraction.
71 An ample selection of $f(\alpha)$ functions have been published along the last decades, ranging from
72 the widely employed first or n^{th} order laws to more sophisticated diffusion or nucleation models
73 ³²⁻³⁴. It is important to remark that Eq. (1) does not consider any particular heating schedule so
74 it should be fulfilled whatever the time-temperature program employed for obtaining the
75 experimental data. Additionally, the reacted fraction or conversion α can be established using
76 data extracted with any technique measuring a property that can be directly related to the
77 reaction rate, most usually the mass loss recorded by thermogravimetry. The standard
78 isothermal method of kinetic analysis follows a model-fitting approach²⁷. Thus, a series of
79 isotherms are recorded at different temperatures and the extracted experimental data are fitted
80 to a set of different kinetic models, according to the following equations, which are obtained by
81 integrating Eq (1):

$$82 \quad \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t k dt \quad (2a)$$

$$83 \quad g(\alpha) = kt \quad (2b),$$

84 where $g(\alpha)$ is the integral form of the kinetic model. The plot of $g(\alpha)$ versus the reaction time
85 (provided that the time for reaching the temperature steady state is negligible with regards to
86 the elapsed time) leads to a straight line whose slope is the rate constant, k . Then, given the
87 Arrhenius dependence of the rate constant with the temperature, the activation energy can be
88 subsequently calculated by plotting the logarithm of the rate constants versus the reverse of
89 their corresponding temperatures:

$$90 \quad \ln k = \ln A - E_a/RT \quad (3)$$

91 Let us assume the experimental kinetic data are fitted with a $G(\alpha)$ function different from the
92 one really obeyed by the reaction, $g(\alpha)$, regardless of the quality of the resulting regression
93 coefficient. In such case, an apparent rate constant, k_a , would be obtained from the plot of $G(\alpha)$
94 as a function of t according to the following equation:

$$95 \quad G(\alpha) = k_a t \quad (4),$$

96 The comparison of Eqs (2b) and (4) leads to the conclusion that the acceptance of a reasonable
97 linear correlation between $G(\alpha)$ and t necessarily implies to accept a linear correlation between
98 $G(\alpha)$ and $g(\alpha)$, that would be expressed according to the following equation:

$$99 \quad G(\alpha) = ag(\alpha) + b \quad (5),$$

100 a and b being constants.

101 It can be concluded from Eqs. (2b), (4) and (5) that, whatever would be the temperature, the
102 apparent constant reaction rate, k_a is related with the actual one, k , through the following
103 relationships:

$$104 \quad \frac{dG(\alpha)}{dt} = k_a = a \frac{dg(\alpha)}{dt} = ak \quad (6).$$

105 Eq. (6) shows that $k_a = ak$. Moreover, taking into account that k fits the Arrhenius equation, it
106 follows:

$$107 \quad k_a = ak = aAe^{-E/RT} \quad (7),$$

108 that could be rearranged in the following form:

$$109 \quad \frac{-\ln k_a}{d(1/T)} = \frac{-\ln k}{d(1/T)} = E/R \quad (8)$$

110 Thus, Eq. (8) clearly demonstrates that the activation energy determined from a set of
111 isothermal α -time plots obtained at different temperatures is independent of the kinetic model
112 previously assumed for performing the kinetic analysis.

113

114 **4. Kinetic analysis of simulated isothermal curves**

115 The time at which a given α value is reached at a certain temperature T can be determined,
116 according to Eq. (2b), from the following expression:

