Applying adiabatic calorimetry for study of energetic materials - is it possible?

Presentation at 11 International Heat Flow Calorimetry Symposium on Energetic Materials, Fraunhofer ICT, Pfinzal-Berghausen, Germany, May 13-16 2019

See also: An in-depth analysis of some methodical aspects of applying pseudo-adiabatic calorimetry

Published in Thermochimica Acta (2109) doi: 10.1016/j.tca.2019.178466

Arcady Kossoy,
CISP Ltd., Saint-Petersburg, Russia,

Topics to be discussed

1. Types of adiabatic calorimeters
2 A little bit of theory and related problems
3 Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality
   - Equilibrium
   - Temperature uniformity
   - Phi-factor
4. Study of energetic materials – is adiabatic calorimetry the right method?

Types of adiabatic calorimeters

- ✓ **Accelerating Rate Calorimeter**

  ARC - ***THT, NETZSCH (Germany)***
  Phi-Tec I - ***HEL (UK)***

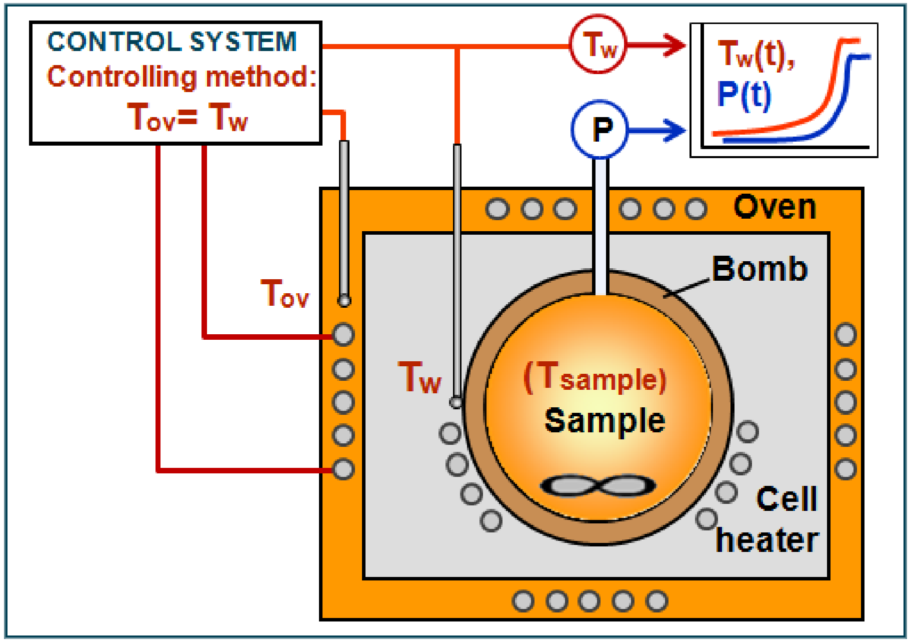
- ✓ **Vent Sizing Package**

  VSP - ***FAI (USA)***
  Phi-Tec II - ***HEL (UK)***

- ✓ **DARC - Differential Accelerating Rate Calorimeter** - ***Omnicalc (USA)***

- ✓ **DEWAR** ***DEKRA (Chilworth) but mostly home-made***

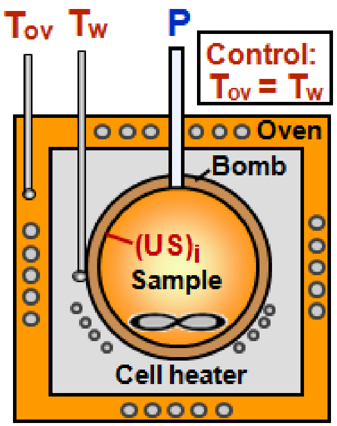
- ✓ **Advanced Reactive System Screening Tool ARSST** - ***FAI (USA)***



A little bit of theory and related problems

1st basic assumption:

Bomb and Sample are the uniform (lumped-parameter systems)



$$(1)\ \begin{cases} m_b \dfrac{d(c_b T_b)}{dt} = (US)_i (T_s - T_b) - W_{loss}; \\ m_s \dfrac{d(c_s T_s)}{dt} = W - (US)_i (T_s - T_b); \\ W = m_s \dfrac{dQ}{dt} \end{cases}$$

c_s, c_b – constants ⇒

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

2nd basic assumtion:

Sample is in equilibrium with the Bomb: $T_s = T_b$ -??

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

$+W_{loss}=0$ ⇒

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

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

2 cornerstone assumptions of adiabatic calorimetry:
equilibrium between sample and bomb and uniformity of a system

Simulation-based analysis

Simulation details

Model: (1) with constant heat capacities - **sample and bomb are uniform**

Bomb: stainless steel sphere, R=1.5 cm, wall thickness - 1 mm; C_p=0.5 J/g/K ; M_b=18.5 g

Sample: low viscous liquid, ρ = 1 g/cm^3; C_p=2 J/g/K; M_s=11.25 g; φ=1.37

Kinetics: 1-st order reaction; K_o=2.9*10^{13} 1/s; E=120 kJ/mol; Q=300 J/g

Internal heat transfer: U=50 W/m^2/K – just guess!

