THERMODYNAMIC PROPERTIES IN THE SERVICE OF PROCESS SIMULATORS

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OBJECTIVES

Illustrate/Distinguish Service & Advice Roles of Properties in Simulation & Design

Suggest How to Make Properties in Service

Efficient

Fast, minimum input, automated

Flexible

Usable in several process applications

Robust

Results reliable for multiple problems

WHY PROPERTIES MODELING?

Competitive Manufacturing Requires

New/Replacement Processes, Products

Economic Efficiency in Time, Effort, Investment

Process Simulators

Allow maximum exploration/optimization

Solve equipment units with *Process Models* of

Constraint equations (Material/Energy/Fugacity)

Thermo Variables are *Conceptuals* ($h, \phi_i, \gamma_i, \ldots$)

Need *Data & Property Models* to relate *Conceptuals*

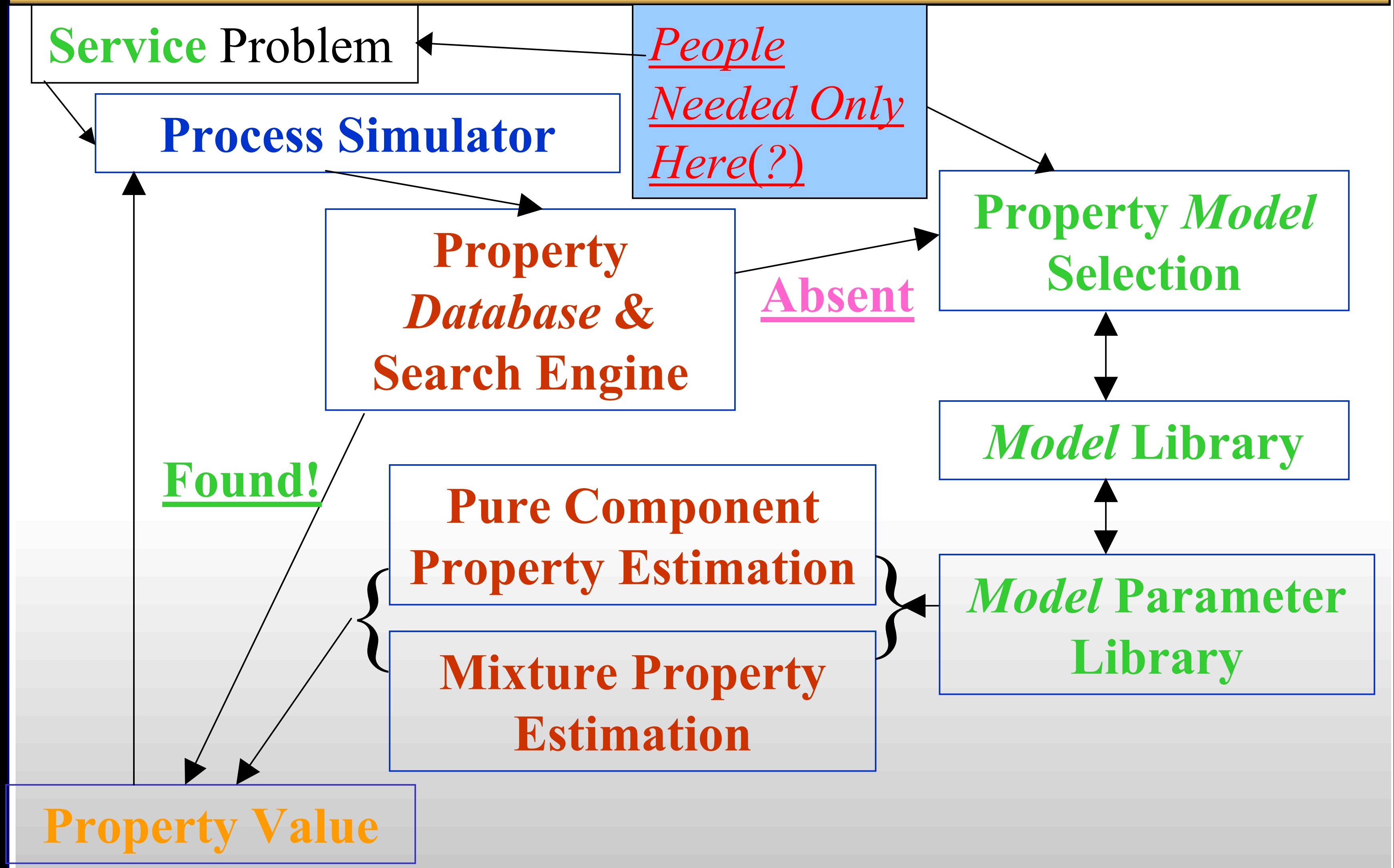
to System/Substance *Measurables* (T, P, $\{x\}, \ldots$)

