

Pharmaceutical
Multiphase Reactors
CHE.782

Design of Multiphase
Flow Processes
669.266

Theory on Intra-Particle Models for Reactive Porous Particles in the „ParScale“ Library

A – Overview
B – Model Details
C – Numerics

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A part of this teaching material has been
prepared for NanoSim (<http://sintef.no/NanoSim/>)

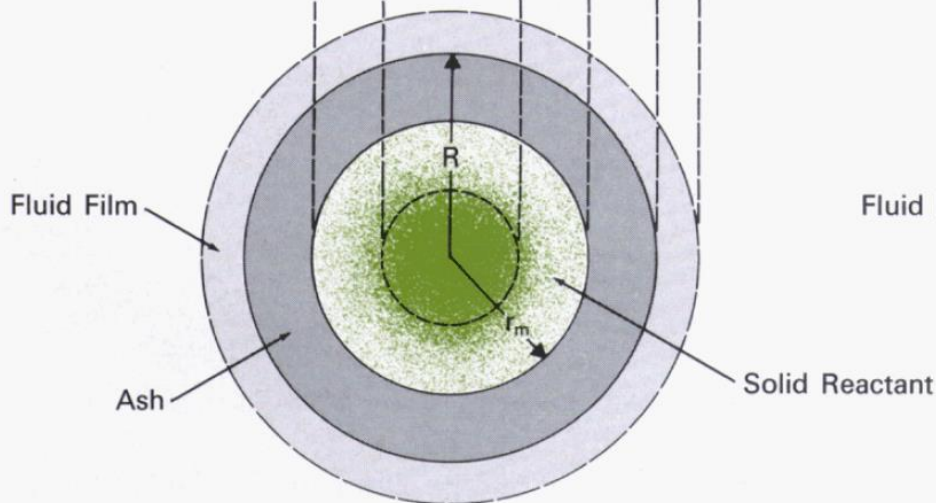
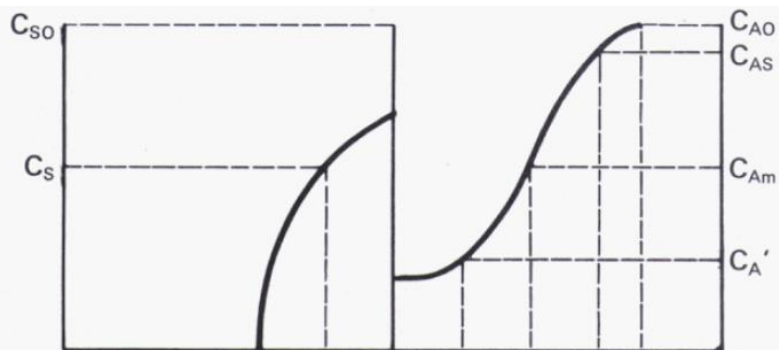


NanoSim - A Multi-scale Simulation-Based Design Platform

Concentration Profiles in a Reacting Particle¹

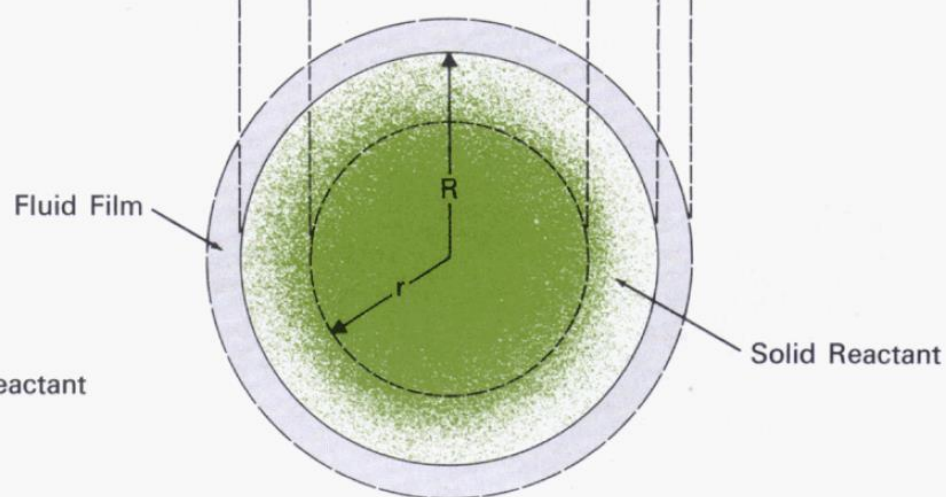
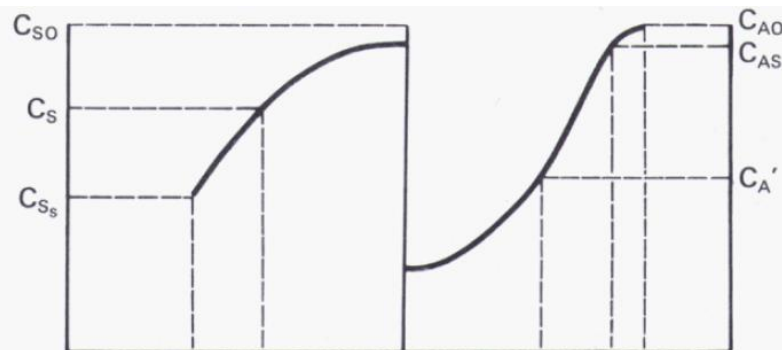
Solid

