Release 2022 R1 Highlights
Chemkin-Pro / MFL

Ansys

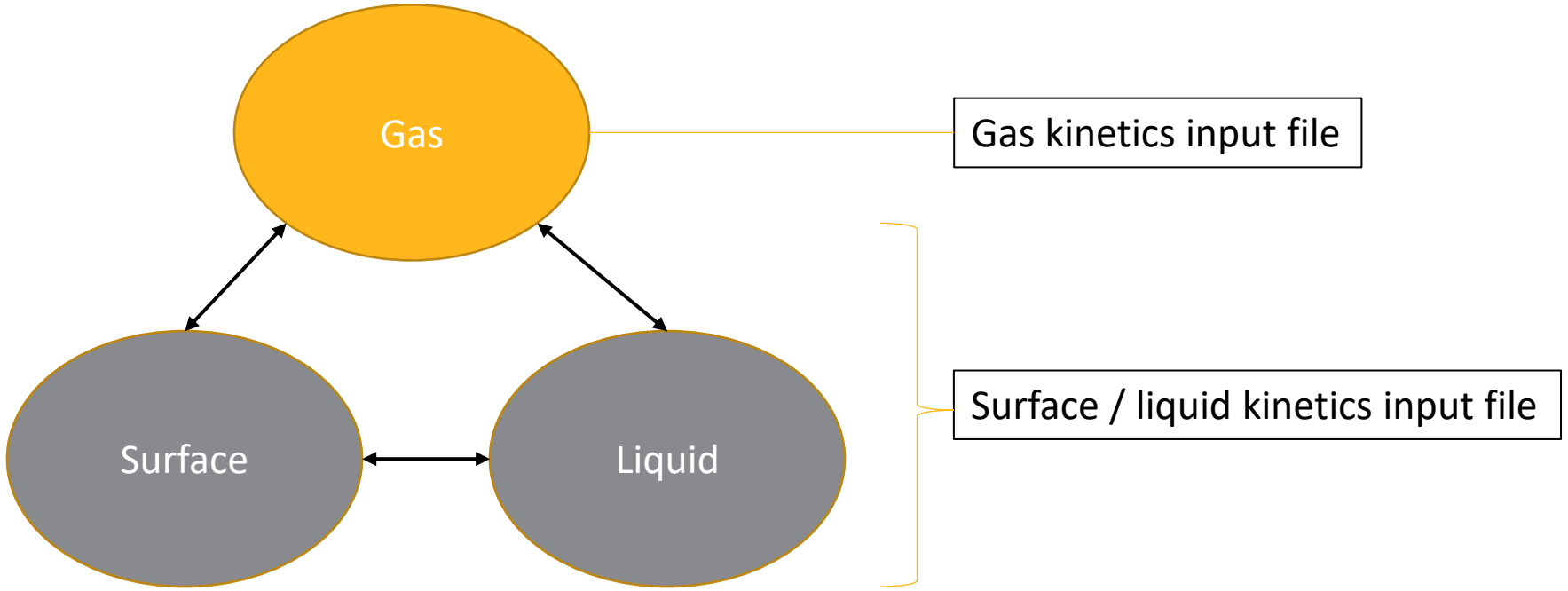
Highlights of changes for Chemkin-Pro / MFL

- New transient **Multiphase Perfectly Stirred Reactor** (PSR) for multiphase chemistry
  - Enables many new applications
- New Multiphase Samples demonstrate capabilities
  - Acid runaway using Closed Batch Multiphase Reactor
  - Urea decomposition using Multiphase PSR
- Chemkin UDFs for chemistry can now be used with Chemkin-CFD solver
  - In **Forte** or **Fluent**
- Improved NO_x predictions with Model Fuel Library PERK* mechanisms