$$117 \quad t = \frac{g(\alpha)}{Ae^{-E/RT}} \quad (9)$$

118 Thus, Eq. (9) was used to numerically construct two sets of simulated curves assuming
119 temperatures of 250, 265, 275 and 300 °C. Figure 1a includes a set of isotherms simulated
120 according to the following kinetic parameters: $E=200$ kJ/mol, $A=10^{16}$ min⁻¹ and a first order
121 kinetic model (F1). On the other hand, isotherms in Figure 1b were constructed assuming the
122 same activation energy and pre-exponential factor as the previous set and an Avrami nucleation
123 kinetic model (A2). The figure clearly shows how the first order trace is convex while the
124 nucleation-driven trace is sigmoidal, as aforementioned. Then, the data from all the curves in
125 Figure 1 were linearly fitted to several theoretical kinetic models, as per Eq (2b), producing the
126 rate constant values listed in Tables 1 and 2, together with their corresponding correlation
127 coefficients. In order to better replicate the analysis procedures most commonly employed in
128 the literature, the fit was limited to data comprising the conversion range $0.1 \leq \alpha \leq 0.9$ since the
129 extreme ranges are more sensitive to experimental errors. Figure 2 includes a selection of plots
130 constructed using data from the 265 °C isothermal curve, providing a clear picture of the results
131 obtained. The linear fits from which slope the rate constants are determined are also marked in
132 the Figure. As expected, only the correct $g(\alpha)$ function produces a flawless linear fit whereas

133 the fit to incorrect models yield non-linear plots with different slopes and, therefore, lead to
134 different rate constants. Nevertheless, it is worth mentioning that 5 out of the 8 models tested
135 yielded significant correlation coefficients, over 0.99. Even more striking are the conclusions
136 reached when the activation energy is determined for each set of rate constants (Tables 1 and 2)
137 as per Eq. (3). Table 3 lists the activation energies and pre-exponential factors obtained,
138 depending on the model used to construct the simulated curves and the model used to fit the
139 data. Results are identical for every case, with the analysis yielding the correct activation
140 energy regardless the model assumed. Thus, the erroneous selection of a kinetic law, and
141 consequently, the erroneous estimation of the rate constants have no influence whatsoever on
142 the obtained activation energy. On the other hand, the pre-exponential factors present a slight
143 variability as it is expected from Eq. (7), although it is still well within the accepted error range
144 given the high numerical value of such constant. It should be warned that any prediction
145 attempt requires the knowledge of correct kinetic model driving the process. Thus, for a given
146 temperature, each kinetic triplet in Table 3 will produce a different α -time curve, with only the
147 right model been able to accurately predict the experimental curve. Nevertheless, it is still
148 possible to make reliable predictions from the model-independent E values obtained by the
149 isothermal method by employing Vyazovkin's isoconversional equation.³⁵

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151 **5. Kinetic analysis of experimental isothermal curves**

152 Next, for further confirmation, real experimental data are tested. Figure 3 includes three
153 isothermal curves, corresponding to the decomposition of polytetrafluoroethylene (Aldrich,
154 product number 182478) recorded at temperatures of 480, 490 and 500 °C in a Q5000IR TA
155 Instruments TGA equipment under a 100 mL min⁻¹ flow of N₂. The plots of $g(\alpha)$ versus the
156 reaction time, as per Eq (2b), for each isothermal curve were built using eight different kinetic
157 models. A selection of these plots is shown as examples in Figure 4. The rate constants, as

158 directly calculated from the slope of the plots, are included in Table 4, as well as the activation
159 energies determined using each set of rate constants, as previously described. Additionally, the
160 plots of the rate constants versus the reverse of the temperature (as per Eq. (3)), from which the
161 activation energies are calculated, are included in Figure 5. These results indicate that, as
162 predicted by the mathematical development presented in a previous section, the same value for
163 the activation energy, 261 ± 1 kJ/mol, is reached whatever the kinetic model used to fit the data.
164 The activation energy here obtained is in agreement with that estimated in a previous study
165 using the same material and employing a combined approach based on both model-fitting and
166 isoconversional methods, thus confirming the validity of the results.³⁶ Additionally, as it
167 happened with the simulated curves, four out of eight models can fit the experimental data with
168 reasonable correlation coefficients.

