Invariants in Multi Phase Reactor Systems

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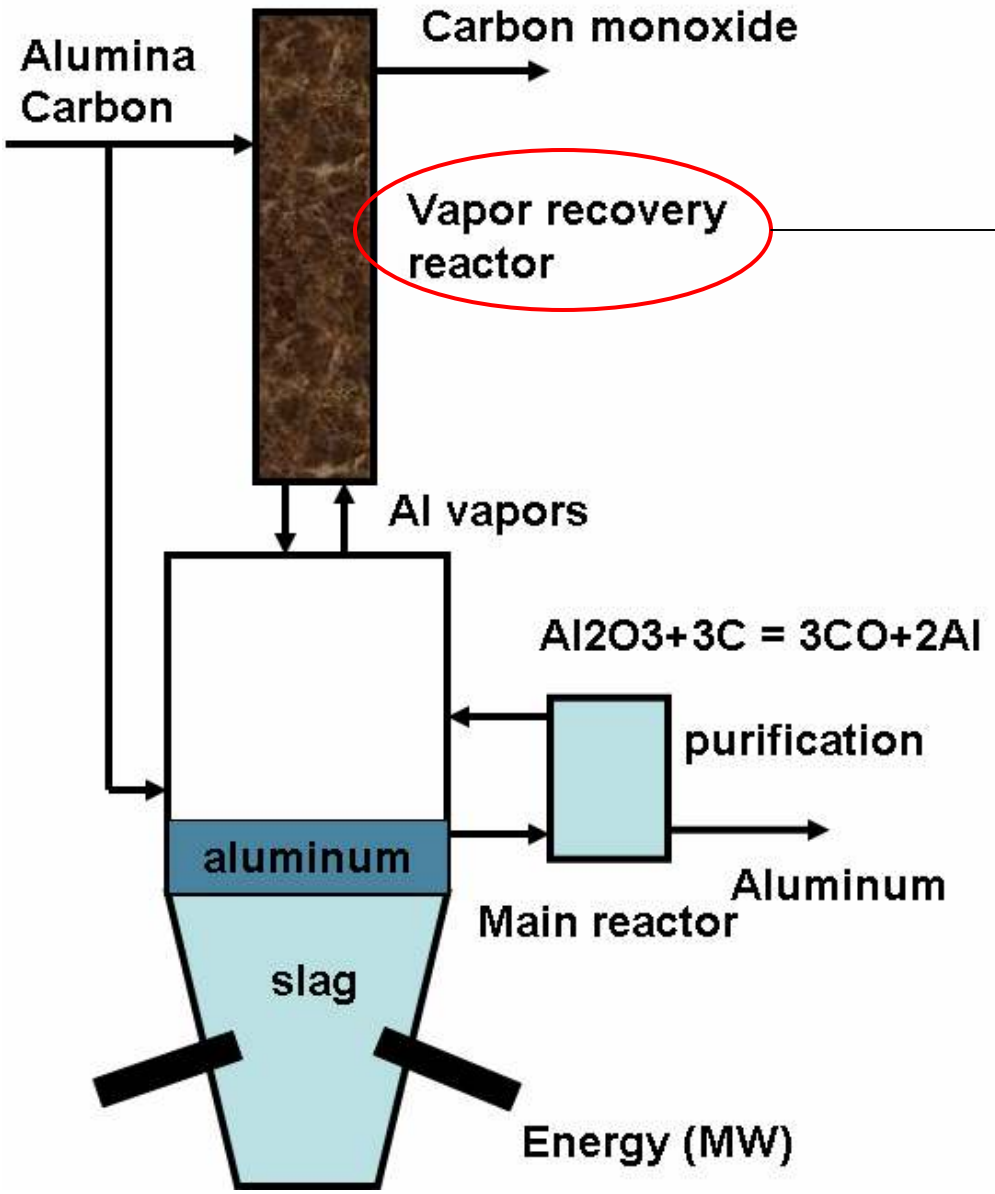
AIChE Annual Meeting
November 7th, 2007

Motivation

- Aluminum most widely used metal next only to Iron.
- Hall electrolytic process for Al production is capital and energy intensive.
- Carbothermic process is a promising alternative.
  - 30% reduction in overall cost (~1300 $/ton Al)
  - 9.8 MWh/ton compared to 13.6 MWh/ton in Hall process

