



Parameter Estimation in gPROMS Using Aspen Properties

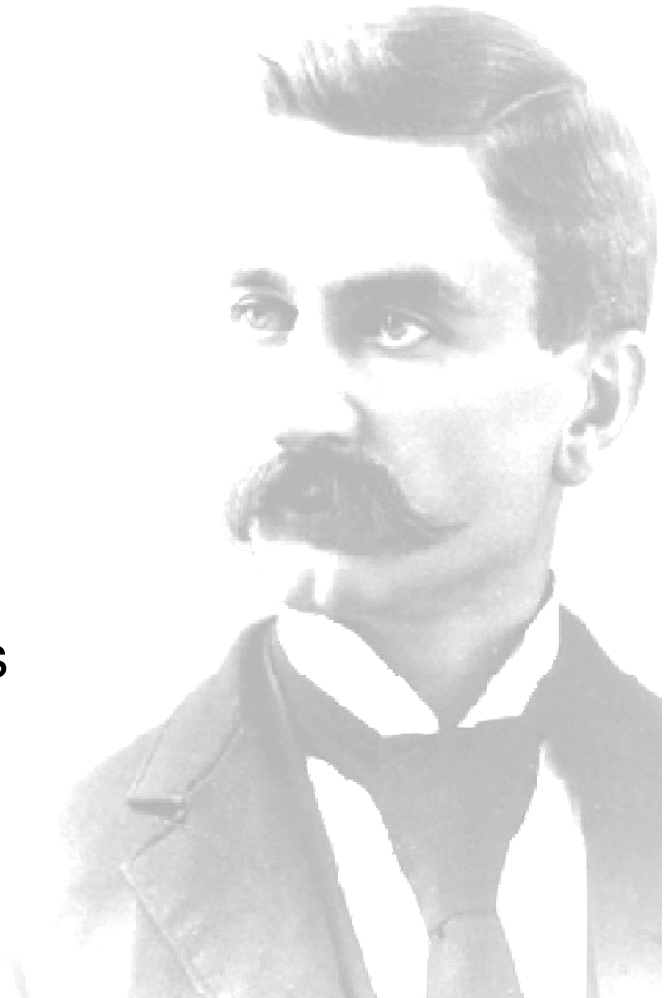
User Experiences

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About Dow ...

- A science and technology leader with annual sales of \$46 billion (2006)
- Founded in 1897 by Herbert H. Dow in Midland, Michigan
- Providing innovative chemical, plastic, and agricultural products in 175 countries
- 165 manufacturing sites in 37 countries
- Employs approximately 42,000 people globally





Outline

- Project background
- Issues
- Workarounds



The purpose of this study is to characterize reaction kinetics



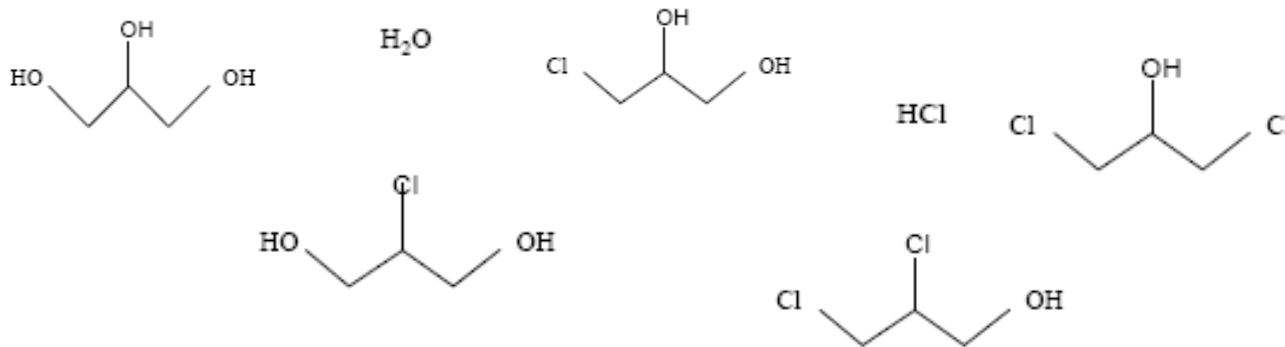
10 equilibrium reactions

40 undetermined reaction rate & Arrhenius constants



The main components are hydrochloric acid, water, glycerin, monochlorohydrin, and dichlorohydrin.