*PERK = Pseudo Elementary Reaction Kinetics

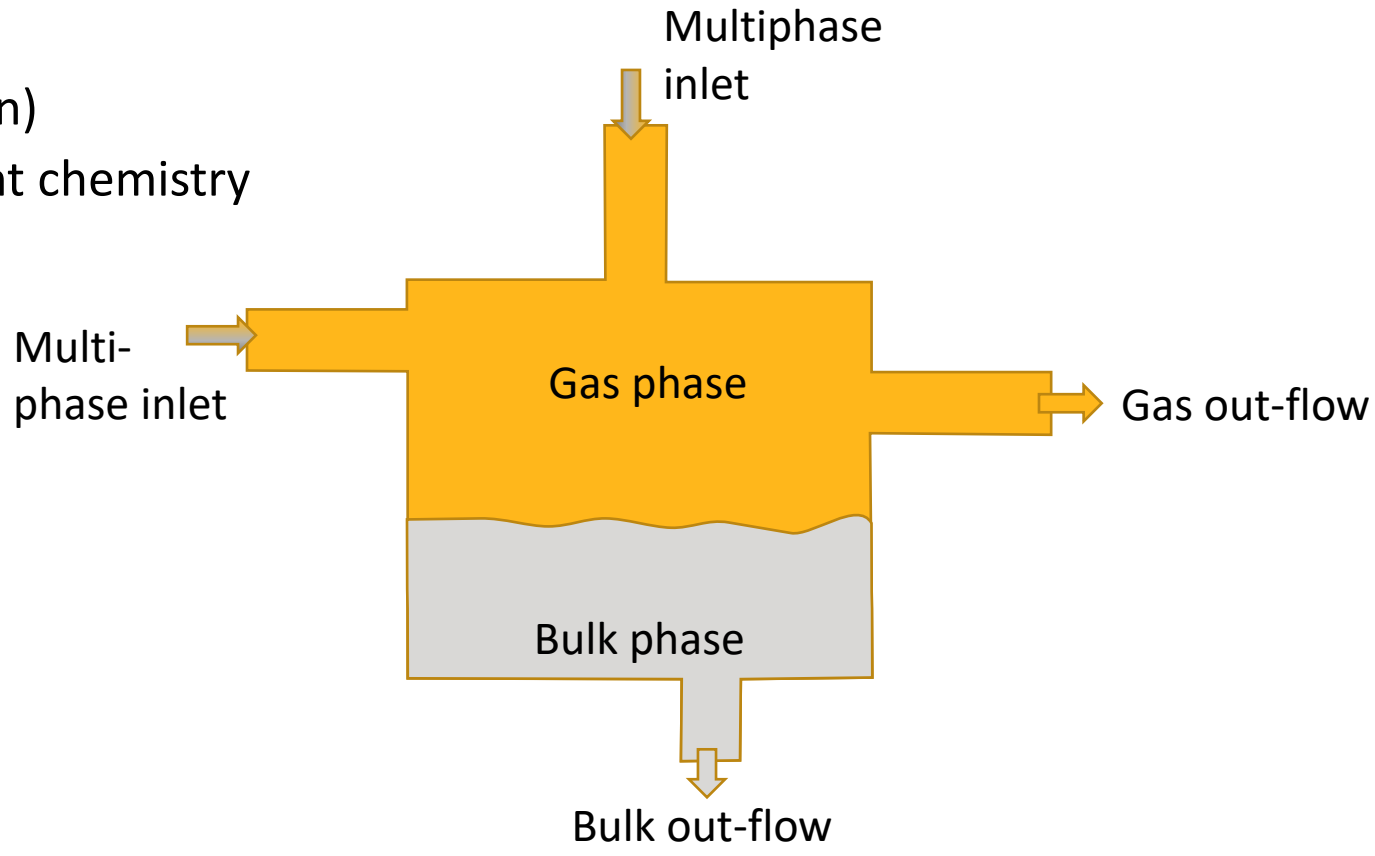
Chemkin-Pro offers a framework for kinetics involving 3 phases

- Multiple phases can be included
  - Reactions supported at the interface between phases
- Liquid properties may be specified with several options
- Special formulations for vapor-liquid equilibrium are available for solutions



Transient Multiphase PSR expands Chemkin-Pro applications

- Allows multiple, multiphase inlets
- Allows multiphase chemical kinetics
  - Including phase change (e.g., vaporization)
  - New reaction-rate formulations or solvent chemistry

