ioMosaic®

Minimizing risk. Maximizing potential.®

DIERS Fall Meeting – October 17, 2022

Best Practices for Calculation of Self Accelerating Reaction Temperatures (T_{SA}) for reaction Systems:

Part I – Data Reduction

Georges A. Melhem, Ph.D., FAIChE

melhem.ioMosaic.com

QMS_7.3_7.4.F06 Rev.9

Meet your presenter

- Over 30 years of Engineering and Process Safety Experience
- Pressure Relief and Flare Systems
- PRV Stability and Fluid Dynamics
- Chemical Reaction Systems
- Fire, Explosion, and Dispersion Dynamics
- Quantitative and Transportation Risk Analysis
- LNG, LPG, and Hydrogen Safety
- Process Safety Management
- Litigation Support & Public Testimony

G. A. Melhem, Ph.D., FAIChE
President and CEO

This tutorial represents part I of a six-part series on “Best Practices for Calculation of Self Accelerating Reaction Temperatures (TSA) for Reaction Systems”

- Part I – Data Reduction
- Part II – Kinetic Model Development
- Part III – Semenov Approach, Simplified and Dynamic
- Part IV - Kamenetskii Approach, 1D/2D, Simplified and Dynamic
- Part V – Case Studies
- Part VI – UN and DOT Requirements

What you are expected to learn from this tutorial includes

- How to prepare a forever green chemical reaction data set
- How to process, visualize, and reduce the data set
- How to analyze the reduced data set
- How to calculate thermal stability indicators
- How to calculate T_{NR}, T_{SA}, and t_{MR}
- How to generate summary reports and graphics

Key References:

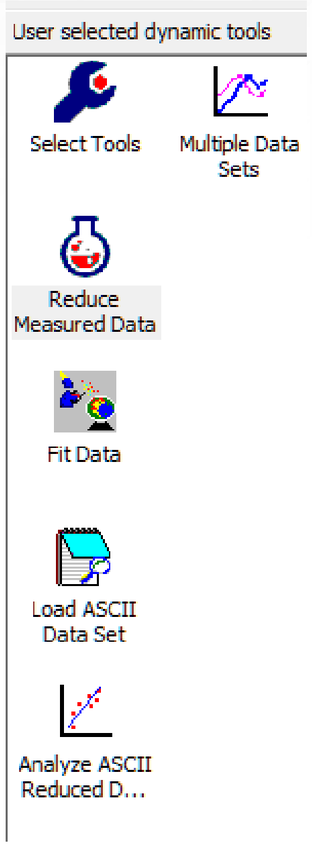
G. A. Melhem, S. Grenier, and L. Ding, *"Thermal stability indicators",* an ioMosaic Corporation white paper, August 2021.

G. A. Melhem, "*Development of kinetic models – Part I. Thermal Stability*", an ioMosaic Corporation white paper, August 2022.

G. A. Melhem, "*Development of kinetic models – Part II. Pressure Relief Systems*", an ioMosaic Corporation white paper, August 2022.

We use a variety of calorimetry data in the development of process safety information (PSI)

- Typical instruments used include the ARC, APTAC, VSP2, DSC, TGA, TAM, etc.
- Measured data is provided in a variety of formats
- Many formats have been obsoleted over time and access to old data can be lost
- We have developed a universal data taxonomy and data reduction tools that can be used in conjunction with SuperChems to preserve this valuable data
- The data reduction tools include visualization, regression, and simplified kinetic model development
- Data can be exchanged and does not require special tools to read and process



The universal taxonomy is based on flat ASCII files with keywords - Identification

Keyword	Function	Usage
C	Provide a comment that is not reported in data summary	C = “This is a comment”
Instrument	Define instrument, ARC, APTAC, RSST, ARSST, VSP, VSP2, DSC, TGA, VariPhi, OTHER	Instrument = “ARC"
Author	Define data set author	Author = “G. A. Melhem”
Date	Define data set date	Date = “October 18, 2022”
Comment	Provide a comment that is reported in data summary	Comment = “This is comment 1” Comment = “This is comment 2”
SampleDescription	Overall sample description	SampleDescription = “EO + Water + NaOH”

The universal taxonomy is based on flat ASCII files with keywords - Time

Keyword	Function	Usage
TimeLocation	Specify index of time data	TimeLocation = 0
TimeUnit	Specify time unit, hr, min, s, day, week, yr	TimeUnit = hr
TimeOffset	Offset time data	TimeOffset = 5.3
TimeStart	Specify starting time for data reduction	TimeStart = 0
TimeEnd	Specify ending time for data reduction	TimeEnd = 7000

The universal taxonomy is based on flat ASCII files with keywords – Mass (always in grams)

Keyword	Function	Usage
MassLocation	Specify mass data index	MassLocation = 2
MassPercentLocation	Specify mass percent data index (optional)	MassPercentLocation = 3
MassRateLocation	Specify change of mass with respect time index (optional)	MassRateLocation = 4

The universal taxonomy is based on flat ASCII files with keywords - Temperature

Keyword	Function	Usage
TempLocation	Specify index of temperature data	TempLocation = 0
TempUnit	Specify temperature unit, C, K, R, F	TempUnit = C
TempOffset	Offset temperature data	TempOffset = 0.0
TempRateLocation	Specify change of temperature with time (optional)	TempRateLocation = 1

