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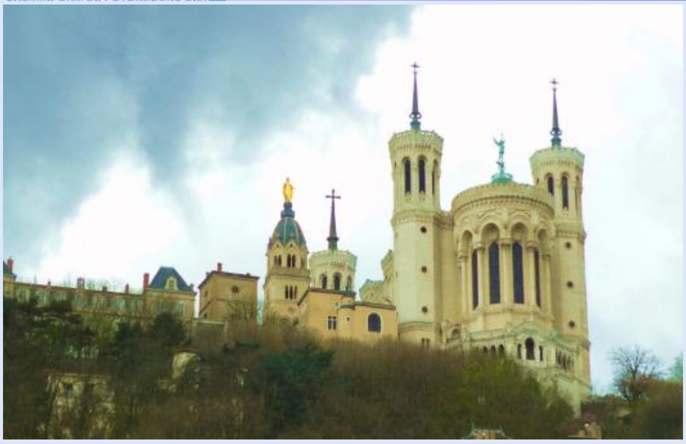

Adiabatic calorimetry – new trends and some peculiarities of application

A. Kossoy

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Topics to be discussed

1. **Types of adiabatic calorimeters**
2. **Something about theory and related problems**
3. **Phi-factor – what is usually supposed and what we have in reality**
4. **Study of energetic materials – is adiabatic calorimetry the right method?**

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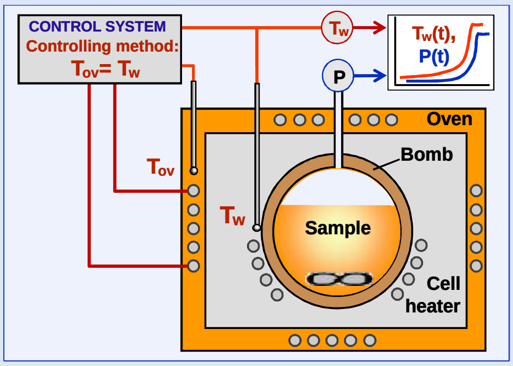
Types of adiabatic calorimeters

- ✓ Accelerating Rate Calorimeter
  ARC - *THT, NETZSCH (Germany)*
  Phi-Tec I - *HEL (UK)*
- ✓ Vent Sizing Package
  VSP - *FAI (USA)*
  Phi-Tec II - *HEL (UK)*
- ✓ New! Differential Accelerating Rate Calorimeter DARC - *Omnicalc (USA)*
- ✓ DEWAR
  Mostly home-made
- ✓ Advanced Reactive System Screening Tool ARSST - *FAI (USA)*



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Types of adiabatic calorimeters

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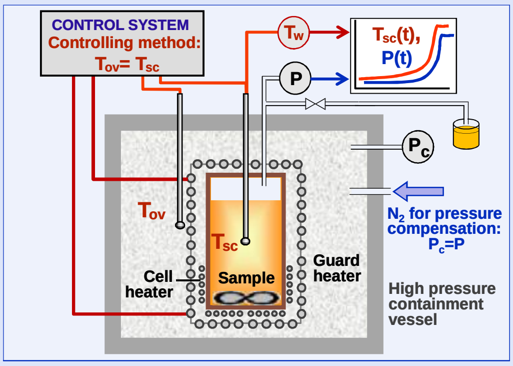
  Phi-Tec I - HEL (UK)
- ✓ Vent Sizing Package
  VSP - FAI (USA)
  Phi-Tec II - HEL (UK)
  Phi-Tec I - HEL (UK) (no P compensation)
- ✓ Differential Accelerating Rate Calorimeter DARC - Omnicalc (USA)
- ✓ DEWAR
  Chilworth (UK), home-made
- ✓ Advanced Reactive System Screening Tool ARSST - FAI (USA)



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Types of adiabatic calorimeters

- ✓ Accelerating Rate Calorimeter
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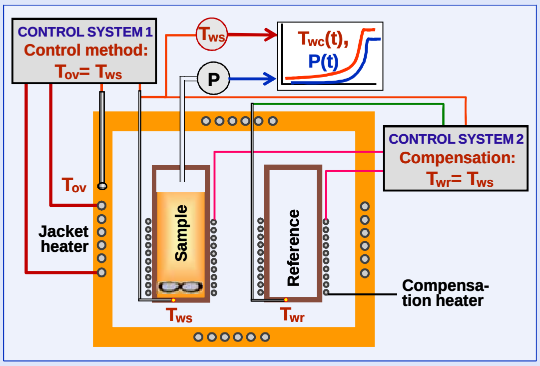
  Phi-Tec I - HEL (UK)
- ✓ Differential Accelerating Rate
  Calorimeter DARC - Omnical (USA)
- ✓ DEWAR
  Chilworth (UK), home-made
- ✓ Advanced Reactive System
  Screening Tool ARSST - FAI (USA)