Gas



Solid

Gas



¹Wen, *Ind Eng Chem* 60 (1968).

Approach	Coordinates	Description
Continuum Model ¹⁻³ [ModelEqn1DSpherical]	1D (3D)	Detailed model with little assumptions (pore structure, carrier particle shape)
Layer Model ^{4,6}	0D (3 or 4 layers)	Drying & reactions occur in different layers, useful for biomass applications
Shrinking Core Model ^{1,5} [ModelEqnShrinkingCore]	0D (1 front)	Reactions take only place at a reaction front, useful for non-porous ash-forming particles and fast reactions (i.e., high temperature)
Uniform Conversion Model ⁵	0D	Reactions take place throughout the particle
Empirical Models ⁵	0D	Parameters (typically 2) based on experiments

Red Bold: Currently implemented in ParScale [Class name]

¹Wen, *Ind Eng Chem* **60** (1968), ²Morell et al, *Chem Eng Sci* **45** (1989), ³Melchiori and Canu, *IEC Res* **53** (2014), ⁴Mehrabian et al., *Fuel Proc Technol* **95** (2012), ⁵Gomez-Barea and Leckner, *Progr Energy Comb Sci* **36** (2010), ⁶Ström and Thunmann, *Appl Energy* **112** (2013).

Modelling approaches

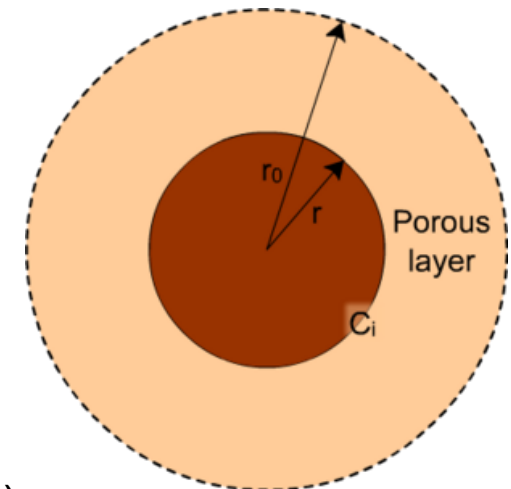
(1) ModelEqn1DSpherical



- Usage documentation „*doc/14_ModelEquation_1_1DSpherical.md*“
- 1-D discretization with fixed number of grid points in **spherical coordinates**
- **Theoretical documentation** „*doc/pdf/1_modelEqn/00_base_model_eqn.pdf*“

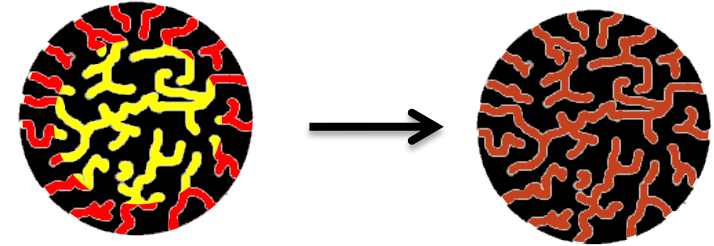
(2) ModelEqnShrinkingCore

- Usage documentation „*doc/14_ModelEquation_2_ShrinkingCore.md*“
- Theoretical documentation „*doc/pdf/1_modelEqn/shrinking_core_model.pdf*“
- **0-D model for reduction** (shrinking due to reaction) of **solid core**



