12 Chemical Akzo Nobel problem

12.1 General information

This IVP is a stiff system of 6 non-linear DAEs of index 1 and has been taken from [Sto98]. The parallel-IVP-algorithm group of CWI contributed this problem to the test set in collaboration with W.J.H. Stortelder. We acknowledge the remarks of Dotsikas Ioannis, which improved the formulation of this problem considerably. The software part of the problem is in the file chemakzo.f available at [MM08].

12.2 Mathematical description of the problem

The problem is of the form

$$M\frac{\mathrm{d}y}{\mathrm{d}t} = f(y), \qquad y(0) = y_0, \quad y'(0) = y_0',$$

with

$$y \in \mathbb{R}^6, \quad 0 \le t \le 180.$$

The matrix M is of rank 5 and given by

$$M = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

and the function f by

$$f(y) = \begin{pmatrix} -2r_1 & +r_2 & -r_3 & -r_4 & & \\ -\frac{1}{2}r_1 & & & -r_4 & -\frac{1}{2}r_5 & +F_{in} \\ r_1 & -r_2 & +r_3 & & & \\ & -r_2 & +r_3 & -2r_4 & & \\ & r_2 & -r_3 & & +r_5 & \\ K_s \cdot y_1 \cdot y_4 - y_6 & & & & & \end{pmatrix},$$

where the r_i and F_{in} are auxiliary variables, given by

$$\begin{aligned} r_1 &= k_1 \cdot y_1^4 \cdot y_2^{\frac{1}{2}}, \\ r_2 &= k_2 \cdot y_3 \cdot y_4, \\ r_3 &= \frac{k_2}{K} \cdot y_1 \cdot y_5, \\ r_4 &= k_3 \cdot y_1 \cdot y_4^2, \\ r_5 &= k_4 \cdot y_6^2 \cdot y_2^{\frac{1}{2}}, \\ F_{in} &= klA \cdot (\frac{p(\mathrm{CO}_2)}{H} - y_2). \end{aligned}$$

The values of the parameters k_1, k_2, k_3, k_4, K, klA, $p(\mathrm{CO}_2)$ and H are

$$\begin{array}{rclrclrcl} k_1 &=& 18.7, & k_4 &=& 0.42, & K_s &=& 115.83, \\ k_2 &=& 0.58, & K &=& 34.4, & p(\mathrm{CO}_2) &=& 0.9, \\ k_3 &=& 0.09, & klA &=& 3.3, & H &=& 737. \end{array}$$

The consistent initial vectors are

$$y_0 = \left(\; 0.444,\, 0.00123,\, 0,\, 0.007,\, 0,\, K_s \cdot y_{0,1} \cdot y_{0,4} \; \right)^{\mathrm{T}} \qquad y_0' = f(y_0).$$

It is clear from the definition of r_1 and r_5 that the function f can not be evaluated for negative values of y_2. In the Fortran subroutine that defines f, we set `IERR=-1` if $y_2 < 0$ to prevent this situation. See page *IV-ix* of the description of the software part of the test set for more details on `IERR`.

12.3 Origin of the problem

The problem originates from Akzo Nobel Central Research in Arnhem, The Netherlands. It describes a chemical process, in which 2 species, FLB and ZHU, are mixed, while carbon dioxide is continuously added. The resulting species of importance is ZLA. In the interest of commercial competition, the names of the chemical species are fictitious. The reaction equations, as given by Akzo Nobel [CBS93], are given in Figure II.12.1. The last reaction equation describes an equilibrium

$$\begin{aligned}
2\,\mathrm{FLB} + \frac{1}{2}\mathrm{CO_2} &\xrightarrow{k_1} \mathrm{FLBT} + \mathrm{H_2O} \\
\mathrm{ZLA} + \mathrm{FLB} &\underset{k_2}{\overset{k_2/K}{\rightleftharpoons}} \mathrm{FLBT} + \mathrm{ZHU} \\
\mathrm{FLB} + 2\,\mathrm{ZHU} + \mathrm{CO_2} &\xrightarrow{k_3} \mathrm{LB} + \mathrm{nitrate} \\
\mathrm{FLB.ZHU} + \frac{1}{2}\mathrm{CO_2} &\xrightarrow{k_4} \mathrm{ZLA} + \mathrm{H_2O} \\
\mathrm{FLB} + \mathrm{ZHU} &\rightleftharpoons \mathrm{FLB.ZHU}
\end{aligned}$$

