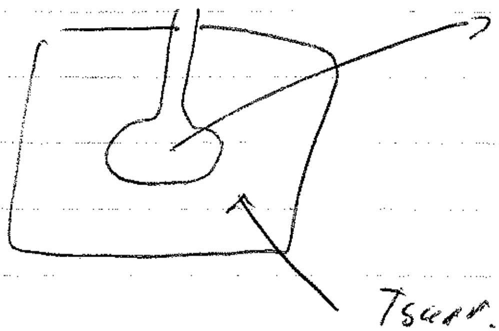
ARC EXPERIMENT



Measure $T_{sample}(t)$

in response to preprogrammed

$T_{surr}(t)$

T_{surr}. T_{surr} is ramped slowly in time!

Detect time when $dT_{sam}/dt > \frac{dT_{surr}}{dt}$

sample heating rate exceeds the ramped

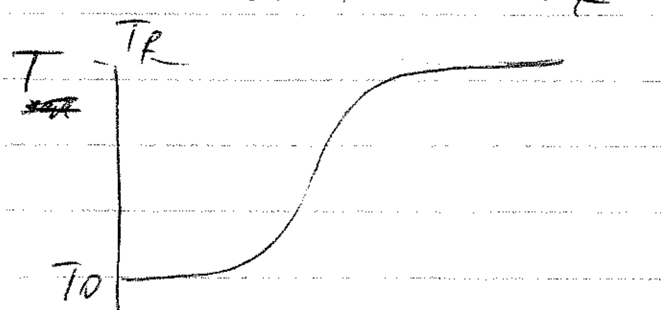
T increase of the surroundings

Let $T = T_{sam}$

$$(1)\quad \underbrace{\left(M_{bomb} C_{P\,steel} + M_{sample} C_{P\,sample}\right)}_{\cancel{\bar\rho C_P}} \frac{dT}{dt} = \underbrace{(-\Delta H_{Rx}) k_0 e^{-E/RT} C_A^{n} V}_{(-r_A)V}$$

Record T_0 $\left(\text{at } \frac{dT_{sam}}{dt} > \frac{dT_{surr}}{dt}\right)$

Record T_R



(2) Adiabatic after T_0

$$\cancel{T = T_0 + \frac{(-\Delta H_{Rx})}{\bar\rho C_P}}$$

$$T = T_0 + \frac{(-\Delta H_{Rx}) C_{A0} x_A}{\bar\rho C_P}$$

$$\boxed{T = T_0 + \Delta T_{ad}\, x_A} \quad (*)$$

Mass Balance

$$(3)\quad C_{A0} \frac{dx_A}{dt} = (-r_A)$$

$$\bar\rho C_P = \frac{M_b C_{Pb} + M_s C_{Ps}}{V}$$

$$\frac{dT}{dt} = \frac{(-\Delta H_{Rx}) V}{M_b C_{Pb} + M_s C_{Ps}} C_{A0} \frac{dx_A}{dt}$$

$$(4)\quad \bar\rho C_P = \rho_s C_{Ps}\left(1 + \frac{M_b C_{Pb}}{M_s C_{Ps}}\right)$$

Solve for x_A

$$x_A = \frac{T-T_0}{\Delta T_{ad}}$$

$$1-x_A = 1 - \frac{T-T_0}{\Delta T_{ad}}$$

$$1-x_A = \frac{T_f - T}{\Delta T_{ad}}$$

let $m = \frac{dT}{dt}$

$$(3) \quad \frac{dT}{dt} = m = \Delta T_{ad} \frac{dx_A}{dt}$$

$$T_{ad} - T_0 = \Delta T_{ad} = \frac{(-\Delta H_{rA}) C_{A0}}{\rho C_p} = \Delta T_{ad}$$

<u>Now</u>

$$m = \frac{dT}{dt} = \Delta T_{ad} \underbrace{k_0 C_{A0}^{n-1} e^{-E/RT}}_{k^*} (1-x_A)^n$$

$$= \Delta T_{ad}\, k^* \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n$$

$$(4) \quad k^* = \frac{m}{\Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} = k_0 C_{A0}^{n-1} e^{-E/RT}$$

known ΔT_{ad}, measured m, T_f, guessed n

plot $\ln k^*$ vs $1/T$

If n guessed correctly, straight line

$(\text{slope}) = E/R$

Consider inflection point $T = T_{I}$ at $t = t_{I} = t^*$

$$\frac{d^2T}{dt^2} = 0 = \Delta T_{ad}\left[\frac{dk^*}{dT}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n + k^* n \left(\frac{T_{ad} - T}{\Delta T_{ad}}\right)^{n-1}\left(-\frac{1}{\Delta T_{ad}}\right)\right]$$

$$\frac{dk^*}{dT} = k_0 C_{A0}^{n-1} \frac{E}{RT^2} e^{-E/RT} = k^* \frac{E}{RT^2}$$

$$\frac{E}{RT_{I}^2}(T_f - T_{I}) - n = 0 \qquad \left(n = \frac{E \overbrace{(T_f - T_{I})}^{\Delta T_{I}}}{R T_{I}^2}\right) \quad (5)$$

Conversion achieved at inflection point

$$(6)\quad x_{Am} = \frac{T_m - T_0}{\Delta T_{ad}} = \frac{(T_f - T_0) - (T_f - T_m)}{\Delta T_{ad}}$$

$$= \frac{\Delta T_f - \Delta T_m}{\Delta T_f} = 1 - \frac{\Delta T_m}{\Delta T_f}$$