169 This finding entails significant implications. The fact that the correct activation energy of a
170 single process would always be obtained from a set of isotherms regardless of the kinetic model
171 chosen to fit the data permits the isothermal method of kinetic analysis to provide the activation
172 energy of any single step reaction without needing any previous knowledge regarding the
173 reaction mechanism. In any case, heat and mass transfer limitations typical of isothermal
174 experiments must still be considered in the experiments design since they will inevitably
175 produce interferences with the real process if not adequately minimized. The ability of the
176 method to yield the correct activation energy regardless of the model used is especially
177 interesting if we consider that most reactions will rarely follow faithfully any theoretical
178 models, which were built upon several ideal assumptions and constraints which are seldom
179 fulfilled in real reactions. For instance, inhomogenous distribution in size and particle shape
180 have been shown to have an important effect on the shape of the experimental curves.³⁷ Such
181 deviations would have consequences in model-fitting methods of kinetic analysis of linear
182 heating rate experiments because the activation energy and the pre-exponential factors provided

183 are heavily dependent on the kinetic model used for the fitting.^{31,38,39} On the other hand, as
184 shown here, the activation energy and pre-exponential factors provided by the isothermal
185 method are independent of the model used to fit the experimental data, hence preventing the
186 distorting effect of non-ideal models or inhomogenous materials.

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188 6. Conclusions

189 It has been proven that the actual activation energy of any single step solid state reaction can
190 be determined from a set of isothermal experiments regardless of the kinetic model of function
191 obeyed by the reaction and/or the kinetic equation previously assumed for performing the
192 kinetic analysis. Thus, the isothermal method of kinetic analysis behaves at all effects as a
193 model-free since the activation energy and the pre-exponential factor can be calculated without
194 a previous knowledge of the kinetic model. Moreover, the kinetic parameters thus obtained
195 would be representative of the reaction even when none of the theoretical models could closely
196 represent the studied process.

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Figure Captions

265 **Figure 1.** Isothermal curves simulated according to the following kinetic parameters:

266 $E=200\text{kJ/mol}$, $A=10^{16}\text{ min}^{-1}$ and (a) F1 kinetic model, $f(\alpha)=(1-\alpha)$ or (b) A2 Avrami model,
267 $f(\alpha)=2(1-\alpha)(-\ln(1-\alpha))^{0.5}$.

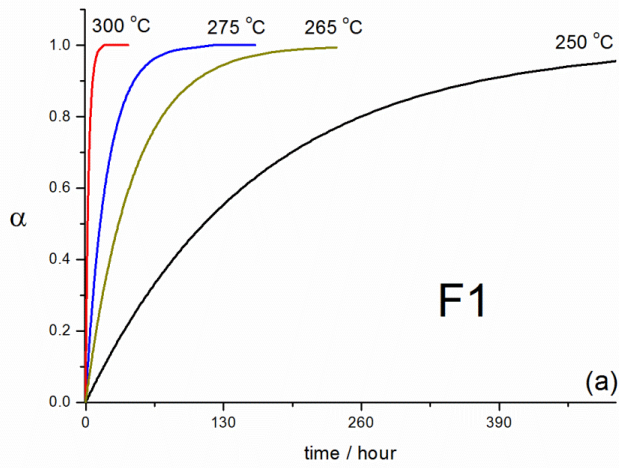
268 **Figure 2.** Fit of the 265°C isothermal curves simulated assuming (a) F1 and (b) A2 models to a
269 set of different kinetic models.

270 **Figure 3.** Isothermal curves corresponding to the degradation of PTFE, recorded at 480, 490
271 and 500°C.

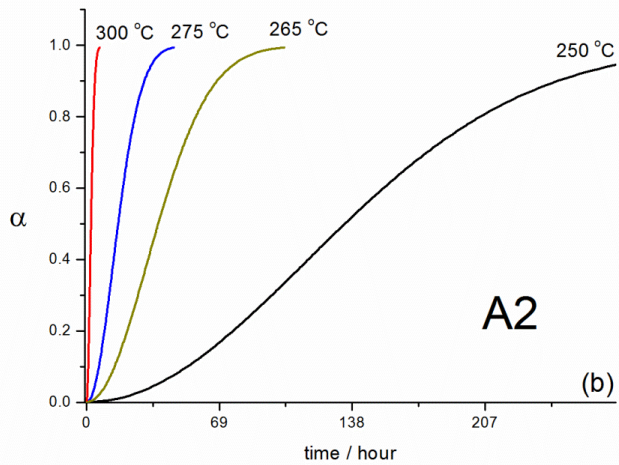
272 **Figure 4.** Fit of the PTFE degradation isothermal curves in Figure 3 to four different kinetic
273 models: first order (F1), phase boundary controlled (R2), two-dimensional diffusion (D2) and
274 nucleation (A2).