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

Initial conditions: T_O= 80 °C, Conversion (t_O)=0

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

1. System with uniform sample and bomb – can we expect equilibrium&

Model used

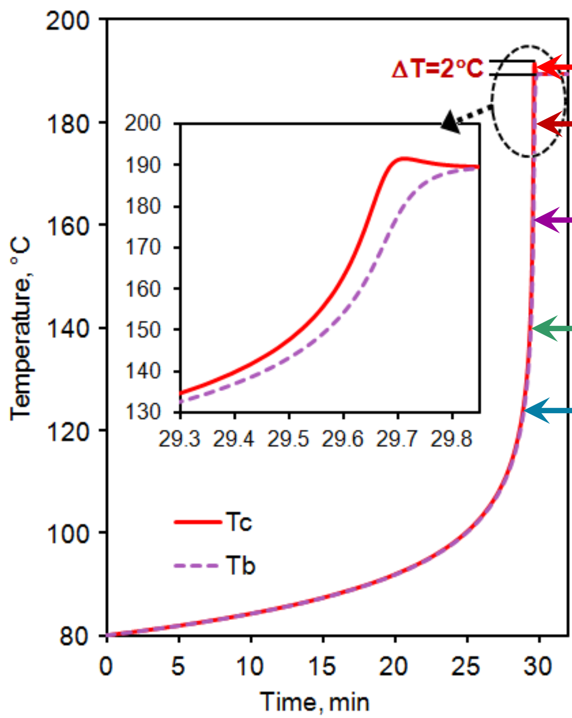
$$c_b m_b \frac{dT_b}{dt} = (US)_i (T_s - T_b);$$

