Presented at the COMSOL Conference 2008 Boston

# COMSOL Conference 2008 Boston
# Fourth Annual Conference on Multiphysics Simulation

**Renaissance Boston Waterfront**
**October 9-11, 2008 Boston, MA**

# Analysis of Heat, Mass Transport, & Momentum Transport Effects in Complex Catalyst Shapes for Gas-Phase Heterogeneous Reactions Using COMSOL Multiphysics

**Session on *Transport Phenomena* - October 9, 2008**

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# Scope & Economics of Catalytic Processes

**Syn & Natural Gas Conversion**

MeOH, DME, MTBE, Paraffins, Olefins, Higher alcohols, ….

**Petroleum Refining**

HDS, HDN, HDM, Dewaxing, Fuels, Aromatics, Olefins, ...

1/3 of USA's GDP

$12 MMMM in Goods

$5.4 MMM in Sales

**Bulk Chemicals**

Aldehydes, Alcohols, Amines, Acids, Esters, LAB's, Inorg Acids, ...

**Polymer Manufacture**

Polycarbonates, PPO, Polyolefins, Specialty plastics

**Fine Chemicals & Pharmaceuticals**

Ag Chem, Dyes, Fragrances, Flavors, Nutraceuticals,...

**Biomass Conversion**

Syn Gas, MeOH, EtOH, Biodiesel, High Value-Added Products

**Environmental Remediation**

De-NOx, De-SOx, HCFC's, DPA, "Green" Processes ..

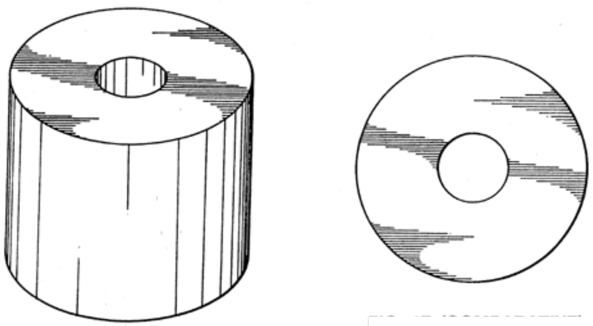
# Motivation

- Various catalyst particle shapes are sold commercially for a wide variety of process technologies

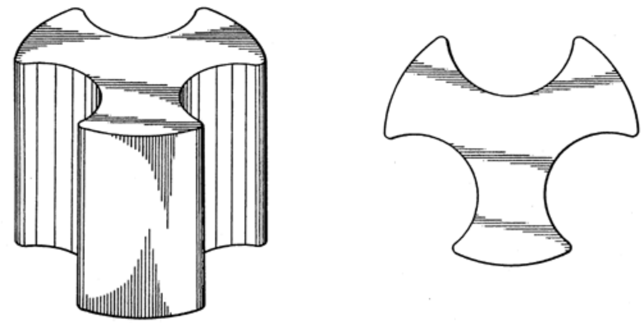

- Preferred shapes are often obtained by empirical methods
- Examine Comsol Multiphysics as a platform for quantifying the effect of catalyst shape on reactor performance

**Applications:** Theoretical, Practical, and Pedagogical

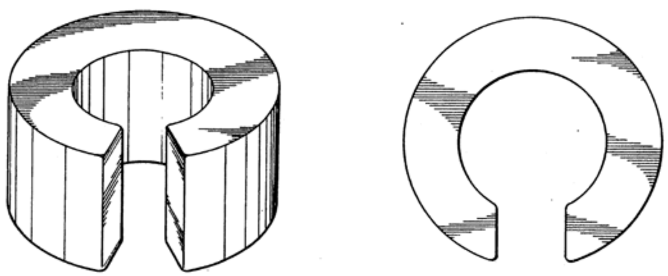
# Examples of Catalyst Shapes - 1



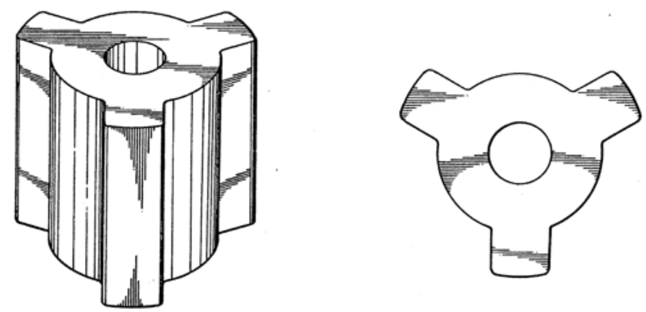
Hollow Cylinder



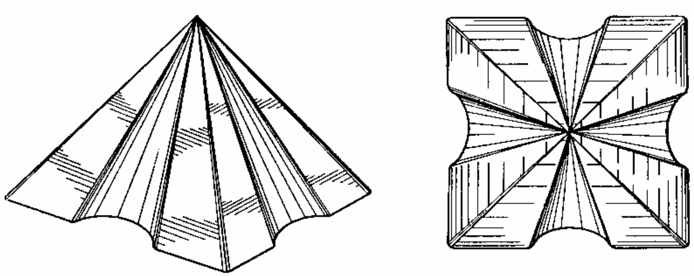
Tri-lobe



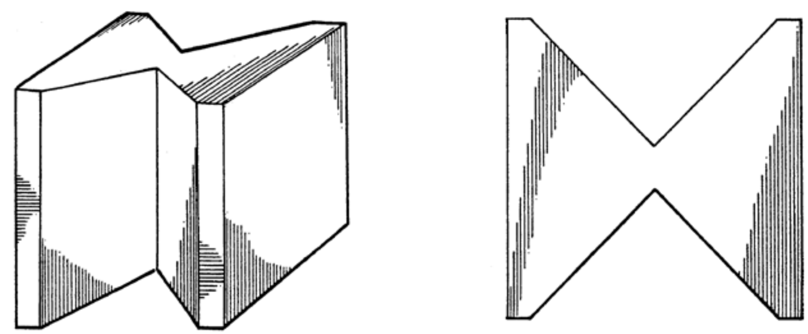
Hollow Cylinder



Ribbed, Hollow Cylinder



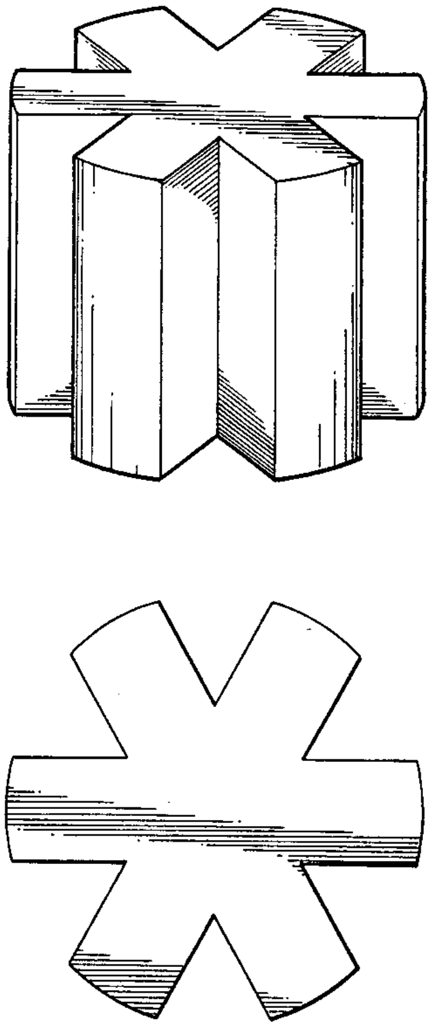
Grooved Pyramid



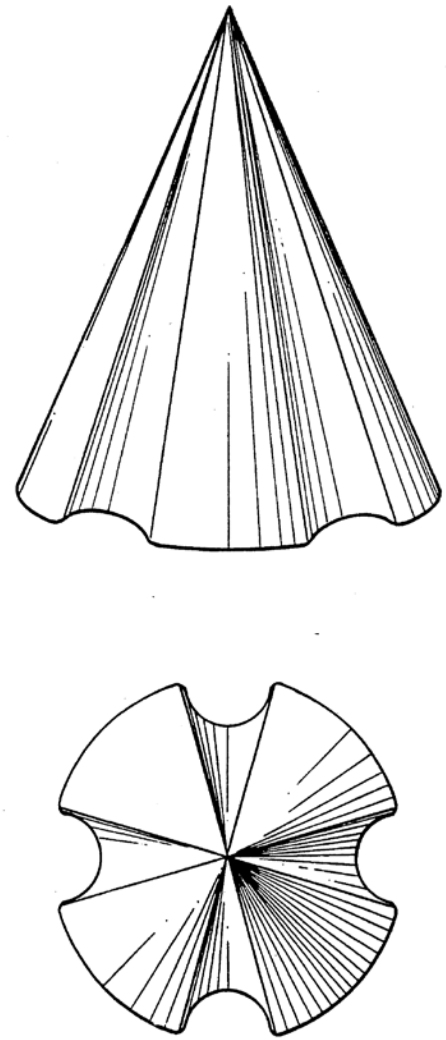
Notched Cube

J. R. Ebner & R. A. Keppel, *Shaped Oxidation Catalyst*, US 5,168,090 Monsanto 1992

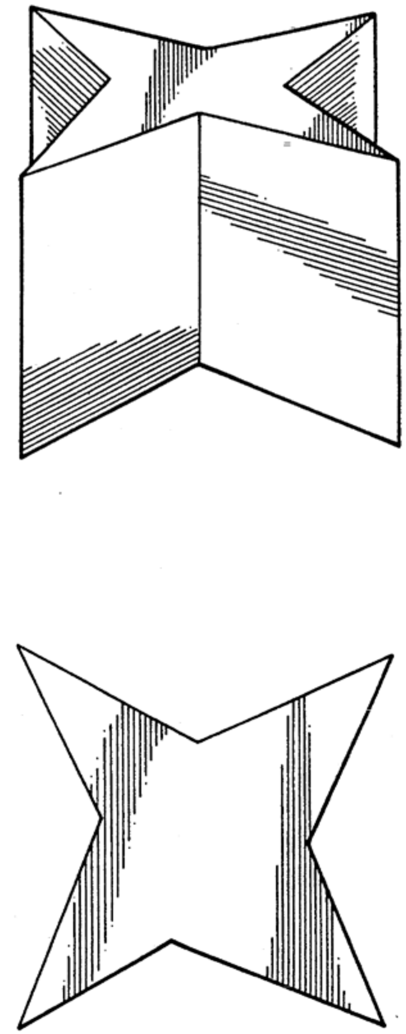
# Examples of Catalyst Shapes - 2



**Notched Cylinder**



**Grooved Cone**

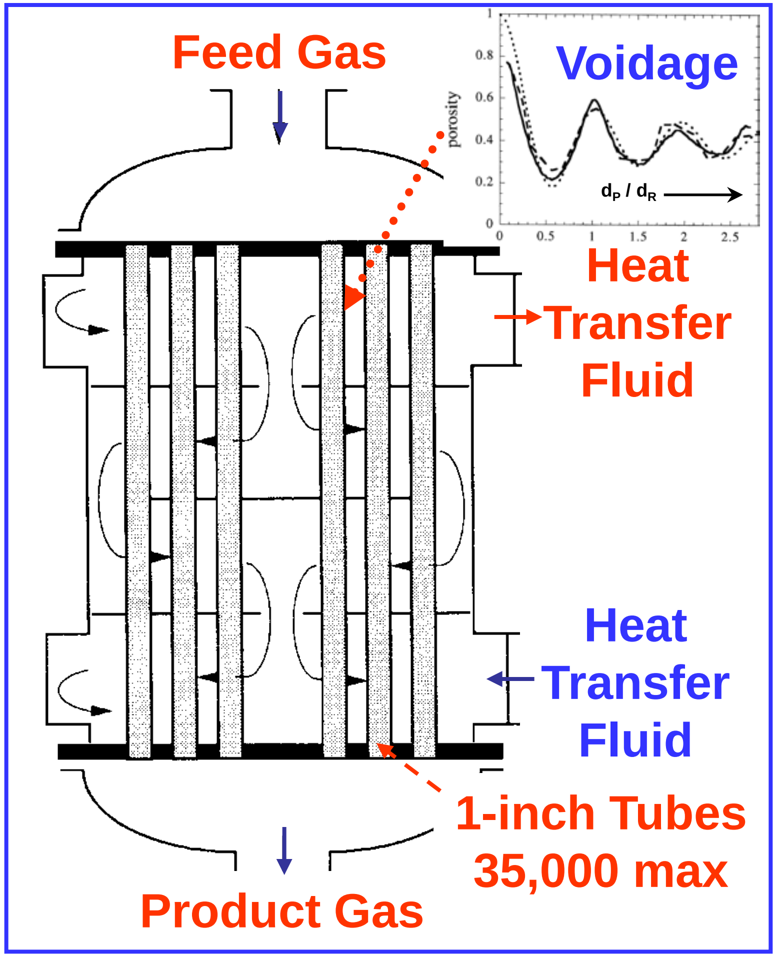


**4-Point Star**

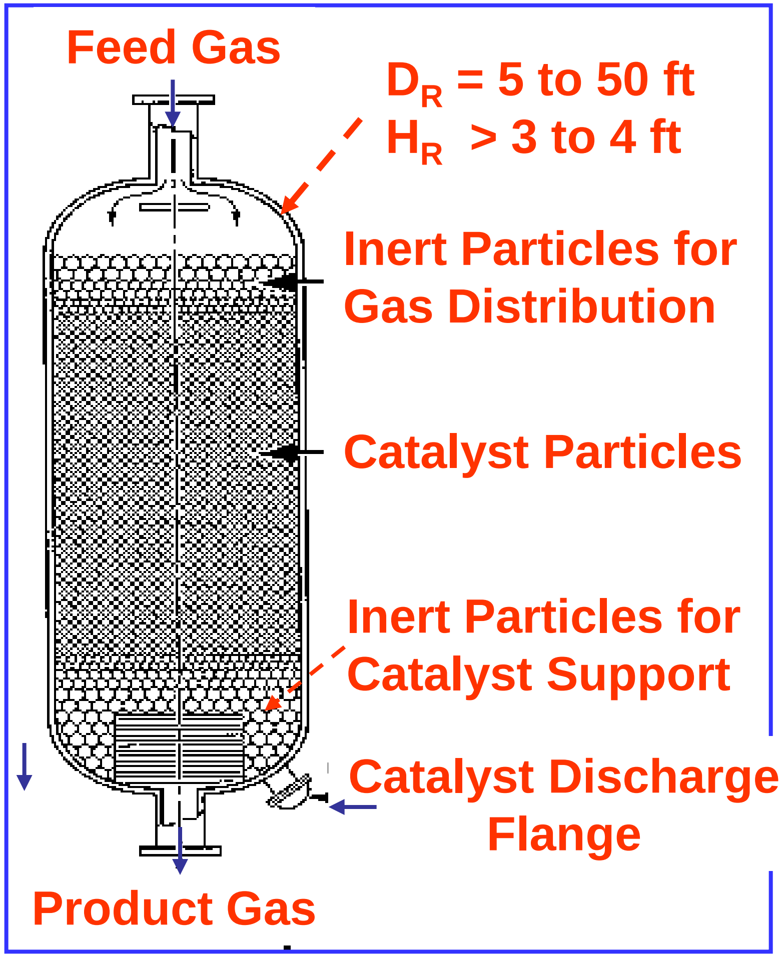
J. R. Ebner & R. A. Keppel, *Shaped Oxidation Catalyst*, US 5,168,090 Monsanto 1992