275 **Figure 5.** Plot of $\ln k$ versus the reverse of their corresponding temperature, constructed for
276 every set of rate constants in Table 4. Activation energy is extracted from the slope of the plots,
277 being identical in every case.

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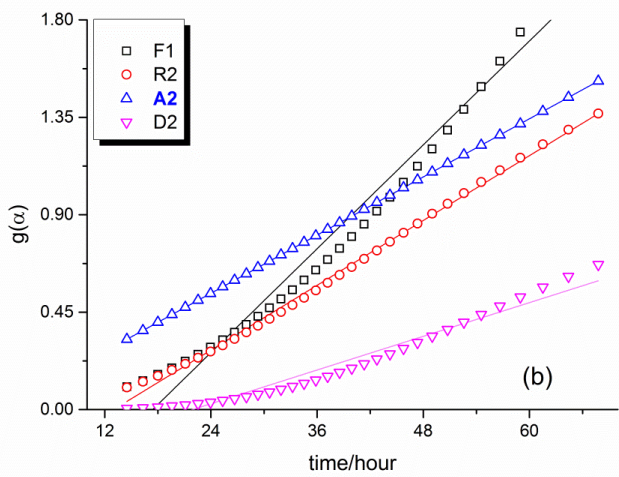
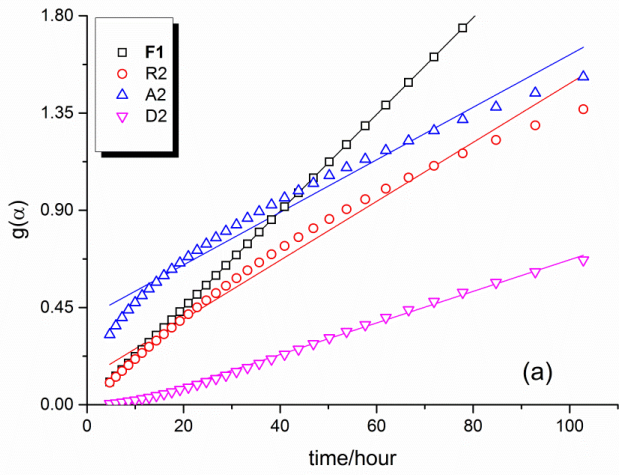


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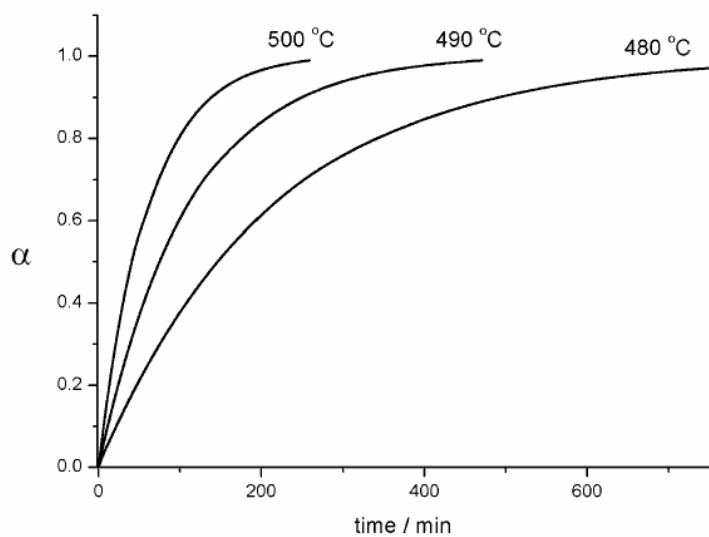
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283 **Figure 1.** Isothermal curves simulated according to the following
 284 kinetic parameters: $E=200\text{kJ/mol}$, $A=10^{16}\text{ min}^{-1}$ and (a) F1 kinetic
 285 model, $f(\alpha)=(1-\alpha)$ and (b) A2 Avrami model, $f(\alpha)=2(1-\alpha)(-\ln(1-\alpha))^{0.5}$.



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Figure 2. Fit of the 265°C isothermal curves simulated assuming (a) F1 and (b) A2 models to a set of different kinetic models.



