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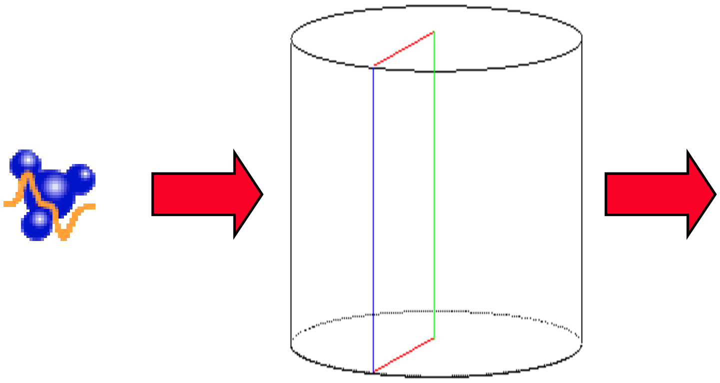
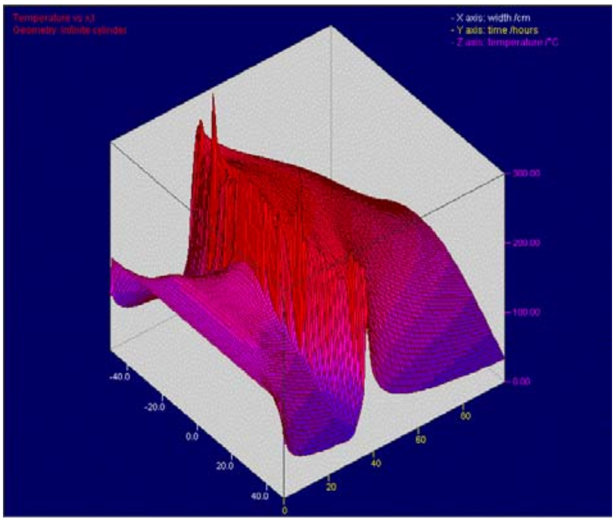
Advanced Kinetics and Technology Solutions

STK-Greifensee Nov. 6th 2002

Thermal hazards & Storage of self-reactive chemicals

FROM MILLIGRAMS TO TONS: THE PREDICTION OF REACTION PROGRESS OF SELF-REACTIVE CHEMICALS





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(AKTS-TA-Software, screen captures)

Summary:

Generally all energetic materials evolve heat during decomposition. Processing, design, quality control, and operational applications all require an understanding of thermal hazards and an ability to predict safety limits.

Several methods have been presented for predictions of the reaction progress of exothermic reactions under adiabatic conditions [1-3]. However, because solid state reactions usually have a multi-step nature, the accurate determination of the kinetic characteristics strongly influences the ability to correctly describe the progress of the reaction [4]. For self-heating reactions, incorrect kinetic description of the process is usually the main source of serious errors in its interpretation. It is hazardous to develop safety predictive models that are based on simplified kinetics determined by thermoanalytical methods.

Applications of finite element methods (FEM) and accurate kinetic description allow determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions. In fact, the assumption that it is safe to handle an energetic material at any temperature below the first appearance of an exothermic signal on the DSC or DTA curve can be often false. The highest safe temperature for handling any energetic material depends on several factors as e.g. its size, shape, and previous thermal history. Due to insufficient thermal convection and limited thermal conductivity, a progressive temperature increase in the sample can easily take place, resulting in a thermal explosion.

Applications of FEM allows the stringent extension from mg of substances to large scales (scale-up) and the simulation in 3D-geometries, the inclusion of thermal conductivity and the consideration of the complex thermal environment. Use of both, kinetics and FEM, allows to determine reaction progress and temperature profiles in storage containers containing any kind of hazardous materials. The reaction progress and temperature can be determined quantitatively at every point in time and in space. This information is essential for the design of containers of self-reactive chemicals, cooling systems and the measures to be taken in the event of a cooling failure.

