

Invariants in Multi Phase Reactor Systems



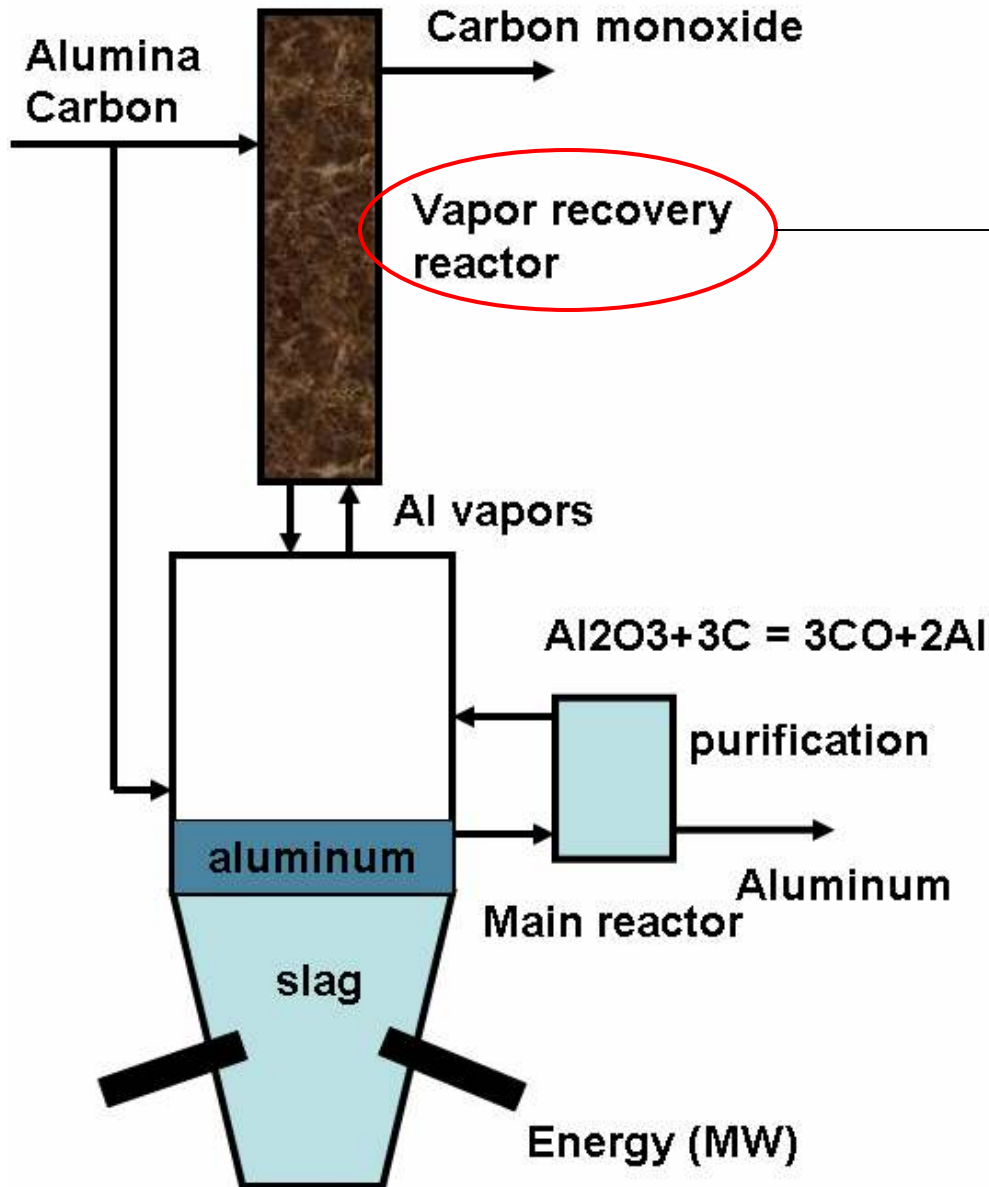
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Motivation

