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Anexo 1. A Integral de Temperatura.

$\xi = 1 - \exp(-\theta)^n \quad onde \quad \theta = K(T) * t$ (A.1.1)

Assumindo que na expressão anterior T = cte durante um intervalo infinitesimal de tempo e diferenciando com relação a t :

$$d\theta = K(T)\,dt = Ko\exp\left(-\frac{E}{R*T}\right)dt \qquad \text{(A.1.2)}$$

Usando a relação $\beta = \frac{dT}{dt}$:

$$\int_{\theta(To)}^{\theta(T)} d\theta' = \theta(T) - \theta(To) = \int_{To}^{T}\frac{Ko}{\beta}\exp\left(-\frac{E}{R*T}\right)dT \qquad \text{(A.1.3)}$$

Propõe-se um mudança de variável na integral da temperatura: $T = \varphi(y) = \frac{E}{Ry}$ Cambio de variável em a integral definida:

$$\int_a^b f(x)dx = \int_\alpha^\beta f[\varphi(y)]\,\varphi'(y)dy \quad onde \;\; x = \varphi(y) \therefore y = \varphi^{-1}(x) \Rightarrow \alpha = = \varphi^{-1}(a), \beta = \varphi^{-1}(b) \Rightarrow y = \frac{E}{RT} \therefore \alpha = \left.\frac{E}{RT}\right|_{To}, \; \beta = \left.\frac{E}{RT}\right|_{T} \qquad \text{(A.1.4)}$$

De esta forma, usando as relações (A.1.4) na equação (A.1.3) resultam:

$$\theta(T) - \theta(To) = \frac{Ko}{\beta}\int_\propto^\beta \exp(-y)\left[\frac{E}{Ry}\right]' dy = -\frac{KoE}{\beta R}\int_\alpha^\beta \frac{\exp(-y)}{y^2}dy \qquad \text{(A.1.5)}$$

Resolvendo a ultima integral por partes, teremos :

$$v = \exp(-y)\,; dv = -\exp(-y)\,dy\,;\; du = \frac{1}{y^2}dy\,; u = -\frac{1}{y}$$

$$\Rightarrow \int_\alpha^\beta \frac{\exp(-y)}{y^2}\,dy = \left.\left(-\frac{\exp(-y)}{y}\right)\right|_\alpha^\beta - \int_\alpha^\beta \frac{\exp(-y)}{y}\,dy$$

Substituindo em (A.1.5) se tem:

$$\theta(T) - \theta(To) = -\frac{KoE}{\beta R}\left\{-\frac{RT}{E}\exp\left(-\frac{E}{RT}\right) + \frac{RTo}{E}\exp\left(-\frac{E}{RTo}\right) - \int_\alpha^\beta \frac{\exp(-y)}{y}\,dy\right\} = -\frac{Ko}{\beta}\left\{-T\exp\left(-\frac{E}{RT}\right) + To\exp\left(-\frac{E}{RTo}\right) - \frac{E}{R}\int_\alpha^\beta \frac{\exp(-y)}{y}\,dy\right\} \qquad \text{(A.1.6)}$$

Lembrando as conhecidas relações [100,101]:

$$E_1(x) = \int_x^\infty \frac{\exp(-y)}{y}\,dy \qquad E_2(x) = \int_1^\infty \frac{\exp(-xy)}{y^2}\,dy \quad E_2\;(x) = \exp(-x) - xE_1(x)$$

$$\exp(-x) = E_{2(x)} + xE_{1\,(x)} = \int_1^\infty \frac{\exp(-xy)}{y^2}\, dy + x\int_x^\infty \frac{\exp(-y)}{y}\, dy \tag{A.1.7}$$

Considerando a x= E/RT , xo = E/RTo e substituindo (A.1.7) em (A.1.6):

$$\theta(T) - \theta(To) = -\frac{Ko}{\beta}\left[-T\left\{\int_1^\infty \frac{\exp(-xy)}{y^2} dy + x\int_x^\infty \frac{\exp(-y)}{y} dy\right\} + To\left\{\int_1^\infty \frac{\exp(-xoy)}{y^2} dy + xo\int_x^\infty \frac{\exp(-y)}{y} dy\right\}\right] - \frac{E}{R}\int_\alpha^\beta \frac{\exp(-y)}{y} dy \tag{A.1.8}$$

Aplicando a propriedade distributiva e agrupando :

$$\theta(T) - \theta(To) = \frac{Ko}{\beta}\left\{T\int_1^\infty \frac{\exp(-\frac{E}{RT}y)}{y^2} dy - To\int_1^\infty \frac{\exp(-\frac{E}{RTo}y)}{y^2} dy - \frac{E}{R}\int_\infty^{\frac{E}{RT}} \exp(-y)\, dy - \frac{E}{R}\int_{\frac{E}{RTo}}^\infty \exp(-y)\, dy + \frac{E}{R}\int_\alpha^\beta \frac{\exp(-y)}{y} dy\right\}$$

Simplificando as ultimas três integrais, teremos :

$$\theta(T) - \theta(To) = \frac{Ko}{\beta}\left\{T\int_1^\infty \frac{\exp(-\frac{E}{RT}y)}{y^2} dy - To\int_1^\infty \frac{\exp(-\frac{E}{RTo}y)}{y^2} dy\right\} = \frac{Ko}{\beta}\left[TE_2\left(\frac{E}{RT}\right) - ToE_2\left(\frac{E}{RTo}\right)\right] \tag{A.1.9}$$

Substituindo a equação (A.1.7) em a equação (A.1.9)

$$\theta(T) - \theta(To) = \frac{Ko}{\beta}\left[T\left(\exp\left(-\frac{E}{RT}\right) - \frac{E}{RT}E_1(\frac{E}{RT})\right) - To\left(\exp\left(-\frac{E}{RTo}\right) - \frac{E}{RTo}E_1(\frac{E}{RTo})\right)\right] \tag{A.1.10}$$

Realizando a aproximação:

$$E_1(x) = \int_x^\infty \frac{\exp(-y)}{\mathrm{y}} dy \cong \frac{\exp(-x)}{x}\left(1 - \frac{1!}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \cdots.\right)$$

$$\theta(T) - \theta(To) = \frac{Ko}{\beta}\left\{T\left[\exp(-\frac{E}{RT}) - \frac{E}{RT}\left(\frac{\exp(-\frac{E}{RT})}{\frac{E}{RT}}\left(1 - \frac{1!}{\frac{E}{RT}} + \frac{2!}{(\frac{E}{RT})^2} - \cdots\right)\right)\right] - To\left[\exp\left(-\frac{E}{RT}\right) - \frac{E}{RTo}\left(\frac{\exp(-\frac{E}{RTo})}{\frac{E}{RTo}}\left(1 - \frac{1!}{\frac{E}{RTo}} + \frac{2!}{(\frac{E}{RTo})^2} - \cdots\right)\right)\right]\right\}$$

Simplificando a ultima equação e considerando somente ate a segunda potencia no desenvolvimento em serie,teremos :

θ(T)-θ(To)=Ko/β$\left\{Texp\left(-\frac{E}{RT}\right)\left(1-1+\frac{RT}{E}-2\left(\frac{RT}{E}\right)^2\right)-Toexp\left(-\frac{E}{RTo}\right)\left(1-1+\frac{RTo}{E}-\right.\right.$

$\left.\left.2\left(\frac{RTo}{E}\right)^2\right)\right\}$

$$\theta(T)-\theta(To)=\frac{KoT}{\beta}\exp\left(-\frac{E}{RT}\right)\left(\frac{RT}{E}-2\left(\frac{RT}{E}\right)^2\right)-\frac{KoTo}{\beta}\exp\left(-\frac{E}{RTo}\right)\left(\frac{RTo}{E}-2\left(\frac{RTo}{E}\right)^2\right)$$

Assumindo que To ≈ 0 (na realidade To << T) , e para o qual θ(To)≈ 0, (na realidade θ(To) << θ(T):

$$\theta(T)=\frac{T^2R}{\beta E}\left(Ko\exp\left(-\frac{E}{RT}\right)\right)\left(1-2\frac{RT}{E}\right) \qquad \text{(A.1.11)}$$

Anexo 2.

Tomando a equação (3.7)

$$\frac{d\xi}{dT} = \frac{1}{P1-Po}\left\{\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) - \frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right\} \qquad \textit{(A.2.1)}$$

Derivando novamente respeito a T:

$$\frac{\mathrm{d}^2\xi}{\mathrm{dT}^2} = \frac{(\mathrm{P1}-\mathrm{Po})\,\frac{\mathrm{d}}{\mathrm{dT}}\left\{\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) - \frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right\} -}{(\mathrm{P1}-\mathrm{Po})^2}$$

$$-\frac{\left\{\left(\frac{dP}{dT}-\frac{dPo}{dT}\right)-\frac{P-Po}{P1-Po}\left(\frac{dP1}{dT}-\frac{dPo}{dT}\right)\right\}\left(\frac{dP1}{dT}-\frac{dPo}{dT}\right)}{(\mathrm{P1}-\mathrm{Po})^2} \qquad \textit{(A.2.2)}$$

Tomando separadamente a derivada do parêntesis :

$$\frac{\mathrm{d}}{\mathrm{dT}}\left\{\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) - \frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right\} = \frac{dA}{dT} - \frac{dB}{dT} \qquad \text{(A.2.3)}$$

Onde *o termo A é dado por:*

$$A = \left(\frac{dP}{dT} - \frac{dPo}{dT}\right) \quad e\ B\ por \quad B = \frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)$$

Então $\quad \frac{dA}{dT} = \frac{d^2P}{dT^2} - \frac{d^2Po}{dT^2} \quad e \qquad \textit{(A.2.4)}$

$$\frac{dB}{dT} = \frac{d}{dT}\left[\frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right] =$$

$$\frac{\left\{\left(\frac{d^2P1}{dT^2}-\frac{d^2Po}{dT^2}\right)(P-Po)+\left(\frac{dP1}{dT}-\frac{dPo}{dT}\right)\left(\frac{dP}{dT}-\frac{dPo}{dT}\right)\right\}(p1-Po)-\left(\frac{dP1}{dT}-\frac{dPo}{dT}\right)(P-Po)\left(\frac{dP1}{dT}-\frac{dPo}{dT}\right)}{(P1-Po)^2} \qquad \textit{(A.2.5)}$$

Substituindo *(A.2.5) e (A.2.4) em* (A.2.3) e o resultado em *(A.2.2) se obtém depois de simplificar:*

$$\frac{d^2\xi}{dT^2} = \frac{1}{P1-Po}\left\{\frac{d^2P}{dT^2} - \frac{2}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) + \frac{2}{(P1-Po)^2}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)^2 (P-Po)\right\} \quad \textit{(A.2.6)}$$

Anexo 3.

Retomando a equação que queremos transformar:

$$\left(\theta\frac{d^2\theta}{dT^2}\right)_{Ti}-[n(\theta^n-1)+1]\left(\frac{\mathrm{d}\theta}{\mathrm{dT}}\right)_{\mathrm{Ti}}^2=-\mathrm{C(T)}\theta\left(\frac{\mathrm{d}\theta}{\mathrm{dT}}\right)_{\mathrm{Ti}} \qquad \text{(A.3.1)}$$

Como: $\theta(T)=\frac{T^2R}{\beta E}\left(Ko\exp\left(-\frac{E}{RT}\right)\right)\left(1-2\frac{RT}{E}\right)=\frac{T^2RK}{\beta E}\left(1-2\frac{RT}{E}\right)$ (A.3.2)

$$\frac{\mathrm{d}\theta}{\mathrm{dT}}=\frac{\mathrm{KoR}}{\beta\mathrm{E}}\frac{\mathrm{d}}{\mathrm{dT}}\left(\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}\mathrm{T}^2(1-\frac{2\mathrm{RT}}{\mathrm{E}})\right)$$

$$\frac{\mathrm{d}}{\mathrm{dT}}\left(\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}\mathrm{T}^2(1-\frac{2\mathrm{RT}}{\mathrm{E}})\right)=$$

$$=-\frac{2e^{-\frac{\mathrm{E}}{RT}}RT^2}{\mathrm{E}}+\frac{e^{-\frac{\mathrm{E}}{RT}}\mathrm{E}(1-\frac{2RT}{\mathrm{E}})}{R}+2e^{-\frac{\mathrm{E}}{RT}}T(1-\frac{2RT}{\mathrm{E}})$$

$$\frac{\mathrm{d}\theta}{\mathrm{dT}}=\frac{\mathrm{RKo}}{\beta\mathrm{E}}\left[-\frac{2e^{-\frac{\mathrm{E}}{RT}}RT^2}{\mathrm{E}}+\frac{e^{-\frac{\mathrm{E}}{RT}}\mathrm{E}(1-\frac{2RT}{\mathrm{E}})}{R}+2e^{-\frac{\mathrm{E}}{RT}}T(1-\frac{2RT}{\mathrm{E}})\right]$$

$$=\frac{\mathrm{RK}}{\beta\mathrm{E}}\left[-\frac{2RT^2}{\mathrm{E}}+\frac{\mathrm{E}(1-\frac{2RT}{\mathrm{E}})}{R}+2T(1-\frac{2RT}{\mathrm{E}})\right]$$

(A.3.3)

$$\frac{\mathrm{d}^2\theta}{\mathrm{dT}^2}=\frac{\mathrm{RKo}}{\beta\mathrm{E}}\left[\frac{e^{-\frac{\mathrm{E}}{RT}}(\mathrm{E}^3-6\mathrm{E}R^2T^2-12R^3T^3)}{\mathrm{E}R^2T^2}\right]=\frac{\mathrm{RK}}{\beta\mathrm{E}}\frac{(\mathrm{E}^3-6\mathrm{E}R^2T^2-12R^3T^3)}{\mathrm{E}R^2T^2} \qquad \text{(A.3.4)}$$

Calculando o termino da equação:

$$n(\theta^n-1)+1$$

E Como já se conhece que: $\theta^n\approx 1+nln\theta+n^2(ln\theta)^2/2.$

$\mathrm{n}(\theta^{\mathrm{n}}-1)+1=\mathrm{n}\left(1+\mathrm{nln}\theta+\frac{\mathrm{n}^2(\mathrm{ln}\theta)^2}{2}-1\right)+1=\mathrm{n}^2\mathrm{ln}\theta+\frac{\mathrm{n}^3(\mathrm{ln}\theta)^2}{2}+1=$
$1+n^2(\mathrm{Ln[bTx]}+\mathrm{Ln}[1-2x])+\frac{1}{2}n^3(\mathrm{Ln[bTx]}+\mathrm{Ln}[1-2x])^2$

E como $\ln(1-2x)\cong-2x \;\; Se\; x\ll 1$

$\mathrm{n}(\theta^{\mathrm{n}}-1)+1=1+n^2(\mathrm{Ln[bTx]}+\mathrm{Ln}[1-2x])+\frac{1}{2}n^3(\mathrm{Ln[bTx]}+\mathrm{Ln}[1-2x])^2=1+$
$n^2(\mathrm{Ln[bTx]}-2x)+\frac{1}{2}n^3(\mathrm{Ln[bTx]}-2x)^2$ (A.3.5)

Onde temos designado: $x = \frac{RT}{E}$ e $b = \frac{K}{\beta}$

Fazendo uso de esta representação as equações anteriores podem se escrever como:

$$\frac{d\theta}{dT} = b(1 - 6x^2) \quad \text{(A.3.3b)}$$

$$\theta = \frac{T^2RK}{\beta E}\left(1 - 2\frac{RT}{E}\right) = bTx(1 - 2x) \quad \text{(A.3.2 b)}$$

$$\frac{d^2\theta}{dT^2} = \frac{\mathrm{RK}}{\beta\mathrm{E}}\frac{(\mathrm{E}^3 - 6\mathrm{E}R^2T^2 - 12R^3T^3)}{\mathrm{E}R^2T^2} = \frac{\mathrm{bR}}{\mathrm{E}}(\mathrm{x}^{-2} - 12\mathrm{x} - 6) \quad \text{(A.3.4 b)}$$

$$\theta\frac{d^2\theta}{dT^2} = -2\mathrm{b}^2\mathrm{x} + \mathrm{b}^2 - 6\mathrm{b}^2x^2 + 24\mathrm{b}^2\mathrm{x}^4 \quad \text{(A.3.6)}$$

Tinindo presente que x << 1(em o rango de trabalho) e por tanto depreciando as potencias superiores de x e substituindo (A.3.5), (A.3.3b), (A.3.2 b) e (A.3.4 b) ou (A.3.6) em a equação (A.3.1) , se obtém :

$$b^2(1 - 2x) - \left(n^2\ln\theta + \frac{n^3}{2}(\ln\theta)^2 + 1\right)b^2 = -C(T)b^2Tx$$

Simplificando e substituindo (A.3.5) em a ultima equação :

$$2x + n^2(\ln(\mathrm{bTx}) - 2x) + \frac{n^3}{2}(\ln(\mathrm{bTx}) - 2x)^2 = c(T)Tx \quad \text{(A.3.7)}$$

E esta ultima expressão a podemos escrever como:

$$\ln(bTx) - 2x + \frac{n}{2}\left(ln^2(bTx) - 4xln(bTx) + 4x^2\right) = \frac{CTx}{n^2} - \frac{2x}{n^2}$$

E desprezado a $4x^2$

$$\ln(bTx) - 2x + \frac{n}{2}\left(ln^2(bTx) - 4xln(bTx)\right) = \frac{CTx}{n^2} - \frac{2x}{n^2}$$

$$\ln(bTx) = \frac{CTx}{n^2} - \frac{2x}{n^2} + 2x - \frac{n}{2}\left(ln^2(bTx) - 4xln(bTx)\right)$$

$$\ln(bTx) = \frac{CTx}{n^2} + 2x\left(1 - \frac{1}{n^2}\right) + \frac{n}{2}\left(4xln(bTx) - ln^2(bTx)\right)$$

$$\ln(bTx) = \frac{CTx}{n^2} + 2x\left(1 - \frac{1}{n^2}\right) + 2nx\left(\ln(bTx) - \frac{ln^2(bTx)}{4x}\right)$$

E para os valores típicos de trabalho o ultimo somando dentro do parêntesis é sempre menor que o primeiro e se pode depreciar.