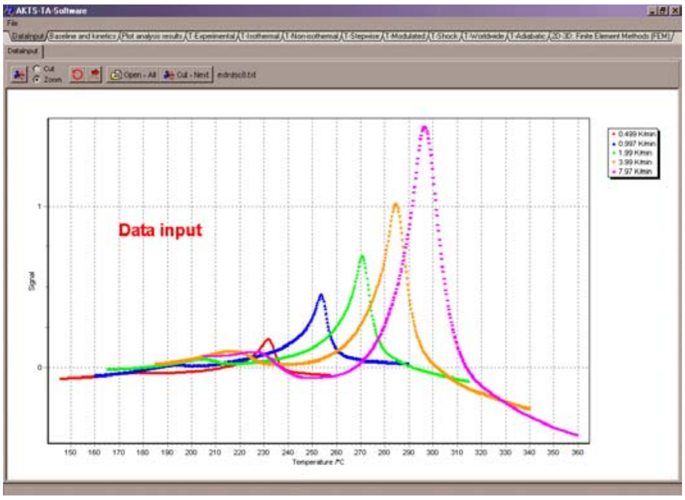
Applications of FEM and kinetics of complex reactions for the determination of the heat balances and consulting on the choice of the best container size for safe storage and transport temperatures will be illustrated by on-line calculations carried out during the lecture.