FIGURE II.12.1: *Reaction scheme for Chemical Akzo Nobel problem.*

$$K_s = \frac{[\mathrm{FLB.ZHU}]}{[\mathrm{FLB}] \cdot [\mathrm{ZHU}]}.$$

The value of K_s plays a role in parameter estimation. The other equations describe reactions with velocities given by

$$\begin{aligned}
r_1 &= k_1 \cdot [\mathrm{FLB}]^4 \cdot [\mathrm{CO_2}]^{\frac{1}{2}}, && \text{(II.12.1)} \\
r_2 &= k_2 \cdot [\mathrm{FLBT}] \cdot [\mathrm{ZHU}], \\
r_3 &= \frac{k_2}{K} \cdot [\mathrm{FLB}] \cdot [\mathrm{ZLA}], \\
r_4 &= k_3 \cdot [\mathrm{FLB}] \cdot [\mathrm{ZHU}]^2, && \text{(II.12.2)} \\
r_5 &= k_4 \cdot [\mathrm{FLB.ZHU}]^2 \cdot [\mathrm{CO_2}]^{\frac{1}{2}}, && \text{(II.12.3)}
\end{aligned}$$

respectively. Here the square brackets '[ ]' denote concentrations. One would expect from the reaction scheme in Figure II.12.1, that reaction velocities r_1, r_4 and r_5 would read

$$\begin{aligned}
r_1 &= k_1 \cdot [\mathrm{FLB}]^2 \cdot [\mathrm{CO_2}]^{\frac{1}{2}}, \\
r_4 &= k_3 \cdot [\mathrm{FLB}] \cdot [\mathrm{ZHU}]^2 \cdot [\mathrm{CO_2}], \\
r_5 &= k_4 \cdot [\mathrm{FLB.ZHU}] \cdot [\mathrm{CO_2}]^{\frac{1}{2}}.
\end{aligned}$$

However, it turns out that the chemical process under consideration is modeled more appropriately using (II.12.1)–(II.12.3).

The inflow of carbon dioxide per volume unit is denoted by F_{in}, and satisfies

$$F_{in} = klA \cdot (\frac{p(CO_2)}{H} - [CO_2]),$$

where klA is the mass transfer coefficient, H is the Henry constant and $p(CO_2)$ is the partial carbon dioxide pressure. $p(CO_2)$ is assumed to be independent of $[CO_2]$. The parameters k_1, k_2, k_3, k_4, K, klA, K_s, H and $p(CO_2)$ are given constants*.

The process is started by mixing 0.444 mol/liter FLB with 0.007 mol/liter ZHU. The concentration of carbon dioxide at the beginning is 0.00123 mol/liter. Initially, no other species are present. The simulation is performed on the time interval [0, 180 minutes].

Identifying the concentrations [FLB], $[CO_2]$, [FLBT], [ZHU], [ZLA], [FLB.ZHU] with $y_1, \ldots, y_6$, respectively, one easily arrives at the mathematical formulation of the preceding section.

12.4 Numerical solution of the problem

Tables II.12.1–II.12.2 and Figures II.12.2–II.12.6 present the reference solution at the end of the integration interval, the run characteristics, the behavior of the solution over the integration interval and the work-precision diagrams, respectively. The reference solution was computed by PSIDE on a Cray C90, using double precision, `rtol = atol` 10^{-19}. To get more insight in the exact behavior of the second component, we included a plot of y_2 on $[0, 3]$ in Figure II.12.2. For the work-precision diagrams, we used: rtol = $10^{-(8+m/4)}$, $m = 0, 1, \ldots, 20$; atol = rtol; h0 = rtol for BIMD, GAMD, MEBDFDAE, MEBDFI, RADAU and RADAU5. The failed runs are in Table II.12.3; listed are the

TABLE II.12.1: *Reference solution at the end of the integration interval.*

y_1	0.1150794920661702	y_4	$0.3656156421249283 \cdot 10^{-3}$
y_2	$0.1203831471567715 \cdot 10^{-2}$	y_5	$0.1708010885264404 \cdot 10^{-1}$
y_3	0.1611562887407974	y_6	$0.4873531310307455 \cdot 10^{-2}$