Depois de substituir $x = \frac{RT}{E}$ e $b = \frac{K}{\beta}$. se obtém a expressão final de trabalho .

$$\ln\left(\frac{\mathrm{Ti}^2}{\beta}\right)_{\mathrm{Ti}} = ln\left(\frac{E}{RKo}\right) + \frac{E}{RT_i} + \frac{C}{n^2}\frac{RT_i{}^2}{E} + 2\frac{RTi}{E}\left\{1 - \frac{1}{n^2} + nln\left[\frac{RKT_i{}^2}{\beta E}\right]\right\}$$

Anexo 4

Se adotarmos o formalismo de KJMA para a função transformada; a seguinte justificação do método de Kissinger pode ser dada:

$$\xi = 1 - \exp\left(-\theta^n\right) \qquad \text{(A.4.1)}$$

Por isso:

$$\frac{d\xi}{dt} = \frac{d\xi}{d\theta}\frac{d\theta}{dt} \qquad \text{(A.4.2)}$$

Como é conhecida, a segunda derivada da função transformada noponto de inflexão é nula:

$$\left(\frac{d^2\xi}{dt^2}\right)_{Tp} = \frac{d}{dt}\left(\frac{d\xi}{d\theta}\frac{d\theta}{dt}\right) = \frac{d\theta}{dt}\frac{d}{dt}\frac{d\xi}{d\theta} + \frac{d\xi}{d\theta}\frac{d^2\theta}{dt^2} = \frac{d\theta}{dt}\frac{d}{d\theta}\left(\frac{d\xi}{d\theta}\right)\frac{d\theta}{dt} + \frac{d\xi}{d\theta}\frac{d^2\theta}{dt^2} = 0 \qquad \text{(A.4.3)}$$

A equação anterior pode ser resumida:

$$\left(\frac{d^2\xi}{dt^2}\right)_{Tp} = \left(\frac{d^2\xi}{d\theta^2}\left(\frac{d\theta}{dt}\right)^2\right)_{Tp} + \left(\frac{d\xi}{d\theta}\frac{d^2\theta}{dt^2}\right)_{Tp} = 0 \qquad \text{(A.4.4)}$$

Retomando a equação (5) :

$$d\theta = K(T)\,dt = Ko\exp\left(-\frac{E}{R*T}\right)dt \qquad \text{(A.4.5)}$$

È evidente de aqui que :2

$$\left(\frac{d\theta}{dt}\right)^2 = K(T)^2 \qquad \text{(A.4.6)}$$

$$\frac{d^2\theta}{dt^2} = K(T)\frac{E}{RT^2}\frac{dT}{dt} \qquad \text{(A.4.7)}$$

Dividindo (A.4.6) por (A.4.7):

$$\left(\frac{d\theta}{dt}\right)^2 \Big/ \frac{d^2\theta}{dt^2} = \frac{KRT^2}{E\beta} \approx \theta \qquad \text{(A.4.8)}$$

Já que: $\theta(T) = \frac{T^2R}{\beta E}\left(Ko\exp\left(-\frac{E}{RT}\right)\right)\left(1 - 2\frac{RT}{E}\right) = K(T)\frac{T^2R}{\beta E}\left(1 - 2\frac{RT}{E}\right) \approx \frac{KRT^2}{E\beta}$ (A.1.11)

Se RT/E<<1

Inserindo a equação (A.4.8) na equação (A.4.4):

$$\left(\frac{d^2\xi}{dt^2}\right)_{Tp} = \left(\theta\frac{d^2\theta}{dt^2}\frac{d^2\xi}{d\theta^2} + \frac{d\xi}{d\theta}\frac{d^2\theta}{dt^2}\right)_{Tp} = 0$$

De donde finalmente obtém-se que:

$$\left(\theta\frac{d^2\xi}{d\theta^2} + \frac{d\xi}{d\theta}\right)_{Tp} = 0 \qquad \text{(A.4.9)}$$

A solução de esta equação é ϑp=1. Por isso a temperatura Tp onde a taxa da reação é máxima, ou seja, no ponto de inflexão da curva ξ VS T(ou t) ,ocorre sempre com boa aproximação, para o mesmo valor de ξ para diferentes taxas de aquecimento $\beta = \frac{dT}{dt}$ é por isto é razoável substituir Ti (valor do ponto de inflexão nas curvas dilatométricas P vs T (ou t)) por Tp ,o ponto de inflexão da curva ξ VS T(ou t)[42].

Este mesmo resultado foi obtido por T. Ozawa (1984) [79] assumindo que a fração transformada segue uma distribuição de Poisson. Também foi obtido por Farjas J, Roura P (2006) [55] ver a equações (51) e (52).

Estes razoamentos constituem uma justificativa para o método de Kissinger de determinação da energia de ativação.Em efeito sim tomamos a expressão (A.1.11) obtida diretamente da integral de temperatura , sem recorrer a nenhum modelo cinético:

$$\theta_f = K(T)\frac{{T_f}^2 R}{\beta E}\left(1 - 2\frac{RT_f}{E}\right)$$

E tomamos um estado fixo da transformação, digamos f, Tf. Como normalmente RTf/E<<1:

$$\theta_f \approx K(T)\frac{{T_f}^2 R}{\beta E} = Koexp(-\frac{E}{RT})\frac{{T_f}^2 R}{\beta E} \qquad \text{(A.4.10)}$$

Aplicando logaritmo natural a (A.4.10) e agrupando convenientemente:

$$ln\frac{{T_f}^2}{\beta} = \frac{E}{RT_f} + ln\frac{E}{RKo} + ln\theta_f \qquad \text{(A.4.10)}$$

O resultado (A.4.10) será usado para determinar E=E(f). Note que para o ponto de inflexão T=Tp, $\theta_{f(Tp)}$=1 o logaritmo de $\theta_{f(Tp)}$ se anula .Esta é uma equação do tipo de Kissinger. Que pode ser usada também para calcular Ko.

Anexo 5 Calculo da Energia de Ativação por Regressão Linear

```
R = 0.00831;
TgKelvin[x_] := 273.15 + x;
ϕ1 = 5;
ϕ2 = 10;
ϕ3 = 15;
ϕ4 = 20;
ϕ5 = 30;
T1 = 138.5;
T2 = 145.8;
T3 = 151.2;
T4 = 155.35;
T5 = 159.3;
rapienfria = {ϕ1, ϕ2, ϕ3, ϕ4, ϕ5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; flujo = rapienfria[[i]];
 listay = AppendTo[listay, {Te^-1, Log[Te^2 / flujo]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
result = NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
l = Normal[result]
Print["Pendiente =", " ", pend = l[[2, 1]]]
Print["intercepto =", " ", Interc = l[[1]]]
 Print["Energiaactiva=", " ", Energiaactiva1 = pend * R]
 Print["Ko =", " ", (Energiaactiva1 * Exp[-Interc]) / R]
nlm = NonlinearModelFit[listay, a + b x, {a, b}, {x}] [
  {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
   "ParameterTStatistics", "ParameterConfidenceIntervals",
   "ParameterConfidenceIntervalTable"}]
Print["valor de energia superior =", R * nlm[[6, 2, 2]]]
Print["valor de energia inferior =", R * nlm[[6, 2, 1]]]

Show[ListPlot[listay],
 Plot[result[x], {x, 0.0023050803004043903`, 0.002433`}],
 Frame -> True, AxesLabel -> {1/Ti, LnTi^2/ϕ}]
Plot[result[x], {x, 0.0024292481476982874, 0.0023124060585038735},
 Epilog :> Point[listay], PlotStyle -> {Red, Thick},
 Frame -> True, AxesLabel -> {1/Ti, LnTi^2/ϕ}]
NonlinearModelFit[listay, a + b x, {a, b}, {x}] [
 {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
```

```
  "ParameterTStatistics", "ParameterConfidenceIntervalTable"}]
lm = LinearModelFit[listay, x, x]
listasalida = {};
listasalida = lm[{"AdjustedRSquared", "RSquared", "FitResiduals"}]
√listasalida[[2]]
Listares = {};
Listares = listasalida[[3]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
listasalida2 = {};
listasalida2 =
  lm[{"FitResiduals", "SinglePredictionConfidenceIntervalTable",
    "ParameterConfidenceRegion"}];
errors = listasalida2[[1]]
tablasimpledeintecnf = listasalida2[[2]]
Observed = {}
Do[Observed = AppendTo[Observed, tablasimpledeintecnf[[1, 1, i, 1]]],
 {i, 2, 6}]
Observed
predicted = {};
Do[predicted = AppendTo[predicted, tablasimpledeintecnf[[1, 1, i, 2]]],
 {i, 2, 6}]
predicted
ListPlot[Transpose[{predicted, errors}], PlotStyle → PointSize[0.02`]]
gplaj = Plot[lm[x], {x, 0.0024292481476982874, 0.0023124060585038735}];
ci = {}
Do[ci = AppendTo[ci, tablasimpledeintecnf[[1, 1, i, 4]]], {i, 2, 6}]
ci
(xval = First /@ listay; predicted = Transpose[{xval, predicted}];
 lowerCI = Transpose[{xval, First /@ ci}];
 upperCI = Transpose[{xval, Last /@ ci}]);
gfrs = ListPlot[{listay, predicted, lowerCI, upperCI},
  Joined → {False, True, True, True}, PlotStyle → {Automatic,
    Automatic, Dashing[{0.05`, 0.05`}], Dashing[{0.05`, 0.05`}]}]
Show[gfrs, gplaj]
```

Out[17]= {411.65, 418.95, 424.35, 428.5, 432.45}

Out[20]= {{0.00242925, 10.4309}, {0.00238692, 9.77292}, {0.00235655, 9.39307}, {0.00233372, 9.12485}, {0.00231241, 8.73774}}

Out[21]= FittedModel[$\boxed{-23.7799 + 14\,075.7\,x}$]

Out[22]= $-23.7799 + 14\,075.7\,x$

Pendiente = 14 075.7

intercepto = −23.7799

Energiaactiva= 116.969

Ko = 2.99184×10^{14}

Out[25]= Null^2

Out[26]=

	DF	SS	MS
Model	2	452.148	226.074
Error	3	0.00641532	0.00213844
Uncorrected Total	5	452.154	
Corrected Total	4	1.67397	

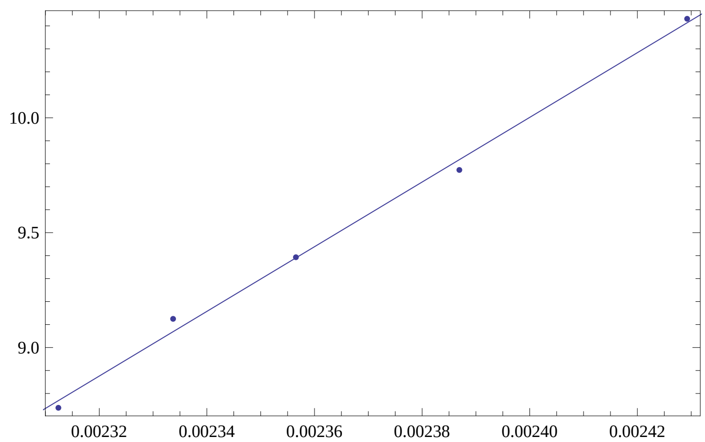
```
{0.00027503, 0.000100808}, 0.999976, 0.999986,
{-19.9553, 27.9249}, {{-27.5722, -19.9875}, {12 471.6, 15 679.9}},
```

	Estimate	Standard Error	Confidence Interval
a	−23.7799	1.19165	{−27.5722, −19.9875}
b	14 075.7	504.057	{12 471.6, 15 679.9}

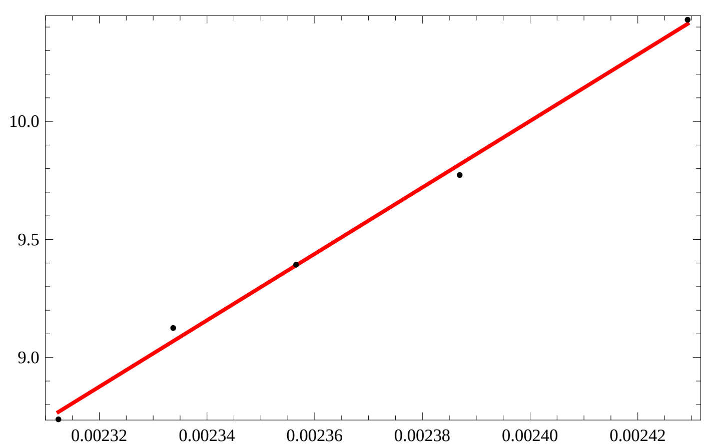
```
valor de energia superior =130.3

valor de energia inferior =103.639
```

Out[29]=



Out[30]=



Out[31]= {

	DF	SS	MS
Model	2	452.148	226.074
Error	3	0.00641532	0.00213844
Uncorrected Total	5	452.154	
Corrected Total	4	1.67397	

,

{0.00027503, 0.000100808}, 0.999976, 0.999986, {-19.9553, 27.9249},

	Estimate	Standard Error	Confidence Interval
a	−23.7799	1.19165	{−27.5722, −19.9875}
b	14 075.7	504.057	{12 471.6, 15 679.9}

}

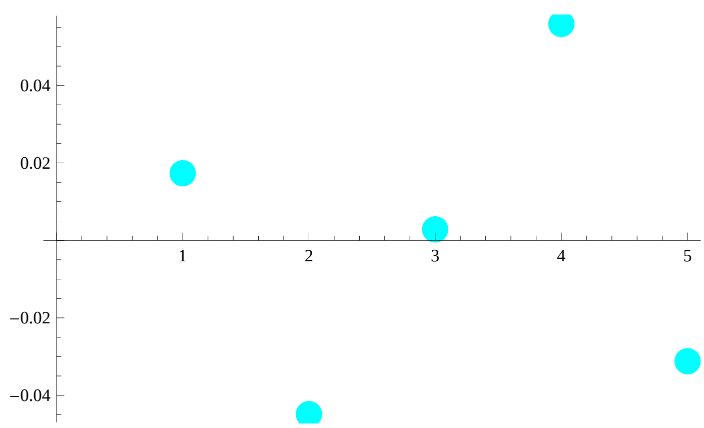
Out[32]= FittedModel[$-23.7799 + 14\,075.7\,x$]

Out[34]= {0.99489, 0.996168, {0.0173364, -0.0448505, 0.00283999, 0.0558729, -0.0311988}}

Out[35]= 0.998082

Out[37]= {0.0173364, -0.0448505, 0.00283999, 0.0558729, -0.0311988}

Out[38]=



Out[41]= {0.0173364, -0.0448505, 0.00283999, 0.0558729, -0.0311988}

Out[42]=

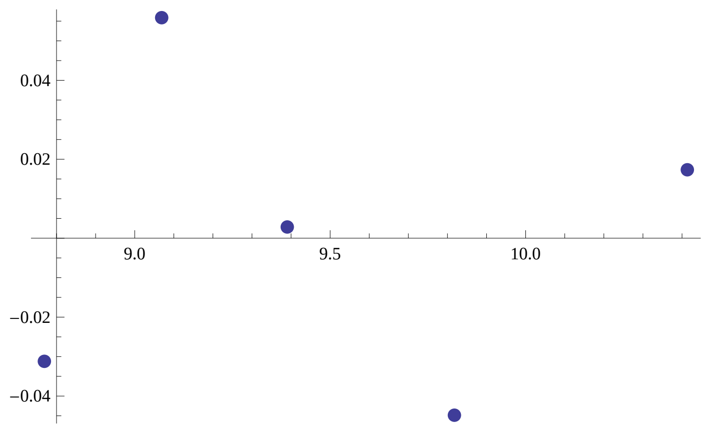
Observed	Predicted	Standard Error	Confidence Interval
10.4309	10.4136	0.0604607	{10.2212, 10.606}
9.77292	9.81777	0.0519837	{9.65233, 9.9832}
9.39307	9.39023	0.0507876	{9.2286, 9.55186}
9.12485	9.06898	0.0528725	{8.90071, 9.23724}
8.73774	8.76893	0.0568893	{8.58789, 8.94998}

Out[43]= { }

Out[45]= {10.4309, 9.77292, 9.39307, 9.12485, 8.73774}

Out[48]= {10.4136, 9.81777, 9.39023, 9.06898, 8.76893}

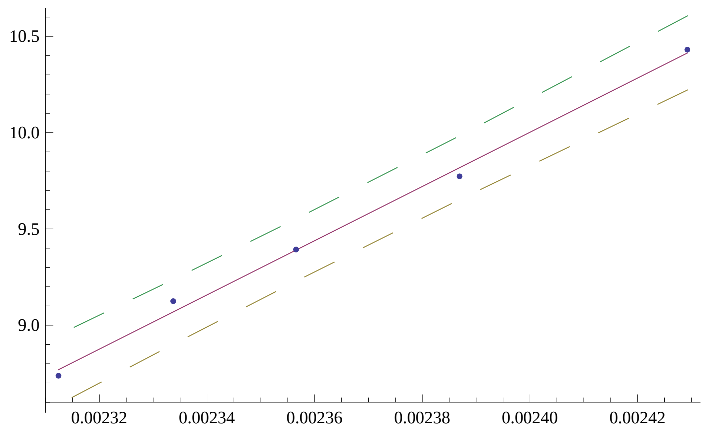
Out[49]=



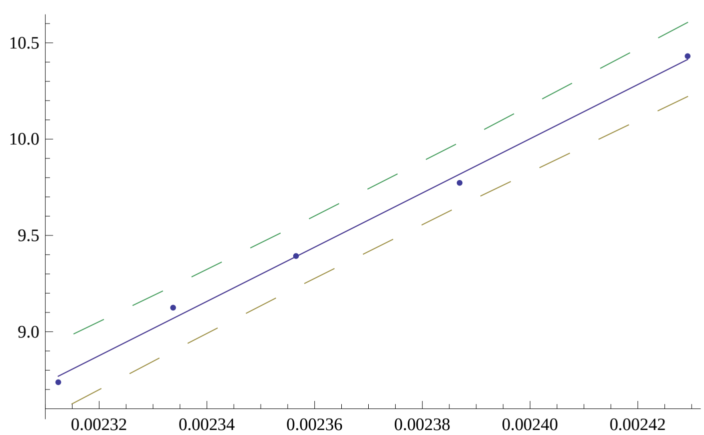
Out[51]= { }

Out[53]= {{10.2212, 10.606}, {9.65233, 9.9832}, {9.2286, 9.55186}, {8.90071, 9.23724}, {8.58789, 8.94998}}