- Complex, electrolyte system
- Contains all the “cats and dogs” you’d find in a real industrial process

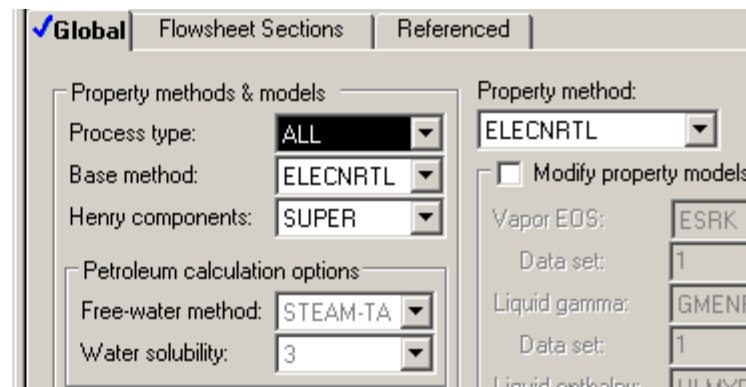
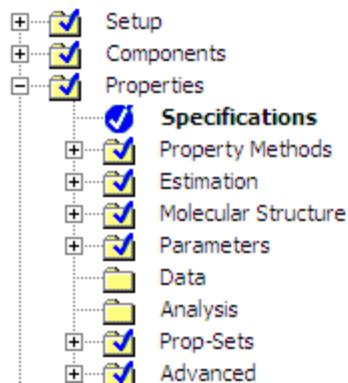


- Many intermediate/trace components



The component list includes over 70 components!

- Property package a collaborative effort between R&D and engineering
- Includes ionic and nonionic species





We use the ElecNRTL property method in Aspen Plus

- Phase equilibrium

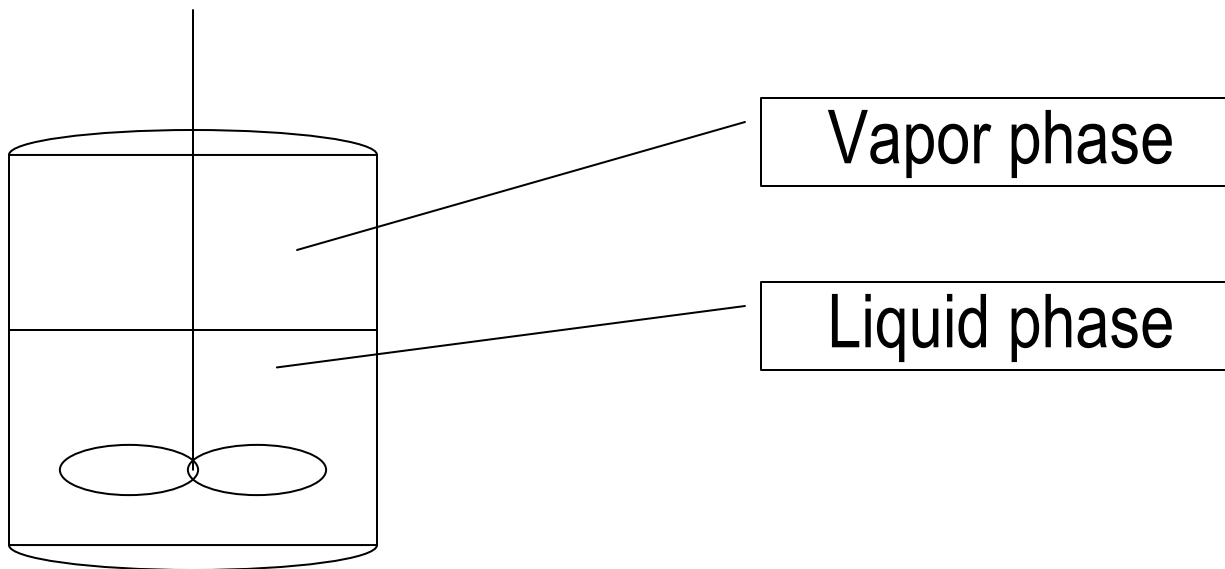
- Ion chemistry

= one of the most complex physical property packages out there!