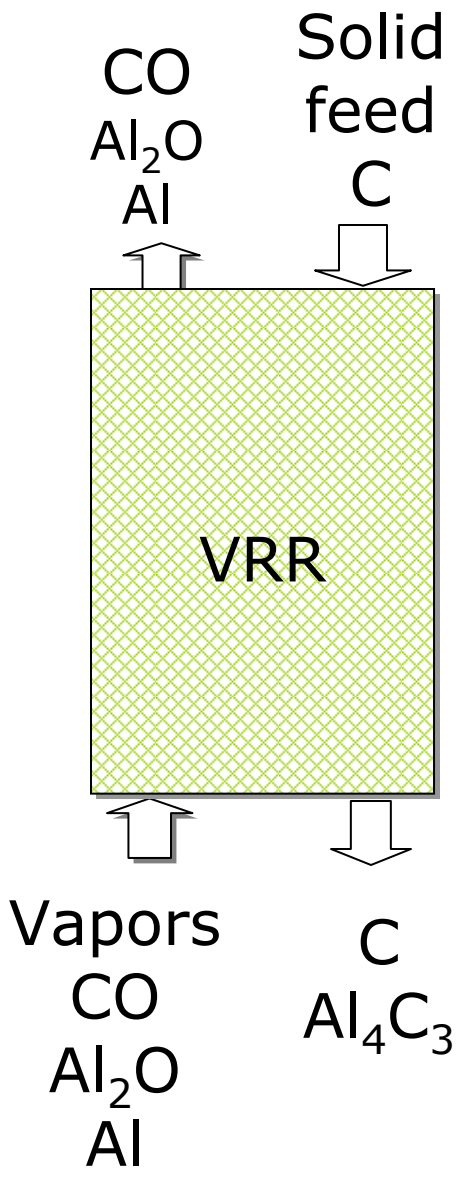
Carbothermic Aluminum Process



VRR is essential for the process to be economically feasible as aluminum in vapors could represent *25%* of the aluminum metal converted

The objective is to develop a model for the VRR that can be used process design scale up, process optimization and control

Vapor Recovery Reactor



- Countercurrent moving bed reactor
- React the gases with solid carbon at high temperatures to form carbide

$$4Al + 3C \rightarrow Al_4C_3$$

$$2Al_2O + 5C \rightarrow Al_4C_3 + 2CO$$

VRR- Modeling Premises

Compounds present

Solid: Al_4C_3 C Al_2O_3

Liquid: Slag (Al_4C_3 + Al_2O_3)

Gas: CO Al Al_2O

- Multi phase reactor with solid carbon, aluminum vapors and slag present.
- Operating temperatures are high so we assume thermodynamic equilibrium Hence we model VRR as an **equilibrium reactor** with flow of mass and energy.
- **Problem**: How do we write the balance equations with different products present depending on the temperature range and composition.
  - Moving phase boundary
  - Kinetic expressions

Element Mass Balance

- Balance equation for compounds

  Rate of Change = Flux in – Flux out + Rate of production

  Rate of production not defined for equilibrium systems as changes are instantaneous

- Balance equation for elements

  Rate of Change = Flux in – Flux out

  - Elemental balance involves only 3 equations for *Al*, *C* and *O* as compared with 9 equations for compound mass balance.
  - No reaction kinetics term involved in balance.

- Use thermodynamic mapping to calculate compound concentrations from element moles