- 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

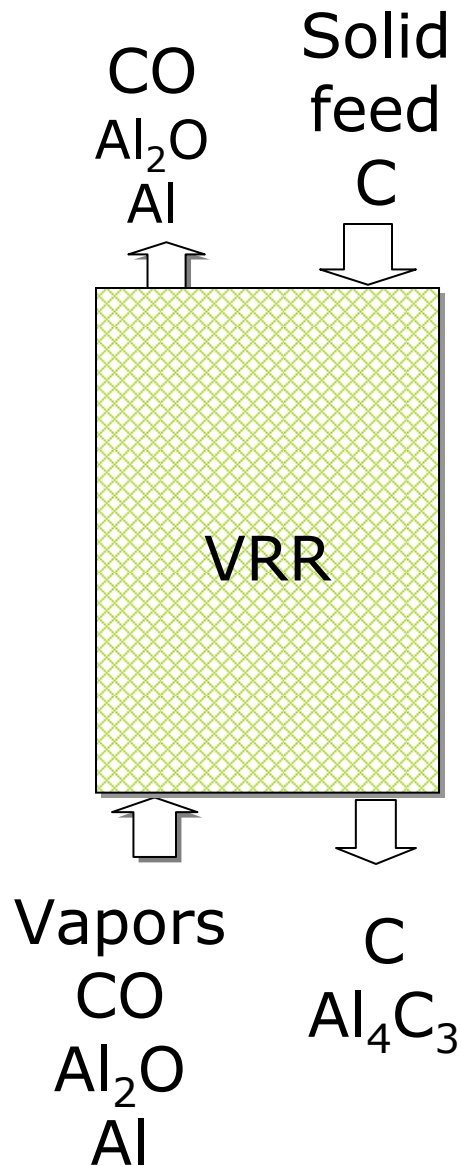
Carbothermic Aluminum Process



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



VRR- Modeling Premises

Compounds present

Solid: Al_4C_3 C Al_2O_3

Liquid: Slag ($\text{Al}_4\text{C}_3 + \text{Al}_2\text{O}_3$)

Gas: CO Al Al_2O

Temperatures	Temperatures
$T > 2810$	$T > 2810$
$2285 \leq T < 2810$	$2285 \leq T < 2810$
$2200 < T < 2280$	$2200 < T < 2280$
$T < 2200$	$T < 2200$