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

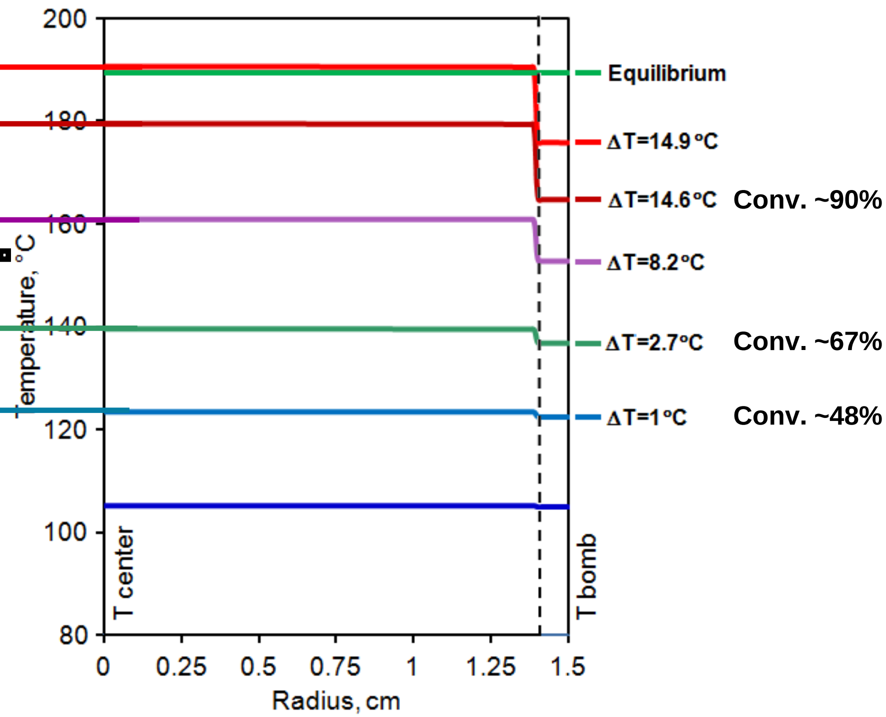
$$W = m_s \frac{dQ}{dt}$$

~~$$c_s m_s \varphi \frac{dT_s}{dt} = W;$$~~

~~$$\varphi = 1 + (c_b m_b)/(c_s m_s)$$~~



Sample (Ts) and bomb (Tb) Temperatures



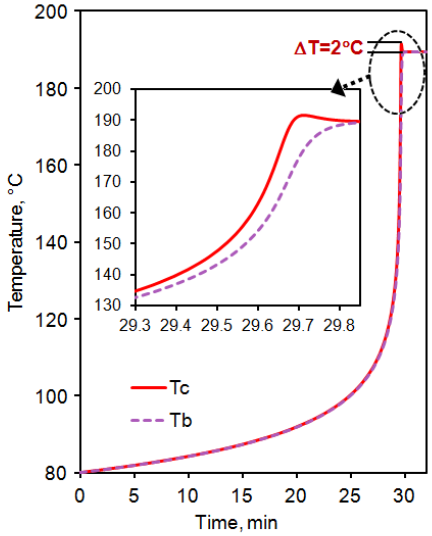
Temperature profiles, ΔT=Ts-Tb

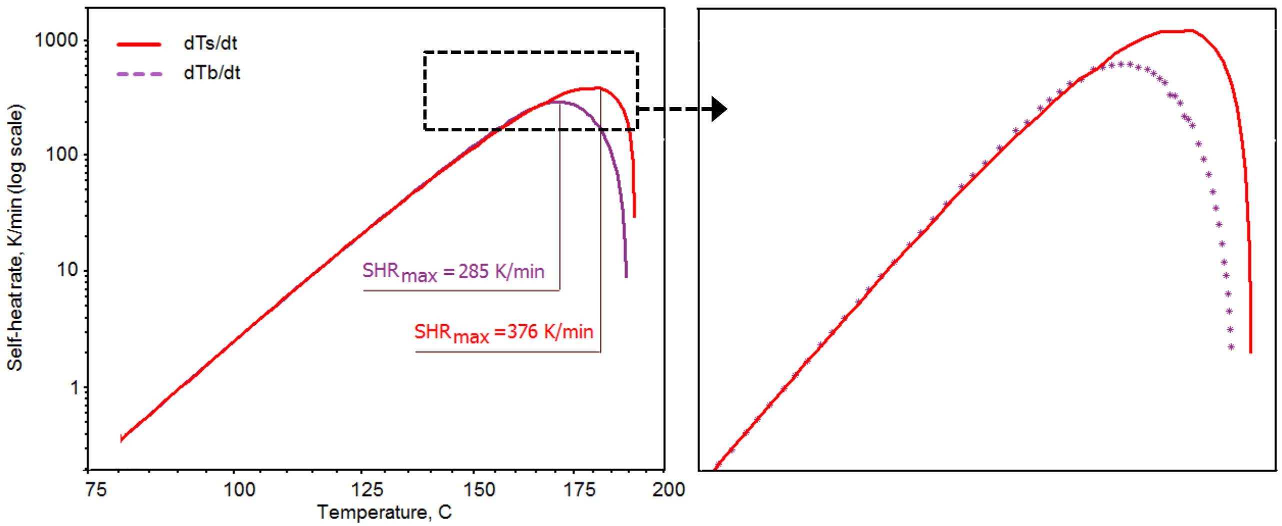
Equilibrium is not provided!

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

1. System with uniform sample and bomb

What happens in the bomb (Ts, dTs/dt) and what we observe (Tb, dTb/dt)





Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

2. Sample uniformity – reality or myth?

Simulation-based analysis

Simulation details (distributed-parameter system)

Model: Partial differential equation of thermal conductivity with kinetic energy source

Bomb: stainless steel sphere, R=1.5 cm, wall thickness - 1 mm; ρ = 7 g/cm^3; C_p=0.45 J/g/K; λ=500 W/m/K; M_b=18.5 g. **Note:** λ was taken very big deliberately

Sample: solid substance, ρ = 1 g/cm^3; C_p=2 J/g/K; λ=0.15 W/m/K; M_s=11.25 g; φ=1.37

Kinetics: 1-st order reaction; K_o=2.9*10^{13} 1/s; E=120 kJ/mol; Q=300 J/g

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

Initial conditions: T_O= 60 °C, Conversion (t_O)=0

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

2. Sample uniformity – reality or myth?

Model used:

Partial differential equation of thermal conductivity with kinetic energy source

$$\rho c \frac{\partial T}{\partial t} = div(\lambda gradT) + W$$

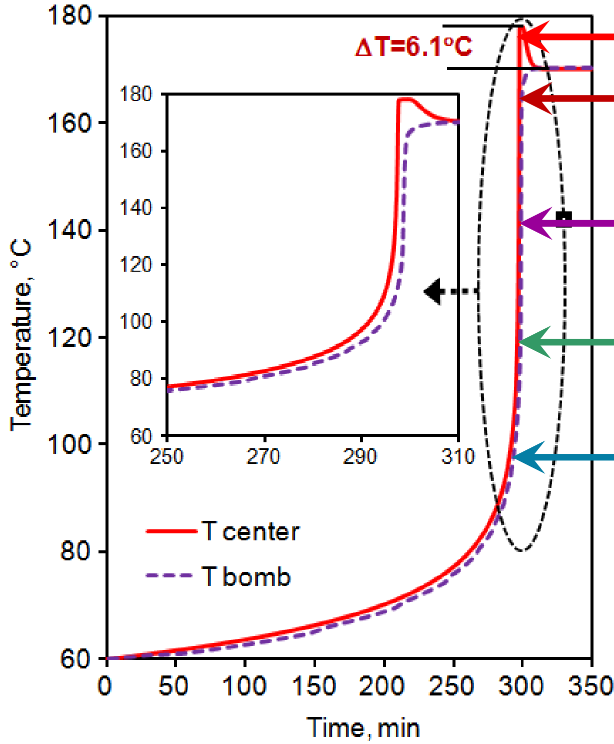
$$W = Q^{\infty} r; \quad r = k_0(1-\alpha)exp(-\frac{E}{RT})$$