TABLE II.12.2: *Run characteristics.*

solver	rtol	atol	h0	mescd	scd	steps	accept	#f	#Jac	#LU	CPU
BIMD	10^{-10}	10^{-10}	10^{-10}	12.39	10.61	41	41	1177	41	41	0.0039
DDASSL	10^{-10}	10^{-10}		10.04	8.33	522	515	649	38		0.0039
GAMD	10^{-10}	10^{-10}	10^{-10}	11.89	9.82	35	35	1737	35	35	0.0039
MEBDFI	10^{-10}	10^{-10}	10^{-10}	11.42	9.76	274	273	916	32	32	0.0029
PSIDE-1	10^{-10}	10^{-10}		11.41	9.91	87	85	1671	15	204	0.0039
RADAU	10^{-10}	10^{-10}	10^{-10}	10.71	8.39	43	41	696	30	43	0.0010

name of the solver that failed, for which values of m this happened, and the reason for failing.

*Apart from H, which is generally known, all parameters have been estimated by W. Stortelder [Sto95].

TABLE II.12.3: *Failed runs.*

solver	m	reason
PSIDE-1	14,16,17,18,19,20	stepsize too small

References

[CBS93] CBS-reaction-meeting Köln. Handouts, May 1993. Br/ARLO-CRC.

[MM08] F. Mazzia and C. Magherini. *Test Set for Initial Value Problem Solvers, release 2.4.* Department of Mathematics, University of Bari and INdAM, Research Unit of Bari, February 2008. Available at http://www.dm.uniba.it/~testset.

[Sto95] W.J.H. Stortelder, 1995. Private communication.

[Sto98] W.J.H. de Stortelder. *Parameter Estimation in Nonlinear Dynamical Systems.* PhD thesis, University of Amsterdam, March 12, 1998.