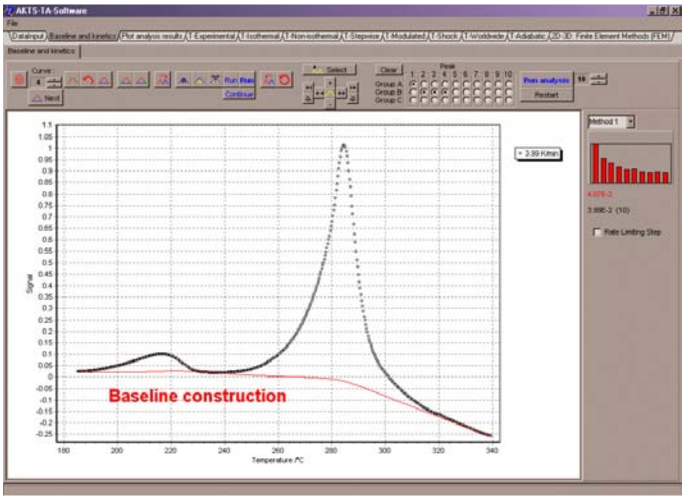
REFERENCES

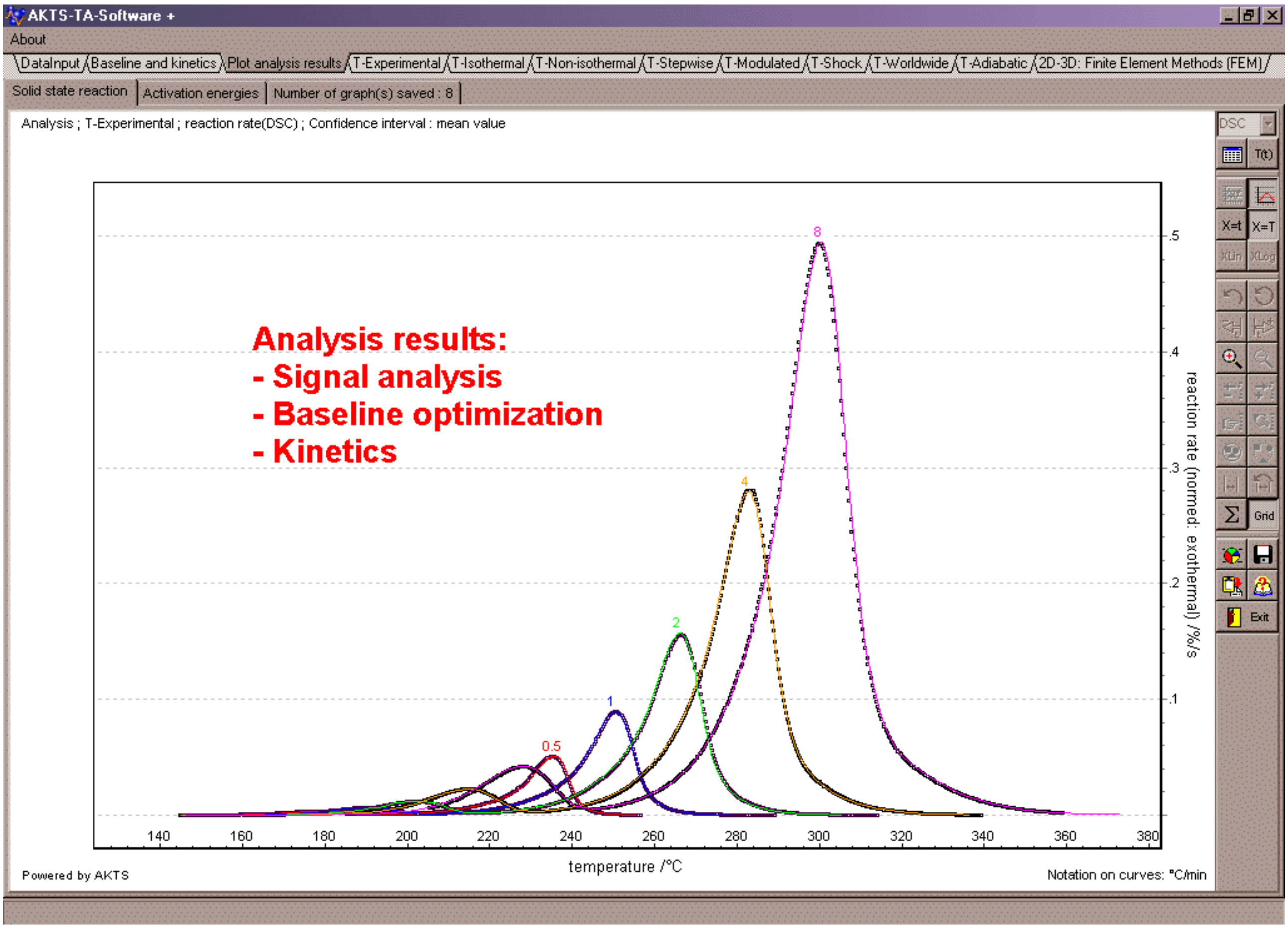
[1] N. Semenov, Einige Probleme der chemischen Kinetik und Reaktionsfähigkeit, Akademieverlag, Berlin, 1961.
[2] D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York, London, 1969.
[3] T. Grewer, Thermochim. Acta, 225 (1993) 165.
[4] B. Roduit, Thermochim. Acta, 388 (2002) 377.

Analysis process:

A full kinetic analysis of a solid state reaction has at least three major stages: (1) experimental collection of data; (2) computation of kinetic parameters using the data from stage 1; and (3) predictions of the reaction progress for required temperature profiles applying determined kinetic parameters.

