2
Analysis of Thermoluminescence Data

Introduction

In this chapter, the analytical expressions presented in Chapter 1 will be used in several detailed numerical exercises. A variety of methods will be used to analyze the same TL glow-curve data, and the results from the different methods will be compared with each other.

Chen and McKeever [1] have provided an excellent summary of how to systematically analyze TL glow curves, by following these steps:

(1) Ensure that the temperature measurement during the TL glow peak is accurate, by optimizing the thermal contact between the sample and the heating element.
(2) Eliminate the possibility of nearby overlapping peaks, by using a thermal cleaning process. Thermal quenching effects must also be accounted for, if present, and corrected using theoretical considerations. The study of emission spectra during the TL glow curve provides also valuable information about the TL process.
(3) Characterize the isolated glow peak by evaluating the three parameters E, s, and b using several of the standard methods of analysis. Methods utilizing the whole glow peak should be preferred over methods based on only a few points on the glow curve. It is essential to carry out this analysis for different trap filling, by studying, for example, samples irradiated at different doses.
(4) It is important to get good agreement between several methods of analysis. Any discrepancies should be examined in more detail.
(5) In order to resolve discrepancies and obtain more information about the processes involved, the analysis should be carried out for glow peaks measured under different heating rates, various irradiation doses, powdered and bulk samples, etc.
(6) Additional information should be obtained using experimental methods based on different physical processes, such as isothermal decay techniques, dose-dependence measurements, excitation and emission spectra, and simultaneous TL-TSC (thermally stimulated current) measurements.

Exercises 2.1–2.3 contain a detailed example of analyzing first-order TL data using three different methods: peak shape methods, variable heating rate methods, and isothermal decay techniques. Similarly, examples of analyzing second- and general-order TL glow curves are given in Exercises 2.4–2.6. Although the material in these exercises may seem to be repeated at times, we have chosen to provide complete and self-contained exercises for easy reference, instead of constantly referring the reader to previous sections of the book.

Extra attention has been paid to include an error analysis of the data whenever possible, because there seems to be a general lack of such detailed examples of error analysis in the TL literature. Exercises 2.7 and 2.9 present examples of the effect of experimental background on the accuracy of the initial rise (IR) method, and of the propagation of errors in the peak shape methods of analysis. Exercise 2.8 is a simulated study of the well-known "15% TL intensity" rule of thumb which is commonly used in experimental TL work.

Exercise 2.1: Analysis of a First-Order TL Peak

You are given the experimental data in Table 2.1 and Figure 2.1, for a TL glow curve (TL versus temperature T), and a known heating rate $\beta = 1\,\mathrm{K\,s^{-1}}$.

(a) Apply the IR method to find the activation energy E. The value for E obtained using the IR method is assumed to be independent of the order of kinetics.
(b) Apply Chen's peak shape equations to find the activation energy E, using the shape parameters τ, δ, and ω. By assuming that the experimental error in the quantities τ, δ, and ω is $\Delta T = 2$ K, estimate the error $\Delta\mu$ in the value of the geometrical shape factor μ.

   Show that the values of μ and $\Delta\mu$ are consistent with the assumption that the TL glow curve obeys first-order kinetics.
(c) By using the experimental data, apply the whole glow-peak method to find E, s, and the order of kinetics b. Graph $\ln(I/n^b)$ versus $1/T$ for various values of

TABLE 2.1. The experimental data for a first-order TL glow curve

T(C)	$TL_{experimental}$	T(C)	$TL_{experimental}$
20	7.56×10^4	85	8.07×10^7
25	1.28×10^5	90	1.20×10^8
30	2.44×10^5	95	1.71×10^8
35	4.54×10^5	100	2.31×10^8
40	8.29×10^5	105	2.90×10^8
45	1.49×10^6	110	3.26×10^8
50	2.61×10^6	115	3.15×10^8
55	4.51×10^6	120	2.43×10^8
60	7.65×10^6	125	1.34×10^8
65	1.27×10^7	130	4.49×10^7
70	2.09×10^7	135	6.75×10^6
75	3.35×10^7	140	2.57×10^5
80	5.27×10^7	145	2.73×10^3

FIGURE 2.1. The first-order TL glow curve.
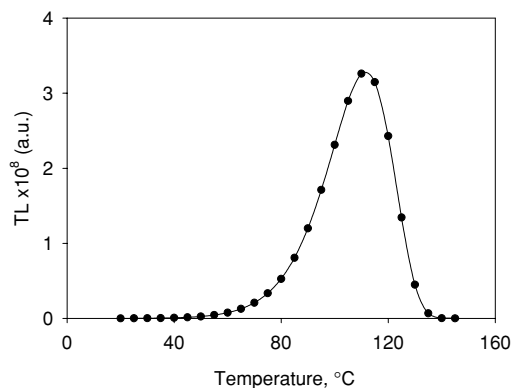
b between 0.8 and 1.2, and find the correct value of b that gives a linear graph. From the slope and intercept of the graph $\ln(I/n^b)$ versus $1/T$ calculate E and s. Verify that the given TL glow curve corresponds to first-order kinetics.

(d) Using the experimental values of I_M (maximum TL intensity) and T_M (temperature of maximum intensity), do a curve fitting to the given numerical data. Use the following analytical equation developed by Kitis et al for first-order kinetic peaks [2]. The expression relies on two experimentally measured quantities, I_M and T_M:

$$
I(T) = I_M \exp\left[1 + \frac{E}{kT} \cdot \frac{T - T_M}{T_M} - \frac{T^2}{T_M^2} \right.
$$
$$
\left. \times \left(1 - \frac{2kT_M}{E} \right) \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M} \right) - \frac{2kT_M}{E} \right]. \quad (2.1)
$$

The activation parameter E can be treated as an adjustable parameter in this expression. Graph both the experimental data and the calculated first-order TL glow curve on the same graph and compare them. Calculate the figure of merit (FOM) of the TL glow curve.

(e) Can it be concluded for this material that this TL peak will always follow first-order kinetics?

Solution

(a) *The IR method.* We calculate in Table 2.2. the values of $1/kT$ ($T = $ temperature in K, $k = $ Boltzman constant) and the values of the natural logarithm of the TL data, ln(TL) in a spreadsheet.

We next graph the ln(TL) versus $1/kT$ data as shown in Figure 2.2.

A very important consideration when applying the IR method is deciding how many data points to use for the regression analysis of the graph ln(TL) versus $1/kT$. We obtain the activation energy E by graphing ln(TL) versus $1/kT$ for the initial part of the data. By performing a regression line analysis using the *first 16 data points* up to a temperature of 100°C, we obtain the graph in Figure 2.3.

TABLE 2.2. Calculated values of $1/kT$ and the values of ln(TL) for first-order glow curve

T(C)	$TL_{experimental}$	$1/kT$(eV^{-1})	ln(TL)	T(C)	$TL_{experimental}$	$1/kT$(eV^{-1})	ln(TL)
20	7.56×10^4	39.47	11.23	85	8.07×10^7	32.42	18.11
25	1.28×10^5	38.94	11.66	90	1.20×10^8	31.97	18.60
30	2.44×10^5	38.30	12.41	95	1.71×10^8	31.54	18.86
35	4.54×10^5	37.68	12.93	100	2.31×10^8	31.11	19.26
40	8.29×10^5	37.08	13.63	105	2.90×10^8	30.70	19.38
45	1.49×10^6	36.49	14.11	110	3.26×10^8	30.30	19.60
50	2.61×10^6	35.93	14.78	115	3.15×10^8	29.91	19.47
55	4.51×10^6	35.38	15.22	120	2.43×10^8	29.53	19.31
60	7.65×10^6	34.85	15.85	125	1.34×10^8	29.16	18.62
65	1.27×10^7	34.33	16.26	130	4.49×10^7	28.80	17.62
70	2.09×10^7	33.83	16.85	135	6.75×10^6	28.44	15.62
75	3.35×10^7	33.35	17.23	140	2.57×10^5	28.10	12.45
80	5.27×10^7	32.88	17.78	145	2.73×10^3	27.76	7.91

When the first 16 data points are used (intensity up to a temperature of 100°C, corresponding to a TL intensity equal to approximately 70% of the maximum TL intensity), the value of the activation energy $E = 0.976 \pm 0.004$ eV is obtained with a value of the regression coefficient $R^2 = 0.9997$.

By performing a similar regression line analysis using only the *first 11 data points* up to a temperature of 75°C, we obtain the graph in Figure 2.4.

When the first 11 data points are used (up to a temperature of 75°C, corresponding to a TL intensity equal to approximately 9% of the maximum TL intensity), a value of $E = 0.986 + 0.003$ eV is obtained, with an R^2 value of 0.9997. Both graphs in Figures 2.3 and 2.4 give an equally good fit with the same value of R^2.
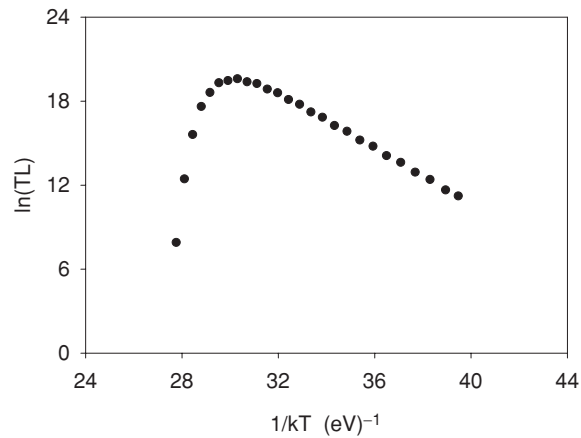

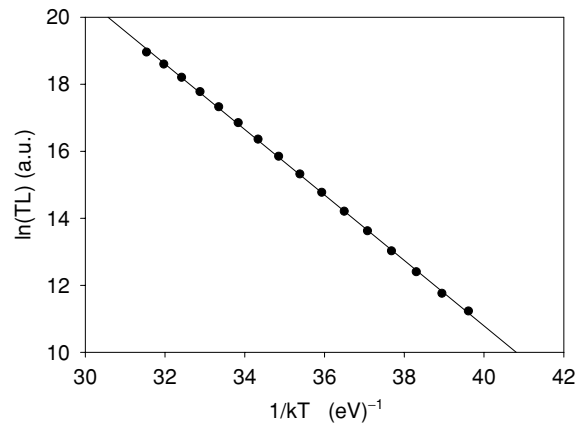FIGURE 2.2. The IR method applied to the first-order TL glow curve.

FIGURE 2.3. Applying the IR method to the first 16 experimental points.

The example above shows that the value of the activation energy E obtained from the IR method by doing a regression analysis of the data is very sensitive to the number of points used in the analysis. Exercise 2.7 is an example of the influence of the experimental background on the results of the IR method.

As a general practical rule, application of the IR technique should be restricted to the portion of the TL glow curve corresponding to about 5–10% of the maximum TL intensity. Exercise 2.8 is a detailed simulation of this so-called "15% intensity" rule of thumb commonly used in the IR method.

(b) *Chen's peak shape equations.* From the given experimental data for a TL glow peak, we can estimate the three temperatures required for Chen's peak shape equations:

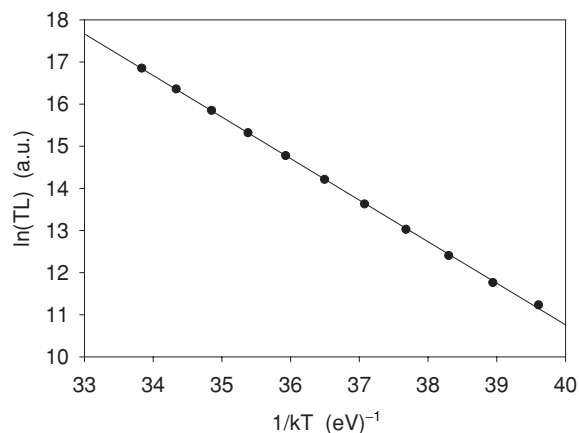$$T_1 = 92°C = 365\,\text{K}, \quad T_2 = 122°C = 395\,\text{K}, \quad T_M = 110°C = 383\,\text{K},$$

FIGURE 2.4. Applying the IR method to the first 11 experimental points.

where

T_M = peak temperature at the maximum TL intensity,

T_1, T_2 = temperatures on either side of T_M, corresponding to the half-maximum intensity.

We first calculate the quantities μ, τ, δ, and ω:

$$\tau = T_M - T_1 = 18\,\text{K},$$
$$\delta = T_2 - T_M = 12\,\text{K},$$
$$\omega = T_2 - T_1 = 30\,\text{K},$$
$$\mu = \delta/\omega = 12/30 = 0.40.$$

Using the value of τ:

$$E = \frac{1.51kT_M^2}{\tau} - 1.58(2kT_M) = 1.060 - 0.104 = 0.956 \text{ eV}.$$

Using the value of δ:

$$E = \frac{0.976kT_M^2}{\delta} = 1.028 \text{ eV}.$$

Using the value of ω:

$$E = \frac{2.52kT_M^2}{\omega} - 2kT_M = 1.062 - 0.066 = 0.996 \text{ eV}.$$

The value of the geometrical shape factor $\mu = 0.40$ is very close to the value expected for a first-order TL peak which is equal to $\mu = \delta/\omega = 0.42$.

Using the known experimental error $\Delta T = 2$ K or the quantities τ, δ, and ω, we can do an error analysis of the values of μ. By taking the logarithmic derivative of the equation $\mu = \delta/\omega$, we find the relative error $\Delta\mu/\mu$:

$$\ln \mu = \ln \delta - \ln \omega$$

$$\left|\frac{\Delta\mu}{\mu}\right| = \left|\frac{\Delta\delta}{\delta}\right| + \left|\frac{\Delta\omega}{\omega}\right| = \left|\frac{2}{12}\right| + \left|\frac{2}{30}\right| = 0.167 + 0.067 = 0.234.$$

This leads to a value of $\mu \pm \Delta\mu = 0.40 \pm 0.09$. This value is consistent with the assumption of first-order kinetics.

In order to estimate the error ΔE in the activation energy E, we take the logarithmic derivative of the equation $E = 0.976kT_M^2/\delta$:

$$\left|\frac{\Delta E}{E}\right| = 2\left|\frac{\Delta T_M}{T_M}\right| + \left|\frac{\Delta\delta}{\delta}\right| = 2\left|\frac{2}{383}\right| + \left|\frac{2}{12}\right| = 0.010 + 0.167 = 0.177.$$

This gives a rather large error in $\Delta E = 0.177E = 0.177(1.028) = 0.18$ eV.

A much more detailed error analysis of the peak shape equations is given in Exercise 2.9.

(c) *The whole glow-peak method.* In the whole glow-peak area method, the area $n(T)$ under the glow peak is calculated starting at temperature T, to the maximum temperature available, as shown in Figure 2.5. In the data shown in Table 2.1, the maximum available temperature is 145°C.

FIGURE 2.5. Applying the whole glow-peak method.
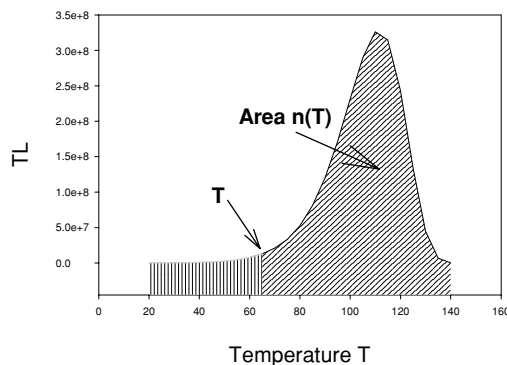
The area $n(T)$ under the glow peak can be approximated by using the sum of all the data points from any temperature T upwards, up to the maximum temperature available in the data. According to equation (1.21), this sum must be multiplied by the temperature interval ΔT and must be also divided by the heating rate β. In our case, we are given $\Delta T = 5$ K and $\beta = 1$ K s^{-1}.

In the spreadsheet example shown in Table 2.3, column C labeled "Area" is calculated using the command:

$$\text{Cell C1} = \text{sum(B1:B26)}^{*}5/1,$$
$$\text{Cell C2} = \text{sum(B2:B26)}^{*}5/1, \text{ etc.}$$

Once the "Area" column is calculated, column D labeled "ln(TL/Area)" can be calculated by using the command:

$$\text{Cell D1} = \ln(\text{B1/C1}),$$
$$\text{Cell D2} = \ln(\text{B2/C2}), \text{ etc.}$$

Additional columns are created in the spreadsheet for the quantities of ln(TL/Area^{b}) and for several values of the kinetic order $b = 1.2, 1.1, 1.0,$ and 0.9. Not all columns are shown for the sake of saving space.

In Figure 2.6, graphs of ln(TL/Area^{b}) versus $1/kT$ are drawn for several values of the kinetic order $b = 1.2, 1.1, 1.0,$ and 0.9.

The graphs in Figure 2.6 corresponding to $b = 0.9, 1.0,$ and 1.2 clearly deviate from straight lines at low values of $1/kT$, and must be rejected.