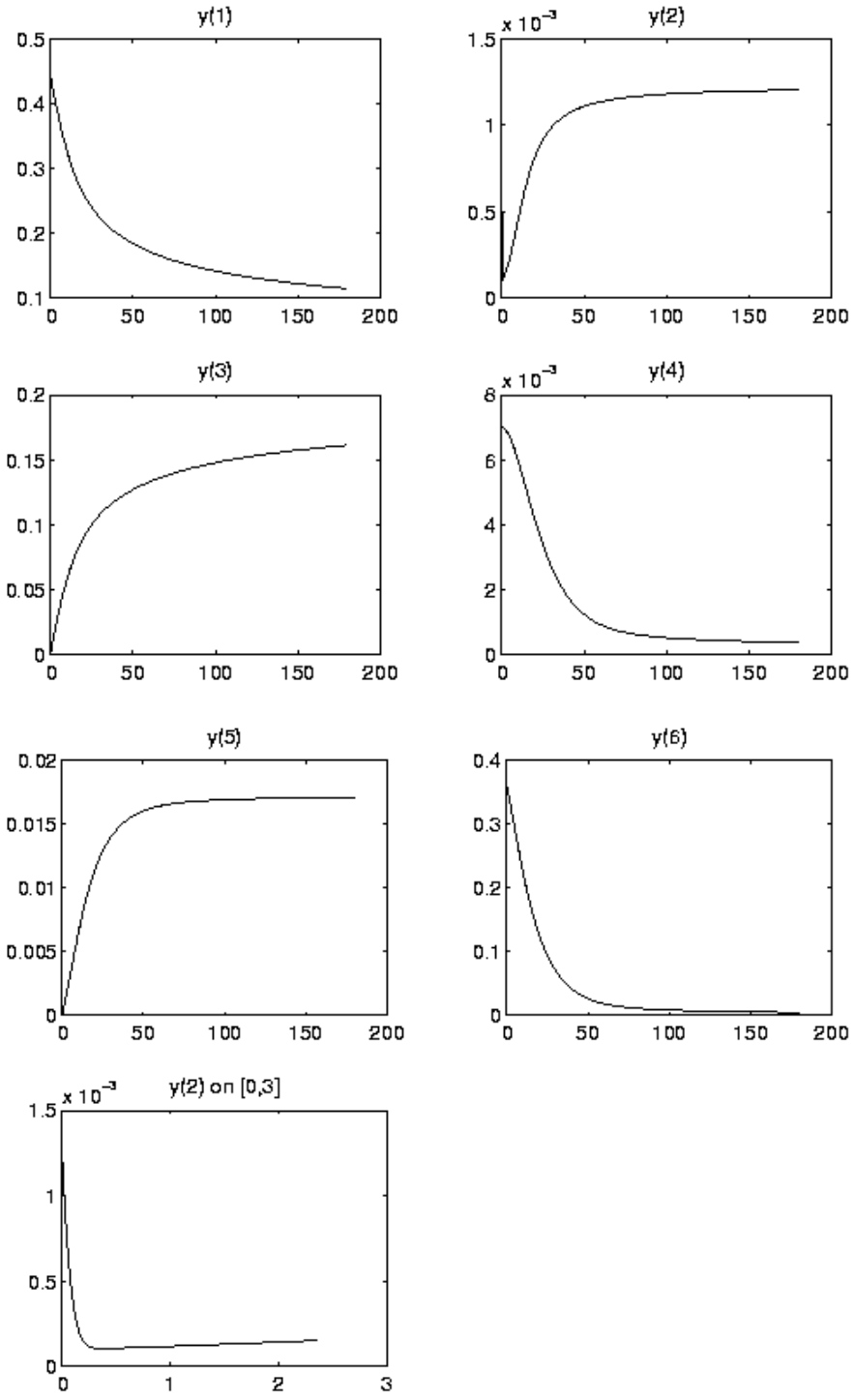

FIGURE II.12.2: *Behavior of the solution over the integration interval.*