- ❑ 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

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

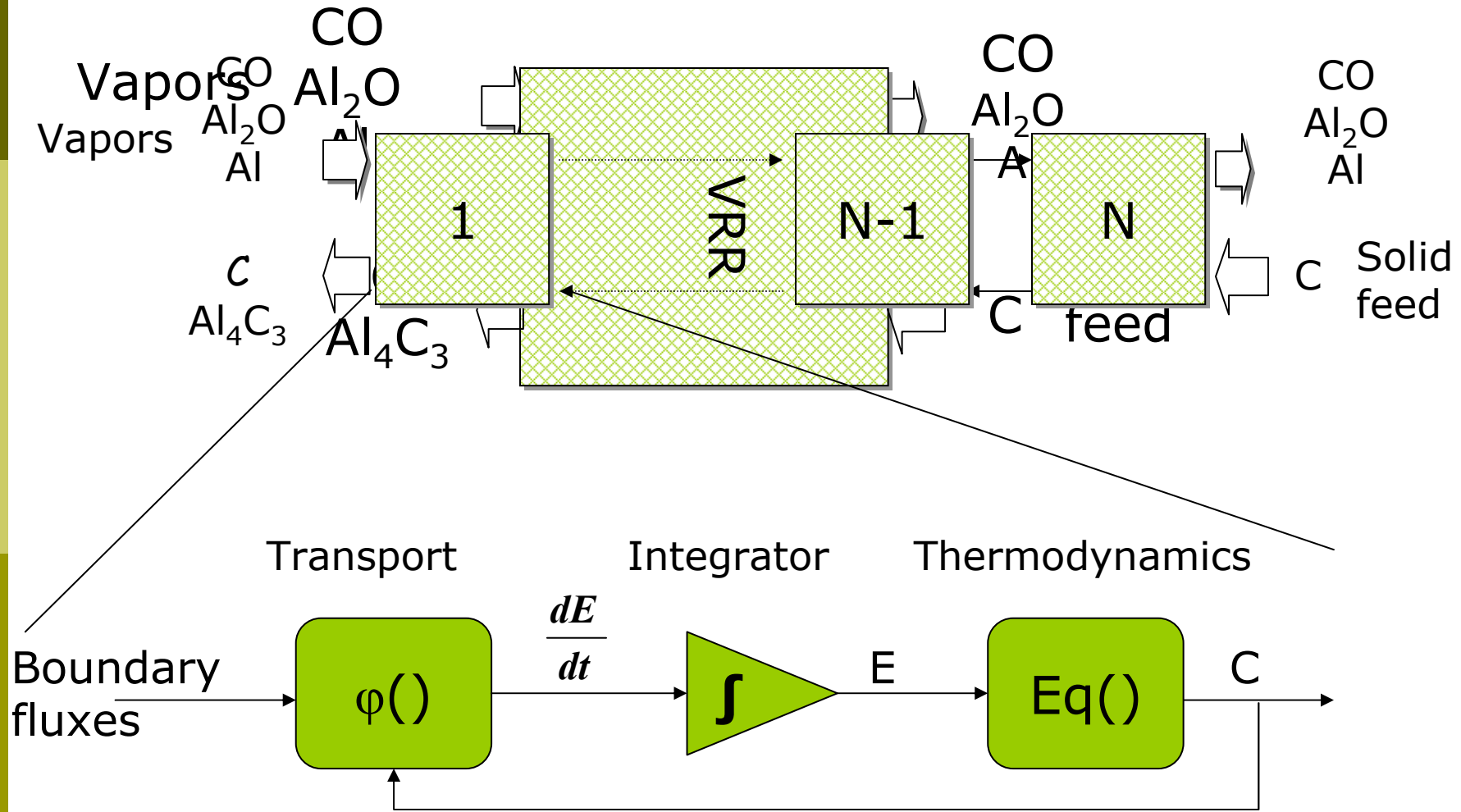
Thermodynamics

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