The $b = 1.1$ graph has the highest value of R^2 and therefore gives the best fit. The data leads us to conclude that the given TL glow peak is described by $b = 1.1$ kinetics. Due to experimental uncertainties in the data and also due to the fact that only 27 data points are available on the TL glow curve, we can say that to a good approximation this can be considered a *first-order* kinetics TL peak. A regression line is fitted to the best line corresponding to $b = 1.1$, to obtain the best slope and the best intercept, as shown in Figure 2.7:

$$\text{Best intercept} = 24.579 \pm 0.11,$$
$$\text{Best slope } E = 0.979 \pm 0.003 \text{ eV.}$$

TABLE 2.3. The quantities $\ln(I/n)$ and $1/kT$ for first-order glow curve

	A	B	C	D	E	
	T(C)	TL$_{experimental}$	Area	ln(TL/Area)	$1/kT$	ln(TL/Area$^{1.1}$)
1	20	7.56×10^4	1.05×10^{10}	-11.84	39.61	-14.15
2	25	1.28×10^5	1.05×10^{10}	-11.31	38.94	-13.62
3	30	2.44×10^5	1.05×10^{10}	-10.67	38.30	-12.98
4	35	4.54×10^5	1.05×10^{10}	-10.05	37.68	-12.35
5	40	8.29×10^5	1.05×10^{10}	-9.45	37.08	-11.75
6	45	1.49×10^6	1.05×10^{10}	-8.86	36.49	-11.17
7	50	2.61×10^6	1.05×10^{10}	-8.30	35.93	-10.61
8	55	4.51×10^6	1.05×10^{10}	-7.75	35.38	-10.06
9	60	7.65×10^6	1.04×10^{10}	-7.22	34.85	-9.53
10	65	1.27×10^7	1.04×10^{10}	-6.71	34.33	-9.01
11	70	2.09×10^7	1.03×10^{10}	-6.21	33.83	-8.51
12	75	3.35×10^7	1.02×10^{10}	-5.72	33.35	-8.03
13	80	5.27×10^7	1.01×10^{10}	-5.25	32.88	-7.56
14	85	8.07×10^7	9.81×10^9	-4.80	32.42	-7.10
15	90	1.20×10^8	9.41×10^9	-4.36	31.97	-6.66
16	95	1.71×10^8	8.81×10^9	-3.94	31.54	-6.23
17	100	2.31×10^8	7.95×10^9	-3.54	31.11	-5.82
18	105	2.90×10^8	6.80×10^9	-3.16	30.70	-5.42
19	110	3.26×10^8	5.35×10^9	-2.80	30.30	-5.04
20	115	3.15×10^8	3.72×10^9	-2.47	29.91	-4.67
21	120	2.43×10^8	2.15×10^9	-2.18	29.53	-4.33
22	125	1.34×10^8	9.31×10^8	-1.94	29.16	-4.00
23	130	4.49×10^7	2.60×10^8	-1.75	28.80	-3.69
24	135	6.75×10^6	3.50×10^7	-1.65	28.44	-3.38
25	140	2.57×10^5	1.30×10^6	-1.62	28.10	-3.03
26	145	2.73×10^3				
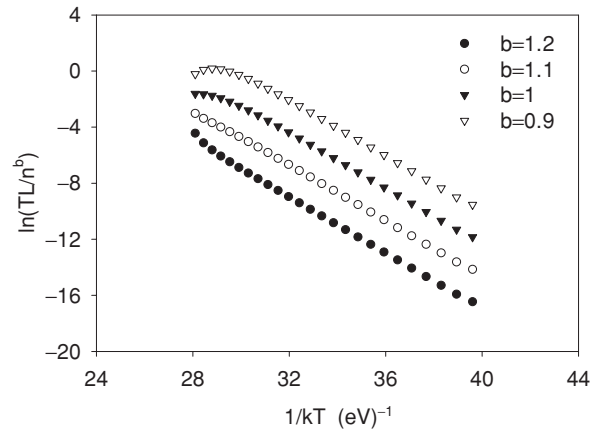
FIGURE 2.6. Applying the whole glow-peak method for different kinetic parameters b.
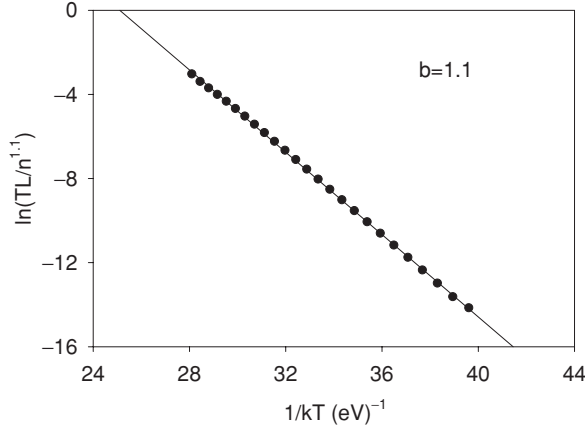
FIGURE 2.7. The value of $b = 1.1$ provides the best least squares fit in the whole glow-curve method of analysis.

This value of E is in reasonably good agreement with the value of $E = 0.986 \pm 0.003$ eV obtained from the IR method. The frequency factor s is calculated from the y-intercept of the graph in Figure 2.7:

$$s = \beta e^{(\text{intercept})} = 1e^{24.579} = 4.7 \times 10^{10}\ \text{s}^{-1}.$$

The errors Δs can be calculated from the uncertainties in the intercept of the regression line as follows:

$$\Delta\ (\text{intercept}) = \frac{\partial(\ln s)}{\partial s}\Delta s = \frac{\Delta s}{s} = 0.11.$$

This gives a typical large 11% error for the value of the frequency factor, with the final value of s reported as $s = (4.7 \pm 0.5) \times 10^{10}\ \text{s}^{-1}$.

(d) *Glow-curve fitting using the Kitis et al equation.* The given TL data can be analyzed by using the following analytical equation developed by Kitis et al [2] for TL peaks following first-order kinetics. The expression relies on two experimentally measured quantities, I_M (the maximum TL intensity) and T_M (the temperature corresponding to the maximum TL intensity):

$$I(T) = I_M \exp\left[1 + \frac{E}{kT}\cdot\frac{T - T_M}{T_M} - \frac{T^2}{T_M^2}\right.$$
$$\left. \times\left(1 - \frac{2kT_M}{E}\right)\exp\left(\frac{E}{kT}\cdot\frac{T - T_M}{T_M}\right) - \frac{2kT_M}{E}\right]. \quad (2.2)$$

For the given experimental data, $T_M = 384$ K and $I_M = 3.26 \times 10^8$. By treating the activation parameter E as an adjustable parameter, we calculate several graphs with values of $E = 0.9, 1.0, 1.1,$ and 1.2 eV. The calculations can be set up easily in a spreadsheet as shown in Table 2.4. Only the first 5 rows are shown for the sake of brevity.

TABLE 2.4. Calculations for glow-curve fitting for several E values

	A	B	C	D	E	F	G	H	I	J	K	L
			$I(T)$	$I(T)$	$I(T)$	$I(T)$						
1	$T(K)$	$TL_{\text{experimental}}$	$E = 1$ eV	$E = 0.9$ eV	$E = 1.1$ eV	$E = 1.2$ eV						
2							$E =$	1	eV	0.9	1.1	1.2
3	293	7.56×10^4	6.96×10^4	1.77×10^5	2.74×10^4	1.08×10^4						
4	298	1.28×10^5	1.35×10^5	3.21×10^5	5.69×10^4	2.39×10^4						
5	303	2.44×10^5	2.57×10^5	5.72×10^5	1.15×10^5	5.17×10^4	$T_M =$	384	K			
6	308	4.54×10^5	4.79×10^5	1.00×10^6	2.28×10^5	1.09×10^5	$I_M =$	3.26×10^8				
7	313	8.29×10^5	8.74×10^5	1.72×10^6	4.43×10^5	2.24×10^5						

Columns A and B contain the experimental data points for the TL glow curve, while columns C–F contain the calculated data points using equation (2.2) for four values of the energy parameter E ($E = 0.9$, 1.0, 1.1, and 1.2 eV).

The following expression is used to calculate the values of the fitted data in column C, using equation (2.2) for first-order kinetics:

Cell C3 = $H$6*EXP(1+$H$2/(0.00008617*A3)

         *((A3-$H$5)/$H$5)-((A3*A3)/($H$5*$H$5))

         *(1-2*0.00008617*$H$5/$H$2)*EXP($H$2/(0.00008617*A3)

         *((A3-$H$5)/$H$5))-2*0.00008617*$H$5/$H$2).

This expression refers to cell A3 which contains the absolute temperature $T(K)$. Also, note that cell H2 in the spreadsheet contains the value of the energy parameter $E = 1.0$ eV, cell H5 contains the value of the experimental parameter $T_M = 384$ K, and cell H6 contains the value of the experimental maximum height parameter $I_M = 3.26 \times 10^8$. The above spreadsheet expression refers to the values contained in these cells by using the Excel commands $H$2, $H$5, $H$6, correspondingly.

The user controls the value of the parameter E by changing the value in cell H2, and the whole spreadsheet calculation is automatically updated.

The graphs calculated for $E = 0.9$, 1.0, 1.1, and 1.2 eV are shown in Figure 2.8.

It can be seen that when the value of E is too low (graph corresponding to $E = 0.9$ eV), the calculated TL points lie above the experimental data. This is also evident by inspection of the calculated $I(T)$ values in Table 2.4. On the other hand, when the value of E is too high (graphs corresponding to $E = 1.1$ and 1.2 eV), the calculated TL points lie clearly below the experimental data.

This procedure is a simple example of a glow-curve fitting procedure, in which we find the value of E that yields the best fit to experimental data obeying first-order kinetics.

A more precise numerical method of performing the same fitting procedure is by calculating the FOM for the graphs above. The FOM is defined as [2]

$$\text{FOM} = \frac{\sum_p \left| y_{\text{experimental}} - y_{\text{fit}} \right|}{\sum_p y_{\text{fit}}}, \quad (2.3)$$
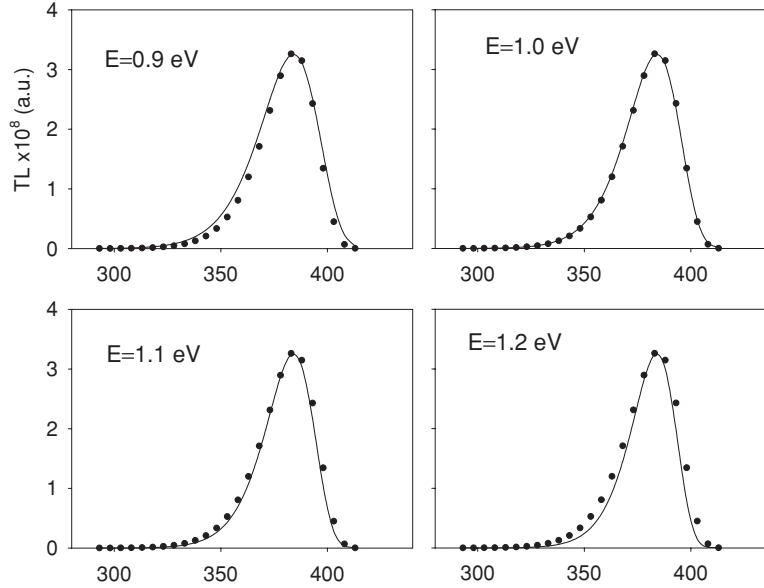
FIGURE 2.8. Calculated first-order TL glow peaks for different E-values.

where $y_{\text{experimental}}$ and y_{fit} represent the experimental TL intensity data and the values of the fitting function, respectively. The summation extends over all the available experimental points.

Table 2.5 shows an example of a FOM calculation as applied to the previous data. Column A contains the experimental data points and columns B and C contain the calculated data points using equation (2.2) for first-order kinetics, for two values of the energy parameter E ($E = 1.0$ and 0.9 eV).

Columns E and F contain the calculation of the quantity $|\text{TL}_{\text{experimental}} - \text{TL}_{\text{calculated}}|$, and cells E29 and F29 contain the calculated values of the FOM. The expressions used in this example are

$$\text{Cell E3} = \text{ABS}(A3 - B3)$$
$$\text{Cell F3} = \text{ABS}(A3 - C3)$$
$$\text{Cell E29} = \text{SUM}(E3:E27)/\text{SUM}(B3:B27)$$
$$\text{Cell F29} = \text{SUM}(F3:F27)/\text{SUM}(C3:C27).$$

The FOM for the value of the parameter $E = 1.0$ eV is equal to $0.026 = 2.6\%$, almost four times smaller than the FOM $= 0.094 = 9.4\%$ for the case $E = 0.9$ eV.

The frequency factor s can be calculated by using the value of $E = 1.0$ eV and the temperature of maximum TL intensity $T_{\text{M}} = 384$ K in equation (1.8) for first-order kinetics:

$$s = \frac{\beta E}{kT_{\text{M}}^2} \exp\left(\frac{E}{kT_{\text{M}}}\right) = \frac{(1)1}{(8.617 \times 10^{-5})(384)^2} \exp\left(\frac{1}{(8.617 \times 10^{-5})384}\right)$$
$$= 1.05 \times 10^{12} \, \text{s}^{-1}$$

TABLE 2.5. Example of a FOM calculation for first-order glow curve

	A	B	C	D	E	F
1	$TL_{experimental}$	$I(T)$ $E = 1$ eV	$I(T)$ $E = 0.9$ eV		$\|TL_{experimental} - I(t)\|$ $E = 1$ eV	$\|TL_{experimental} - I(t)\|$ $E = 0.9$ eV
2						
3	7.56×10^4	6.96×10^4	1.77×10^5		6.01×10^3	1.07×10^5
4	1.28×10^5	1.35×10^5	3.21×10^5		6.83×10^3	1.86×10^5
5	2.44×10^5	2.57×10^5	5.72×10^5		1.30×10^4	3.15×10^5
6	4.54×10^5	4.79×10^5	1.00×10^6		2.42×10^4	5.23×10^5
7	8.29×10^5	8.74×10^5	1.72×10^6		4.41×10^4	8.46×10^5
8	1.49×10^6	1.56×10^6	2.90×10^6		7.88×10^4	1.34×10^6
9	2.61×10^6	2.75×10^6	4.82×10^6		1.38×10^5	2.07×10^6
10	4.51×10^6	4.75×10^6	7.87×10^6		2.38×10^5	3.13×10^6
11	7.65×10^6	8.05×10^6	1.26×10^7		4.02×10^5	4.59×10^6
12	1.27×10^7	1.34×10^7	2.00×10^7		6.64×10^5	6.56×10^6
13	2.09×10^7	2.19×10^7	3.10×10^7		1.07×10^6	9.05×10^6
14	3.35×10^7	3.52×10^7	4.72×10^7		1.68×10^6	1.20×10^7
15	5.27×10^7	5.52×10^7	7.03×10^7		2.55×10^6	1.51×10^7
16	8.07×10^7	8.44×10^7	1.02×10^8		3.67×10^6	1.77×10^7
17	1.20×10^8	1.25×10^8	1.44×10^8		4.93×10^6	1.89×10^7
18	1.71×10^8	1.77×10^8	1.94×10^8		5.92×10^6	1.74×10^7
19	2.31×10^8	2.37×10^8	2.49×10^8		5.84×10^6	1.25×10^7
20	2.90×10^8	2.93×10^8	2.98×10^8		3.62×10^6	5.24×10^6
21	3.26×10^8	3.25×10^8	3.25×10^8		1.16×10^6	1.79×10^5
22	3.15×10^8	3.08×10^8	3.12×10^8		6.59×10^6	3.52×10^6
23	2.43×10^8	2.35×10^8	2.51×10^8		7.99×10^6	1.66×10^7
24	1.34×10^8	1.32×10^8	1.61×10^8		2.81×10^6	2.91×10^7
25	4.49×10^7	4.79×10^7	7.50×10^7		3.03×10^6	2.70×10^7
26	6.75×10^6	9.60×10^6	2.29×10^7		2.85×10^6	1.34×10^7
27	2.57×10^5	8.39×10^5	4.00×10^6		5.83×10^5	3.16×10^6
28						
29				FOM =	0.026	0.094

The resolution of the Kitis et al fitting method can be refined by repeating this process of calculating the FOM for different values of E spaced much closer together (e.g. $E = 1.01$, 1.00, 0.99, etc.) and finding the value of E that minimizes the value of the FOM.

Finally, we summarize in Table 2.6 the results of the various methods for analyzing the given experimental data.

TABLE 2.6. Summary of the results of various analysis methods for first-order glow curve

	E(eV)	s(s^{-1})	Comments below
Initial rise method	0.986 ± 0.003		[1, 5]
Chen's τ-method	0.956		[2, 5]
Chen's δ-method	1.03 ± 0.18		[2, 5]
Chen's ω-method	0.996		[2, 5]
Whole glow-peak method	0.979 ± 0.003	$(4.7 \pm 0.5) \times 10^{10}$	[3]
Fitting method using Kitis et al equation (equation (2.21))	1.1 ± 0.1	1.05×10^{12}	[4, 5]

Comments on the Results of Exercise 2.1

1. The value of E obtained from the IR method is independent of the kinetics of the TL glow peak.

   The presence of thermal quenching affects the value of E obtained in the IR method. A possible correction method for the value of E is given in Chapter 5.

   It is best to use the IR method with samples irradiated at low doses, i.e. samples away from saturation conditions [3].

   The test dose used to obtain the TL glow curve is our "probe" of the material, and must always be as small as possible, so that on one hand it does not disturb the system and on the other it can give us a statistically satisfactory signal. Typical values of test doses may be in the mGy or μGy range.

2. The value of E obtained with peak shape methods can be influenced by the presence of smaller satellite peaks.

3. The whole glow-curve method yields information on both E and the pre-exponential factor s. By using the values of E, s, and n_0 (obtained from the area under the glow curve), it is possible to compare directly the experimental data with the TL intensity obtained using equation (1.5) (see also Exercises 2.4–2.6 in this chapter for second- and general-order kinetics).

4. The Kitis et al method is based on two experimentally measured parameters, T_M and I_M. The activation energy E is treated as a fitting parameter. The method can be easily adopted on a computer to yield high accuracy for E.

5. The pre-exponential factor s can be calculated from the value of T_M, E, and β by using equation (1.8). The estimated uncertainties $\Delta s/s$ from equation (1.8) can be very large (50–100%), even when the uncertainty $\Delta E/E$ is very small.

(e) Can it be concluded for this material that this TL peak will always follow first-order kinetics?

In general, one cannot assume that the studied TL glow curve of this material will always follow first-order kinetics. The analysis should be carried out for glow peaks measured under different heating rates, various irradiation doses, powdered and bulk samples, etc.

Some of the criteria for first-order kinetics are:

 I. *Peak shape*: First-order peaks have $\mu = 0.42$.
 II. *Peak shift*: In first-order TL glow peaks, the location of maximum TL intensity does not shift in temperature for different irradiation doses.
III. *Isothermal decay results*: These can provide valuable independent information about the kinetics of the TL process involved at different temperatures. First-order kinetics corresponds to exponential isothermal decay curves.

Exercise 2.2: Heating Rate Method for First-Order Kinetics

You are given the data in Figure 2.9 for four experimental TL glow curves measured with different heating rates (TL versus Temperature T, and known heating rates $\beta_1 = 0.5$, $\beta_2 = 1$, and $\beta_3 = 2$, and $\beta_3 = 3 \, \mathrm{K \, s^{-1}}$). It is known that this TL peak follows first-order kinetics.
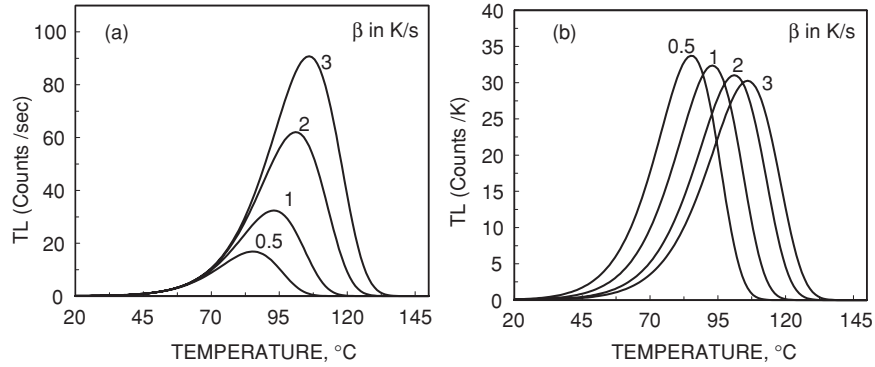
FIGURE 2.9. The experimental TL glow curves for different heating rates. (a) The *y*-axis is represented as counts/s and (b) the *y*-axis is represented as counts/K.

(a) Discuss the observed changes in the peak position and peak shape for different heating rates.
(b) Apply the two-heating rate equation for E (equation (1.26)), to obtain a quick estimate of the activation energy E.
(c) Apply also the $I_M - T_M$ variation method (equation (1.31)), to obtain a quick estimate of the activation energy E.
(d) By applying the heating rate method of analysis find the kinetic parameters E and s, and their uncertainties ΔE and Δs.

Solution

(a) The data of Figure 2.9 show that as the heating rate increases, the glow peaks shift to higher temperatures, and the height of the TL peak changes. Because in a typical TL experiment, one collects the TL signal as a function of time, the *y*-axis in Figure 2.9(a) is represented in counts/s. These units of counts/s are not suitable for graphing the actual TL glow curve which is a function of temperature, so it is necessary to convert into temperature units. This is done by dividing each of the graphs in Figure 2.9(a) by the corresponding heating rate β, and one obtains the *y*-axis in counts/K as shown in Figure 2.9(b).