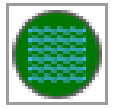


Two new Samples demonstrate Chemkin's Multiphase capabilities

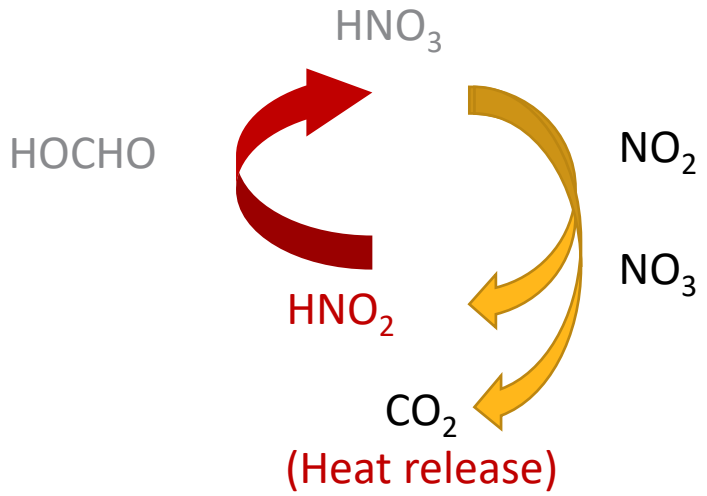
- Acid runaway in a Multiphase 0-D batch reactor
- Urea decomposition in a Multiphase PSR
  - Involves solvent kinetics

New Sample for Industrial safety: simulating runaway processes

- Example: Runaway process of nitric acid (HNO_3) with formic acid (HOCHO)
  - Nitric acid is a popular chemical in industrial processes
    - Cleaning agent, for metal extraction
    - Strong oxidizer – may lead to explosive reaction when mixed with certain compounds
  - Reaction time is ~hours at temperatures ~40 ˚C
- Liquid kinetics mechanism from recent publications:
  - Autocatalysis step from *Ando et al., 2021*
  - HNO3 dissociation based on other publications