The universal taxonomy is based on flat ASCII files with keywords - Pressure

Keyword	Function	Usage
PresLocation	Specify index of pressure data	PresLocation = 0
PresUnit	Specify pressure unit, atm, bara, dyn/cm2, ftH2O, g/cm2, inHg, inH2O, kg/cm2a, kPa, Mpa, mmHg, Pa, psia, psig, lb/ft2, pdls/ft2, barg, kPag,Mpag, kg/cm2g, mbara, mbarg	PresUnit = psia
PresRateLocation	Specify change of pressure with time (optional)	PresRateLocation = 1

The universal taxonomy is based on flat ASCII files with keywords – Operating Mode

Keyword	Function	Usage
ModeLocation	Specify index of operating mode data	ModeLocation = 0
ModeIdle	Specify numeric value of Idle mode	ModeIdle = 13
ModeCalibrate	Specify numeric value of calibration mode	ModeCalibrate = 14
ModeManual	Specify numeric value of manual mode	ModeManual = 15
ModeExotherm	Specify numeric value of exotherm mode, this is needed for automatic calculations by SuperChems	ModeExotherm = 4
ModeWait	Specify numeric value of wait mode	ModeWait = 3
ModeCool	Specify numeric value of cool mode	ModeCool = 2
ModeSearch	Specify numeric value of search mode	ModeSearch = 6
ModeEndotherm	Specify numeric value of endotherm mode	ModeEndotherm = -1
ModeSelect	Specify numeric value of data to be selected	ModeSelect = 4

The universal taxonomy is based on flat ASCII files with keywords (Sample Chemicals, multiple entries)

Keyword	Function	Usage
SampleName	Component name	SampleName = “1,3-Butadiene”
SampleCAS	CAS number, preferred	SampleCAS = “12456-23”
SampleID	SuperChems databank ID number (not recommended)	SampleID = -1
SampleDesc	Chemical description	SampleDesc = “Proprietary Blend”
SampleCP	Heat capacity in cal/g/C	SampleCP = 0.5 cal/g/C
SampleVolume	Sample volume in ml	SampleVolume = -1 ml
SampleMass	Sample mass, in gms	SampleMass = 2.3 gm
….		….
FinalTotalMass	Final mass after test is completed and test cell is opened	FinalTotalMass = 0.6 gm

Only of sample identification keyword is required. Use -1 for properties for automatic calculation by SuperChems. Keywords must be provided in this order. Multiple chemicals are allowed using multiple entries.

The universal taxonomy is based on flat ASCII files with keywords (Pad Gas)

Keyword	Function	Usage
PadGasName	Pad gas component name	PadGasName = “Nitrogen”
PadGasCAS	CAS number, preferred	PadGasCAS = “12456-23”
PadGasID	SuperChems databank ID number (not recommended)	PadGasID = -1

Only one pad gas entry is allowed.

The universal taxonomy is based on flat ASCII files with keywords (Test Cell)

Keyword	Function	Usage
TestCellMaterialName	Material name	TestCellMaterialName = “Hastelloy-C”
TestCellMaterialCAS	CAS number, preferred	TestCellMaterialCAS = “12456-23”
TestCellMaterialID	SuperChems databank ID number (not recommended)	TestCellMaterialID = 1291
TestCellCP	Heat capacity in cal/g/C	TestCellCP = 0.1 cal/g/C
TestCellVolume	Test cell volume in ml	TestCellVolume = 9.8 ml
TestCellMass	Test cell mass, in gms	TestCellMass = 17.0 gm

Only one test cell data set is allowed

The universal taxonomy is based on flat ASCII files with keywords (Fittings)

Keyword	Function	Usage
FittingsMaterialName	Material name	FittingsMaterialName = “STEEL”
FittingsMaterialCAS	CAS number, preferred	FittingsMaterialCAS = “12456-23”
FittingsMaterialID	SuperChems databank ID number (not recommended)	FittingsMaterialID = 1291
FittingsCP	Heat capacity in cal/g/C	FittingsCP = 0.1 cal/g/C
FittingsMass	Fittings mass, in gms	FittingsMass = 0.1 gm

Only one fittings data set is allowed

The universal taxonomy is based on flat ASCII files with keywords (Foil)

Keyword	Function	Usage
FoilMaterialName	Material name	FoilMaterialName = “Aluminum”
FoilMaterialCAS	CAS number, preferred	FoilMaterialCAS = “12456-23”
FoilMaterialID	SuperChems databank ID number (not recommended)	FoilMaterialID = -1
FoilCP	Heat capacity in cal/g/C	FoilCP = -1 cal/g/C
FoilMass	Foil mass, in gms	FoilMass = 0.05 gm

Only one foil data set is allowed

The universal taxonomy is based on flat ASCII files with keywords (Stirrer)

Keyword	Function	Usage
StirrerMaterialName	Material name	StirrerMaterialName = “STEEL”
StirrerMaterialCAS	CAS number, preferred	StirrerMaterialCAS = “12456-23”
StirrerMaterialID	SuperChems databank ID number (not recommended)	StirrerMaterialID = -1
StirrerCP	Heat capacity in cal/g/C	StirrerCP = -1 cal/g/C
StirrerMass	Stirrer mass, in gms	StirrerMass = 1.0 gm
StirringStateLocation	Stirring state data location	StirringStateLocation = 11
StirringPowerLocation	Stirring power data location, mW	StirringPowerLocation = 12
StirringSpeedLocation	Stirring speed data location, RPM	StirringSpeedLocation = 13