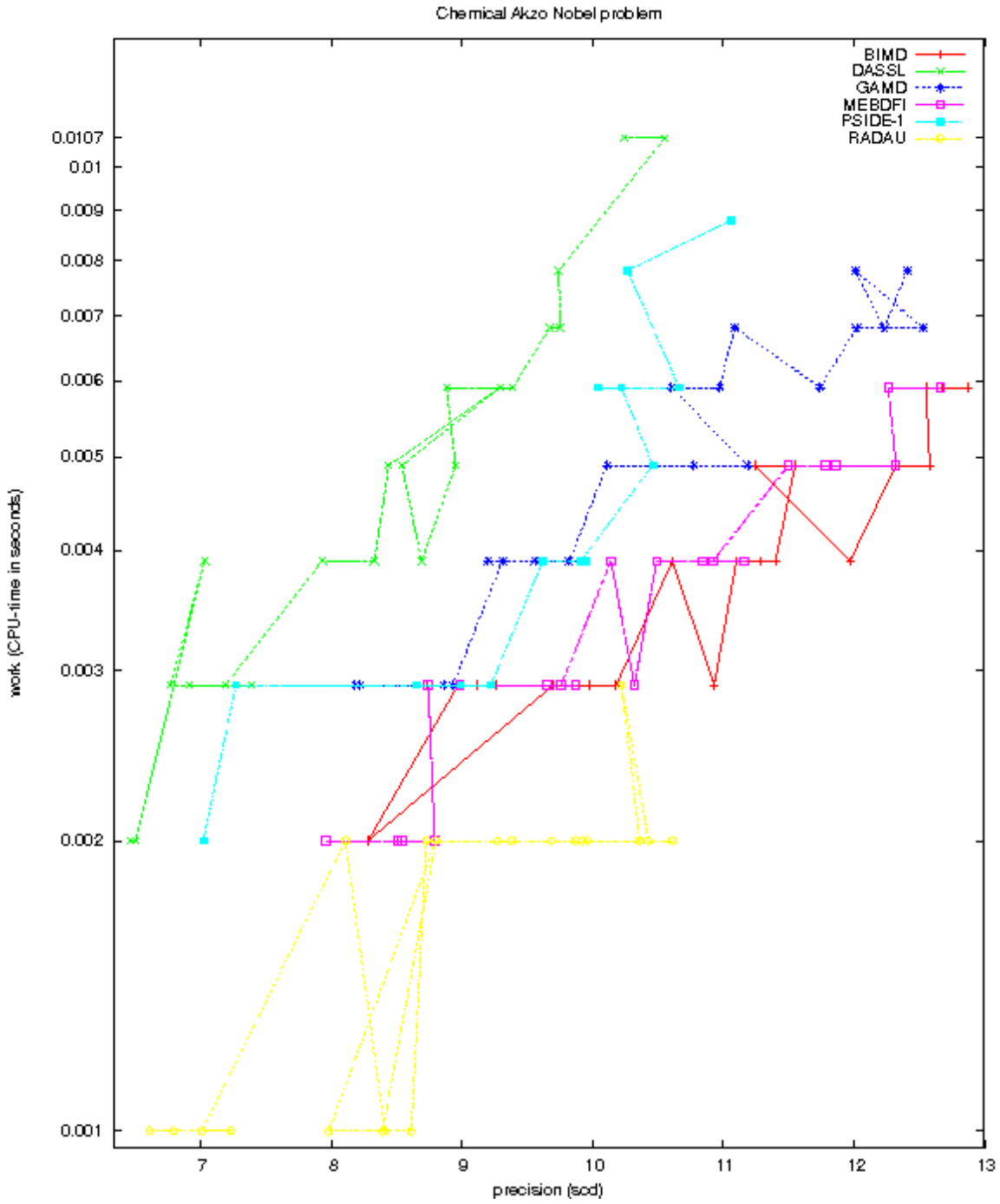

FIGURE II.12.3: *Work-precision diagram (scd versus CPU-time).*

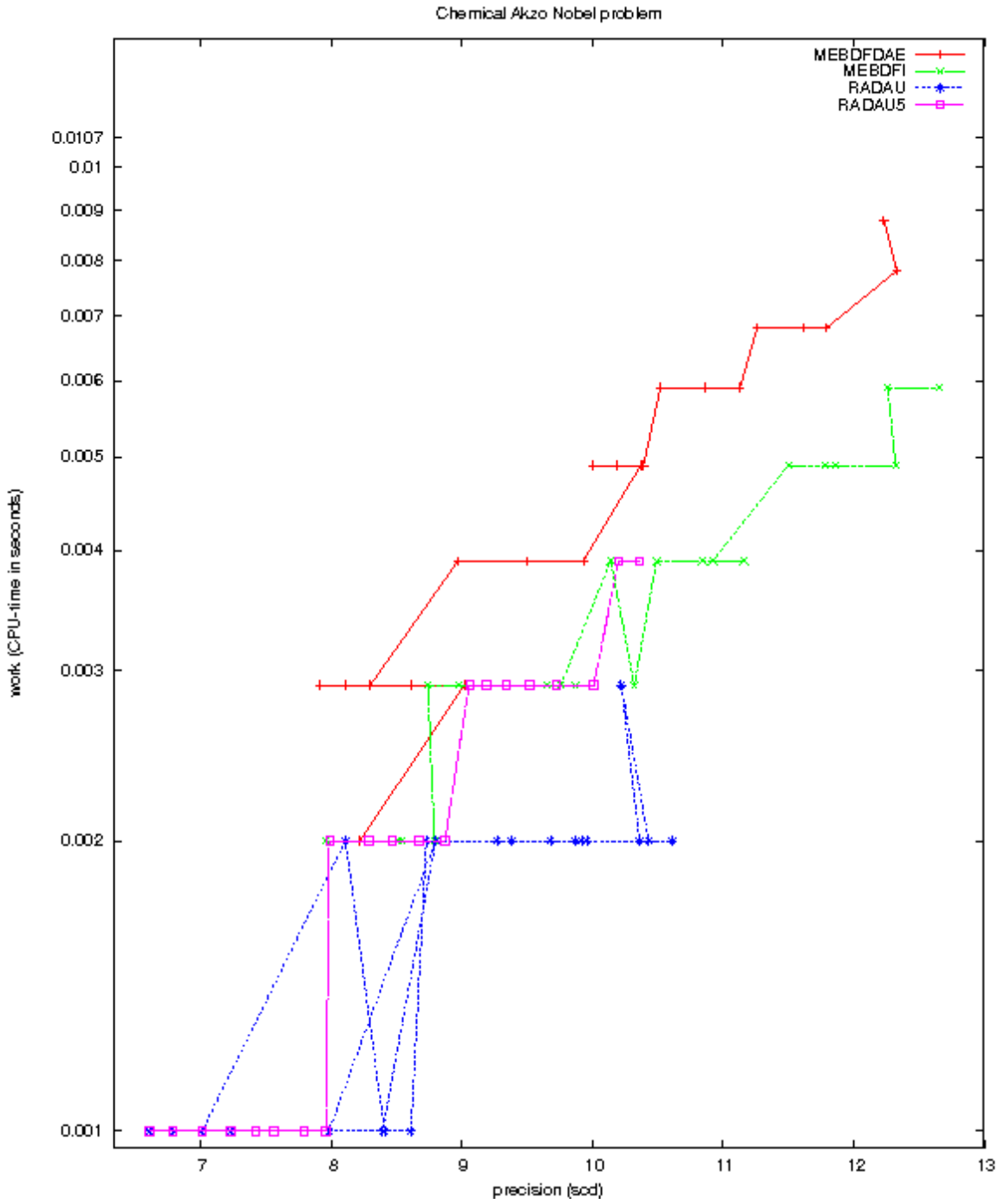