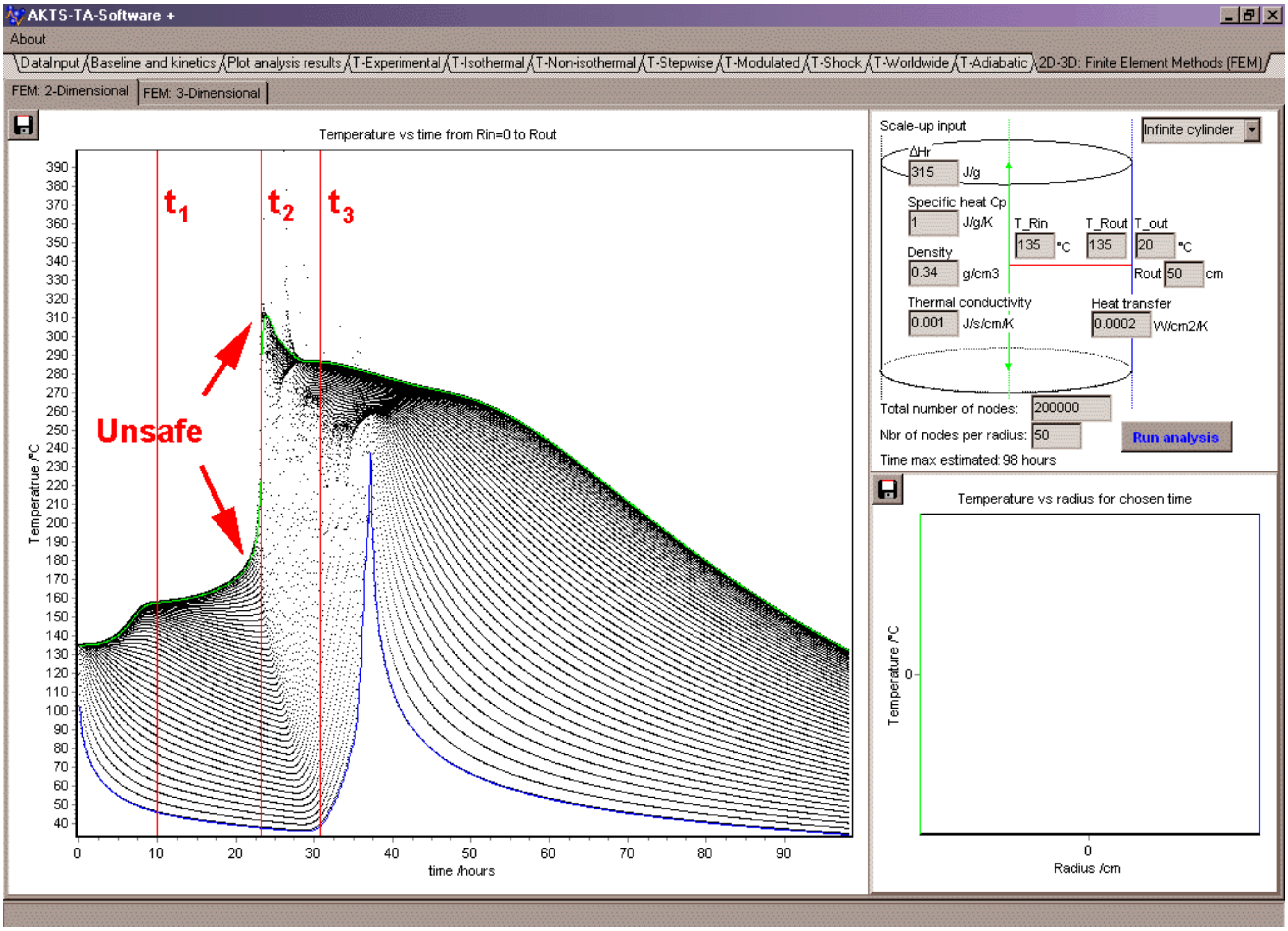






Applications of finite element methods (FEM):

Applications of FEM and accurate kinetic description allow determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions.