Model Formulation

Conservation Laws

$$\frac{dU}{dt} = \sum_{j=1}^{N_c} \Delta(h_j F_j)$$

$$\frac{dE_i}{dt} = \sum_{j=1}^{N_c} e_{ij} \Delta(F_j)$$

$$\Delta(x) = x^{inflow} - x^{outflow}$$

The state of VRR is represented as

$$Z = \begin{pmatrix} U \\ V \\ E_{Al} \\ E_C \\ E_O \end{pmatrix}$$

Transport

$$F_j = v^{\alpha} A C_{\alpha j} - D_{\alpha j} A \nabla C_{\alpha j}$$

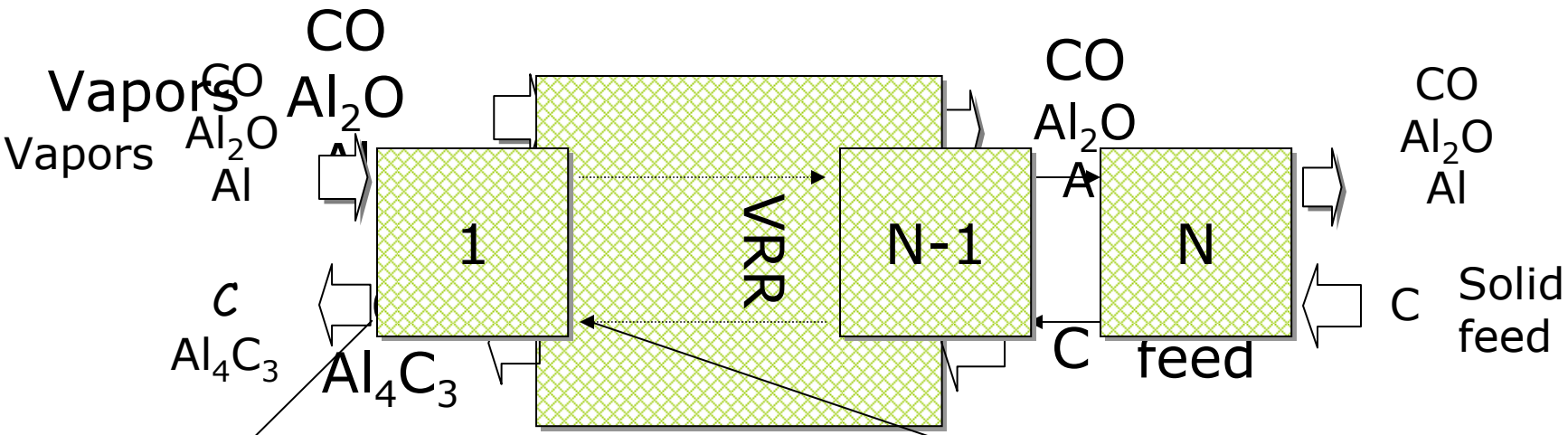
Thermodynamics

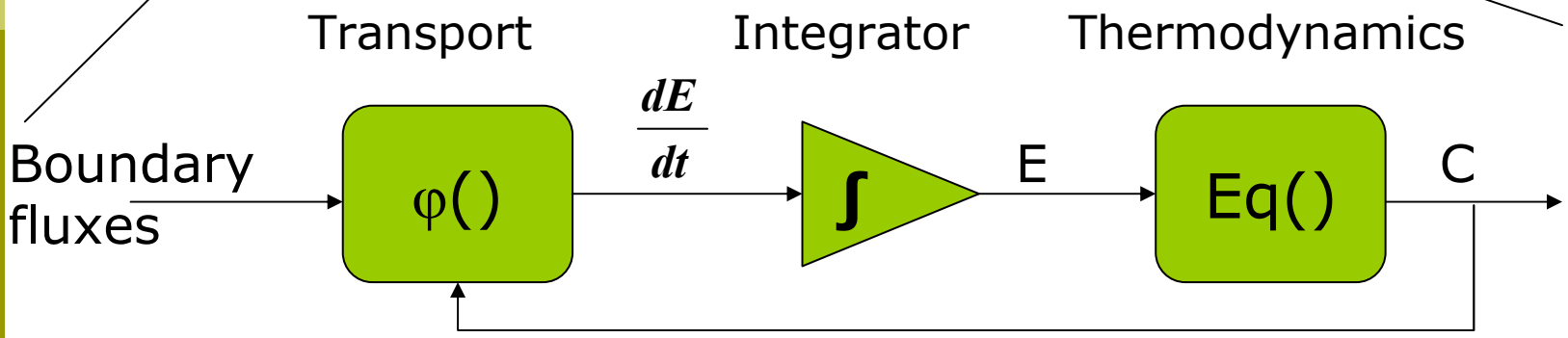
$$(T, P, C_j) = Eq(U, V, E_i)$$

Gibbs free energy minimization

Model Framework

Grid into N sub-regions or equilibrium stages





Model of an Equilibrium Stage based on Element balance

Model Simplifications

$$\frac{dE_i}{dt} = \sum_{j=1}^{N_c} e_{ij} \Delta F_j$$

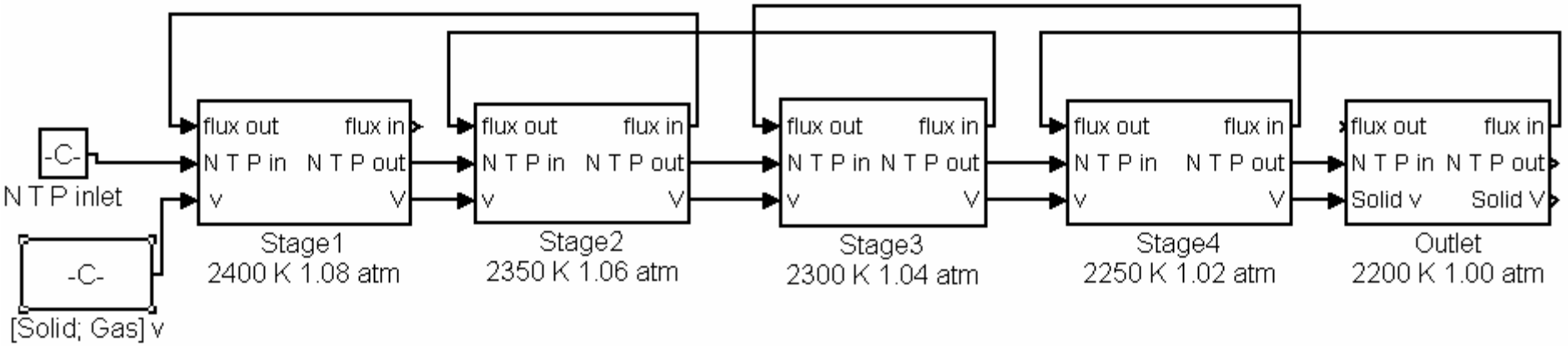