The area under the peaks in Figure 2.9(a) is proportional to the heating rate β, whereas the area under the glow curves in Figure 2.9(b) is constant.

The temperatures T_M for the maximum TL intensity and the corresponding intensities I_M are found from the curves of Figure 2.9(a) and (b), and are listed in Table 2.7.

(b) We can calculate the energy E from the two-heating rate equation (equation (1.26))

$$E = k\frac{T_{M1}T_{M2}}{T_{M1} - T_{M2}} \ln\left[\frac{\beta_1}{\beta_2}\left(\frac{T_{M2}}{T_{M1}}\right)^2\right]. \qquad (1.26)$$

TABLE 2.7. Calculation of $\ln(T_M^2/\beta)$ and $1/kT_M$ for first-order glow curve

$\beta(\text{K s}^{-1})$	$T_M(^\circ\text{C})$	$T_M(\text{K})$	$\ln(T_M^2/\beta)$	$1/kT_M(\text{eV})^{-1}$	$I_M(\text{counts/s})$	$I_M(\text{counts/K})$
0.5	84	357	12.449	32.507	17	34
1	92	365	11.800	31.794	32	32
2	100	373	11.150	31.113	62	31
3	104	377	10.766	30.782	90	30

Inserting $T_{M1} = 357$ K, $T_{M2} = 365$ K, $\beta_1 = 0.5$ K s^{-1}, $\beta_2 = 1$ K s^{-1}, we obtain

$$E = 8.617 \times 10^{-5}\,(357)(365)/(357 - 365)\ln[0.5(365)^2/1(357)^2] = 0.911\ \text{eV}.$$

(c) We can also estimate the energy E from the two-intensities equation (equation (1.31))

$$E = \frac{kT_{m1}T_{m2}}{T_{m1} - T_{m2}}\ln\frac{I_{m1}}{I_{m2}}. \tag{1.31}$$

Inserting $T_{M1} = 357$ K, $T_{M2} = 365$ K, $I_{M1} = 34$ (counts/K), $I_{M2} = 32$ (counts/K), we obtain

$$E = 8.617 \times 10^{-5}\,(357)(365)/(357 - 365)\ln[(34/32)0.5] = 0.89\ \text{eV}.$$

(d) We calculate the quantities $1/kT_M$ ($k = $ Boltzmann constant) and $\ln(T_M^2/\beta)$ shown in Table 2.7 with $\beta = $ given heating rates. As discussed in Chapter 1, equation (1.27) shows that the slope of the graph $\ln(T_M^2/\beta)$ versus $1/kT_M$ will be equal to the activation energy E, and that the y-intercept will be equal to $\ln(E/sk)$.

From the slope and intercept of the graph $\ln(T_M^2/\beta)$ versus $1/kT_M$, in Figure 2.10, we can calculate the kinetic parameters E and s as follows:
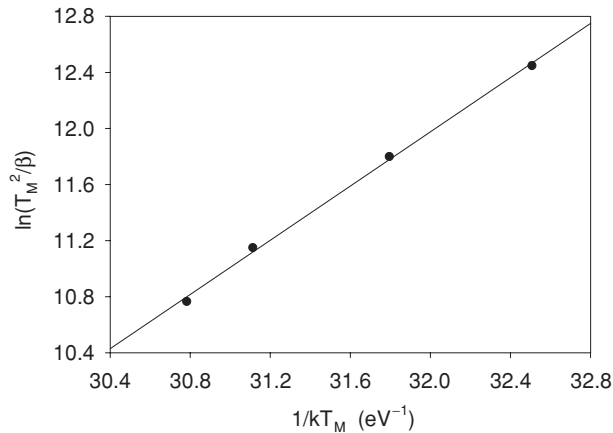
FIGURE 2.10. Graph of $\ln(T_M^2/\beta)$ versus $1/kT_M$ to determine E and s.

From the slope of the graph, $E = 0.9668$ eV.

From the value of the y-intercept $= \ln(E/sk)$, we obtain

$$s = E e^{\text{intercept}/k} = 0.9668 e^{(18.962)/(8.617 \times 10^{-5})} = 1.9 \times 10^{12} \text{ s}^{-1}.$$

The values of E and s obtained above can be checked for self-consistency as follows. Because the temperature T_M of the maximum TL intensity is known from the experimental data, the value of s can be calculated in an independent manner by rearranging equation (1.8) to obtain

$$s = \frac{\beta E}{kT_M^2} \exp\left(\frac{E}{kT_M}\right). \tag{2.4}$$

By using the values of $E = 0.9668$ eV, $T_M = 84°C = 357$ K, $\beta = 0.5$ K s^{-1} in equation (2.4):

$$s = \frac{(0.5)(0.9668)}{(8.617 \times 10^{-5})(357)^2} \exp\left(\frac{0.9668}{(8.617 \times 10^{-5})357}\right) = 2.1 \times 10^{12} \text{ s}^{-1}.$$

This value of s is very close to the value of $s = 1.9 \times 10^{12}$ s^{-1} obtained above using the y-intercept of the graph, indicating that the results of the heating rate method are self-consistent with the assumption of first-order kinetics.

(d) The errors ΔE and Δs can be calculated from the uncertainties in the slope and y-intercept of the best-fitting regression lines.

From the slope of the regression line, $E = 0.967 \pm 0.029$ eV.

This corresponds to a percent error in E of $100(\Delta E/E) = 100(0.029/0.967) = 3\%$.

By taking the logarithmic derivative of the equation $s = E \exp(\text{intercept})/k$, we obtain

$$\ln s = \ln E + \text{intercept} - \ln k,$$

$$\left|\frac{\Delta s}{s}\right| = \left|\frac{\Delta E}{E}\right| + |\Delta(\text{intercept})| = \left|\frac{0.0288}{0.9668}\right| + |0.91| = 0.94. \tag{2.5}$$

This leads to a very large (but nevertheless typical) uncertainty in s, of the order of 94%.

As a general comment on applying the heating rate methods of analysis, we wish to point out that the methods based on the variation of I_M with the heating rate β are easy to use. These methods are perhaps also more reliable than the methods based on the changes of T_M with the heating rate, because they would be less affected by the presence of nearby overlapping TL peaks. It is rather strange that these I_M-based methods have not been very popular in the TL literature. In our opinion, this is due most probably to confusion between the theoretical heights I_M and the corresponding heights measured in an experiment. These latter heights must be divided by the heating rate β as was shown in this exercise, in order to correct the units and to normalize the areas under the TL glow peaks.

When using theoretical methods involving I_M, the units of the height I_M are in counts/s. However, in experimental data, one measures I_M in units of counts/K.

If one tries to apply the I_M methods of analysis using the experimental data in counts/K, these methods fail dramatically to yield the correct values of E. For correct application of the method, the experimental values of counts/K must be changed into counts/s by multiplying with the heating rate β.

This important point has not been emphasized or clarified enough in the TL literature.

Exercise 2.3: Isothermal Method for First-Order Kinetics

You are given the experimental data in Table 2.8 for the isothermal decay curves of a TL peak, which were measured for four different temperatures of $T = 50°C, 60°C, 70°C$, and $80°C$.

(a) Show that these data are consistent with the assumption that the TL glow peak follows first-order kinetics.
(b) Find the kinetic parameters E and s.

Solution

(a) Figure 2.11 shows the given data for the four different temperatures $T = 50°C, 60°C, 70°C$, and $80°C$.

As discussed in Chapter 1, the isothermal decay curves for TL peaks following first-order kinetics are exponential functions of time, given by

$$I = I_0 \exp(-s \cdot \exp(-E/kT) \cdot t). \qquad (2.6)$$

This equation tells us that a graph of $\ln(I)$ versus time t will be linear for first-order kinetics peaks, and that the slope of the line will be

$$|slope| = s \cdot \exp(-E/kT). \qquad (2.7)$$

By taking the natural logarithm of this equation, we obtain

$$\ln(|slope|) = \ln s - E/kT. \qquad (2.8)$$

TABLE 2.8. Data for the isothermal decay curves of a first-order TL peak

| t(s)	TL, $T = 50°C$	TL, $T = 60°C$	TL, $T = 70°C$	TL, $T = 80°C$
0	2.48×10^6	7.22×10^6	1.94×10^7	4.74×10^7
20	2.47×10^6	7.11×10^6	1.87×10^7	4.26×10^7
40	2.45×10^6	7.01×10^6	1.79×10^7	3.83×10^7
60	2.44×10^6	6.91×10^6	1.72×10^7	3.45×10^7
80	2.43×10^6	6.80×10^6	1.65×10^7	3.10×10^7
100	2.42×10^6	6.70×10^6	1.58×10^7	2.78×10^7
120	2.40×10^6	6.61×10^6	1.52×10^7	2.50×10^7
140	2.39×10^6	6.51×10^6	1.46×10^7	2.25×10^7
160	2.38×10^6	6.41×10^6	1.40×10^7	2.02×10^7
180	2.37×10^6	6.32×10^6	1.34×10^7	1.82×10^7
200	2.36×10^6	6.23×10^6	1.29×10^7	1.63×10^7
220	2.35×10^6	6.13×10^6	1.24×10^7	1.47×10^7
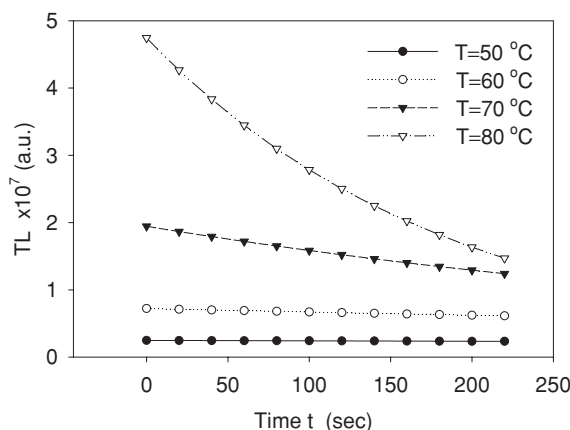
FIGURE 2.11. The isothermal decay curves for first-order TL data.

The graph of the $\ln(|\text{slope}|)$ versus $1/kT$ should be a straight line with slope $= -\text{E}$ and y-intercept $= \ln s$.

We first find $\ln(\text{TL})$ for each isothermal curve as shown in Table 2.9.

By graphing the $\ln(\text{TL})$ versus time, we obtain straight lines as shown in Figure 2.12, indicating that the given isothermal TL data obey first-order kinetics. We next find the regression lines through each of the graphs shown in Figure 2.12.

(b) Next, we tabulate in Table 2.10 the slopes of these linear graphs and calculate the natural logarithm of the slopes, $\ln(|\text{slope}|)$. Finally, we graph in Figure 2.13 the $\ln(|\text{slope}|)$ versus $1/kT$, where $T =$ temperature (in K) at which the isothermal decay curves were measured.

The slope of the regression line gives the activation energy E:

$$E = 1.007 \pm 0.002 \text{ eV.}$$

TABLE 2.9. The $\ln(\text{TL})$ data for each isothermal curve

| t(s)	TL, $T = 50°C$	$\ln(\text{TL})$, $T = 50°C$	TL, $T = 60°C$	$\ln(\text{TL})$, $T = 60°C$	TL, $T = 70°C$	$\ln(\text{TL})$, $T = 70°C$	TL, $T = 80°C$	$\ln(\text{TL})$, $T = 80$
0	2.48×10^6	14.726	7.22×10^6	15.796	1.94×10^7	16.783	4.74×10^7	17.683
20	2.47×10^6	14.722	7.11×10^6	15.782	1.87×10^7	16.750	4.26×10^7	17.594
40	2.45×10^6	14.718	7.01×10^6	15.771	1.79×10^7	16.718	3.83×10^7	17.498
60	2.44×10^6	14.712	6.91×10^6	15.749	1.72×10^7	16.674	3.45×10^7	17.380
80	2.43×10^6	14.705	6.80×10^6	15.735	1.65×10^7	16.629	3.10×10^7	17.264
100	2.42×10^6	14.701	6.70×10^6	15.720	1.58×10^7	16.584	2.78×10^7	17.150
120	2.40×10^6	14.696	6.61×10^6	15.707	1.52×10^7	16.548	2.50×10^7	17.059
140	2.39×10^6	14.690	6.51×10^6	15.699	1.46×10^7	16.511	2.25×10^7	16.961
160	2.38×10^6	14.687	6.41×10^6	15.683	1.40×10^7	16.462	2.02×10^7	16.863
180	2.37×10^6	14.681	6.32×10^6	15.660	1.34×10^7	16.420	1.82×10^7	16.754
200	2.36×10^6	14.675	6.23×10^6	15.645	1.29×10^7	16.385	1.63×10^7	16.634
220	2.35×10^6	14.673	6.13×10^6	15.632	1.24×10^7	16.346	1.47×10^7	16.527
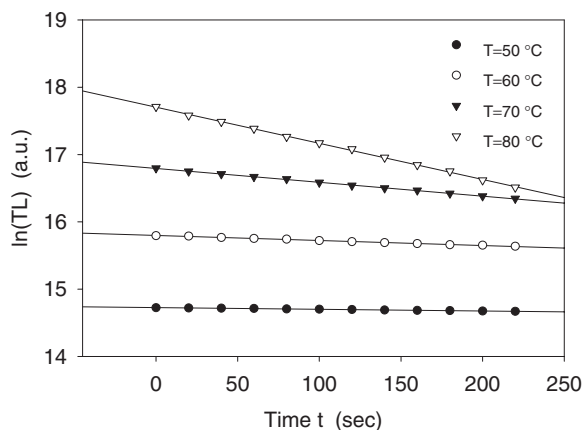
FIGURE 2.12. The isothermal decay curves on semilog scale for first-order TL data.

And the frequency factor s can be found from the intercept of the regression line:

$$\text{Intercept} = \ln(s) = 27.87 \pm 0.07.$$

Therefore,

$$s = \exp(27.87) = 1.3 \times 10^{12} \text{ s}^{-1}.$$

The error in the frequency factor Δs can be calculated from the uncertainties in the intercept of the regression line as follows:

$$\Delta(\text{intercept}) = \Delta s/s = 0.07.$$

This gives a rather unusually small error of 7% for the value of the frequency factor s.

Self-Consistency Check of E and s Values

The values of s and E can be checked for self-consistency as follows: We can calculate theoretical slopes of the isothermal decay curves using the E and s values and compare them with the experimental slopes obtained from the graphs. Theoretically, the slopes of the graphs $\ln(\text{TL})$ versus time t should be given by equation (2.7)

$$\text{slope} = s \exp\left(\frac{-E}{kT}\right).$$

TABLE 2.10. The slopes of linear isothermal graphs

$T(°C)$	$|slope|(s^{-1})$	$1/kT$ (eV^{-1})	$\ln(|Slope|)$	Calculated $|slope|(s^{-1})$	%Difference in slopes
50	2.46×10^{-4}	35.93	-8.31	2.49×10^{-4}	1.2
60	7.35×10^{-4}	34.85	-7.22	7.33×10^{-4}	-0.3
70	2.04×10^{-3}	33.83	-6.19	2.02×10^{-3}	-0.8
80	5.33×10^{-3}	32.88	-5.23	5.28×10^{-3}	-1.0
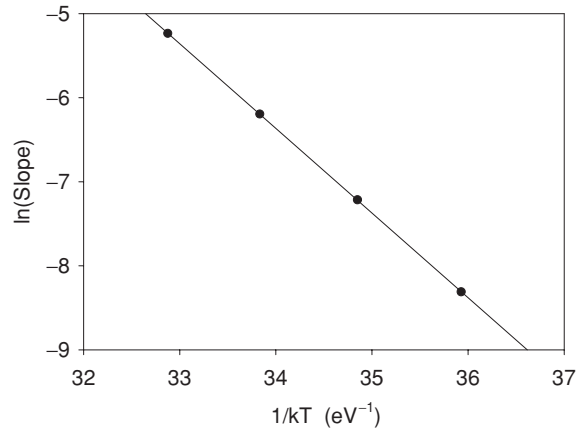
FIGURE 2.13. The ln(|slope|) versus $1/kT$ graph for first-order TL data.

By using the values of $E = 1.007$ eV and $s = 1.3 \times 10^{12}$ s^{-1} in equation (2.7), we obtain the theoretical values of the slopes shown on the fifth column of Table 2.10. The last column in Table 2.10 shows that the percent difference between the theoretical and experimental slopes in columns 2 and 5 is very small, of the order of 1%, indicating that the isothermal decay data are consistent with first-order kinetics.

Exercise 2.4: Analysis of a Second-Order TL Peak

You are given in Table 2.11 and Figure 2.14 the experimental data for a TL glow curve (TL versus Temperature T), which was measured with a heating rate $\beta = 1$ K s^{-1}.

(a) Apply the IR method to find the activation energy E. The value for E obtained using the IR method is assumed to be independent of the order of kinetics.

TABLE 2.11. The experimental data for a second-order TL glow curve

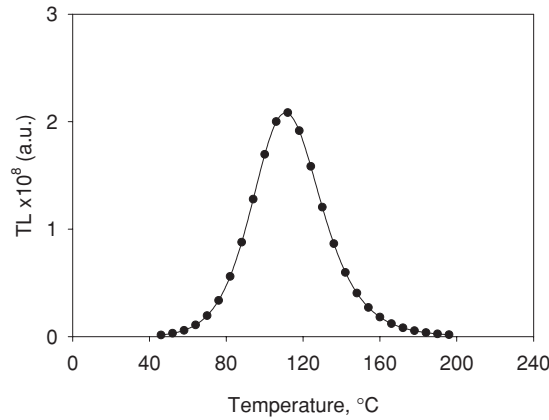| $T(°C)$	TL (a.u.)	$T(°C)$	TL (a.u.)
46	1.58×10^6	124	1.58×10^8
52	3.09×10^6	130	1.20×10^8
58	5.87×10^6	136	8.64×10^7
64	1.09×10^7	142	5.98×10^7
70	1.95×10^7	148	4.05×10^7
76	3.37×10^7	154	2.71×10^7
82	5.60×10^7	160	1.81×10^7
88	8.78×10^7	166	1.21×10^7
94	1.28×10^8	172	8.17×10^6
100	1.70×10^8	178	5.53×10^6
106	2.00×10^8	184	3.77×10^6
112	2.08×10^8	190	2.59×10^6
118	1.92×10^8	196	1.79×10^6

FIGURE 2.14. The second-order TL glow curve.

(b) Apply Chen's peak shape equations for second-order kinetics to find the activation energy E, using the shape parameters τ, δ, and ω. By assuming that the experimental error in the quantities τ, δ, and ω is $\Delta T = 2$ K, estimate the error $\Delta\mu$ in the value of the geometrical shape factor μ.

Show that the values of μ and $\Delta\mu$ are consistent with the assumption that the TL glow curve obeys second-order kinetics.

(c) Apply the whole glow-peak method to the data given and find E, s, and the order of kinetics b. Verify that the given TL glow curve corresponds to second-order kinetics.

(d) Using the values of I_M (maximum TL intensity) and T_M (temperature of maximum intensity) from the data table, do a curve fitting to the given numerical data. Use the following analytical equation developed by Kitis et al [2] for second-order kinetics:

$$I(T) = 4I_M \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)$$

$$\times \left[\frac{T^2}{T_M^2} \cdot \left(1 - \frac{2kT}{E}\right) \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right) + 1 + \frac{2kT_M}{E}\right]^{-2}. \quad (2.9)$$

The activation parameter E in this expression can be treated as an adjustable parameter.