# Typical Packed Bed Reactor Configurations

## Multi-tubular




## Adiabatic




**Overall Goal:** Maximize activity and selectivity while minimizing pressure drop & cost

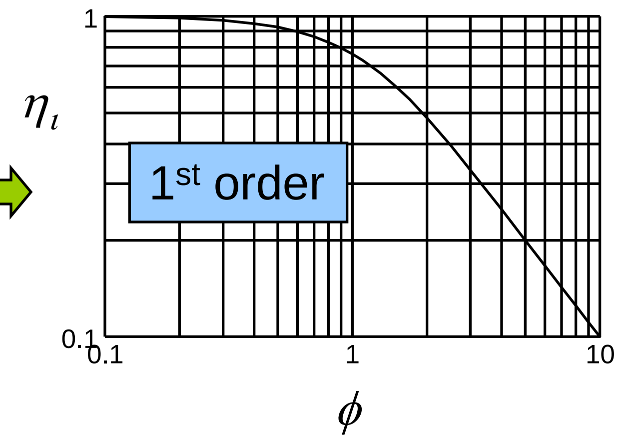
# Catalyst Shape

## -A Key Reactor Process Design Parameter-

### Catalyst Effectiveness Factor (Maximize)

$$\eta_i = \frac{\text{observed rate}}{\text{rate without internal gradients}} = \frac{\int_0^{V_p} r_v(c,T)\,dV}{r_{v,chem}(c_s,T_s)\cdot V_p}$$

$$\phi^2 = \left(\frac{V_P}{S_P}\right)^2 \frac{k_1}{D_{EA}} = \frac{\text{Characterisic time for diffusion}}{\text{Characteristic time for reaction}}$$

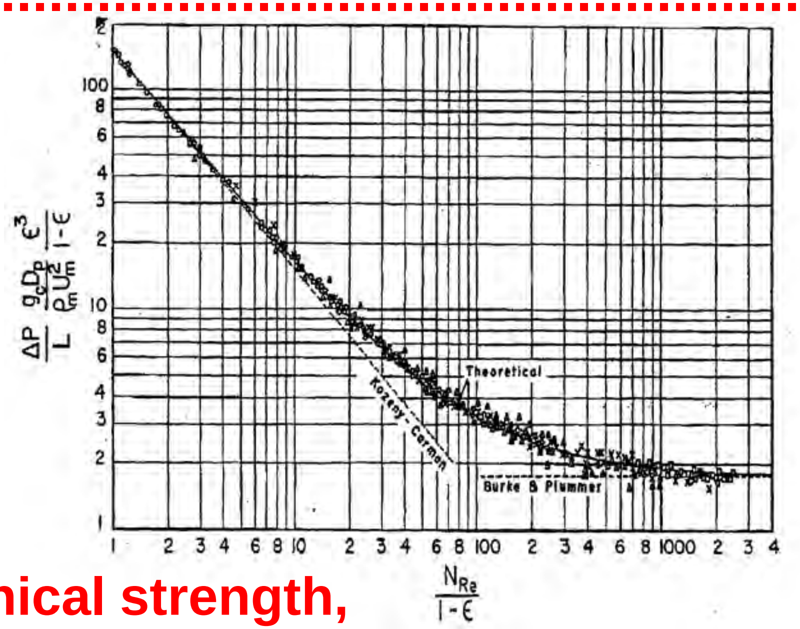



### Catalyst Bed Pressure Drop (Minimize)

$$\frac{\Delta P}{L} = 150\,\frac{(1-\varepsilon)^2}{\varepsilon^3}\,\frac{\mu\, U_M}{D_P^2} + 1.75\,\frac{1-\varepsilon}{\varepsilon^3}\,\frac{G\, U_M}{D_P}$$

**Ergun Equation & Updated Forms**

(Ergun, 1952; Levec, 2005a, 2005b)




**Other key parameters:** **Forming, mechanical strength, heat transfer, pore size distribution,**

# Approaches to Catalyst Particle Modeling

- **Numerous papers on modelling of transport-kinetic interactions in catalyst particles**

  Rutherford Aris, "On shape factors for irregular particles – I. The steady-state problem. Diffusion & reaction. *Chem. Engng. Sci*. **6**: 262-268 (1957)

- **Variety of solution methods & numerical techniques**

  Analytical, semi-analytical, finite difference, finite element, method of lines, etc

  P. A. Ramachandran, "Boundary integral element method for linear diffusion-reaction problems with discontinuous boundary conditions. *Chem. Eng. J.* **47**: 169 (1991).

- **Some approaches are driven by process applications**

  J. S. S. Mohammadzadeh and A. Zamaniyan, "Catalyst shape as a design parameter for methane-steam reforming catalyst." Inst Chem Eng (UK), **80** (2002)

- **Comsol Multiphysics provides powerful platform for multi-scale modeling and parametric analysis**

# Transport & Reaction in Porous Catalysts

- **Widely studied & analyzed since Thiele's & Aris' classic papers and monograph on the subject**


E. W. Thiele, "Relation between catalytic activity and size of particle." *Ind. Eng. Chem.* **31**: 916-920 (1939).

Rutherford Aris, "On shape factors for irregular particles – I. The steady-state problem. Diffusion & reaction. *Chem. Engng. Sci.* **6**: 262-268 (1957).

Rutherford Aris, *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts.* Volume 1 and Volume 2, Oxford: Clarendon Press (1975).


**Species Mass Balance**

$$\nabla \bullet \overline{N}_j = \nabla \bullet \left(- D_{ej,m} \nabla C_j\right) = \left(\sum_{i=1}^{nr} \upsilon_{i\,j}\, r_i\right) S_g\, \rho_g$$

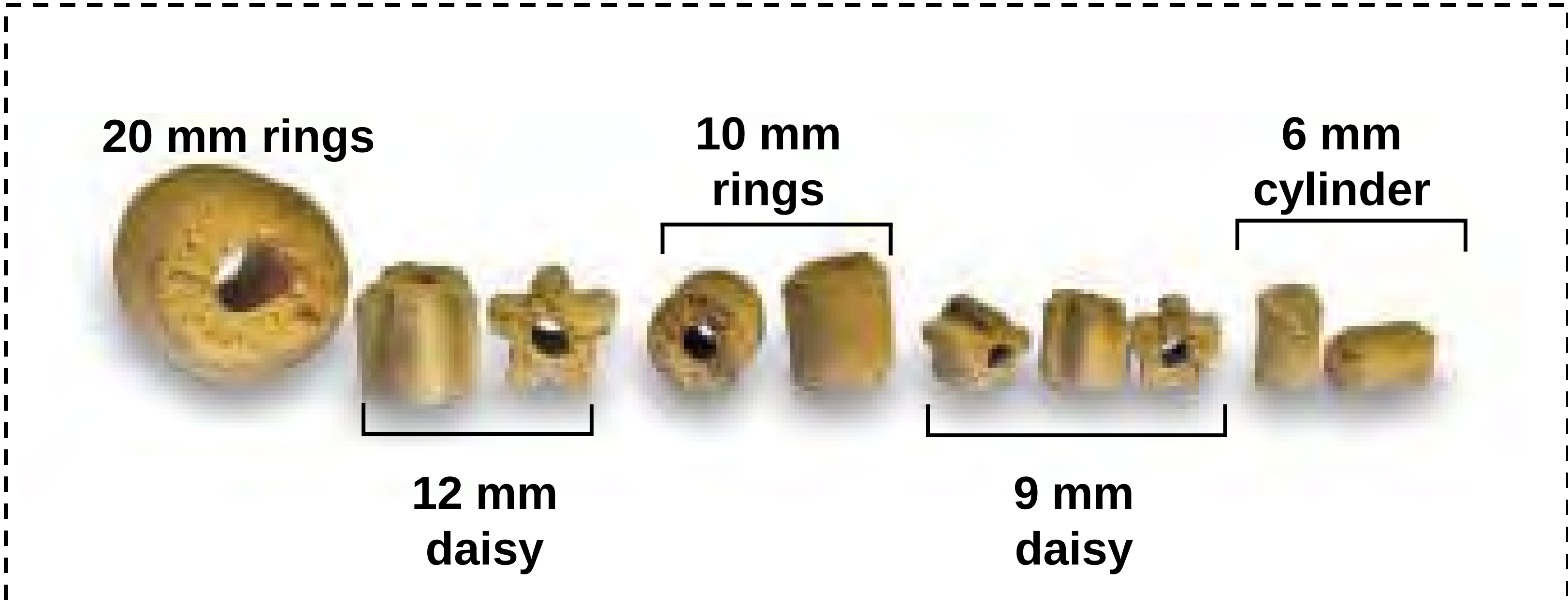
**Energy Balance**

$$\nabla \bullet \overline{q} = \nabla \bullet \left(- k_{eff} \nabla T\right) = - \left(\sum_{i=1}^{nr} -(\Delta H_{rxn,i})\, r_i\right) S_g\, \rho_g$$

- Homogeneous pellet
- Effective transport coefficients

**Note:** Other flux and constitutive relations can be used for more realistic solutions

# Case Study: $SO_2$ Oxidation Catalysts




## Key Features

- Alkali metal-promoted (K or Cs) vanadium pentoxide ($V_2O_5$) on silica support

## Key Selection Factors

- Pressure drop
- Dust capacity
- Ignition & activity

→

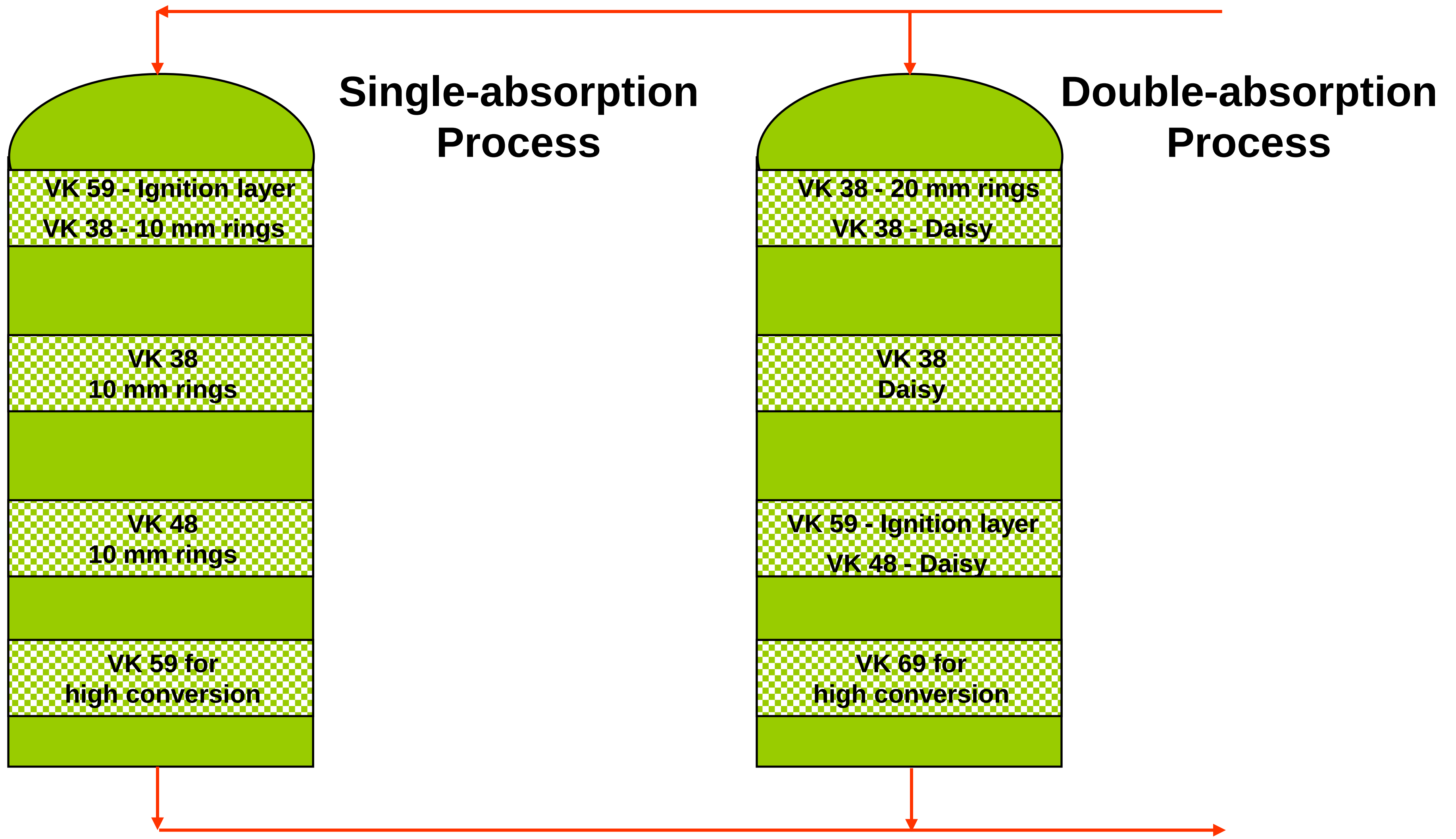
- Strength of $SO_2$ feed gas
- Plant configuration (Single vs double absorption)

→

No other engineering data is provided

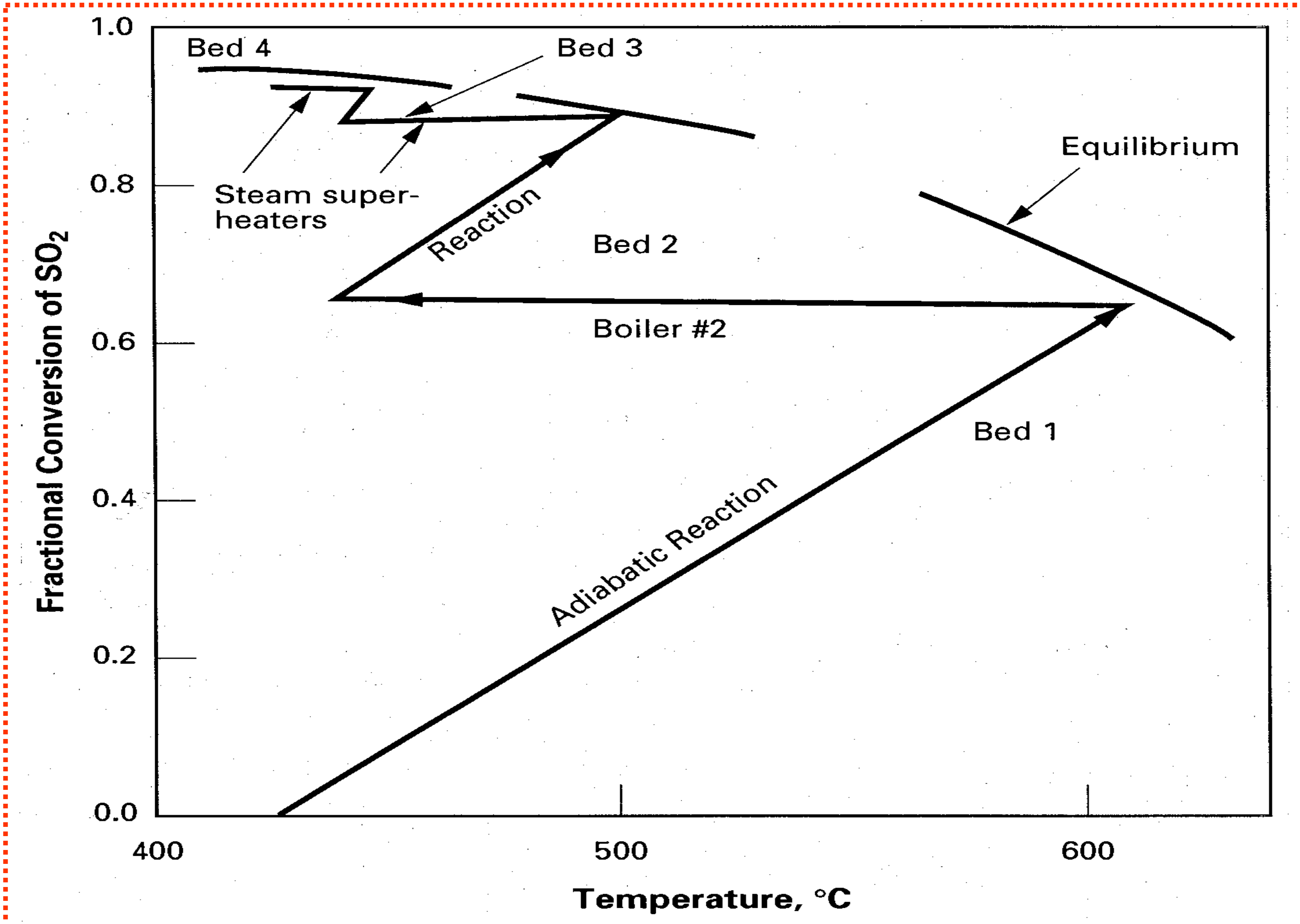
**Reference:** "VK Series - Sulphuric Acid Catalysts for Today and for the Future," Product Brochure, Haldor Topsoe, Inc.