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Figure 3. Isothermal curves corresponding to the degradation of PTFE, recorded at 480, 490 and 500°C.

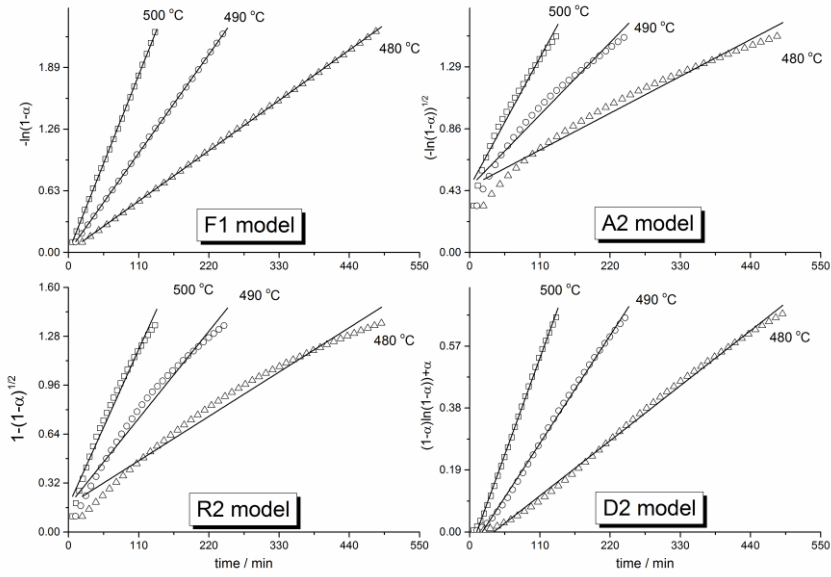


Figure 4. Fit of the PTFE degradation isothermal curves in Figure 3 to four different kinetic models: first order (F1), phase boundary controlled (R2), two-dimensional diffusion (D2) and nucleation (A2).

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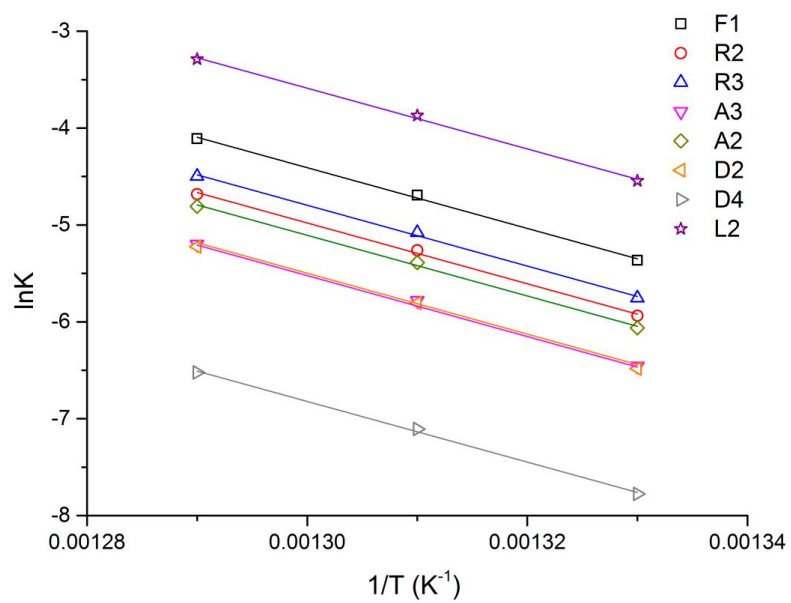


Figure 5. Plot of $\ln k$ versus the reverse of their corresponding temperature, constructed for every set of rate constants in Table 4. Activation energy is extracted from the slope of the plots, being identical in every case.

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320 **Table 1.** Rate constants and correlation factors obtained from fitting simulated curves in Figure
 321 1a (assuming a F1 model) to different kinetic models, according to Eq. (2a).