Graph both the experimental data and the calculated second-order TL glow curve on the same graph and compare them.

Calculate the FOM for the TL glow curve.

(e) Can it be concluded from the above analysis that this material will always follow second-order kinetics?

Solution

(a) *The IR method.* We calculate in Table 2.12 the values of $1/kT$ (T = temperature in K) and the values of ln(TL) in a spreadsheet.

TABLE 2.12. Calculated values of $1/kT$ and the values of $\ln(\text{TL})$

$T(^\circ\text{C})$	$\text{TL}_{\text{experimental}}$	$1/kT$ (eV^{-1})	$\ln(\text{TL})$	$T(^\circ\text{C})$	$\text{TL}_{\text{experimental}}$	$1/kT$ (eV^{-1})	$\ln(\text{TL})$
46	1.58×10^6	36.38	14.27	124	1.58×10^8	29.23	18.88
52	3.09×10^6	35.71	14.94	130	1.20×10^8	28.80	18.61
58	5.87×10^6	35.06	15.59	136	8.64×10^7	28.37	18.27
64	1.09×10^7	34.44	16.20	142	5.98×10^7	27.96	17.91
70	1.95×10^7	33.83	16.78	148	4.05×10^7	27.57	17.52
76	3.37×10^7	33.25	17.33	154	2.71×10^7	27.18	17.12
82	5.60×10^7	32.69	17.84	160	1.81×10^7	26.80	16.71
88	8.78×10^7	32.15	18.29	166	1.21×10^7	26.44	16.31
94	1.28×10^8	31.62	18.67	172	8.17×10^6	26.08	15.92
100	1.70×10^8	31.11	18.95	178	5.53×10^6	25.73	15.53
106	2.00×10^8	30.62	19.11	184	3.77×10^6	25.39	15.14
112	2.08×10^8	30.14	19.15	190	2.59×10^6	25.06	14.77
118	1.92×10^8	29.68	19.07	196	1.79×10^6	24.74	14.40

We next graph in Figure 2.15(a) the $\ln(\text{TL})$ versus $1/kT$ data and find a regression line through the first 7 data points, as shown in Figure 2.15(b).

The slope of the regression line gives the activation energy E as

$$E = 0.969 \pm 0.006 \text{ eV}, \qquad \text{with } R^2 = 0.9997.$$

(b) *Chen's peak shape equations.* From the given experimental data, we can estimate the temperatures

$$T_1 = 91^\circ\text{C} = 364 \text{ K}, \quad T_2 = 133^\circ\text{C} = 406 \text{ K}, \quad T_\text{M} = 112^\circ\text{C} = 385 \text{ K},$$

where

$T_\text{M} = $ peaktemperature at the maximum TL intensity,

$T_1, T_2 = $ temperatures on either side of T_M, corresponding to the half-maximum intensity.
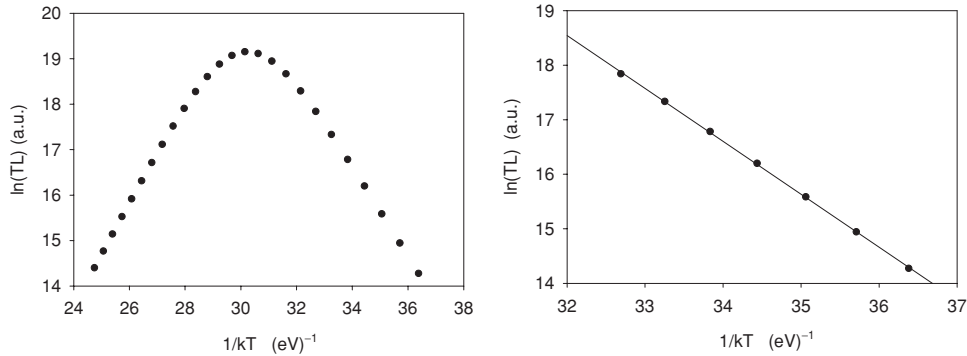

FIGURE 2.15. IR method analysis.

We next calculate the quantities μ, τ, δ, and ω:

$$\tau = T_M - T_1 = 21 \text{ K}, \quad \delta = T_2 - T_M = 21 \text{ K}, \quad \omega = T_2 - T_1 = 42 \text{ K},$$
$$\mu = \delta/\omega = 21/42 = 0.50.$$

The calculated value of the geometrical shape factor $\mu = \delta/\omega = 0.50$ is very close to the theoretical value for a second-order TL peak $\mu = \delta/\omega = 0.52$.

Using the known experimental error $\Delta T = 2 \text{ K}$ for the quantities τ, δ, and ω, we can do an error analysis of the values of μ. As in the case of first-order kinetics,

$$\left| \frac{\Delta \mu}{\mu} \right| = \left| \frac{\Delta \delta}{\delta} \right| + \left| \frac{\Delta \omega}{\omega} \right| = \left| \frac{2}{21} \right| + \left| \frac{2}{42} \right| = 0.095 + 0.048 = 0.143.$$

This leads to a value of $\mu \pm \Delta \mu = 0.50 \pm 0.07$, which is consistent with second-order kinetics within the accuracy of the given TL data.

We apply Chen's equation for second-order kinetics.

Using the value of τ:

$$E = \frac{1.81 k T_M^2}{\tau} - 2(2kT_M) = 1.101 - 0.133 = 0.968 \text{ eV}.$$

Using the value of δ:

$$E = \frac{1.71 k T_M^2}{\delta} = 1.040 \text{ eV}.$$

Using the value of ω:

$$E = \frac{3.54 k T_M^2}{\omega} - 2kT_M = 1.077 - 0.066 = 1.011 \text{ eV}.$$

In order to find the error ΔE in the activation energy E, we take the logarithmic derivative of the equation $E = 1.71 k T_M^2 / \delta$:

$$\left| \frac{\Delta E}{E} \right| = 2 \left| \frac{\Delta T_M}{T_M} \right| + \left| \frac{\Delta \delta}{\delta} \right| = 2 \left| \frac{2}{385} \right| + \left| \frac{2}{21} \right| = 0.010 + 0.095 = 0.105.$$

This gives a rather large 10.5% error of $\Delta E = 0.105 E = 0.105(1.040) = 0.11 \text{ eV}$.

(c) *The whole glow-peak method*. We graph $\ln(I/n^b)$ versus $1/T$ for various values of b between 1.8 and 2.1, and find the value of b that gives a linear graph. As in the case of first-order kinetics, $n(T)$ is the area under the glow peak and it is calculated starting at a temperature T, up to the maximum temperature available in the experimental data. In the data shown in Table 2.13, the maximum available temperature is 196°C.

By following the same procedure as in the case of first-order kinetics, we set up a spreadsheet to calculate the quantities $\ln(I/n^b)$ and $1/kT$ as shown in Table 2.13.

Additional columns are created in the spreadsheet for the quantities of $\ln(TL/n^b)$ for several values of the kinetic order $b = 2.0, 2.1, 1.9,$ and 1.8.

Finally, several graphs are drawn of $\ln(TL/\text{Area}^b)$ versus $1/kT$ as shown in Figure 2.16.

It is clear that all four graphs in Figure 2.16 deviate from straight lines, especially at low values of $1/kT$ (which correspond to large temperatures located on the high-temperature end of the TL glow peak). These deviations are due to experimental

TABLE 2.13. The quantities $\ln(I/n^b)$ and $1/kT$

|		A	B	C	D	E	F	G
1	$T(°C)$	$1/kT$ $(eV)^{-1}$	Area	$\ln(TL/Area)$	$\ln(TL/n^2)$	$\ln(TL/n^{2.1})$	$\ln(TL/n^{1.9})$	$\ln(TL/n^{1.8})$
2	46	36.38	9.96×10^9	−8.75	−31.77	−34.07	−29.47	−27.17
3	52	35.71	9.95×10^9	−8.08	−31.10	−33.40	−28.80	−26.49
4	58	35.06	9.94×10^9	−7.43	−30.45	−32.75	−28.15	−25.85
5	64	34.44	9.90×10^9	−6.82	−29.83	−32.13	−27.53	−25.23
6	70	33.83	9.84×10^9	−6.22	−29.23	−31.53	−26.93	−24.63
7	76	33.25	9.72×10^9	−5.66	−28.66	−30.96	−26.36	−24.06
8	82	32.69	9.52×10^9	−5.14	−28.11	−30.41	−25.81	−23.52
9	88	32.15	9.18×10^9	−4.65	−27.59	−29.88	−25.30	−23.00
10	94	31.62	8.65×10^9	−4.21	−27.10	−29.38	−24.81	−22.52
11	100	31.11	7.89×10^9	−3.84	−26.63	−28.91	−24.35	−22.07
12	106	30.62	6.87×10^9	−3.54	−26.19	−28.45	−23.92	−21.66
13	112	30.14	5.67×10^9	−3.30	−25.76	−28.01	−23.52	−21.27
14	118	29.68	4.42×10^9	−3.14	−25.35	−27.57	−23.13	−20.91
15	124	29.23	3.27×10^9	−3.03	−24.94	−27.13	−22.74	−20.55
16	130	28.80	2.32×10^9	−2.96	−24.52	−26.68	−22.37	−20.21
17	136	28.37	1.60×10^9	−2.92	−24.11	−26.23	−21.99	−19.87
18	142	27.96	1.08×10^9	−2.89	−23.69	−25.77	−21.61	−19.53
19	148	27.57	7.19×10^8	−2.88	−23.27	−25.31	−21.23	−19.19
20	154	27.18	4.76×10^8	−2.86	−22.84	−24.84	−20.85	−18.85
21	160	26.80	3.13×10^8	−2.85	−22.41	−24.36	−20.45	−18.50
22	166	26.44	2.04×10^8	−2.82	−21.95	−23.87	−20.04	−18.13
23	172	26.08	1.31×10^8	−2.78	−21.47	−23.34	−19.60	−17.73
24	178	25.73	8.21×10^7	−2.70	−20.92	−22.74	−19.10	−17.28
25	184	25.39	4.89×10^7	−2.56	−20.27	−22.04	−18.50	−16.73
26	190	25.06	2.63×10^7	−2.32	−19.40	−21.11	−17.69	−15.99
27	196							
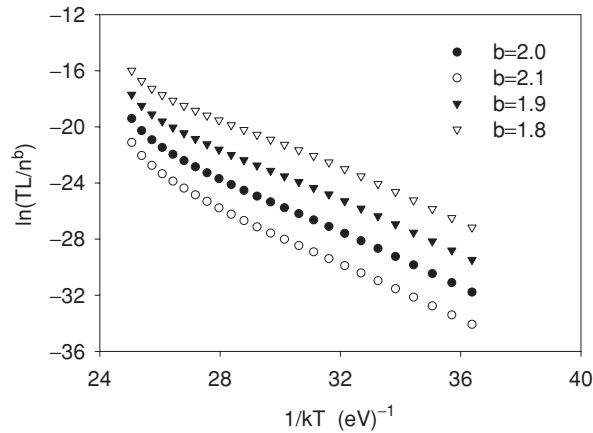
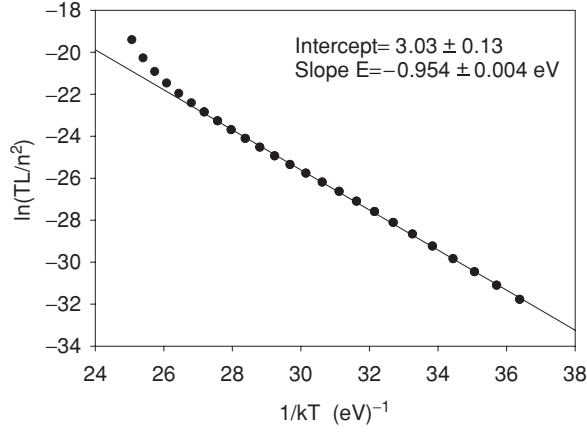FIGURE 2.16. Graphs of $\ln(TL/Area^b)$ versus $1/kT$ for several values of kinetic order b.

FIGURE 2.17. The parameters E and s' can be calculated from the whole glow-peak method.

uncertainties in the data, and also to the fact that only 26 data points are available on the TL glow curve.

A regression line is fitted to the four graphs above:

$$b = 1.8: \quad R^2 = 0.9983$$
$$b = 1.9: \quad R^2 = 0.9992$$
$$b = 2.0: \quad R^2 = 0.9990$$
$$b = 2.1: \quad R^2 = 0.9979.$$

The regression line for $b = 1.9$ gives the largest regression coefficient R^2, with a value that is very close to the regression coefficient for the case $b = 2.0$. Within the accuracy of the given experimental data and within the framework of the whole glow-peak method of analysis, we can conclude that the given TL glow peak data follow second-order kinetics.

The values of E and s' can be calculated from the best-fitting regression line shown in Figure 2.17:

$$\text{Best intercept} = 3.03 \pm 0.13,$$
$$\text{Best slope } E = -0.954 \pm 0.004 \text{ eV}.$$

According to equation (1.23), the value of s' can be calculated from the intercept of the regression line:

$$s' = \beta e^{(\text{intercept})} = 1e^{(3.03)} = 20.697.$$

The whole glow-peak method yields information about both the activation energy E and the effective frequency factor $s' = s/N$ appearing in equation (1.6):

$$I(T) = n_0^2 \frac{s}{N} \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{n_0 s}{\beta N} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-2}. \quad (1.6)$$

Since TL data analysis of a glow curve cannot yield a value for the *absolute* concentration n_0 of traps in the material, the factors s/N and n_0 appearing in equation (1.6) represent *two empirical fitting parameters* for second-order glow peaks. The value of n_0 can be obtained from the area under the glow curve as follows:

$$\frac{\text{Area}}{\beta} = \frac{1}{\beta} \int_{T_0}^{T_f} I \, dT = \int_{t_0}^{t_f} I \, dt = \int_{t_0}^{t_f} -\left(\frac{dn}{dt}\right) dt$$
$$= n(t_0) - n(t_f) = n_0 - 0 = n_0. \tag{2.10}$$

In our example, the area can be estimated by summing the TL intensities multiplied by the temperature interval $\Delta T = 6$ K between TL measurements, and dividing by the heating rate $\beta = 1$ K s^{-1}:

$$n_0 \approx \frac{1}{\beta} \int_{T_0}^{T_f} I \, dT = \frac{1}{\beta} \sum I(T)\Delta T = \frac{1}{1} \sum I(T)(6K) = 9.96 \times 10^9. \tag{2.11}$$

By using the values of $E = 0.954$ eV, $s' = 20.697$, $n_0 = \text{Area} = 9.96 \times 10^9$, and $\beta = 1$ K s^{-1}, it is possible to calculate the TL intensity using equation (1.6), and to compare this result directly with the given experimental data. The integral in equation (1.6) can be calculated using numerical integration methods, as shown for example in Chapter 3. As an alternative method, the series approximation given in equation (1.52) can be used to evaluate the integral.

The result of the comparison is shown in Figure 2.18, where the calculated $I(T)$ from equation (1.6) is compared with the original experimental data. Figure 2.18 shows that the calculated parameters E, s', and n_0 from the whole glow-peak method, as well as the second-order equation (equation (1.6)), describe the given experimental data in a satisfactory manner.
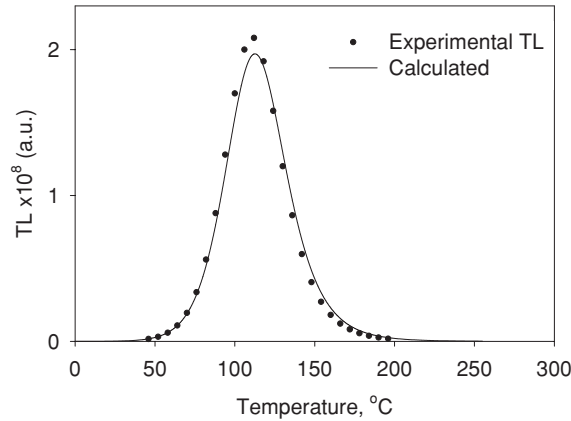

FIGURE 2.18. Comparison of calculated TL intensity using equation (1.6) (solid line), and original experimental data (individual data points). The parameters used in equation (1.6) were calculated using the whole glow-peak method.

TABLE 2.14. Calculations for glow-curve fitting for several E values

A	B	C	D	E	F	G	H	I	J	K	L
		$I(T)$	$I(T)$	$I(T)$	$I(T)$						
1 T(K)	$TL_{experimental}$	$E = 1$ eV	$E = 0.9$ eV	$E = 1.1$ eV	$E = 1.2$ eV						
2						$E =$	1	eV	0.9	1.1	1.2
3 319	1.58×10^6	1.49×10^6	2.63×10^6	8.45×10^5	4.76×10^5						
4 325	3.09×10^6	3.02×10^6	4.97×10^6	1.83×10^6	1.10×10^6						
5 331	5.87×10^6	5.94×10^6	9.11×10^6	3.85×10^6	2.48×10^6	$T_M =$	380	K			
6 337	1.09×10^7	1.13×10^7	1.62×10^7	7.83×10^6	5.39×10^6	$I_M =$	2.08×10^8				
7 343	1.95×10^7	2.08×10^7	2.78×10^7	1.54×10^7	1.13×10^7						

The observed discrepancies between experiment and calculation in Figure 2.18 are due to the several approximations involved in applying the whole glow-peak method, and to the approximation of the area using equation (2.11).

(d) *Glow-curve fitting using the Kitis et al equation.* We use the analytical equation developed by Kitis et al [2], which relies on two experimentally measured quantities, $I_M = 2.08 \times 10^8$ and $T_M = 380$ K:

$$I(T) = 4I_M \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)$$

$$\times \left[\frac{T^2}{T_M^2} \cdot \left(1 - \frac{2kT}{E}\right) \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right) + 1 + \frac{2kT_M}{E}\right]^{-2}. \quad (2.12)$$

The activation parameter E is treated in this equation as an adjustable parameter. We calculate several graphs with values of $E = 0.9$, 1.0, 1.1, and 1.2 eV. The calculations can be easily set up in a spreadsheet as shown in Table 2.14. Only the first 5 rows are shown for the sake of brevity.

Columns A and B contain the experimental data points for the TL glow curve, whereas columns C–F contain the calculated data points using equation (2.12) for second-order kinetics and for four values of the energy parameter E ($E = 0.9$, 1.0, 1.1, and 1.2 eV).

The following equation is used to calculate the values of the fitted data in column C, using equation (2.12) for second-order kinetics:

Cell C3 = 4*$H$6*EXP($H$2/(0.00008617*B3)*((B3-$H$5)/
$H$5))*((B3*B3)/($H$5*$H$5))*((1-2*0.00008617*
$H$5/$H$2)*EXP($H$2/(0.00008617*B3)*((B3-$H$5)/
$H$5))+1+2*0.00008617*$H$5/$H$2)^-2.