Only one stirrer data set is allowed

The universal taxonomy is based on flat ASCII files with keywords (Heating)

Keyword	Function	Usage
HeaterOffsetLocation	Data location index, %	HeaterOffsetLocation = -1
HeaterPowerLocation	Data location index, W	HeaterPowerLocation = 5
SensitivityLocation	Data location index. uV/mW	SensitivityLocation = 6
HeatFlowLocation	Data location index. mW/mg	HeatFlowLocation = 7
HeaterOff	Time of when heating is turned off	HeaterOff = 235 min
HeatTemp	Heating start temperature	HeatTemp = 25 C
HeatRate	Heating rate	HeatRate = 2 C/min
…		

A sample flat ASCII data file is provided below for an ARC data set

```
Author =  "A. Iskandar"
Date   =  "06/26/2020"

Instrument =  ARC

TestDescription = "acrylonitrile + styrene + methyl ethyl ketone + alpha methyl styrene"
TestDescription = "Test Number 06232020-2  Acyrylonitrile + Styrene + MEK + AMS"
TestDescription = "Project # 20109"
TestDescription = "AMS Inihibited with 15 ppm TBC"
TestDescription = "AN Inihibited with 35-45 ppm MEHQ. ST Inihibited with TBC, most likely 15 ppm."

Comment =  "The Methyl EthylKetone, Alpha Methylstyrene, Styrene and Acrylonitrile were"
Comment =  "transfered into the test cell under a nitrogen atmosphere."
Comment =  "The headspace of the test cell was changed to nitrogen prior to starting the test."
Comment =  "The test had 109.7 psia of non-condensible gas at 26.4C."
Comment =  "The weightloss was measured to be 0.3417g which includes material stuck in the pressure transfer lines and gas vented."

SampleID = 724
SampleDesc = -1
SampleCP = -1
SampleVolume = -1
SampleMass =  0.712

SampleID = 181
SampleDesc = -1
SampleCP = -1
SampleVolume = -1
SampleMass =  0.533

SampleID = 269
SampleDesc = -1
SampleCP = -1
SampleVolume = -1
SampleMass =  0.09

SampleID = 182
SampleDesc = -1
SampleCP = -1
SampleVolume = -1
SampleMass =  1.712

PadGasName = "Nitrogen"

FinalTotalMass =  2.7053 Lost 0.3417
```

```
TestCellMaterialName = STEEL 971 Stainless Steel
TestCellMass =  17.492
TestCellVolume =  9.107
TestCellCP = -1

FittingsMaterialName = Titanium 1239
FittingsMass =  6.5464
FittingsCP = -1

FoilMaterialName = Aluminum 964
FoilMass =  0.0
FoilCP = -1

StirrerMaterial = 971 Iron
StirrerMass =  0.2068
StirrerCP = -1

StirringStateLocation =  -1
StirringPowerLocation =  -1
StirringSpeedLocation =  7

TimeLocation =  0
TimeUnit =  min
TimeOffset =  0.0
TimeStart =  0.01027
TimeEnd =  3718.28833

TempLocation =  1
TempRateLocation =  10
TempUnit =  C
TempOffset =  0

PresLocation =  6
PresUnit =  psia
PresRateLocation =  -1

ModeLocation =  14
ModeSelect =  -1
ModeExotherm =  4
ModeHeat =  1
ModeWait =  2
ModeCool =  0
ModeSearch =  3
ModeEndotherm =  -1
ModeIdle =  -1
ModeCalibrate =  -1
ModeManual =  -1
```

A sample flat ASCII data file is provided below for an ARC data set (continued)