# Typical Process Configurations




**Source:** "VK Series - Sulphuric Acid Catalysts for Today and for the Future," Haldor Topsoe, Inc

# Equilibrium Conversion for $SO_2$ Oxidation



# Reaction Kinetics for $SO_2$ Oxidation

$$-r_{SO2} = \frac{k_1\, p_{O2}\, p_{SO2} \left(1 - \dfrac{p_{SO3}}{p_{SO2}\sqrt{p_{O2}}\, K_P}\right)}{22.414\left(1 + K_2\, p_{SO2} + K_3 p_{SO3}\right)^2} \qquad \frac{kmol\ SO_2}{kg\ catalyst\ -\ hr}$$

Hougen-Watson Mechanism; RLS = Adsorbed $O_2$ & $SO_{2;}$ *T = 420 - 590°C*

## Kinetic Parameters

$$k_1 = exp(12.160 - 5473 / T)$$

$$K_2 = exp(-9.953 - 8619 / T)$$

$$K_3 = exp(-71.745 - 52596 / T)$$

$$K_P = exp(11{,}300 / T - 10.68)$$

*Units: T [K] p [atm]*

## Molten Salt Chemistry

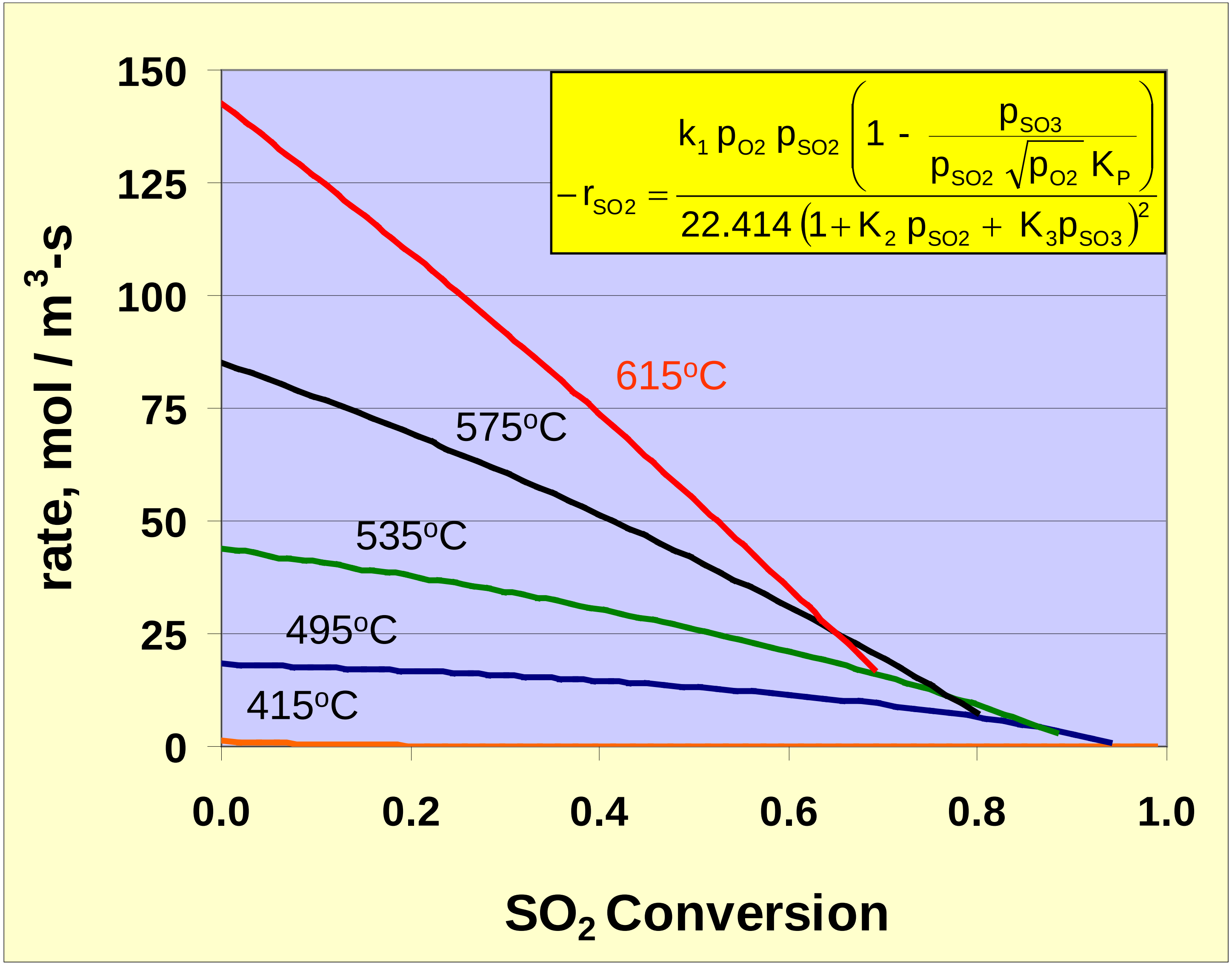
$$K_2SO_4 + SO_3 \longrightarrow K_2S_2O_7$$

$$K_2S_2O_7 + V_2O_5 \longrightarrow K_wV_xS_yO_z$$

$$SO_2 + 2\,V^{5+} + O^{2-} \longrightarrow SO_3 + 2\,V^{4+}$$

$$1/2\ O_2 + 2\,V^{4+} \longrightarrow O^{2-} + 2\,V^{5+}$$

# Reaction Rate *vs* $SO_2$ Conversion



# Constants

Constants

| Name | Expression | Value | Description |
|---|---|---|---|
| p_SO3_0 | P*y_SO3_0 | 0 | |
| p_N2_0 | P*y_N2_0 | 0.814 | |
| c_SO2_0 | p_SO2_0/Rg/T0_K*10^6 | 1.37221 | |
| c_O2_0 | p_O2_0/Rg/T0_K*10^6 | 1.899983 | |
| c_SO3_0 | p_SO3_0/Rg/T0_K*10^6 | 0 | |
| c_N2_0 | p_N2_0/Rg/T0_K*10^6 | 14.320242 | |
| Rg | 22400/273.15 | 82.006224 | atm cc/m... |
| k_eff | 7e-4 | 7e-4 | cal/(cm-s-C) |
| k_eff_comsol | k_eff*0.239*10^2 | 0.01673 | W/(m-K) |
| T0_C | 420 | 420 | Celsius |
| T0_K | T0_C+273.15 | 693.15 | K |
| k1 | exp(12.16-5473/T0_K) | 71.10532 | |
| K2 | exp(-9.953+8619/T0_K) | 11.959644 | |
| K3 | exp(-71.745+52596/T0_K) | 62.46958 | |
| Kp | exp(11300/T0_K-10.68) | 276.548898 | |
| r_SO2_f_max | k1*p_O2_0*p_SO2_0/(22.414*(1+K2*p_SO2_0+K3*p_SO3_0)^2) | 0.007153 | |
| r_SO2_b_max | k1/Kp*p_O2_0^0.5*p_SO3_0/(22.414*(1+K2*p_SO2_0+K3*p_SO3_0)^2) | 0 | |
| r_SO2_max | r_SO2_f_max-r_SO2_b_max | 0.007153 | |
| r_SO2_coms... | r_SO2_max*10^6/3600*rho_cat | 2.642731 | |
| dhr_410 | -98963.2 | -98963.2 | at 410c J... |
| dhr_618 | -98958.9 | -98958.9 | at 618c J... |
| dhr_avg | (dhr_410+dhr_618)/2 | -98961.05 | J/mol |
| Q_rxn_max | dhr_avg*r_SO2_comsol_max | -2.615274e5 | J/m^3-s |

OK Cancel Apply Help

Partial pressures & concentrations at pellet surface conditions

Effective conductivity

Reaction rate constants

Maximum reaction rate

Maximum heat generation rate

# Global Expressions

**Global Expressions**

| Name | Expression | Unit | Description |
|---|---|---|---|
| p_SO2 | c_SO2*Rg*T0_K/10^6 | $mol/m^3$ | |
| p_O2 | c_O2*Rg*T0_K/10^6 | $mol/m^3$ | |
| p_SO3 | c_SO3*Rg*T0_K/10^6 | $mol/m^3$ | |
| p_N2 | c_N2*Rg*T0_K/10^6 | $mol/m^3$ | |
| R_SO2_f | k1*p_O2*p_SO2/(22.414*(1+K2*p_SO2+K3*p_SO3)^2) | | |
| R_SO2_b | k1/Kp*p_O2^0.5*p_SO3/(22.414*(1+K2*p_SO2+K3*p_SO3)^2) | | |
| R_SO2_comsol | R_SO2*10^6/3600*rho_cat | | |
| Q_rxn | dhr_avg*R_SO2_comsol | | |
| R_SO2 | R_SO2_f-R_SO2_b | | |
| p_SO2_noniso | c_SO2*Rg*T/10^6 | $K \cdot mol/m^3$ | |
| p_O2_noniso | c_O2*Rg*T/10^6 | $K \cdot mol/m^3$ | |
| p_SO3_noniso | c_SO3*Rg*T/10^6 | $K \cdot mol/m^3$ | |
| p_N2_noniso | c_N2*Rg*T/10^6 | $K \cdot mol/m^3$ | |
| r_so2_noniso_f | k1*p_O2_noniso*p_SO2_noniso/(22.414*(1+K2*p_SO2_noniso+K3*p_SO3_nonis... | 1 | |
| r_so2_noniso_b | k1/Kp*p_O2_noniso^0.5*p_SO3_noniso/(22.414*(1+K2*p_SO2_noniso+K3*p_SO... | | |
| r_so2_noniso | r_so2_noniso_f-r_so2_noniso_b | | |
| r_so2_noniso_comsol | r_so2_noniso*10^6/3600*rho_cat | | |

OK | Cancel | Apply | Help

Partial pressures at pellet surface temperature

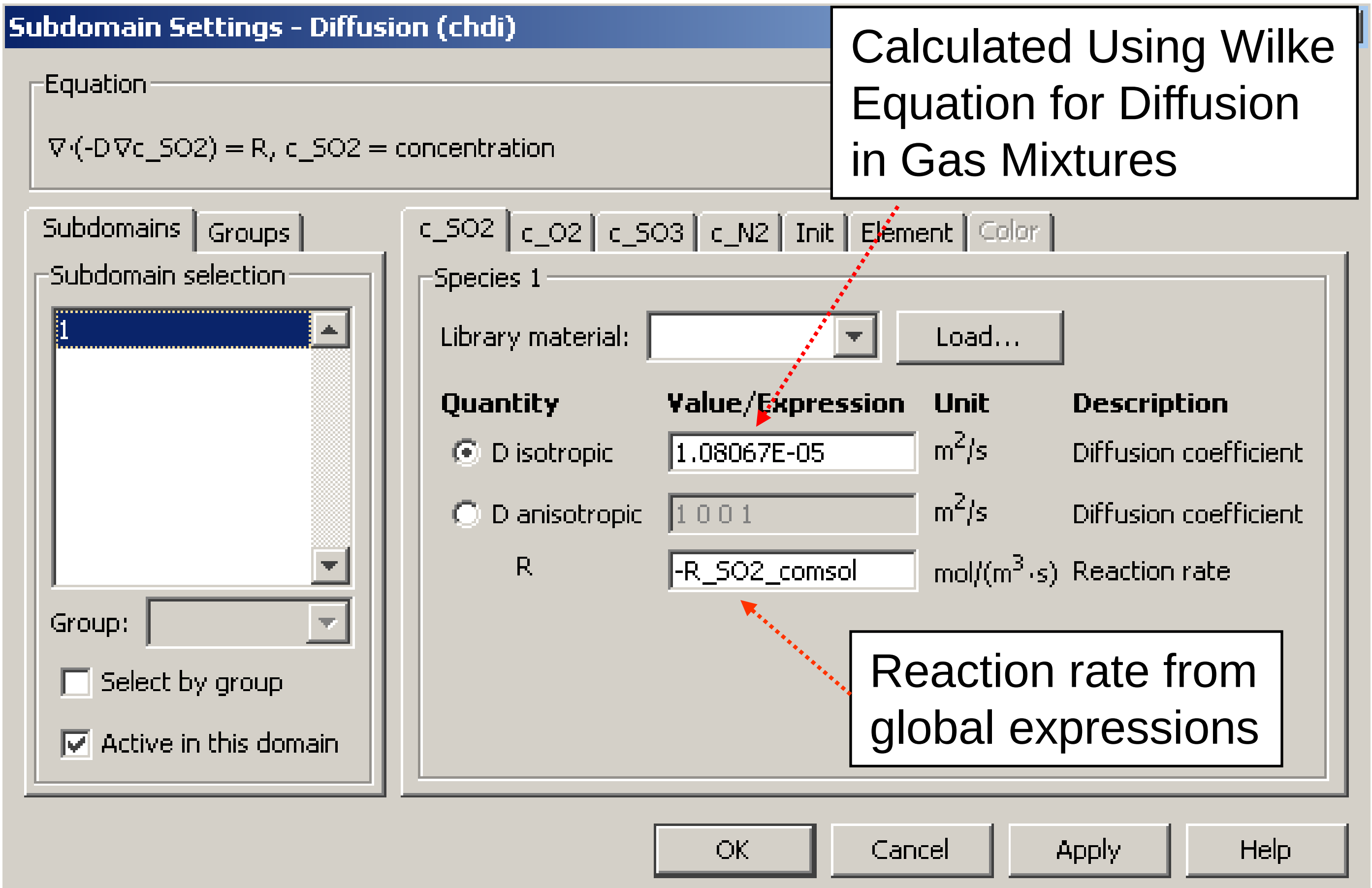
Reaction rate at pellet surface

Heat generation

Partial pressures at local temperature

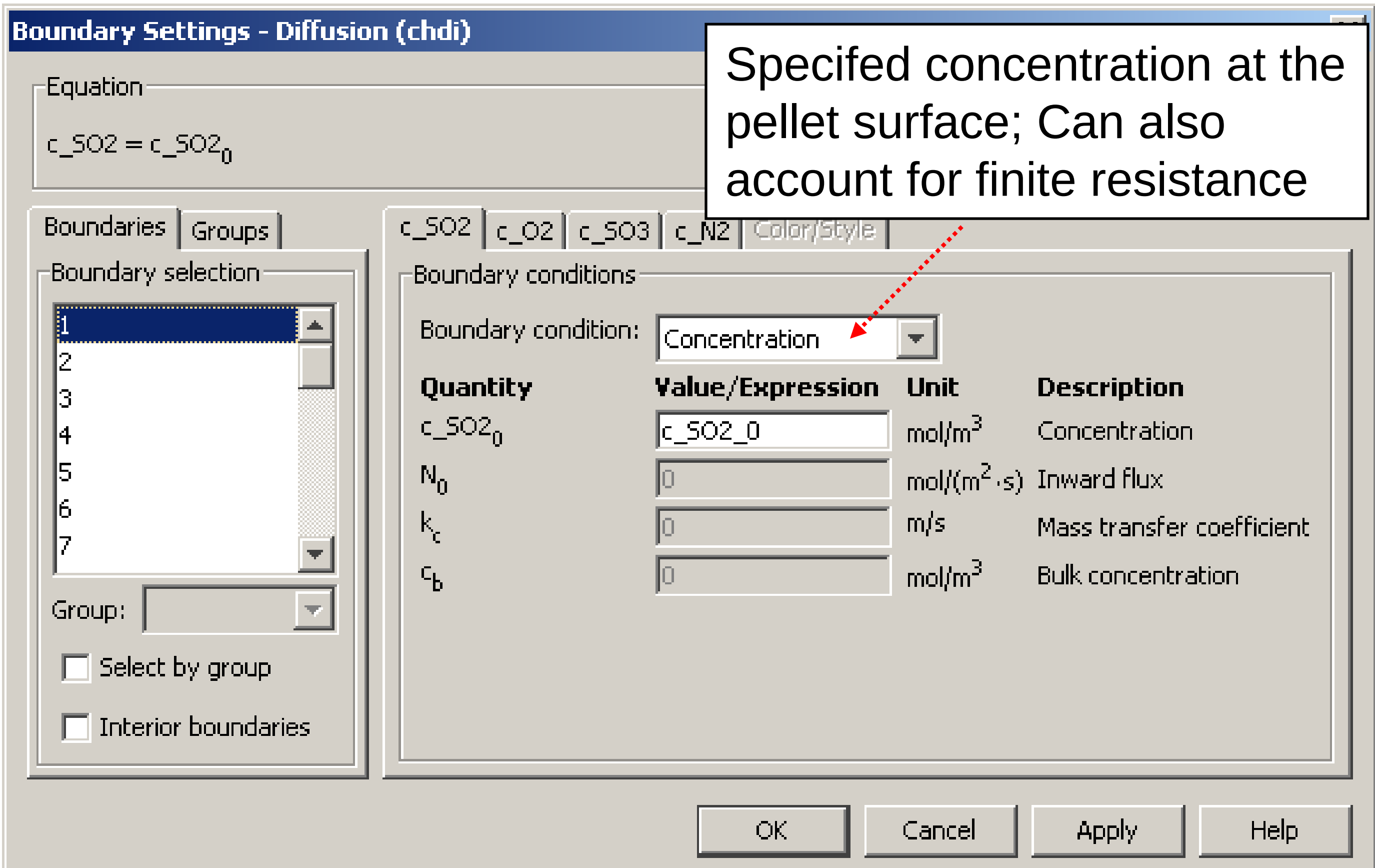
Reaction rate at pellet (c,T)