Physical Models

Chemistry Models (e.g. Fe_2O_3 reaction)



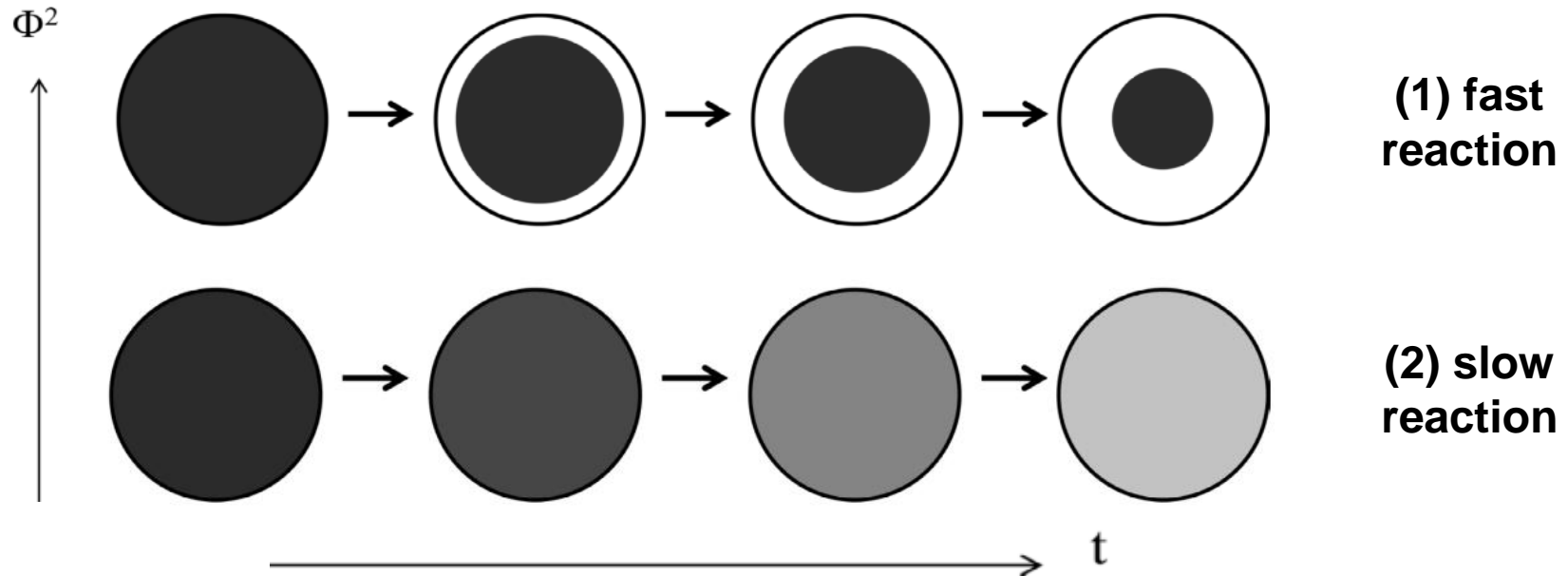
- Possible combination with (1) and (2)
- Usage documentation „doc/15_Chemistry.md“
 - Single reaction „doc/15_Chemistry_1_SingleReaction.md“
 - Multi reaction „doc/15_Chemistry_10_MultiReaction.md“
 - Grain models „doc/15_Chemistry_2_grainModel.md“
- Theoretical documentation „ doc/pdf/2_modelChem“

Phase Change Models (e.g. Drying)



- Possible combination with (1) and (2)
- Usage documentation „doc/18_PhaseChange.md “
 - Evaporation „doc/18_PhaseChange_1_Evaporation.md “
 - Equilibrium „doc/18_PhaseChange_2_Equilibrium_Sharp.md “
- Theoretical documentation „ doc/pdf/2_modelChem“

Continuum Model - Basics



- Possible modeling of **fast reactions** (1) with diffusion limitation inside the particle
- (2) **slow reaction** where reaction rate is determining for overall conversion⁷

⁷Forgber, *PARTICLES, Barcelona* (2015).

