ABE 201
Biological Thermodynamics 1

Degree of Freedom Analysis

and

Multiple Unit Operations

Topics for Today

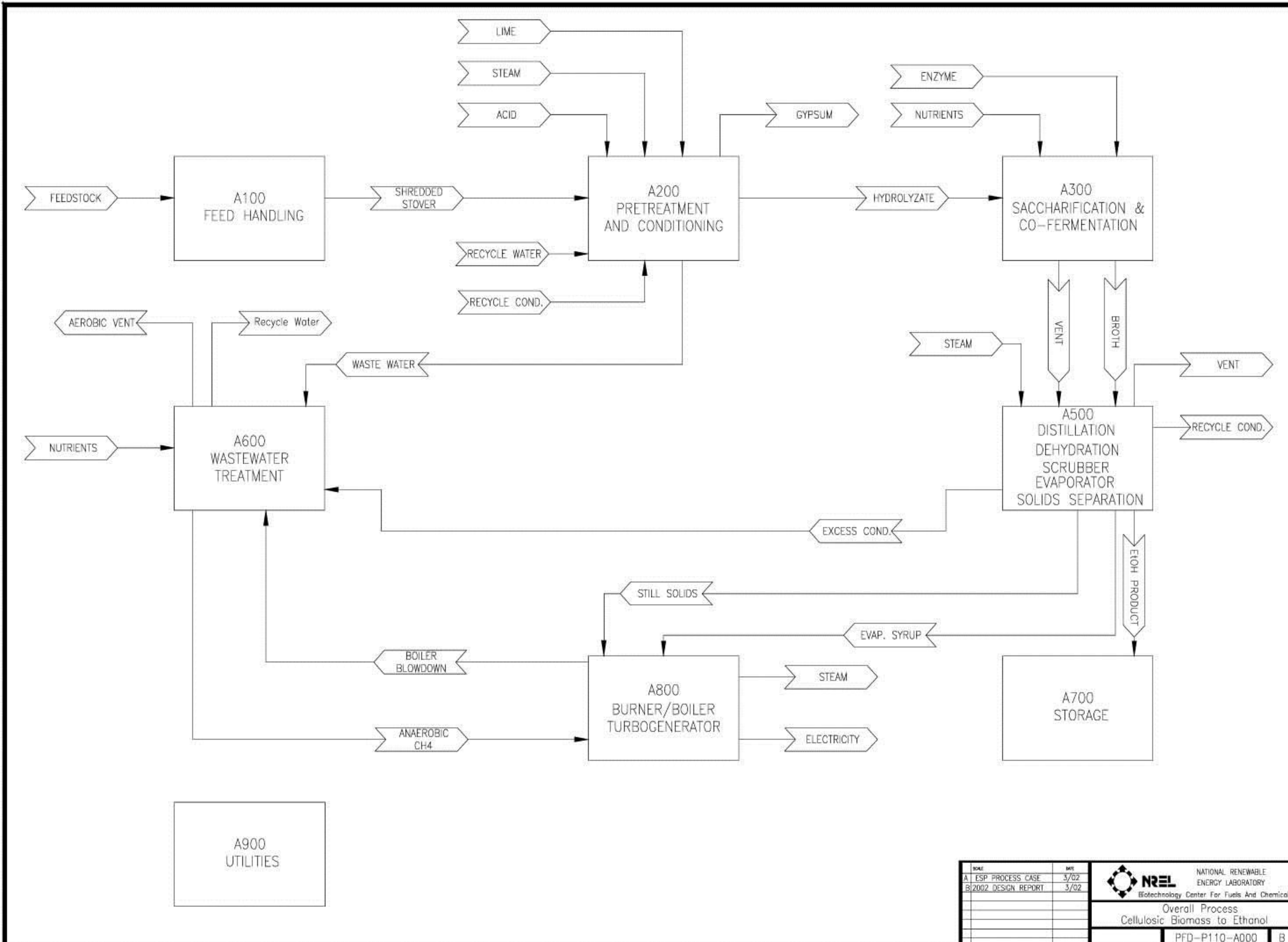
Analyzing complex biological processes

– Defining systems and subsystems

– Using Degree of Freedom Analysis

Complex Biological Systems

- Biological processes have multiple unit operations
- Processes can be broken into multiple systems for analysis
- Determine which individual system (unit) to solve first by degree of freedom analysis
- Solve each of the systems, in order by DOF