20 batch reaction experiments

Thermodynamics characterized by physical property package





Challenge:
Develop kinetic parameter estimator

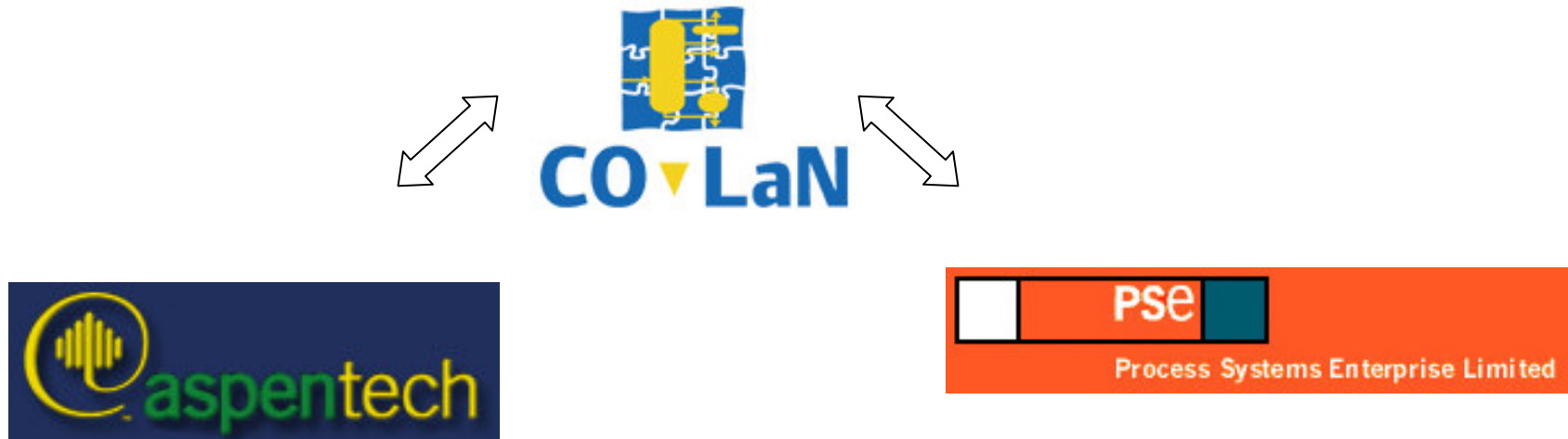
- Simultaneously fits 40 parameters
- Simulates 20 batch reactions that are vapor-liquid
- Uses Aspen Properties ElecNRTL package that has a component list that has >70 components

...and **estimator must run in a maximum CPU time of a few hours!**



We combined the fast numerical engine from gPROMS with the robust physical property package from Aspen Technology

gPROMS has a fast integrator and robust maximum likelihood parameter estimator





We modeled the batch reactor as a liquid-vapor stirred tank

$$\frac{dn_i^{VAP}}{dt} = F_i^{IN} + k^{MT} (x_i \gamma_i P_i^{sat} - y_i \phi_i P)$$

$$\frac{dn_i^{liq}}{dt} = r_i V^{LIQ} - k^{MT} (x_i \gamma_i P_i^{sat} - y_i \phi_i P)$$

The rate-based approach is easier to initialize in a dynamic simulator



The property requirements are:

- Molecular weight
- Liquid
 - Liquid mass density
 - Liquid-phase activity coefficient
- Vapor
 - Vapor molar volume
 - Vapor-phase fugacity coefficient