Note that cell H2 in the spreadsheet contains the value of the energy parameter $E = 1.0$ eV, cell H5 contains the value of the experimental parameter $T_M = 380$ K, and cell H6 contains the value of the experimental maximum height parameter $I_M = 2.08 \times 10^8$. The above spreadsheet expression refers to the values contained in these cells by using the Excel expressions $H$2, $H$5, $H$6, correspondingly.
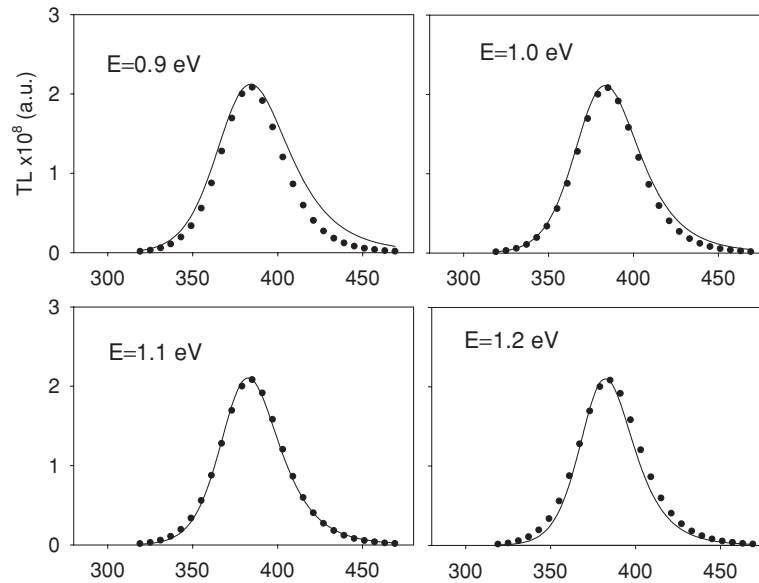
FIGURE 2.19. Experimental data and fitted graphs calculated for several values of E.

Similar expressions are entered in the columns D, E, and F, and the Excel command **Fill Down** is used to fill the rest of these columns.

The graphs calculated for E = 0.9, 1.0, 1.1, and 1.2 eV are shown in Figure 2.19, together with the given experimental data.

It can be seen in Figure 2.19 that when the value of E is too low (graph corresponding to $E = 0.9$ eV), the calculated TL points lie well above the experimental data. This is also evident by inspection of the $I(T)$ data in Table 2.14. On the other hand, when the value of E is too high (graph corresponding to $E = 1.2$ eV), the calculated TL points lie below the experimental data.

This procedure is a simple example of a single glow-curve fitting procedure, in which we find the value of E that yields the best fit to experimental data obeying second-order kinetics.

A more precise numerical method of performing a fitting procedure is by calculating the FOM, using a similar calculation to the one employed for first-order kinetics (Exercise 2.1).

Table 2.15 shows an example of a FOM calculation as applied to the previous data. Column A contains the experimental data points and columns B and C contain the calculated data points using equation (2.12) for second-order kinetics and for two values of the energy parameter E ($E = 1.1$ and 0.9 eV).

Columns E and F contain the calculation of the quantity $|TL_{experimental} - TL_{calculated}|$, and cells E29 and F29 contain the calculated values of the FOM.

The expressions used in this example are

$$Cell\ E3 = ABS(A3-B3)$$
$$Cell\ F3 = ABS(A3-C3)$$

TABLE 2.15. Example of a FOM calculation

	A	B	C	D	E	F
		$I(T)$	$I(T)$		$|TL_{experimental} - I(t)|$	$|TL_{experimental} - I(t)|$
1	$TL_{experimental}$	$E = 0.9$ eV	$E = 1.1$ eV		$E = 0.9$ eV	$E = 1.1$ eV
2						
3	1.58×10^6	2.63×10^6	8.45×10^5		1.05×10^6	7.38×10^5
4	3.09×10^6	4.97×10^6	1.83×10^6		1.88×10^6	1.26×10^6
5	5.87×10^6	9.11×10^6	3.85×10^6		3.23×10^6	2.03×10^6
6	1.09×10^7	1.62×10^7	7.83×10^6		5.34×10^6	3.03×10^6
7	1.95×10^7	2.78×10^7	1.54×10^7		8.36×10^6	4.10×10^6
8	3.37×10^7	4.59×10^7	2.90×10^7		1.22×10^7	4.77×10^6
9	5.60×10^7	7.20×10^7	5.17×10^7		1.60×10^7	4.24×10^6
10	8.78×10^7	1.06×10^8	8.61×10^7		1.82×10^7	1.74×10^6
11	1.28×10^8	1.45×10^8	1.30×10^8		1.68×10^7	2.42×10^6
12	1.70×10^8	1.81×10^8	1.75×10^8		1.14×10^7	5.81×10^6
13	2.00×10^8	2.06×10^8	2.05×10^8		5.41×10^6	5.28×10^6
14	2.08×10^8	2.12×10^8	2.09×10^8		3.98×10^6	6.81×10^5
15	1.92×10^8	2.01×10^8	1.87×10^8		9.36×10^6	4.38×10^6
16	1.58×10^8	1.77×10^8	1.52×10^8		1.86×10^7	6.65×10^6
17	1.20×10^8	1.47×10^8	1.14×10^8		2.68×10^7	5.95×10^6
18	8.64×10^7	1.18×10^8	8.26×10^7		3.13×10^7	3.86×10^6
19	5.98×10^7	9.16×10^7	5.80×10^7		3.18×10^7	1.74×10^6
20	4.05×10^7	7.01×10^7	4.03×10^7		2.96×10^7	1.97×10^5
21	2.71×10^7	5.32×10^7	2.79×10^7		2.60×10^7	7.11×10^5
22	1.81×10^7	4.02×10^7	1.93×10^7		2.20×10^7	1.14×10^6
23	1.21×10^7	3.04×10^7	1.34×10^7		1.82×10^7	1.26×10^6
24	8.17×10^6	2.30×10^7	9.38×10^6		1.48×10^7	1.21×10^6
25	5.53×10^6	1.75×10^7	6.61×10^6		1.19×10^7	1.08×10^6
26	3.77×10^6	1.33×10^7	4.70×10^6		9.57×10^6	9.31×10^5
27	2.59×10^6	1.02×10^7	3.37×10^6		7.65×10^6	7.78×10^5
28	1.79×10^6	7.90×10^6	2.43×10^6		6.11×10^6	6.39×10^5
29				FOM =	0.178	0.040

$$\text{Cell E29} = \text{SUM(E3:E28)/SUM(B3:B28)}$$
$$\text{Cell F29} = \text{SUM(F3:F28)/SUM(C3:C28)}.$$

The FOM for the value of the parameter $E = 1.1$ eV is equal to $0.040 = 4\%$, almost four times smaller than the FOM $= 0.178 = 17.8\%$ for the case $E = 0.9$ eV.

The frequency factor s can be calculated by using the value of $E = 1.1$ eV and the temperature of maximum TL intensity $T_M = 380$ K in equation (1.9) for second-order kinetics ($b = 2$):

$$s = \frac{\beta E}{kT_M^2 \left(1 + \dfrac{2kT_M}{E}\right)} \exp\left(\frac{E}{kT_M}\right)$$

TABLE 2.16. Summary of the results of various analysis methods for
second-order data

	E (eV)	s or s'	Comments below
Initial rise method	0.969 ± 0.006		[1, 4]
Chen's τ-method	0.968		[2, 4]
Chen's δ-method	1.04 ± 0.11		[2, 4]
Chen's ω-method	1.011		[2, 4]
Whole glow-peak method	0.954 ± 0.004	$s' = 20.697$	[3]
Fitting method using Kitis et al. second-order equation (equation (2.12))	1.1 ± 0.1	$s = 1.38 \times 10^{12} \text{ s}^{-1}$	[4]

$$= \frac{1(1)}{(8.617 \times 10^{-5})(380)^2 \left(1 + \dfrac{2(8.617 \times 10^{-5})380}{1}\right)}$$

$$\times \exp\left(\frac{1}{(8.617 \times 10^{-5})380}\right) = 1.38 \times 10^{12} \text{ s}^{-1}. \qquad (2.13)$$

The resolution of the Kitis et al fitting method can be refined by repeating this process of calculating the FOM for different values of E spaced much closer together (e.g., $E = 1.01, 1.00, 0.99$, etc.) and then attempt to minimize the value of the FOM.

Finally, we summarize in Table 2.16 the results of the various methods for analyzing the given second-order experimental data.

Comments on the Results of Exercise 2.4

1. The value of E obtained from the IR method is independent of the kinetics of the TL glow peak.

   As in the case of first-order kinetics, the presence of thermal quenching affects the value of E obtained in the IR method.

   A possible correction method for the value of E when thermal quenching is present is given in Chapter 5.

   It is best to use the IR and peak shape methods with samples irradiated at low doses [3].

2. The value of E obtained with peak shape methods can be influenced by the presence of smaller satellite peaks.

3. The whole glow-curve method yields information on both E and the pre-exponential factor s. Because TL cannot yield a value for the absolute concentration n_0, the quantities $s' = s/N$ and n_0 appearing in equation (1.6) represent *empirical fitting parameters* for second-order glow peaks. The value of n_0 can be obtained from the area under the glow curve.

   By using the values of E, $s' = s/N$, and n_0 obtained from the whole glow-peak method, it is possible to compare directly the experimental data with the TL intensity obtained using equation (1.6), as was shown in this exercise.

4. The pre-exponential factor *s* in these methods can be calculated from the value of T_M, E, and β by using equation (2.13). The estimated uncertainties $\Delta s/s$ from equation (2.13) can be very large (50–100%), even when the uncertainty $\Delta E/E$ is very small.

(e) Can we conclude that this TL peak follows second-order kinetics?

Chen et al [4] have provided a list of criteria that should be checked before claiming that a certain TL glow peak is of second-order.

Unfortunately, the TL literature contains many publications claiming a certain kinetic order for TL glow curves, based solely on peak shape analysis of a single glow curve.

The criteria for second-order kinetics were listed by Chen et al. [4] as follows:

I. *Peak shape*: Second-order peaks exhibit $\mu = 0.52$.
II. *Peak shift*: In most non-first-order TL glow peaks, the location of maximum TL intensity shifts toward higher temperatures for lower trap filling (smaller doses). One must be aware that the observed maximum shift in the experimental data can also be due to the presence of smaller satellite peaks.
III. *Superlinearity effects*: Second-order peaks may exhibit slight superlinearity effects at low doses.
IV. $I_M - T_M$ *dependence*: In second-order peaks, a graph of $\ln\left[I_M \left(\dfrac{T_M^2}{\beta} \right)^2 \right]$

   versus $1/kT_M$ will yield a straight line of slope E (equation (1.29)).
V. *Isothermal decay results*: These can provide valuable independent information about the kinetics of the TL process involved at different temperatures. As discussed in Chapter 1, different kinetic orders correspond to different mathematical behaviors for the isothermal decay laws.

   For second-order isothermal decay, a graph of $(I_t/I_0)^{-1/2}$ versus time should yield a straight line of slope E.

   The TL-like presentation of isothermal decay data can provide useful information about the kinetics and the kinetic parameters. A numerical example using this type of presentation is given in Chapter 5.

Exercise 2.5: Isothermal Method for Second-Order Kinetics

Even though this exercise refers specifically to isothermal data following second-order kinetics, the exact same method of analysis can be used for general-order kinetics data.

A TL material is irradiated with a certain dose D, and the sample is heated rapidly to a temperature of 60°C. The temperature is then kept constant while the emitted light is measured as a function of time t. The experiment is then repeated with the same dose D and for two additional temperatures of 70°C and 80°C. The following isothermal decay data in Table 2.17 is obtained for three different temperatures T = 60°C, 70°C, and 80°C.

TABLE 2.17. Isothermal decay data for second-order kinetics

t(s)	TL, $T = 60°$C	TL, $T = 70°$C	TL, $T = 80°$C
0	6.40×10^6	1.40×10^7	2.30×10^7
100	5.57×10^6	1.02×10^7	1.25×10^7
200	4.92×10^6	7.84×10^6	8.10×10^6
300	4.20×10^6	6.18×10^6	5.45×10^6
400	3.92×10^6	4.90×10^6	3.99×10^6
500	3.54×10^6	4.13×10^6	2.90×10^6
600	3.10×10^6	3.47×10^6	2.39×10^6
700	2.91×10^6	2.95×10^6	1.94×10^6
800	2.70×10^6	2.56×10^6	1.80×10^6
900	2.44×10^6	2.21×10^6	1.34×10^6

(a) Show that these data are consistent with the assumption that this TL peak follows second-order kinetics.

(b) Find the kinetic parameters E and s.

Solution

(a) The graphs in Figure 2.20 show the given data for the three temperatures $T = 60°$C, $70°$C, and $80°$C.

We can rule out the possibility of first-order kinetics by graphing ln(TL) versus time as shown in Figure 2.21. The graphs obtained are nonlinear, indicating that the data do not conform to first-order kinetics.

As discussed in Chapter 1, the isothermal decay curves for TL peaks following general-order kinetics with a kinetic-order parameter b are given by

$$\left(\frac{I_t}{I_0}\right)^{\frac{1-b}{b}} = 1 + s' n_0^{b-1}(b-1)t \exp\left(-\frac{E}{kT}\right), \qquad (1.38)$$
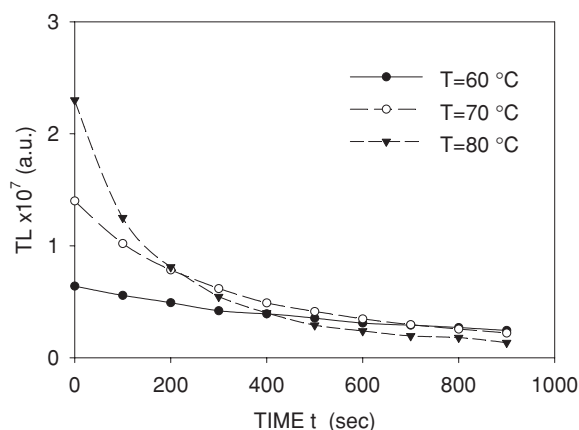

FIGURE 2.20. The isothermal data for three different temperatures and for second-order kinetics.
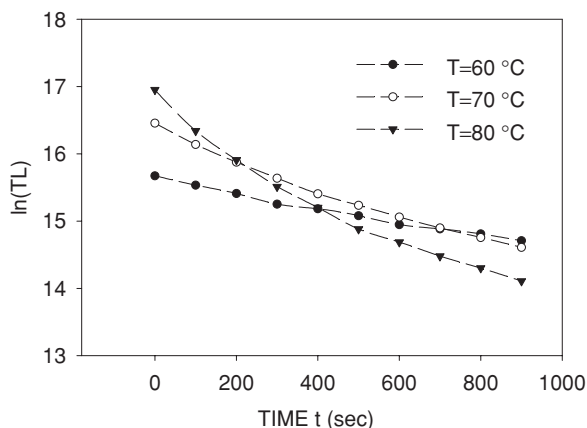
FIGURE 2.21. The ln(TL) versus time graphs for a second-order TL glow curve.

where

I_0 = initial TL intensity,
I_t = the TL intensity at time t,
$s' = s/N$ = effective frequency factor,
E = activation energy,
n_0 = initial trapped charged population,
T = temperature of isothermal decay.

This equation indicates that a plot of the quantity $(I_t/I_0)^{(1-b)/b}$ versus time t should be a straight line when a suitable value of b is found. After the determination of value of b, we will graph $(I_t/I_0)^{(1-b)/b}$ versus time t for the three different decay temperatures, and obtain a set of straight lines of slope m given by

$$m = s'n_0^{b-1}(b-1)\exp\left(-\frac{E}{kT}\right). \tag{1.39}$$

The activation energy E and the effective frequency factor $s'' = s'n_0^{b-1}$ will be determined from the slope and intercept of the plot of $\ln(m)$ versus $1/kT$.

Table 2.18 shows the calculation of the quantities $(I_t/I_0)^{(1-b)/b}$ for the isothermal decay data at $T = 70^{\circ}C$, and for four different values of the kinetic-order parameter $b = 1.6$, 1.8, 2.0, and 2.2. The graph in Figure 2.22 shows these quantities as a function of time t.

It can be seen that all four graphs yield satisfactory linear fits, with the following regression coefficients:

$$\begin{aligned}
b &= 1.6: & R &= 0.9986 \\
b &= 1.8: & R &= 0.9995 \\
b &= 2.0: & R &= 0.9999 \\
b &= 2.2: & R &= 0.9998.
\end{aligned}$$

TABLE 2.18. Calculation of the quantities $(I_t/I_0)^{(1-b)/b}$ for the isothermal decay data

t(s)	$T = 70°C$	$(I/I_0)^{(1-b)/b}$ $b = 2.0$	$(I/I_0)^{(1-b)/b}$ $b = 1.8$	$(I/I_0)^{(1-b)/b}$ $b = 1.6$	$(I/I_0)^{(1-b)/b}$ $b = 2.2$
0	1.40×10^7	1.000	1.000	1.000	1.000
100	1.02×10^7	1.172	1.151	1.126	1.189
200	7.84×10^6	1.337	1.294	1.243	1.372
300	6.18×10^6	1.505	1.438	1.359	1.562
400	4.90×10^6	1.690	1.595	1.482	1.773
500	4.13×10^6	1.842	1.721	1.581	1.947
600	3.47×10^6	2.010	1.860	1.688	2.142
700	2.95×10^6	2.178	1.998	1.793	2.338
800	2.56×10^6	2.338	2.128	1.891	2.526
900	2.21×10^6	2.515	2.270	1.997	2.735

This example illustrates one of the possible difficulties with isothermal decay data: It may be difficult to obtain an exact estimate of the best linear fit, because small differences may occur between the graphs for various values of b. The above values of R indicate that the graph corresponding to $b = 2.0$ represents the best linear fit, and therefore the given TL data are consistent with second-order kinetics.

The above type of analysis must be carried out for all available isothermal decay data. Once the kinetic order b is ascertained by the above type of analysis, we graph $(I_t/I_0)^{(1-b)/b} = (I_t/I_0)^{-1/2}$ versus time t, and find the slopes of the resulting linear graphs.

These graphs are shown in Figure 2.23 for the available isothermal decay data at $T = 60°C$, $70°C$, and $80°C$. We next find the regression lines through each of the graphs in Figure 2.23.

(b) We now tabulate in Table 2.19 the slopes of these linear graphs and calculate the natural logarithm of the slopes, ln(slope). Finally, we graph in Figure 2.24 the
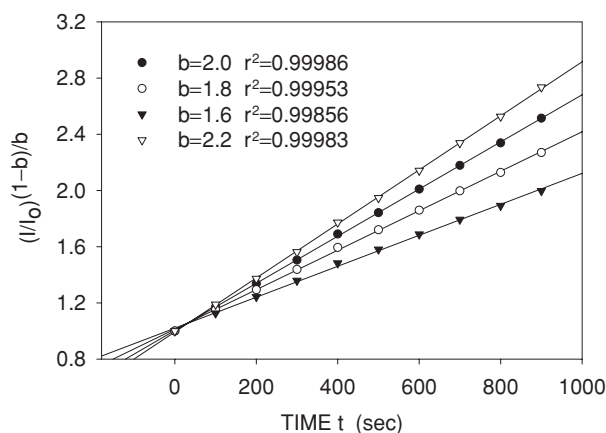

FIGURE 2.22. Graphs calculated for several values of kinetic order b.