Shrinking Core Model - Basics

(a) Uniform conversion model (UCM)



- x_c and ρ_c vary uniformly with t
- $d_p = \text{const} = d_{p0}$
- $x_c = X$
- $c_s = c(r)$
- $\eta_i = 1$

(b) Shrinking unreacted particle model (SUPM)



- Reaction at particle surface
- Ash (if exists) peels off
- $d_p = d_{p0}(1-x_c)^{1/3}$
- Valid for relatively non-porous char

(c) Shrinking unreacted core model (SUCM)



- Reaction at core surface
- Ash layer remains attached
- $d_p = d_{p0}$
- $d_c = d_{p0}(1-x_c)^{1/3}$
- Valid for initially non-porous char

(d) Progressive model with shrinking (reacting) particle (PMSP)



- Reaction throughout the particle
- Ash (if exists) peels off
- $d_p = d_p(x_c)$
- Extension of SUPM for porous char

(e) Progressive model with shrinking (reacting) core (PMSC)



- Reaction throughout the particle
- Ash layer remains attached
- $d_p = d_{p0}$ but $d_c = d_c(x_c)$
- Extension of SUCM for porous char

Time

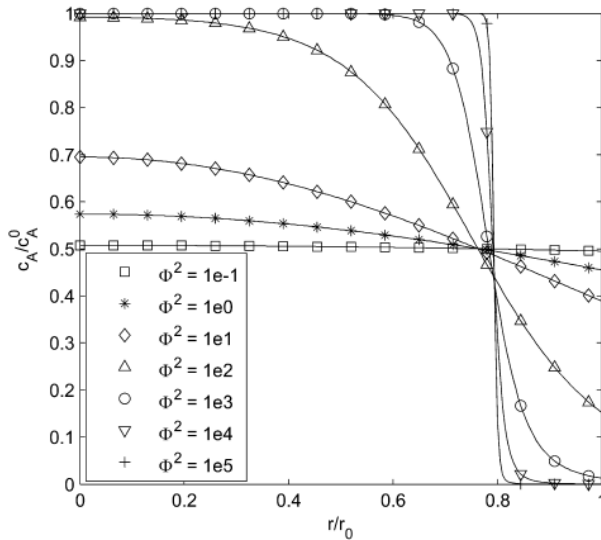
Implemented in
ParScale

NOT
Implemented in
ParScale (yet)