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

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

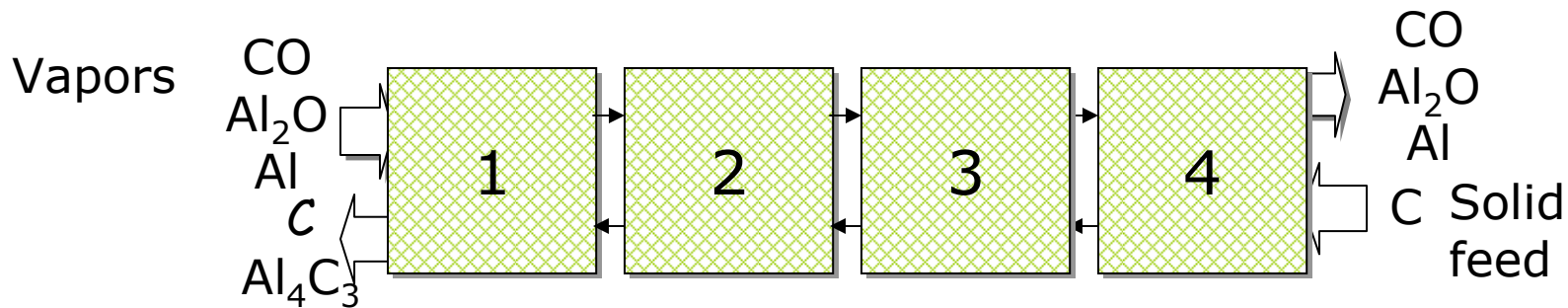
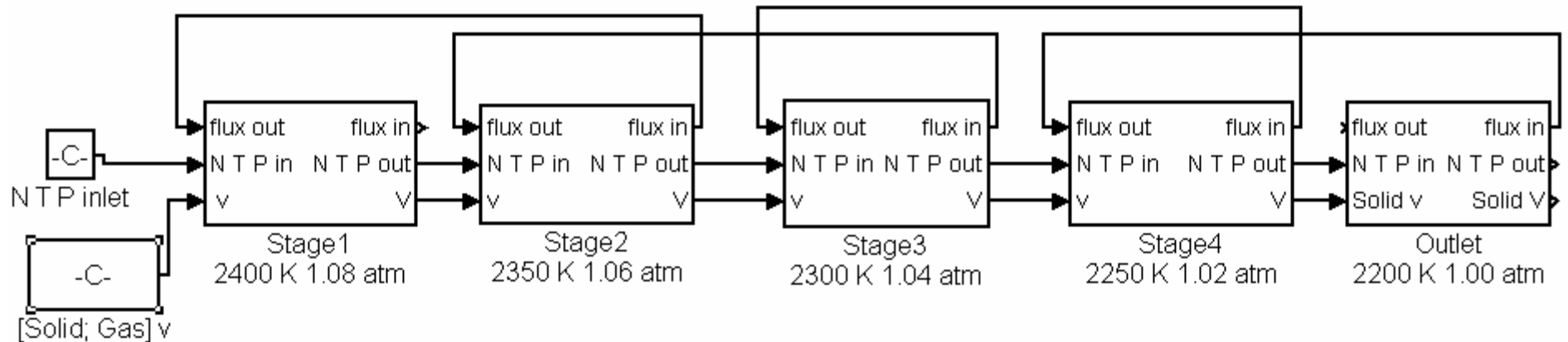
$$F_j = v^\alpha A C_{\alpha j}$$