BC of 2nd kind: $q|_S = 0$

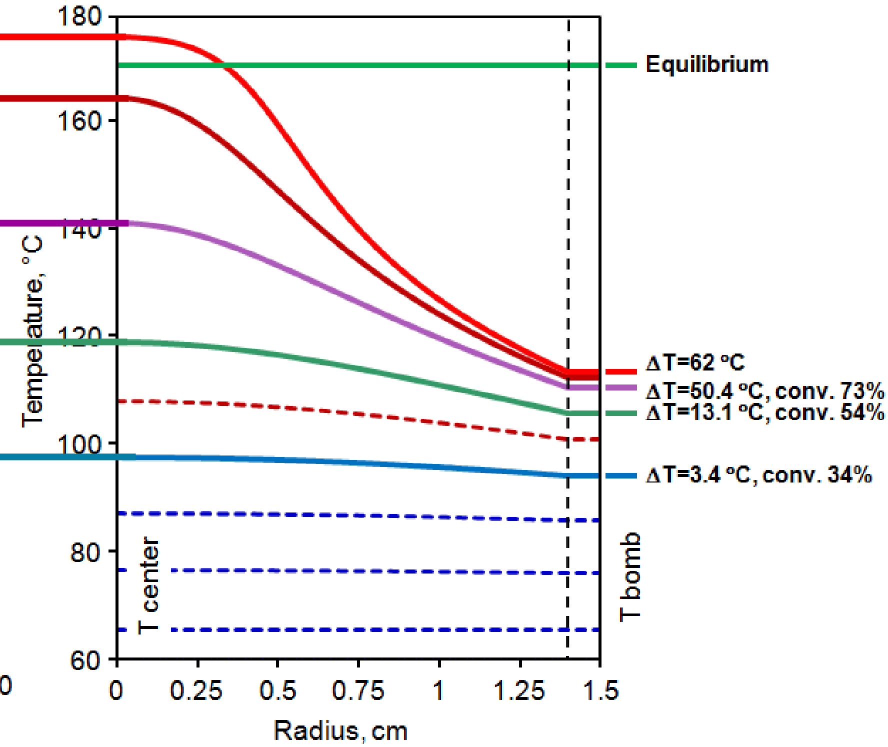
$$c_b m_b \frac{dT_b}{dt} = (US)_i (T_s - T_b);$$

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

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



Sample center (Tc) and bomb (Tb) Temperatures



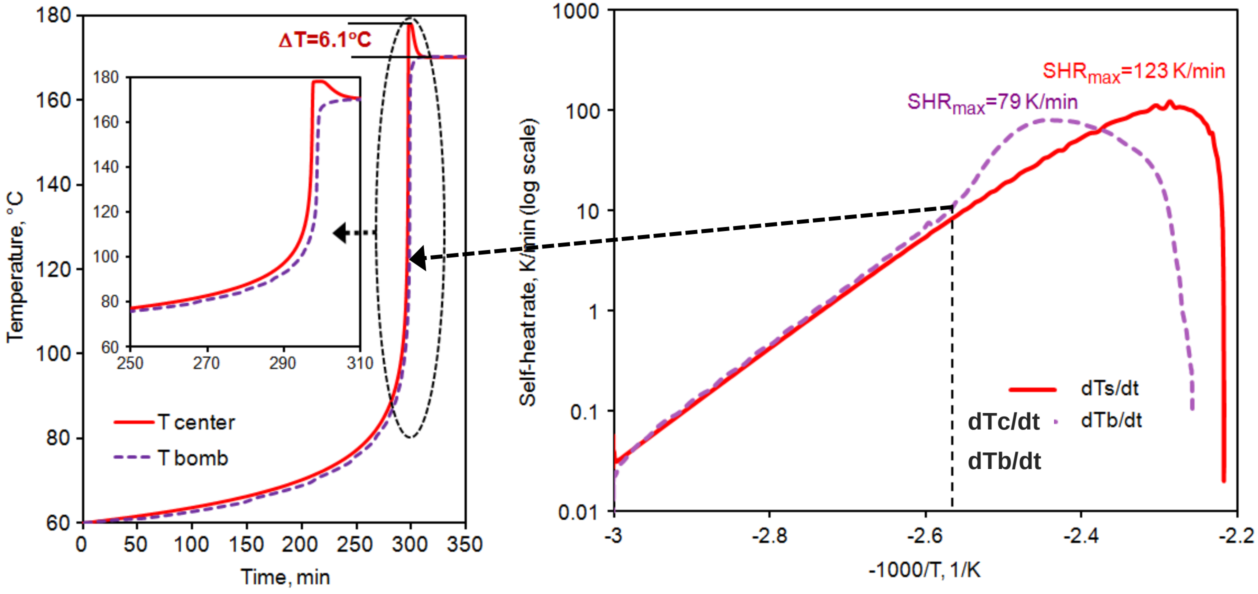
Temperature profiles, ΔT=Tc-Tb

Uniformity? Perhaps for liquids with very intensive agitation but for solids – no way!

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

2. Sample uniformity – reality or myth?

What happens in the bomb (Ts, dTs/dt) and what we observe (Tb, dTb/dt)



Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

2. Equilibrium and Sample uniformity – can they be provided?

Low viscous liquids :

Possible uniformity if intensive forced mixing is provided but the system "bomb+sample" can easily deviate from equilibrium;

Solids or viscous liquids:

Most likely system is non - uniform and hence non – equilibrium;

Obvious remedy:

An instrument with phi = 1. Examples: the Differential ARC and several other devices all based on power compensation of thermal inertia. Panacea? Alias! NO!

Obstacles:

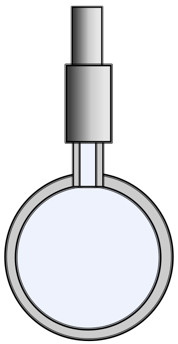
1. **Technically hardly possible to get really phi=1 in all the experiments**
2. **At phi=1 T_{max} and SHR_{max} can easily exceed technical limits even for reactions with very moderate energy release**
3. **No way to test EM!**

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?