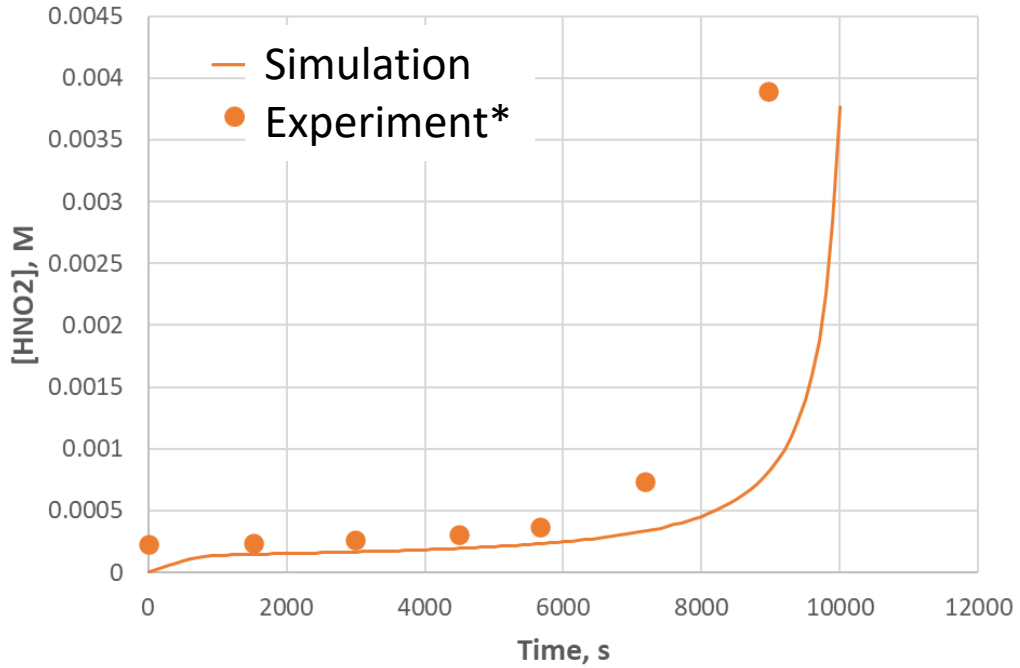


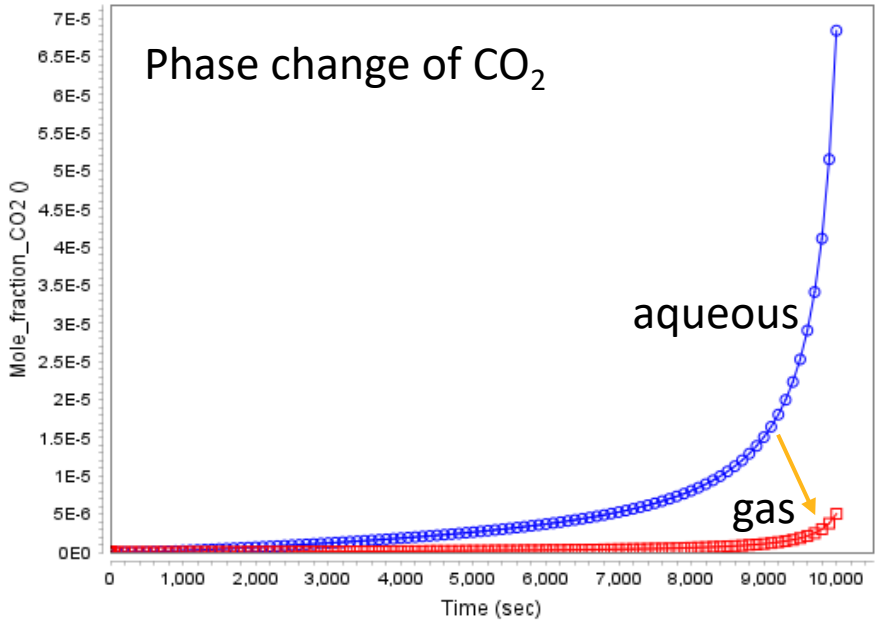
Closed Multiphase Batch Reactor



The acid-runaway simulation captures observed behavior

- Temperature increases due to the rapid rise of HNO_2
- Provides insights into the phase change of products during the reaction



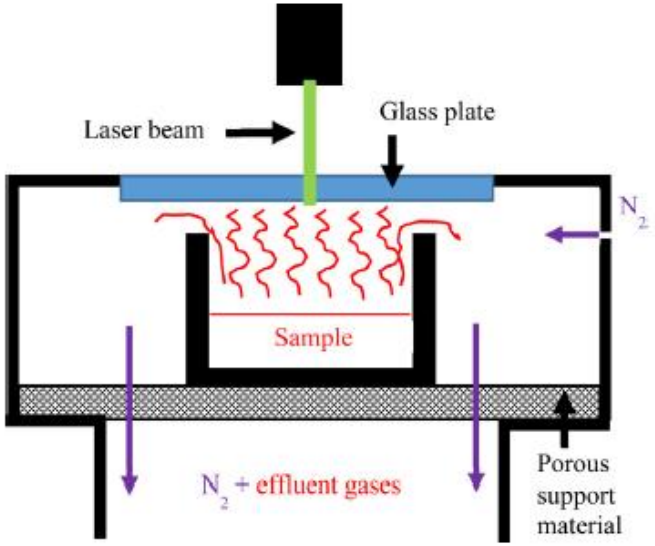


**Data from Ando et al., 2021*

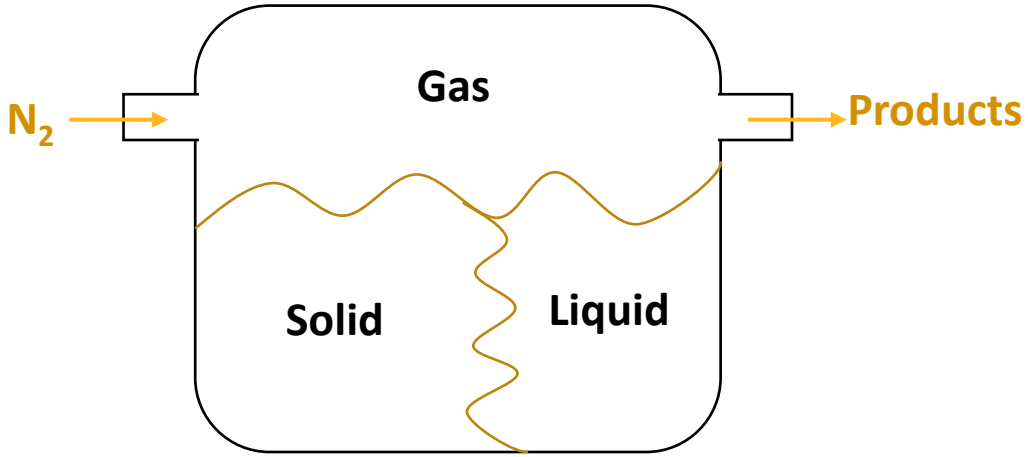
New Sample for simulating urea decomposition