Infinite cylinder

ΔHr 315 J/g

Specific heat Cp 1 J/g/K

Density 0.34 g/cm3

Thermal conductivity 0.001 J/s/cm/K

T_Rin 135 °C

T_Rout 135

T_out 20 °C

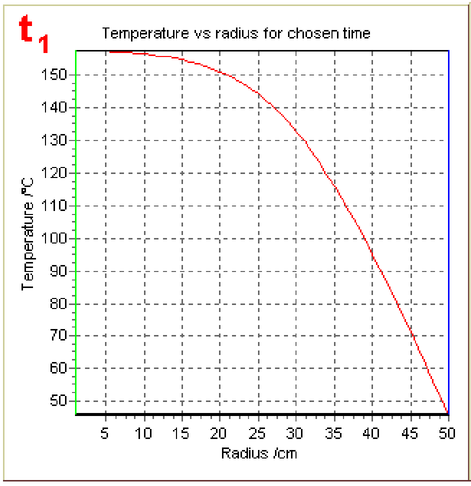
Rout 50 cm

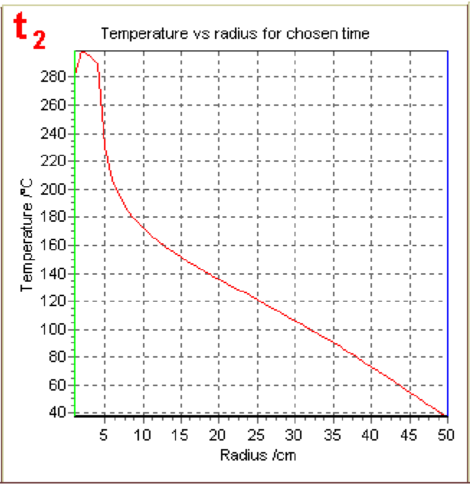
Heat transfer 0.0002 W/cm2/K