Out[54]=



Out[55]=



(* **Anexo 5 b***) Calculo da Energia de Ativação por Regressão Linear, Processo II


```
R = 0.00831;
TgKelvin[x_] := 273.15 + x;
ϕ1 = 5;
ϕ2 = 10;
ϕ3 = 15;
ϕ4 = 20;
ϕ5 = 30;
T1 = 311.2`;
T2 = 320.4`;
T3 = 326;
T4 = 330.`;
T5 = 335.7`;
rapienfria = {ϕ1, ϕ2, ϕ3, ϕ4, ϕ5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; flujo = rapienfria[[i]];
 listay = AppendTo[listay, {Te^-1, Log[Te^2 / flujo]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
result = NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
l = Normal[result]
Print["Pendiente =", " ", pend = l[[2, 1]]]
Print["intercepto =", " ", Interc = l[[1]]]
Print["Energiaactiva=", " ", Energiaactiva1 = pend * R]
Print["Ko =", " ", (Energiaactiva1 * Exp[-Interc]) / R]
nlm = NonlinearModelFit[listay, a + b x, {a, b}, {x}] [
  {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
   "ParameterTStatistics", "ParameterConfidenceIntervals",
   "ParameterConfidenceIntervalTable"}]
Print["valor de energia superior =", R * nlm[[6, 2, 2]]]
Print["valor de energia inferior =", R * nlm[[6, 2, 1]]]

Show[ListPlot[listay],
 Plot[result[x], {x, 0.0017113031573543255`, 0.001642440666830911`}],
 Frame → True, AxesLabel → {1/Ti, LnTi^2/ϕ}]
Plot[result[x], {x, 0.0017113031573543255`, 0.001642440666830911`},
 Epilog :→ Point[listay], PlotStyle → {Red, Thick},
 Frame → True, AxesLabel → {1/Ti, LnTi^2/ϕ}]
NonlinearModelFit[listay, a + b x, {a, b}, {x}] [
 {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
```

```
  "ParameterTStatistics", "ParameterConfidenceIntervalTable"}]
lm = LinearModelFit[listay, x, x]
listasalida = {};
listasalida = lm[{"AdjustedRSquared", "RSquared", "FitResiduals"}]
√listasalida[[2]]
Listares = {};
Listares = listasalida[[3]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
listasalida2 = {};
listasalida2 =
  lm[{"FitResiduals", "SinglePredictionConfidenceIntervalTable",
    "ParameterConfidenceRegion"}];
errors = listasalida2[[1]]
tablasimpledeintecnf = listasalida2[[2]]
Observed = {}
Do[Observed = AppendTo[Observed, tablasimpledeintecnf[[1, 1, i, 1]]],
 {i, 2, 6}]
Observed
predicted = {};
Do[predicted = AppendTo[predicted, tablasimpledeintecnf[[1, 1, i, 2]]],
 {i, 2, 6}]
predicted
ListPlot[Transpose[{predicted, errors}], PlotStyle → PointSize[0.02`]]
gplaj = Plot[lm[x], {x, 0.0017113031573543255`, 0.001642440666830911`}];
ci = {}
Do[ci = AppendTo[ci, tablasimpledeintecnf[[1, 1, i, 4]]], {i, 2, 6}]
ci
(xval = First /@ listay; predicted = Transpose[{xval, predicted}];
 lowerCI = Transpose[{xval, First /@ ci}];
 upperCI = Transpose[{xval, Last /@ ci}]);
gfrs = ListPlot[{listay, predicted, lowerCI, upperCI},
  Joined → {False, True, True, True}, PlotStyle → {Automatic,
    Automatic, Dashing[{0.05`, 0.05`}], Dashing[{0.05`, 0.05`}]}]
Show[gfrs, gplaj]
```

```
Out[127]= {584.35, 593.55, 599.15, 603.15, 608.85}

Out[130]= {{0.0017113, 11.1316}, {0.00168478, 10.4697},
           {0.00166903, 10.083}, {0.00165796, 9.8086}, {0.00164244, 9.42195}}

Out[131]= FittedModel[ -31.3166 + 24804. x ]

Out[132]= -31.3166 + 24804. x

          Pendiente = 24804.

          intercepto = -31.3166

          Energiaactiva= 206.121
```

Ko = 9.8892×10^{17}

Out[135]= Null^2

Out[136]=

	DF	SS	MS
Model	2	520.173	260.087
Error	3	0.0000121801	4.06004×10^{-6}
Uncorrected Total	5	520.173	
Corrected Total	4	1.71133	

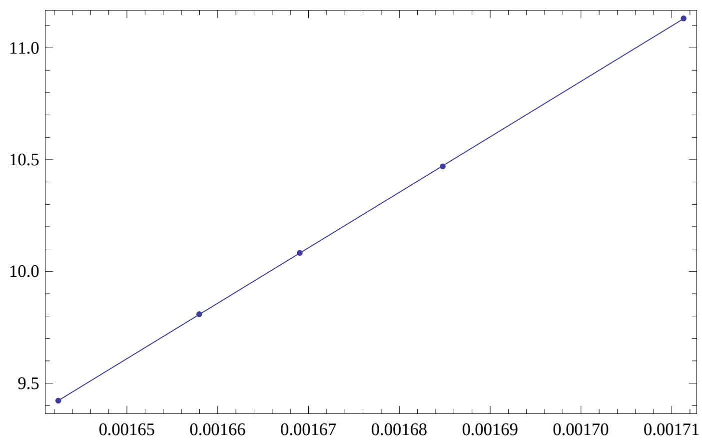
{1.87586×10^{-8}, 8.05874×10^{-9}}, 1., 1., {-489.878, 649.232},
{{-31.5201, -31.1132}, {24 682.4, 24 925.5}},

	Estimate	Standard Error	Confidence Interval
a	−31.3166	0.0639274	{−31.5201, −31.1132}
b	24 804.	38.2051	{24 682.4, 24 925.5}

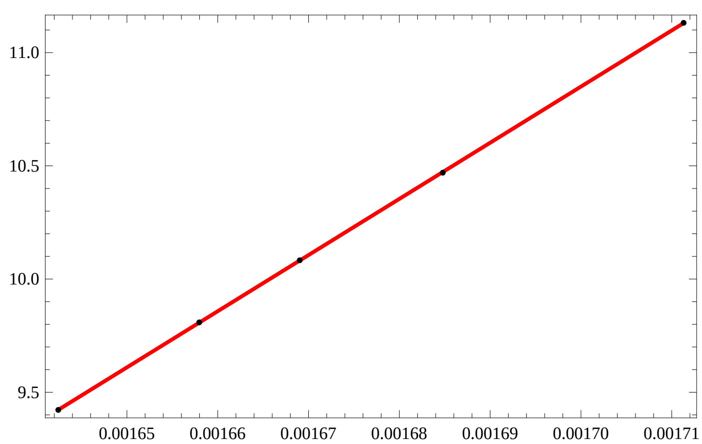
valor de energia superior =207.131

valor de energia inferior =205.111

Out[139]=



Out[140]=



Out[141]=

	DF	SS	MS
Model	2	520.173	260.087
Error	3	0.0000121801	4.06004×10^{-6}
Uncorrected Total	5	520.173	
Corrected Total	4	1.71133	

$\{1.87586\times10^{-8}, 8.05874\times10^{-9}\}$, 1., 1., {-489.878, 649.232},

	Estimate	Standard Error	Confidence Interval
a	-31.3166	0.0639274	{-31.5201, -31.1132}
b	24 804.	38.2051	{24 682.4, 24 925.5}

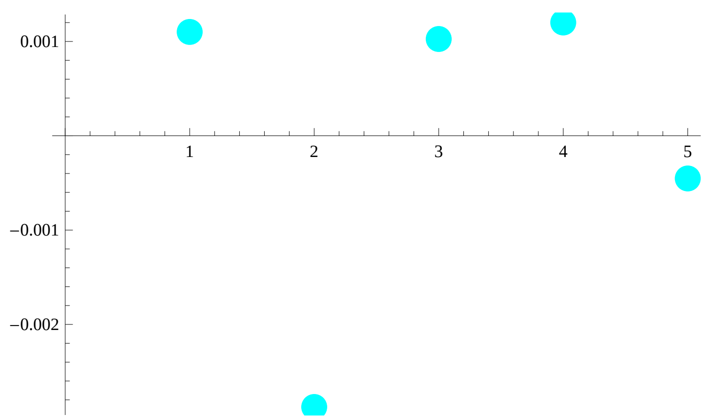
Out[142]= FittedModel[$-31.3166 + 24804.\,x$]

Out[144]= {0.999991, 0.999993, {0.00110094, -0.00287542, 0.00102605, 0.00120099, -0.000452557}}

Out[145]= 0.999996

Out[147]= {0.00110094, -0.00287542, 0.00102605, 0.00120099, -0.000452557}

Out[148]=



Out[151]= {0.00110094, -0.00287542, 0.00102605, 0.00120099, -0.000452557}

Out[152]=

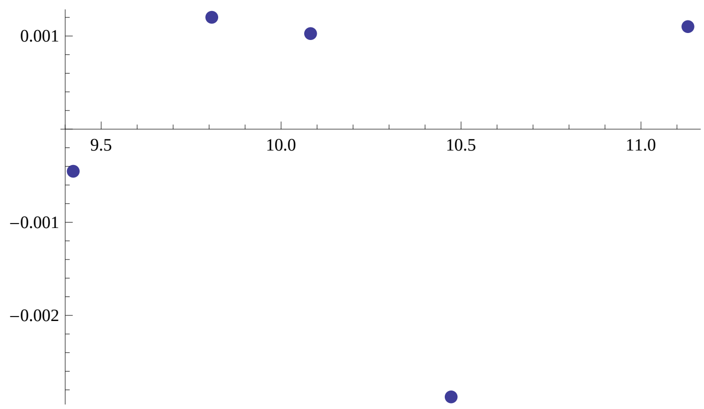
Observed	Predicted	Standard Error	Confidence Interval
11.1316	11.1305	0.00264613	{11.122, 11.1389}
10.4697	10.4725	0.00225189	{10.4654, 10.4797}
10.083	10.0819	0.00221275	{10.0749, 10.089}
9.8086	9.8074	0.00228181	{9.80014, 9.81466}
9.42195	9.4224	0.00249887	{9.41445, 9.43035}

Out[153]= { }

Out[155]= {11.1316, 10.4697, 10.083, 9.8086, 9.42195}

Out[158]= {11.1305, 10.4725, 10.0819, 9.8074, 9.4224}

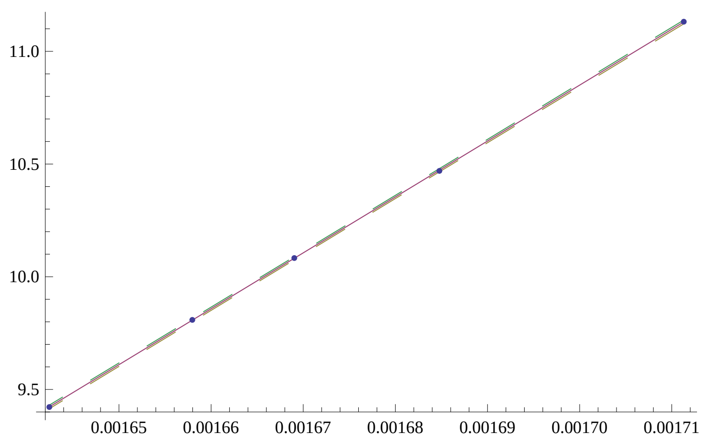
Out[159]=



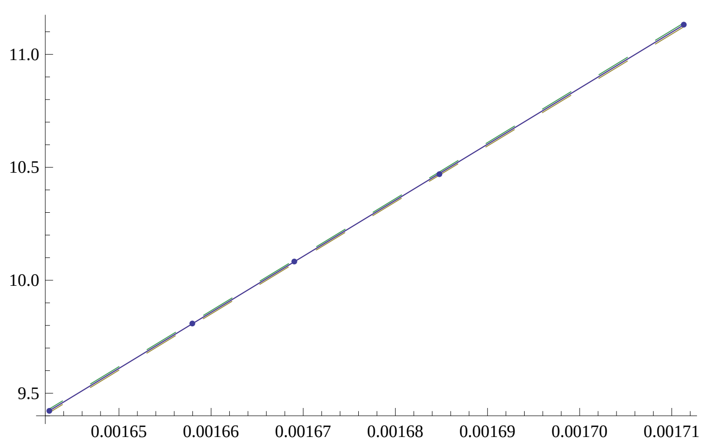
Out[161]= { }

Out[163]= {{11.122, 11.1389}, {10.4654, 10.4797},
{10.0749, 10.089}, {9.80014, 9.81466}, {9.41445, 9.43035}}

Out[164]=



Out[165]=



- **(* Anexo 6 ,tuda a equação e com parametros *)**

```
R = 0.00831;
TgKelvin[x_] := 273.15 + x;
β1 = 5;
β2 = 10;
β3 = 15;
β4 = 20;
β5 = 30;
T1 = 138.5;
T2 = 145.8;
T3 = 151.2;
T4 = 155.35;
T5 = 159.3;
rapienfria = {β1, β2, β3, β4, β5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; flujo = rapienfria[[i]];
 listay = AppendTo[listay, {Te^-1, Log[Te^2 / flujo]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
resul = NonlinearModelFit[listay,
   Ener/R * y + Log[Ener/(R * Ko)], {{Ener, 115}, {Ko, 1 * 10^14}}, {y}]
resul[[1, 2]]
resul[[1, 2, 1, 2]]
resul[[1, 2, 2, 2]]
listasalida = {};
listasalida =
 resul[{"BestFitParameters", "FitResiduals", "ParameterConfidenceIntervals",
   "ParameterConfidenceIntervalTable", "ParameterTable"}]
residuos = listasalida[[2]]
valoresdex = First /@ listay
Lsitgraresiduos = {};
Do[Lsitgraresiduos = AppendTo[Lsitgraresiduos, {valoresdex[[i]], residuos[[i]]}],
 {i, 1, Length[residuos]}]
ListPlot[Lsitgraresiduos, AxesLabel → {Xexp, Residuos},
 PlotStyle → {Hue[0.7], PointSize[0.02]}]
```

```
{411.65, 418.95, 424.35, 428.5, 432.45}

{{0.00242925, 10.4309}, {0.00238692, 9.77292},
 {0.00235655, 9.39307}, {0.00233372, 9.12485}, {0.00231241, 8.73774}}

FittedModel[ -23.7799 + 14075.7 y ]
```

$\{Ener \to 116.969,\ Ko \to 2.99184 \times 10^{14}\}$

```
116.969
```

2.99184×10^{14}

$\{\{Ener \to 116.969,\ Ko \to 2.99184 \times 10^{14}\},$
$\{0.0173364,\ -0.0448505,\ 0.00283999,\ 0.0558729,\ -0.0311988\},$
$\{\{116.745,\ 117.194\},\ \{2.99184 \times 10^{14},\ 2.99184 \times 10^{14}\}\},$

	Estimate	Standard Error	Confidence Interval
Ener	116.969	0.0705728	{116.745, 117.194}
Ko	2.99184×10^{14}	8.04844×10^{-16}	$\{2.99184 \times 10^{14}, 2.99184 \times 10^{14}\}$

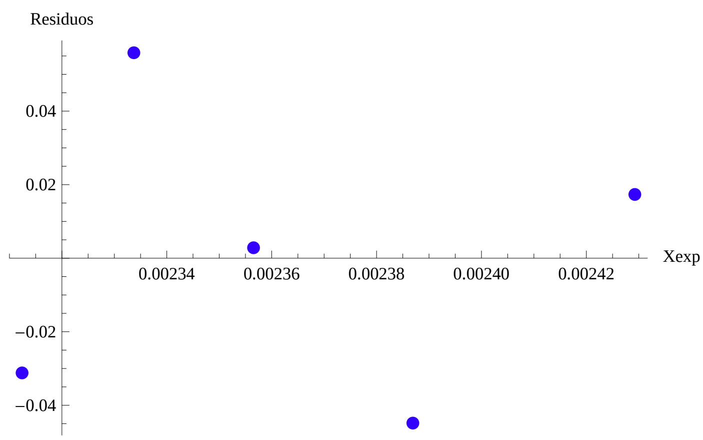
,

	Estimate	Standard Error	t Statistic	P-Value
Ener	116.969	0.0705728	1657.43	4.84358×10^{-10}
Ko	2.99184×10^{14}	8.04844×10^{-16}	3.71729×10^{29}	4.2933×10^{-89}

}

$\{0.0173364,\ -0.0448505,\ 0.00283999,\ 0.0558729,\ -0.0311988\}$

$\{0.00242925,\ 0.00238692,\ 0.00235655,\ 0.00233372,\ 0.00231241\}$



Anexo 7 Calculo dos Residuos

Para calcular os valores dos residuais Res1 e Res2 em a equação (13) é necessário calcular o valor do parâmetro Q, em neste caso o parâmetro P é a longitude da mostra, l:

$$Q(T_i) = 2\,\frac{\dfrac{dp_1}{dT} - \dfrac{dp_o}{dT}}{p_1 - p_o} = 2\,\frac{(\alpha_1 l_1 - \alpha_0 l_0)}{l_1 - l_0} \cong \frac{\Delta\alpha}{\dfrac{\Delta l}{l_o}} \qquad (7.1)$$

Onde α_0 e α_1 são os coeficientes da dilatação lineal da amostra antes e depois da transformação , observar a figura 2.1. Para estruturas poliméricas tem sido verificada a seguinte relação [99]

$$\alpha = \alpha_1 V_1 + \alpha_2 V_2 + \alpha_3 V_3 + ... \qquad (7.2)$$

Onde α_i e V_i são respectivamente o coeficiente de dilatação lineal e a fração de volume da fase i-enésima . Antes de iniciar a transformação veja a figura 3.2, segmento AO a equação (7.2) pode-se escrever da seguinte forma:

$$\alpha_o = \alpha_m V_m + \alpha_{ar} V_{ar} \qquad (7.3)$$

E depois da transformação, processo I, veja novamente a figura 3.2:

$$\alpha_1 = \alpha_e V_e + \alpha_{fe} V_{fe} + \alpha_{ar} V_{ar} \qquad (7.4)$$

Onde os sub índices (m,ar,e,fe), refreasse ao Martensita(m), Austenita residual (ar),carbetos Épsilon(e) e Ferrita(Fe) respectivamente.É certo que :

$$V_m + V_{ar} = 1 \quad , \; Ve + V_{fe} + V_{ar} = 1 \qquad (7.5)$$

Por isso em a equação (7.1) :

$$\Delta\alpha = \alpha_1 - \alpha_0 \qquad (7.6)$$

É muito Bom conhecido que os câmbios relativos do volumem referidos ao volume inicial da amostra ficam relacionados com os câmbios relativos da longitude por a simples relação

$$\delta V/V = 3\,\delta l/l.$$

Para transformações isomorfas. Pero não se comete um grão erro se aplicamos ela em este caso [82]. O cambio de volume se deve a que em o processo I o cambio das fases esta dado por:

$(\alpha'_{0.5} + \gamma_{r\,0.04} \rightarrow \alpha_{0.2} + \varepsilon + \gamma_{r\,0.04})$ Muito perto da temperatura Ti (tabela 3.2)

É possível calcular a fração de volume da fase que se tem formado (O carboneto Épsilon), Ve, sim as seguintes considerações são assumidas: Nomear os termos N^e ,N^{fe}, N^m como o numero de átomos de ferro em as fases Épsilon , Ferrita e Martensita respectivamente, E seja também ν^e, ν^{fe} ,ν^m o volume de um átomo de ferro em as fases Épsilon, Ferrita e Martensita respectivamente. Assume-se um revenido isotérmico, então a seguinte relação é valida:

$$\frac{\Delta V}{V} = 3\frac{\Delta l}{l_o} = \frac{N^e v^e + N^{fe} v^{fe} + N^{ar} v^{ar} - (N^e v^m + N^{fe} v^m + N^{ar} v^{ar})}{N^m v^m} \qquad (7.7)$$

Tendo presente a conservação de sítios:

$$N^m = N^{fe} + N^e \ , \ 1 = \frac{N^{fe}}{N^m} + \frac{N^e}{N^m} = \frac{N^{fe}}{N^m} + y \ , \ y = \frac{N^e}{N^m} \qquad (7.8)$$

Onde y $y = \dfrac{N^e}{N^m}$ é a fração de átomos de ferro que tem sido transformada em carbonetos épsilon . e agora a relação (VII.7) pode-se escrever como :

$$\frac{\Delta V}{V} = 3\frac{\Delta l}{l_o} = \frac{y(v^e - v^m) + (1-y)(v^{fe} - v^m)}{v^m} \qquad (7.9)$$

A fração de volume que se tem formado de carbetos Épsilon :

$$V_E = \frac{N^e v^e}{N^m v^m} = y\frac{v^e}{v^m} \qquad (\mathrm{VII.10})$$

Se se tem presente (7.10) e pode derivar se que :

$$V_E = \frac{N^e v^e}{N^m v^m} = y\frac{v^e}{v^m} = \left\{ \frac{\left(3\frac{\Delta l}{l_o} + 1\right) v^m - v^{fe}}{v^e - v^{fe}} \right\} \frac{v^e}{v^m} \qquad (7.11)$$

Em a relação anterior Δ l/lo é obtido diretamente do registro do dilatómetro extrapolando ate o ponto de inflexão da curva , veja a figura 2.1,os valores de referencia P_1 e P_o são obtidos de esta forma como é indicado em a figura 2.1. Posteriormente se subtraí o valor P1 de Po.Os valores ν^{e}, ν^{fe}, ν^{m} , assim como todos os α_i são obtidos da literatura[82]

ν^{m} = 11.897 A^3 /Fe α_m=11.5*10^{-6} C^{-1}

ν^{fe} =11.77 A^3 /Fe α_{fe}=14.5*10^{-6} C^{-1} ; α_{ar} =23*10^{-6} C^{-1};

ν^{e} =13.827 A^3 /Fe α_E= α_θ= 12.5*10^{-6} C^{-}

Em a tabela seguinte se mostram os valores do parâmetro Q calculados para cada curva do registro dilatométrico para o primeiro processo. A fração de volume dos carbonetos Epsilon ε, Ve , se calcula usando a equação (7.11) e a fração de volume de Ferrita , V_{Fe} se calcula usando a relação (7.5). A fração de volume da martensita e da Austenita residual é em todos os casos: V_{ar} = 0.04 ; V_m = 0.96 .

Como poderá apreciar se o parâmetro Q é aproximadamente ≈ - 0.01 para o primeiro processo do revenido. Para o segundo processo do revenido (terceiro estado do revenido) o parâmetro Q = 0. Pois a seguinte reação se desenvolve durante o segundo processo:

$$\epsilon \ \rightarrow \ \theta', \quad \alpha + \epsilon + \theta \ \rightarrow \alpha + \theta + \theta'$$

Onde θ e α são a Cementita e a Ferrita respectivamente. A Cementita que se origina da decomposição dos carbonetos Épsilon se designa por θ'.Então

$$\alpha_0 = V_{fe}\alpha_{fe} + \alpha e Ve + \alpha_{\theta'} V_{\theta'} \quad \text{e} \quad \alpha_1 = V_{fe}\alpha_{fe} + V_\theta \alpha_\theta + \alpha_{\theta'} V_{\theta'}$$

De esta forma $\Delta\alpha = \alpha_1 - \alpha_0 = \alpha_\theta V_\theta - V_c \alpha_c = 0$ devido a que Ve =V_θ e $\alpha_e = \alpha_\theta$ e por tanto Q = 0.Em resume :

Tabela A 7.1: Valores do parâmetro Q , para o primeiro processo.

β	$\Delta l/l_o \times 10^{-4}$	V_c(%)	V_{fe}(%)	$\alpha_1 \times 10^{-6}$	$\alpha_0 \times 10^{-6}$	$Q \times 10^{-2}$
5	-4.2	9.8	86.2	14.5	11.8	-1.3
10	-3.86	9.9	86.1	14.5	11.8	-1.6
15	-4.52	9.7	86.3	14.5	11.8	-1.3
20	-4.4	9.8	86.2	14.5	11.8	-1.1
30	-4.5	9.7	86.3	14.5	11.8	-1.1

E finalmente os valores dos residuals se mostram em a tabela A VII.2

Tabela A7.2: Processo I (I): E=117KJ/mol ; n =1; Ko=2.99*10^{14} min^{-1} ; Q=-0.01. Processo (II): E=206 KJ/mol; Ko=9.5*10^{17}; n=0.66; Q= 0.0; Res1=0.0

Process (I)				Process (II)	
β	T_i, K	Res1	Res2	T_i, K	Res2
5	411.6	0.12	0.00018	584.3	-0.061
10	418.9	0.124	-0.0035	593.5	-0.0627
15	424.3	0.128	-0.00067	599.1	-0.063
20	428.5	0.13	0.0028	603.1	-0.064
30	432.4	0.13	-0.0027	608.8	-0.064

$$RES_1 = \frac{Q}{n^2}\frac{RTi^2}{E}$$

$$RES_2 = 2\frac{RT_i}{E} * \left\{1 - \frac{1}{n^2} + nln\left[\frac{Ti^2RK(Ti)}{\beta E}\right]\right\}$$

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- **(* Anexo 8 Haciendo una estimacion del parametro cf de Farjas *)**

```
Clear[Ko, Cf, Ener];
αp = 0.632;
Na = 6.02 * 10^23;
Kb = 1.381 * 10^-23;
R = 0.00831;
Ener = 116.969;
TgKelvin[x_] := 273.15 + x;
β1 = 5;
β2 = 10;
β3 = 15;
β4 = 20;
β5 = 30;
T1 = 138.5;
T2 = 145.8;
T3 = 151.2;
T4 = 155.35;
T5 = 159.3;
rapienfria = {β1, β2, β3, β4, β5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; flujo = rapienfria[[i]];
 listay = AppendTo[listay, {Te^-1, Log[flujo / Te^2]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
resul = NonlinearModelFit[listay,
   -(Ener/R) * y + Log[(R * Ko * Cf)/Ener], {{Ko, 2.99184 * 10^14}, {Cf, 1.01}}, {y}]
Listasali = {};
Listasali = resul[{"BestFitParameters", "ANOVATable", "EstimatedVariance",
    "FitResiduals", "ParameterTable", "ParameterConfidenceIntervals",
    "ParameterConfidenceIntervalTable", "RSquared", "AdjustedRSquared"}]
tablaAnov = resul["ANOVATable"];
valorSS = tablaAnov[[1, 1, 3, 3]];
valorST = tablaAnov[[1, 1, 5, 3]];
Print["valordeR=", Sqrt[1 - valorSS/valorST]]
Listares = {};
Listares = Listasali[[4]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
```

```
{411.65, 418.95, 424.35, 428.5, 432.45}

{{0.00242925, -10.4309}, {0.00238692, -9.77292},
 {0.00235655, -9.39307}, {0.00233372, -9.12485}, {0.00231241, -8.73774}}
```

FittedModel[$23.7798 - 14\,075.7\,y$]

{{Ko → 2.99552×10^{14}, Cf → 0.998674},

	DF	SS	MS
Model	2	452.148	226.074
Error	3	0.00641532	0.00213844
Uncorrected Total	5	452.154	
Corrected Total	4	1.67397	

,

0.00213844, {−0.0173389, 0.0448496, −0.0028397, −0.0558717, 0.0312008},

	Estimate	Standard Error	t Statistic	P-Value
Ko	2.99552×10^{14}	6.87889×10^{-17}	4.35466×10^{30}	2.6706×10^{-92}
Cf	0.998674	0.0206532	48.3544	0.0000194757

,

{{2.99552×10^{14}, 2.99552×10^{14}}, {0.932946, 1.0644}},

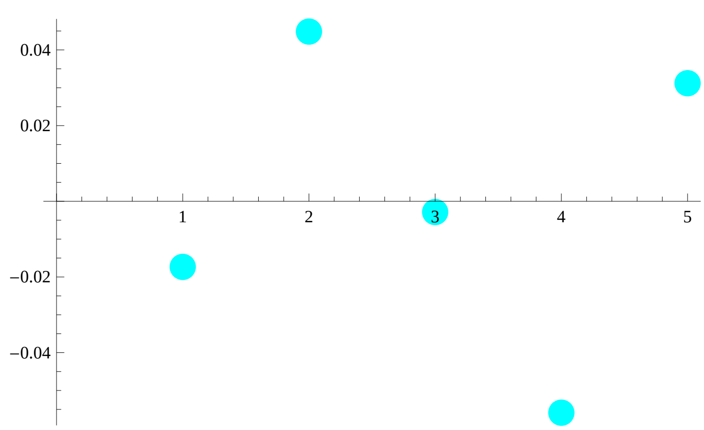
	Estimate	Standard Error	Confidence Interval
Ko	2.99552×10^{14}	6.87889×10^{-17}	{2.99552×10^{14}, 2.99552×10^{14}}
Cf	0.998674	0.0206532	{0.932946, 1.0644}

,

0.999986, 0.999976}

valordeR=0.998082

{−0.0173389, 0.0448496, −0.0028397, −0.0558717, 0.0312008}



⋮

```
(* Anexo 8 b Processo II ,
Haciendo una estimacion del parametro cf de Farjas*)
Clear[Ko];
αp = 0.632;
Na = 6.02 * 10^23;
Kb = 1.381 * 10^-23;
R = 0.00831;
Ener = 206.121;
TgKelvin[x_] := 273.15 + x;
β1 = 5;
β2 = 10;
β3 = 15;
β4 = 20;
β5 = 30;
T1 = 311.2;
T2 = 320.4;
T3 = 326;
T4 = 330;
T5 = 335.7;
rapienfria = {β1, β2, β3, β4, β5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; flujo = rapienfria[[i]];
 listay = AppendTo[listay, {Te^-1, Log[flujo / Te^2]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
resul = NonlinearModelFit[listay,
   -Ener/R * y + Log[(R * Ko * Cf)/Ener], {{Ko, 9.88979 * 10^17}, {Cf, 0.9}}, {y}]
Listasali = {};
Listasali = resul[{"BestFitParameters", "ANOVATable", "EstimatedVariance",
    "FitResiduals", "ParameterTable", "ParameterConfidenceIntervals",
    "ParameterConfidenceIntervalTable", "RSquared", "AdjustedRSquared"}]
tablaAnov = resul["ANOVATable"];
valorSS = tablaAnov[[1, 1, 3, 3]];
valorST = tablaAnov[[1, 1, 5, 3]];
Print["valordeR=", Sqrt[1 - valorSS/valorST]]
Listares = {};
Listares = Listasali[[4]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
```

```
{584.35, 593.55, 599.15, 603.15, 608.85}
```

{{0.0017113, -11.1316}, {0.00168478, -10.4697}, {0.00166903, -10.083}, {0.00165796, -9.8086}, {0.00164244, -9.42195}}

FittedModel[$\boxed{31.3167 - 24\,804.\,y}$]

{{Ko → 9.79972 × 10^{17}, Cf → 1.00915},

	DF	SS	MS
Model	2	520.173	260.087
Error	3	0.0000121801	4.06004×10^{-6}
Uncorrected Total	5	520.173	
Corrected Total	4	1.71133	

, 4.06004 × 10^{-6},

{-0.00110045, 0.00287557, -0.0010261, -0.00120119, 0.000452166},

	Estimate	Standard Error	t Statistic	P-Value
Ko	9.79972×10^{17}	0.	∞	$0. \times 10^{-308}$
Cf	1.00915	0.000909361	1109.74	1.61365×10^{-9}

,

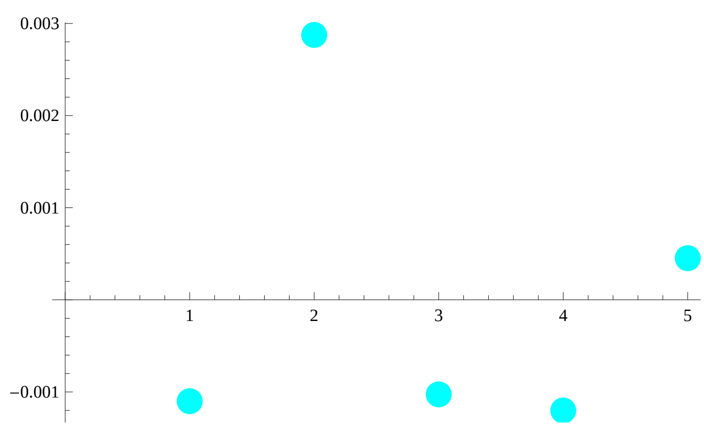
{{9.79972 × 10^{17}, 9.79972 × 10^{17}}, {1.00626, 1.01205}},

	Estimate	Standard Error	Confidence Interval
Ko	9.79972×10^{17}	0.	$\{9.79972 \times 10^{17}, 9.79972 \times 10^{17}\}$
Cf	1.00915	0.000909361	{1.00626, 1.01205}

, 1., 1.}

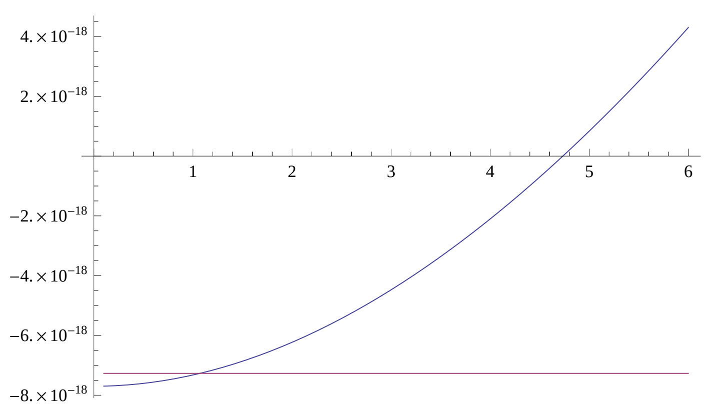
valordeR=0.999996

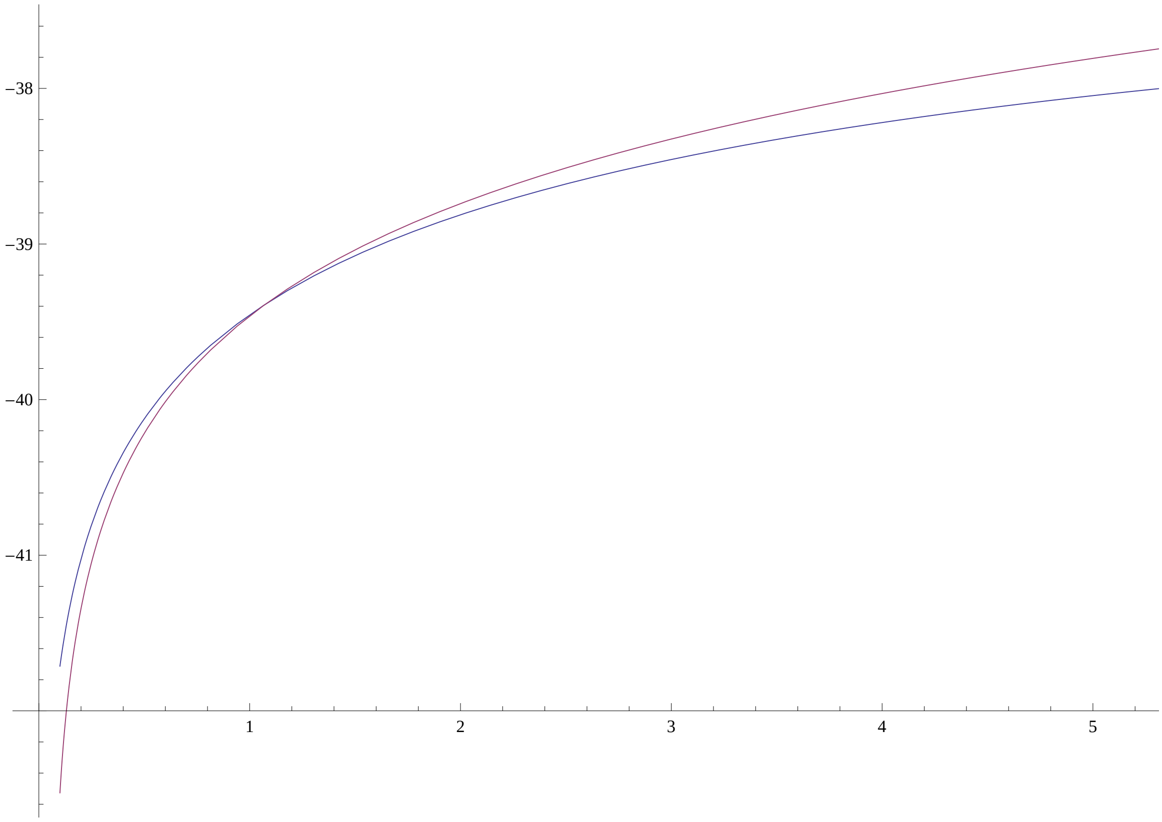
{-0.00110045, 0.00287557, -0.0010261, -0.00120119, 0.000452166}



