As stated in an earlier chapter, thermal desorption method is amenable for estimation of kinetic parameters. The kinetic triplet normally considered in thermal methods includes the activation energy, frequency factor and the functional dependence of the conversion. In these three parameters, the importance of activation energy and frequency factor need not be re-emphasized. Since heating rate β is related by the relation dT/dt between temperature and time, kinetic analysis seems to be feasible. In addition normally in thermal desorption measurements, the system is far from equilibrium and hence once can use only kinetic expressions for treating such measurements. Normally in every temperature programmed measurement, β, the heating rate is constant and it is possible to obtain the temperature of desorption rate maximum T_{max} (= maximum rate of desorption).

Polanyi-Wigner equation can be expressed as

$$(r_{des}) = -\frac{d\theta}{dt} = \vartheta_n\ (\theta) \exp\ (-[\Delta E_{des}^{PW}(\theta)]/RT)\ (\theta)^{n(\theta)} \qquad (1)$$

Since $\beta = \frac{dT}{dt}$ or $dt = (\frac{1}{\beta})\ dT$, equation (1) can be rewritten as

$$\frac{d\theta}{dT} = -\frac{1}{\beta}\ \vartheta_n \exp\ [-[\Delta E_{des}^{PW}(\theta)]/RT]\ (\theta)^{n(\theta)}$$

At the maximum of the desorption rate at T_{max}

$$\frac{dr_{des}}{dt}\ |T_{max} = 0$$

This condition must be satisfied since $r_{max} = -\frac{d\theta}{dt} = -\beta \frac{d\theta}{dT}$

$$0 = \frac{d^2\theta}{dT^2}\ \Big|T_{max} = n.\theta^{n-1}.\frac{d\theta}{dT} + \theta^n\{-\Delta E_{des}/RT_{max}^2\}$$

However

$$\frac{d\theta}{dT} = -\frac{1}{\beta}\vartheta_n\ .\exp\{-\Delta E_{des}^{PW}/RT\}.\ \theta^n$$

And hence substituting this value of $\frac{d\theta}{dT}$ $and\ solve\ for$ $\{\Delta E_{des}/RT_{max}^2\}$ one gets,

$$\frac{\Delta E_{des}}{RT_{max}^2} = \frac{1}{\beta}\vartheta_n\ .n.\ \theta^{n-1}\exp\{-\Delta E_{des}^{PW}/RT_{max}\}.$$

When the reaction order is taken as 1 (n=1) then T_{max} $is\ independent\ of\ the\ coverage\ but\ depends\ only\ on\ the\ heating\ rate$

Therefore one can write that

$$\frac{\Delta E_{des}}{RT_{max}^{2}} = \frac{1}{\beta}\,.\,\vartheta_{1.\exp\{-}\frac{\Delta E_{des}}{\mathrm{R}T_{max}})$$

Taking logarithm and rearrangement gives

$$(\ln\frac{\widetilde{T_{max}^{2}}}{\beta}) = \frac{\Delta E_{des}}{\mathrm{R}T_{max}} + (\ln\frac{\Delta\tilde{E}_{des}}{\tilde{\vartheta}\tilde{R}})$$

In this expression to make it dimensionless each parameter is divided by its own unit, for example $\tilde{T} = T/K)$

Now if one were to plot (ln $\frac{T_{max}^{2}}{\beta}$) $versus$ $\frac{1}{T_{max}}$ for a series of heating rate β, then from the slope of the straight line plot one can calculate ΔE_{des} and $\vartheta_{\vartheta 1}$ can be obtained from the intercept.

The corresponding expression for a second order desorption process is

$$\frac{\Delta E_{des}}{RT_{max}^{2}} = \frac{2}{\beta}.\vartheta_{2}.\,\theta(T_{max}).\exp\left(-\frac{\Delta E_{des}}{\mathrm{R}T_{max}}\right)$$

Since in a second order desorption process, the trace is symmetric with respect to T_{max} and hence the θ at T_{max} is half the value of desorption. Inserting that the total θ desorbed = 2.θ, the expression obtained is

$$(\ln\frac{\widetilde{T_{max}^{2}}}{\beta}) = \frac{\Delta E_{des}}{\mathrm{R}T_{max}} + (\ln\frac{\Delta Edes}{\widetilde{\vartheta_{2\,R}\theta_{0}}})$$

Plotting Left hand side versus $1/T_{max}$ as function of heating rate will provide means for calculating ΔE_{des} from the value of the slope and if θ_0 is known, then the frequency factor ϑ_2 can be calculated from the value of the intercept.

However Redhead derived a simplified relation between $\Delta E_{des}\ versus \frac{1}{T_{max}}$. He made the assumption that activation parameters are independent of surface coverage and the desorption followed first order kinetics.

He used the following equation

$\frac{\Delta E_{des}}{RT_{max}^{2}} = \frac{1}{\beta}\,.\,\vartheta_{1}.\exp\left\{-\frac{\Delta E_{des}}{RT_{max}}\right\}$ and solved for ΔE and obtained a relation

$$\Delta E_{des} = RT_{max}\{(\ln[\,\vartheta_{1}T_{max}\,/\beta]) - \ln\frac{\Delta E_{des}}{RT_{max}}\}$$

The { ln $\frac{\Delta E_{des}}{RT_{max}}$} is small compared to the first term ln $\frac{\vartheta_{1}\, T_{max}}{\beta}$ especially when $10^{8} < \frac{\vartheta_1}{\beta} < 10^{13}$ K^{-1}. Therefore one can extract the value of the activation energy ΔE_{des} from a single desorption trace at a particular heating rate β and observing T_{mzx} and using the same to calculate ΔE_{des}.

Another simplified method has also been introduced by Habenshaden and Kuppers. If one were to evaluate the leading edge of the desorption trace at the same value of θ, then one can plot ln $\widetilde{r_{des}}$ versus 1/T according to the logarithmic form of Polanyi-Wigner equation

{ln $\tilde{r}_{des} = -\frac{\Delta E_{des}}{RT} = \ln\tilde{\vartheta}\ + n.\ \ln\tilde{\theta}$

The slope of this Arrhenius type of plot the value of ΔE_{des} can be calculated. From the intercept of this plot the value of the frequency factor can be calculated if one knows the order of desorption kinetics and also the coverage where the leading edge has been measured.

Even though there is advantages since the assumptions made are limited, a general drawback of this procedure is that the leading edge has the signal/noise data plugged and hence the error involved may be greater when low coverages are considered for leading edge analysis.

There is yet another way of analyzing thermal desorption trace by using a plot of

{ln - $\frac{\widetilde{r_{des}}}{\widetilde{\theta^{n}}}$ } versus 1/T for various values of n = 1, 2, or 3. Assuming the activation parameters are independent of temperature and coverage, then a straight line will be obtained if the correct value of n is used. Since

{ln –(d$\tilde{\theta}/dt)/\widetilde{\theta_n}$} = - $\frac{\Delta E_{des}}{RT}$ + {ln $\tilde{\vartheta}_n$}

The value of activation energy ΔE_{des} and ϑ_n can be determined.