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Model Fitted to	250°C		265°C		275°C		300°C	
	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²
F1	0.0062	1.000	0.0224	1.000	0.0507	1.000	0.3441	1.000
R2	0.0038	0.981	0.0136	0.980	0.0309	0.980	0.2097	0.980
R3	0.0044	0.991	0.0160	0.991	0.0362	0.991	0.2456	0.991
A2	0.0034	0.970	0.0122	0.970	0.0275	0.970	0.1868	0.970
A3	0.0024	0.944	0.0085	0.944	0.0192	0.944	0.1305	0.944
D2	0.0020	0.996	0.0073	0.996	0.0165	0.996	0.1124	0.996
D4	0.0005	0.993	0.0020	0.993	0.0044	0.993	0.0300	0.993
L2	0.0145	0.996	0.0524	0.996	0.1186	0.996	0.8060	0.996

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325 **Table 2.** Rate constants and correlation factors obtained from fitting the simulated curves in
 326 Figure 1b (assuming a A2 model) to different kinetic models, according to Eq. (2a).

327

Model Fitted to	250°C		265°C		275°C		300°C	
	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²
F1	0.0111	0.970	0.0400	0.970	0.0905	0.970	0.6147	0.970
R2	0.0069	0.997	0.0250	0.997	0.0565	0.997	0.3836	0.997
R3	0.0080	0.992	0.0290	0.992	0.0656	0.992	0.4458	0.992
A2	0.0062	1.000	0.0224	1.000	0.0507	1.000	0.3441	1.000
A3	0.0044	0.996	0.0158	0.996	0.0358	0.996	0.2430	0.996
D2	0.0036	0.953	0.0130	0.953	0.0293	0.953	0.1994	0.953
D4	0.0010	0.936	0.0034	0.936	0.0078	0.936	0.0529	0.936
L2	0.0263	0.988	0.0947	0.988	0.2143	0.988	1.4563	0.988

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332 **Table 3.** Activation energies, pre-exponential factors and correlation coefficients obtained from
 333 the plot of the different rate constants in Tables 1 and 2 versus the reverse of their
 334 corresponding temperature, as per Eq.(3).

Model used to simulate the curves						
F1				A2		
Model fitted to	E (kJ mol ⁻¹)	A (min ⁻¹)	r ²	E (kJ mol ⁻¹)	A (min ⁻¹)	r ²
F1	200	5x10 ¹⁶	1.000	200	1x10 ¹⁷	1.000
R2	200	5x10 ¹⁶	1.000	200	6x10 ¹⁶	1.000
R3	200	4x10 ¹⁶	1.000	200	8x10 ¹⁶	1.000
A2	200	3x10 ¹⁶	1.000	200	6x10 ¹⁶	1.000
A3	200	2x10 ¹⁶	1.000	200	4x10 ¹⁶	1.000
D2	200	2x10 ¹⁶	1.000	200	4x10 ¹⁶	1.000
D4	200	5x10 ¹⁵	1.000	200	1x10 ¹⁶	1.000
L2	200	1x10 ¹⁷	1.000	200	3x10 ¹⁷	1.000

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337 **Table 4.** Rate constants and correlation factors calculated from the fit of the experimental
 338 curves corresponding to the degradation of PTFE (Figure 3) to a set of theoretical kinetic
 339 models. The activation energy and correlation coefficients obtained from the plot of the rate
 340 constants versus the reverse of the temperature (Eq.(3)) are also included.

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Model Fitted to	480°C		490°C		500°C		Result of Isothermal analysis	
	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	k (min ⁻¹)	r ²	E (kJ mol ⁻¹)	r ²
F1	0.0047	1.000	0.0092	1.000	0.0164	0.999	261±10	0.997
R2	0.0026	0.978	0.0052	0.979	0.0093	0.982	261±11	0.996
R3	0.0032	0.990	0.0062	0.990	0.0111	0.993	261±11	0.996
A2	0.0023	0.973	0.0046	0.974	0.0082	0.977	260±11	0.996
A3	0.0016	0.951	0.0031	0.952	0.0055	0.955	261±12	0.996
D2	0.0015	0.997	0.0030	0.998	0.0054	0.998	262±11	0.996
D4	0.0004	0.997	0.0008	0.997	0.0015	0.997	260±10	0.997
L2	0.0106	0.996	0.0208	0.997	0.0373	0.997	261±10	0.996

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