THERMODYNAMICS II: MODELING

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Objectives of Presentation

Brief overview of thermodynamic modeling approaches
- Basics
- Strategies

Assumptions about audience
- Familiar with chemical processing
- More interested in fundamentals than details

Goals of Modeling I.

Want "good enough" values of "practical" process designs, product behaviors

How **Complicated**?

"As Simple as Possible, But No Simpler"

Accuracy/Information **will vary effort**

- always just meet your objectives

How **Generalized**?

Seek Consistency, But Know **Sensitivities**

Must Optimize

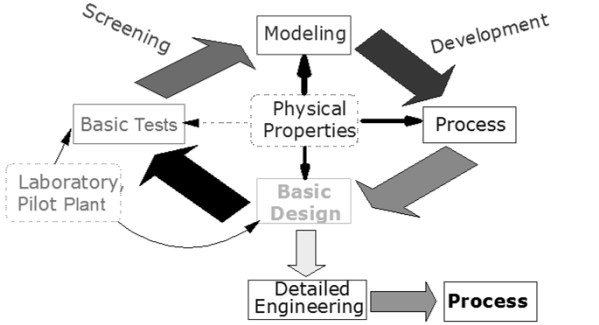
Accuracy/reliability vs. "convenience"

Goals of Modeling II.

How to economize? Minimize:

- **Measurement**
  - Data *Essential* - Might Be Best for Everything But Too Much to Do & Too Costly
- **Decisions/Specialization**
  - Apply Concepts/Relations to Wide *Range* of Properties/Conditions/Processes
- **Computer Resources**
  - Calculation Time & Memory

Properties Central to Process Development Cycle

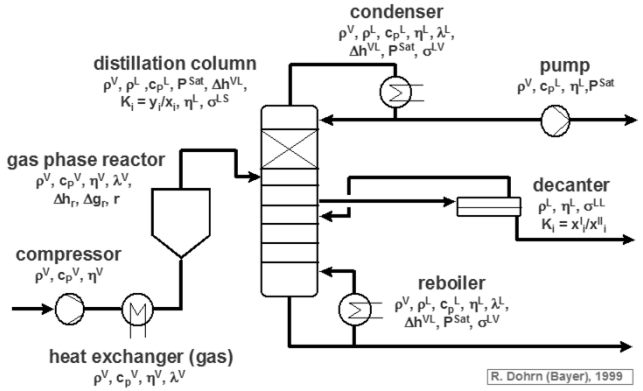


Typical turnaround: 1-3 years

MITSUBISHI CHEMICAL

Adapted From T. Ishikawa, 1999

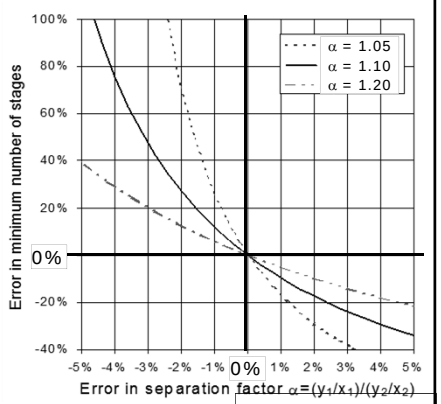
EXAMPLE PROPERTIES NEEDS



Same properties in different units - generalize

Physical Property Sensitivity I.

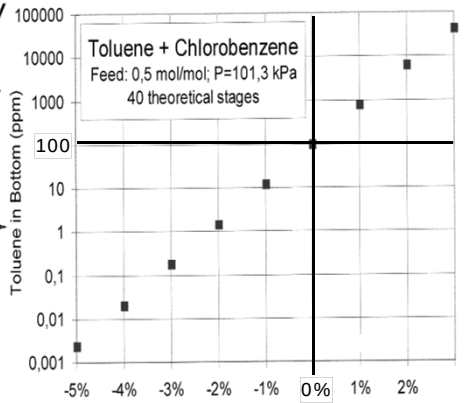
Number of stages in distillation badly in error when wrong by few % if $\alpha \sim 1$



R. Dohrn (Bayer), 1999

Physical Property Sensitivity II.

Product purity can depend on property input - ±1% in T_c changes x_{BT} by order of magnitude!



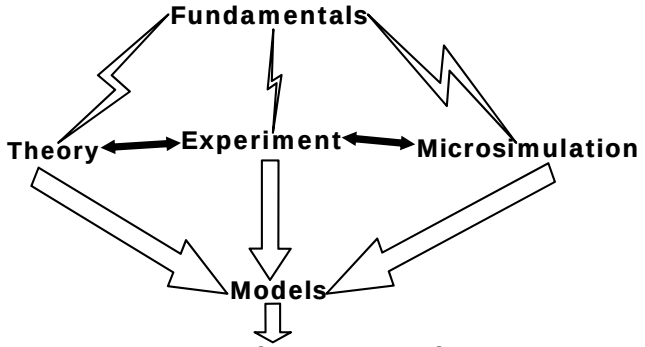
R. Dohrn (Bayer), 1999

Modeling Allows Asking "What If?"