$$F_j = v^{\alpha} A C_{\alpha j}$$

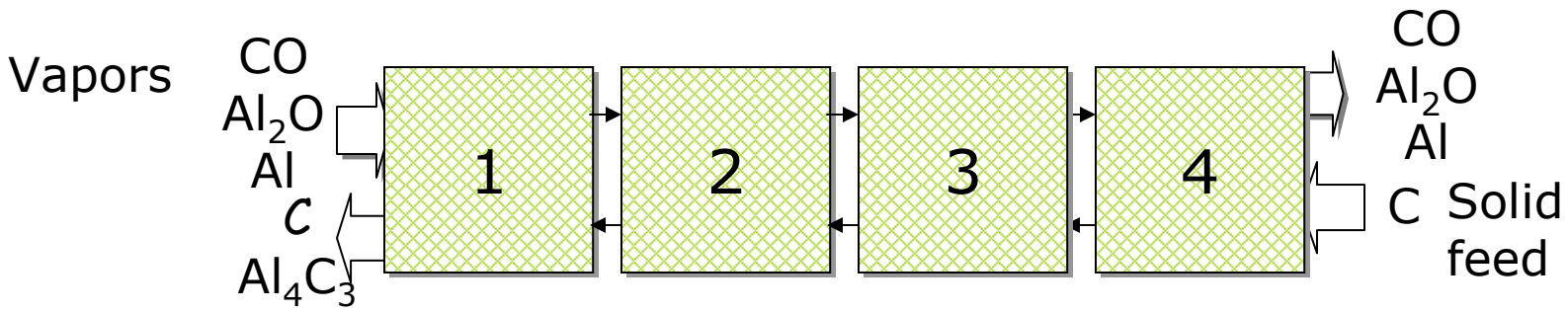
$$C_j = Eq(T, P, E_i)$$

- It was assumed that the reactor is operating isothermally. The temperature profile was assumed to be linear with 2400 K at gas inlet decreasing to 2200 K at solid inlet.
- Pressure was assumed to be 1 atm.
- The diffusive flow was neglected in the transport equations.
- The Eq function was developed based on Gibbs free energy minimization. (formulation)

Simplified 4 stage VRR model simulated in Simulink

Dynamic Simulation of VRR

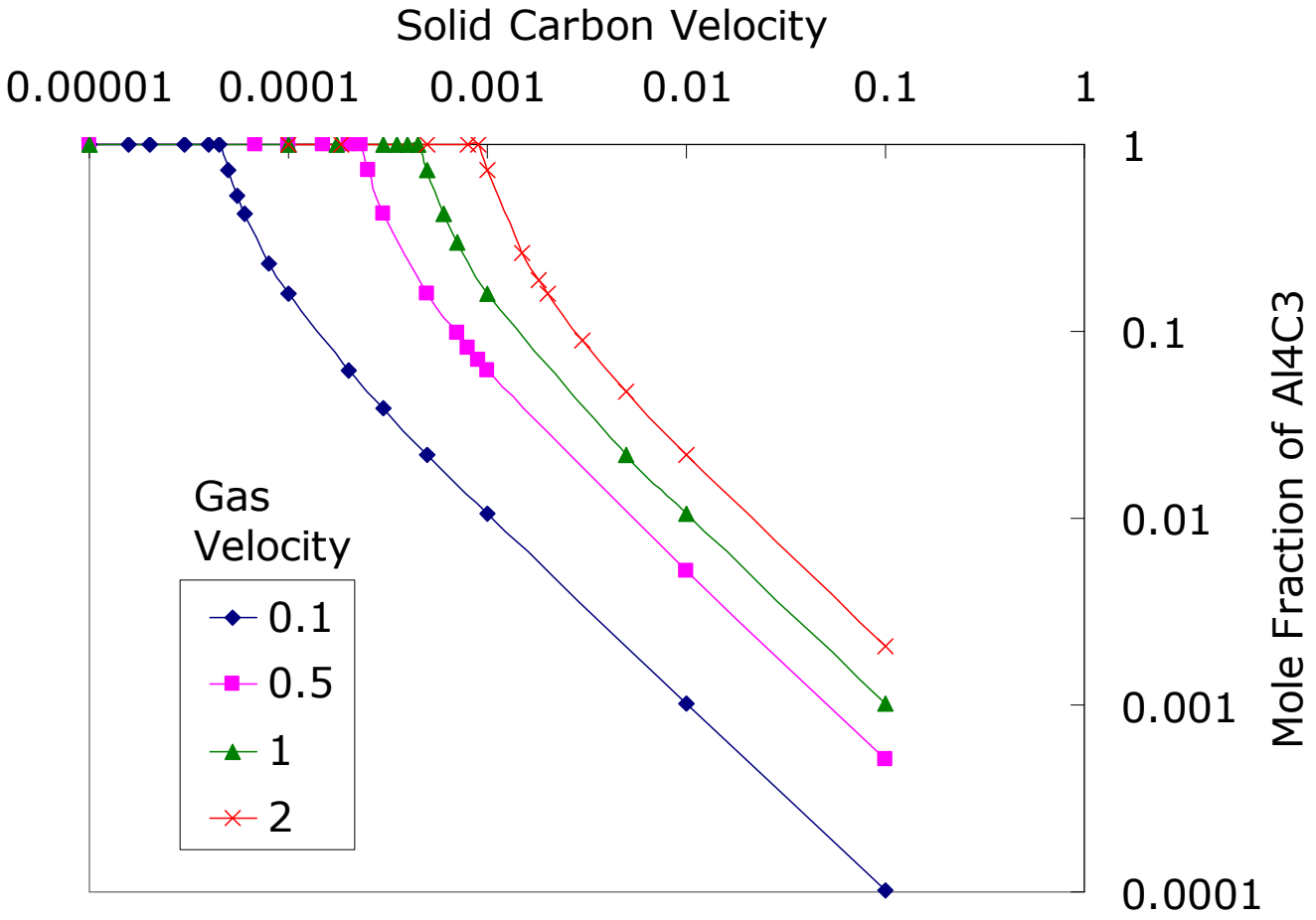




Simulations were done for different values of solid and gas velocity

The output mole fraction of aluminum carbide was noted once the simulation reached steady state