- Includes phase-change and kinetics of urea decomposition
  - Solid urea → Ammonia gas, 20 → 600 ˚C with a heating rate of 10 ˚C/min
  - Nitrogen is the carrier gas

Experiment of Krum et al.*

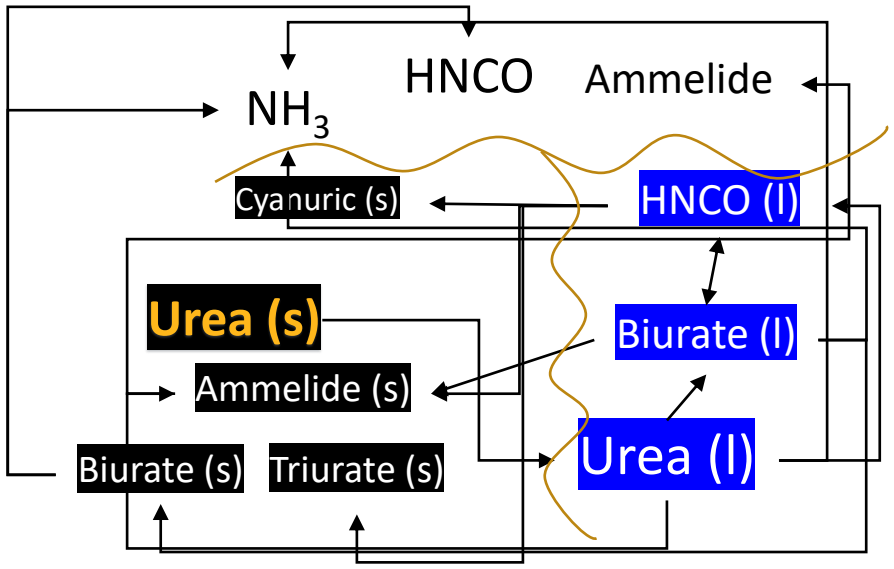


Chemkin-Pro Multiphase PSR



* *Krum et al. Chem. Eng. Sci. (2021) 230, 116138.*

Urea kinetics, involving 3 phases, are derived from publications



Derived from: Brack et al. Chem. Eng. Sci. (2014) 106, 1-8.