USES OF PROPERTY MODELS

Have *Process* simulation & *System* design problems

Simulation (Service)		Design (Advice)
Simulation/Design Find Process Alternatives	Problem	Set Design Target Find System Feasibility
Fixed compounds Bounded *T*, *P*,{ *x*}	Constraints	Any compounds Unbounded *T*, *P*, {*x*}
Generalized or ***System***-Specific Models	Options	Generalized or ***Problem***-Specific Models

SERVICE TOOLS FOR PROPERTY PROBLEMS



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SERVICE CASES DEPEND UPON KNOWN INFORMATION (DATA/PARAMETERS)

Forward Problems (Service Role)

- Select Appropriate Model

How to be efficient, reliable, & accurate?

MANY MODELS

Pure Component

P^{Sat}, v^{Sat}, T_c

. . . .

EoS Models

SRK

PHC

SAFT

. . . .

Mixing Rules

vdW, G^E

. . . .

G^E Models

Wilson

UNIQUAC

Electrolyte

NRTL

. . . .

Group Methods

UNIFAC-I

ASOG

. . . .

ISSUES FOR SERVICE MODELS

Large model libraries may be needed

Increases application range

Causes model selection/validation uncertainties

Requires many data/parameters

Generalized models may be

Computationally expensive

Unnecessarily complex, especially derivatives

Efficiency/reliability improvements

Simpler models with tuned parameters
generated on-line & validated

Sensitivity analysis of parameters

EXAMPLE: CO_2 & ACRYLIC ACID

VLE separation feasibility & conditions?

Limited pure component, binary data available

Model selection suggests EoS, specifically SAFT

Corresponding states form, no binary parameter

But takes large computational resources

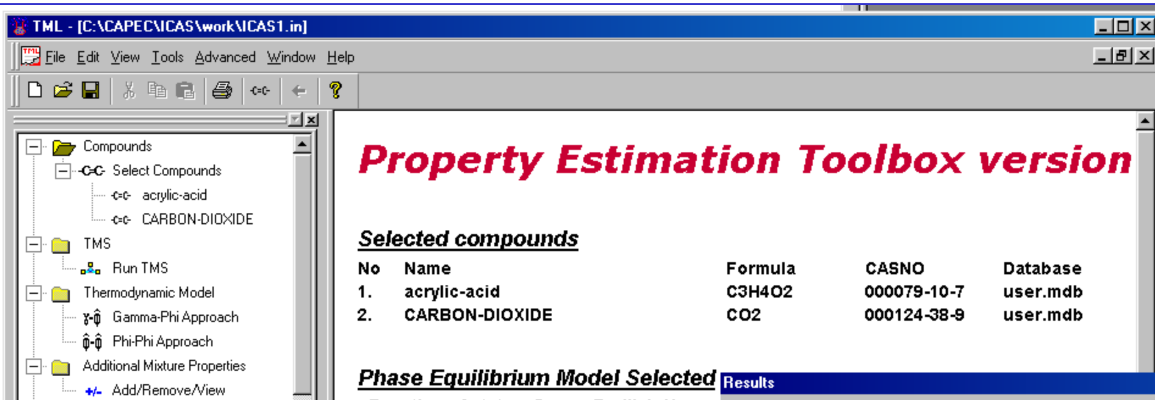
Questions:

Use directly or to set up simpler model?