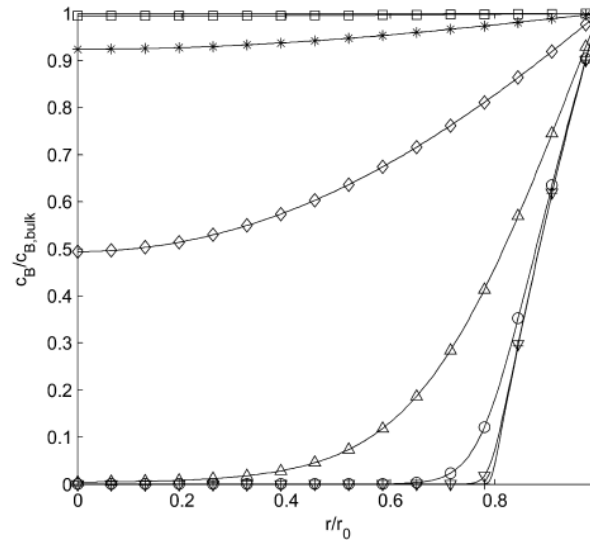
Comparison of Models

Solid

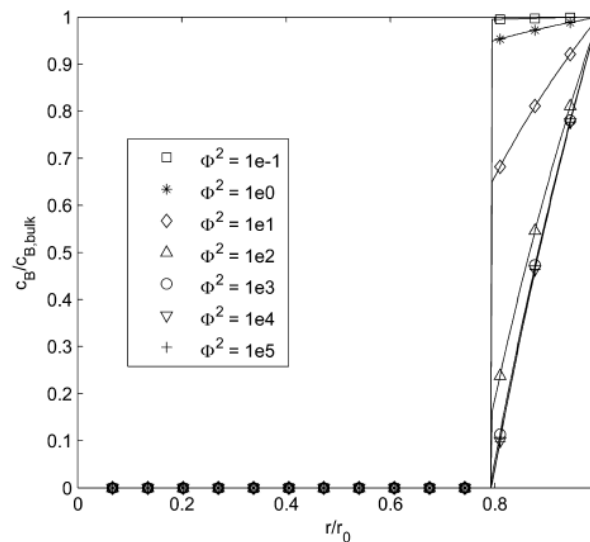
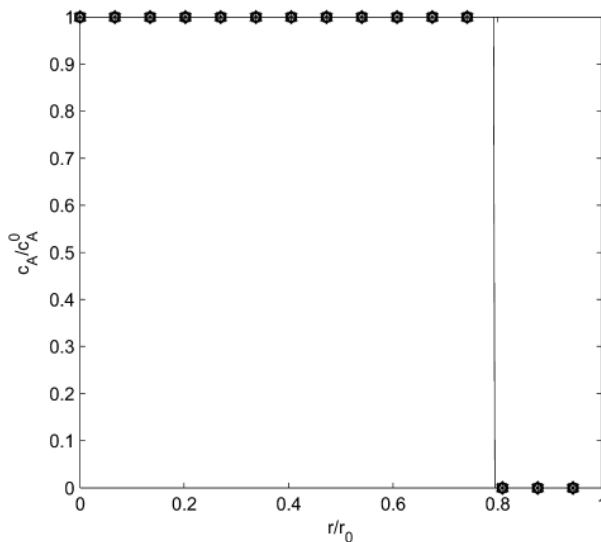
1D-CM



Gas



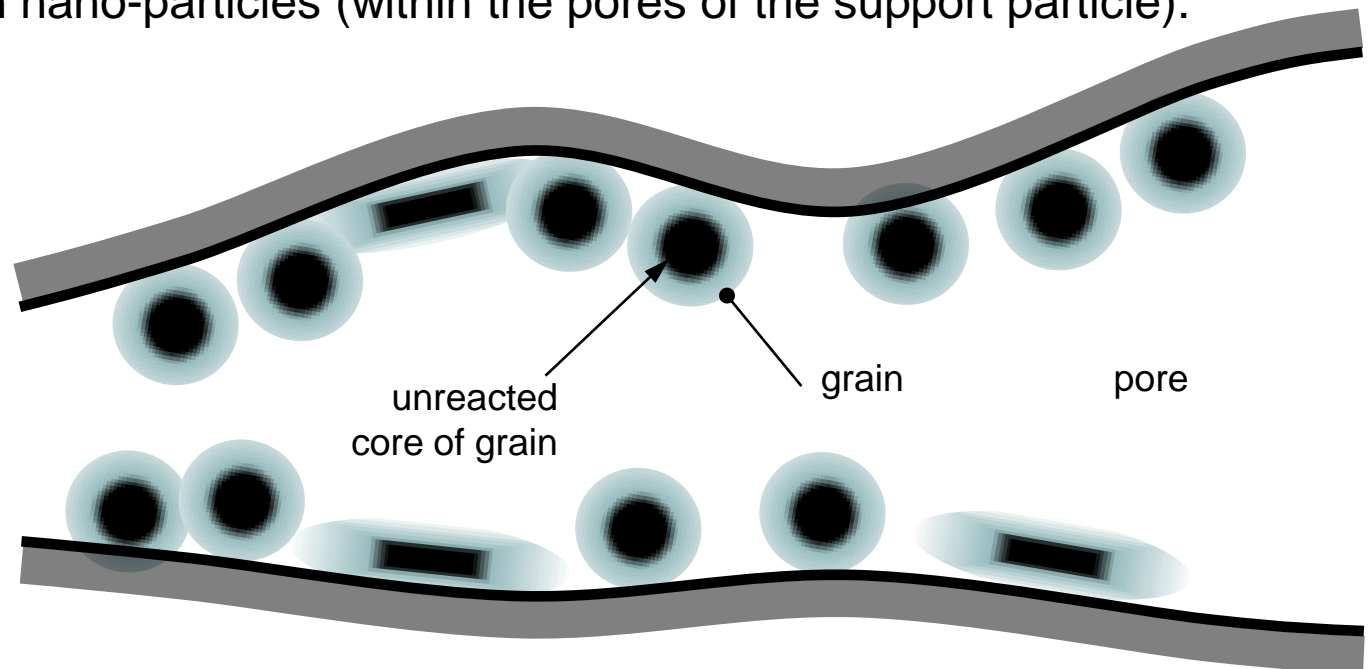
SCM



Simulated concentration profiles for a fixed solid conversion of $X = 0.5$ (Melchiori and Canu³)