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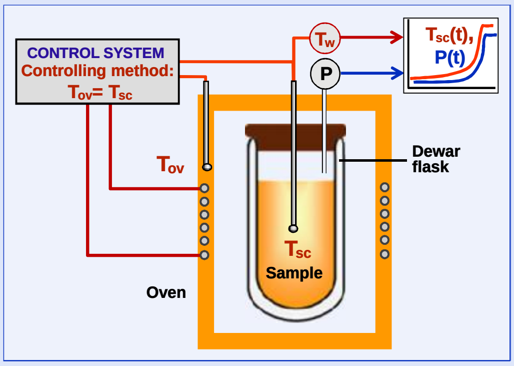

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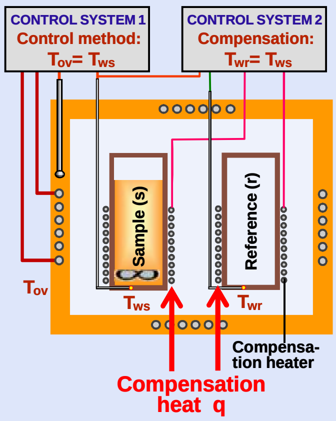
Something about theory and related problems

Differential Accelerating Rate Calorimeter DARC, principle of the method *)



1. $t=0, T=T_{onset}$. <u>Start of reaction. Heat release</u>

   $Q_r(0)=Q_r$ ì $T_s=T_{onset}+Q_r/(C_s+C_w)$ ì $T_{ws}-T_{wr}$ = aT_o

2. <u>Compensation starts</u>

   $q_o=C_w$aT_o ì T_{ws} increase = $q_o/(C_s+C_w)$= aT_1

   $q_1=C_w$aT_1= $C_w q_o/(C_s+C_w)$ = ¨ q_o= C_w ¨ a T_o

   ¨ = $C_w q_o/(C_s+C_w)$

3. <u>Cycle</u>

   $q_i=C_w$aT_i=C_w ¨ ^{i}a T_o, aT_i= ¨ ^{i}a T_o

   $\overset{n}{\underset{iZo}{\text{ģ}}}$ aT_i ZaT_o $\overset{n}{\underset{iZ0}{\text{ģ}}}$ ¨ ^{n} ZaT_o¨ (1 J ¨ ^{n}) ü ^{n}ü ì ã û ì aT_o¨

*) Arata Kimura & Teruhito Otsuka, Performance evaluation of differential accelerating rate calorimeter for the thermal runaway reaction of di-tert-butyl peroxide, J Therm Anal Calorim (2013) V. 113:1585-1591

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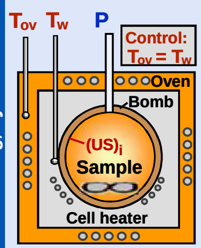
Something about theory and related problems

<u>Main assumption: Bomb and Sample are the uniform (lumped) systems</u>



$$c_b m_b \frac{dT_b}{dt} = (US)_i(T_s - T_b) - W_{loss};$$

$$c_s m_s \frac{dT_s}{dt} = W - (US)_i(T_s - T_b);$$

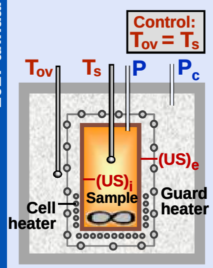
$$W = m_s \frac{dQ}{dt}$$

⇨

$$c_s m_s \frac{dT_s}{dt} + c_b m_b \frac{dT_b}{dt} = W - W_{loss};$$

Assuming that T_b=T_s and W_{loss}=0

$$c_s m_s \text{¨} \frac{dT_s}{dt} = W; \quad \text{¨} = 1 + (c_b m_b)/(c_s m_s)$$



$$c_b m_b \frac{dT_b}{dt} = (US)_e(T_{ov} - T_b) + (US)_i(T_s - T_b) - W_{loss};$$

$$c_s m_s \frac{dT_s}{dt} = W - (US)_i(T_s - T_b);$$

⇩

$$c_s m_s \frac{dT_s}{dt} + c_b m_b \frac{dT_b}{dt} = (US)_e(T_{ov} - T_b) + W - W_{loss};$$

Assuming that T_b=T_{ov}=T_s and W_{loss}=0

$$c_s m_s \text{¨} \frac{dT_s}{dt} = W; \quad \text{¨} = 1 + (c_b m_b)/(c_s m_s)$$

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Something about theory and related problems

Assumption: Sample is in equilibrium with the Bomb (Ts=Tb) -??