TABLE 2.19. The slopes of linear isothermal graphs
and their natural logarithms ln(slope)

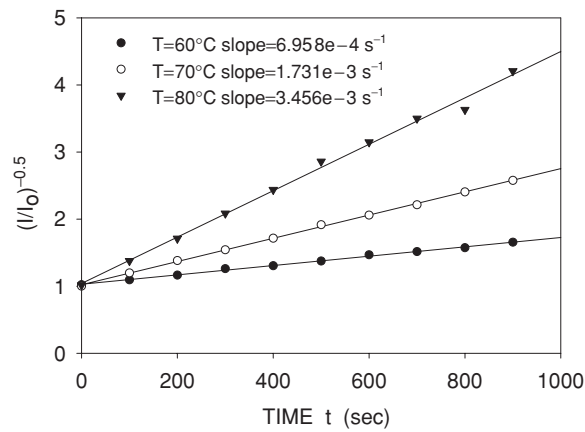| $T(°C)$	slope (s^{-1})	$1/kT$ (eV^{-1})	ln (Slope)
60	6.9580×10^{-4}	34.8498	-7.2704
70	1.7310×10^{-4}	33.8337	-6.3591
80	3.4560×10^{-4}	32.8753	-5.6676

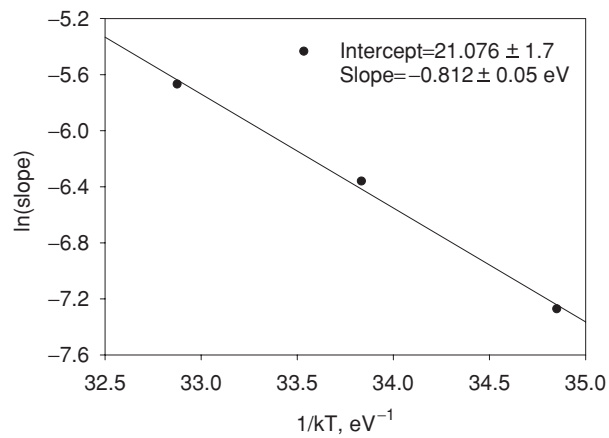FIGURE 2.23. Calculated graphs for kinetic order $b = 2.0$ and for second-order TL data.

FIGURE 2.24. The ln(slope) versus $1/kT$ graph to determine E for second-order TL data.

ln(slope) versus $1/kT$, where $T =$ temperature (K) at which the isothermal decay curves were measured.

The slope of the regression line gives the activation energy E:

$$E = 0.812 \pm 0.050 \, \text{eV}.$$

And the frequency factor $s'' = s'n_0^{b-1}$ can be found from the intercept of the regression line:

$$\text{Intercept} = \ln((b-1)\,s'') = 21.1 \pm 1.7.$$

Therefore, by substituting in our case $b = 2$,

$$s'' = \exp(21.1) = 1.46 \times 10^9 \, \text{s}^{-1}.$$

The errors $\Delta s''$ can be calculated from the uncertainties in the intercept of the regression line as follows:

$$\Delta \, (\text{intercept}) = \frac{\partial(\ln s'')}{\partial s''} \Delta s'' = \frac{\Delta s''}{s''} = 1.7.$$

This gives a typical large error for the value of the effective frequency factor $s'' = s'n_0^{b-1}$.

Once again, it is noted that the parameter $s'' = s'n_0^{b-1}$ cannot yield any additional information on the kinetics of the TL process, but rather represents an empirical fitting parameter for equation (1.38).

## *Exercise 2.6: Analysis of a General-Order TL Peak*

You are given the experimental data in Table 2.20 and Figure 2.25 for a TL glow curve (TL versus temperature T), and the known heating rate $\beta = 1\text{K s}^{-1}$.

(a) Apply the IR method to find the activation energy E. The value for E obtained using the IR method is assumed to be independent of the order of kinetics.

TABLE 2.20. Experimental data for general-order kinetics TL peak

$T(°C)$	$TL_{\text{experimental}}$	$T(°C)$	$TL_{\text{experimental}}$
0	8.38×10^5	130	3.96×10^7
10	2.06×10^6	140	1.96×10^7
20	4.74×10^6	150	9.19×10^6
30	1.03×10^7	160	4.22×10^6
40	2.09×10^7	170	1.93×10^6
50	3.98×10^7		
60	6.97×10^7		
70	1.09×10^8		
80	1.49×10^8		
90	1.70×10^8		
100	1.57×10^8		
110	1.18×10^8		
120	7.32×10^7		

FIGURE 2.25. The general-order TL glow curve.
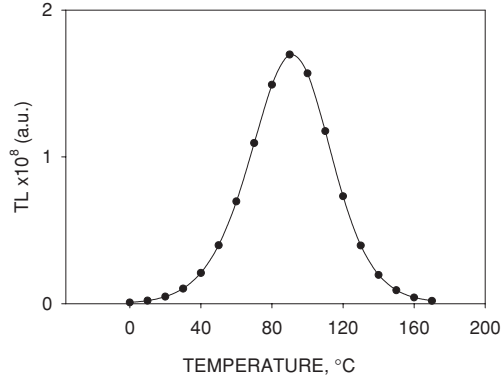
(b) Apply Chen's peak shape equations to find the activation energy E, using the shape parameters τ, δ, and ω. By assuming that the experimental error in the quantities τ, δ, and ω is $\Delta T = 2$ K estimate the error $\Delta\mu$ in the value of the geometrical shape factor μ.

   Show that the values of μ and $\Delta\mu$ are consistent with the assumption that the TL glow curve obeys general-order kinetics.

(c) By using the experimental data, apply the whole glow-peak method to find E, s, and the order of kinetics b. Graph $\ln(I/n^b)$ versus $1/T$ for various values of b and find the correct value of b that gives a linear graph.

   From the slope and intercept of the graph $\ln(l/n^b)$ versus $1/T$, calculate the kinetic parameters.

   Verify that the given TL glow curve corresponds to general-order kinetics.

(d) Using the experimental values of I_M (maximum TL intensity) and T_M (temperature of maximum intensity), do a curve fitting to the given numerical data. Use the following analytical equation developed by Kitis et al [2] for general-order kinetic peaks. The expression relies on two experimentally measured quantities I_M and T_M:

$$I(T) = I_M b^{b-1} \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)$$

$$\times \left[(b-1)\frac{T^2}{T_M^2}\left(1 - \frac{2kT}{E}\right)\exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)\right.$$

$$\left. + 1 + (b-1)\frac{2kT_M}{E}\right]^{-\frac{b}{b-1}}. \tag{2.14}$$

The activation parameter E can be treated as an adjustable parameter. Graph both the experimental data and the calculated general order TL glow curve on the same graph and compare them. Calculate the FOM for the TL glow curve.

(e) Can it be concluded from the above analysis that this material will always follow general-order kinetics?

TABLE 2.21. The values of $1/kT$ and of the natural logarithm of the TL data, ln(TL)

$T(°C)$	$TL_{experimental}$	$1/kT(eV^{-1})$	ln(TL)	$T(°C)$	$TL_{experimental}$	$1/kT(eV^{-1})$	ln(TL)
0	8.38×10^5	42.51	13.64	130	3.96×10^7	28.80	17.49
10	2.06×10^6	41.01	14.54	140	1.96×10^7	28.10	16.79
20	4.74×10^6	39.61	15.37	150	9.19×10^6	27.43	16.03
30	1.03×10^7	38.30	16.15	160	4.22×10^6	26.80	15.26
40	2.09×10^7	37.08	16.86	170	1.93×10^6	26.20	14.47
50	3.98×10^7	35.93	17.50				
60	6.97×10^7	34.85	18.06				
70	1.09×10^8	33.83	18.51				
80	1.49×10^8	32.88	18.82				
90	1.70×10^8	31.97	18.95				
100	1.57×10^8	31.11	18.87				
110	1.18×10^8	30.30	18.58				
120	7.32×10^7	29.53	18.11				

Solution

(a) *The IR method.* We calculate in Table 2.21 the values of $1/kT$ (T = temperature (K), k = Boltzman constant) and the values of the natural logarithm of the TL data, ln(TL).

We next graph the ln(TL) versus $1/kT$ data and find a regression line through the first 7 data points, as shown in Figure 2.26.

The slope of the regression line gives the activation energy E as

$$E = 0.580 \pm 0.006 \text{ eV}, \quad \text{with } R^2 = 0.9996.$$

(b) *Chen's peak shape equations.* From the given experimental data for a TL glow peak, we can estimate the three temperatures required for Chen's peak shape equations:

$$T_1 = 64°C = 337 \text{ K}, \quad T_2 = 117°C = 390 \text{ K}, \quad T_M = 91°C = 364 \text{ K},$$
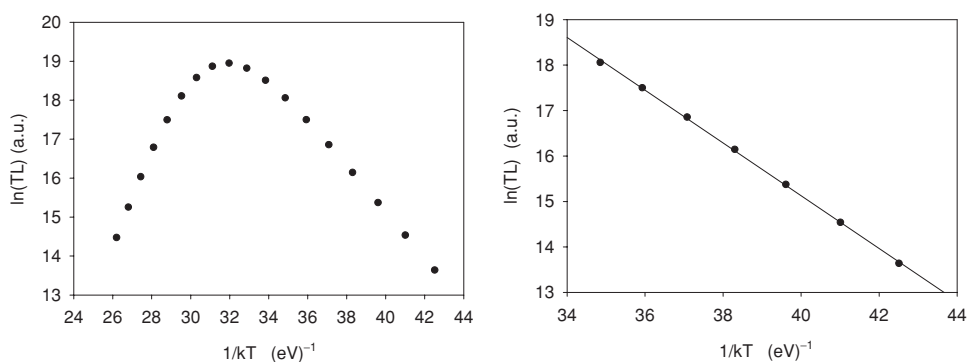

FIGURE 2.26. The IR analysis for general-order kinetics data.

where

T_M = peak temperature at the maximum TL intensity,

T_1, T_2 = temperatures on either side of T_M, corresponding to the half-maximum
intensity.

We next calculate the quantities μ, τ, δ, and ω:

$$\tau = T_M - T_1 = 27\,\text{K}, \quad \delta = T_2 - T_M = 26\,\text{K},$$
$$\omega = T_2 - T_1 = 53\,\text{K}, \quad \mu = \delta/\omega = 26/53 = 0.490.$$

The calculated value of the geometrical shape factor $\mu = \delta/\omega = 0.490$ corresponds to a value of μ for a general-order TL peak with an approximate value of $b = 1.6$ (Figure 1.14).

Using the known experimental error $\Delta T = 2$ K for the quantities τ, δ, and ω, we can do an error analysis of the values of μ. As in the similar examples for first- and second-order kinetics data,

$$\left|\frac{\Delta\mu}{\mu}\right| = \left|\frac{\Delta\delta}{\delta}\right| + \left|\frac{\Delta\omega}{\omega}\right| = \left|\frac{2}{26}\right| + \left|\frac{2}{53}\right| = 0.077 + 0.038 = 0.115.$$

This leads to a value of $\mu + \Delta\mu = 0.490 \pm 0.056$ which is consistent with general-order kinetics, within the accuracy of the TL experiment.

In order to find the activation energy E, we apply Chen's equation for general-order kinetics:

$$E_\alpha = c_\alpha \left(\frac{kT_M^2}{\alpha}\right) - b_\alpha(2kT_M), \tag{2.15}$$

where α is τ, δ, or ω and the values of c_α and b_α are summarized below

$$c_\tau = 1.510 + 3.0(\mu - 0.42), \quad b_\tau = 1.58 + 4.2(\mu - 0.42)$$
$$c_\delta = 0.976 + 7.3(\mu - 0.42), \quad b_\delta = 0$$
$$c_\omega = 2.52 + 10.2(\mu - 0.42), \quad b_\omega = 1. \tag{2.16}$$

Using the value of τ:

$$E = \frac{1.720kT_M^2}{\tau} - 1.874(2kT_M) = 0.727 - 0.117 = 0.610 \text{ eV}.$$

Using the value of δ:

$$E = \frac{1.487kT_M^2}{\delta} = 0.653 \text{ eV}.$$

Using the value of ω:

$$E = \frac{3.234kT_M^2}{\omega} - 2kT_M = 0.671 - 0.062 = 0.609 \text{ eV}.$$

TABLE 2.22. Calculation of the quantities $\ln(I/n_b)$ and $1/kT$ for general-order data

T(°C)	TL	$1/kT$	Area	$\ln(\text{TL}/n^{1.2})$	$\ln(\text{TL}/n^{1.4})$	$\ln(\text{TL}/n^{1.5})$	$\ln(\text{TL}/n^{1.6})$
0	8.38×10^5	42.51	9.99×10^8	−13.99	−18.60	−20.90	−23.20
10	2.06×10^6	41.01	9.98×10^8	−13.09	−17.70	−20.00	−22.30
20	4.74×10^6	39.61	9.96×10^8	−12.25	−16.86	−19.16	−21.46
30	1.03×10^7	38.30	9.91×10^8	−11.47	−16.08	−18.38	−20.68
40	2.09×10^7	37.08	9.81×10^8	−10.75	−15.35	−17.65	−19.95
50	3.98×10^7	35.93	9.60×10^8	−10.08	−14.68	−16.98	−19.28
60	6.97×10^7	34.85	9.20×10^8	−9.47	−14.06	−16.35	−18.65
70	1.09×10^8	33.83	8.50×10^8	−8.93	−13.50	−15.78	−18.07
80	1.49×10^8	32.88	7.41×10^8	−8.45	−13.00	−15.27	−17.54
90	1.70×10^8	31.97	5.92×10^8	−8.05	−12.55	−14.80	−17.05
100	1.57×10^8	31.11	4.22×10^8	−7.72	−12.16	−14.37	−16.59
110	1.18×10^8	30.30	2.65×10^8	−7.46	−11.80	−13.97	−16.14
120	7.32×10^7	29.53	1.48×10^8	−7.23	−11.45	−13.56	−15.67
130	3.96×10^7	28.80	7.45×10^7	−7.02	−11.11	−13.15	−15.19
140	1.96×10^7	28.10	3.49×10^7	−6.82	−10.75	−12.72	−14.68
150	9.19×10^6	27.43	1.53×10^7	−6.58	−10.35	−12.24	−14.12
160	4.22×10^6	26.80	6.15×10^6	−6.27	−9.85	−11.65	−13.44
170	1.93×10^6	26.20					

In order to find the error ΔE in the activation energy E, we take the logarithmic derivative of the equation $E = \dfrac{1.487kT_{\text{M}}^2}{\delta}$:

$$\left|\frac{\Delta E}{E}\right| = 2\left|\frac{\Delta T_{\text{M}}}{T_{\text{M}}}\right| + \left|\frac{\Delta \delta}{\delta}\right| = 2\left|\frac{2}{364}\right| + \left|\frac{2}{26}\right| = 0.011 + 0.077 = 0.088.$$

This gives an error ΔE of the order of 8.8% or $\Delta E = 0.088E = 0.082(0.653) = 0.060$ eV.

(c) *The whole glow-peak method.* We graph $\ln(I/n^b)$ versus $1/T$ for various values of b between 1.2 and 1.6, and find the correct value of b that gives a linear graph. As in the case of first-order kinetics, $n(T)$ is the area under the glow peak and it is calculated starting at a temperature T, up to the maximum temperature available in the glow curve. In the data shown in Table 2.22, the maximum available temperature is 170°C.

By following the same procedure as in the case of first-order kinetics, we set up an Excel spreadsheet to calculate the quantities $\ln(I/n^b)$ and $1/kT$ as shown in Table 2.22, for several values of the kinetic order $b = 1.2, 1.4, 1.5$ and 1.6.

Finally, graphs of $\ln(\text{TL}/\text{Area}^b)$ versus $1/kT$ are drawn in Figure 2.27 for several values of the kinetic order $b = 1.2, 1.4, 1.5$, and 1.6.

The graphs corresponding to $b = 1.5$ and 1.6 best approximate straight lines. The $b = 1.5$ graph has the highest value of R^2 and therefore gives the best fit. A regression line is fitted to the data corresponding to $b = 1.5$ in Figure 2.28, to obtain the best slope and the best intercept:

$$\text{Best intercept} = 3.345 \pm 0.17,$$
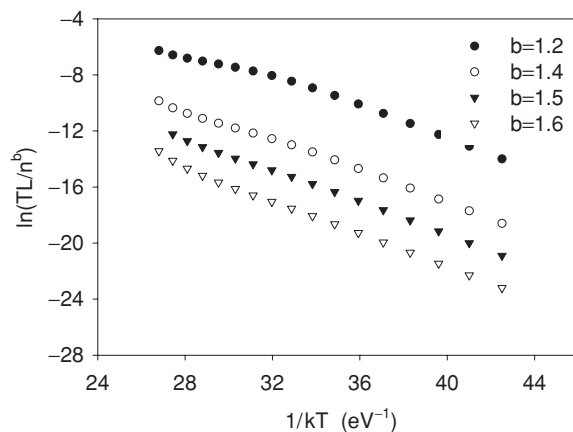$$\text{Best slope } E = -0.568 \pm 0.005 \text{ eV}.$$

FIGURE 2.27. Graphs for several values of kinetic order *b*.

It is noted that this value of $E = 0.568 \pm 0.005$ eV is in good agreement with the value of $E = 0.580 \pm 0.006$ eV obtained from the IR method.

Within the accuracy of the given experimental data and within the framework of the whole glow-peak method of analysis, we can conclude that the given TL glow peak follows general-order kinetics described by $b = 1.5$.

The value of s' can be calculated from the best-fitting regression line shown in Figure 2.28:

$$s' = \beta e^{(\text{intercept})} = 1e^{(3.345)} = 28.36.$$

The whole glow-peak method yields information about both the activation energy E and the effective frequency factors s' and $s'' = s'n_0^{b-1}$ appearing in
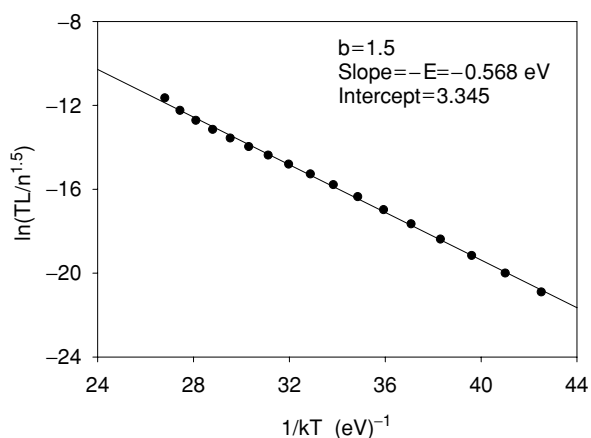

FIGURE 2.28. The value of $b = 1.5$ gives the best fit for the whole glow-curve analysis. The parameters E and s' can be calculated from this graph.

equation (1.7):

$$I(T) = s''n_0 \exp\left(-\frac{E}{kT}\right)\left[1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\frac{b}{b-1}}. \quad (1.7)$$

Because TL data analysis of a glow curve cannot yield a value for the *absolute* concentration n_0 of traps in the material, the quantities s'', b, and n_0 appearing in equation (1.7) represent *three empirical fitting parameters* for general-order glow peaks.

The value of n_0 can be estimated from the area under the glow curve as in Exercise 2.4, by summing the TL intensities multiplied by the temperature interval ΔT between TL measurements, and by dividing with the heating rate β:

$$n_0 \approx \frac{1}{\beta}\int_{T_0}^{T_f} I\,dT = \frac{1}{\beta}\sum I(T)\Delta T = \frac{1}{1}\sum I(T)(10\,\text{K}) = 9.99 \times 10^9.$$

By using the values of $E = 0.56$ eV, $s' = 28.36$, $n_0 = \text{Area} = 9.99 \times 10^9$, and $\beta = 1$ K s^{-1}, it is possible to calculate the TL intensity using equation (1.7), and to compare this result directly with the given experimental data.