# Subdomain Settings -Diffusion Model-



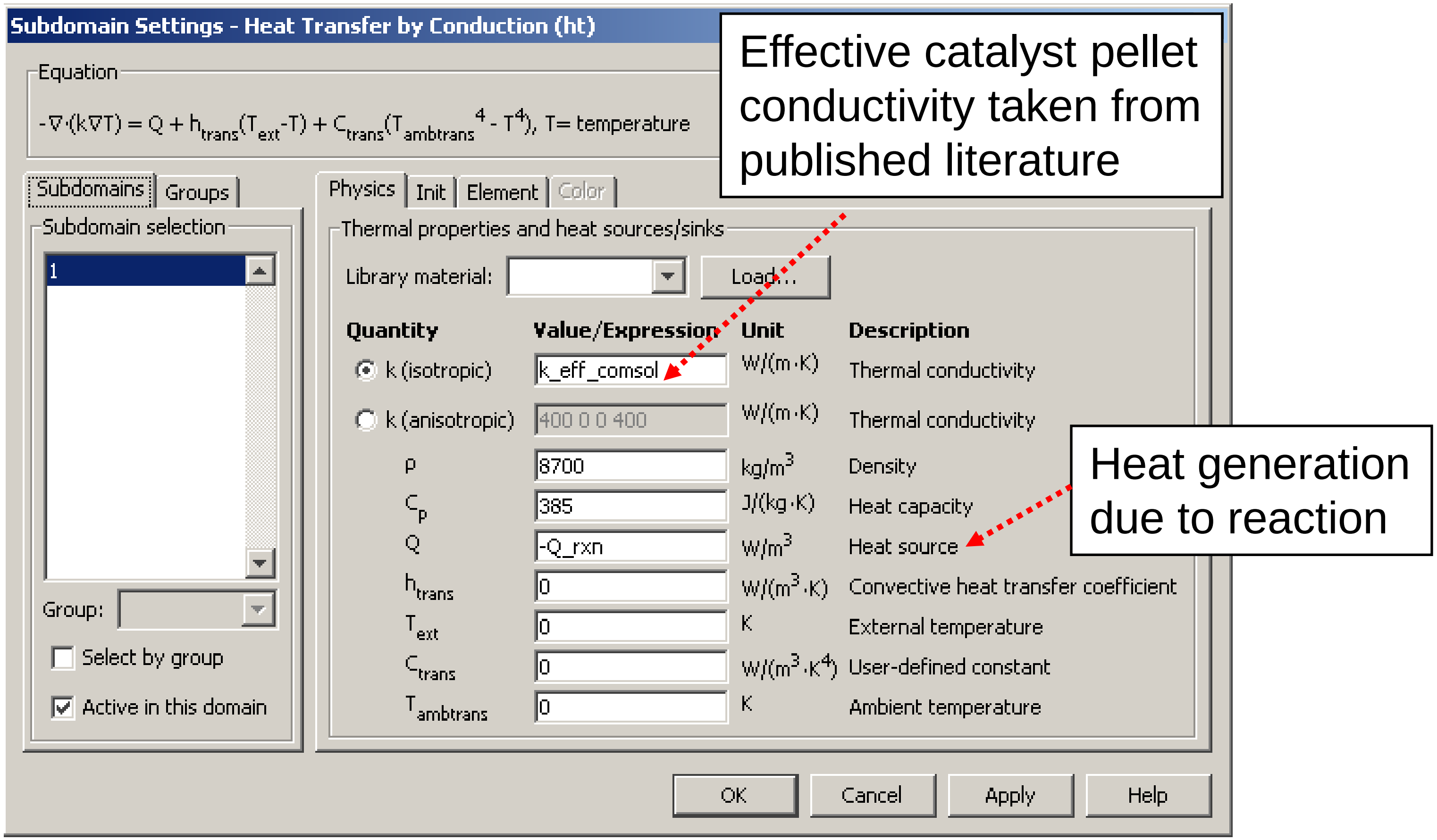

- Repeat for each Specie

# Boundary Settings -Diffusion Model-



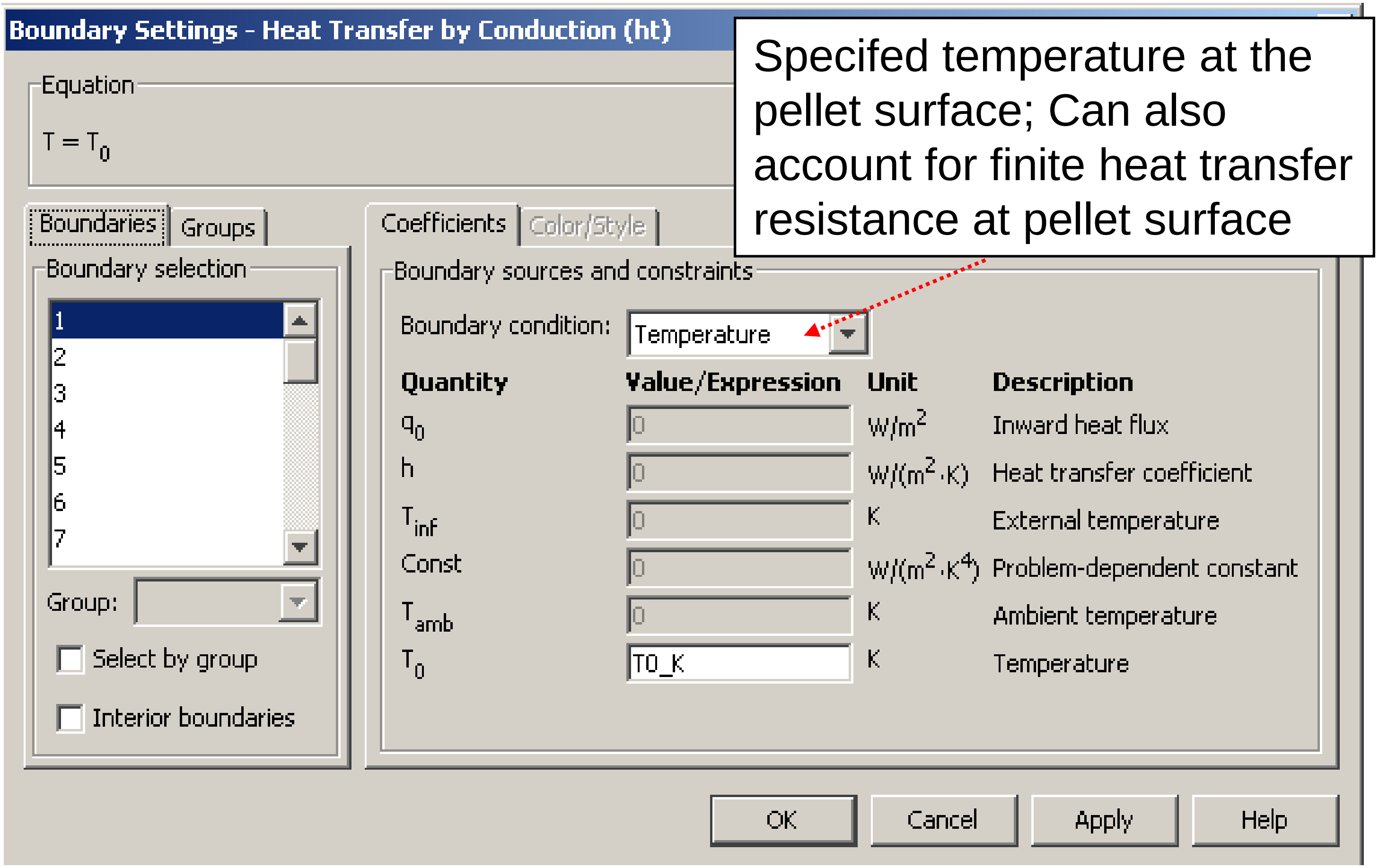

- Repeat for each Specie
- Repeat for each Boundary

# Subdomain Settings
# -Steady State Heat Conduction Model-



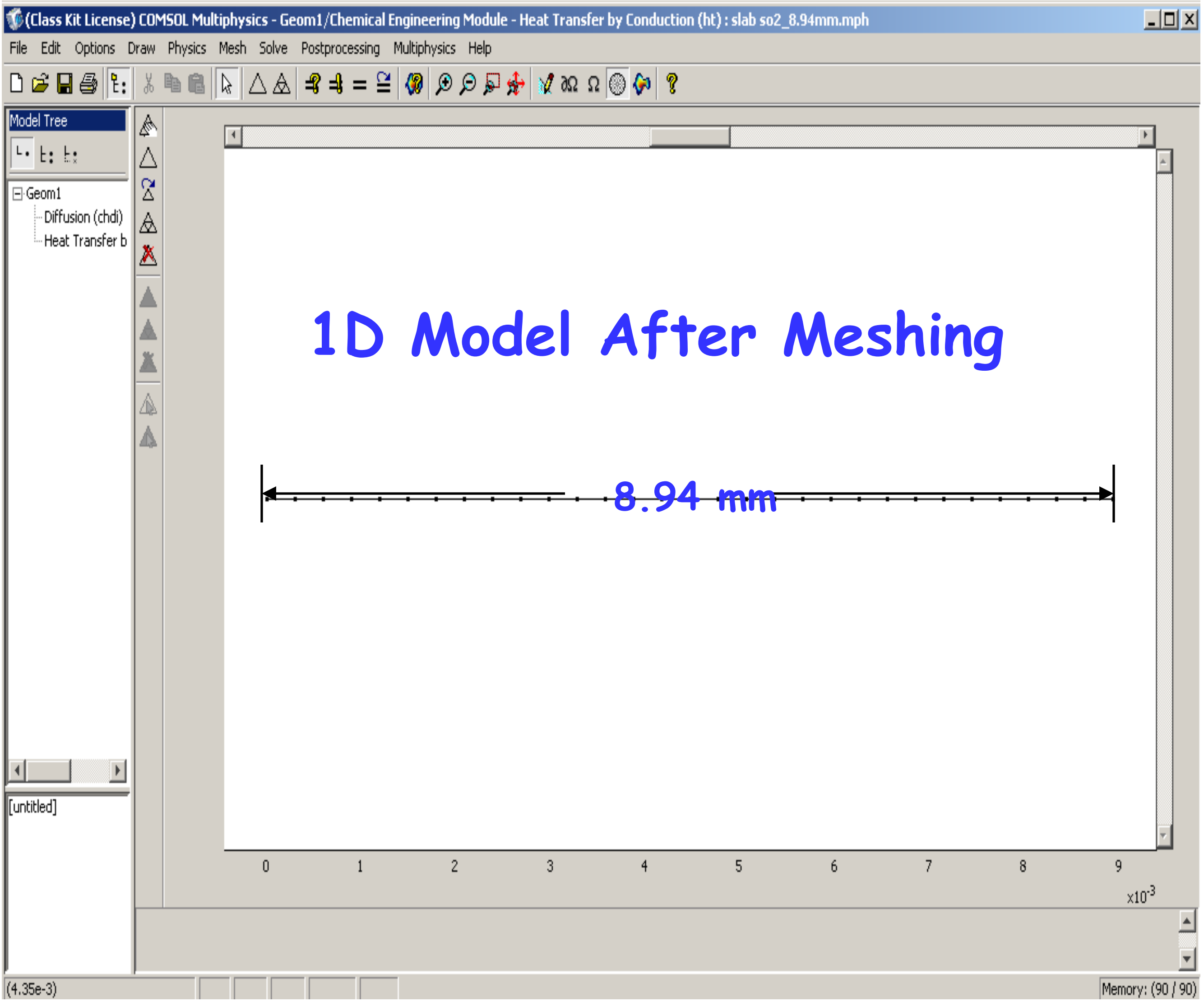

- Repeat for each Specie