1. ARC-type

$$c_b m_b \frac{dT_b}{dt} = (US)_i (T_s - T_b);$$
$$c_s m_s \frac{dT_s}{dt} = W - (US)_i (T_s - T_b);$$

$$\Rightarrow \quad c_s m_s \frac{dT_s}{dt} + c_b m_b \frac{dT_b}{dt} = W;$$

Simulation details

Bomb: stainless steel sphere, R=1.6 cm, wall thickness - 1 mm; M_b=22.6 g

Sample: low viscous liquid, ° = 1 g/cm^3; C_p=2 J/g/K; M_s=13.6 g; ¨=1.383

Kinetics: 1-st order reaction; K_o=5.32*10^{11} 1/s; E=120 kJ/mol; Q=400 J/g

Internal heat transfer coefficient: U=100 W/m^2/K

Boundary conditions:
adiabatic on the outer side of the bomb (ARC control method T_{ov}=T_b)

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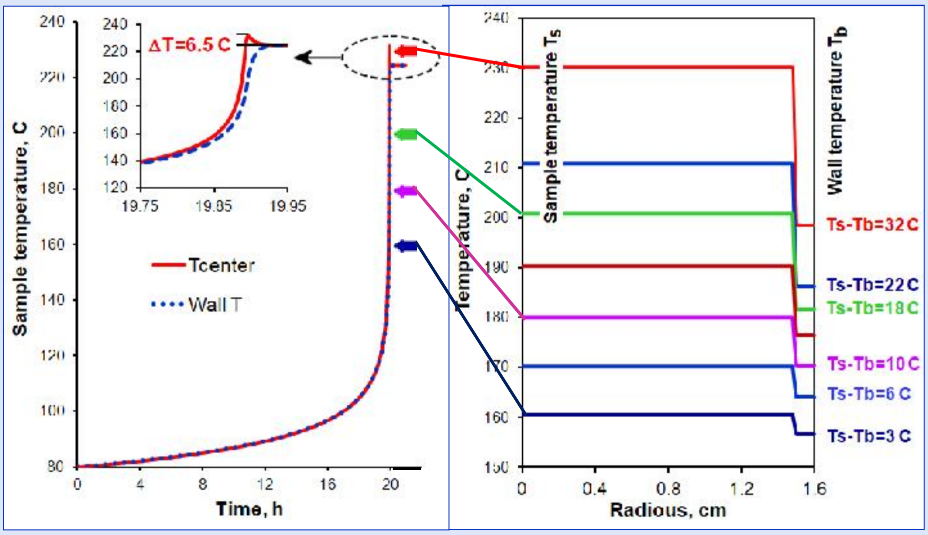
Something about theory and related problems

Assumption: Sample is in equilibrium with the Bomb (Ts=Tb) -??



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Something about theory and related problems

Assumption: Sample is in equilibrium with the Bomb (Ts=Tb) -??

2. VSP-type

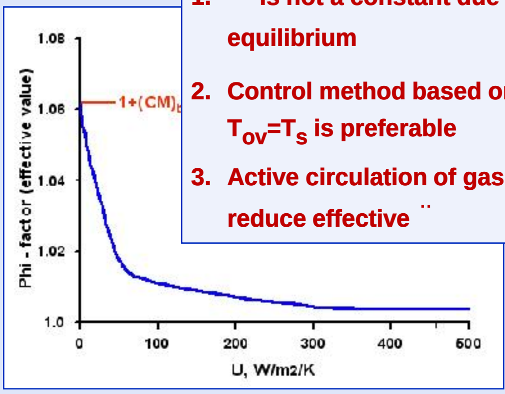
$$c_b m_b \frac{dT_b}{dt} = (US)_e(T_{ov} - T_b) + (US)_i(T_s - T_b);$$

$$c_s m_s \frac{dT_s}{dt} = W - (US)_i(T_s - T_b);$$

$$\ldots US)_e(T_{ov} - T_b) + W;$$

$$\ldots = T_s;$$

…change



1. ¨ is not a constant due to deviation form equilibrium
2. Control method based on maintenance $T_{ov}=T_s$ is preferable
3. Active circulation of gas in the oven can reduce effective ¨

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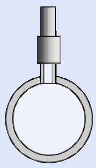
Phi-factor – what is it really?