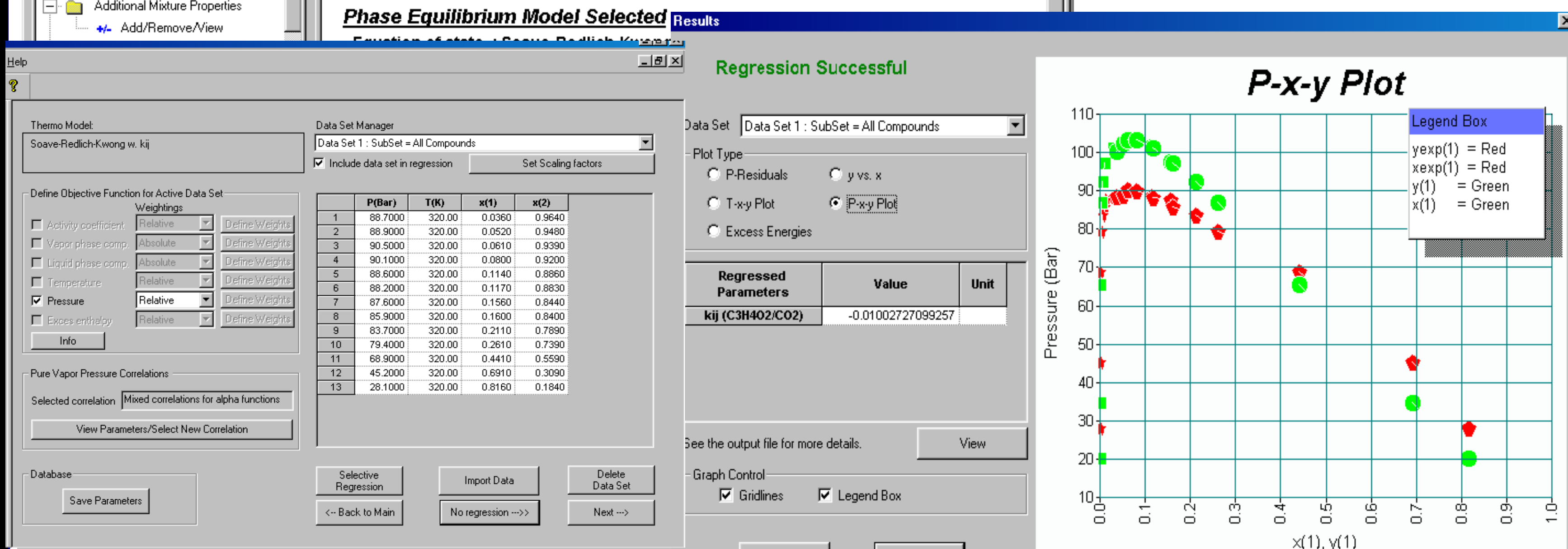
What is efficient procedure to generate model?

SAFT REFERENCE; SRK APPLICATION

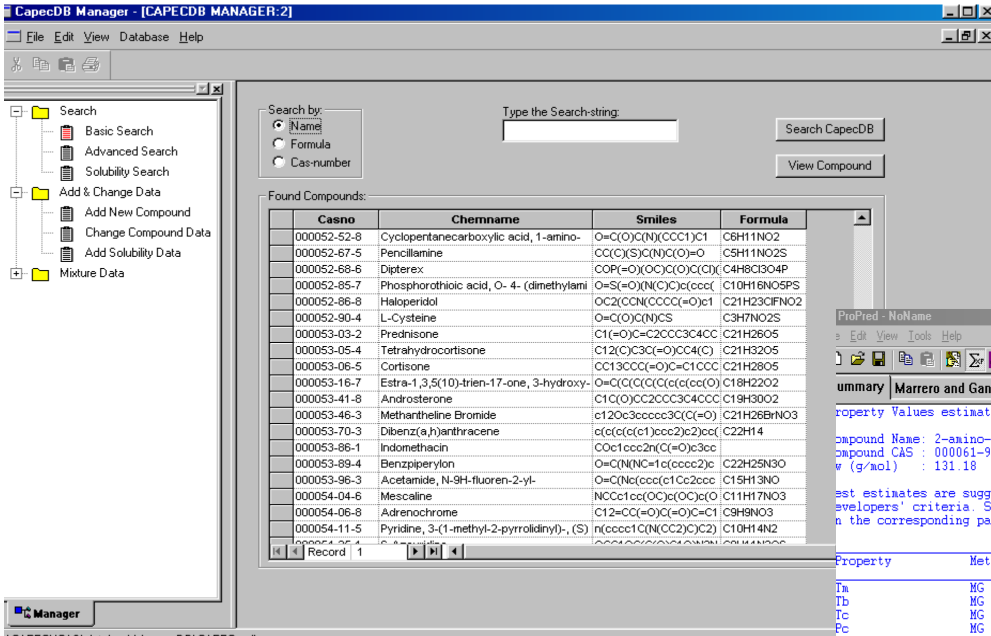
VLE data from SAFT, use to fit SRK k_{12} – fast/reliable