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

- 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

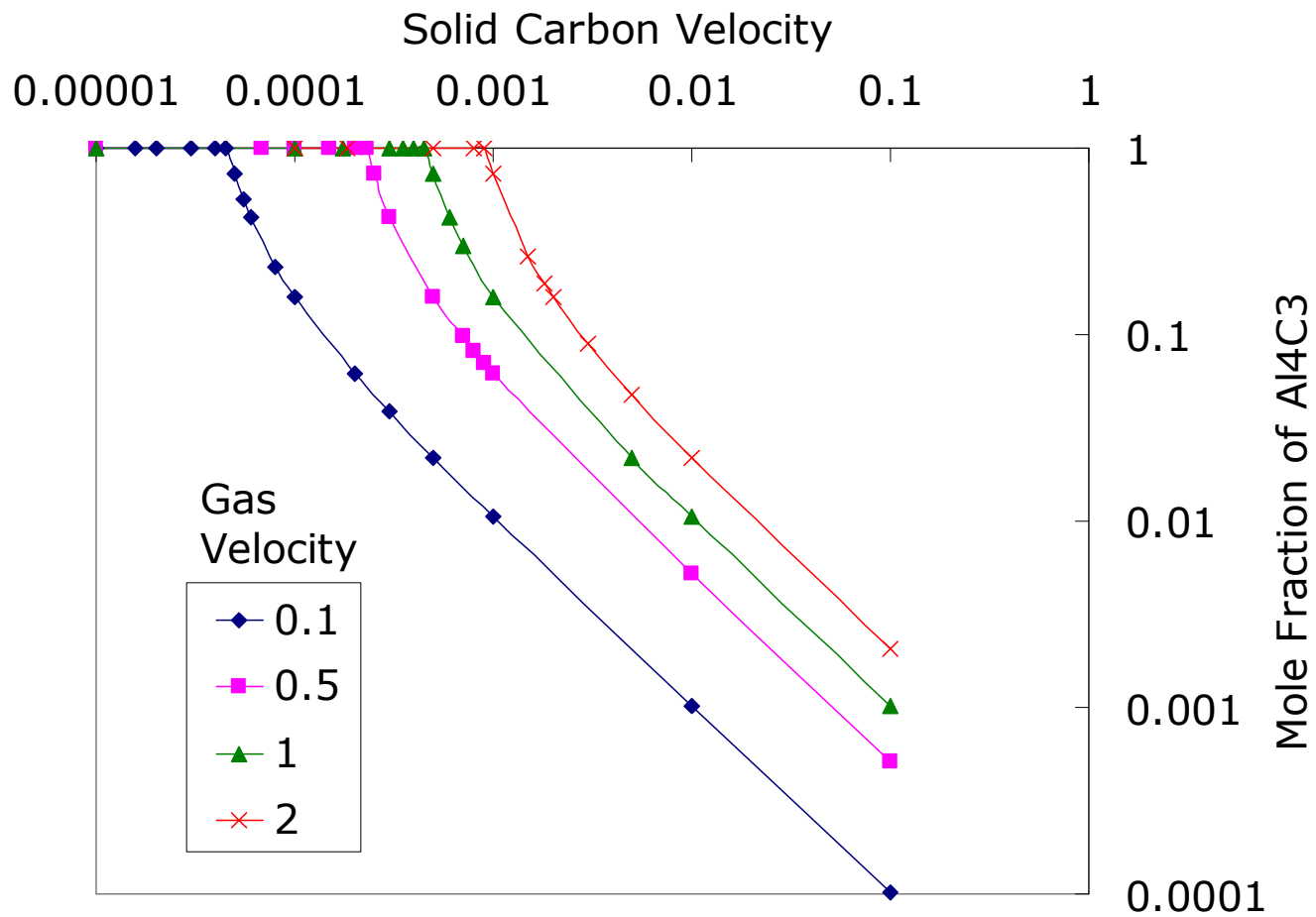
Dynamic Simulation of VRR



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

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

Carbon element mole balance

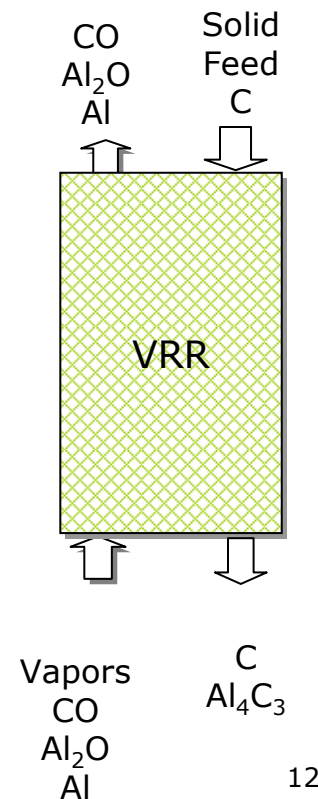
$$F_{C_s}^{in} + F_{CO_g}^{in} = F_{C_s}^{out} + F_{CO_g}^{out} + 3F_{Al_4C_{3s}}^{out}$$