With reliable property models, can

- Think *differently*, try *innovative* approaches
  - Explore broadest context of problems
  - Find consequences of errors on *everything*
  - See requirements to get quantitative description
    - # parameters, amount of data, computation resources?
- Find out what variables influence & inform
  - Make use of derivatives (sign tells direction)
    - Entropy always increases with volume $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V > 0$
  - Clever single/collected properties simplify relations
    - "Think density, not pressure"
    - Use dimensionless variables
      - Careful with T/T_c, etc., Corresponding States

Structure to Organize Applications



Structure Uses Bridges from Fundamentals to Modeling

Experiment -

- Only direct measure of Nature's behavior
- But use of results limited to *correlations*

Theory

- Gives *approximate* results for *idealized* systems
- Collects variables in parametrizable ways

Microsimulation (*e.g.*, Quantum, MC, MD)

- Is essentially *exact* molecular physics/chemistry
  - but must use *approximate* microinteractions

Models

- Capture essence of behavior in reliable math form

Strategy: Pushing Ahead

Contemporary research *combines* tools

Theory suggests simulations & experiment

- Experiment validates simulations
- Simulations predict responses to changes
- Extensions of theory organize/codify models
- Models describe structure & behavior of system

Modeling Basics I.

Always True Macroscopic **Fundamentals**

Macroscopic **Process / Product** Descriptions

- Thermostatic **States**
  - ► Stable (Equilibrium), Metastable, Nonequilibrium
- Thermostatic **Properties**
  - ► Measurables (T, P, $\{x\}$, ρ, . . .)
  - ► Conceptuals (Energy, Entropy, Fugacity, . . .)
- Tendencies for **Change**
  - ► Heat, Mass & Momentum Transfer
  - ► Reaction

Modeling Basics II.

Process Independent: Thermodynamic

Initial ➡ Equilibrium

Finite Changes of Properties, Species

Process Dependent: Pseudothermodynamic

Initial ➡ **Transition State** ➡ Equilibrium

Process Evolution: Transport

Heat, Mass & Momentum Transfer, Kinetics

Differential Size/Time Changes of State/Properties

Modeling Basics III. Mathematical Implementation

Sometimes True Property Models Relate

Conceptuals to Measurables using Parameters

Results Depend on Decisions of

Expansion and Parameterization + Values,

e.g.,VLE:

Basic **(Always True)**

$$f_i^V = f_i^L$$

Expanded **(Rigorous)**

Approximated

$$y_i \cancel{\phi_i} P = x_i \gamma_i \cancel{\phi_i^S} P_i^S \exp\left[\int_{P_i^S}^{P} \frac{\bar{V}_i^L}{RT} dP\right]$$

Model **(Not Rigorous)**

$$y_i P = x_i \exp[A(1-x_i)^2] \exp[a_i - b_i/T]$$

Errors of **omission/commission** occur!

Some Models for Fugacities in Phase & Reaction Equilibria

- Ideal gases, fugacity = partial pressure: $f_i^{ig} = x_i P$
- Fugacity coefficient corrects for nonideality via EoS, *e.g.*,

$$\phi_i \equiv \frac{f_i}{x_i P} = \exp\left\{\int_0^P \left[\frac{\bar{V}_i(T,P,\{x\})}{RT} - \frac{1}{P}\right]_{T,x} dP\right\}$$

  - Alternative complex formula for usual EoS: $P(T,v,\{x\})$
- If EoS not adequate for both V&L or have ig vapor, choose ideal solution standard state (T; P^0,$\{x\}^0$)

$$f_i^{is}(T,P,\{x\}) = x_i f_i^0(T,P)$$

- Activity coefficient corrects for nonideality via g^E

$$\gamma_i \equiv \frac{f_i}{x_i f_i^0} = \exp\left\{\frac{\partial\{Ng^E/RT\}}{\partial N_i}\bigg|_{T,P,N_{j\neq i}}\right\}$$

  - Typically, f_i^0 set to P^S, with consistent pressure corrections
- "g^E mixing rules" for EoS parameters match set of $\{\phi_i P\}$ from EoS to set of $\{\gamma_i \phi_i^S P_i^S\}$ from g^E & $\{P^S\}$ at a condition(many ways)

Conclusions

Thermodynamic property modeling essential to describe Nature

Modeling basis from fundamentals via experiment, theory, microsimulation

Essentials are EoS, c_p^{ig}, $\Delta g_i^0{}_f$

- Augmented by g^E, P^S, *etc.*
- Many current models "good enough"
- But complex systems demand more

Success demands use of <u>all</u> tools

- Parameters from data & assumption – be strategic!
- Know uncertainties/sensitivities to error
- <u>Best effort via teams</u> that represent range of contributions & fulfill complementary roles

Some Alternative References

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