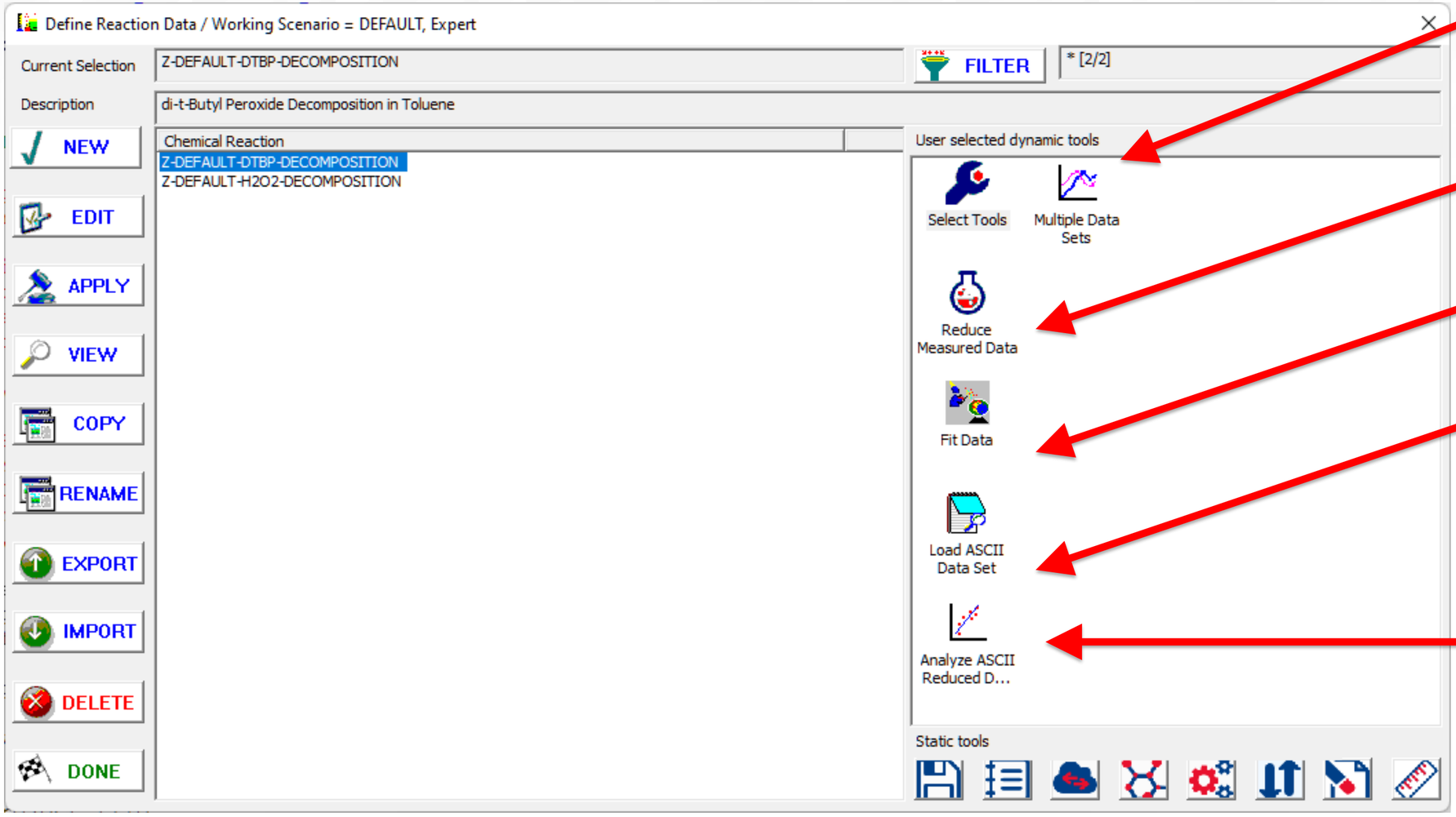
C Elasp C Time C (min)	Sample Temp (ºC)	TempSide Heater (ºC)	Temp Top Heater (ºC)	Bottom Heater (ºC)	Spare T/C (ºC)	Sample Pressure (psia)	Stirrer RPM (V)	Not Avail ()	Not Avail ()	Sample TempRate (ºC)	PowerTop Heater (W)	Side Heater (W)	Base Heater (W)	Heater Mode (ModeValue)
"START"														
0.01027	25.51703	23.05807	23.14580	23.21298	25.38579	14.70925	300.00000	0.00000	0.00000	0.01279	0.76541	1.01815	0.93169	1
0.29992	25.51458	23.50858	23.57947	23.62097	25.29669	14.72123	300.00000	0.00000	0.00000	-0.00847	1.04630	0.97567	0.91977	1
1.07788	25.58615	24.90608	25.01926	25.02425	25.28609	14.76992	300.00000	0.00000	0.00000	0.09865	0.53285	0.91162	0.62253	1
1.24476	25.61270	25.12823	25.25347	25.25723	25.29604	14.78186	300.00000	0.00000	0.00000	0.09865	0.59598	0.87545	0.65919	1
1.42336	25.64230	25.35302	25.46811	25.48243	25.30934	14.79436	300.00000	0.00000	0.00000	0.11148	0.74711	0.88085	0.71366	1
1.81534	25.70451	25.80817	25.85828	25.91994	25.34597	14.82314	300.00000	0.00000	0.00000	0.13426	1.02648	0.89520	0.83020	1
2.25211	25.78819	26.26977	26.31689	26.35127	25.39597	14.85535	300.00000	0.00000	0.00000	0.15412	0.78386	0.91450	0.92644	1
2.73455	25.88616	26.73184	26.78453	26.78370	25.45934	14.89015	300.00000	0.00000	0.00000	0.17191	0.88683	0.90752	0.95297	1
3.54187	26.05756	27.42746	27.45474	27.45356	25.57946	14.94670	300.00000	0.00000	0.00000	0.19651	0.85141	0.85308	0.95334	1

....

....