Thermal inertia ¨ ù 1 + $(c_b M_b)/(c_s M_s)$

Problem # 1 – how to determine thermal inertia?

What is bomb mass M_b=?



The best solution – calibration.
It is applied for DEWAR but not for other instruments
Why ?

How to determine phi for DEWAR?

Problem # 2 – how to minimize thermal inertia?

1. **Reduce value of $c_b M_b$ – VSP, Phi-Tec II, DEWAR**
2. **Apply power-compensation – DARC**
3. **Apply advanced control method (e.g. gas circulation in the oven)**
4. **Apply math methods for phi correction**

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Phi-factor – what is it really?

Thermal inertia ¨ ù 1 + (c_bM_b)/(c_sM_s)

Problem # 3 – ¨ - Constant or Variable ?

1st reason why ¨ may vary:

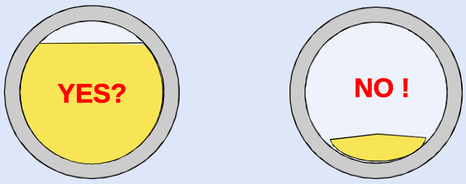
C_b= f(T)

C_s= f(T, t): mixture composition varies in time

2nd reason why ¨ may vary:

Lack of equilibrium between sample and bomb

¨ ù Constant ? ¨ ù Constant ?



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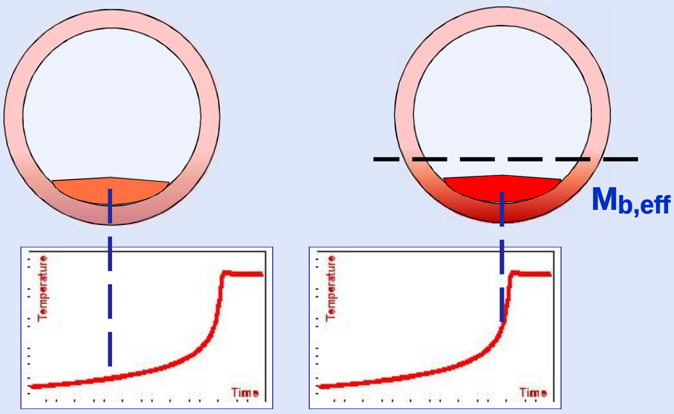
Phi-factor – what is it really?

Thermal inertia ¨ ù 1 + (c_bM_b)/(c_sM_s)

Problem # 3 – ¨ - Constant or Variable ?

$¨_1$ ù 1 + (c_bM_b)/ (c_sM_s) **>> $¨_2$ ù 1 + ($c_bM_{b,eff}$)/ (c_sM_s) !!**



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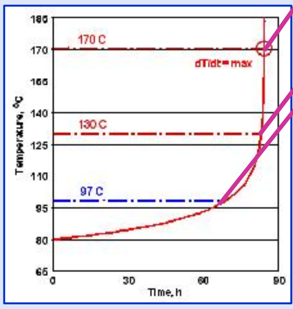
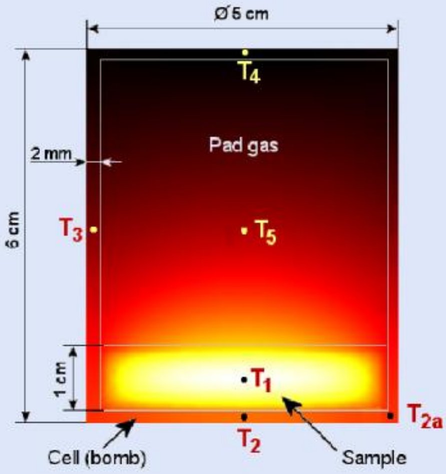
Phi-factor – what is it really?

Thermal inertia ¨ ù 1 + $(c_bM_b)/(c_sM_s)$

Problem # 3 – ¨ - Constant or Variable ?