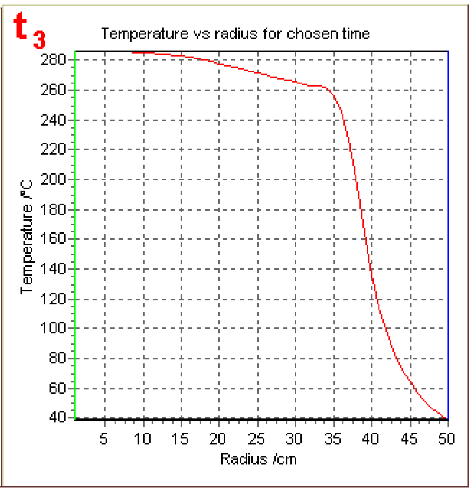
Total number of nodes: 200000

Nbr of nodes per radius: 50

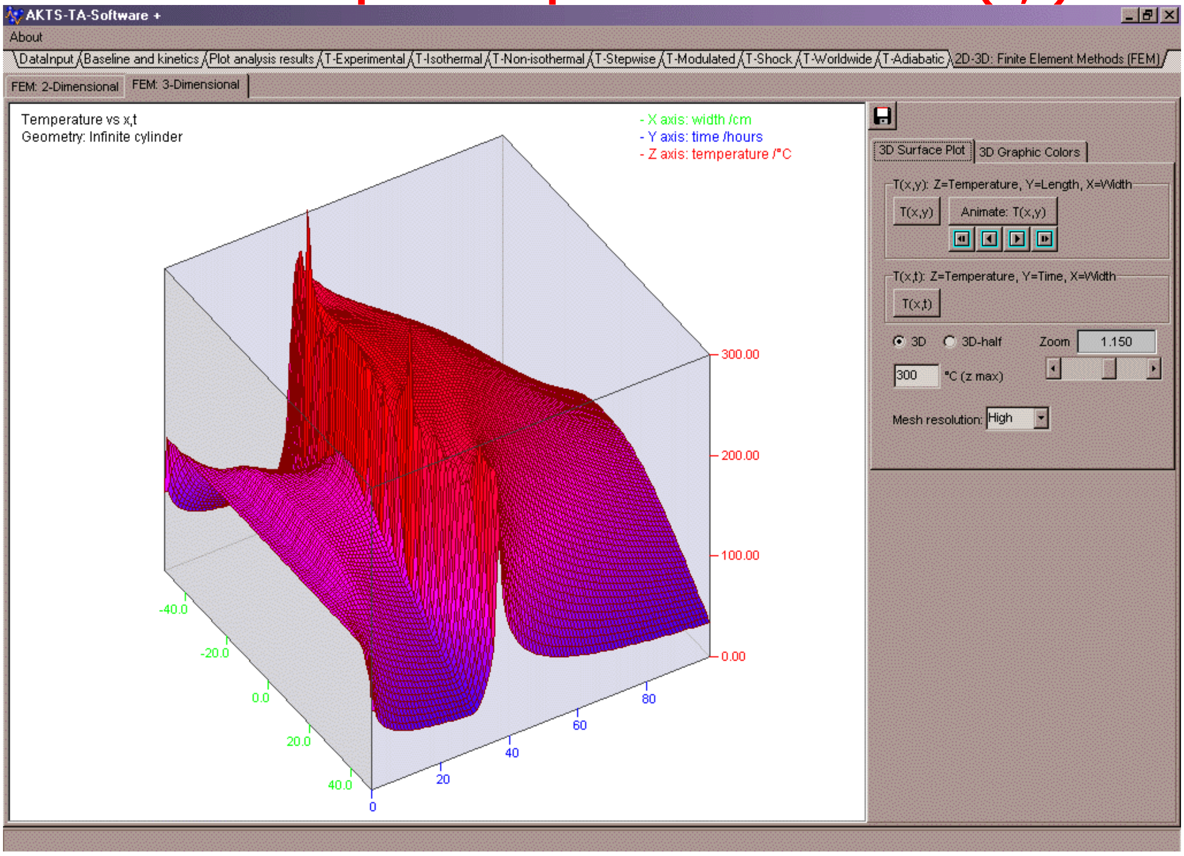
Time max estimated: 98 hours







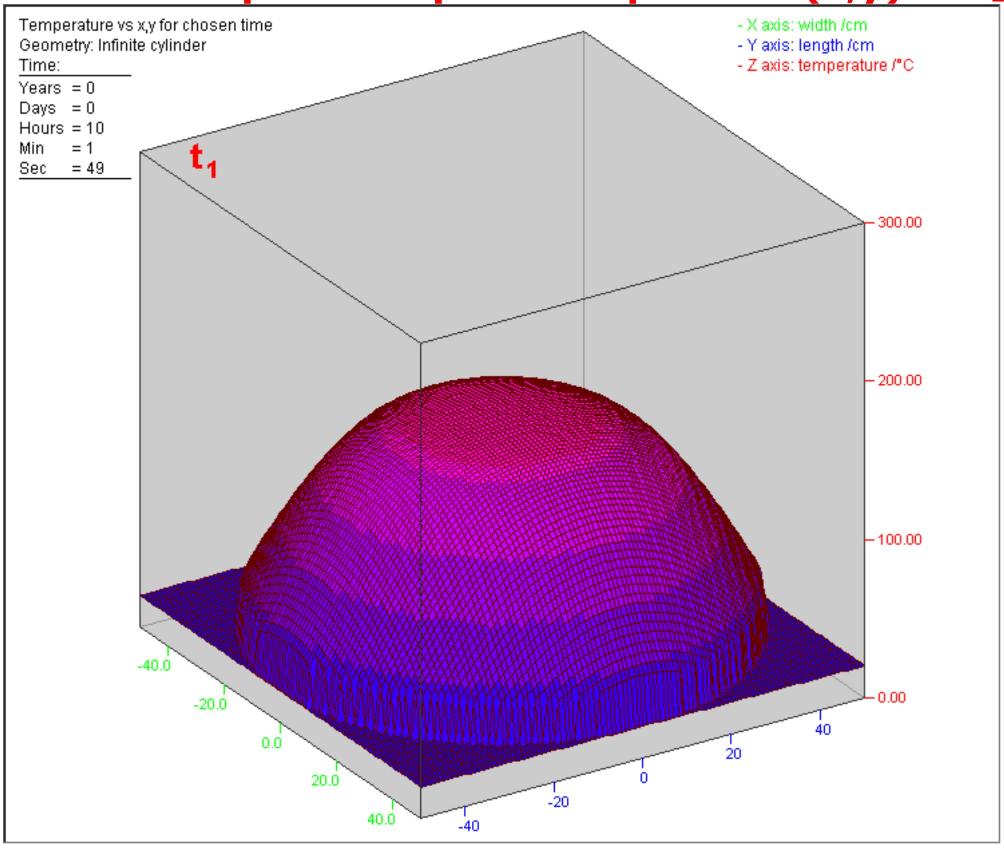
3D Surface plot: temperature evolution T(x,t)