# Boundary Settings
# -Steady State Heat Conduction Model-

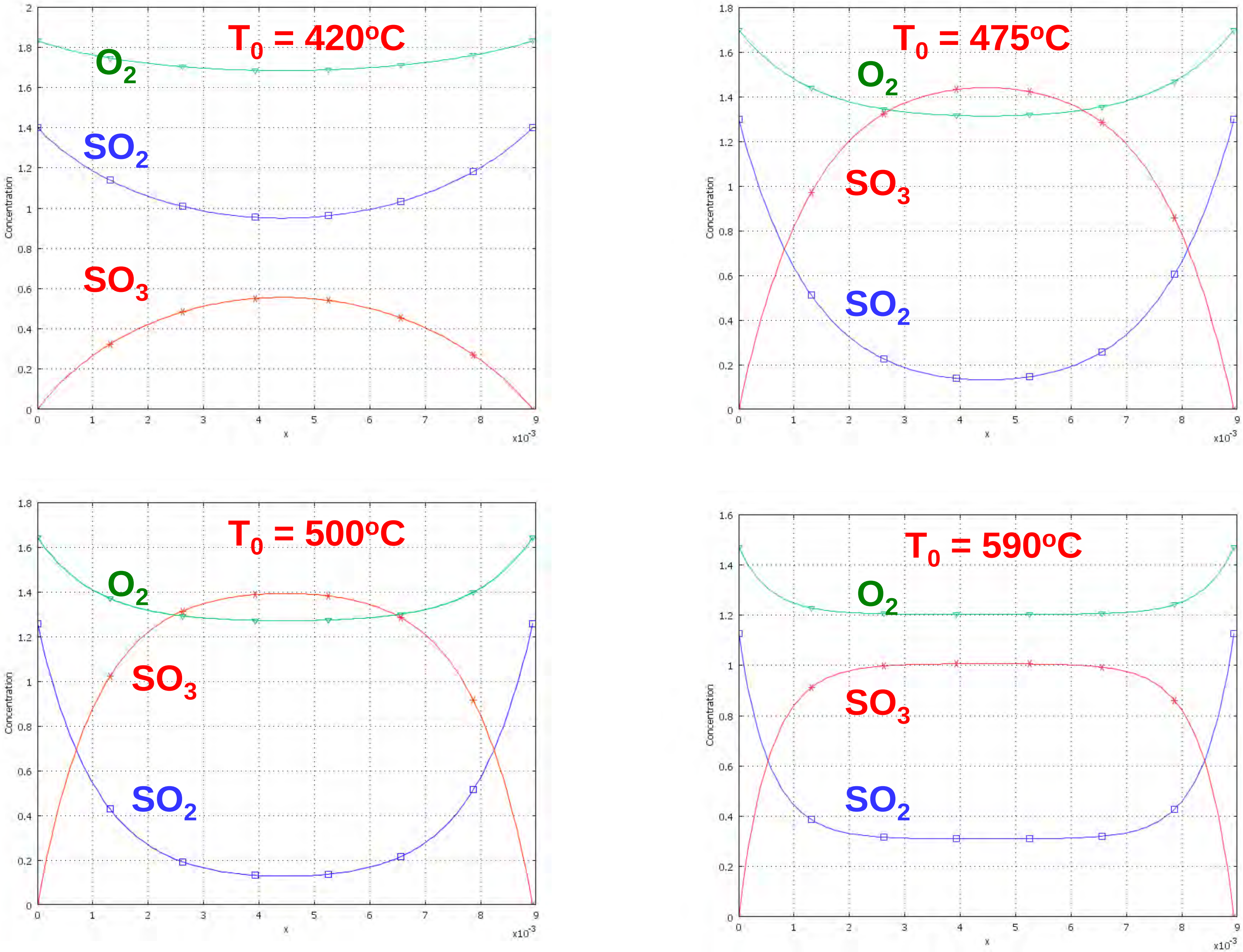



- Repeat for each Boundary

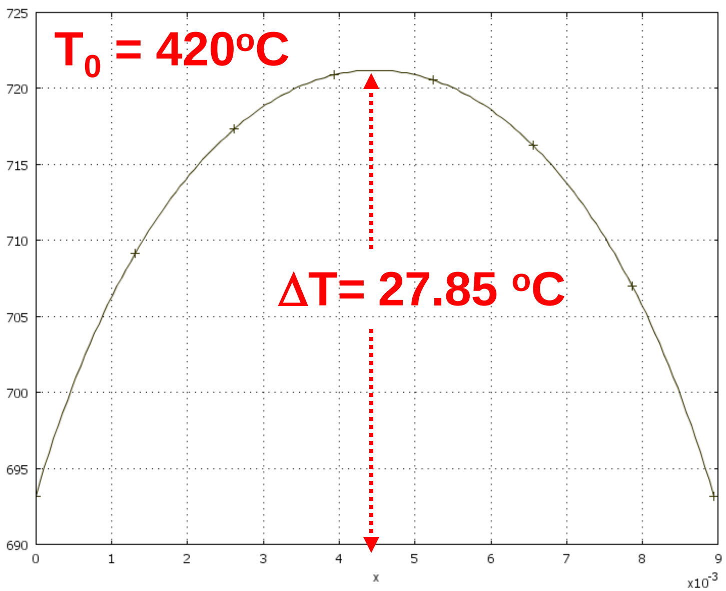
# Comsol Setup - Nonisothermal Slab

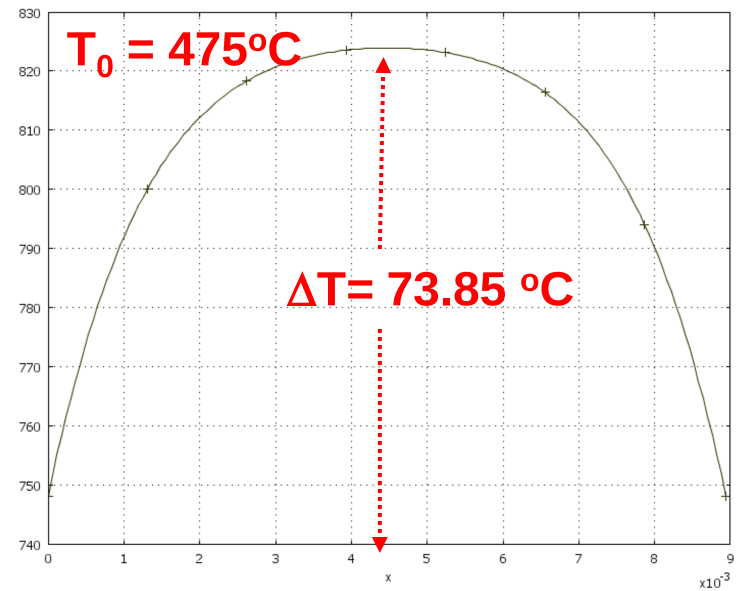


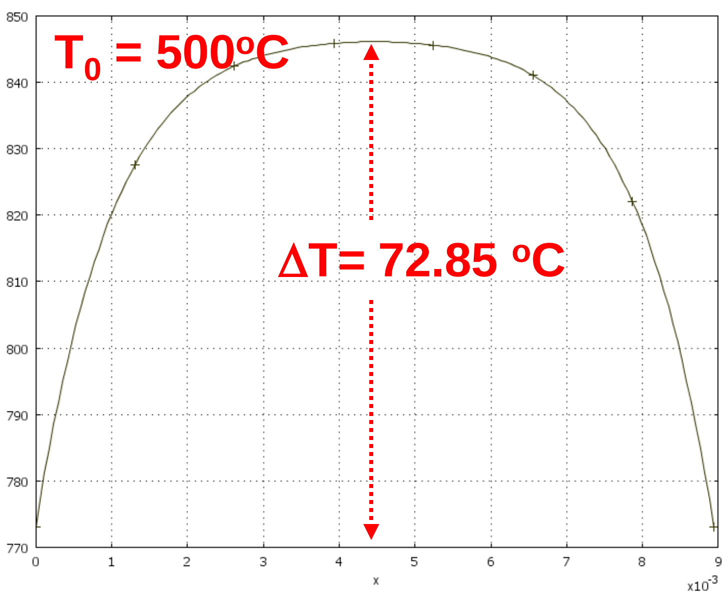
# Conc. Profiles - Nonisothermal Slab

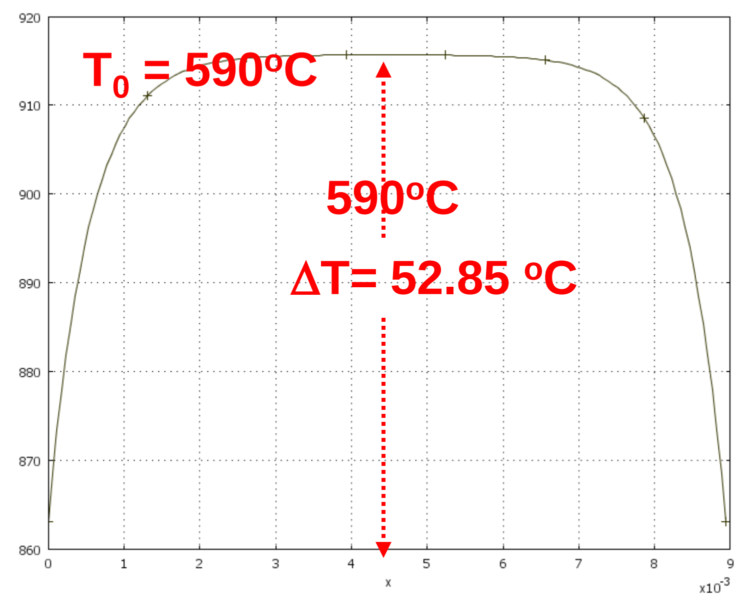


# Slab Pellet Temperature Profiles

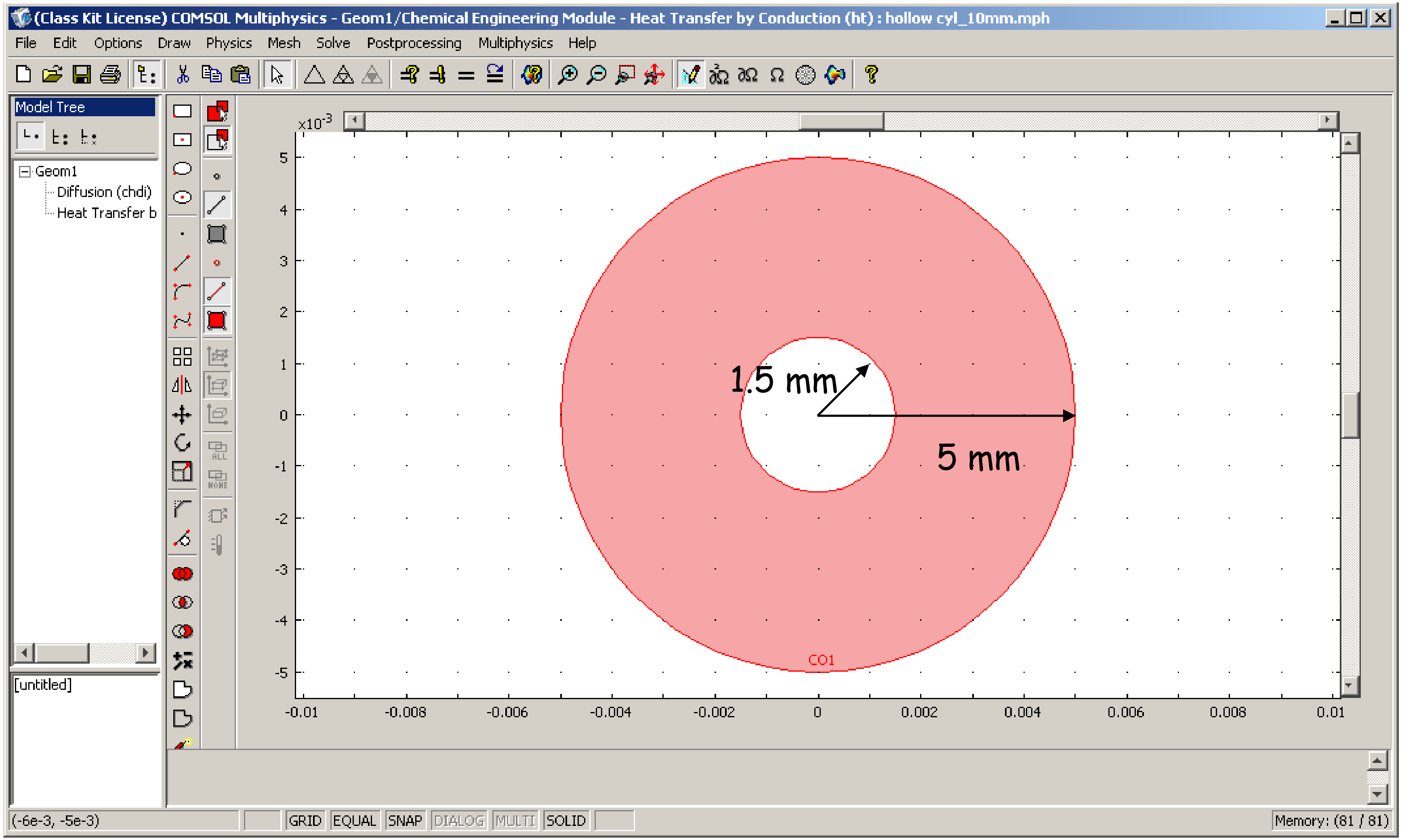