(* Anexo 9 Hallando a n Primer Proceso *)

```
Ene = 116.969`;
R = 0.00831`; Ko = 2.85 * 10^14; Tp = 428.5; β = 20; Cf = 1;
Clear[n]
P[x_] := N[ExpIntegralE[2, x]]/x; Vx = Ene/(R Tp);
f1[n_] = -n (Ko Cf)^n (Ene/(R β))^(n-1) P[Vx]^n Exp[-Vx] + ((n - 1) (β R) Exp[-Vx])/Ene;
f2[x_] = -(β Ene P[Vx])/(R Tp^2);
f1b[n_] = n Log[Ko Cf P[Vx]] + (n - 1) Log[Ene/(R β)] + Log[n] - Vx;
f2b[n_] = Log[((β Ene) P[Vx])/(R Tp^2) + ((n - 1) (β R) Exp[-Vx])/Ene];
Plot[{f1[x], f2[x]}, {x, 0.1`, 6}, PlotRange → All]
Plot[{f1b[x], f2b[x]}, {x, 0.1`, 6}, PlotRange → All]
FindRoot[
  -n (Ko Cf)^n (Ene/(R β))^(n-1) P[Vx]^n Exp[-Vx] + ((n - 1) (β R) Exp[-Vx])/Ene == -(β Ene P[Vx])/(R Tp^2), {n, 1}]
FindRoot[n Log[Ko Cf P[Vx]] + (n - 1) Log[Ene/(R β)] + Log[n] - Vx ==
  Log[((β Ene) P[Vx])/(R Tp^2) + ((n - 1) (β R) Exp[-Vx])/Ene], {n, 1}]
```





{n → 1.07022}

{n → 1.07022}

■ **(* Anexo 9 b Programa para calcular os erros de n ,atualiçado para β=5 Processo II*)**

```
n = 0.66;
Ene = 206.211;
R = 0.00831;
Ko = 9.51 * 10^17;
Tp = 584.35;
β = 5;
Cf = 1.00;
DeltaT = 0.1;
δEne = 0.2;
```

$$P[x\_] := \frac{N[\mathrm{ExpIntegralE}[2, x]]}{x}$$

$$Vx = \frac{Ene}{R * Tp};$$

deltan =

$$\left(n * (Ko * Cf)^{n} * \left(\frac{Ene}{\beta * R}\right)^{n-1} * Exp[-Vx] * P[Vx]^{n} * \frac{Ene}{R * Tp^{2}} * \left(\frac{n * (P[Vx])^{-1} * Exp[-Vx]}{Vx^{2}} + 1\right) + \frac{\beta * Exp[-Vx]}{Tp^{2}} * n + \frac{2 * \beta * Ene * P[Vx]}{R * Tp^{3}} \right) \Big/ \left(\left(\frac{Ene}{\beta * R}\right)^{n-1} * P[Vx]^{n} * Exp[-Vx] * (Ko * Cf)^{n} * \left(1 + Log\left[\left(\frac{Ko * Cf * Ene * P[Vx]}{\beta * R}\right)^{n}\right]\right) + \frac{\beta * R * Exp[-Vx]}{Ene} \right) * DeltaT + \left(\left((Ko * Cf)^{n} * \left(\frac{Ene}{\beta * R}\right)^{n-1} * Exp[-Vx] * P[Vx]^{n} * \left(\frac{n * (n-1)}{Ene} + \frac{n^{2} * (P[Vx])^{-1} * Exp[-Vx] * R * Tp}{Ene\hat{}2} + \frac{n}{R * Tp}\right) + \frac{(n-1) * \beta * R * Exp[-Vx]}{Ene} * \left(\frac{1}{Ene} + \frac{1}{R * Tp}\right) + \frac{\beta * P[Vx]}{R * Tp\hat{}2} + \frac{\beta * Exp[-Vx]}{Ene * Tp} \right) * \delta Ene \right) \Big/ \left(\left(\frac{Ene}{\beta * R}\right)^{n-1} * P[Vx]^{n} * Exp[-Vx] * (Ko * Cf)^{n} * \left(1 + Log\left[\left(\frac{Ko * Cf * Ene * P[Vx]}{\beta * R}\right)^{n}\right]\right) + \frac{\beta * R * Exp[-Vx]}{Ene} \right)$$

```
n + deltan
n - deltan
```

0.0444671

0.704467

0.615533

▪ (* Anexo 10 Calculo Dos Erros en KO *)

In[1]:=
```
Ene = 116.969;
Cf = 1.0;
β = 10;
R = 0.00831;
Ti = 418.95;
deltaCf = 0.01;
deltaEne = 0.2;
deltaP = 5 * 10^-19;
ListaLefFTTeor = {};
listLefFTexpS = {};
```

$$Pt[T\_] = \frac{N\left[ExpIntegralE\left[2, \frac{Ene}{R*T}\right]\right]}{\frac{Ene}{R*T}};$$

```
Pt[Ti];
```

$$valorKO = \frac{R*\beta}{Cf*Ene*Pt[Ti]}$$

$$deltaKo2 = R*\beta*\left(\frac{deltaCf}{(Cf\wedge 2)\ Ene*Pt[Ti]} + \frac{deltaP}{(Pt[Ti]\wedge 2)*Ene*Cf} + \frac{deltaEne}{Cf*Pt[Ti]*Ene\wedge 2}\right)$$

```
Print["Ko+δKo2 = ", valorKO + deltaKo2]
Print["Ko-δKo2 = ", valorKO - deltaKo2]
```

Out[13]= 3.31005×10^{14}

Out[14]= 8.09857×10^{13}

Ko+δKo2 = 4.11991×10^{14}

Ko−δKo2 = 2.50019×10^{14}

■ (* Anexo 10 b Calculo Dos Erros en KO *)

```
deltaKo = (R * β)/(Pt[Ti]) * (deltaCf/((Cf^2) * Ene) + deltaEne/(Cf * Ene^2));
Print["Ko+δKo = ", valorKO + deltaKo]
Print["Ko-δKo = ", valorKO - deltaKo]
Ene = 206.211;
Cf = 1.0;
β = 30;
R = 0.00831;
Ti = 608.85;
deltaCf = 0.01;
deltaEne = 0.2;
deltaP = 5 * 10^-22;
ListaLefFTTeor = {};
listLefFTexpS = {};
Pt[T_] = N[ExpIntegralE[2, Ene/(R*T)]] / (Ene/(R*T));
Pt[Ti];
valorKO = (R * β)/(Cf * Ene * Pt[Ti])

deltaKo2 = R * β * (deltaCf/((Cf^2) Ene * Pt[Ti]) + deltaP/((Pt[Ti]^2) * Ene * Cf) + deltaEne/(Cf * Pt[Ti] * Ene^2))

Print["Ko+δKo2 = ", valorKO + deltaKo2]
Print["Ko-δKo2 = ", valorKO - deltaKo2]
```

1.05592×10^{18}

4.72712×10^{17}

Ko+δKo2 = 1.52863×10^{18}

Ko-δKo2 = 5.83209×10^{17}

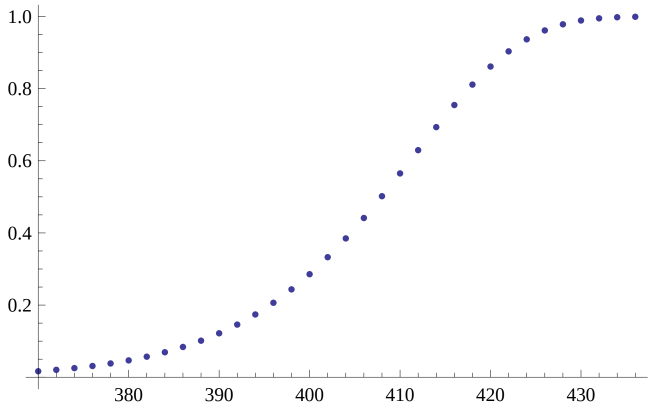
Anexo 11

```
(*O programa usado para calcular no. Neste programa
 α (T) é a função de interpolação obtida da data experimentai ,
a mesma é diferente para cada taxa de aquecimento β *)
```

```
In[28]:= Ene = 116.969;
Ko = 2.99184 * 10^14;
Cf = 1.0;
β = 5;
R = 0.00831;
```

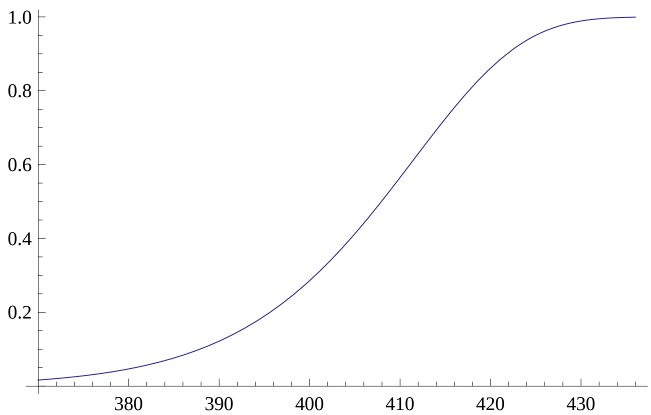
```
In[33]:= Listaexpft = {{370, 0.01651760622200371`}, {372, 0.02043987958258464`},
    {374, 0.025225522215615692`}, {376, 0.031046125340003616`},
    {378, 0.03810190930459556`}, {380, 0.046624631722749665`},
    {382, 0.056880022112787865`}, {384, 0.06916931528982617`},
    {386, 0.08382929198766287`}, {388, 0.10123003753123139`},
    {390, 0.12176940521334956`}, {392, 0.14586294026377278`}, {394, 0.1739278227326989`},
    {396, 0.20635929206972237`}, {398, 0.2434981299979856`}, {400, 0.2855882535426786`},
    {402, 0.33272449952435434`}, {404, 0.3847924728116796`}, {406, 0.44140504078160203`},
    {408, 0.5018436741797023`}, {410, 0.5650169974865198`}, {412, 0.6294526878466693`},
    {414, 0.6933405814716751`}, {416, 0.754642170512299`}, {418, 0.8112721570151054`},
    {420, 0.8613401219962658`}, {422, 0.9034165591934372`}, {424, 0.9367643587650922`},
    {426, 0.9614660315452251`}, {428, 0.9783911188275345`}, {430, 0.9889923252021308`},
    {432, 0.9949813145170145`}, {434, 0.9979864940641315`}, {436, 0.9993027587390773`}};
gflistexp = ListPlot[Listaexpft]
α = Interpolation[Listaexpft]
gfinterft = Plot[α[x], {x, 370.`, 436.`}]
Show[gfinterft, gflistexp]
```

Out[34]=

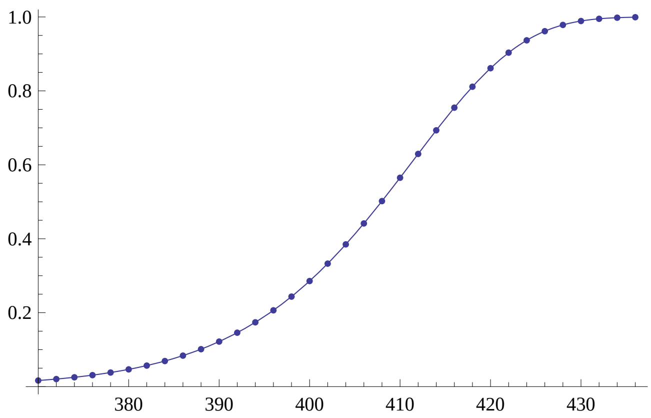



```
Out[35]= InterpolatingFunction[{{370., 436.}}, <>]
```

Out[36]=



Out[37]=



In[38]:=
```
fnte[T_] = 1 - α[T];
derivadafnt[T_] = ∂T (fnte[T]);
LefTFTTeor[T_, no_] = (-derivadafnt[T] * β/Ko * Exp[Ene/(R * T)]) ^ (1/no)
```

Out[40]= $1.67121 \times 10^{-14\,\frac{1}{no}} \left(e^{14075.7/T}\ \text{InterpolatingFunction}[\{\{370., 436.\}\}, <>][T]\right)^{\frac{1}{no}}$

In[41]:=
```
Listaexp = {};
Do[Listaexp = AppendTo[Listaexp, {T, fnte[T]}], {T, 370, 436, 2}]
```

In[43]:=
```
ajuste = NonlinearModelFit[Listaexp, LefTFTTeor[T, no], {{no, 0.5}}, {T}]

Listasali = {};
Listasali = ajuste[{"BestFitParameters", "ANOVATable", "EstimatedVariance",
    "FitResiduals", "ParameterTable", "ParameterConfidenceIntervals",
    "ParameterConfidenceIntervalTable", "RSquared", "AdjustedRSquared"}]
```

Out[43]= FittedModel[$1.68459 \times 10^{-14} \left(e^{14075.7/T}\ \text{InterpolatingFunction}[\{\{370., 436.\}\}, <>][T]\right)^{0.999749}$]

Out[45]= {{no → 1.00025},

	DF	SS	MS
Model	1	14.8838	14.8838
Error	33	4.75437×10^{-6}	1.44072×10^{-7}
Uncorrected Total	34	14.8838	
Corrected Total	33	4.71203	

,

1.44072×10^{-7}, {-0.0018203, 0.000500081, -0.000428471, -0.000391476, -0.00035212, -0.000310149, -0.000265375, -0.000217722, -0.000167283, -0.000114383, -0.0000596717, -4.2072×10^{-6}, 0.0000504468, 0.000102146, 0.000148132, 0.000185079, 0.000209271, 0.00021696, 0.000204945, 0.000171386, 0.000116764, 0.0000448067, -0.0000369459, -0.000117398, -0.000183372, -0.000222449, -0.000226709, -0.000196155, -0.000140031, -0.0000746016, -0.0000174813, 0.0000191555, 0.0000327884, -0.0000958284},

	Estimate	Standard Error	t Statistic	P-Value
no	1.00025	0.000319933	3126.44	7.21434×10^{-92}

, {{0.9996, 1.0009}},

	Estimate	Standard Error	Confidence Interval
no	1.00025	0.000319933	{0.9996, 1.0009}

, 1., 1.}

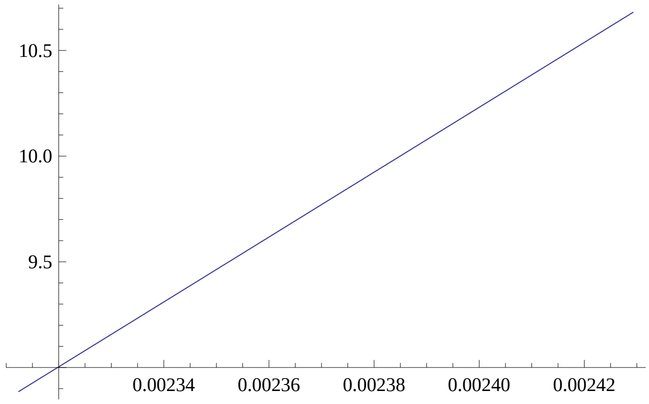
Anexo 12(*calculodeEFriedmanIprocesom7.nb*)

```
In[1]:= R = 0.00831;
TgKelvin[x_] := 273.15 + x;
ϕ1 = 5;
ϕ2 = 10;
ϕ3 = 15;
ϕ4 = 20;
ϕ5 = 30;
T1 = 138.5;
T2 = 145.8;
T3 = 151.2;
T4 = 155.35;
T5 = 159.3
vdyi1 = 4.431 * 10^-6;
vdyi2 = 4.95 * 10^-6;
vdyi3 = 4.463 * 10^-6;
vdyi4 = 4.494 * 10^-6;
vdyi5 = 4.95 * 10^-6;
rapienfria = {ϕ1, ϕ2, ϕ3, ϕ4, ϕ5};
valoresdeyie = {vdyi1, vdyi2, vdyi3, vdyi4, vdyi5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; valordey = valoresdeyie[[i]];
 listay = AppendTo[listay, {Te^-1, -Log[rapienfria[[i]] * valordey]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
resul = NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
l = Normal[resul]
NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
Print["Pendiente =", " ", pend = l[[2, 1]]]
Print["intercepto =", " ", Interc = l[[1]]]
Print["Energiaactiva=", " ", Energiaactiva1 = pend * R]

Out[12]= 159.3

Out[23]= {411.65, 418.95, 424.35, 428.5, 432.45}

Out[26]= {{0.00242925, 10.7174}, {0.00238692, 9.91354},
 {0.00235655, 9.61164}, {0.00233372, 9.31704}, {0.00231241, 8.81493}}

Out[27]= FittedModel[ -26.602 + 15 347.1 x ]

Out[28]= -26.602 + 15 347.1 x

Out[29]= FittedModel[ -26.602 + 15 347.1 x ]
```

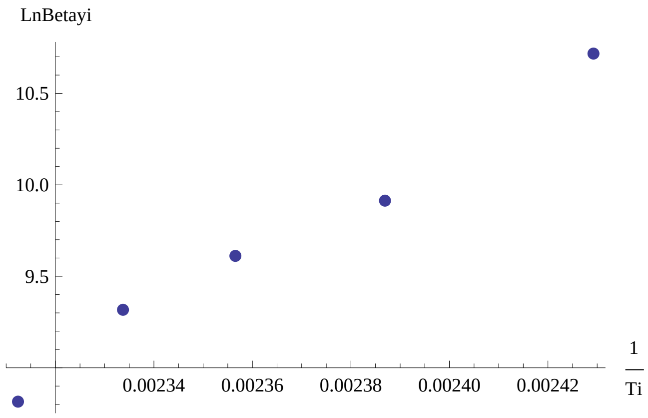
```
Pendiente = 15 347.1

intercepto = -26.602

Energiaactiva = 127.534
```

In[33]:=
```
ajuste[x_] := Interc + pend * x
Gf1 = Plot[ajuste[x], {x, 0.0024292481476982874, 0.0023124060585038735`}]
Gf2 = ListPlot[listay, PlotStyle -> PointSize[0.02], AxesLabel -> {Ti^-1, LnBetayi}]
Show[Gf1, Gf2, AxesLabel -> {Ti^-1, LnBetayi}]
NonlinearModelFit[listay, a + b x, {a, b}, {x}][
 {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
  "ParameterTStatistics", "ParameterConfidenceIntervalTable"}]
```

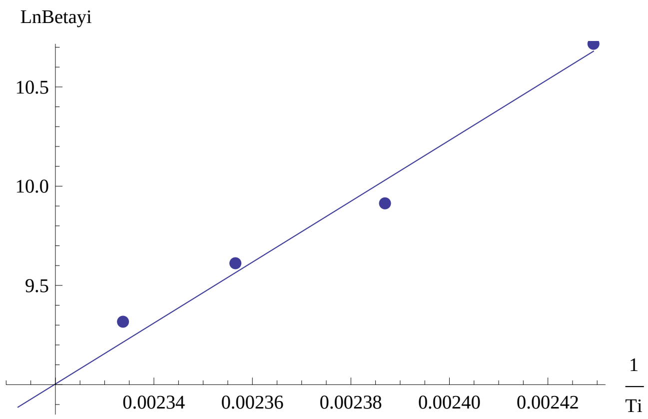
Out[34]=



Out[35]=



Out[36]=



Out[37]= {

	DF	SS	MS
Model	2	470.002	235.001
Error	3	0.0330961	0.011032
Uncorrected Total	5	470.036	
Corrected Total	4	2.01548	