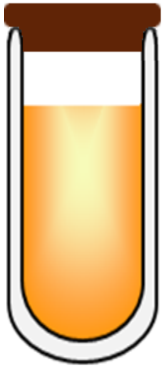
Classical definition: Thermal inertia $\varphi \approx 1 + (c_b M_b)/(c_s M_s)$

Problem # 1 – how to determine thermal inertia?



What is bomb mass M_b=?

How to determine phi for DEWAR?



The best solution – calibration.

It is applied for DEWAR but not for other instruments

Why ?

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?

Classical definition: Thermal inertia $\varphi \approx 1 + (c_b M_b)/(c_s M_s)$

Problem # 2 – φ - Constant or Variable ?

1st reason why φ may vary:

C_b= f(T)

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

Dependency C(T) can be easily taken into account.

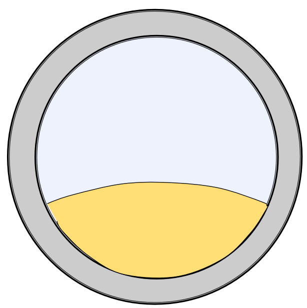
Dependency C_s(composition) – more difficult challenge but certain solutions can be found.

Note: if C_s or/and C_b are variables φ in present form cannot be used

2nd reason why φ may vary:

Lack of equilibrium between sample and bomb even if C_s and C_b are constants

3rd reason why φ may vary:



Sample occupies only part of the bomb volume even if C_s and C_b are constants

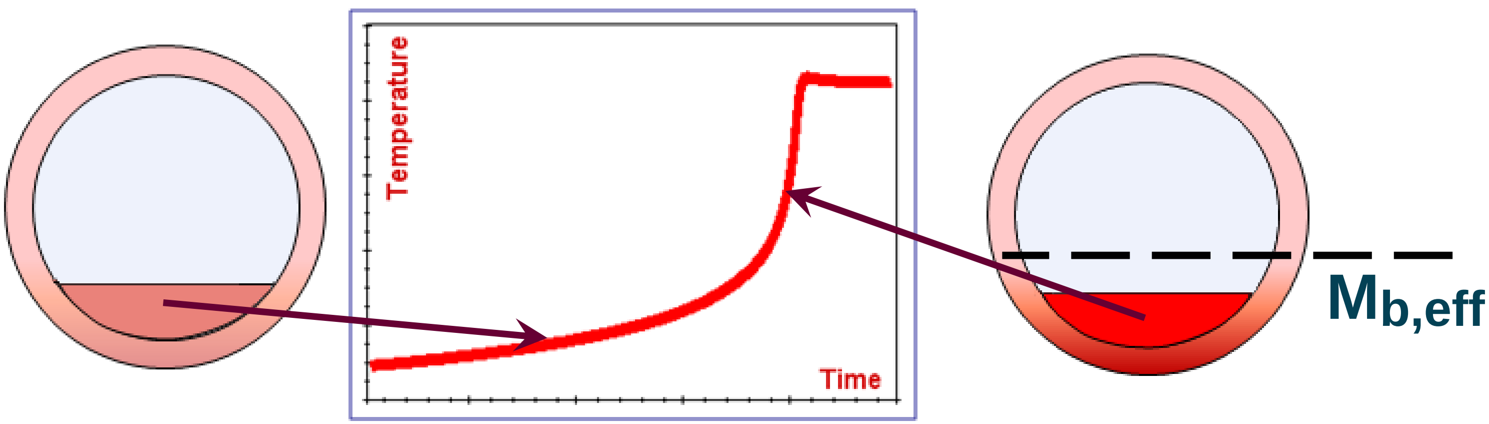
Let me show why

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?

Classical definition: Thermal inertia $\varphi \approx 1 + (c_b M_b)/(c_s M_s)$

Problem # 3 – φ - Constant or Variable ?



$\varphi_0 \approx 1 + (c_b M_b)/\ (c_s M_s)$ >> $\varphi \approx 1 + (c_b M_{b,eff})/\ (c_s M_s)$!!

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?

Simulation-based analysis

Simulation details

Model: Partial differential equation of thermal conductivity with kinetic energy source

Bomb: stainless steel barrel, R=2.6 cm, height=6.2 cm, V=100 ml,
wall thickness - 2 mm; ρ = 7 g/cm^3; C_p=0.5 J/g/K; λ=20 W/m/K; M_b=187 g

Sample: solid substance, ρ = 1 g/cm^3; C_p=2 J/g/K; λ=1 W/m/K; M_s=31.49 g; φ=2.48