Dynamic Simulation Results



Steady State Analysis of VRR

Aluminum element mole balance

$$F^{in}_{Al_g} + 2F^{in}_{Al_2O_g} + 2F^{in}_{Al_2O_{3s}} = F^{out}_{Al_g} + 2F^{out}_{Al_2O_g} + 4F^{out}_{Al_4C_{3s}}$$

Carbon element mole balance

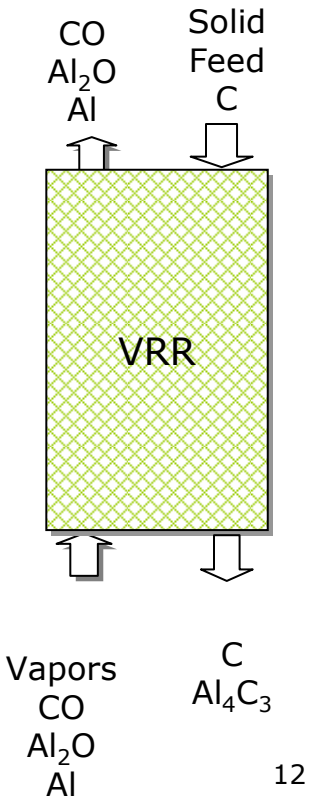
$$F^{in}_{C_s} + F^{in}_{CO_g} = F^{out}_{C_s} + F^{out}_{CO_g} + 3F^{out}_{Al_4C_{3s}}$$

Oxygen element mole balance

$$F^{in}_{Al_2O_g} + F^{in}_{CO_g} + 3F^{in}_{Al_2O_{3s}} = F^{out}_{Al_2O_g} + F^{out}_{CO_g}$$

Recovery

$$\gamma = \frac{F^{in}_{Al_g} - F^{out}_{Al_g}}{F^{in}_{Al_g}} = \frac{F^{in}_{Al_2O_g} - F^{out}_{Al_2O_g}}{F^{in}_{Al_2O_g}}$$



Design Relation

$$F^{out}_{Al_4C_{3s}} = \frac{1}{4}(\gamma F^{in}_{Al_g} + 2\gamma F^{in}_{Al_2O_g} + 2F^{in}_{Al_2O_{3s}})$$

$$F^{out}_{CO_g} = \gamma F^{in}_{Al_2O_g} + F^{in}_{CO_g} + 3F^{in}_{Al_2O_{3s}}$$

$$F^{out}_{C_s} = F^{in}_{C_s} - \frac{9}{2}F^{in}_{Al_2O_{3s}} - \frac{3}{4}\gamma F^{in}_{Al_g} - \frac{5}{2}\gamma F^{in}_{Al_2O_g}$$