, {0.00223905, 0.00089751}, 0.999883, 0.99993, {-9.82844, 13.405},

	Estimate	Standard Error	Confidence Interval
a	-26.602	2.70663	{-35.2157, -17.9883}
b	15 347.1	1144.88	{11 703.5, 18 990.6}

}

In[38]:=
```
lm = LinearModelFit[listay, x, x]
listasalida = {};
listasalida = lm[{"AdjustedRSquared", "RSquared", "FitResiduals"}]
√listasalida[[2]]
Listares = {};
Listares = listasalida[[3]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
listasalida2 = {};
listasalida2 = lm[{"FitResiduals",
    "SinglePredictionConfidenceIntervalTable ", "ParameterConfidenceRegion "}];
errors = listasalida2[[1]]
tablasimpledeintecnf = listasalida2[[2]]
Observed = {}
Do[Observed = AppendTo[Observed, tablasimpledeintecnf[[1, 1, i, 1]]], {i, 2, 6}]
Observed
predicted = {};
Do[predicted = AppendTo[predicted, tablasimpledeintecnf[[1, 1, i, 2]]], {i, 2, 6}]
predicted
ListPlot[Transpose[{predicted, errors}], PlotStyle → PointSize[0.02`]]
gplaj = Plot[lm[x], {x, 0.0024292481476982874, 0.0023124060585038735`}];
ci = {}
Do[ci = AppendTo[ci, tablasimpledeintecnf[[1, 1, i, 4]]], {i, 2, 6}]
ci
(xval = First /@ listay; predicted = Transpose[{xval, predicted}];
 lowerCI = Transpose[{xval, First /@ ci}]; upperCI = Transpose[{xval, Last /@ ci}]);
gfrs = ListPlot[{listay, predicted, lowerCI, upperCI}, Joined → {False, True, True, True},
  PlotStyle → {Automatic, Automatic, Dashing[{0.05`, 0.05`}], Dashing[{0.05`, 0.05`}]}]
Show[gfrs, gplaj, AxesLabel -> {Ti^-1, LnBetayi}]
```

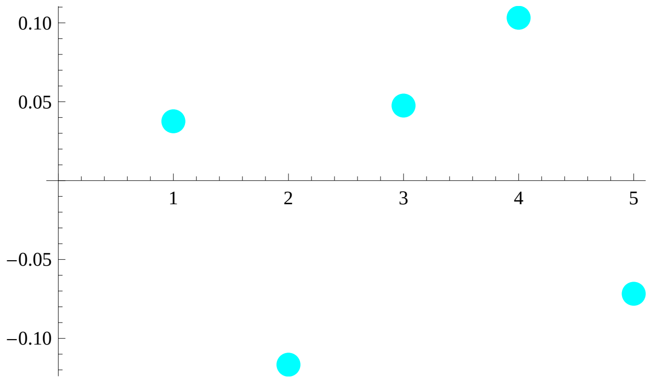
Out[38]= FittedModel[$-26.602 + 15\,347.1\,x$]

Out[40]= {0.978105, 0.983579, {0.0376074, -0.116685, 0.0475738, 0.103236, -0.0717323}}

Out[41]= 0.991756

Out[43]= {0.0376074, -0.116685, 0.0475738, 0.103236, -0.0717323}

Out[44]=



Out[47]= {0.0376074, -0.116685, 0.0475738, 0.103236, -0.0717323}

Out[48]=

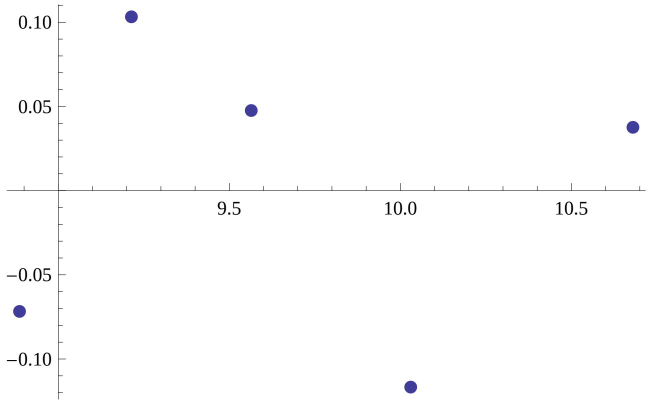
Observed	Predicted	Standard Error	Confidence Interval
10.7174	10.6798	0.137326	{10.2428, 11.1169}
9.91354	10.0302	0.118072	{9.65447, 10.406}
9.61164	9.56407	0.115355	{9.19695, 9.93118}
9.31704	9.2138	0.12009	{8.83162, 9.59598}
8.81493	8.88666	0.129214	{8.47544, 9.29787}

Out[49]= { }

Out[51]= {10.7174, 9.91354, 9.61164, 9.31704, 8.81493}

Out[54]= {10.6798, 10.0302, 9.56407, 9.2138, 8.88666}

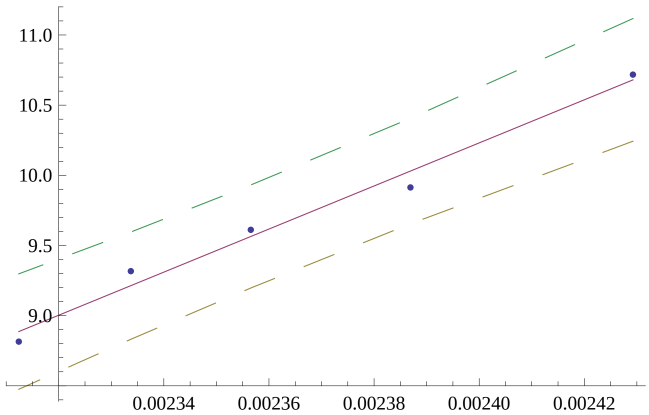
Out[55]=



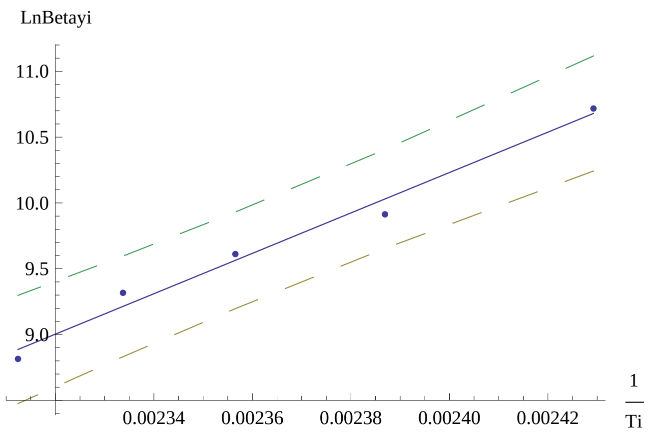
Out[57]= { }

Out[59]= {{10.2428, 11.1169}, {9.65447, 10.406},
{9.19695, 9.93118}, {8.83162, 9.59598}, {8.47544, 9.29787}}

Out[60]=


11.0
10.5
10.0
9.5
9.0
0.00234
0.00236
0.00238
0.00240
0.00242

Out[61]=


LnBetayi
11.0
10.5
10.0
9.5
9.0
0.00234
0.00236
0.00238
0.00240
0.00242
1/Ti

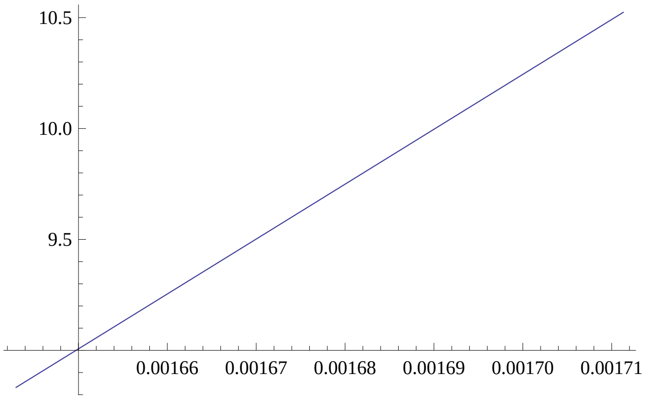
- **Processo II**

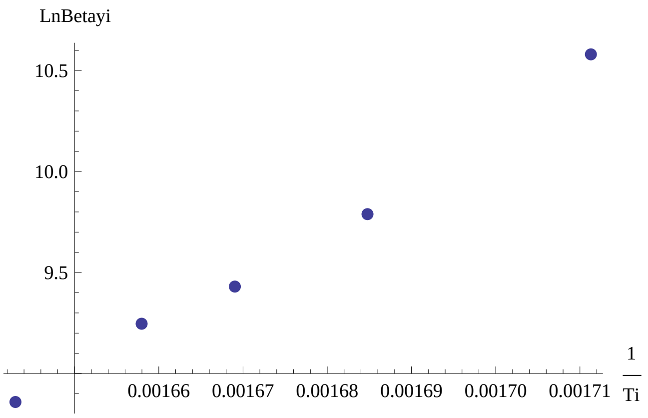
```
R = 0.00831;
TgKelvin[x_] := 273.15 + x;
ϕ1 = 5;
ϕ2 = 10;
ϕ3 = 15;
ϕ4 = 20;
ϕ5 = 30;
T1 = 311.2;
T2 = 320.4;
T3 = 326;
T4 = 330;
T5 = 335.5
vdyi1 = 5.083 * 10^-6;
vdyi2 = 5.606 * 10^-6;
vdyi3 = 5.349 * 10^-6;
vdyi4 = 4.822 * 10^-6;
vdyi5 = 4.736 * 10^-6;
rapienfria = {ϕ1, ϕ2, ϕ3, ϕ4, ϕ5};
valoresdeyie = {vdyi1, vdyi2, vdyi3, vdyi4, vdyi5};
listatepgradCent = {T1, T2, T3, T4, T5};
TemperaturaKelvin = {};
Do[ti = listatepgradCent[[i]];
 TemperaturaKelvin = AppendTo[TemperaturaKelvin, TgKelvin[ti]],
 {i, 1, Length[listatepgradCent]}]
TemperaturaKelvin
listay = {};
Do[Te = TemperaturaKelvin[[i]]; valordey = valoresdeyie[[i]];
 listay = AppendTo[listay, {Te^-1, -Log[rapienfria[[i]] * valordey]}],
 {i, 1, Length[TemperaturaKelvin]}]
listay
resul = NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
l = Normal[resul]
NonlinearModelFit[listay, a + b * x, {a, b}, {x}]
Print["Pendiente =", " ", pend = l[[2, 1]]]
Print["intercepto =", " ", Interc = l[[1]]]
Print["Energiaactiva=", " ", Energiaactiva1 = pend * R]
```

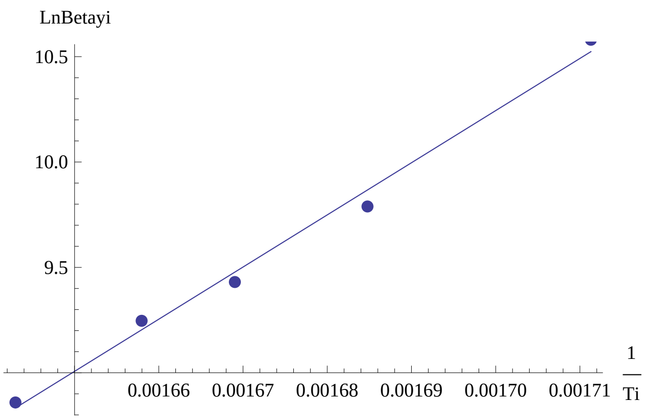
```
335.5

{584.35, 593.55, 599.15, 603.15, 608.65}

{{0.0017113, 10.5802}, {0.00168478, 9.78909},
 {0.00166903, 9.43055}, {0.00165796, 9.24659}, {0.00164298, 8.85912}}

FittedModel[ -31.8238 + 24 745.8 x ]

-31.8238 + 24 745.8 x

FittedModel[ -31.8238 + 24 745.8 x ]
```

```
Pendiente = 24745.8

intercepto = -31.8238

Energiaactiva= 205.638
```

```
ajuste[x_] := Interc + pend * x
Gf1 = Plot[ajuste[x], {x, 0.0017113031573543255, 0.0016429803663846217}]
Gf2 = ListPlot[listay, PlotStyle -> PointSize[0.02], AxesLabel -> {Ti^-1, LnBetayi}]
Show[Gf1, Gf2, AxesLabel -> {Ti^-1, LnBetayi}]
NonlinearModelFit[listay, a + b x, {a, b}, {x}][
 {"ANOVATable", "ParameterPValues", "AdjustedRSquared", "RSquared",
  "ParameterTStatistics", "ParameterConfidenceIntervalTable"}]
```







	DF	SS	MS
Model	2	460.671	230.335
Error	3	0.0140447	0.00468157
Uncorrected Total	5	460.685	
Corrected Total	4	1.69722	

{0.000700773, 0.000320283}, 0.999949, 0.99997, {-14.5722, 18.9613},

	Estimate	Standard Error	Confidence Interval
a	-31.8238	2.18387	{-38.7739, -24.8738}
b	24 745.8	1305.07	{20 592.5, 28 899.1}

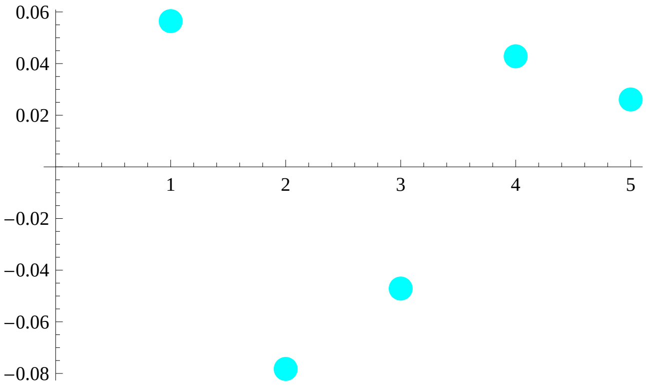
```
lm = LinearModelFit[listay, x, x]
listasalida = {};
listasalida = lm[{"AdjustedRSquared", "RSquared", "FitResiduals"}]
√listasalida[[2]]
Listares = {};
Listares = listasalida[[3]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.04]}]
listasalida2 = {};
listasalida2 = lm[{"FitResiduals",
    "SinglePredictionConfidenceIntervalTable", "ParameterConfidenceRegion"}];
errors = listasalida2[[1]]
tablasimpledeintecnf = listasalida2[[2]]
Observed = {}
Do[Observed = AppendTo[Observed, tablasimpledeintecnf[[1, 1, i, 1]]], {i, 2, 6}]
Observed
predicted = {};
Do[predicted = AppendTo[predicted, tablasimpledeintecnf[[1, 1, i, 2]]], {i, 2, 6}]
predicted
ListPlot[Transpose[{predicted, errors}], PlotStyle → PointSize[0.02`]]
gplaj = Plot[lm[x], {x, 0.0017113031573543255, 0.0016429803663846217}];
ci = {}
Do[ci = AppendTo[ci, tablasimpledeintecnf[[1, 1, i, 4]]], {i, 2, 6}]
ci
(xval = First /@ listay; predicted = Transpose[{xval, predicted}];
 lowerCI = Transpose[{xval, First /@ ci}]; upperCI = Transpose[{xval, Last /@ ci}]);
gfrs = ListPlot[{listay, predicted, lowerCI, upperCI}, Joined → {False, True, True, True},
  PlotStyle → {Automatic, Automatic, Dashing[{0.05`, 0.05`}], Dashing[{0.05`, 0.05`}]}]
Show[gfrs, gplaj, AxesLabel -> {Ti^-1, LnBetayi}]
```

FittedModel[$-31.8238 + 24\,745.8\,x$]

{0.988966, 0.991725, {0.0564464, -0.0782511, -0.0471187, 0.0428255, 0.0260978}}

0.995854

{0.0564464, -0.0782511, -0.0471187, 0.0428255, 0.0260978}



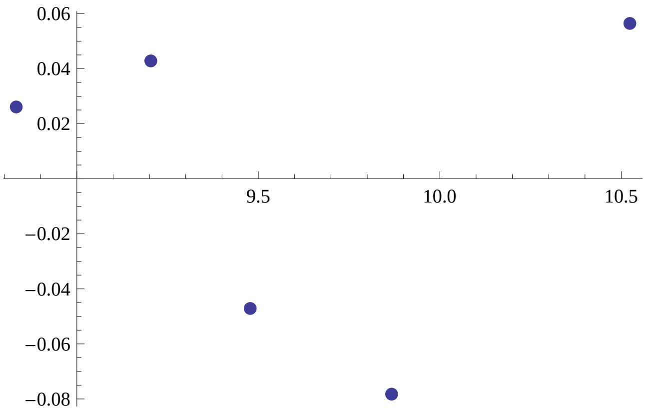
{0.0564464, -0.0782511, -0.0471187, 0.0428255, 0.0260978}

Observed	Predicted	Standard Error	Confidence Interval
10.5802	10.5237	0.0899403	{10.2375, 10.81}
9.78909	9.86734	0.0764576	{9.62402, 10.1107}
9.43055	9.47767	0.0751508	{9.23851, 9.71683}
9.24659	9.20376	0.0775495	{8.95697, 9.45056}
8.85912	8.83302	0.084702	{8.56346, 9.10258}

{}

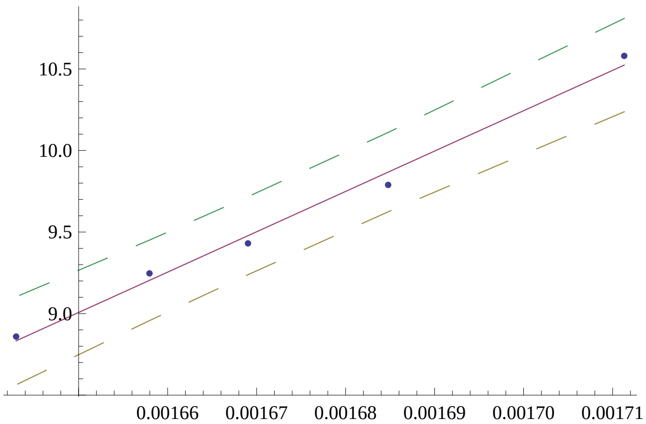
{10.5802, 9.78909, 9.43055, 9.24659, 8.85912}