3698.47998	44.45153	45.97464	43.88140	44.97168	43.71076	127.62756	0.00000	0.00000	0.00000	-0.16586	0.00000	0.00000	0.00000	0
3700.36646	44.12178	45.62494	43.56129	44.63720	43.38284	127.31181	0.00000	0.00000	0.00000	-0.16324	0.00000	0.00000	0.00000	0
3702.25293	43.79672	45.27971	43.24603	44.30772	43.05953	126.99734	0.00000	0.00000	0.00000	-0.16067	0.00000	0.00000	0.00000	0
3704.61108	43.40299	44.85644	42.85992	43.90828	42.66356	126.61069	0.00000	0.00000	0.00000	-0.15757	0.00000	0.00000	0.00000	0
3706.49780	43.08344	44.52288	42.55454	43.61774	42.35167	126.31036	0.00000	0.00000	0.00000	-0.15516	0.00000	0.00000	0.00000	0
3708.38428	42.77441	44.19381	42.25493	43.33002	42.04438	126.01554	0.00000	0.00000	0.00000	-0.15267	0.00000	0.00000	0.00000	0
3710.27100	42.46944	43.86936	41.96059	43.03098	41.74275	125.72382	0.00000	0.00000	0.00000	-0.15043	0.00000	0.00000	0.00000	0
3712.62915	42.10185	43.47036	41.59769	42.65861	41.37130	125.36585	0.00000	0.00000	0.00000	-0.14755	0.00000	0.00000	0.00000	0
3714.51563	41.80218	43.15628	41.31287	42.36635	41.07955	125.08096	0.00000	0.00000	0.00000	-0.14520	0.00000	0.00000	0.00000	0
3716.40186	41.49388	42.84778	41.03292	42.07859	40.79258	124.80350	0.00000	0.00000	0.00000	-0.14301	0.00000	0.00000	0.00000	0
3718.28833	41.22810	42.54331	40.75578	41.79048	40.50894	124.52996	0.00000	0.00000	0.00000	-0.14089	0.00000	0.00000	0.00000	0
"END"														

The data reduction tools in SuperChems were upgraded and enhanced



View multiple data sets from multiple instruments

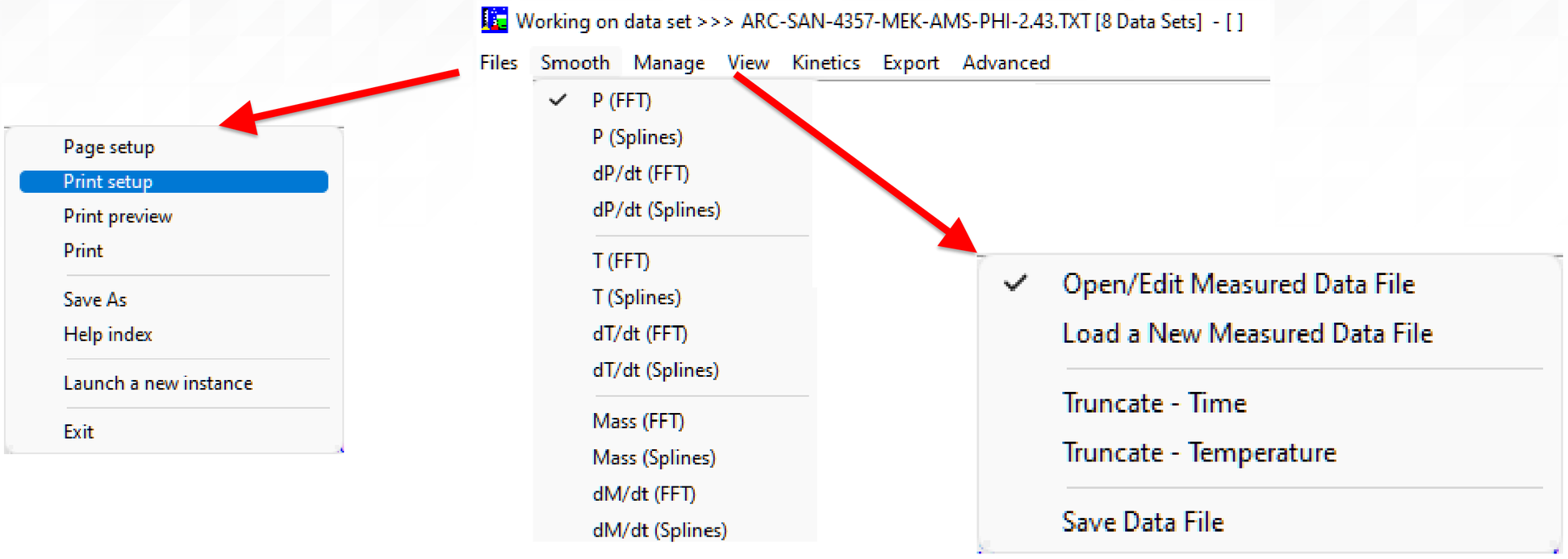
Access data reduction tool

Detailed kinetic model fitting tool

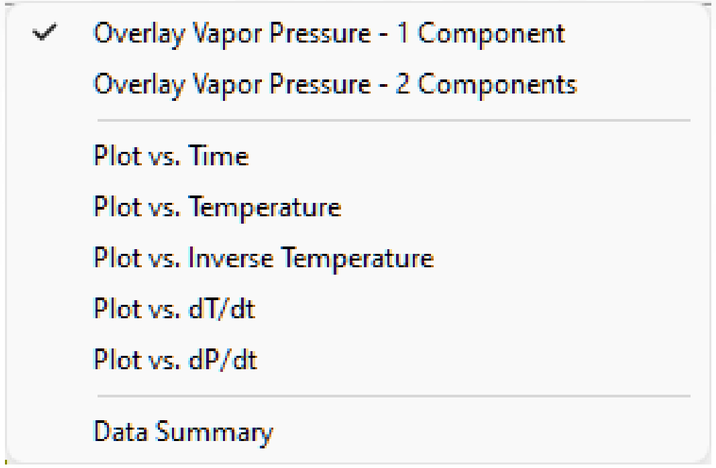
Load a reduced data set for further processing and regression