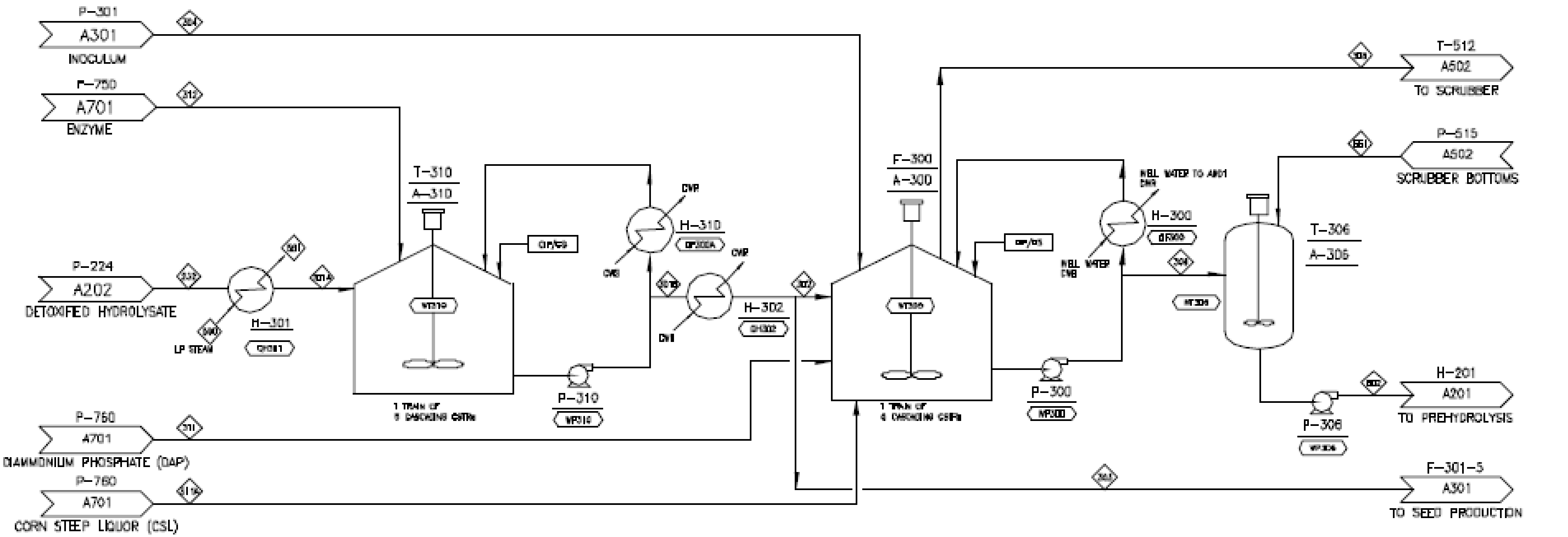

LIME
STEAM
ACID
GYPSUM
ENZYME
NUTRIENTS
FEEDSTOCK
A100
FEED HANDLING
SHREDDED STOVER
A200
PRETREATMENT
AND CONDITIONING
HYDROLYZATE
A300
SACCHARIFICATION &
CO-FERMENTATION
RECYCLE WATER
RECYCLE COND.
AEROBIC VENT
Recycle Water
VENT
BROTH
STEAM
WASTE WATER
VENT
A500
DISTILLATION
DEHYDRATION
SCRUBBER
EVAPORATOR
SOLIDS SEPARATION
RECYCLE COND.
NUTRIENTS
A600
WASTEWATER
TREATMENT
EXCESS COND.
EtOH PRODUCT
STILL SOLIDS
EVAP. SYRUP
BOILER BLOWDOWN
A800
BURNER/BOILER
TURBOGENERATOR
STEAM
ELECTRICITY
A700
STORAGE
ANAEROBIC CH4
A900
UTILITIES
SCALE
DATE
A ESP PROCESS CASE 3/02
B 2002 DESIGN REPORT 3/02
NATIONAL RENEWABLE
ENERGY LABORATORY
Biotechnology Center For Fuels And Chemicals
Overall Process
Cellulosic Biomass to Ethanol
PFD-P110-A000
B