T2, C	T2a, C	T3, C	T4, C	T5, C	T_{max}=T1, C
156.8	155	151	148	151	170
126.5	126.3	125.7	125.1	125.8	130
97.21	97.2	97.13	97.1	97.2	97.33





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Applying adiabatic calorimetry for energetic materials

Main Problem - high energy release

Conditions of ARC experiment:

Bomb mass ~22 g; bomb Cp~0.5 J/g/K
Sample mass ~10 g; sample Cp~2 J/g/K
¨=1.55

Typical reactive mixture: Reaction heat - 200ö600 J/g
Max temperature rise - 70 ö200 C
Max SHR~100 K/min

Energetic material:Reaction heat - 1000ö3000 J/g
Max temperature rise - 350 ö950 C and more!
Max SHR~600 ö1000 K/min and more!

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Applying adiabatic calorimetry for energetic materials

Main Problem - high energy release

What to do? Increase ¨ :

Bomb mass ~22 g; bomb Cp~0.5 J/g/K

Sample mass ~x g; sample Cp~2 J/g/K

Energetic material: Reaction heat – 2000, 3000 and 4000 J/g

Max temperature rise: keep ~300 – 340 C

Max SHR ??

Q, J/g	Ms, g	¨	aTmax
2000	1	6.5	~300
3000	0.6	10.2	~300
4000	0.45	13.2	~300

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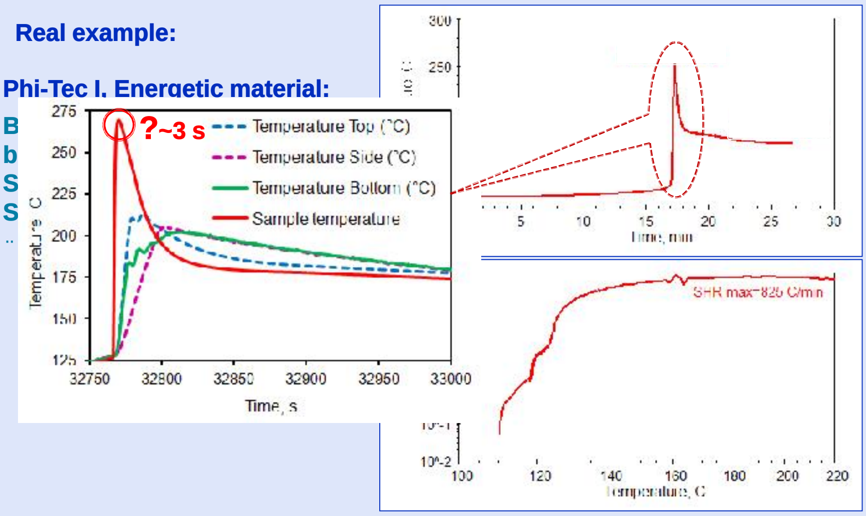
Applying adiabatic calorimetry for energetic materials

Main Problem - high energy release

Real example:

Phi-Tec I. Energetic material:

B
b
S
S
¨



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Applying adiabatic calorimetry for energetic materials

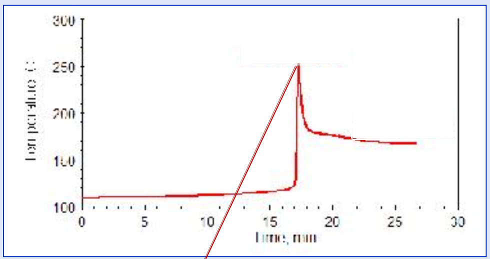
Main Problem - high energy release

Real example:

Phi-Tec I, Energetic material:

Bomb mass - 24.4 g;
bomb Cp - 0.42 J/g/K
Sample mass - 0.5 g;
Sample Cp - 2 J/g/K

¨=11



Q=1255 J/g if ¨$_{eff}$ ~ 4: about 36% of calculated value

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Conclusions

1. **Adiabatic calorimetry:**
   - **is known for almost 50 years**
   - **showed its usefulness**
   - **Is used extensively everywhere**
2. **Nevertheless:**
   - **still a lot of methodical problems**
   - **they must be resolved**
3. **Application of the method to energetic materials:**
   - **Is doomed to failure without applying specialized methods**
   - **no such methods are available at the moment**


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Thank you for your attention!
Comments?
Questions?
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