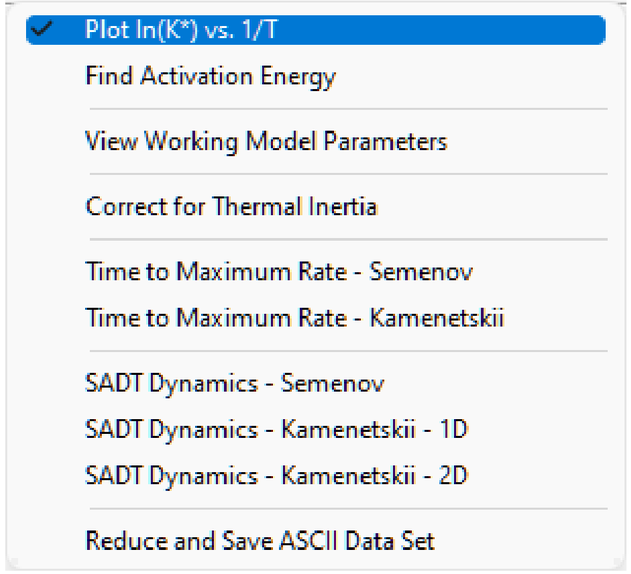
Access data regression tools

Measured data can be filtered, smoothed, truncated, and re-written as different data sets

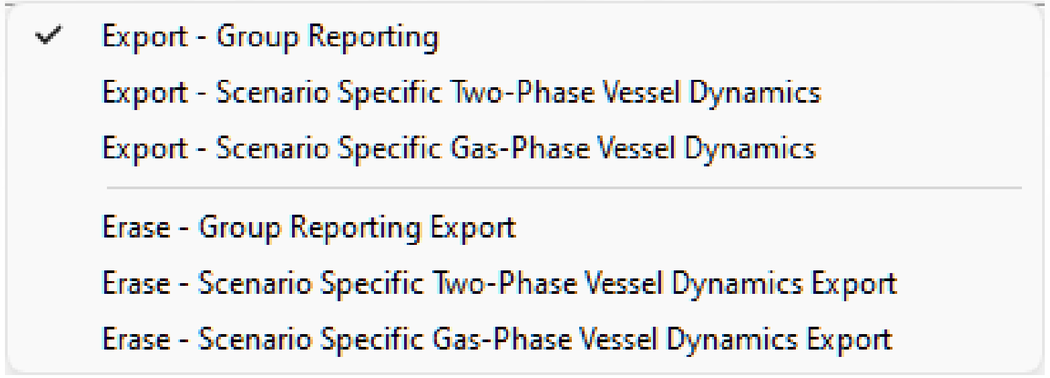


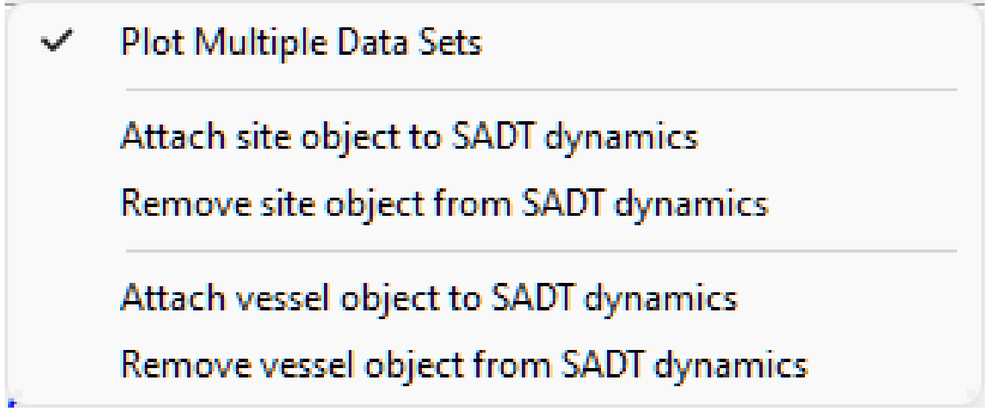
The view and kinetics options provide visualization, simplified, and detailed data analysis and modeling