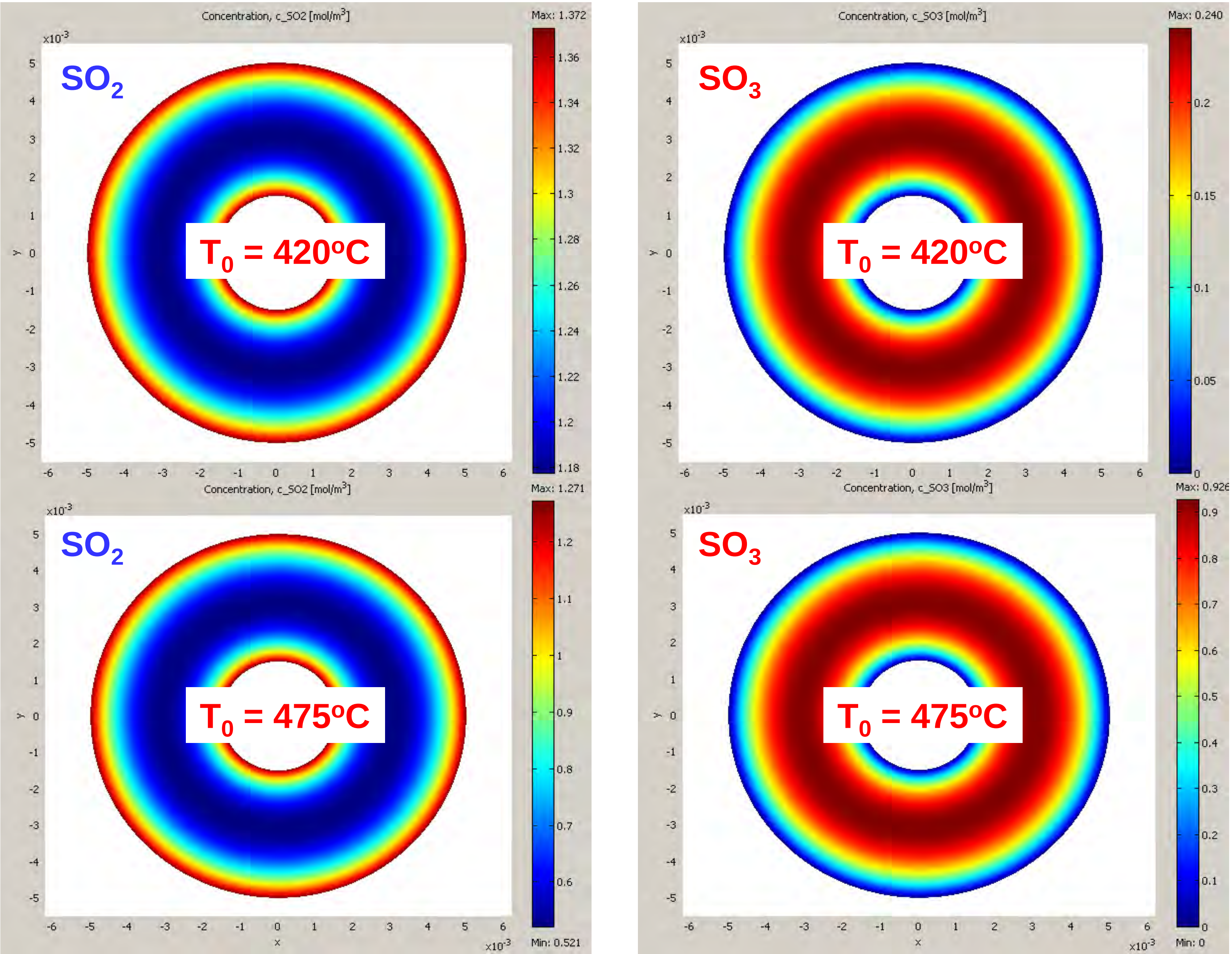



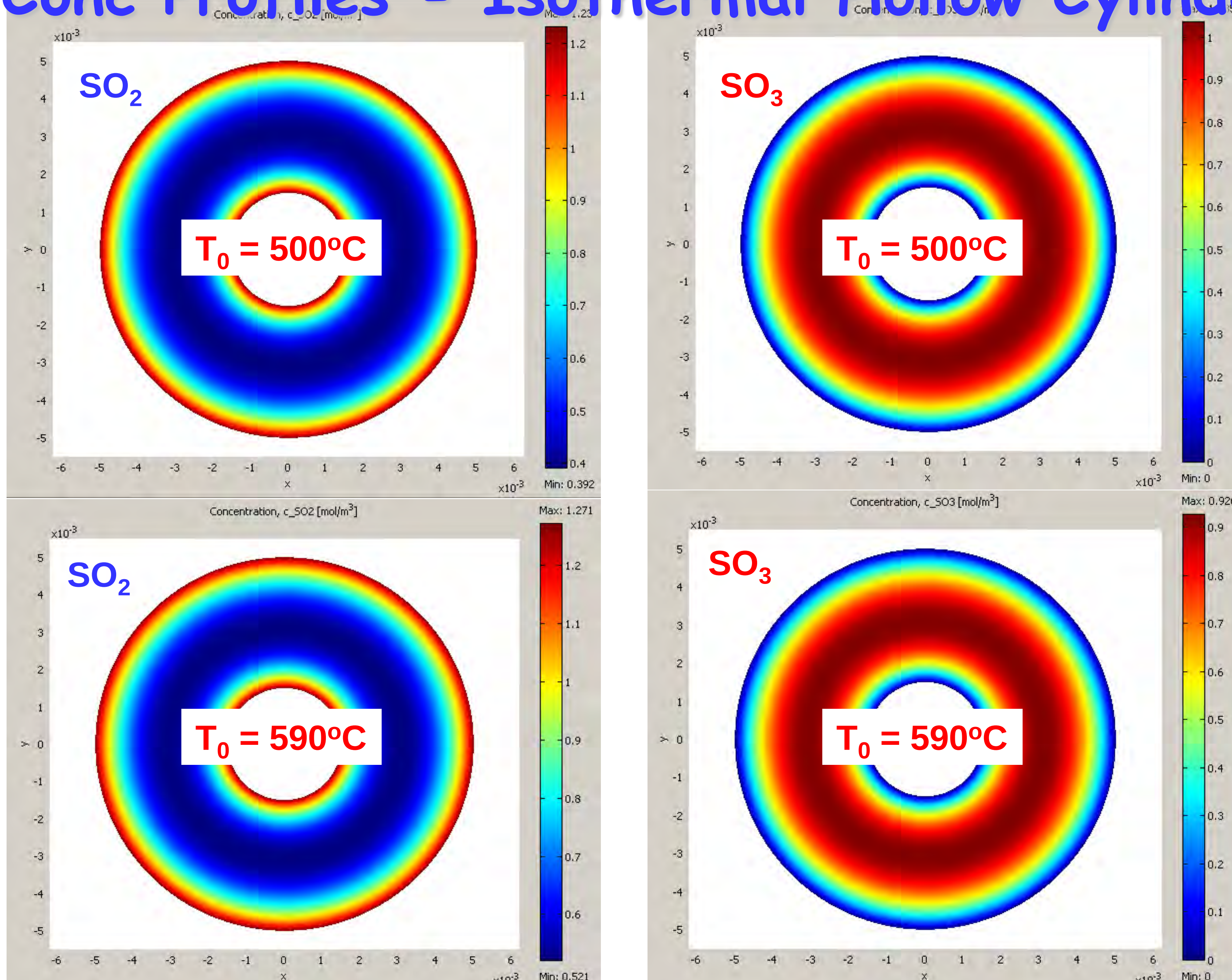
# Comsol Setup
# -Nonisothermal Hollow Cylinder-



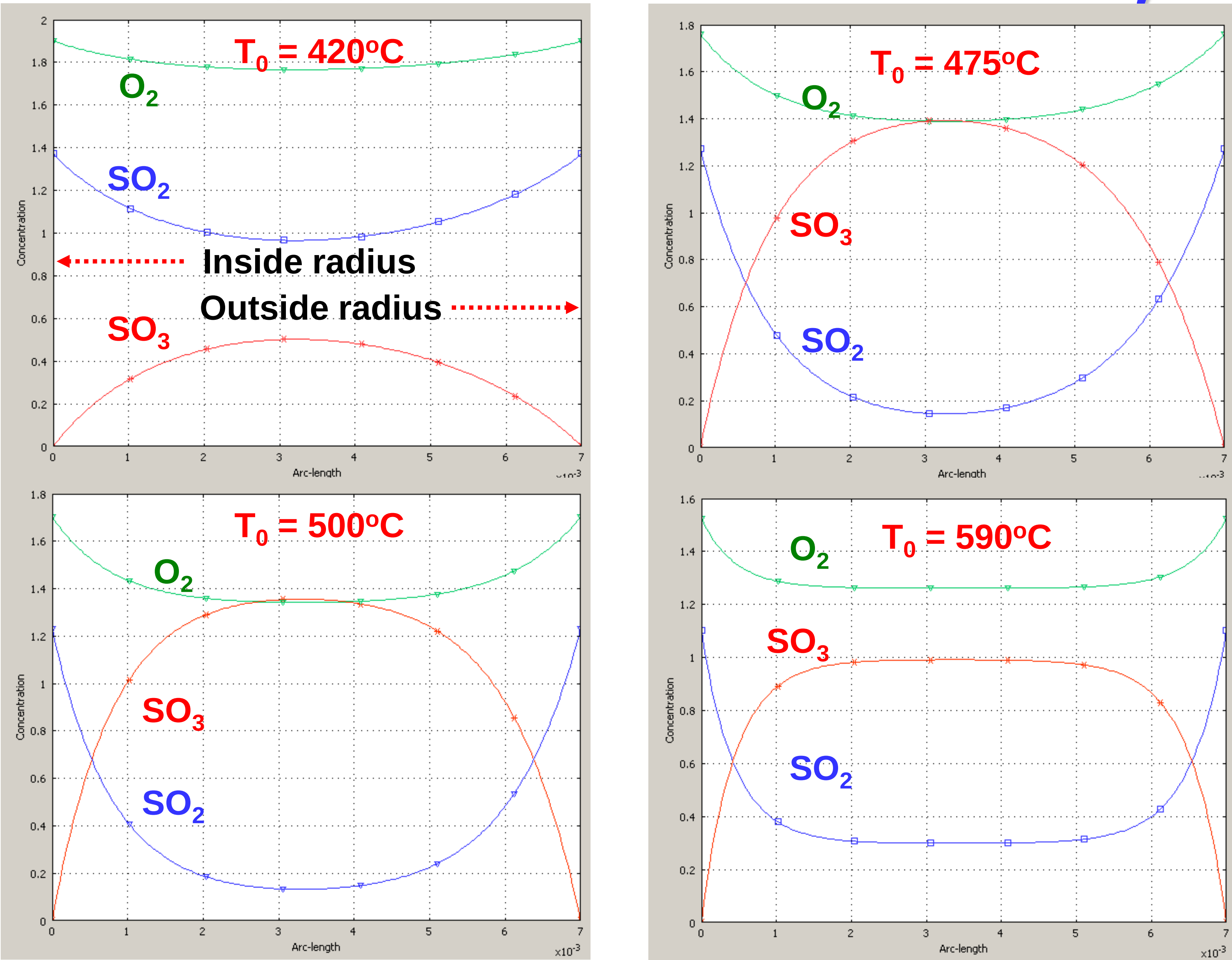
# Conc Profiles - Isothermal Hollow Cylinder



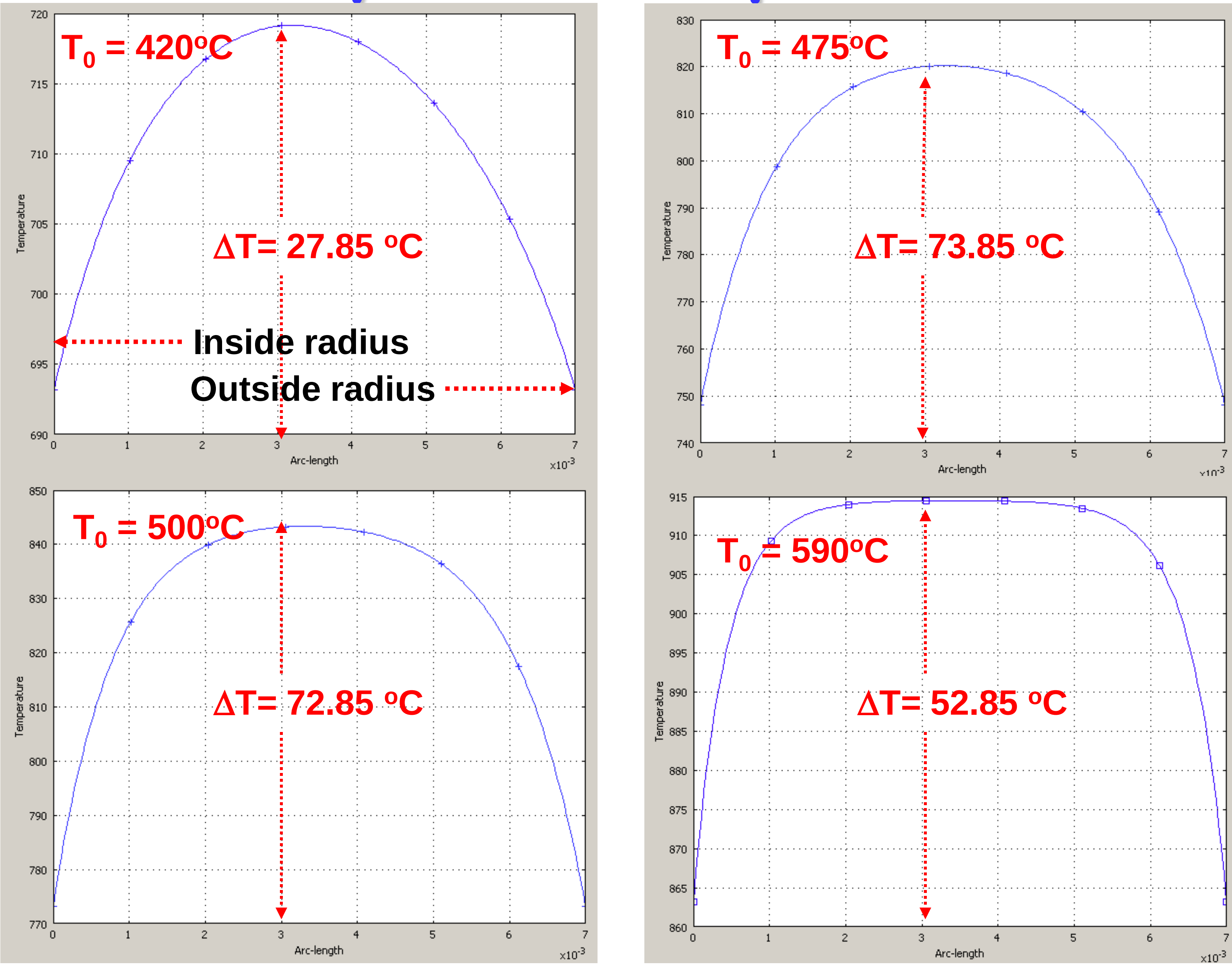
# Conc Profiles - Isothermal Hollow Cylinder



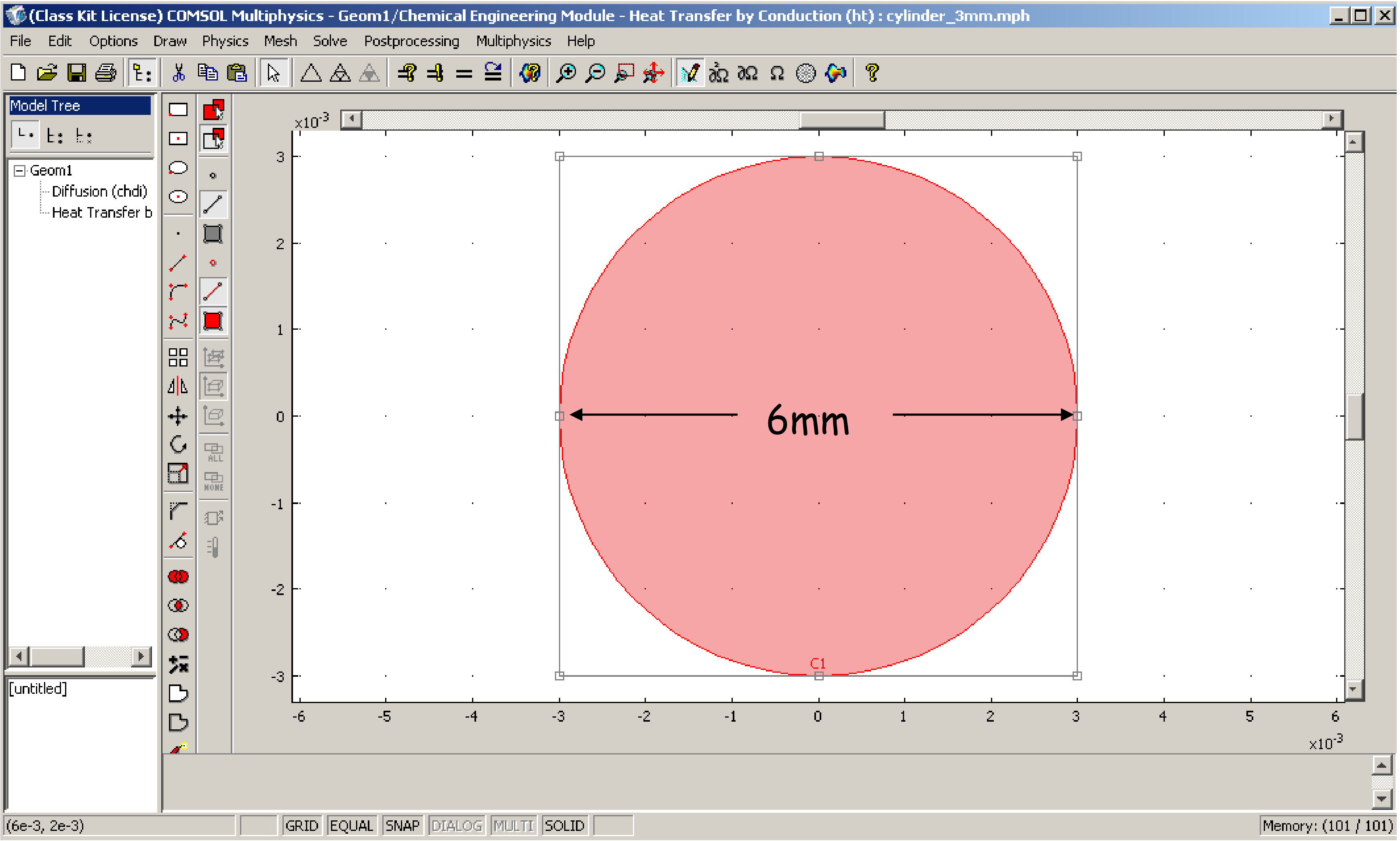
# Conc. Profiles - Nonisothermal Hollow Cylinder