Critical time to point of "no return" point of explosion (inflection point)

$$\frac{dT}{dt} = \Delta T_{ad}\, k_0 C_{A0}^{n-1} \left(\frac{T_{ad} - T}{\Delta T_{ad}}\right)^n e^{-E/RT}$$

Replace $k_0 e^{-E/RT} = k_0' T^2 e^{-E/RT}$

Solve of for T_m

$$nRT_m^2 + ET_m - ET_f = 0$$

True T_m of system

$$T_m = \frac{E}{2nR}\left[\sqrt{1 + \frac{4nRT_f}{E}} - 1\right] =$$

$$= \frac{E}{2nR}\left[\sqrt{1 + \frac{4nR(T_0 + \Delta T_{adsss})}{E}} - 1\right)$$

$$\Delta T_{adsss} = \Delta T_{ad}(1 + \phi) > \Delta T_{ad_{\text{measured}}}$$

$$7)\quad t^* = \frac{R}{E k_0' \Delta T_{ad}^{1-n} C_{A0}^{n-1}} \int_{T_0}^{T_m} \frac{E}{RT^2} e^{E/RT} (T_f - T)^{-n}\, dT$$

$$\approx \frac{RT^2}{E k_0' T^2 \Delta T_{ad}^{1-n} C_{A0}^{n-1} (T_f - T)^n e^{-E/RT}}\Bigg|_{T_m}^{T_0} =$$

$$t^* = \frac{RT_0^2}{E\,m_0} - \cancel{\frac{RT_m^2}{E\,m_m}} \to 0$$

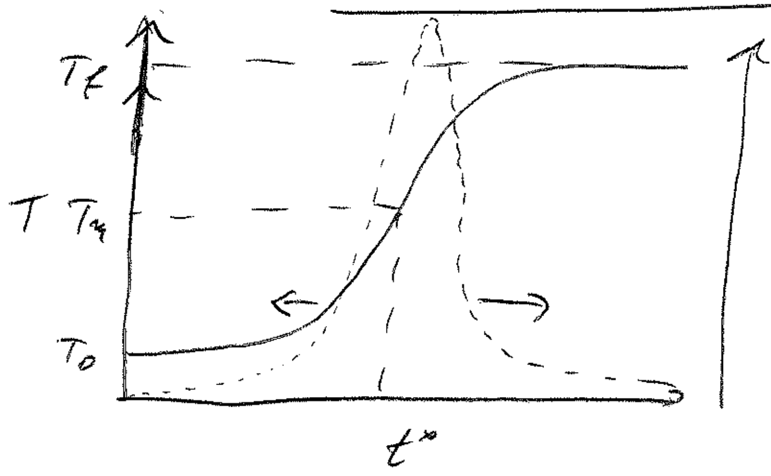
$$\boxed{t^* = \frac{RT_0^2}{E\,m_0}} \quad (8)$$

Now correct to heat capacity of bomb

→ note $m_{system} = m_{exp}(1+\phi)$

$$\boxed{t^*_{system} = t^*_{exp} / (1+\phi)}$$

Summary of ARC



$m = \frac{dT}{dt}$ $\qquad T_m = T_{inf}$

From graph

$$T_f - T_0 = \Delta T_{ad} = \frac{(-\Delta H_{rA})\, C_{A0}}{\rho C_p (1+\phi)}$$

$$\phi = \frac{M_{wall}\, C_{wall}}{M_{fluid}\, C_p}$$

Adiabatic governing equation

$$\rho C_p (1+\phi) \frac{dT}{dt} = (-\Delta H_{rA})\, k_0 e^{-E/RT} C_{A0}^{n} (1-x_A)^n$$

with $\quad x_A = \frac{T-T_0}{\Delta T_{ad}} \quad$ so $\quad 1-x_A = \frac{C_A}{C_{A0}} = \frac{T_f - T}{\Delta T_{ad}}$

$$m = \frac{dT}{dt} = \Delta T_{ad}\, \underbrace{k_0 C_{A0}^{n-1} e^{-E/RT}}_{k^*} \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n$$

Can do $\ln \frac{dT}{dt}$ vs $\frac{1}{T}$

as $e^{-E/RT}$ dominates $\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n$

but it is better to use k^*

$$\boxed{k^* = k_0 C_{A0}^{n-1} e^{-E/RT} = \frac{m}{\Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n}}$$

guess n until
$\ln k^*$ vs $\frac{1}{T}$ is a straight line.

From $\frac{d^2T}{dt^2} = 0 \Longrightarrow \boxed{m = \frac{E(T_f - T_m)}{R T_m^2}}$

$$T_M = T_m = \frac{E}{2nR}\left[\sqrt{1 + \frac{4nRT_f}{E}} - 1\right]$$

Critical time to explosion or
time to point of no return

$$t^* = \frac{1}{\Delta T_{ad} k_0 C_{A0}^{n-1}} \int_{T_0}^{T_m} \frac{e^{E/RT}}{\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} dT$$

Conservative estimate based on $n = 0$ and k approximate yields

$$t_0^* = \frac{RT_0^2}{E(m_0)_0} - \frac{RT_m^2}{E(m_m)_0} = \frac{RT_0^2}{E(m_0)_0}$$

$$= \frac{T_0}{\delta \frac{(-R_A)_0}{C_{A0}} \Delta T_{ad}} - \frac{C_{A0}}{\delta(-R_A)_0}$$

So $\boxed{\frac{\delta\, t_0^* (-R_{A0})}{C_{A0}} = \frac{\delta\, t_0^*}{\tau_R} = Da^* \delta = 1}$