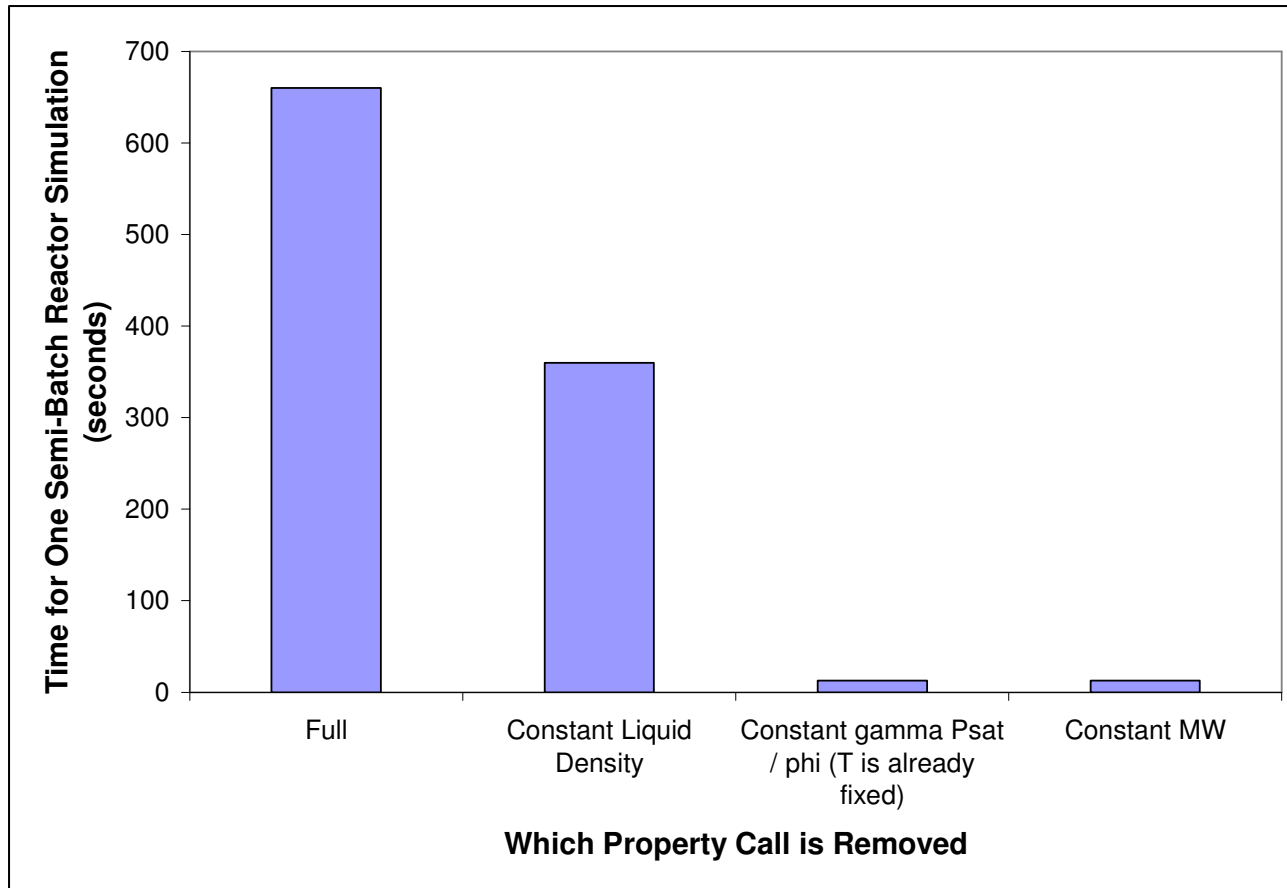
We compared the execution times of a single batch reactor experiment

We ran four cases:

- All needed property calls
 - » Molecular weight, liquid density, saturation pressures, fugacity coefficients, activity coefficients
- Removed call to liquid density
- Removed call to K-values (saturation pressures, fugacity coefficient, activity coefficients)
- Removed call to molecular weight



We found that property calls took an enormous amount of time





Observations

- Simulating a single experiment once takes longer than 10 minutes – this is not acceptable for estimating 40 parameters with 20 batch experiments (**estimation time > 1 week**)
- Simulating a single experiment once without property calls takes about 13 seconds

SPEEDUP OF 50X



How do we get speedup but still leverage physical properties package?

- Create an **empirical emulator**, i.e., translate the theoretical functions into simpler empirical ones

- We can leverage **genetic programming (GP)** technology developed in Dow





What does GP do?

- Given a set of inputs and outputs, it:
 - Constructs a series of **analytical, nonlinear equations** with **varying levels of complexity**
 - These equations use **different combinations of input variables**
 - Gives us Pareto optimal, analytical, nonlinear equations that **best fit the data**
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What do we do?