FIGURE II.12.4: *Work-precision diagram (scd versus CPU-time).*

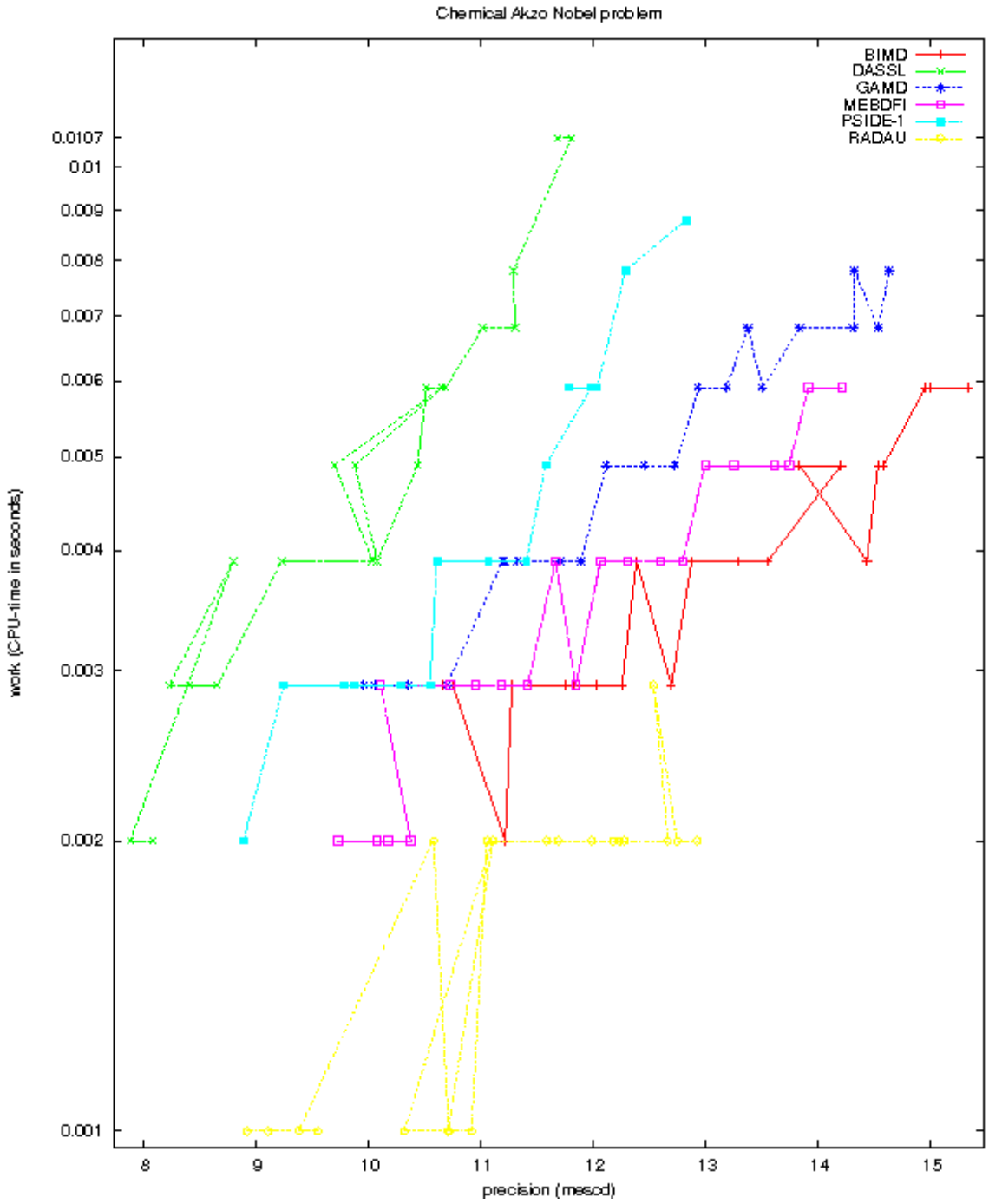

FIGURE II.12.5: *Work-precision diagram (mescd versus CPU-time).*

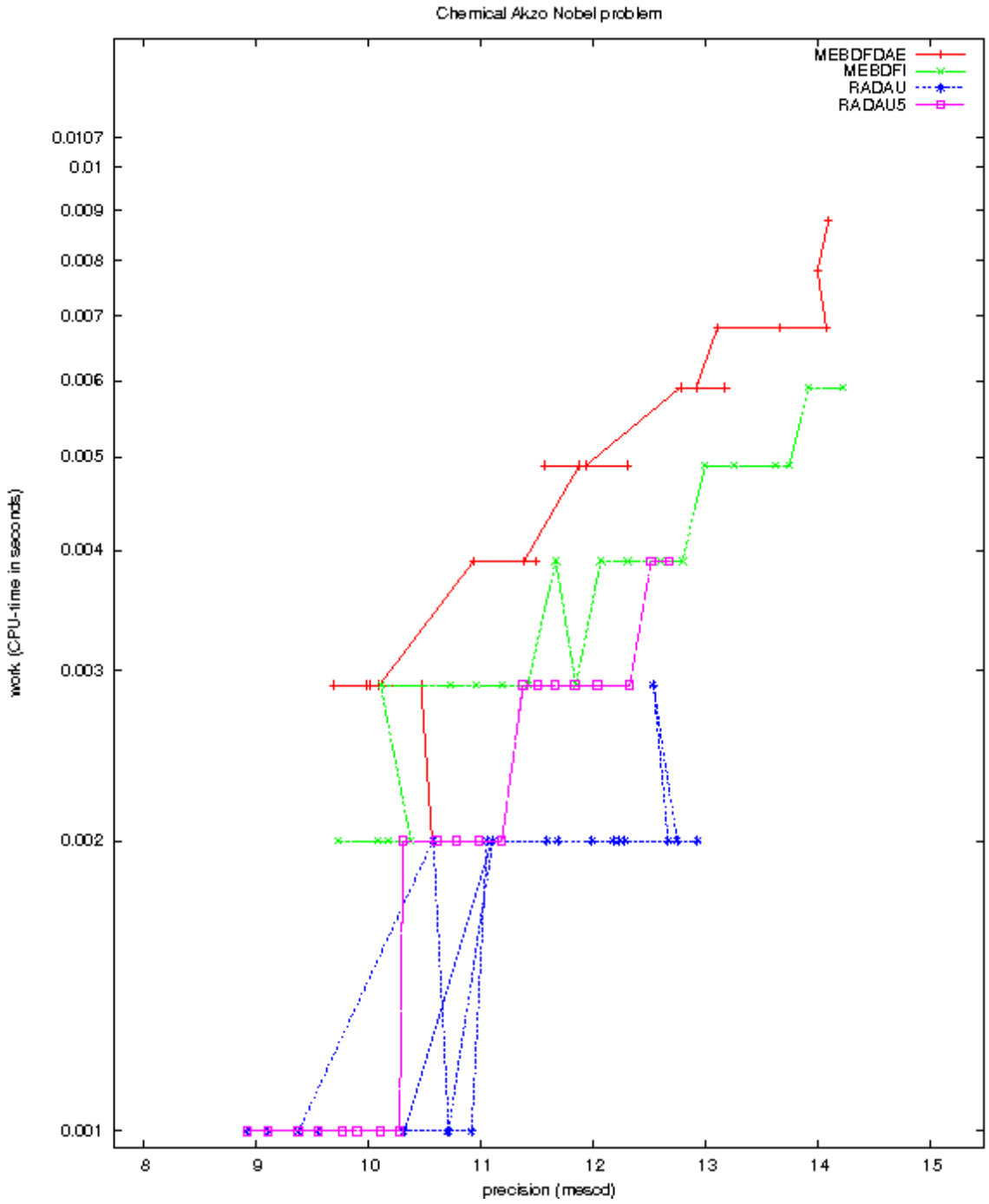

FIGURE II.12.6: *Work-precision diagram (mescd versus CPU-time).*