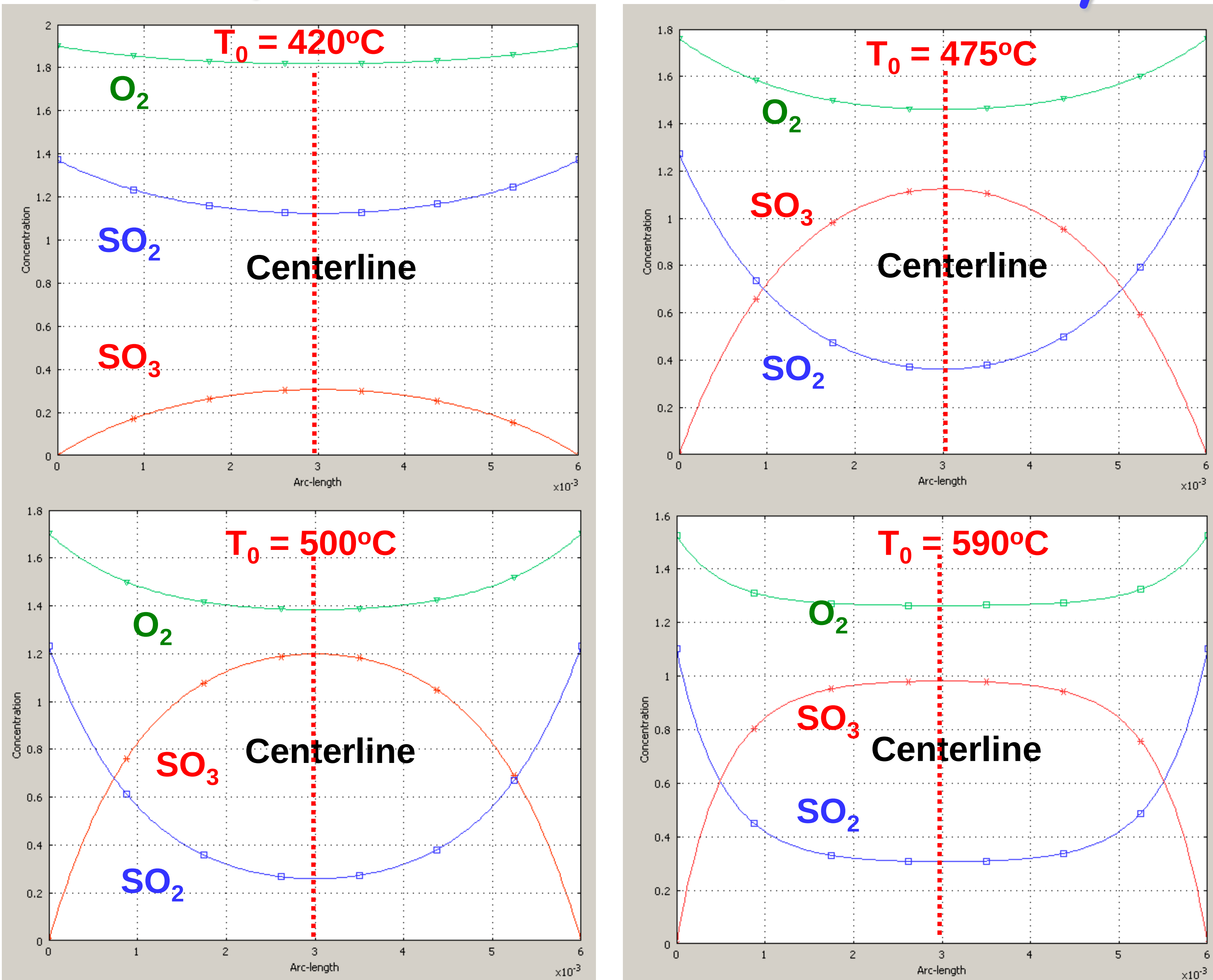
# Hollow Cylinder Temperature Profiles



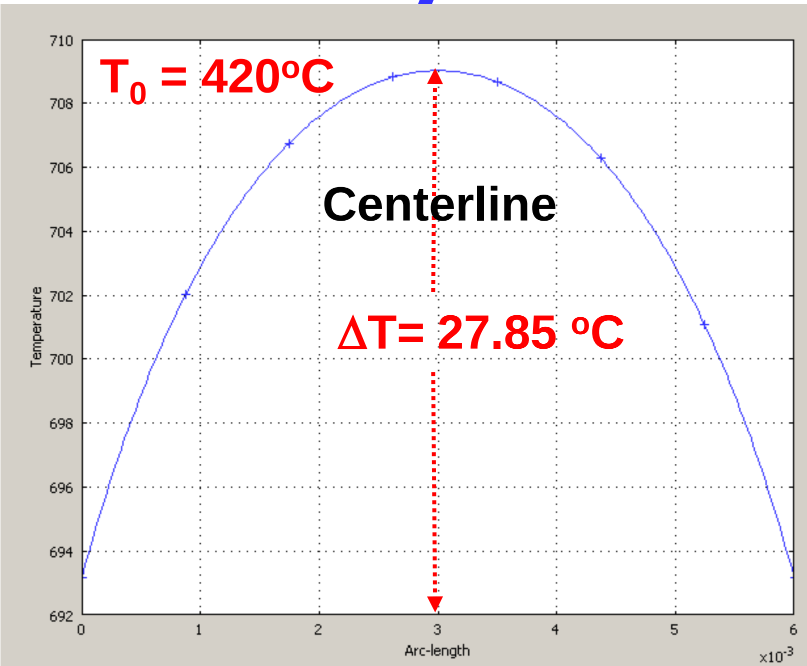
# Comsol Setup
# -Nonisothermal Solid Cylinder-

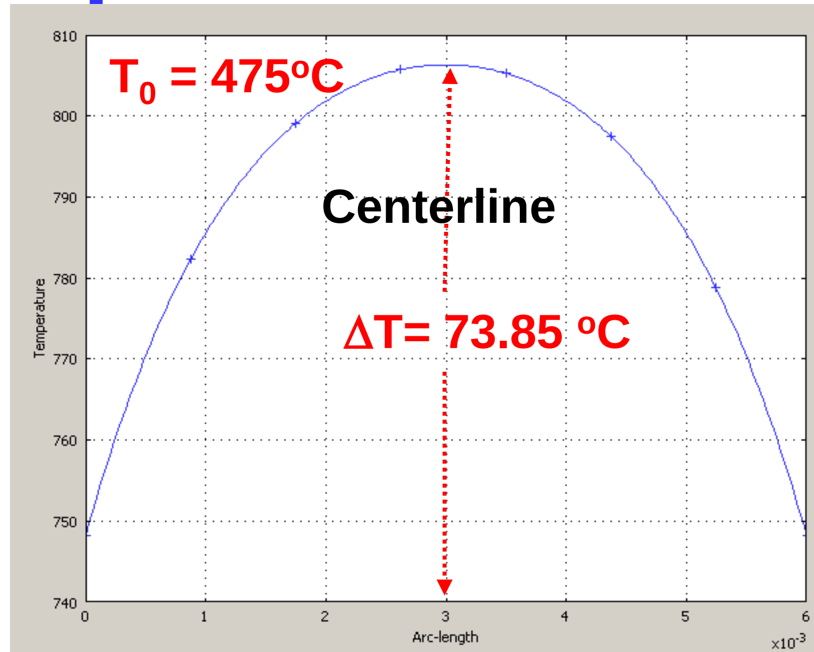


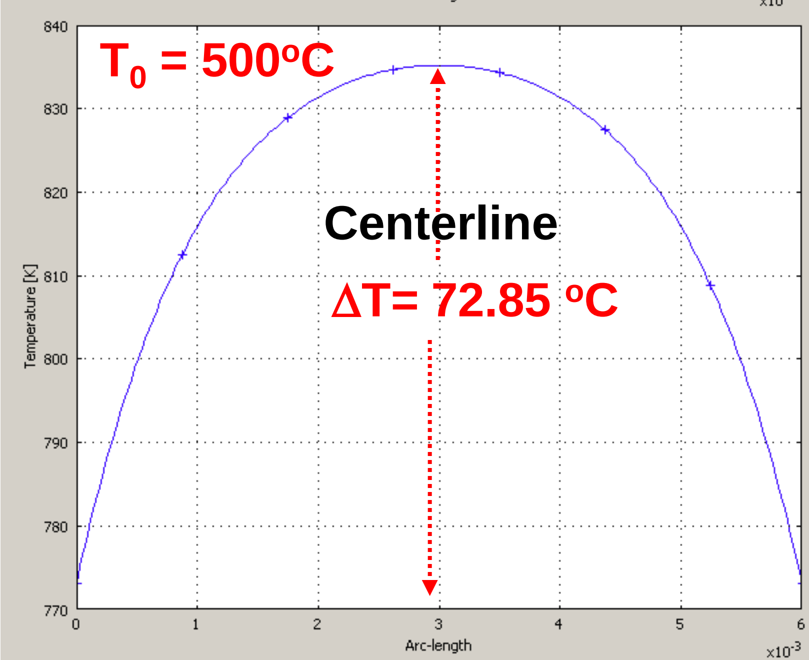
# Conc. Profiles - Nonisothermal Solid Cylinder