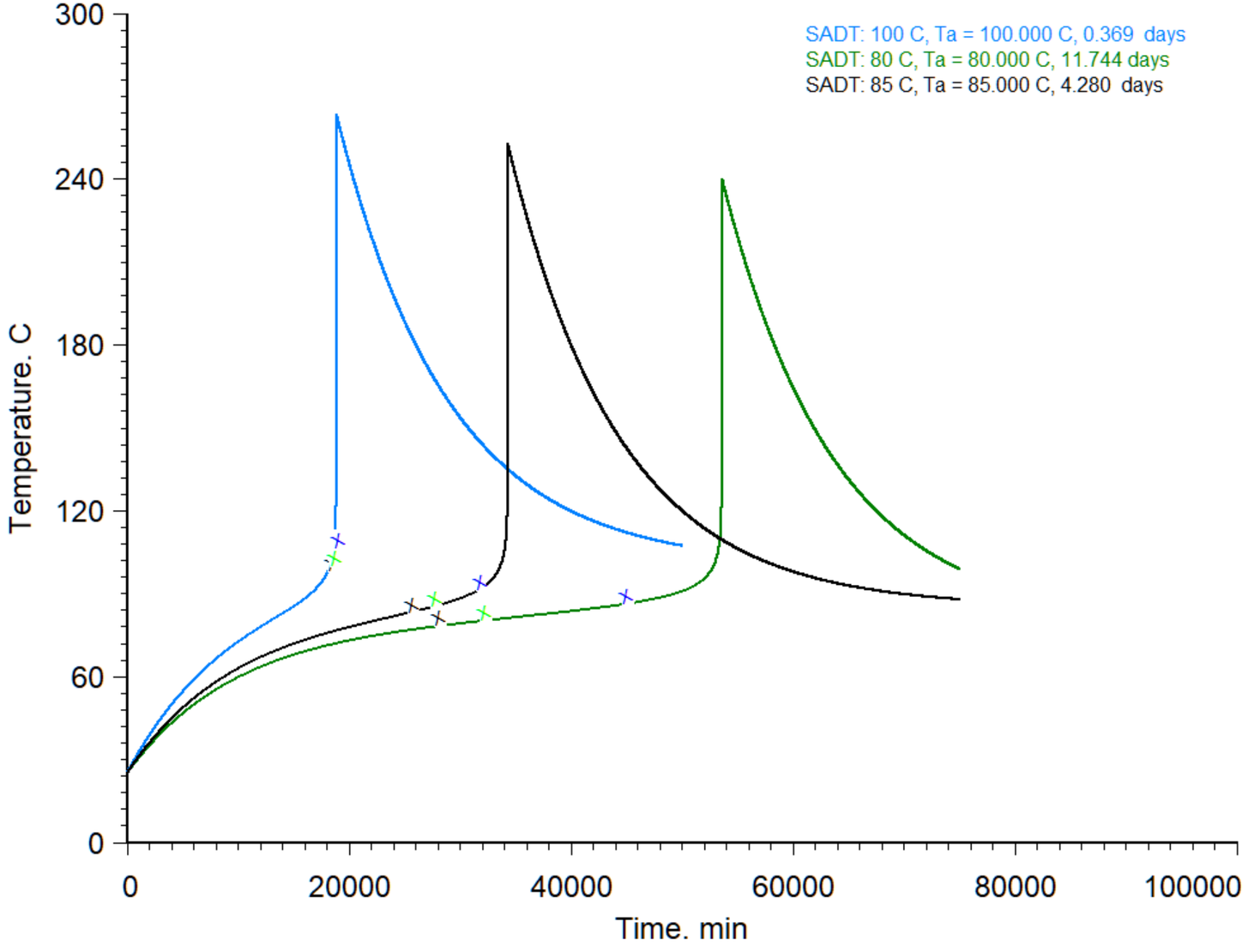


Multiple data sets can be visualized with advanced features enabling time dependent meteorological data sets to be used