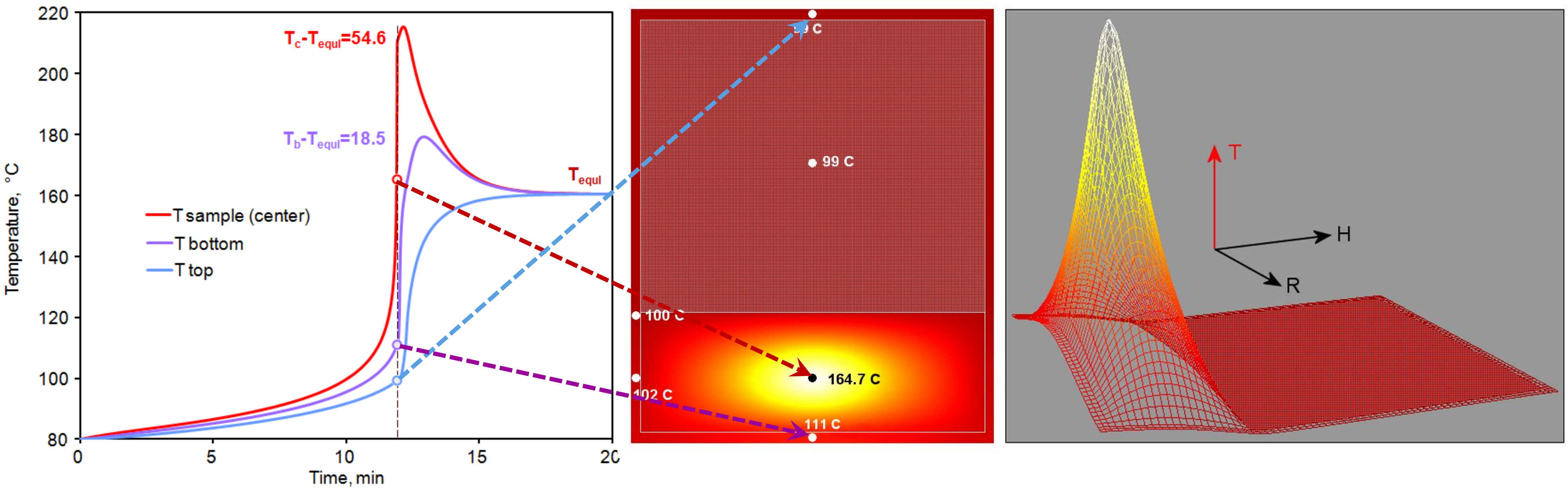
Kinetics: 1-st order reaction; K_o=7.9*10^{13} 1/s; E=120 kJ/mol; Q=400 J/g

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

Initial conditions: T_O= 80 °C, Conversion (t_O)=0

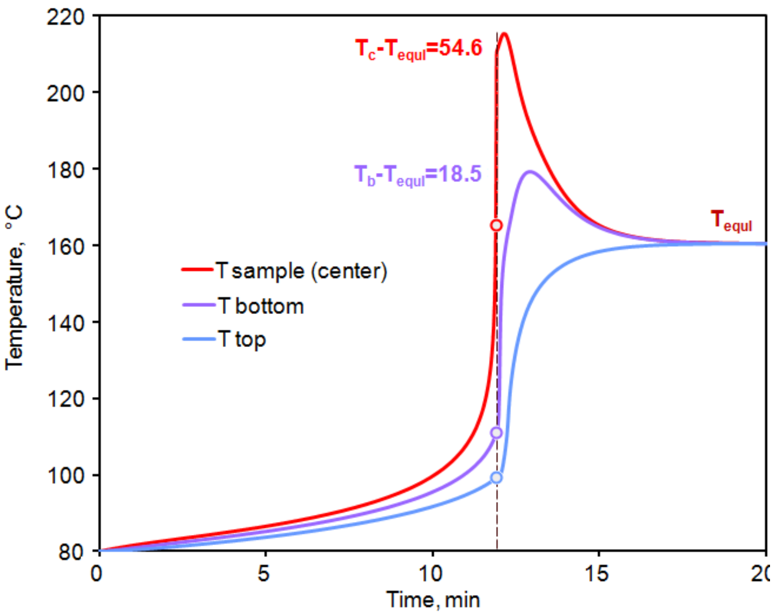
Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?

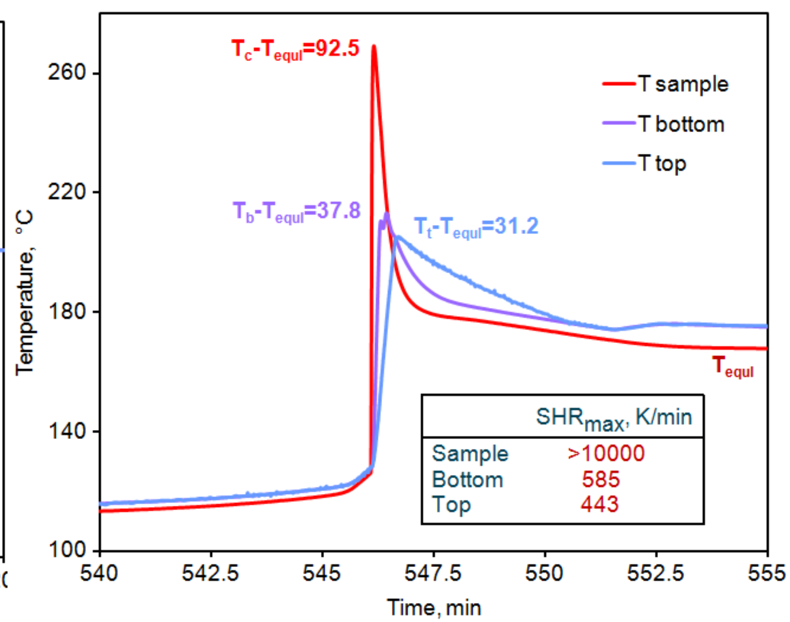


Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?