Oxygen element mole balance

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

Recovery

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



Design Relation

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

Output compositions
calculated from overall
mass balances

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

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

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

Transport
relations

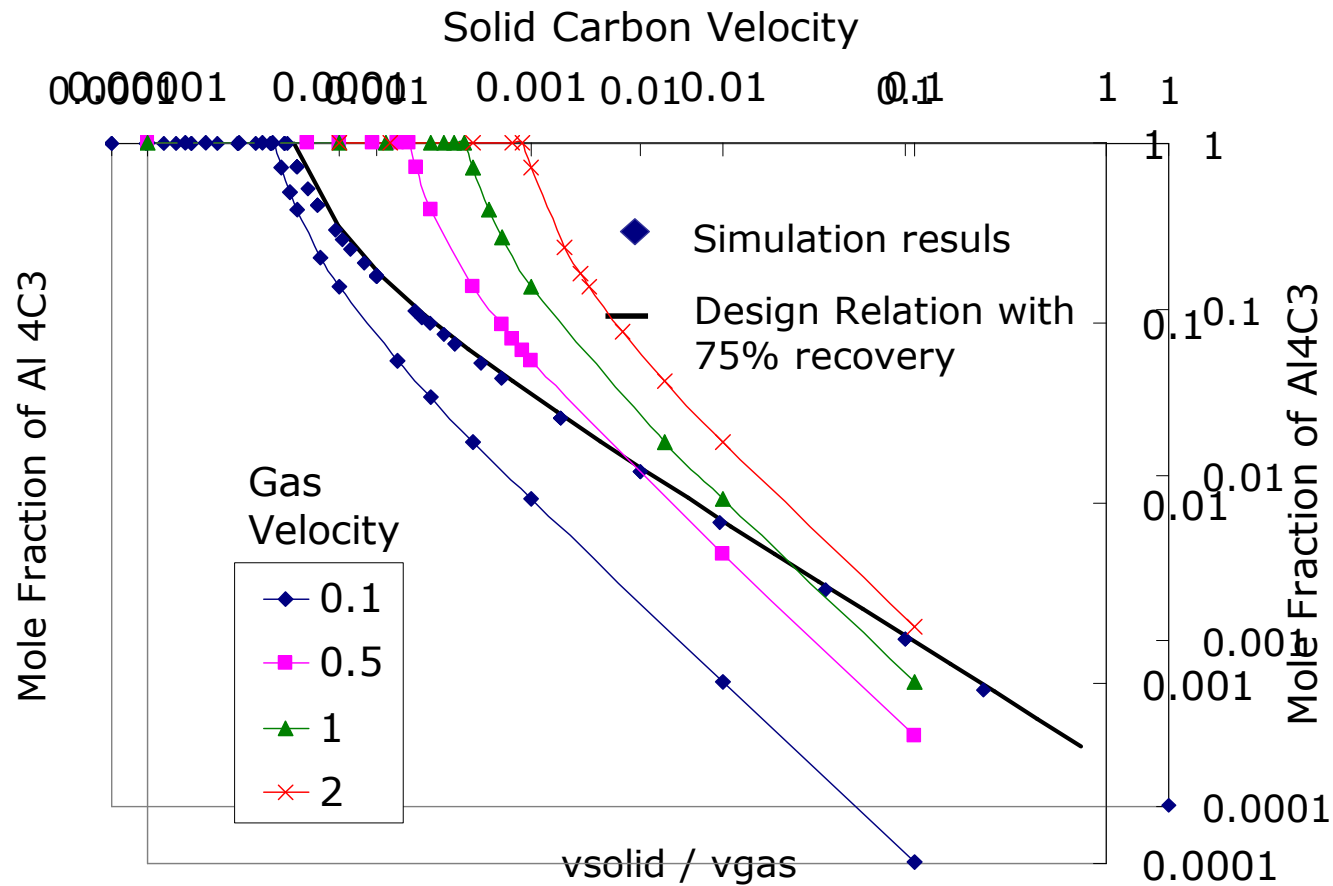
$$F_{solid} = v^{solid} * Area * C_{solid}$$

Design Relation

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

**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

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

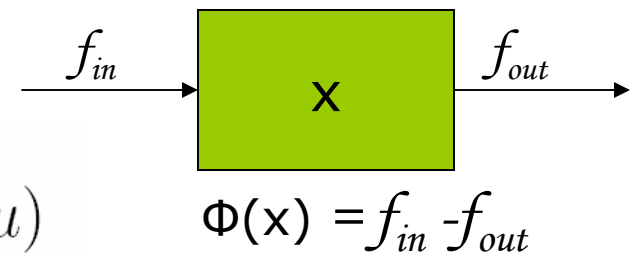
$$y = h(x)$$

An inventory ν is defined as an additive continuous function

$$\nu : X \rightarrow \mathfrak{R}^+$$

From continuity we have

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



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

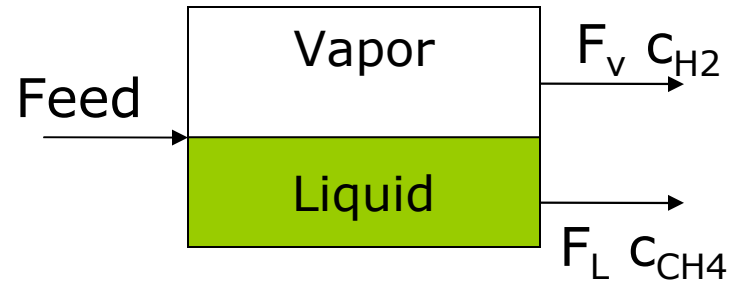
For a chemical process, there exists another set of invariants, the elements or atoms that are neither created nor destroyed in a chemical reaction.