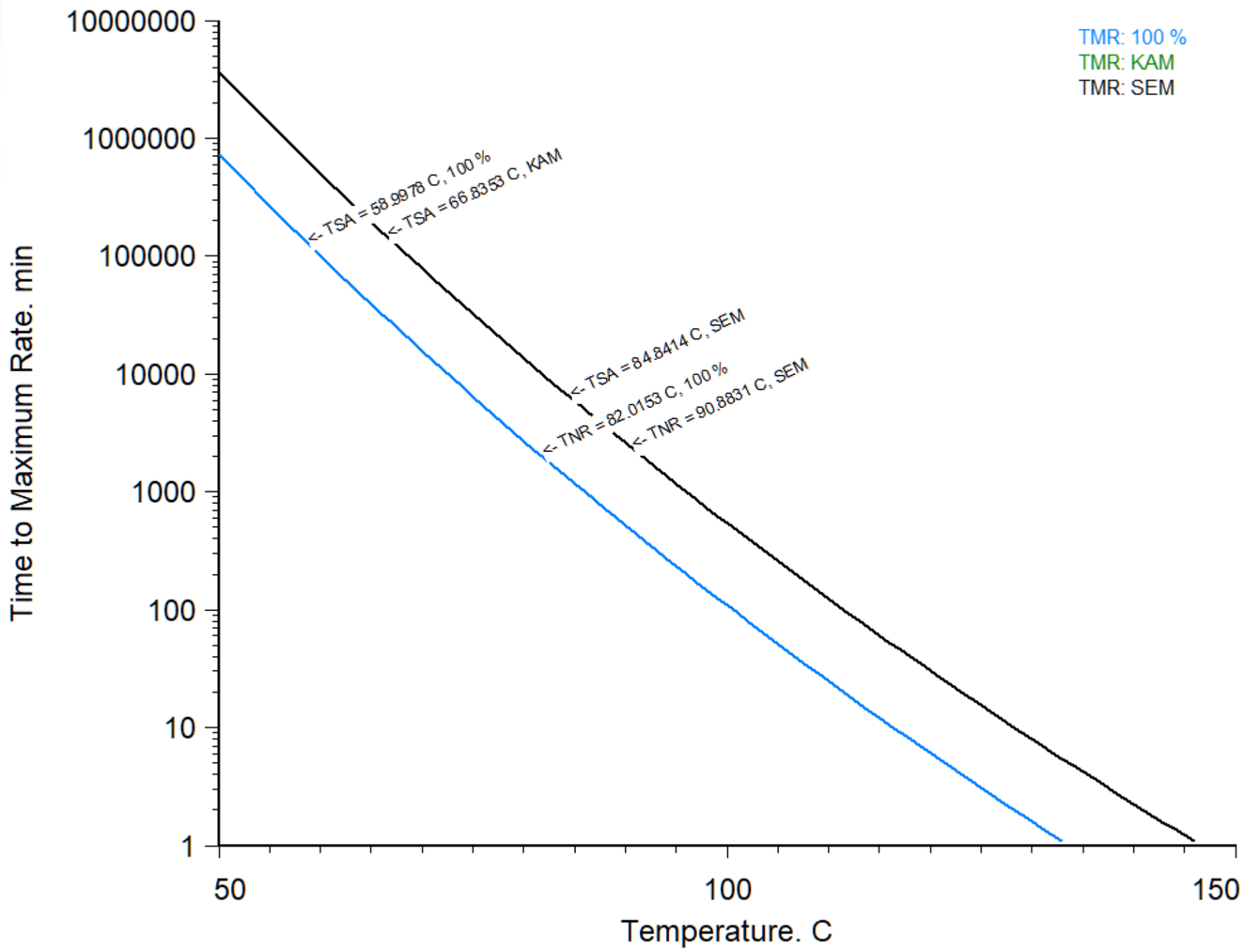




An SADT multiple data set calculated using simplified kinetics



Quick estimates of TSA and TNR can be obtained following data reduction



Conclusions and recommendation

- A complete framework for the reduction, analysis, kinetic model development, and scaleup of chemical reactivity data is now provided in SuperChems v11.5

Recommended additional reading

- G. A. Melhem, *"Relief systems last line of defense, only line of defense?"*, Process Safety Progress, vol 25, No. 4, December 2006
- G. A. Melhem and Peter Howell, *"Designing Emergency Relief Systems for Runaway Reactions",* Chemical Engineering Progress, September 2005
- G. A. Melhem, "*Calculate phase and chemical equilibria using Process Safety Office® SuperChems Expert™"*, an ioMosaic Corporation white paper, March 2021.
- G. A. Melhem, "*Polymerization modeling for emergency relief systems"*, an ioMosaic Corporation white paper, July 2020.
- G. A. Melhem, *"Polymerization reactions inhibitor modeling – styrene and butyl acrylate incidents case studies"*, an ioMosaic Corporation white paper, July 2020.
- G. A. Melhem, *"Quickly develop chemical interaction matrices with SuperChems"*, an ioMosaic Corporation white paper, March 2018.
- G. A. Melhem, *"Systematic evaluation of chemical reaction hazards"*, an ioMosaic Corporation white paper, August 2022.

Recommended additional reading (continued)

- G. A. Melhem, "*An advanced method for the estimation of reaction stoichiometry and rates from ARC data*", an ioMosaic Corporation white paper, August 2022.
- G. A. Melhem, S. Grenier, and L. Ding, "*Thermal stability indicators*", an ioMosaic Corporation white paper, August 2022.
- G. A. Melhem, "*Development of kinetic models – Part I. Thermal Stability*", an ioMosaic Corporation white paper, August 2022.
- G. A. Melhem, "*Development of kinetic models – Part II. Pressure Relief Systems*", an ioMosaic Corporation white paper, August 2022.
- G. A. Melhem, "*Advanced pressure relief design using computer simulation*", an ioMosaic Corporation white paper, August 2022.

For more information, please contact

G. A. Melhem, Ph.D., FAIChE
melhem@iomosaic.com
C: 603-475-3646

ioMosaic Corporation
93 Stiles Road
Salem, NH 03079

Worldwide Locations

Let's talk about your safety needs. Want to schedule a meeting or ask us a question? Call us or email us and we'll be in touch right away.

Salem Office

93 Stiles Road
Salem, NH 03079 US

Tel: 603.893.7009
Fax: 603.386.6522
Email: sales@iomosaic.com

Houston Office

1900 St. James Place, Suite 700
Houston, TX 77056 US

Tel: 713.490.5220
Fax: 832.553.7283
Email: sales@iomosaic.com

Minneapolis Office

401 North 3rd Street, Suite 410
Minneapolis, MN 55401 US

Tel: 612.338.1669
Fax: 832.553.7283
Email: sales@iomosaic.com

Bahrain Office

Suite 161 / 162 / 163 – Platinum Tower,
Building 190 Road 2803 Block 428
Al Seef, Kingdom of Bahrain

Tel: +973.17.561480
Fax: 973.17.911473
Email: sales@iomosaic.com

UK Office

16-18 Queen Square
Bath, BA1 2HN UK

Tel: +44 (0)1225 530 510
Fax: +44 (0)1225 430 225
Email: sales@iomosaic.com

California Office

2001 Addison Street, 3rd Floor
Berkeley, CA 94704 US

Tel: 510.646.0035
Fax: 832.553.7283
Email: sales@iomosaic.com

About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training, and software development.

ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

For more information on ioMosaic, please visit: **www.ioMosaic.com**