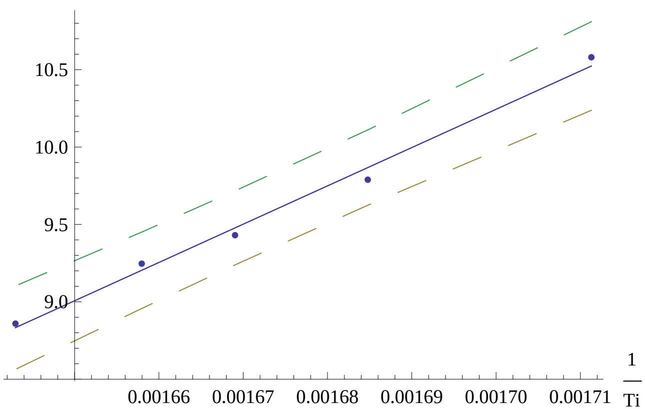
{10.5237, 9.86734, 9.47767, 9.20376, 8.83302}



{}

{{10.2375, 10.81}, {9.62402, 10.1107},
{9.23851, 9.71683}, {8.95697, 9.45056}, {8.56346, 9.10258}}


10.5
10.0
9.5
9.0
0.00166
0.00167
0.00168
0.00169
0.00170
0.00171


LnBetayi
10.5
10.0
9.5
9.0
0.00166
0.00167
0.00168
0.00169
0.00170
0.00171
1/Ti

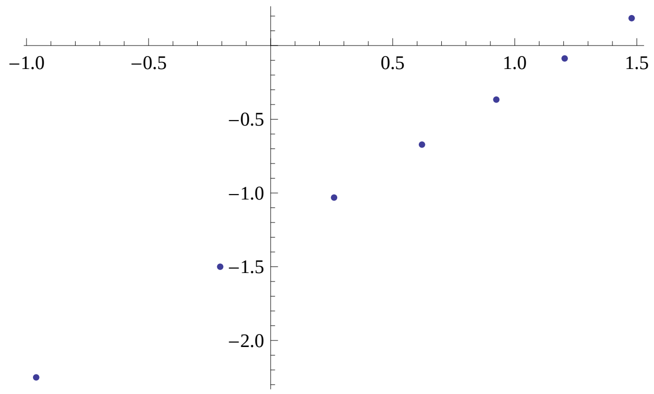
r

■ Anexo 13 Hallando a n(T) y K(T)

```
dTdq1 = 0.382727;
dTdq2 = 0.81325;
dTdq3 = 1.29671;
dTdq4 = 1.85862;
dTdq5 = 2.52029;
dTdq6 = 3.33453;
dTdq7 = 4.38734;
ξ1 = 0.1;
ξ2 = 0.2;
ξ3 = 0.3;
ξ4 = 0.4;
ξ5 = 0.5;
ξ6 = 0.6;
ξ7 = 0.7;
```

```
Listadedtdq = {dTdq1, dTdq2, dTdq3, dTdq4, dTdq5, dTdq6, dTdq7}
ListadeFraT = {ξ1, ξ2, ξ3, ξ4, ξ5, ξ6, ξ7}
Listatrabajo = {};
Do[Listatrabajo =
  AppendTo[Listatrabajo, {Log[Listadedtdq[[i]]], Log[Log[1/(1 - ListadeFraT[[i]])]]}],
 {i, 1, Length[ListadeFraT]}]
Listatrabajo
ListPlot[Listatrabajo]
resul =
 NonlinearModelFit[Listatrabajo, interc + pendt * x, {{interc, -0.1}, {pendt, 3}}, {x}]
Listasali = {};
Listasali = resul[{"BestFitParameters", "ANOVATable", "EstimatedVariance",
    "FitResiduals", "ParameterTable", "ParameterConfidenceIntervals",
    "ParameterConfidenceIntervalTable", "RSquared", "AdjustedRSquared"}]
tablaAnov = resul["ANOVATable"];
valorSS = tablaAnov[[1, 1, 3, 3]];
valorST = tablaAnov[[1, 1, 5, 3]];
Print["valordeR=", Sqrt[1 - valorSS/valorST]]
Listares = {};
Listares = Listasali[[4]]
ListPlot[Listares, PlotStyle → {Hue[0.5], PointSize[0.02]}]
```

```
{0.382727, 0.81325, 1.29671, 1.85862, 2.52029, 3.33453, 4.38734}

{0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7}

{{-0.960433, -2.25037}, {-0.206717, -1.49994},
 {0.25983, -1.03093}, {0.619834, -0.671727},
 {0.924374, -0.366513}, {1.20433, -0.0874216}, {1.47872, 0.185627}}
```



FittedModel[$-1.2913 + 0.999365\,x$]

{{interc → -1.2913, pendt → 0.999365},

	DF	SS	MS
Model	2	9.00443	4.50222
Error	5	7.13862×10^{-6}	1.42772×10^{-6}
Uncorrected Total	7	9.00444	
Corrected Total	6	4.3283	

, 1.42772×10^{-6},

{0.000756846, -0.00205363, 0.000705308, 0.000133459, 0.0010013, 0.000312728, -0.000856011},

	Estimate	Standard Error	t Statistic	P-Value
interc	−1.2913	0.000527318	−2448.81	2.1554×10^{-16}
pendt	0.999365	0.000573968	1741.15	1.1861×10^{-15}

,

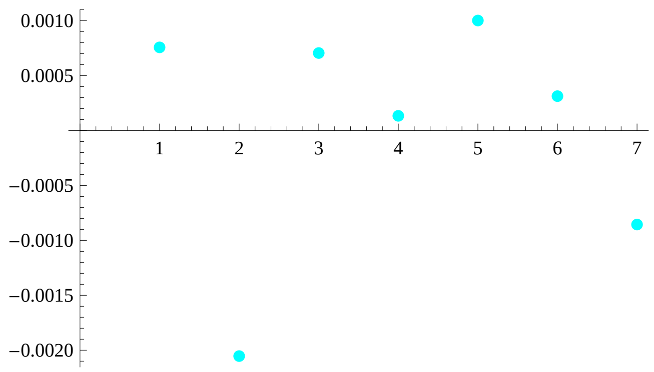
{{-1.29266, -1.28995}, {0.997889, 1.00084}},

	Estimate	Standard Error	Confidence Interval
interc	−1.2913	0.000527318	{−1.29266, −1.28995}
pendt	0.999365	0.000573968	{0.997889, 1.00084}

, 0.999999, 0.999999}

valordeR=0.999999

{0.000756846, -0.00205363, 0.000705308,
0.000133459, 0.0010013, 0.000312728, -0.000856011}



```
varK
valon
```

```
varK
```

```
valon
```

Anexo 14 a Dilatação Relativa, Processo I

β = 5

T	l(T)
387.871	0.0000359
395.631	0.0000718
400.636	0.0001077
404.554	0.0001436
407.942	0.0001795
411.089	0.0002154
414.214	0.0002513
417.787	0.0002872
421.823	0.0003231
430	0.000359

valor de L1= $(\delta l/l)_{fin1}$ =0.000359

β = 10

T	l(T)
395.028	0.0000364
403.72	0.0000728
408.264	0.0001092
412.329	0.0001456
415.846	0.000182
419.113	0.0002184
422.358	0.0002548
425.861	0.0002912
430.263	0.0003276
439	0.000364

valor de L1= $(\delta l/l)_{fin1}$ =0.000364

β = 15

T	l(T)
399.335	0.0000394
407.553	0.0000788
412.858	0.0001182
417.013	0.0001576
420.609	0.000197
423.949	0.0002364
427.268	0.0002758
430.851	0.0003152
435.355	0.0003546
444.4	0.000394

valor de L1= $(\delta l/l)_{fin1}$ =0.000394

$\beta = 20$

T	l(T)
402.447	0.0000412
410.791	0.0000824
416.18	0.0001236
420.4	0.0001648
424.053	0.000206
427.447	0.0002472
430.819	0.0002884
434.461	0.0003296
439.039	0.0003708
447	0.000412

valor de L1= $(\delta l/l)_{fin1}$ =0.000412

$\boldsymbol{\beta} = \mathbf{30}$

T	l(T)
406.914	0.0000418
415.442	0.0000836
420.95	0.0001254
425.266	0.0001672
429.001	0.000209
432.473	0.0002508
435.924	0.0002926
439.65	0.0003344
444.335	0.0003762
454	0.000418

valor de L1= $(\delta l/l)_{fin1}$ =0.000418

Anexo 14 b Dilatação Relativa, Processo II

β = 5

T	l(T)
543	0.0000515
555.74	0.000103
564.355	0.0001545
571.13	0.000206
577.15	0.0002575
582.75	0.000309
587.97	0.0003605
593.89	0.000412
601.36	0.0004635
611	0.000515

valor de L1= $(\delta l/l)_{fin1}$ =0.000515

β = 10

T	l(T)
550.49	0.0000529
564.14	0.0001058
573.015	0.0001587
579.995	0.0002116
586.06	0.0002645
591.72	0.0003174
597.36	0.0003703
603.465	0.0004232
611.175	0.0004761
623	0.000529

valor de L1= $(\delta l/l)_{fin1}$ =0.000529

β = 15

T	l(T)
555.28	0.000054
569.17	0.000108
578.2	0.000162
585.31	0.000216
591.485	0.00027
597.245	0.000324
602.98	0.000378
609.21	0.000432
617.06	0.000486
627	0.00054

valor de L1= $(\delta l/l)_{fin1}$ =0.00054

β = **20**

T	l(T)
558.73	0.0000588
572.79	0.0001176
581.935	0.0001764
589.135	0.0002352
595.39	0.000294
601.225	0.0003528
607.04	0.0004116
613.345	0.0004704
621.305	0.0005292
631.4	0.000588

valor de L1= $(\delta l/l)_{fin1}$ =0.000588

β = **30**

T	l(T)
563.67	0.0000601
577.975	0.0001202
587.28	0.0001803
594.61	0.0002404
600.98	0.0003005
606.925	0.0003606
612.84	0.0004207
619.275	0.0004808
627.385	0.0005409
639	0.000601

valor de L1= $(\delta l/l)_{fin1}$ =0.000601

- **Anexo 15 Version CHT a TTT(* e necesario ter processadas as listas das fracT Vs B antes de comenzar,ListaFTVST[q] *)**

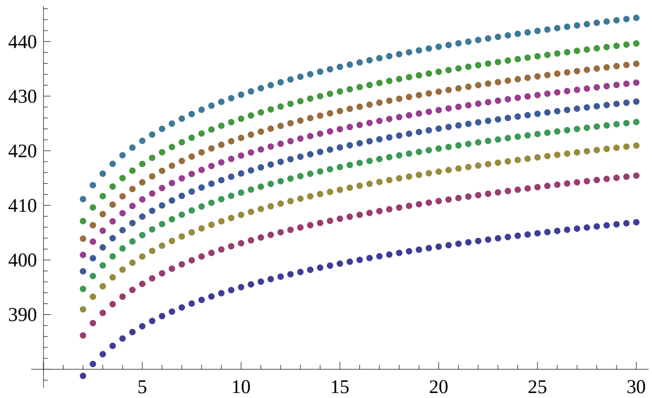
- **Armando (beta T)**

```
ListaBT[0.1] = {};
ListaBT[0.2] = {};
ListaBT[0.3] = {};
ListaBT[0.4] = {};
ListaBT[0.5] = {};
ListaBT[0.6] = {};
ListaBT[0.7] = {};
ListaBT[0.8] = {};
ListaBT[0.9] = {};
ListaBTp[0.1] = {};
ListaBTp[0.2] = {};
ListaBTp[0.3] = {};
ListaBTp[0.4] = {};
ListaBTp[0.5] = {};
ListaBTp[0.6] = {};
ListaBTp[0.7] = {};
ListaBTp[0.8] = {};
ListaBTp[0.9] = {};


(* Este grupo esta llenando las listas BT para cada fracion transformada*)
Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 1, If[z >= 0.9, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.9] = AppendTo[ListaBTp[0.9], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.9] = AppendTo[ListaBT[0.9],
    {-ListaBTp[0.9][[i, 2]], ListaBTp[0.9][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.9]]}];


Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.9, If[z >= 0.8, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.8] = AppendTo[ListaBTp[0.8], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.8] = AppendTo[ListaBT[0.8],
```

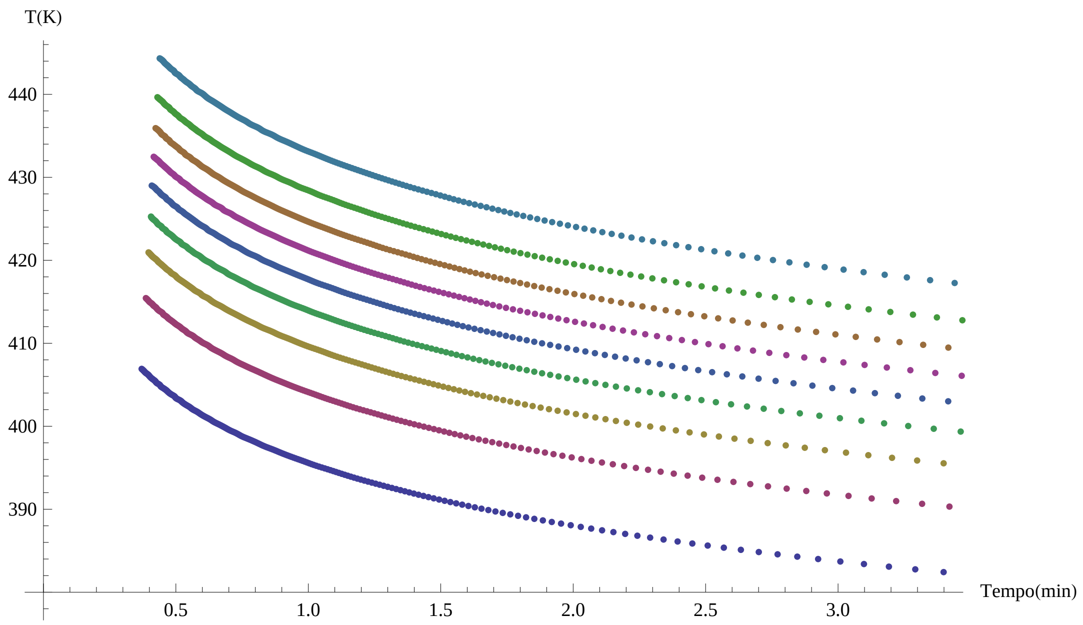
```
    {-ListaBTp[0.8][[i, 2]], ListaBTp[0.8][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.8]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.8, If[z >= 0.7, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.7] = AppendTo[ListaBTp[0.7], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.7] = AppendTo[ListaBT[0.7],
    {-ListaBTp[0.7][[i, 2]], ListaBTp[0.7][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.7]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.7, If[z >= 0.6, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.6] = AppendTo[ListaBTp[0.6], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.6] = AppendTo[ListaBT[0.6],
    {-ListaBTp[0.6][[i, 2]], ListaBTp[0.6][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.6]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.6, If[z >= 0.5, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.5] = AppendTo[ListaBTp[0.5], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.5] = AppendTo[ListaBT[0.5],
    {-ListaBTp[0.5][[i, 2]], ListaBTp[0.5][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.5]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.5, If[z >= 0.4, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.4] = AppendTo[ListaBTp[0.4], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.4] = AppendTo[ListaBT[0.4],
    {-ListaBTp[0.4][[i, 2]], ListaBTp[0.4][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.4]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
```

```
  If[z < 0.4, If[z >= 0.3, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.3] = AppendTo[ListaBTp[0.3], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.3] = AppendTo[ListaBT[0.3],
    {-ListaBTp[0.3][[i, 2]], ListaBTp[0.3][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.3]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.3, If[z >= 0.2, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.2] = AppendTo[ListaBTp[0.2], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.2] = AppendTo[ListaBT[0.2],
    {-ListaBTp[0.2][[i, 2]], ListaBTp[0.2][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.2]]}];

Do[
 Clear[z];
 ListaprovBT[q] = {};
 Do[z := ListaFTVST[q][[i, 2]];
  If[z < 0.2, If[z >= 0.1, ListaprovBT[q] = AppendTo[ListaprovBT[q], ListaFTVST[q][[i]]]]],
  {i, 1, Length[ListaFTVST[q]]}]; Lo = Sort[ListaprovBT[q], #1[[2]] < #2[[2]] &];
 menorL = Lo[[1]]; ListaBTp[0.1] = AppendTo[ListaBTp[0.1], {menorL, q}], {q, 5, 30, 5}]
Do[ListaBT[0.1] = AppendTo[ListaBT[0.1],
    {-ListaBTp[0.1][[i, 2]], ListaBTp[0.1][[i, 1, 1]]}], {i, 1, Length[ListaBTp[0.1]]}];

ListPlot[{ListaBT[0.9], ListaBT[0.8], ListaBT[0.7], ListaBT[0.6], ListaBT[0.5],
  ListaBT[0.4], ListaBT[0.3], ListaBT[0.2], ListaBT[0.1]}, PlotStyle → PointSize[0.01],
 AxesLabel → {"β,( ºK min^-1)", "T,( K ) "}, Joined → True, PlotMarkers → Automatic]
ListamemofqT = {};
Do[ListamemofqT = AppendTo[ListamemofqT, ListaBT[valξ]], {valξ, 0.1, 0.6, 0.1}]
Do[ListamemofqT = AppendTo[ListamemofqT, ListaBT[valξ]], {valξ, 0.8, 0.9, 0.1}]
ListamemofqT >> "D:\\Jorge\\Tesis\\noisotermico\\modelar los
   parametros cineticos\\modelandoAISI1050farjas\\QvsTPafijPro1.nb"
```

```
ListagfqT[0.7] = {{2., 403.906}, {2.5, 406.37}, {3., 408.40500000000003}, {3.5, 410.141},
   {4., 411.657}, {4.5, 413.003}, {5.`, 414.214}, {5.5, 415.315}, {6., 416.326},
   {6.5, 417.26}, {7., 418.129}, {7.5, 418.94}, {8., 419.702}, {8.5, 420.42},
   {9., 421.1}, {9.5, 421.744}, {10., 422.358}, {10.5, 422.943}, {11., 423.502},
   {11.5, 424.038}, {12., 424.552}, {12.5, 425.046}, {13., 425.522}, {13.5, 425.981},
   {14., 426.424}, {14.5, 426.853}, {15., 427.26800000000003}, {15.5, 427.67},
   {16., 428.06}, {16.5, 428.438}, {17., 428.806}, {17.5, 429.164}, {18.`, 429.512`},
   {18.5, 429.851}, {19., 430.182}, {19.5, 430.504}, {20., 430.819}, {20.5, 431.127},
   {21., 431.427}, {21.5, 431.721}, {22.`, 432.009`}, {22.5, 432.29}, {23., 432.566},
   {23.5, 432.835}, {24., 433.1}, {24.5, 433.359}, {25., 433.614}, {25.5, 433.864},
   {26.`, 434.109`}, {26.5, 434.349}, {27., 434.586}, {27.5, 434.818}, {28., 435.047},
   {28.5, 435.271}, {29., 435.492}, {29.5, 435.71}, {30.`, 435.924`}};
ListamemofqTr = {};
ListamemofqTr = << "D:\\Jorge\\Tesis\\noisotermico\\modelar los
     parametros cineticos\\modelandoAISI1050farjas\\QvsTPafijPro1.nb";
ListamemofqTr = AppendTo[ListamemofqTr, ListagfqT[0.7]];

ListagfqT[0.1] = ListamemofqTr[[1]];
ListagfqT[0.2] = ListamemofqTr[[2]];
ListagfqT[0.3] = ListamemofqTr[[3]];
ListagfqT[0.4] = ListamemofqTr[[4]];
ListagfqT[0.5] = ListamemofqTr[[5]];
ListagfqT[0.6] = ListamemofqTr[[6]];
ListagfqT[0.8] = ListamemofqTr[[7]];
ListagfqT[0.9] = ListamemofqTr[[8]];
ListagfqT[0.7] = ListamemofqTr[[9]];
ListPlot[{ListagfqT[0.1], ListagfqT[0.2], ListagfqT[0.3], ListagfqT[0.4],
  ListagfqT[0.5], ListagfqT[0.6], ListagfqT[0.7], ListagfqT[0.8`], ListagfqT[0.9]}]
```



```
Do[
 funTenq[valξ] = Interpolation[ListagfqT[valξ], Method → "Spline"],
 {valξ, 0.1, 0.6, 0.1}]
Do[
 funTenq[valξ] = Interpolation[ListagfqT[valξ], Method → "Spline"],
 {valξ, 0.8, 0.9, 0.1}]
funTenq[0.7] = Interpolation[ListagfqT[0.7], Method → "Spline"];

Do[ListagfTtiem[valξ] = {};
 Do[ListagfTtiem[valξ] =
   AppendTo[ListagfTtiem[valξ], {funTenq[valξ]'[x], funTenq [valξ][x]}],
  {x, funTenq[valξ][[1, 1, 1]], funTenq[valξ][[1, 1, 2]], 0.1}], {valξ, 0.1, 0.6, 0.1}]
Do[ListagfTtiem[valξ] = {};
 Do[ListagfTtiem[valξ] =
   AppendTo[ListagfTtiem[valξ], {funTenq[valξ]'[x], funTenq [valξ][x]}],
  {x, funTenq[valξ][[1, 1, 1]], funTenq[valξ][[1, 1, 2]], 0.1}], {valξ, 0.8, 0.9, 0.1}]

ListagfTtiem[0.7] = {};
Do[ListagfTtiem[0.7] =
  AppendTo[ListagfTtiem[0.7], {funTenq[0.7]'[x], funTenq [0.7][x]}],
 {x, funTenq[0.7][[1, 1, 1]], funTenq[0.7][[1, 1, 2]], 0.1}]
ListPlot[{ListagfTtiem[0.1], ListagfTtiem[0.2], ListagfTtiem[0.3],
  ListagfTtiem[0.4], ListagfTtiem[0.5], ListagfTtiem[0.6], ListagfTtiem[0.7],
  ListagfTtiem[0.8], ListagfTtiem[0.9]}, AxesLabel → {"Tempo(min)", "T(K)"}]
ListamemofTTiempo = {};
Do[ListamemofTTiempo = AppendTo[ListamemofTTiempo, ListagfTtiem[valξ]],
 {valξ, 0.1, 0.7, 0.1}]
Do[ListamemofTTiempo = AppendTo[ListamemofTTiempo, ListagfTtiem[valξ]],
 {valξ, 0.8, 0.9, 0.1}]
ListamemofTTiempo >> "D:\\Jorge\\Tesis\\noisotermico\\modelar los parametros
   cineticos\\modelandoAISI1050farjas\\TvsTiemPafijPro1menpunt.nb"
```