VSP bomb partly filled with solid - simulation



Real Phi-Tec I experiment with EM

Experiment's parameters

Test Cell: ARC type

Bomb mass = 24.3729g

Sample mass = 0.511 g

Sample Cp = 2 J/g/K

phi = 11.01

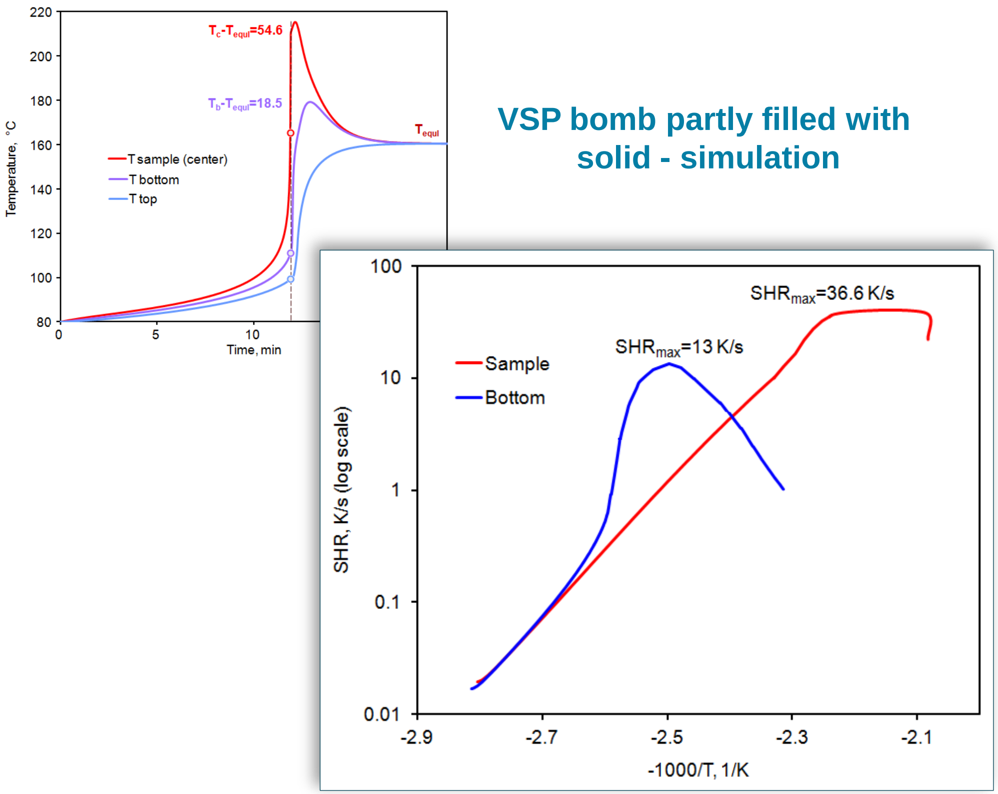
Q (from T_{equl})=1250 J/g

Phi $_{eff}$ at T_{max} =1250/2/140=

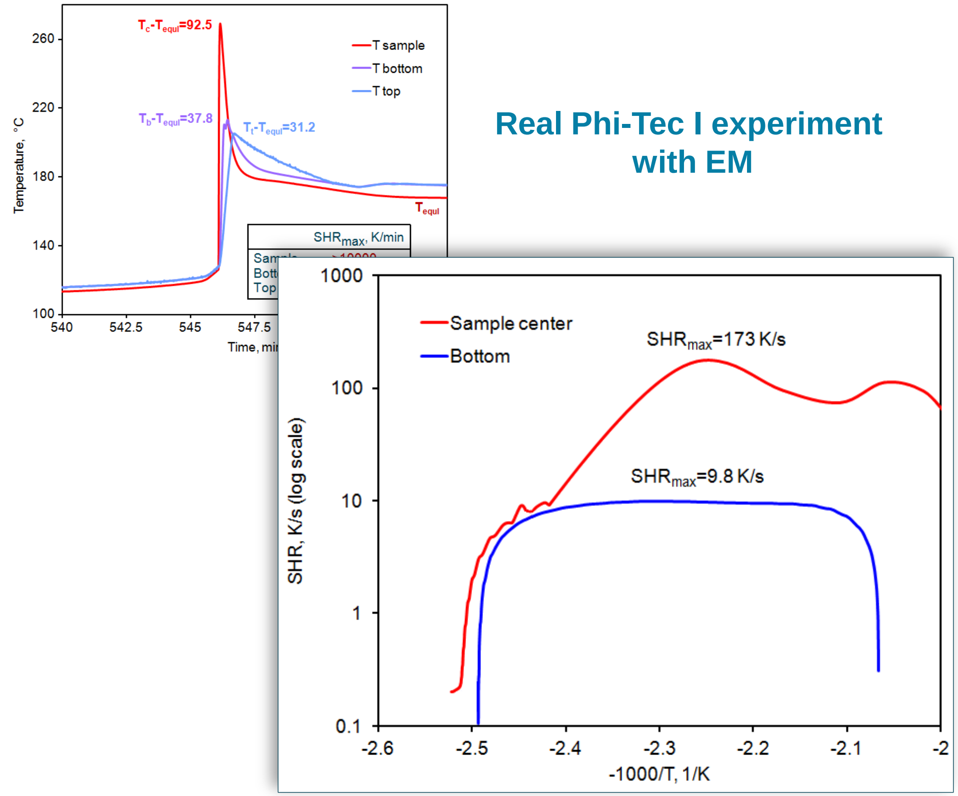
= 4.4 Compare with 11 !!!