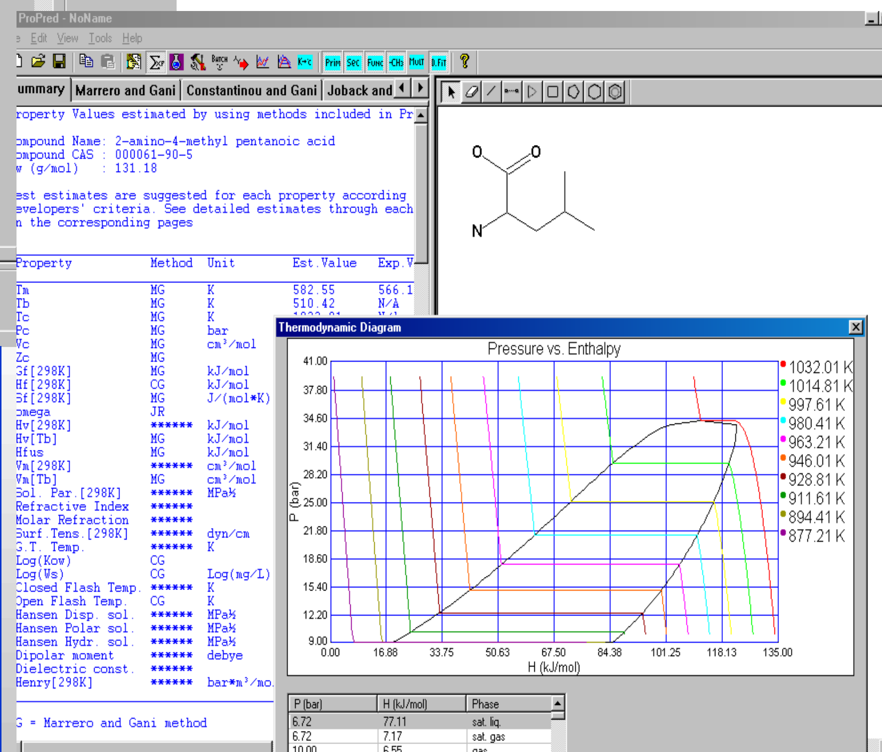


Values passed to Database, Parameter library for use in other applications



CASE: PARAMETERS UNKNOWN



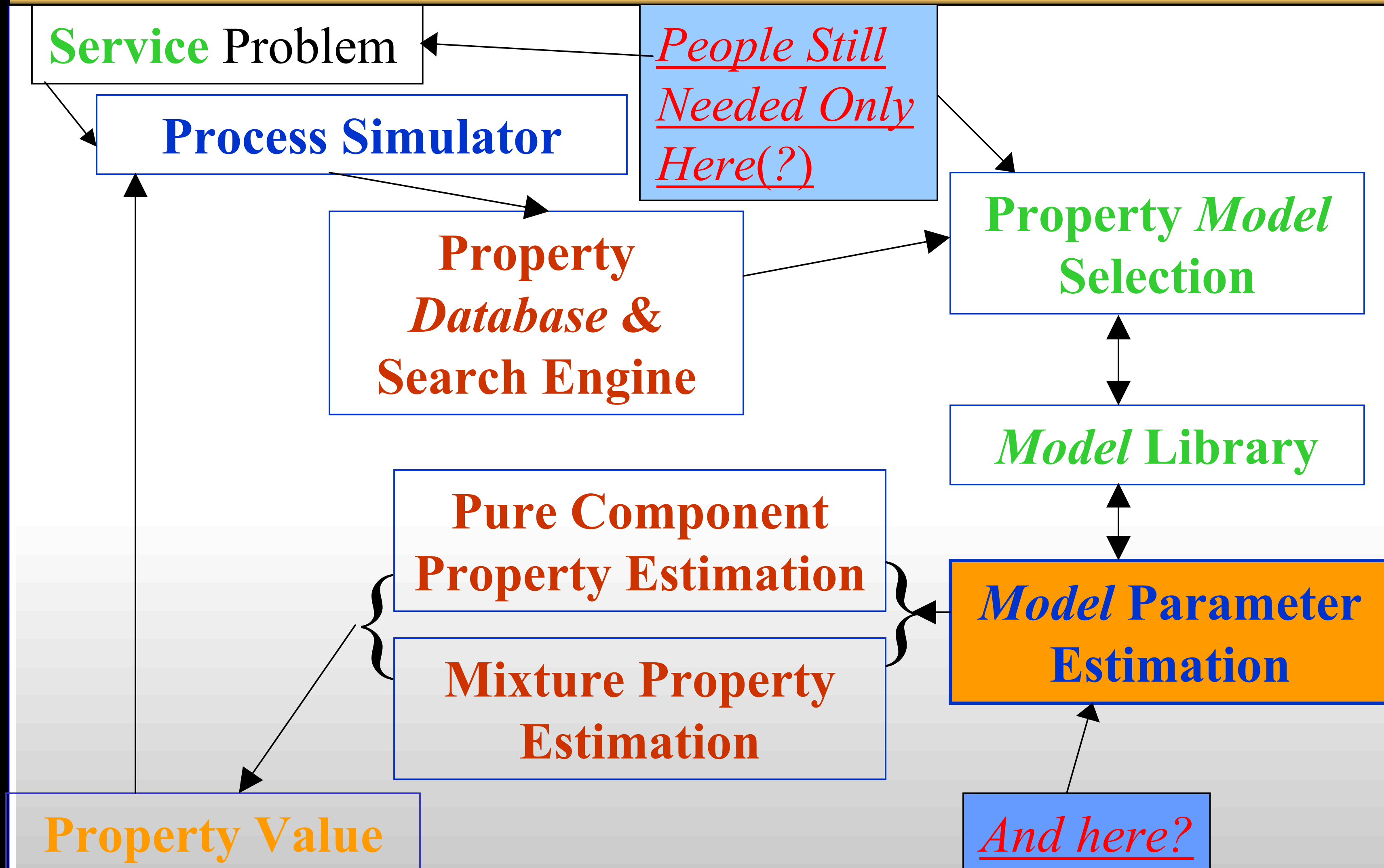


Though much information available, no data nor model parameters for case of interest

Must *estimate* parameters

Should be efficient!

SERVICE TOOLS FOR PROPERTY PROBLEMS



EXAMPLE: H_2O/ KCl/EtOH/Ampicillin

Effect of ethanol on solubility of ampicillin

Limited pure/binary/ternary SLE data available

Speciation identified

Model selection suggests Electrolyte NRTL

Most binary parameters known

Questions:

Procedure of greatest efficiency?

Minimum parameters to be fitted?

SYSTEM DEFINITION & PROPERTIES

Comp. No.	Name	Phase	Ion type	Salt type	Other spec.
1	H2O	Vapor / solvent	-		
2	Ampicillin	Liquid / solid	Dipole	Organic	
3	KCl	Solid	-	Inorganic	
4	EtOH	Vapor / solvent	-		
5	H+	Liquid	Cation		
6	OH-	Liquid	Anion		
7	Ampicillin+	Liquid	Cation		
8	Ampicillin-	Liquid	Anion		
9	K+	Liquid	Cation		
10	Cl-	Liquid	Anion		

	Properties name	SLE	Models
Pure Properties	Born radius	*	Data
	Density	*	Racket
	Dielectric constant	*	Correlation
Mixture Properties	Activity coefficient	*	electrolyte NRTL
	Solubility	*	Solubility product