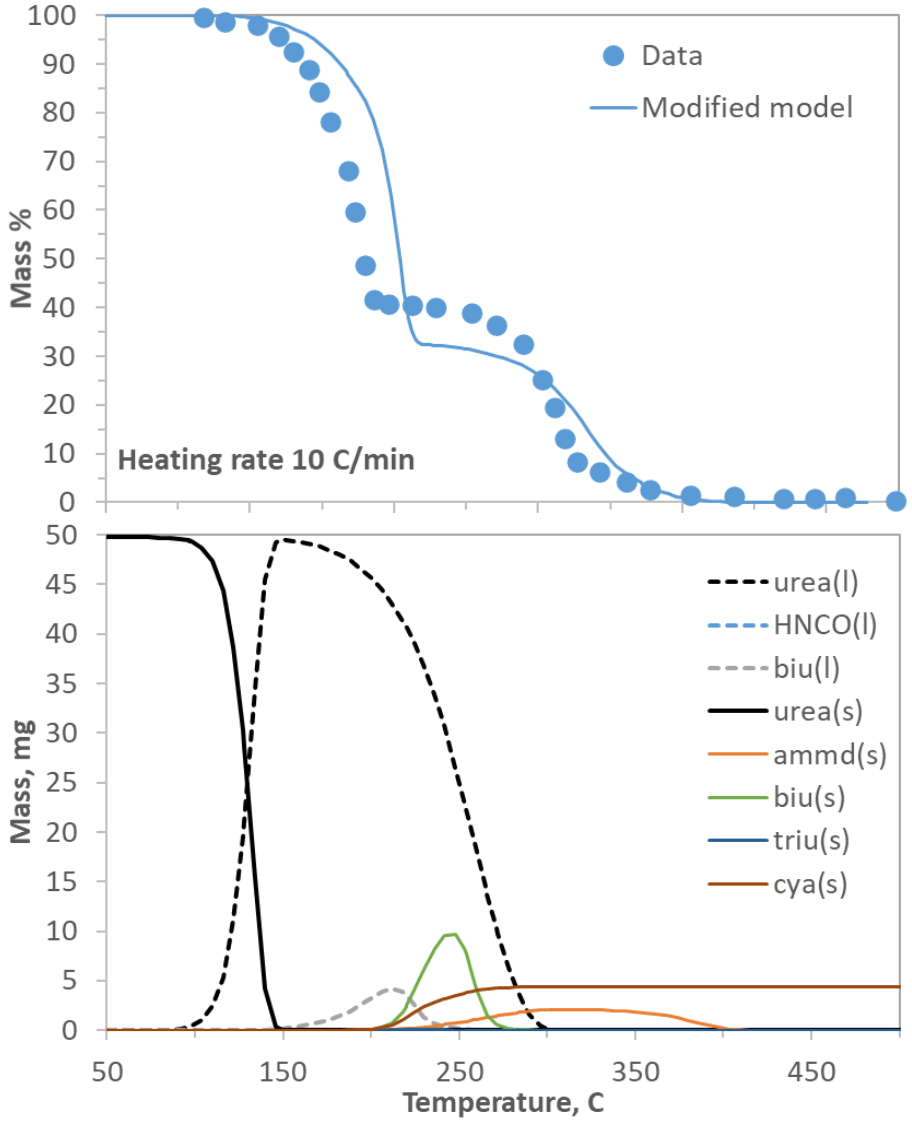
Chemkin kinetics input files

```
MATERIAL/UreaSolution/

BULK/ ureaLiquid/ LIQUID
     urea(l)
     HNCO(l) !Isocynic acid
     biu(l)  !Biurate liquid

BULK/ urea_s/           !Solid phase
     urea(s)  /1.32/    !Density in g/cm3
     ammd(s)  /1.573/   !Ammelide
     biu(s)   /1.47/    !Biurate
     triu(s)  /1.547/   !Triurate
     cya(s)   /2.50/    !Cyunaric acid

LIQPROPERTIES ALL
! Enthalpy, en
! Other proper
! Some propert
!   Use consta
!
urea(l)
 CriticalPrope
 AcentricFac=0
 RefLiqEnthalp
 RefLiqEntropy
```

```
REACTION    KJOUL/MOL
!!!!!!! Urea decomposition kinetics based on Brack et al. 2016 !!!!
cya(s) => 3 HNCO                                1.00e03  0.0  118.42
biu(l) => urea(l) + HNCO(l)                     1.11e20  0.0  208.23
urea(l) + HNCO(l) => biu(l)                     3.52e11  0.0   75.45
urea(l) => HNCO(l) + NH3                        2.00e04  0.0   75.45
  FORD/ urea(l)  0.7/
2 biu(l) => ammd(s) + HNCO(l) + NH3 + H2O       3.64e26  0.0  257.76
biu(l) + HNCO(l) => cya(s) + NH3                9.40e20  0.0  158.68
biu(l) + HNCO(l) => triu(s)                     1.10e15  0.0  116.97
triu(s) => cya(s) + NH3                         1.24e18  0.0  194.94
urea(l) + 2 HNCO(l) => ammd(s) + H2O            1.27e20  0.0  110.40
biu(l) => biu(s)                                8.20e26  0.0  271.50
biu(s) => biu(l)                                3.16e09  0.0  122.00
biu(s) => 2 HNCO + NH3                          5.63e24  0.0  266.38
urea(s) => urea(l)                              1.00e15  1.5  160.00
ammd(s) => ammd(g)                              1.00e14  0.0  201.67

HNCO(l)=HNCO    1.0  0.0  0.
  VLE/ HENRY 1 26. -4089.26  298.15/
  UNITS/MOLAR_ATM/
```