Output compositions calculated from overall mass balances

$$F_{vapors} = v^{gas} * Area * C_{vapors}$$

$$F_{solid} = v^{solid} * Area * C_{solid}$$

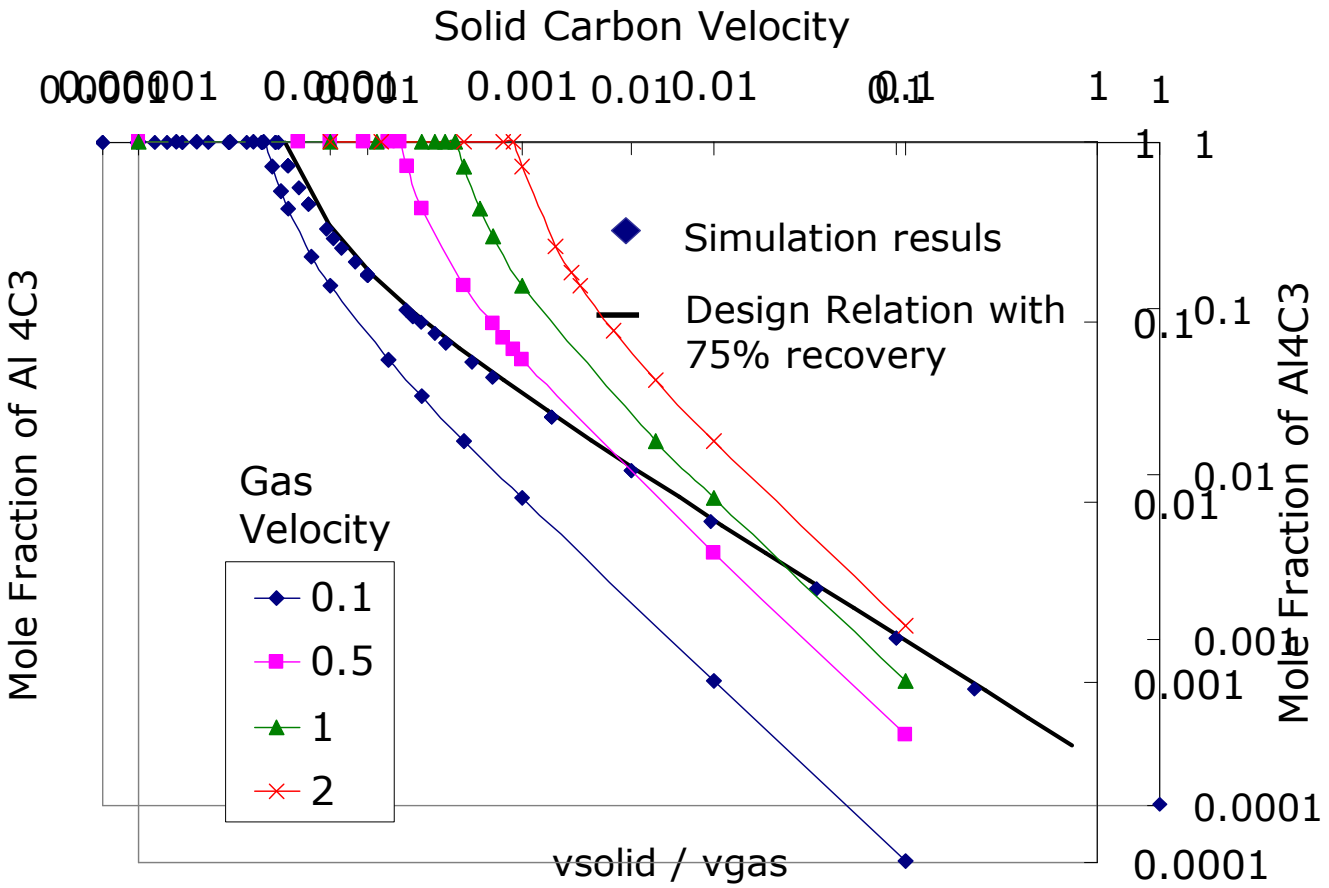
Transport relations

Design Relation

$$x^{out}_{Al_4C_{3s}} = \frac{\frac{1}{4}(\gamma C^{in}_{Al_g} + 2\gamma C^{in}_{Al_2O_g} + 2C^{in}_{Al_2O_{3s}})}{\left(\frac{v^{solid}}{v^{gas}}\right)(C^{in}_{C_s} - 4C^{in}_{Al_2O_{3s}}) - \frac{1}{2}\gamma C^{in}_{Al_g} - 2\gamma C^{in}_{Al_2O_g}}$$

Dimensionless group on which output depends

Comparison with Simulation



"There is nothing so practical as a good theory."