- Construct γ/ϕ vs. T, P, x data using ElecNRTL
 - Ranges of inputs given by experimental measurements

- Create a model of the data using GP

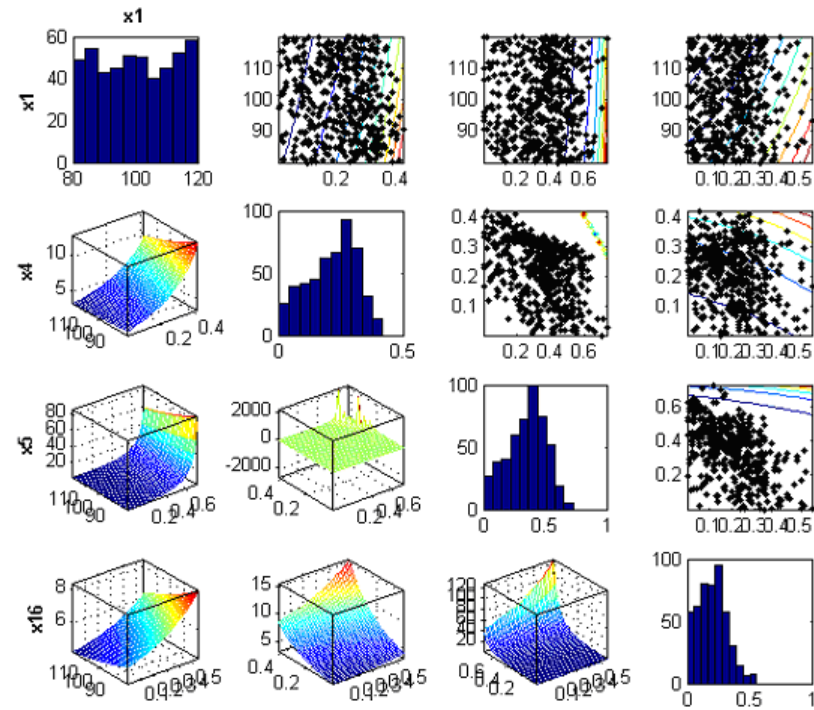
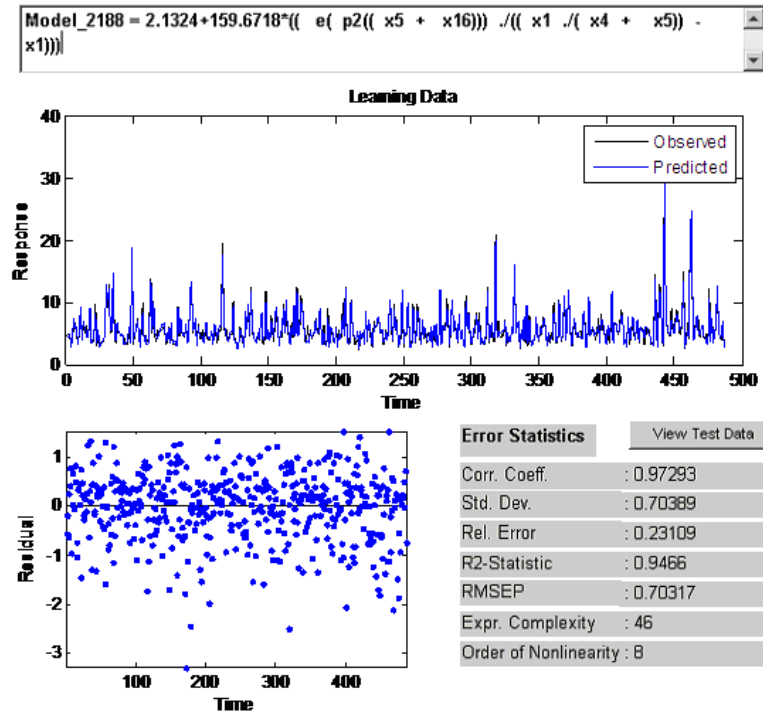


Use Aspen OSE workbook to automagically do 600 flash calculations (inputs randomly generated in Excel)