Anexo 16 Método A1

Considerando que $P_{0}= (\delta l/l)_{0}$ e $P_{1} = (\delta l/l)_{1}$ dependem da temperatura, como é mostrado na fig (3.2) e diferenciando a equação (3.1) com relação a T obtêm-se :

$$\frac{d\xi}{dT} = \frac{d}{dT}[(P - Po)(P1 - Po)^{-1}] =$$

$$= \frac{d(P - Po)}{dT}(P1 - Po)^{-1} + (P - Po)\frac{d}{dT}(P1 - Po)^{-1} =$$

$$= \left\{\frac{dP}{dT} - \frac{dPo}{dT}\right\}(P1 - Po)^{-1} + (P - Po)\left\{-1(P1 - Po)^{-2}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right\} \Rightarrow$$

$$\frac{d\xi}{dT} = \frac{1}{P1-Po}\left\{\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) - \frac{P-Po}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\right\} \qquad (3.7)$$

E diferenciando novamente a equação (3.7) respeito a T teremos (Anexo 2, eq. (A.2.6)):

$$\frac{d^2\xi}{dT^2} = \frac{1}{P1-Po}\left\{\frac{d^2P}{dT^2} - \frac{2}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) + \frac{2}{(P1-Po)^2}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)^2 (P - Po)\right\} \qquad (3.8)$$

Quando T=Ti ; $\left|\frac{dP}{dT}\right|_{Ti}$ é máximo e P não é muito grande pois $\boldsymbol{P} \in [\boldsymbol{Po}, \boldsymbol{P1}]$ e por esta razão $\left|\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\left(\frac{P-Po}{P1-Po}\right)\right|_{Ti} \ll \left|\frac{dP}{dT} - \frac{dPo}{dT}\right|_{Ti}$ o ultimo termino nas equações (7) e (8) podem ser desprezado.Alem disso em T=Ti , $\left(\frac{d^2P}{dT^2}\right)_{Ti} = \mathbf{0}$, então a equação (3.8) se transforma em :

$$\left(\frac{d^2\xi}{dT^2}\right)_{Ti} = -\frac{2}{(P1-Po)^2}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\left(\frac{dP}{dT} - \frac{dPo}{dT}\right) = -\frac{2}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right)\left(\frac{d\xi}{dT}\right)_{Ti}$$

Que pode ser escrita como:

$$\left(\frac{d^2\xi}{dT^2}\right)_{Ti} = -\boldsymbol{C}(\boldsymbol{T})\left(\frac{d\xi}{dT}\right)_{Ti} \quad \text{onde:} \quad \boldsymbol{C}(\boldsymbol{T}) = \frac{2}{P1-Po}\left(\frac{dP1}{dT} - \frac{dPo}{dT}\right) \qquad (3.9)$$

Lembrando que: $\boldsymbol{\beta} = \frac{dT}{dt}$; podemos escrever:

$$\frac{d\xi}{dT} = \beta^{-1}\frac{d\xi}{dt} \quad \text{e} \quad \frac{d^2\xi}{dT^2} = \beta^{-2}\frac{d^2\xi}{dt^2} \tag{3.10}$$

Usando agora a equação (3.4): $\xi = 1 - exp(-\theta)^n$

$$\frac{d\xi}{dt} = exp\,(-\theta^n)\theta^{n-1}n\frac{d\theta}{dt} \quad \text{e}$$

$$\frac{d^2\xi}{dt^2} = \left(\frac{d\theta}{dt}\right)^2 exp(-\theta^n)\{-n^2\theta^{2n-2} + n(n-1)\theta^{n-2}\} + n\theta^{n-1}\,exp(-\theta^n)\frac{d^2\theta}{dt^2}$$
(3.11).

Substituindo (11) em (10) e o resultado em (9) , obtém se a equação diferencial :

$$\left(\theta\frac{d^2\theta}{dT^2}\right)_{Ti} - [n(\theta^n - 1) + 1]\left(\frac{d\theta}{dT}\right)_{Ti}^2 = -C(T)\theta\left(\frac{d\theta}{dT}\right)_{Ti} \tag{3.12}$$

Como n esta compreendido no intervalo (1,4) , e como na faixa de trabalho onde ,ξ , sofreu câmbios significativos(perto do ponto de inflexão , onde ($d\xi/dT$) é máxima) ,$\theta \approx 1$, então é possível fazer a seguinte aproximação para $\theta^n = exp\,(n\,ln(\theta))$ que pode ser desenvolvido na serie de potencias :

$$exp(u) = 1 + \frac{u}{1!} + \frac{u^2}{2!} + \frac{u^3}{3!} \quad \Rightarrow \theta^n = exp(n\,ln(\theta)) = 1 + \frac{nln\theta}{1!} + \frac{(nln\theta)^2}{2!} + \frac{(nln\theta)^3}{3!} + \ldots$$

Fazendo uso desta aproximação e substituindo a equação (3.6) em a equação (3.12) e como RT/E <<1,desprezando as potencias superiores de RT/E, depois de algumas simplificações (Ver Anexo 3) se obtém[17] [48]:

$$ln\frac{Ti^2}{\beta} = ln\frac{E}{RKo} + \frac{E}{RT} + RES_{1+}RES_2 \tag{3.13}$$

Onde: $RES_1 = \frac{Q}{n^2}\frac{RTi^2}{E}$, $RES_2 = 2\frac{RT_i}{E} * \left\{1 - \frac{1}{n^2} + nln\left[\frac{Ti^2RK(Ti)}{\beta E}\right]\right\}$ e

$$Q(Ti) = 2\left(\frac{\frac{dP_1}{dT} - \frac{dP_o}{dT}}{P_1 - P_o}\right)_{Ti}$$

Anexo 17

Para uma transformação que envolve nucleação e crescimento e assumindo que os núcleos da nova fase ficam aleatoriamente distribuídos, Avrami,M [22,69,70], obteve a equação:

$$\boldsymbol{\xi = 1 - exp[-v_{ext}]} \qquad (3.14)$$

Onde V_{ext} é o volume total por unidade de volume no tempo t desprezando a sobreposição dos grãos em crescimento:

$$\boldsymbol{v_{ext} = \int_0^t N(\tau) v(t,\tau)\, d\tau} \qquad (3.15)$$

Onde N(τ) é a velocidade da nucleação por unidade de volume e V(t,τ) é o volume transformado por um único núcleo, que há nascido em o tempo τ ,durante o tempo t:

$$\boldsymbol{v(z,t) = \sigma \left(\int_\tau^t G(z)\, dz \right)^m} \qquad (3.16)$$

Onde σ é um fator de forma (por exemplo,σ =4/3 π para um grão esférico), G(z) é a velocidade de crescimento e m depende do mecanismo de crescimento (por exemplo, m = 3 para um crescimento em três dimensiones).

Na maior parte das situações praticas é possível assumir uma dependência do tipo de Arrhenius da temperatura para N(z) e G(z) [1]:

$$\boldsymbol{N = Noexp[-\frac{EN}{KbT}]} \quad \text{e} \quad \boldsymbol{G = Goexp[-\frac{EG}{KbT}]} \qquad (3.17)$$

Só é possível escrever a equação de velocidade de uma reação na forma da equação (3.2) para o caso iso-cinético , o que é equivalente quando os parâmetros cinéticos não dependem do tempo ou da temperatura. De um modo simultâneo a mesma equação pode ser aplicada a uma reação não isotérmica quando a taxa de transformação depende só da temperatura e não da historia térmica [71,72,73].Esta condição é satisfeita especialmente na saturação de sítios para a nucleação , quando a nucleação ocorre antes do crescimento dos cristais[11] ou para a situação iso-cinética , especialmente quando N e G possuem a mesma energia de ativação [55].

Para uma velocidade de aquecimento constante $\boldsymbol{\beta = \frac{dT}{dt} = Cte}$ e substituindo a equação (3.17) na equação (3.16):

$$\boldsymbol{v(\tau,t) = \sigma\left(\int_{\tau}^{t} G(z)\, dz\right)^{m} = \sigma\left(\int_{\tau}^{t} Go\; exp\;(-\frac{E}{KbT}) dz\right)^{m}} \qquad (3.18)$$

E como $\boldsymbol{\beta = \frac{dT}{dz} = cte \Rightarrow T = To + \beta z}$,se usamos esta relação na equação (3.18) :

$$\boldsymbol{v(\tau,t) = \frac{\sigma Go^{m}}{\beta^{m}}\left(\int_{T_o}^{T} exp\;(-\frac{E}{K_bT}) dT\right)^{m}} \qquad (3.19)$$

E esta integral é a mesma que aparece em o anexo 1 (A.1.3) , tomando o resultado (A.1.9):

$$\boldsymbol{v(\tau,t) = \frac{\sigma Go^{m}}{\beta^{m}}\left\{T\int_{1}^{\infty}\frac{exp\;(-\frac{E}{KbT}\mu)}{\mu^{2}}\, d\mu - To\int_{1}^{\infty}\frac{exp\;(-\frac{E}{KbT}\mu)}{\mu^{2}}\, d\mu\right\}^{m}} \qquad (3.20)$$

Depois de multiplicar e dividir cada somando na eq. (3.20) por K/E:

$$\boldsymbol{v(\tau.t) = \sigma\left(\frac{GoE}{K\beta}\right)^{m}\left(\frac{\int_{1}^{\infty}\frac{exp\;(-\frac{E}{KbT}\mu)}{\mu^{2}}d\mu}{\frac{E}{KbT}} - \frac{\int_{1}^{\infty}\frac{exp\;(-\frac{E}{KbT}\mu)}{\mu^{2}}d\mu}{\frac{E}{KbTo}}\right)^{m}} \qquad (3.21)$$

Usando a definição (A.1.7):

$\boldsymbol{E_2(x) = \int_{1}^{\infty}\frac{exp(-xy)}{y^{2}}\, dy}$ y tomando $\boldsymbol{x = \frac{E}{KbT} = \frac{E}{RT}}$, lembrando que R = NaKb onde Na é o numero de Avogadro e R a constante universal dos gases.Agora as unidades de E são (Kj mol^{-1}).

$$\boldsymbol{v(\tau,t) = \sigma\left(\frac{GoE}{K\beta}\right)^{m}\left(\frac{E_2(x)}{x} - \frac{E_2(x_o)}{x_o}\right)^{m}} \qquad (3.22)$$

Definindo :

$$\boldsymbol{P(x) = \frac{E_{2(x)}}{x} = \int_{x}^{\infty}\frac{exp\;(-u)}{u^{2}}\, du} \qquad (3.23)$$

O volume transformado de um só núcleo, equação (3.22), se pode escrever:

$$\boldsymbol{v(\tau,t) = \sigma\left(\frac{GoE}{K\beta}\right)^{m}\left[P\left(\frac{Eg}{RT}\right) - P\left(\frac{Eg}{RTo}\right)\right]^{m}} \qquad (3.24)$$

E a fração de volume estendido, V $_{ext}$, pode ser calculado substituindo as equações (3.17) e (3.24) na equação (3.15).

$$V_{ext} = \int_0^t N(\tau)v(z,\tau)\, d\tau = \int_0^t Noexp(-\frac{En}{RT'})\, \sigma \left(\frac{GoE}{K\beta}\right)^m \left[P\left(\frac{Eg}{RT}\right) - P\left(\frac{Eg}{RT'}\right)\right]^m d\tau$$

(3.25)

E como $\beta = \frac{dT'}{d\tau} = cte \Rightarrow T' = To + \beta\tau, dT' = \beta d\tau \;\; e\; alem \;\; y = \frac{Eg}{RT} \;; w = \frac{Eg}{RT'} \Rightarrow$

$$dw = -\frac{Eg}{RT'^2} dT' \qquad (3.26).$$

Substituindo (3.26) na equação (3.25) se obtém:

$$V_{ext} = -\frac{No\sigma Go^m}{\beta}\left(\frac{Eg}{\beta R}\right)^m \int_0^t exp\,(-\frac{En}{RT'}\frac{Eg}{Eg})(P(y) - P(w))^m \frac{RT'^2}{Eg} dw \qquad (3.27)$$

Multiplicando e dividindo a Eq. (3.27) por Eg/R.

$$V_{ext} = -\frac{No\sigma Go^m}{\beta}\left(\frac{Eg}{\beta R}\right)^m \frac{Eg}{R}\int_0^t exp\,(-\frac{En}{RT'}\frac{Eg}{Eg})(P(y) - P(w))^m \frac{dw}{\frac{Eg^2}{R^2T'^2}} \qquad (3.28)$$

$$V_{ext} = No\sigma Go^m \left(\frac{Eg}{R\beta}\right)^{m+1} \int_w^\infty exp\,(-\frac{En}{Eg}w')\frac{1}{w'^2}(P(y) - P(w'))^m dw' \qquad (3.29)$$

Esta integral pode ser analiticamente resolvida se Em=Eg. Neste caso:

$$\frac{dP(w')}{dw'} = -\frac{exp\,(-w')}{w'^2}$$

Então a equação (3.29) pode-se escrever como:

$$V_{ext} = No\sigma Go^m \left(\frac{Eg}{R\beta}\right)^{m+1} \int_w^\infty -dP(w')(P(y) - P(w'))^m$$

$$V_{ext} = \frac{No\sigma Go^m}{m+1}\left(\frac{Eg}{R\beta}\right)^{m+1} P(y)^{m+1} = \left[Ko\frac{E}{R\beta}P(\frac{E}{RT})\right]^{m+1} \qquad (330)$$

Assumindo que P(∞) = 0 e $Ko = \left(\frac{No\sigma Go^m}{m+1}\right)^{\frac{1}{m+1}}$ (3.31)

Esta ultima relação ,intuitivamente se sugere que:

$$\boldsymbol{K} = \left(\frac{\sigma N G^{m}}{m+1}\right)^{\frac{1}{m+1}} \tag{3.32}$$

Substituindo na eq.(32) a eq. (17) :

$$\boldsymbol{K} = \left(\frac{No\sigma Go^{m}}{m+1}\right)^{\frac{1}{m+1}} \boldsymbol{exp}\left(-\frac{E}{RT}\right) \quad \text{.Onde} \quad \boldsymbol{E} = \frac{En+mEg}{m+1} \tag{3.33}$$

Substituindo a equação (3.30) em a equação (3.14) :

$$\boldsymbol{\xi} = \mathbf{1} - \boldsymbol{exp}\left\{-\left[Ko\frac{E}{R\beta}P\left(\frac{E}{RT}\right)\right]^{m+1}\right\} \tag{3.34}$$