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really?



VSP bomb partly filled with solid - simulation



Real Phi-Tec I experiment with EM

Thermal mode of adiabatic experiment – what is usually assumed and what we have in reality

3. Phi-factor – what is it really? Variable more often than not

What can be done?

Most likely we have to follow Vechot L.N., Saha N., at all and answer YES to their question Is it the time to say bye to the φ-factor?

Process Safety and Envir. Protection., (2018) 113 193-203.

Applying adiabatic calorimetry for energetic material

Main problem – high energy release

What to do?

1. Use thermal dilution – good idea but

Hard to find inert material (solid or liquid) that wouldn't affect a reaction

2. Increase φ by using small samples

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	M_S, g	φ	ΔT_{max}, °C
2000	1	6.5	~300
3000	0.6	10.2	~300
4000	0.45	13.2	~300

3. Special construction of the bomb – perhaps possible but not available – has to be designed

Alas! This method won't work because of 2 reasons:

- **nonequilibrium state of the system**
- **non-uniformity of the system**

Applying adiabatic calorimetry for energetic material

Final example

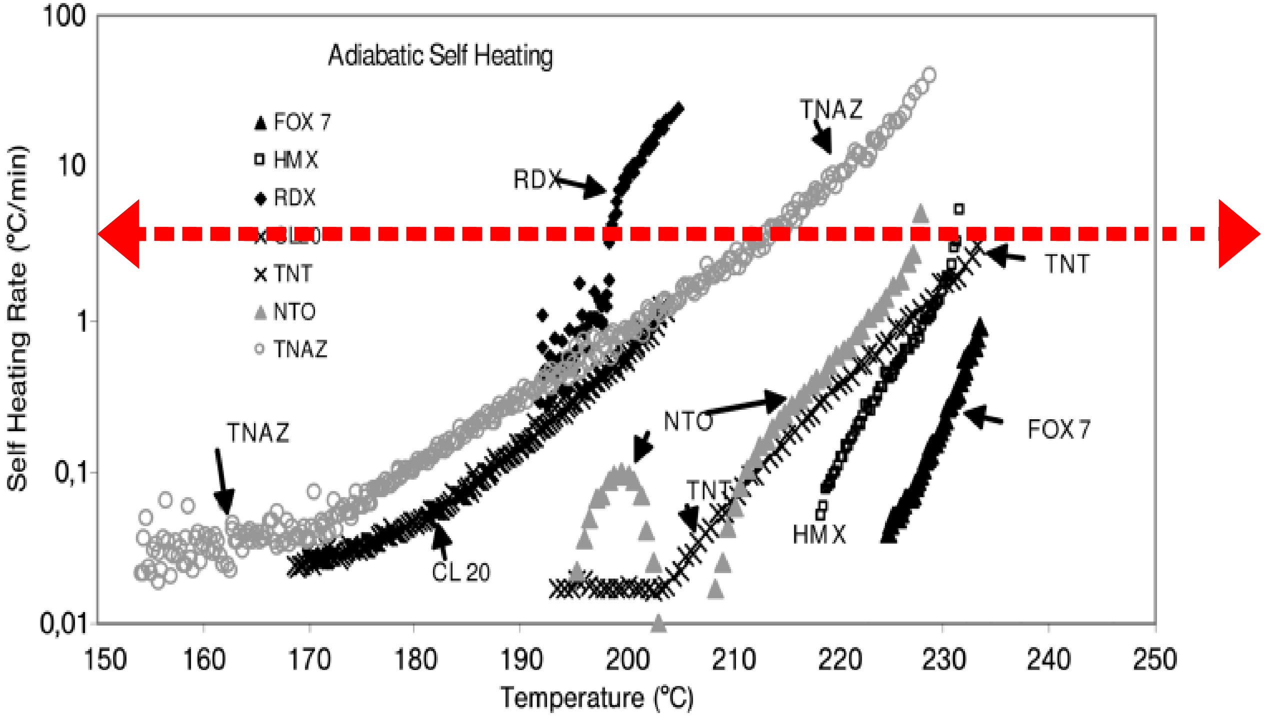


Figure 1.1. Adiabatic self-heating rate of various energetic materials.
Energetic Materials. Edited by Ulrich Teipel, 2005 WILEY-VCH Verlag GmbH & Co. KG, A, Weinheim
Chapter 1 New Energetic Materials, by Horst H. Krause

Don't you think that SHRs are surprisingly small for such highly energetic materials?

For comparison: max value of self-heat rate for 20% solution of DTBP in toluene ~ 250 K/min!

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
   - meantime one should be aware about the serious limitations and be careful not to go out of the limits
3. Application of the method to energetic materials:
   - Is doomed to failure without applying specialized methods
   - no such methods are available at the moment

All the simulations in this project were made by ThermEx software from the CISP® TSS-ARKS series