Los Alamos National Laboratory Chemistry Division

Periodic Table of the Elements

1A 1 H Hydrogen 1.008	2A 4 Be Beryllium 9.012																	3A 5 B Boron 10.81	4A 6 C Carbon 12.01	5A 7 N Nitrogen 14.01	6A 8 O Oxygen 16.00	7A 9 F Fluorine 18.99	2 He Helium 4.003
3 Li Lithium 6.941	12 Mg Magnesium 24.31																	13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	3B 21 Sc Scandium 44.96	4B 22 Ti Titanium 47.88	5B 23 V Vanadium 50.94	6B 24 Cr Chromium 52.00	7B 25 Mn Manganese 54.94	8B 26 Fe Iron 55.85		27 Co Cobalt 58.93	28 Ni Nickel 58.69	11B 29 Cu Copper 63.55	12B 30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.64	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80					
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium 98.91	44 Ru Ruthenium 101.1	45 Rh Rhodium 106.4	46 Pd Palladium 106.3	47 Ag Silver 107.87	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3						
55 Cs Cesium 132.9	56 Ba Barium 137.3	57 La* Lanthanum 138.9	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.8	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 196.97	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222						
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac~ Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Ds Darmstadtium (271)	111 Uu Ununium (272)	112 Uub Unbium (277)	114 Uuq Unquadium (286)	116 Uuh Unhexium (288)	118 Uuo Unoctium (?)									
Lanthanide Series*			58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium 144.9	62 Sm Samarium 150.4	63 Eu Europium 151.9	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 174.9							
Actinide Series~			90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium 237.0	94 Pu Plutonium 244.0	95 Am Americium 243.0	96 Cm Curium 247.0	97 Bk Berkelium 247.0	98 Cf Californium 251.0	99 Es Einsteinium 252.0	100 Fm Fermium 257.0	101 Md Mendelevium 258.0	102 No Nobelium 259.0	103 Lr Lawrencium 260.0							