Name	Value
1.FLOW	6.48E-03
1.FLOW	1.74E-01
1.FLOW	0.001668605
1.FLOW	8.52E-03
1.FLOW	0.439807583
1.FLOW	1.02E-03
1.FLOW	3.25E-05
1.FLOW	5.48E-03
1.FLOW	1.70E-04
1.FLOW	1.59E-02
1.FLOW	0.406623225
1.FLOW	8.00E-03
1.FLOW	4.93E-03
1.FLOW	0.691868598
ASDF_TEMP	109.7043401
ASDF PRES	7.956661169



Create optimal nonlinear functions that fit the data





Models are quite good, with R² values greater than 0.9

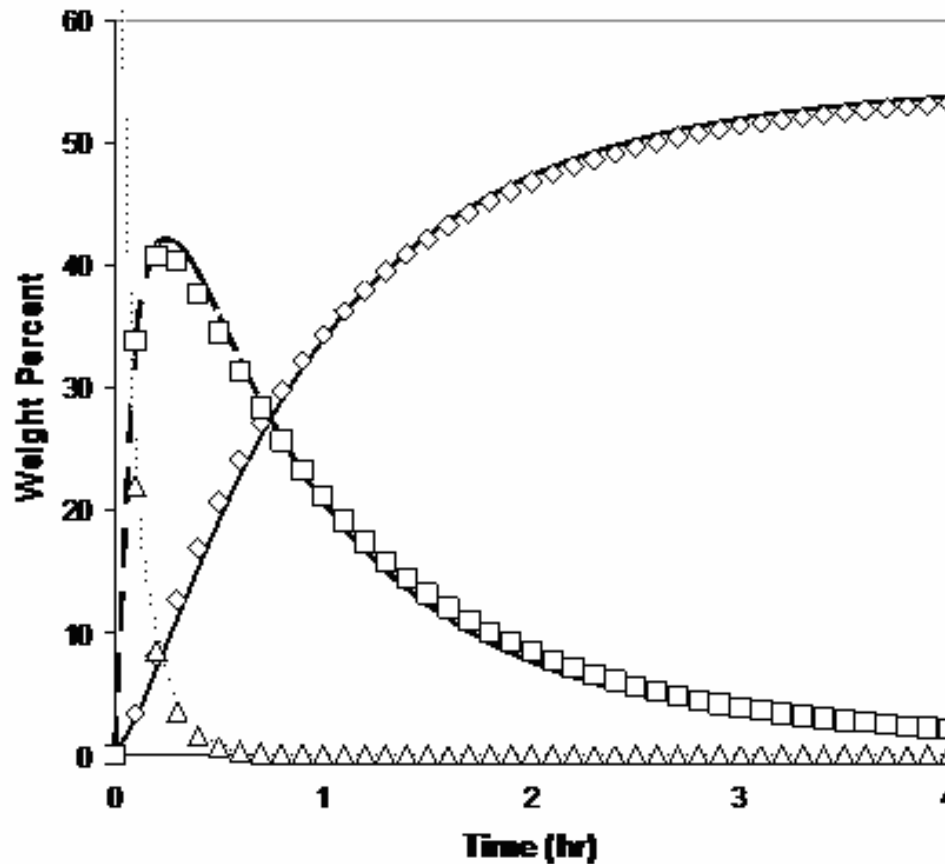
$$\frac{\gamma}{\phi}(a) = 2.1324 + 159.6718 \frac{\exp((x(c) + x(d))^2)}{\left(\frac{T}{x(b) + x(c)} - T \right)}$$

$$\frac{\gamma}{\phi}(b) = 0.0033029 + 2.116x(b)^{3.6535} (\exp(x(e)))^{3.3325}$$

Develop K-value models (function of x and T) for key volatile components



Simulation results using ElecNRTL and GP-derived models are virtually the same





Conclusions

- Calling Aspen properties through the CAPE-OPEN interface is slow for large industrial electrolyte systems
- Too slow to solve a very large kinetic parameter estimation problem
- Worked around by encapsulating the physical properties package in an empirical emulator



Suggestion for Improvement

- Employ some kind of component list manager
 - Useful when some components in the component list are not used
 - Unused components left in an equation-oriented model greatly slow the simulation