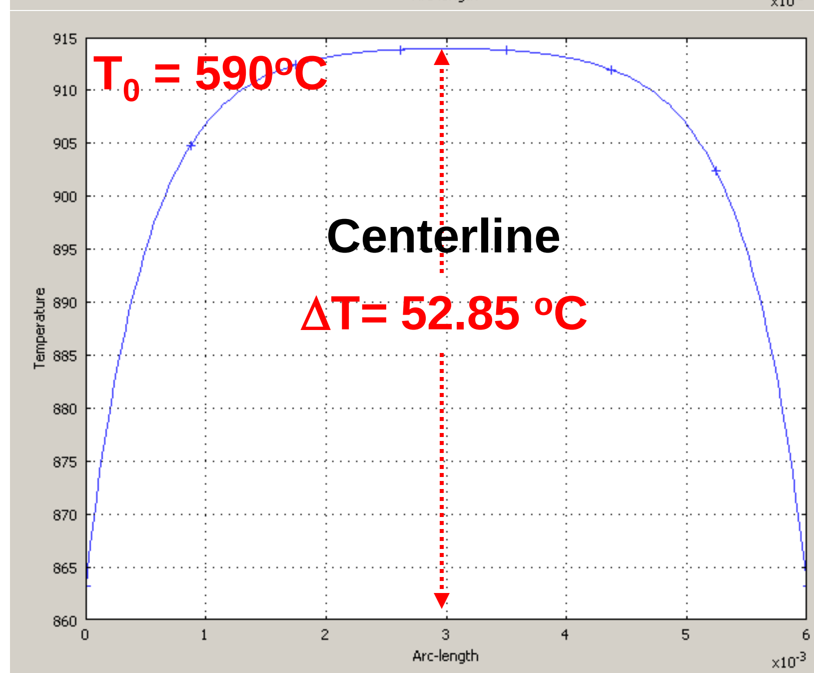


# Solid Cylinder Temperature Profiles

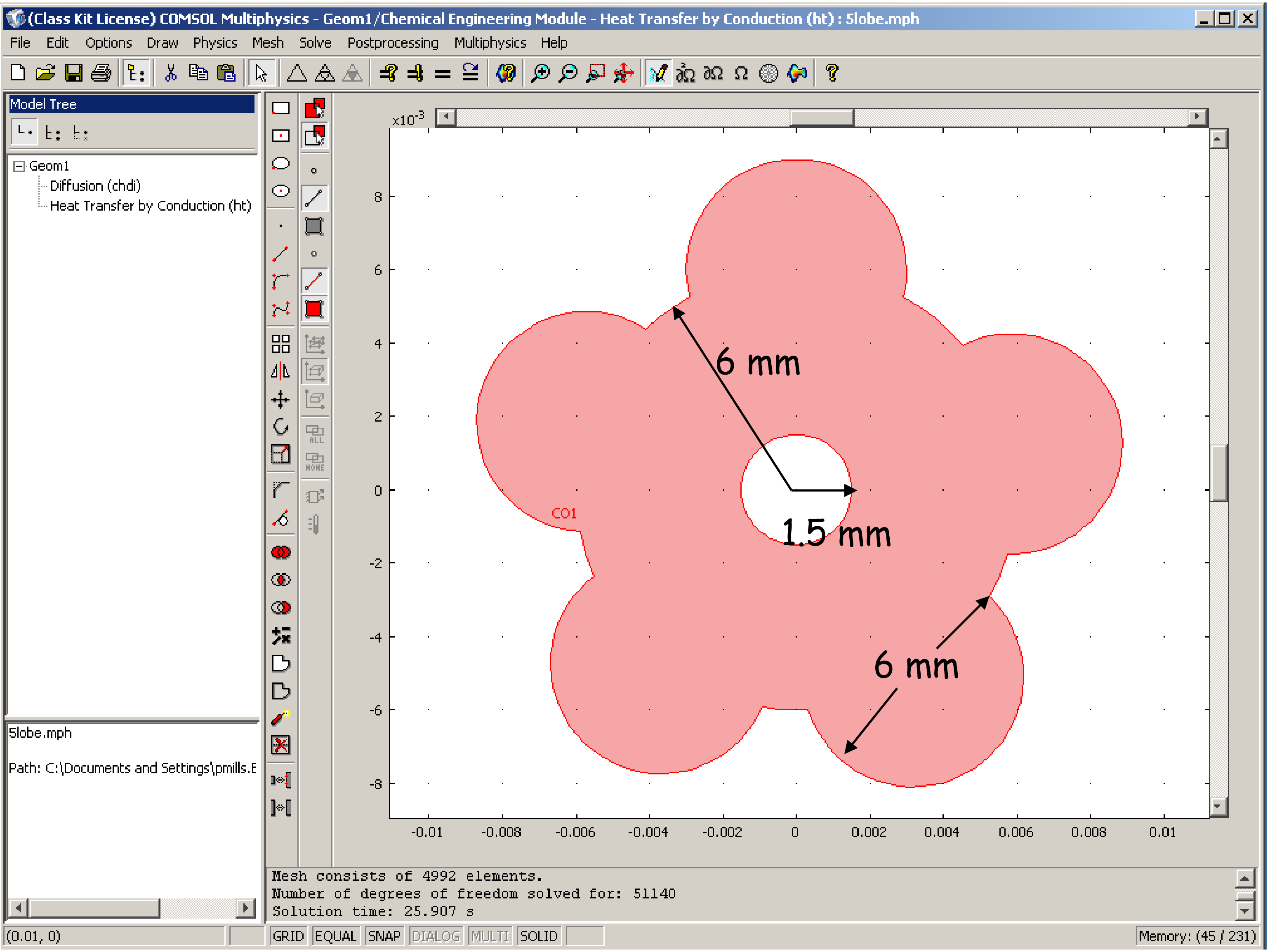


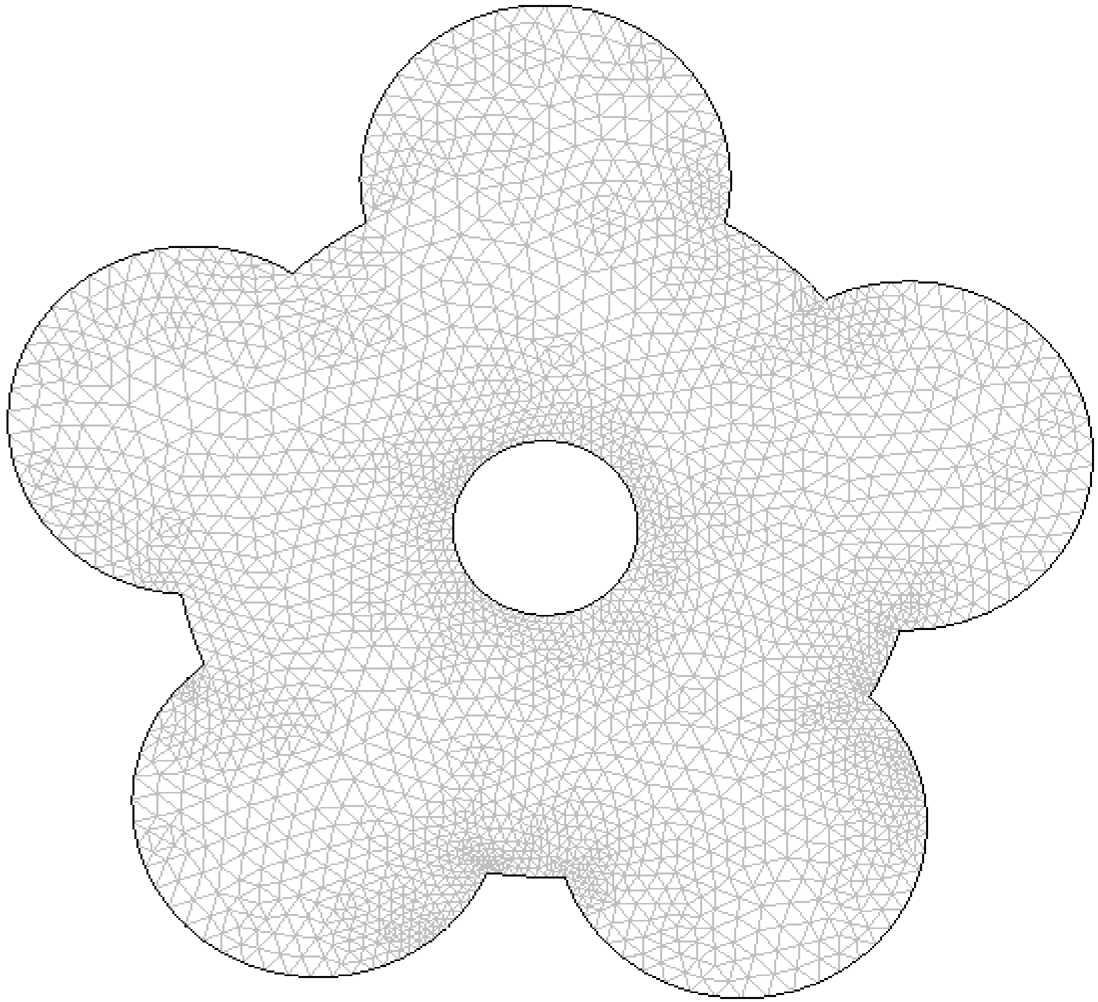



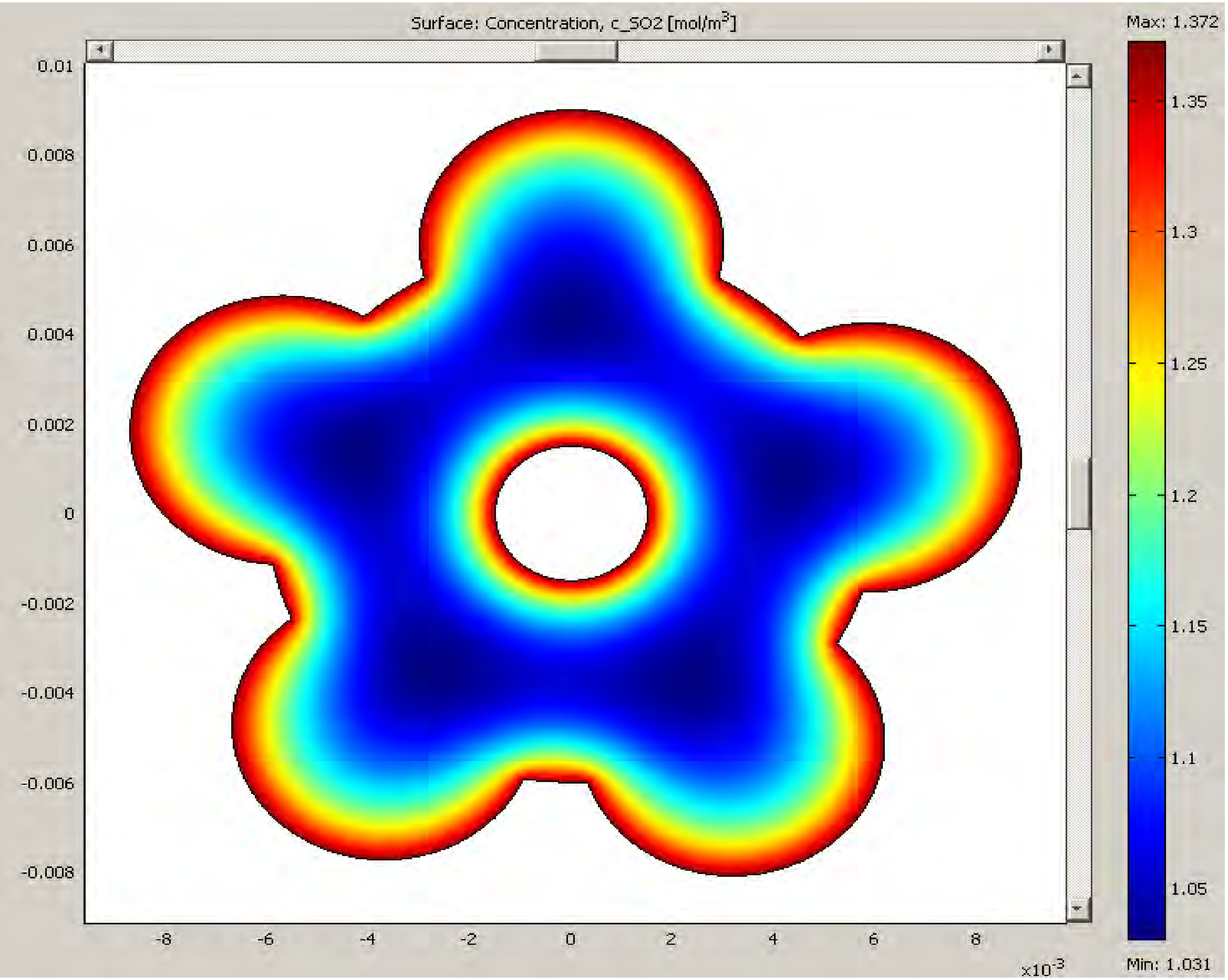
# Comsol Setup
# -Nonisothermal Daisy-



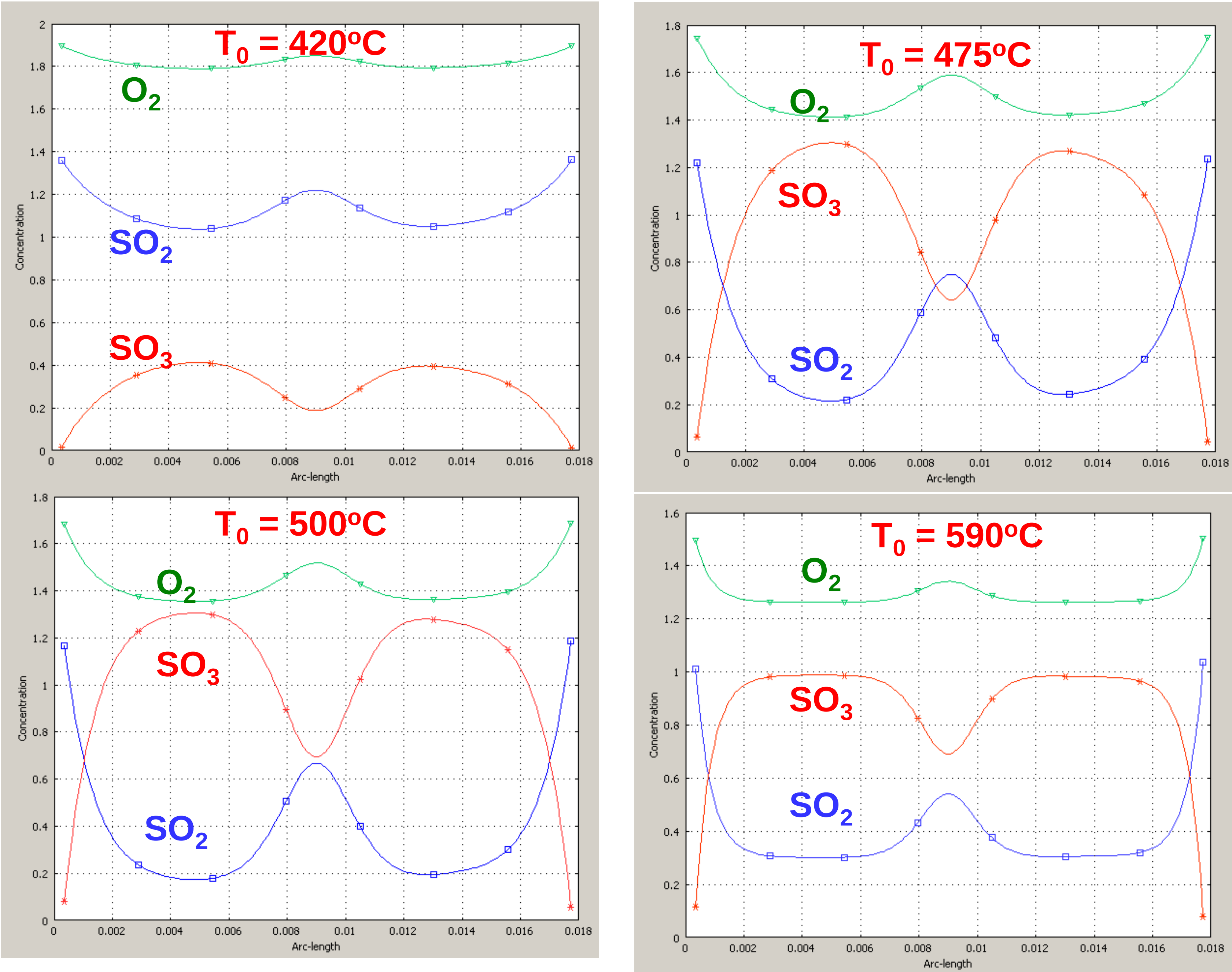
# Mesh Generation



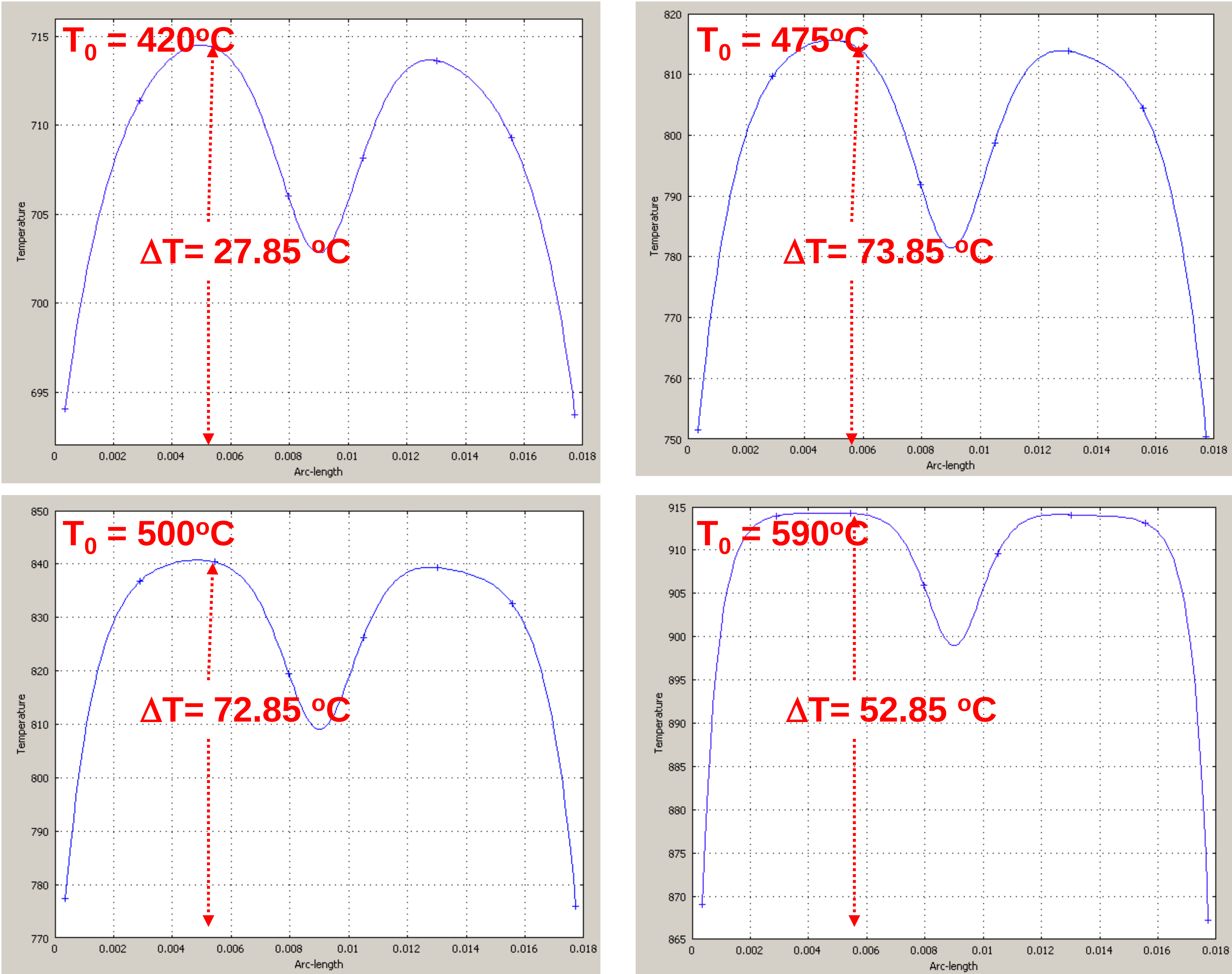
# Surface Concentration Plot for $SO_2$



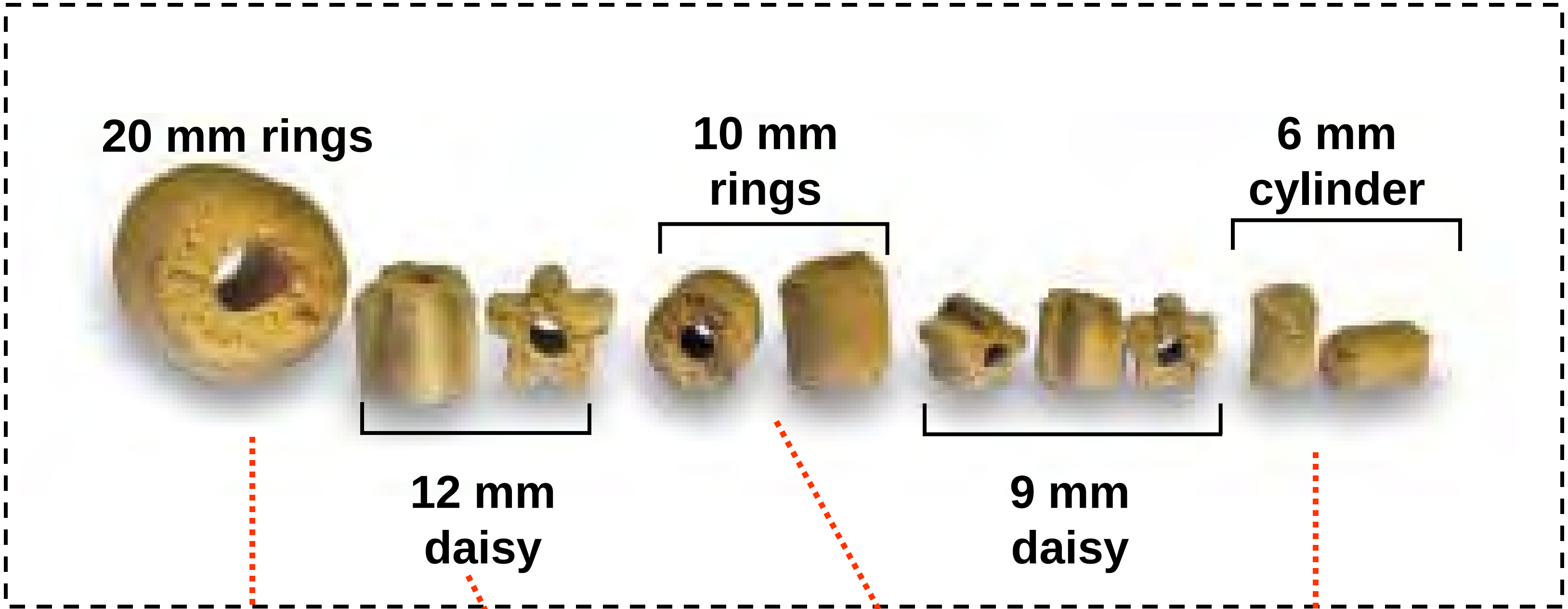
# Conc. Profiles - Nonisothermal Daisy



# Daisy Pellet Temperature Profiles



# Effectiveness Factor Comparison




| | Effectiveness Factors | | | |
|---|---|---|---|---|
| T, °C | 20 mm Hollow | 12 mm Daisy | 10 mm Hollow | 6 mm Solid |
| 420 | 0.363 | 0.449 | 0.589 | 0.592 |
| 475 | 0.387 | 0.498 | 0.684 | 0.679 |
| 500 | 0.300 | 0.393 | 0.562 | 0.565 |
| 590 | 0.146 | 0.193 | 0.283 | 0.302 |

# Summary

- COMSOL Multiphysics provides attractive approach for modeling impact of catalyst particle shape on catalyst effectiveness factors for $SO_2$ oxidation.

# Suggested Areas for Improvement

- Need more detailed algorithm for rates forms with fractional orders since *C* = 0 for x<x* which gives errors
- Techniques for investigating presence of multiple solutions, which are present in many problems, would allow detailed parametric analysis and identification of stability regions.
- Provide user with more flexible choices, such as molar flux models (*e.g.*, Dusty-gas model), particle shape library, transport parameter library, etc.