Simulation results compare well with experimental observations

- Reduction in mass matches data
  - Forming gas-phase products
- Simulation provides more details:
  - Urea solid-to-liquid phase transition
  - Solid and liquid components vs. Temperature

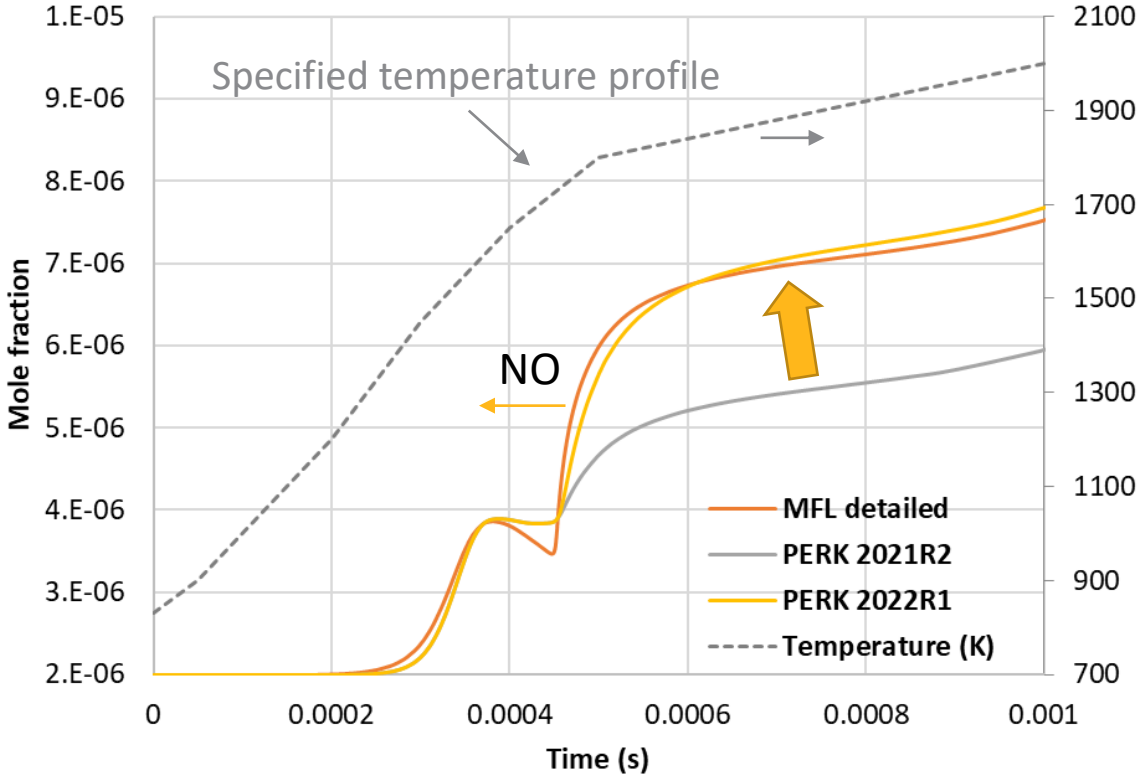


Dashed lines = Liquids
Solid lines = Solids

Improved NO_x predictions using Ansys MFL PERK* models

- PERK mechanisms are small (~30-50 species)
  - Targeted for use in large CFD models
- NO_x kinetics were updated for all PERK mechanisms included in the MFL
  - Added pathways with HNO, amino radicals (NH_2)
  - Updated N_2O reactions
- Predictions of NO_2 now agree well with the MFL full, detailed mechanisms

Chemkin-Pro prediction of NO for gas-turbine combustor conditions



* MFL = Model Fuel Library
PERK = Pseudo Elementary Reaction Kinetics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