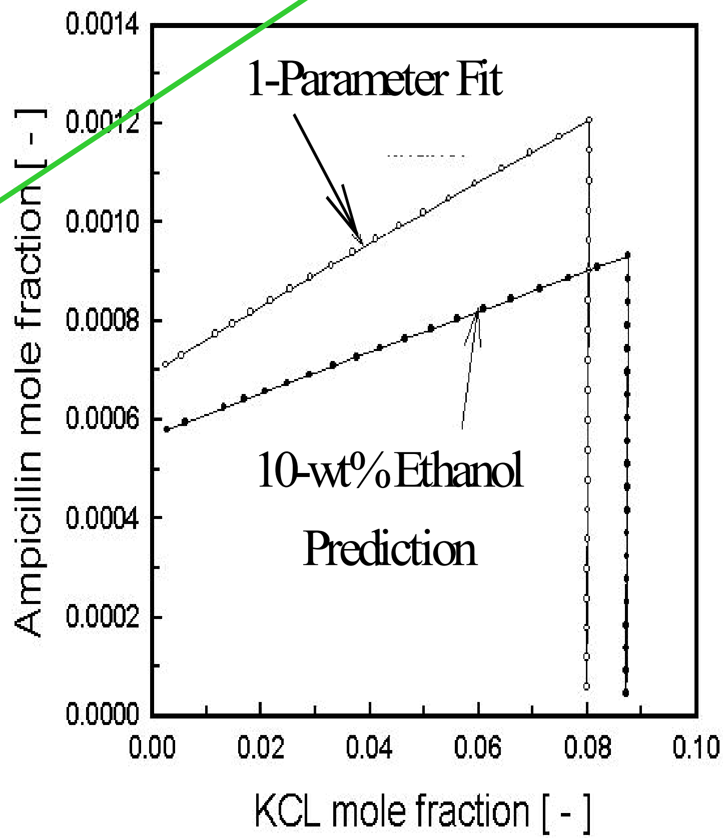
FIT SENSITIVE BINARY PARAMETER(S)

Of 15 parameters in Electrolyte-NRTL H_2O/KCl model,
Ampicillin ternary sensitive to only1;
Minimizes fitting effort

H2O					
(H, OH)					
(H, Cl)					
(K, OH)					
(K, Cl)					
	H2O	(H, OH)	(H, Cl)	(K, OH)	(K, Cl)

H2O					
(H, OH)					
(H, Cl)					
(K, OH)					
(K, Cl)	*				
	H2O	(H, OH)	(H, Cl)	(K, OH)	(K, Cl)

Fitted



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DETERMINATION OF PARAMETER SENSITIVITY

Evaluate sensitivities from

$$\frac{dF}{d\tau_k} = \sum_{j=1}^{NEXP} \frac{dF_j}{d\tau_k} = \sum_{j=1}^{NEXP} \frac{d\left(\sum_{i=1}^{Np} \left| (p_i^{cal} - p_i^{exp}) / p_i^{exp} \right| \right)_j}{d\tau_k}$$

F = function, p = property value, τ = parameter

Fit only parameters *k* with large $dF/d\tau_k$

SERVICE DIFFERS FROM ADVICE IN TARGET/KNOWN INFORMATION

Forward Problems
(Service Role)

- Select Appropriate Model
- Tune/Re-estimate Model Form/Parameters
- Simplify Model When Possible with Accuracy
- Compute Properties & Derivatives

Automate?

Reverse Problems
(Advice Role)

- Select Appropriate Properties & Models
- Estimate Model Parameters
- Compute Properties
- Validate (Data, Theory, Microsimulation)
- Select “Best” System

ISSUES FOR ADVICE MODELS

Must use general models for multiple properties

- Data/parameters often unavailable
- Unknown accuracy/reliability

Efficiency improved with

- Strategy for obtaining information
  - Experiment/Theory/Microsimulation
- On-line model generation/validation

Reliability better via sensitivity-analysis/validation

Some, but not all steps same as service role

MODEL GENERATORS MAY NOT MATCH SERVICE OR ADVICE USER NEEDS

Provide limited testing

- Systems – Known substances
- Properties – Standard EoS, G^E
- Weak Validation – Consistency, limits, multiproperty

Give inefficient formulation

- Theoretical basis without computational strategy
- Excessive # of parameters
- Complex expressions, especially derivatives

Result often correlation with limited prediction

FUTURE PROSPECTS

Properties strategy separate from process simulation?

Advice problem does process once with target

then iteratively finds substances/states

Algorithms for advanced systems need to treat

Simultaneous reactions/mass & heat transfer

Education of generators/users on roles of

Properties & models

Products of model generators

Implementation by model users

CONCLUSIONS

Service & Advice roles exist for properties

Differences in objective, model usage & input

Careful strategies can meet goals to

Maximize productivity

Reduce uncertainty

Elucidate sensitivity

Allow "<u>machines to work & people to think</u>"