Ludwig Boltzmann

Definition: Inventory of a System

High-dimensional dynamic system

$$\dot{x} = f(x) + g(d, x, u)$$

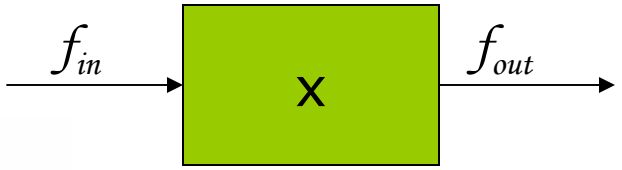
$$y = h(x)$$

An inventory *v* is defined as an additive continuous function

$$\nu : X \rightarrow \Re^{+}$$

From continuity we have

$$\frac{d\nu(x)}{dt} = p_{\nu}(x) + \phi_{\nu}(d, x, u)$$



$\Phi(x) = f_{in} - f_{out}$

Drift or production

$$p_{\nu}(x) = \frac{\partial \nu}{\partial x} f(x)$$

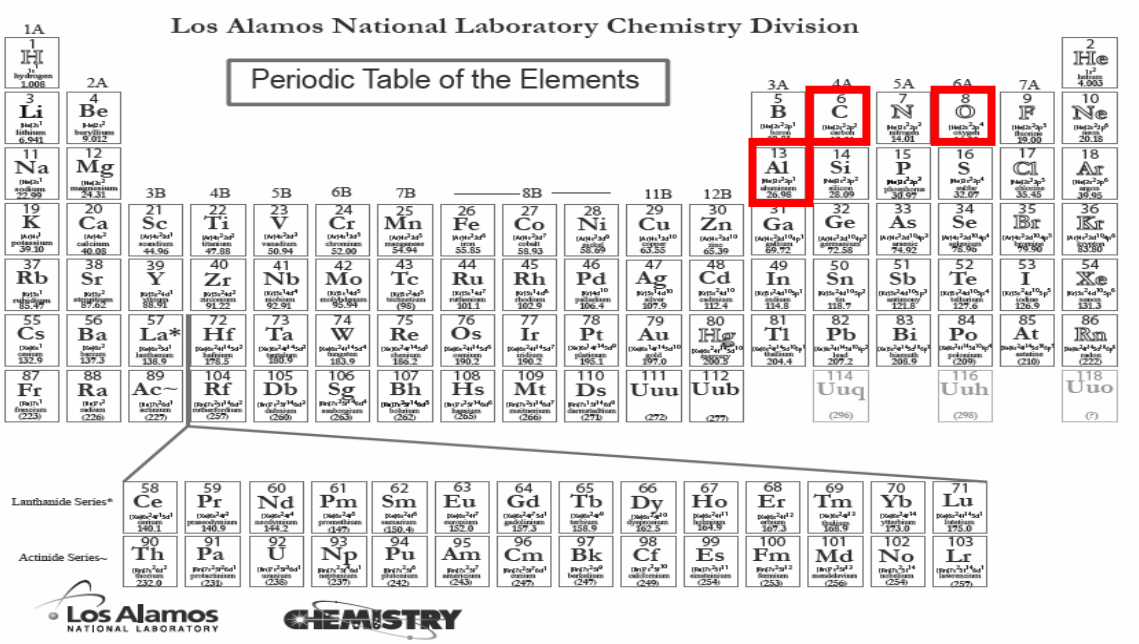
Net flux at boundaries

$$\phi_{\nu}(d, x, u) = \frac{\partial \nu}{\partial x} g(d, x, u)$$

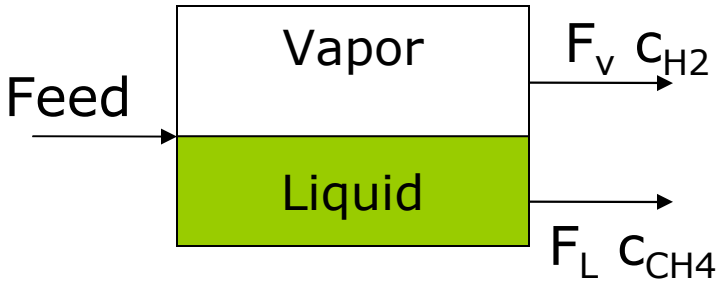
Invariant Inventories

If the drift $p_v(x) = 0$ for all $x \in X$ the inventory is said to be invariant e.g. Energy, Mass

For a chemical process, there exists another set of invariants, the elements or atoms that are neither created nor destroyed in a chemical reaction.



Local Invariants



Flash Drum

Invariants: H_2 and CH_4

We define invariants *I* if they satisfy the following

$$p_I(x) = 0 \text{ for all } x \in X_o$$

X_o is a subspace of X for the process

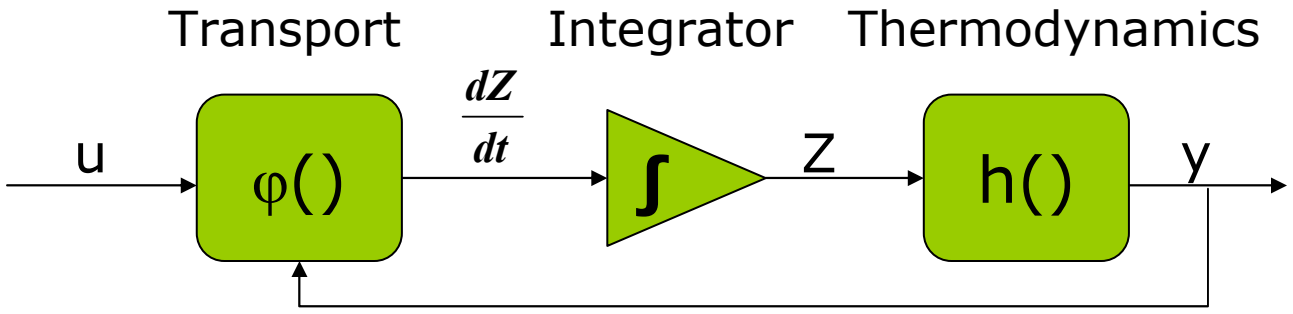
Equilibrium Systems

- Example: Distillation column, VRR
- The state of an equilibrium system can be represented by a vector of invariants