The result is shown in Figure 2.27, where the calculated $I(T)$ from equation (1.7) is compared with the original experimental data. Figure 2.29 shows that the calculated parameters E, s', and b and n_0 from the whole glow-peak method, as well as the general order equation (1.7), describe the given experimental data in a reasonably accurate manner.

The observed discrepancies between experiment and calculation in Figure 2.29 are due to the several approximations involved in applying the whole glow-peak method.
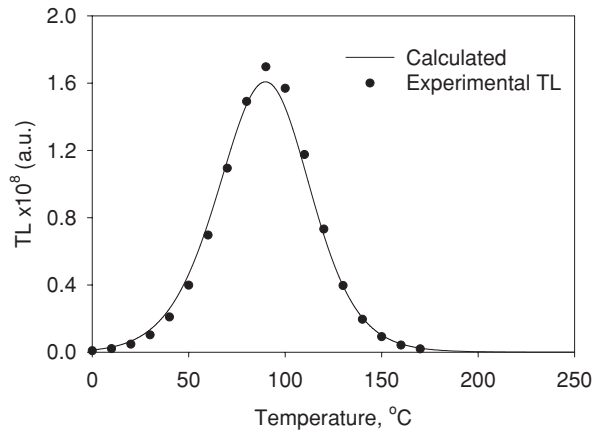

FIGURE 2.29. Comparison of calculated TL intensity using equation (1.7) (solid line), and original experimental data (individual data points). The parameters used in equation (1.7) were obtained from the whole glow-peak method.

(d) *Glow-curve fitting using the Kitis et al equation.* We use the following analytical equation developed by Kitis et al [2] for TL peaks following general-order kinetics. The expression relies on two experimentally measured quantities I_M (the maximum TL intensity) and T_M (the temperature corresponding to the maximum TL intensity):

$$I(T) = I_M b^{b-1} \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)$$

$$\times \left[(b-1)\frac{T^2}{T_M^2} \cdot \left(1 - \frac{2kT}{E}\right) \exp\left(\frac{E}{kT} \cdot \frac{T - T_M}{T_M}\right)\right.$$

$$\left. + 1 + (b-1)\frac{2kT_M}{E}\right]^{-\frac{b}{b-1}}. \tag{2.17}$$

For the given experimental data, $T_M = 364$ K and $I_M = 1.70 \times 10^8$. By treating the activation parameter E as an adjustable parameter, we calculate several graphs with values of $E = 0.4, 0.5, 0.6$, and 0.7 eV. The calculations can be set up easily in a spreadsheet as shown in Table 2.23.

Columns A–C contain the experimental data points for the TL glow curve, whereas columns D–G contain the calculated data points using equation (2.17) for general-order kinetics $b = 1.5$ and for four values of the energy parameter $E(E = 0.4, 0.5, 0.6$, and 0.7 eV).

The following equation is used to calculate the values of the fitted data in column D, using equation (2.17) for general-order kinetics:

Cell D3 = ($I$8^($I$8/($I$8-1)))*$I$6*EXP($I$2/(0.00008617*B3)
        *((B3-$I$5)/$I$5))*((B3*B3)/($I$5*$I$5)
        *(1-2*0.00008617*B3/$I$2)*EXP($I$2/(0.00008617*B3)
        *((B3-$I$5)/$I$5))*($I$8-1)+1+($I$8-1)
        *(2*0.00008617*$I$5/$I$2))^-($I$8/($I$8-1)).

This expression refers to cell B3 which contains the absolute temperature T(K). Also, note that cell I2 in the spreadsheet contains the value of the energy parameter $E = 0.4$ eV, cell I5 contains the value of the experimental parameter $T_M = 364$ K, and cell I6 contains the value of the experimental maximum height parameter $I_M = 1.70 \times 10^8$. The parameter $b = 1.5$ is contained in cell I8. The above spreadsheet expression refers to the values contained in these cells by using the Excel expressions $I$2, $I$5, $I$6, and $I$8, correspondingly.

The user controls the value of the parameter E by changing the value in cell I2, and the whole spreadsheet calculation is automatically updated.

The graphs calculated for $E = 0.4, 0.5, 0.6$, and 0.7 eV are shown in Figure 2.30.

It can be seen in Figure 2.30 that when the value of E is too low (graph corresponding to $E = 0.4$, and 0.5 eV), the calculated TL points lie well above the experimental data. This is also evident by inspection of the calculated columns

TABLE 2.23. Calculations for several values of energy E

|	A	B	C	D	E	F	G	H	I	J
	$T(^\circ\mathrm{C})$	$T(\mathrm{K})$	TL$_{\text{experimental}}$	$I(T)$, $E = 0.4\,\mathrm{eV}$	$I(T) = 0.5\,\mathrm{eV}$	$I(T) = 0.6\,\mathrm{eV}$	$I(T) = 0.7\,\mathrm{eV}$			
1										
2								$E =$	0.4	eV
3	0	273	8.38×10^5	6.44×10^6	2.34×10^6	8.35×10^5	2.95×10^5			
4	10	283	2.06×10^6	1.16×10^7	4.94×10^6	2.05×10^6	8.44×10^5			
5	20	293	4.74×10^6	2.00×10^7	9.85×10^6	4.73×10^6	2.24×10^6	$T_M=$	364	K
6	30	303	1.03×10^7	3.29×10^7	1.86×10^7	1.03×10^7	5.56×10^6	$I_M=$	1.70×10^8	
7	40	313	2.09×10^7	5.12×10^7	3.32×10^7	2.09×10^7	1.29×10^7			
8	50	323	3.98×10^7	7.55×10^7	5.55×10^7	3.97×10^7	2.78×10^7	$b=$	1.5	
9	60	333	6.97×10^7	1.04×10^8	8.61×10^7	6.94×10^7	5.49×10^7			
10	70	343	1.09×10^8	1.34×10^8	1.22×10^8	1.09×10^8	9.64×10^7			
11	80	353	1.49×10^8	1.58×10^8	1.54×10^8	1.49×10^8	1.43×10^8			
12	90	363	1.70×10^8	1.69×10^8	1.69×10^8	1.69×10^8	1.69×10^8			
13	100	373	1.57×10^8	1.65×10^8	1.61×10^8	1.57×10^8	1.52×10^8			
14	110	383	1.18×10^8	1.46×10^8	1.32×10^8	1.18×10^8	1.03×10^8			
15	120	393	7.32×10^7	1.18×10^8	9.47×10^7	7.35×10^7	5.52×10^7			
16	130	403	3.96×10^7	8.79×10^7	6.08×10^7	3.99×10^7	2.50×10^7			
17	140	413	1.96×10^7	6.17×10^7	3.61×10^7	1.98×10^7	1.03×10^7			
18	150	423	9.19×10^6	4.12×10^7	2.03×10^7	9.32×10^6	4.10×10^6			
19	160	433	4.22×10^6	2.67×10^7	1.10×10^7	4.30×10^6	1.61×10^6			
20	170	443	1.93×10^6	1.69×10^7	5.93×10^6	1.97×10^6	6.38×10^5			
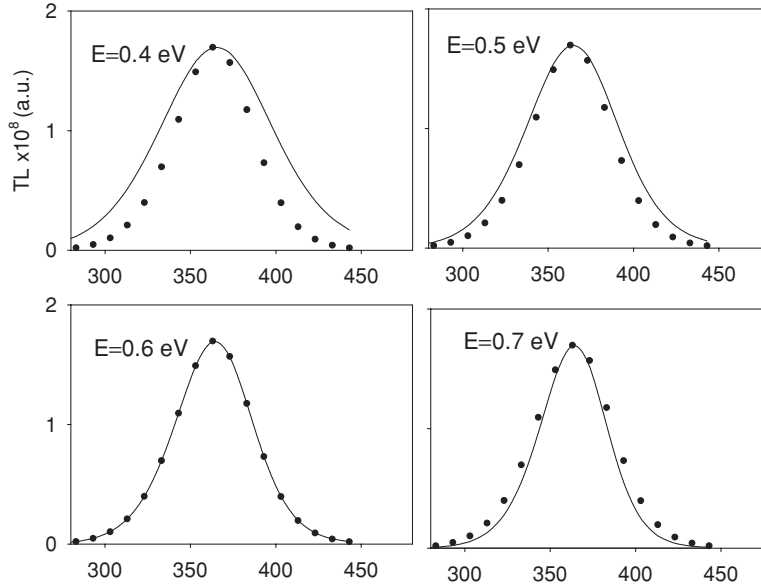
FIGURE 2.30. The experimental data and fitted curves for several values of E.

$I(T)$ in Table 2.23. On the other hand, when the value of E is too high (graph corresponding to $E = 0.7\,\text{eV}$), the calculated TL points lie well below the experimental data.

Table 2.24 shows the FOM calculation as applied to the previous data. Column A contains the experimental data points and columns B–E contain the calculated data points using equation (2.17) for general-order kinetics and for four values of the energy parameter E (E = 0.4, 0.5, 0.6, and 0.7 eV).

Columns F–I contain the calculation of the quantity $|\text{TL}_{\text{experimental}} - \text{TL}_{\text{calculated}}|$, and the cells in the last row contain the calculated values of the FOM.

The FOM for the value of the parameter $E = 0.60\,\text{eV}$ is equal to $0.003 = 0.3\%$, almost 100 times smaller than the FOM $= 0.300 = 30.0\%$ for the case $E = 0.4\,\text{eV}$.

The frequency factor s can be calculated by using the value of $E = 0.60\,\text{eV}$ and the temperature of maximum TL intensity $T_{\text{M}} = 364\,\text{K}$ in equation (1.10), which is applicable for general-order kinetics:

$$s = \frac{\beta E}{k T_{\text{M}}^2 \left(1 + \frac{2k T_{\text{M}}(b-1)}{E}\right)} \exp\left(\frac{E}{k T_{\text{M}}}\right)$$

$$s = \frac{(1)0.60}{(8.617 \times 10^{-5})(364)^2 \left(1 + \frac{2(8.617 \times 10^{-5})364(1.5-1)}{0.60}\right)}$$

$$\times \exp\left(\frac{0.60}{(8.617 \times 10^{-5})364}\right) = 1.05 \times 10^{12}\,s^{-1}. \tag{2.18}$$

TABLE 2.24. The FOM calculation for general-order kinetics TL peak

A	B	C	D	E	F	G	H	I
$TL_{experimental}$	$I(T)$, $E = 0.4$ eV	$I(T)$, $E = 0.5$ eV	$I(T)$, $E = 0.6$ eV	$I(T)$, $E = 0.7$ eV	$\lvert TL_{experimental} - I(T) \rvert$, $E = 0.4$ eV	$\lvert TL_{experimental} - I(T) \rvert$, $E = 0.5$ eV	$\lvert TL_{experimental} - I(T) \rvert$, $E = 0.6$ eV	$\lvert TL_{experimental} - I(T) \rvert$, $E = 0.7$ eV
8.38×10^5	6.44×10^6	2.34×10^6	8.35×10^5	2.95×10^5	5.61×10^6	1.50×10^6	2.61×10^3	5.43×10^5
2.06×10^6	1.16×10^7	4.94×10^6	2.05×10^6	8.44×10^5	9.58×10^6	2.88×10^6	6.48×10^3	1.22×10^6
4.74×10^6	2.00×10^7	9.85×10^6	4.73×10^6	2.24×10^6	1.53×10^7	5.11×10^6	1.47×10^4	2.50×10^6
1.03×10^7	3.29×10^7	1.86×10^7	1.03×10^7	5.56×10^6	2.26×10^7	8.32×10^6	3.19×10^4	4.72×10^6
2.09×10^7	5.12×10^7	3.32×10^7	2.09×10^7	1.29×10^7	3.03×10^7	1.22×10^7	6.71×10^4	8.05×10^6
3.98×10^7	7.55×10^7	5.55×10^7	3.97×10^7	2.78×10^7	3.57×10^7	1.57×10^7	1.30×10^5	1.20×10^7
6.97×10^7	1.04×10^8	8.61×10^7	6.94×10^7	5.49×10^7	3.46×10^7	1.65×10^7	2.28×10^5	1.47×10^7
1.09×10^8	1.34×10^8	1.22×10^8	1.09×10^8	9.64×10^7	2.43×10^7	1.23×10^7	3.46×10^5	1.30×10^7
1.49×10^8	1.58×10^8	1.54×10^8	1.49×10^8	1.43×10^8	8.61×10^6	4.49×10^6	4.15×10^5	5.93×10^6
1.70×10^8	1.69×10^8	1.69×10^8	1.69×10^8	1.69×10^8	3.03×10^5	3.02×10^5	3.24×10^5	3.64×10^5
1.57×10^8	1.65×10^8	1.61×10^8	1.57×10^8	1.52×10^8	8.04×10^6	4.23×10^6	5.75×10^4	4.84×10^6
1.18×10^8	1.46×10^8	1.32×10^8	1.18×10^8	1.03×10^8	2.82×10^7	1.46×10^7	2.22×10^5	1.44×10^7
7.32×10^7	1.18×10^8	9.47×10^7	7.35×10^7	5.52×10^7	4.45×10^7	2.15×10^7	3.46×10^5	1.80×10^7
3.96×10^7	8.79×10^7	6.08×10^7	3.99×10^7	2.50×10^7	4.83×10^7	2.12×10^7	3.14×10^5	1.46×10^7
1.96×10^7	6.17×10^7	3.61×10^7	1.98×10^7	1.03×10^7	4.21×10^7	1.65×10^7	2.20×10^5	9.23×10^6
9.19×10^6	4.12×10^7	2.03×10^7	9.32×10^6	4.10×10^6	3.21×10^7	1.11×10^7	1.34×10^5	5.09×10^6
4.22×10^6	2.67×10^7	1.10×10^7	4.30×10^6	1.61×10^6	2.25×10^7	6.82×10^6	7.59×10^4	2.61×10^6
1.93×10^6	1.69×10^7	5.93×10^6	1.97×10^6	6.38×10^5	1.50×10^7	4.00×10^6	4.11×10^4	1.29×10^6
				FOM =	0.300	0.152	0.003	0.154

TABLE 2.25. Summary of the results of various analysis methods for
general-order data

	E (eV)	Frequency factor (s or s'')	Comments below
Initial rise method	0.580 ± 0.006		[1,4]
Chen's τ-method	0.610		[2,4]
Chen's δ-method	0.653 ± 0.06		[2,4]
Chen's ω-method	0.609		[2,4]
Whole glow-peak method	0.568 ± 0.005	$s' = 28.36$	[3]
Fitting method using Kitis et al equation	0.60 ± 0.1	$s = 1.05 \times 10^{12}\ s^{-1}$	[4]

Finally, we summarize in Table 2.25 the results of the various methods for analyzing the given experimental data for general-order kinetics.

Comments

1. The value of E obtained from the IR method is independent of the kinetics of the TL glow peak.

   As in the case of first- and second-order kinetics, the presence of thermal quenching affects the value of E obtained in the IR method.

   A possible correction method for the value of E is given in Chapter 5.

   It is best to use the IR and peak shape methods with samples irradiated at low doses [3].
2. The value of E obtained with peak shape methods can be influenced by the presence of smaller satellite peaks.
3. The whole glow-curve method yields information on both E and the pre-exponential factor $s'' = n_0^{b-1} s'$. Because TL cannot yield a value for the absolute concentration n_0^{b-1}, the factor s'' and the n_0 appearing in equation (1.7) represent *two empirical fitting parameters* for general-order glow peaks. The value of n_0 can be estimated from the area under the glow curve.

   By using the values of E, s'', and n_0, it is possible to compare directly the experimental data with the TL intensity obtained using equation (1.7).
4. The pre-exponential factor s can be calculated from the values of T_M, E, and β by using equation (2.18). The estimated uncertainties $\Delta s/s$ from equation (2.18) can be very large (50–100%), even when the uncertainty $\Delta E/E$ is very small.

(e) Can it be assumed for this material that this TL peak will always follow general kinetics of order $b = 1.5$?

In general, one cannot assume that the studied TL glow curve of this material will always follow general-order kinetics of the same order found in analyzing one set of data. The analysis should be carried out for glow peaks measured under different heating rates, various irradiation doses, powdered and bulk samples, etc.

Some of the criteria for general-order kinetics are:

I. *Peak shape*: first-order peaks have $\mu = 0.42$, second-order peaks have $\mu = 0.52$, and general-order kinetics have values in-between (see Figure 1.14).

II. *Peak shift*: In most non-first-order TL glow peaks, the location of maximum TL intensity shifts toward higher temperatures for lower trap filling. One must be aware that the observed maximum shift can be also due to the presence of smaller satellite peaks.

III. $I_M - T_M$ *dependence*: In general-order peaks a graph of $\ln \left[I_M^{\,b-1} \left(\dfrac{T_M^2}{\beta} \right)^b \right]$ versus $1/kT_M$ will yield a straight line of slope E (equation (1.28)).

IV. *Isothermal decay results*: These can provide valuable independent information about the kinetics of the TL process involved at different temperatures. General-order kinetics corresponds to decay curves described by a plot of the quantity $\left(\dfrac{I_t}{I_0} \right)^{\frac{1-b}{b}}$ versus time, which should be a straight line when a suitable value of b is found.

Exercise 2.7: Influence of the Background on the Results of the IR Method

Given the experimental data of Table 2.26, estimate the influence of the background on the activation energy obtained using the IR method.

Solution

In Exercise 2.1, it was found that the activation energies calculated using the IR method depend strongly on the number of points chosen, i.e. on the TL intensity I_{start} at the starting temperature of the IR region. From a statistical point of view, the IR region must start from the temperature at which the TL intensity is higher than the background by at least three times the standard deviation of the background signal.

TABLE 2.26. Experimental data-effect of background on IR method

T(K)	TL	T(K)	TL	T(K)	TL	T(K)	TL	T(K)	TL
293.4	5	341	6	353.8	11	357.8	25	379.8	228
297.8	3	345.8	4	354.2	25	358.2	21	382.6	316
302.6	2	350.6	7	354.6	19	360.6	25	385	400
307.4	8	351	8	355	13	363	41	387.4	538
312.2	4	351.4	9	355.4	14	365.4	51	389.8	646
317	4	351.8	10	355.8	11	367.8	46	396.6	1420
321.8	1	352.2	16	356.2	20	370.2	79	401	2152
326.6	7	352.6	15	356.6	25	352.6	110	405.8	3452
331.4	5	353	12	357	15	375	128	410.2	5127
336.2	5	353.4	16	357.4	27	377.4	197	413	6483

TABLE 2.27. Data for the two IR lines

$1/kT$	ln(TL)	ln(TL − bg)	$1/kT$	ln(TL)	ln(TL − bg)
32.58	3.00	2.69	30.95	4.85	4.81
32.54	3.22	2.99	30.75	5.28	5.26
32.51	2.71	2.28	30.56	5.43	5.51
32.47	3.30	3.08	30.33	5.76	5.74
32.43	3.22	2.99	30.14	5.99	5.98
32.40	3.04	2.76	29.96	6.29	6.28
32.18	3.22	2.99	29.77	6.47	6.46
31.97	3.71	3.58	29.26	7.26	7.25
31.76	3.93	3.82	28.94	7.67	7.67
31.55	3.83	3.71	28.60	8.15	8.15
31.35	4.37	4.30	28.29	5.84	8.54
31.15	4.70	4.65	28.10	8.78	8.78

By examining the given data, it is clear that the TL intensity at low temperatures is due to the background only. Therefore, the first 15 points, i.e. the TL in the temperature region [293–350 K] can be used to evaluate the mean value of the background. It is found by averaging these 15 points that the background is equal to bg = 5.2 ± 2.3 counts.