Grain Model

- Classical use: account for the **change of porosity** during conversion.
- Porosity change can occur due to
 - Gasification of solid
 - Differences in the solid density of educts and product
- **Grain size distribution models** have been proposed in literature in order to model the effect of non-uniform grain size.⁸
- Within the NanoSim project: account for the **effect of oxide layer** formation on nano-particles (within the pores of the support particle).



⁸Heesink et al., *CEJ* 53 (1993).

Grain Model

- A variety of grain models to **model gasification kinetics** has accumulated (see the table provided by Gómez-Barea and Ollero⁵).
- Melchiori and Canu³ provide expressions that take grain size, grain shape (sintering!), diffusion in the grain product layer, and the reaction rate into account. This is an **extension of the classical "Grain Model"** of van den Aarsen shown in the table.

Main structural or empirical models applied to gasification kinetics

Name	Abbreviation	$F(X)$	Param.	$\Theta(X)$	Reference
Volumetric model	VM	$(1 - X)$	—	$-\ln(1 - X)$	Adanez and de Diego (1993) Szekely et al. (1976) Adschiri et al. (1986)
Grain model	GM	$(1 - X)^{2/3}$	—	$3(1 - (1 - X)^{1/3})$	van den Aarsen (1985)
Random pore model	RPM	$(1 - X)(1 - \psi_0 \ln(1 - X))^{1/2}$	ψ_0	$(2/\psi_0) (1 - \psi_0 \ln(1 - X))^{1/2}$	Bhatia and Perlmutter (1980)
Struis	MRPM	$f(t) (1 - X) (1 - \psi_0 \ln(1 - X))^{1/2(*)}$	p, α, ψ_0	$(**)$	Struis et al. (2002)
Simons model	SM	$(1 - X) (X + \alpha_0(1 - X))^{1/2}$	α_0	$2 \operatorname{atanh} ((1 - \alpha)x + \alpha)^{1/2}$	Simons (1980)
Johnson model	JM	$(1 - X)^{2/3} e^{\alpha X^2}$	α	NAEF	Johnson (1979)
Dutta model	DM	$[1 \pm 100X^{\gamma\beta} \exp(-\beta \cdot X)] \cdot (1 - X)$	α, β	NAEF	Dutta et al. (1977)
Gardner model	GM	$(1 - X)e^{\alpha X}$	a	NAEF	Gardner et al. (1979)
Chornet model	CM	$\sqrt{X}(1 - X)$	—	$2 \operatorname{atanh} (\sqrt{X})$	Chornet et al. (1979)
Modified volumetric model	MVM	$a^{1/b} b(1 - X)[- \ln(1 - X)]^{(b-1)/b}$	a, b	NAEF	Kasaoka et al. (1985)
Traditional	TM	$(1 - X)^\alpha$	α	$(\alpha - 1)^{-1} [(1 - X)^{1-\alpha} - 1]$	
Polinomial model	PM	$\sum_{i=1}^n a_i X(1 - X)^i$	a_i	NAEF	
					Ollero et al. (2003), Gómez-Barea et al. (2005)

... Implemented in *ParScale*

Discretization in space

- *ParScale* uses **CDS 2nd** order in space $O(\Delta x^2)$
- For more information see „*doc/pdf/1_modelEqn/00_base_model_eqn.pdf*“ (**section 6 Numerics**)

Discretization in time

- *ParScale* depends on **CVODE** (available within SUNDIALS package)
- For more information see „*thirdParty/sundials-2.5.0/doc/cvode/cv_guide.pdf*“ or „*doc/pdf/1_modelEqn/00_base_model_eqn.pdf*“ (section 6 Numerics)
 - 1-5 order backward differencing scheme (**BDS**)
 - **Variable time stepping**, automatic sub-time stepping
 - Robust, suitable for **stiff systems** of ODE's (e.g. fast reactions)

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