Temperature vs x,t
Geometry: Infinite cylinder

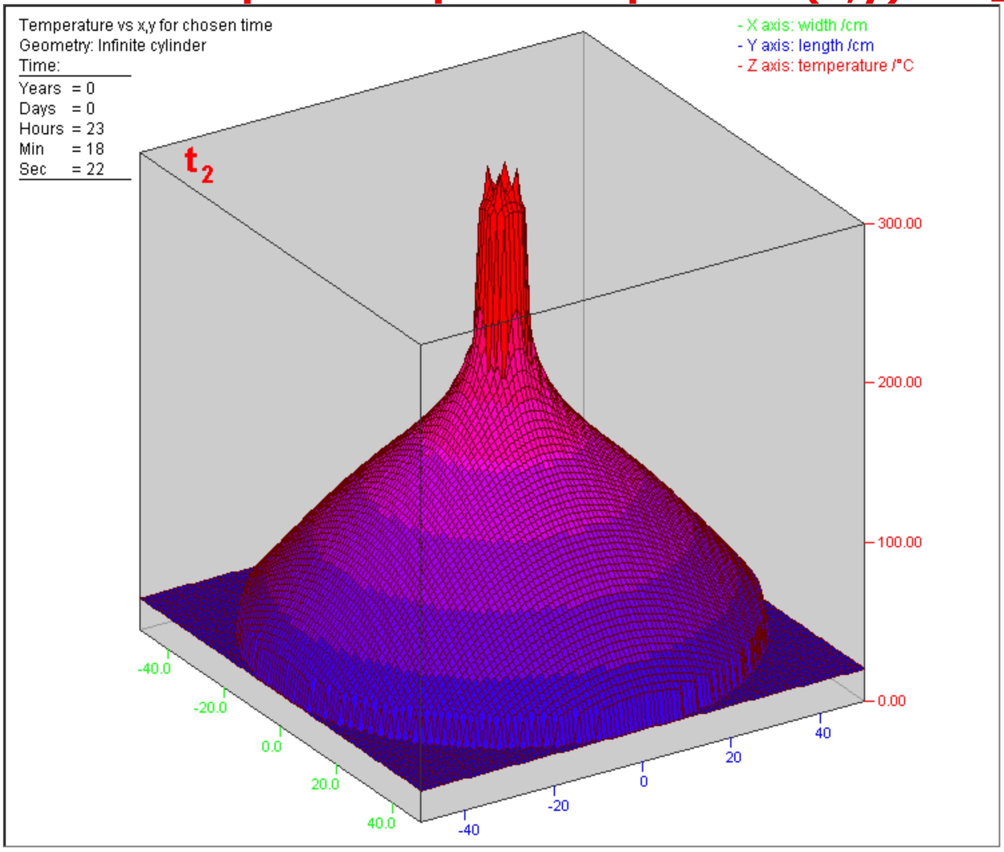
● 3D ○ 3D-half
Zoom 1.150
300 °C (z max)
Mesh resolution: High

3D Surface plot: temperature profile T(x,y) at t_1



Temperature vs x,y for chosen time
Geometry: Infinite cylinder
Time:
Years = 0
Days = 0
Hours = 10
Min = 1
Sec = 49

3D Surface plot: temperature profile T(x,y) at t_2



3D Surface plot: temperature profile T(x,y) at t_3