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

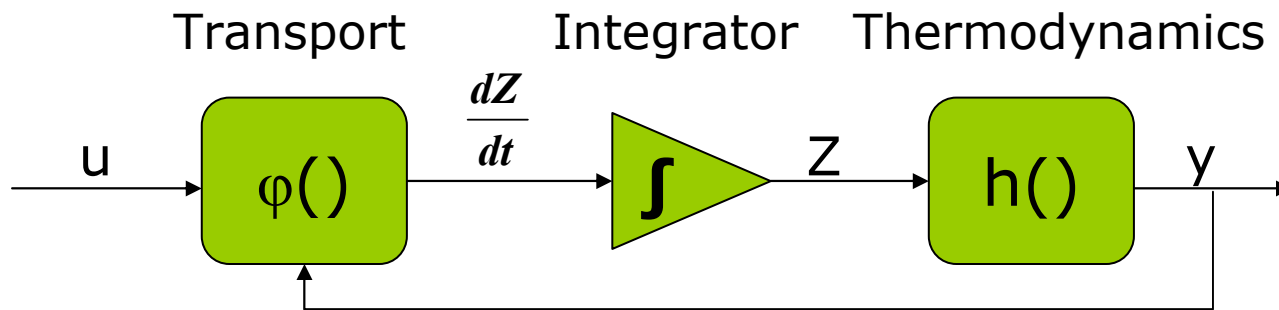
- Example: Distillation column, VRR

- 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

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

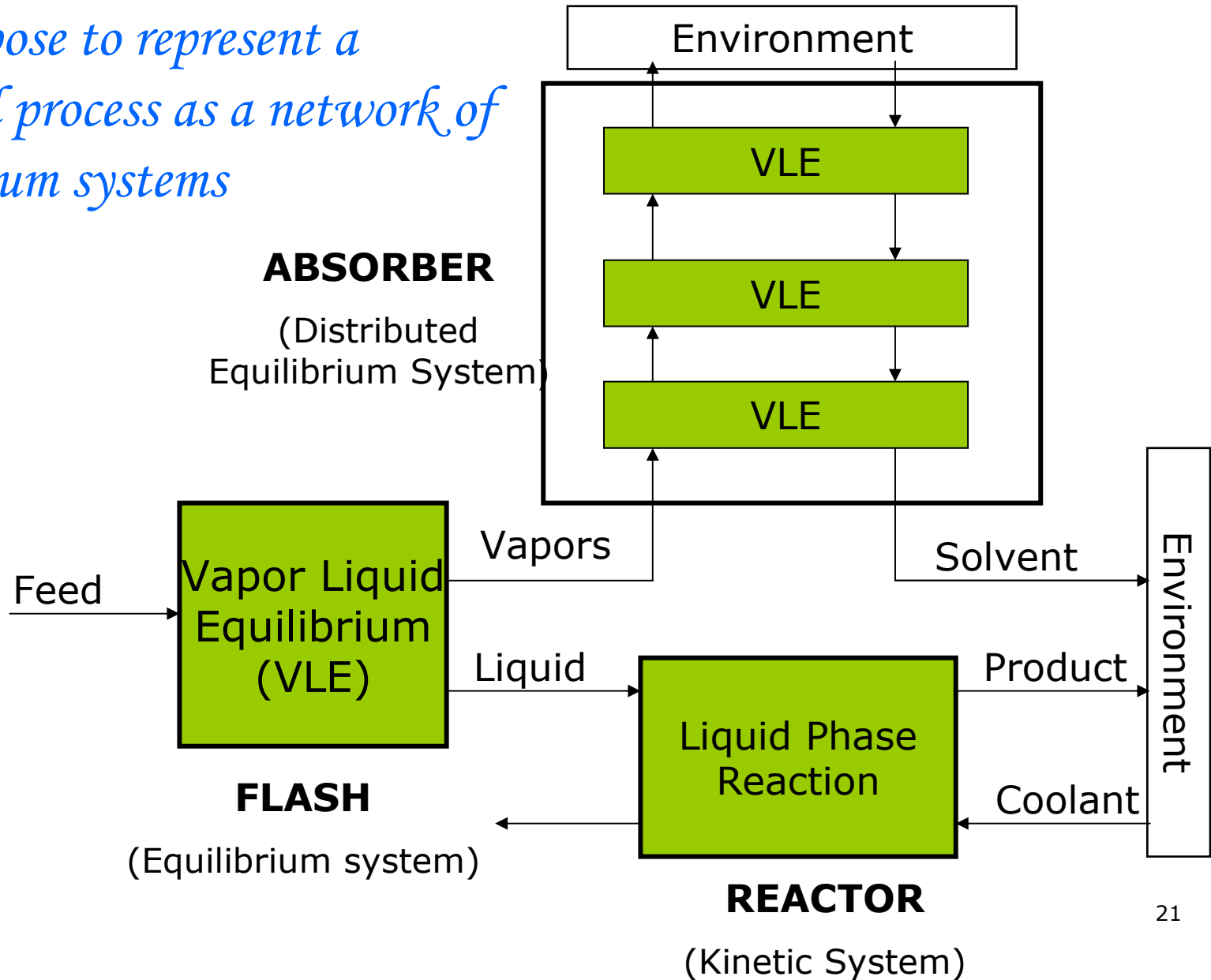


Why Invariants?

- 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 ₄ C ₃ (s) C(s) Gas	Infeasible
C(s) Slag Gas	Infeasible
Al ₂ O ₃ (s) C(s) Gas	Infeasible
Al ₂ O ₃ (s) Slag Gas	Infeasible
Al ₄ C ₃ (s) Slag Gas	-1.0476e+007
C(s) Gas	-1.0181e+007
Al ₄ C ₃ (s) Gas	-1.0255e+007
Al ₂ O ₃ (s) Gas	Infeasible

Output:

Al₄C₃(s) Al₂O₃(s) C(s) Al₄C₃(l) Al₂O₃(l) Al(g) Al₂O(g) CO(g)
 1.5564 0 0 0.5831 3.1090 0.0410 0.0915 3.5815²⁶

Equilibrium Module: Formulation

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

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

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

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