Once the background is evaluated and in order to show its effect on the activation energy calculation, the IR linear fit is applied twice. In the first case, the fit is performed using the TL data as given, by graphing ln(TL) versus $1/kT$, and in the second case, by subtracting the background and graphing ln(TL − bg) versus $1/kT$. The corresponding data for the two fits are shown in Table 2.27.

The resulting IR lines are shown in Figure 2.31, where one can see the different slopes obtained. The activation energy values obtained from each IR line are:
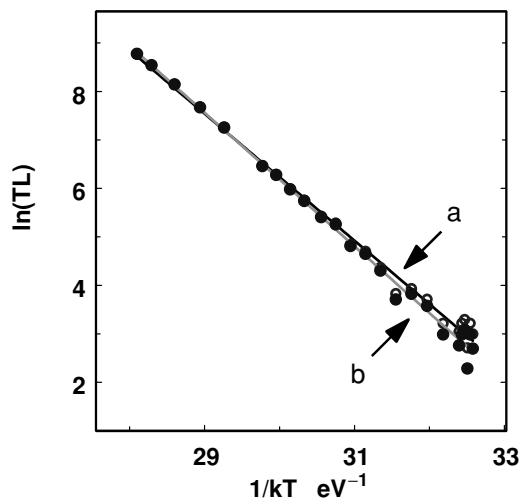

FIGURE 2.31. IR plots: (a) without background subtraction and (b) with background subtracted.

(a) Without background subtraction: $E = 1.3087 \pm 0.022$.
(b) With background subtracted: $E = 1.3780 \pm 0.024$.

It is seen that by ignoring the background, the IR method in this exercise leads to a serious underestimation of the activation energy E by 5%.

Exercise 2.8: Study of the 15% Rule of Thumb for the IR Technique

A well-known rule of thumb for the IR method is that the method holds only up to a temperature that corresponds to a TL intensity lower than 10–15% of the peak maximum intensity, I_M.

Calculate a synthetic glow peak with the trapping parameters $E = 1$ eV, $s = 10^{12}$ s^{-1}, $n_0 = 10^6$ m^{-3} and verify the applicability of the 15% rule by following these steps:

(a) Express the rule of thumb in a mathematical form by examining the two terms in the analytical expression for first-order TL glow peaks.
(b) Express the mathematical condition in (a) as a function of the percent ratio $\%I_{IR}/I_M = (I_{IR}/I_M) \times 100\%$ where I_{IR} is the maximum TL intensity of the IR region.
(c) Examine how the activation energy values obtained by the IR method depend not only on the end of the IR region (i.e. on the $\%I_{IR}/I_M$ value), but also on the starting TL intensity I_{start} of the IR region.

Solution

(a) By substituting the series approximation for the TL integral from equation (1.52) into equation (1.5) for first-order TL glow peaks, we obtain the following analytical expression:

$$I(T) = n_0 \cdot s \cdot \exp\left(-\frac{E}{kT}\right) \cdot \exp\left[-\frac{skT^2}{\beta E} \cdot \exp\left(-\frac{E}{kT}\right) \cdot \left(1 - \frac{2kT}{E}\right)\right].$$

(2.19)

This expression consists of two parts, the increasing IR part $n_0 s \exp(-E/kT)$ and the function $F2(T)$ given by

$$F2(T) = \exp\left[-\frac{skT^2}{\beta E} \cdot \exp\left(-\frac{E}{kT}\right) \cdot \left(1 - \frac{2kT}{E}\right)\right].$$ (2.20)

The IR method holds when the condition $F2(T) \sim 1$ is fulfilled.

Using a spreadsheet program, it is straight forward to evaluate a single TL glow peak with the given parameters, as well as the values of the expression $F2(T)$ at various temperatures T. The result is shown in Figure 2.32 where one can identify the part of the glow peak which must be used for the correct application of the IR method.
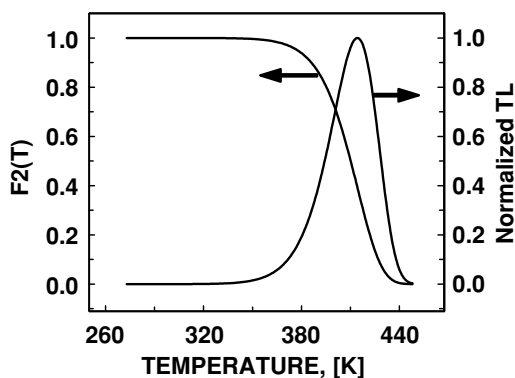
FIGURE 2.32. The function $F2(T)$ with the respective TL glow peak, showing the region where the IR method holds.

(b) The commonly used rule of thumb for the IR method says that the method holds up to the temperature at which the TL intensity is less than 10–15% of the peak maximum intensity I_M. From the data shown in Figure 2.32, one can extract the data for a plot of $F2(T)$ versus the percent ratio $\%I_{IR}/I_M$. The result is shown in Figure 2.33 from which one can conclude that the 15% rule for the IR method holds when $F2(T) > 0.95$.

(c) The IR method is applied to the synthetic glow peak by varying the starting TL intensity I_{start}. The upper limit $\%I_{IR}/I_M$ was left to vary and an IR plot was accepted if its correlation coefficient was better than 0.999. Figure 2.34 shows the resulting activation energies E as a function of the percent ratio $\%I_{IR}/I_M$. The values of I_{start} and $\%I_{IR}/I_M$ for curves (a)–(e) are shown in Table 2.28.

The data for curve (a) in Figure 2.34 show that the 15% I_{IR}/I_{IM} rule of thumb is applicable up to about 26% of the maximum TL intensity. Even at this high ratio of 26%, the activation energy obtained using the IR method is $E = 0.9964$ eV which corresponds to a very small error of 0.36% relative to the reference value of $E = 1$ eV used for the evaluation of the synthetic peak. The corresponding IR plot is shown in Figure 2.35.
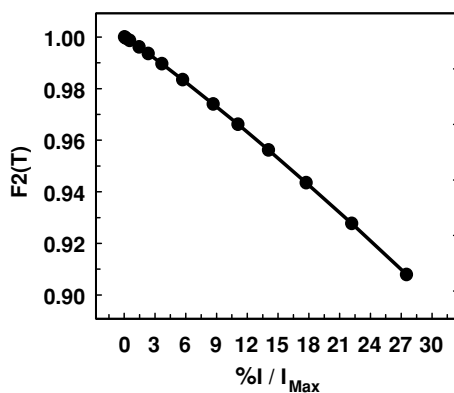

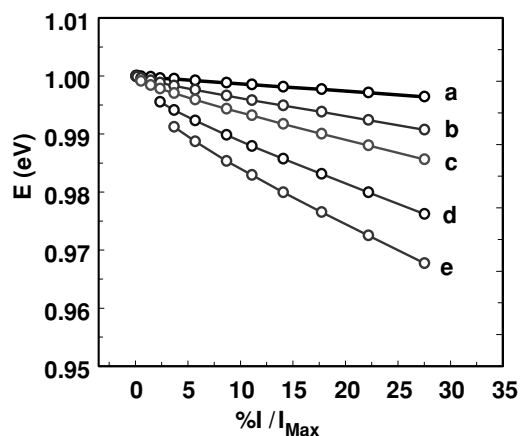FIGURE 2.33. The values of the condition factor $F2(T)$ at various $\%I_{IR}/I_M$.

FIGURE 2.34. Activation energy values E resulting from the IR method by using the conditions given in the Table 2.28.

The results of Figure 2.34 show clearly that the commonly used 15% rule of thumb does not always apply. The correct application of the IR method depends strongly on the extent of the selected IR region. It also depends critically on the clear and accurate definition of the beginning of the IR region. In an experimental situation, this beginning must be defined according to the value of the background of the data, which also affects the results as was shown in the previous exercise.

Exercise 2.9: Error Analysis for Peak Shape Methods

Using a synthetic general-order glow-peak with $E = 1$ eV, $s = 10^{12}$ s^{-1}, and $b = 1.5$

(a) Find how the estimated error in the temperatures T_1, T_M, and T_2 is propagated in the symmetry factor μ, as a function of the error in temperature.
(b) Investigate what the error in temperature ΔT must be, so that one can discriminate between kinetic orders having a difference $\Delta b = 0.1$.
(c) Find how the estimated error in the temperatures T_1, T_M, T_2, and μ is propagated in the values of the activation energies E evaluated using general peak shape methods.

TABLE 2.28. I_{start} and T_{start} for the 15% rule of thumb study

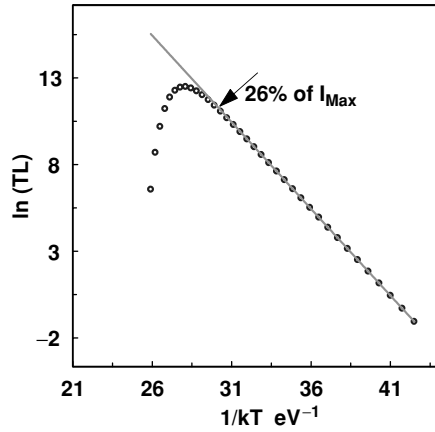| Curve	T_{start} (K)	I_{start}/I_M
a	273	1.3×10^{-6}
b	314	3.13×10^{-4}
c	330	2.0×10^{-3}
d	346	1.0×10^{-2}
e	355	2.3×10^{-2}

FIGURE 2.35. The open circles are the points on the glow peak and the solid line represents the IR line with slop $E = 1$ eV.

Solution

(a) The symmetry factor μ, is defined by the relation

$$\mu = \frac{T_2 - T_M}{T_2 - T_1}. \tag{2.21}$$

The errors on T_1, T_2, and T_M are propagated in the value of μ, according to the expression [5]:

$$\sigma_\mu = \pm \sqrt{\left(\frac{\partial \mu}{\partial T_1} \cdot \Delta T_1\right)^2 + \left(\frac{\partial \mu}{\partial T_2} \cdot \Delta T_2\right)^2 + \left(\frac{\partial \mu}{\partial T_M} \cdot \Delta T_M\right)^2}. \tag{2.22}$$

By evaluating the partial derivatives using equation (2.21) and substituting into equation (2.22), we find the following expression for the standard deviation σ_μ of μ:

$$\sigma_\mu = \pm \sqrt{\left(\frac{T_2 - T_M}{(T_2 - T_1)^2} \cdot \Delta T_1\right)^2 + \left(\frac{T_M - T_1}{(T_2 - T_1)^2} \cdot \Delta T_2\right)^2 + \left(-\frac{1}{T_2 - T_1} \cdot \Delta T_M\right)^2}$$

$$\tag{2.23}$$

Using a spreadsheet program, one can easily generate a synthetic glow peak and evaluate the temperatures T_1, T_2, and T_M by using, for example, the series approximation from equation (1.52) in the general-order equation (1.7).

In experimental situations, the errors in temperature depend on the temperature interval used for sampling the TL signal. For example, if one measures the TL intensity per every 2 K, then the possible error in temperature T_M, T_1, T_2, etc., can be taken to be half of this interval (1 K).

In this exercise, the experimental situation is simulated by generating the synthetic glow peak using different temperature intervals to evaluate the TL intensity. This is shown in column 1 of Table 2.29. In the first row of the table, it is shown

TABLE 2.29. Data table 1 for error propagation in peak shape methods

Step	T_M (K)	T_1 (K)	T_2 (K)	ΔT (K)	μ	σ_μ	$3\sigma_\mu/\Delta\mu$
0.001	384.301	365.29	401.718	0.0005	0.478121	0.000017	0.005
0.005	384.305	365.29	401.715	0.0025	0.477968	0.000084	0.026
0.01	384.31	365.29	401.71	0.005	0.47759	0.00017	0.053
0.05	384.35	365.25	401.7	0.025	0.475995	0.00084	0.26
0.1	384.4	365.3	401.7	0.05	0.475275	0.00168	0.53
0.2	384.6	365.2	401.6	0.1	0.46033	0.00336	1.05
0.3	384.6	365.4	401.7	0.15	0.471074	0.005	1.57
0.4	384.6	365.4	401.8	0.2	0.472527	0.0067	2.1
0.5	385	365.5	401.5	0.25	0.465753	0.0085	2.67
0.6	384.6	365.4	402	0.3	0.475410	0.01	3.14
0.7	385	365.4	401.8	0.35	0.461538	0.012	3.52
0.8	385	365	401.8	0.4	0.456522	0.013	4.08
0.9	385.5	365.7	401.7	0.45	0.450000	0.015	4.71
1	385	365	402	0.5	0.459459	0.0165	5.18

that the first synthetic glow peak was generated by evaluating the TL every 0.001 K. The error in temperature is given by column 5 and was taken equal to one half of the step used in measuring TL ($\Delta T = 0.0005$ K).

For the sake of simplicity in the evaluations, it is assumed that $\Delta T_1 = \Delta T_2 = \Delta T_M = \Delta T$. The values of T_M, T_1, T_2, symmetry factor μ, and its standard deviation σ_μ according to equation (2.23) are listed in columns 2, 3, 4, 6, and 7 of Table 2.29, respectively, for different values of ΔT.

(b) From the first row of Table 2.29, the symmetry factor for $b = 1.5$ is equal to $\mu = 0.478121$. The symmetry factors for the neighboring values of $b = 1.4$ and $b = 1.6$ are found in a similar fashion to be equal to $\mu = 0.468176$ and $\mu = 0.487376$, respectively. The difference between these two symmetry factors for $b = 1.5$ and $b = 1.6$ is $\Delta\mu = 0.00925$.

In order for one to be able to discriminate between these two values, the following condition must be fulfilled.

$$3\sigma_\mu > \Delta\mu. \tag{2.24}$$

The data of Table 2.29 show that this condition holds only when $\Delta T > 0.1$ K. For all values of μ that satisfy the condition $3\sigma_\mu < \Delta\mu$, the respective values of μ_g belong to a kinetic order $b = 1.5$. Therefore, the error in temperature ΔT must be less than 0.2 K in order for the evaluated symmetry factor μ to correspond to the kinetic order $b = 1.5$, and not to 1.4 or 1.6.

(c) The general peak shape method equation for evaluating the activation energy E is given by equation (1.48):

$$E = c_\alpha \cdot \frac{kT_M{}^2}{a} - b_\alpha(2kT_M), \tag{1.48}$$

where α stands for τ, δ, and ω and the coefficients are given by equation (1.49):

$$
\begin{aligned}
c_\tau &= 1.510 + 3.0(\mu - 0.42), \quad b_\tau = 1.58 + 4.2(\mu - 0.42) \\
c_\delta &= 0.976 + 7.3(\mu - 0.42), \quad b_\delta = 0 \\
c_\omega &= 2.52 + 10.2(\mu - 0.42), \quad b_\omega = 1.
\end{aligned}
$$
(1.49)

The errors on T_1, T_2, and T_M are propagated in the value of E, according to the expression:

$$
\sigma_E = \pm \sqrt{\left(\frac{\partial E}{\partial T_M} \cdot \Delta T_M \right)^2 + \left(\frac{\partial E}{\partial a} \cdot \Delta a \right)^2 + \left(\frac{\partial E}{\partial \mu} \cdot \Delta \mu \right)^2}.
$$
(2.25)

Taking into account equation (1.49), equation (2.25) becomes for the case of E_τ

$$
\sigma_{E\tau} = \pm \sqrt{\left(\left(\frac{2 c_\tau k T_M}{\tau} - 2 k b_\tau \right) \cdot \Delta T_M \right)^2 + \left(\frac{c_\tau k T_M^2}{\tau^2} \cdot \Delta \tau \right)^2 + \left(\frac{3 k T_M^2}{\tau} - 8.4 k T_M \right) \cdot \Delta \mu)^2.4}
$$
(2.26)

The corresponding equations for E_δ and E_ω are

$$
\sigma_{E\delta} = \sqrt{\left(\frac{2 c_\delta k T_M}{\delta} \cdot \Delta T_M \right)^2 + \left(\frac{c_\delta k T_M^2}{\delta^2} \cdot \Delta \delta \right)^2 + \left(\frac{7.3 k T_M^2}{\delta} \cdot \Delta \mu \right)^2},
$$
(2.27)

$$
\sigma_{E\omega} = \sqrt{\left(\frac{2 c_\omega k T_M}{\omega} \cdot \Delta T_M \right)^2 + \left(\frac{c_\omega k T_M^2}{\omega^2} \cdot \Delta \omega \right)^2 + \left(\frac{10.2 k T_M^2}{\omega} \cdot \Delta \mu \right)^2}.
$$
(2.28)

For the sake of simplicity, we assume that $\Delta T_1 = \Delta T_2 = \Delta T_M = \Delta T$. The quantities τ, δ, and ω are given by the relations:

$$
\begin{aligned}
\omega &= T_2 - T_1, \\
\delta &= T_2 - T_M, \\
\tau &= T_M - T_1.
\end{aligned}
$$
(2.29)

The error propagation for ω is

$$
\begin{aligned}
\sigma_\omega &= \pm \sqrt{\Delta T_2^2 + \Delta T_1^2} \\
\sigma_\omega &= \pm \Delta T \sqrt{2}
\end{aligned}
$$
(2.30)

with similar expressions for τ and δ. Therefore, in equations (2.26–2.28) one must use

$$
\Delta \tau = \Delta \delta = \Delta \omega = 1.41 \, \Delta T.
$$

The results for the error ΔE are shown in Table 2.30, which continues Table 2.29. The data in Table 2.30 show that the error in the activation energy depends on the peak shape quantity used in the evaluation (τ, δ, or ω). However, as in the previous question of this exercise, the most accurate values of the activation energy (with the lowest errors of 1% or less) are obtained when the temperature is measured with an accuracy better than 0.1 K.

TABLE 2.30. Data table 2 for error propagation in peak shape methods

ΔT	E_τ	$100 \times \sigma_{E\tau}$	E_δ	$100 \times \sigma_{E\delta}$	E_ω	$100 \times \sigma_{E\omega}$
0.0005	1.00672	0.0051	1.02316	0.0099	1.02125	0.0064
0.0025	1.0062	0.025	1.00624	0.0494	1.0208	0.0318
0.005	1.0056	0.051	1.00224	0.0989	1.02025	0.0635
0.025	1.9981	0.252	1.01598	0.495	1.01328	0.317
0.05	0.9971	0.504	1.01531	0.995	1.01247	0.636
0.1	0.9669	0.97	0.9982	2.02	0.9841	1.27
0.15	0.9852	1.49	1.0054	3.02	1.0015	1.92
0.2	0.9877	1.99	1.00742	4.00	1.00375	2.55
0.25	0.9489	2.4	0.9720	5.24	0.9664	3.25
0.3	1.0113	2.99	1.01125	5.91	1.0081	3.78
0.35	0.9488	3.33	0.9725	7.14	0.9666	4.45
0.4	0.9193	3.65	0.9447	8.05	0.9375	4.97
0.45	0.9214	4.19	0.9446	9.59	0.9388	5.84
0.5	0.924	4.56	0.9497	9.91	0.9425	6.15

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