$$Z = \begin{pmatrix} U \\ V \\ I \end{pmatrix}$$

- The model of an equilibrium system in terms of invariants

$$\begin{aligned} \frac{dZ}{dt} &= \phi(y, d, u) \\ y &= h(Z) \end{aligned}$$

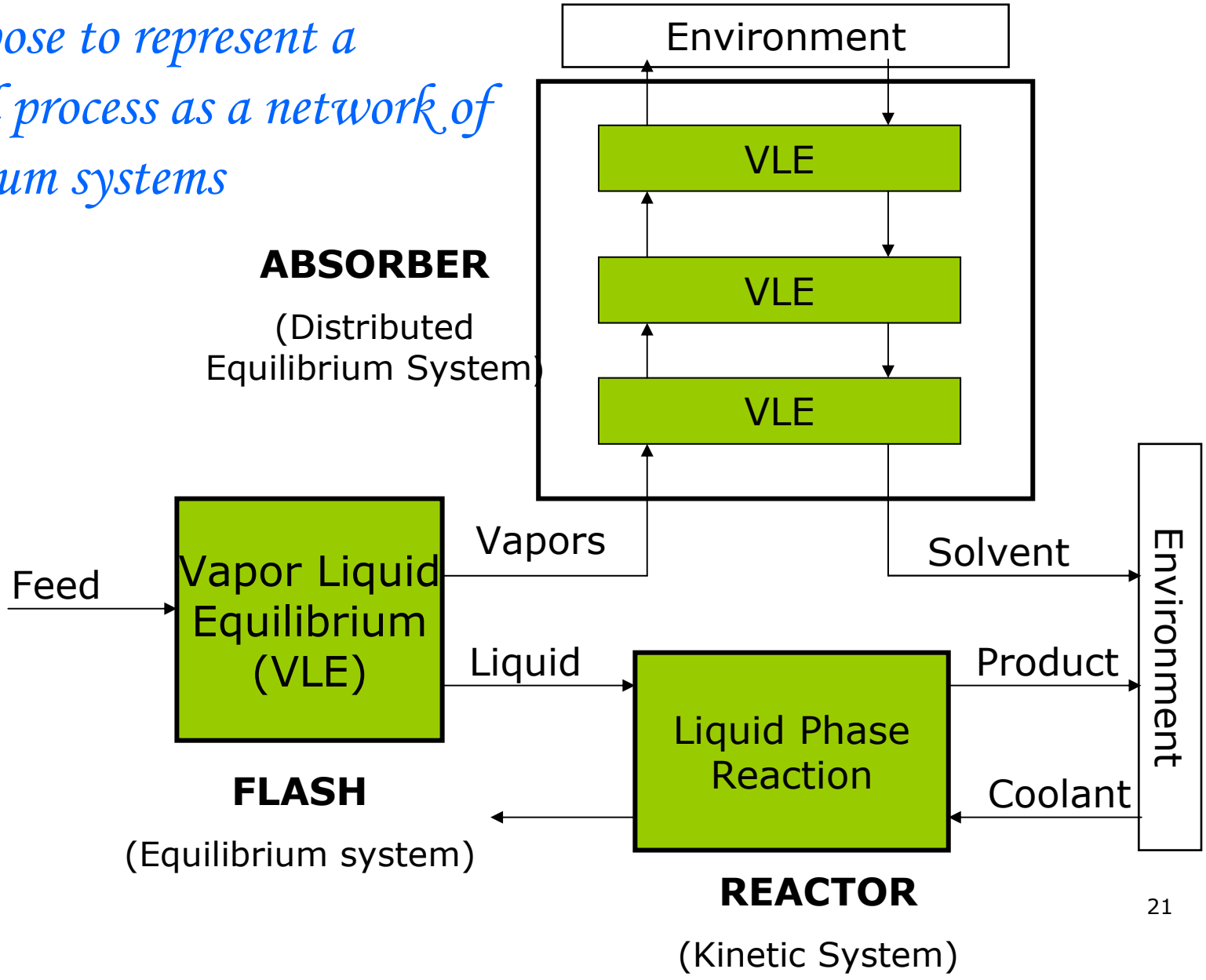


Why Invariants?

- Minimal state representation
- Allows the use the structure of physical processes for modeling.
  - It separates the model into modules of thermodynamics and transport phenomenon.
- A systematic method to choose input-output pair for control which doesn't include the drift p
  - Choose u so that: $\Phi(u,y) = -K_c(v-v^*)$
- Provides a basis for stability
  - Lossless system since $p_v(x) = 0$
- Model reduction

Network of Equilibrium Systems

We propose to represent a chemical process as a network of equilibrium systems



Summary and Conclusions

- Carbothermic Aluminum production can lead to reduction in capital and operating costs.
- Significant amount of vapors escape from main reactor.
- Staged equilibrium VRR model has been developed for process scale up and process control.
- Modeling framework for equilibrium, multi phase reactors based on invariants as state has been developed.
- Generalization to non-equilibrium, kinetic systems is under development.

Thank you

Questions?

Thank you

Questions?

Thank you

Questions?

Equilibrium function

Input:

Al	C	O	T(K)	P(atm)
15	10	13	2200	1

Function:

Phase Combination	Gibbs Energy
Al_4C_3(s) C(s) Gas	Infeasible
C(s) Slag Gas	Infeasible
Al_2O_3(s) C(s) Gas	Infeasible
Al_2O_3(s) Slag Gas	Infeasible
Al_4C_3(s) Slag Gas	-1.0476e+007
C(s) Gas	-1.0181e+007
Al_4C_3(s) Gas	-1.0255e+007
Al_2O_3(s) Gas	Infeasible

Output:

Al_4C_3(s)	Al_2O_3(s)	C(s)	Al_4C_3(l)	Al_2O_3(l)	Al(g)	Al_2O(g)	CO(g)
1.5564	0	0	0.5831	3.1090	0.0410	0.0915	3.5815

Equilibrium Module: Formulation

min $$G_T = \sum_{\alpha} C_\alpha \sum_{j} \mu_j x_j^\alpha$$

s.t.

Chemical equilibrium constraints

$$\mu_j = \sum_i e_{ij} \lambda_i$$

$$\mu_j = \mu_j^{std}(T) \quad \text{for solid phase}$$

$$\mu_j = \mu_j^{std}(T) + RT \ln \gamma_j x_j \quad \text{for liquid phase}$$

$$\mu_j = \mu_j^{std}(T) + RT \ln P x_j \quad \text{for gas phase}$$

Elemental mass balance constraints

$$b_i = \sum_{\alpha} C_\alpha \sum_{j} e_{ij} x_j^\alpha$$

$$\sum_j x_j^\alpha = 1$$

back