Process Flow Diagrams/Sheets “PFD” or “PFS”

- Made of <u>Unit Operations</u>
  - Filtration, Fermentation, Distillation, Centrifugation, Drying
- Example from NREL
  - Processing Facility to Convert Corn Stalks to Biofuel (ethanol) and Biopower (electricity)
  - 25 PFDs with all stream compositions
  - 28 “compounds” tracked and balanced
  - Thermal energy tracked and balanced

28 “Compounds” in Mass Balance

Individual Compounds	Soluble Solids (SS)	Insoluble Solids (IS)
Water	Glucose	Cellulose
Ethanol	Xylose	Xylan
Acetic Acid	Arabinose	Arabinan
Sulfuric Acid	Other Sugars	Other Sugar Polymers
Furfural	Cellobiose	Lignin
HMF	Glucose Oligomers	Gypsum
Carbon Dioxide	Xylose Oligomers	Ca(OH)2
Methane	Other Oligomers	
Oxygen	"Corn Steep Liquor"	
Nitrogen	Other SS	
Others		



COMPONENT	UNITS	232	301A	301B	302	303	304	306	308	311	311A	312	502	551	590	591
Total Flow	kg/hr	428,764	428,764	435,588	392,029	43,559	41,381	412,222	22,420	136	1,067	6,824	448,363	37,130	9,480	9,480
Insoluble Solids	%	11.2%	11.2%	5.0%	5.0%	5.0%	5.7%	5.5%	0.0%	0.0%	0.0%	8.3%	5.0%	0.0%	0.0%	0.0%
Soluble Solids	%	9.0%	9.0%	15.7%	15.7%	15.7%	4.8%	4.0%	0.0%	0.0%	100.0%	0.0%	3.6%	0.0%	0.0%	0.0%
Temperature	C	51	65	65	41	41	41	41	41	20	20	20	41	38	189	148
Pressure	atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.90	0.90	4.42	4.42
Vapor Fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Ethanol	kg/hr	47	47	47	43	5	2,336	24,032	668				24,825	793		
Water	kg/hr	335,811	335,811	339,186	305,269	33,919	33,881	338,544	710			6,266	374,828	36,284	9,480	9,480
Glucose (SS)	kg/hr	2,432	2,432	31,188	28,074	3,119	103	82					82			
Xylose (SS)	kg/hr	18,087	18,087	18,087	16,279	1,809	156	939					939			
Arabinose (SS)	kg/hr	2,528	2,528	2,528	2,275	253	32	217					217			
Other Sugars (SS)	kg/hr	2,982	2,982	2,982	2,688	298	37	254					254			
Cellobiose (SS)	kg/hr	312	312	360	324	36	36	360					360			
Glucose Oligomers (SS)	kg/hr	716	716	1,853	1,668	185	185	1,853					1,853			
Xylose Oligomers (SS)	kg/hr	646	646	646	581	65	65	646					646			
Other Oligomers (SS)	kg/hr	969	969	969	872	97	97	969					969			
Corn Steep Liquor (SS)	kg/hr	270	270	270	243	27	224	1,456	3		1,067		1,459	4		
Others (Soluble Solids)	kg/hr	9,581	9,581	9,581	8,623	958	958	9,581					9,581			
Acetic Acid	kg/hr	4,477	4,477	4,477	4,029	448	527	5,251	6				5,258	7		
Sulfuric Acid	kg/hr	154	154	154	139	15	15	154	0				154	0		
Furfural	kg/hr	576	576	576	518	58	57	568	7				576	8		
HMF	kg/hr	90	90	90	81	9	9	89	1				90	1		
Carbon Dioxide	kg/hr	29	29	29	26	3	40	406	20,769				440	34		
Methane	kg/hr															
Oxygen	kg/hr	0	0	0	0	0	0	0	226				0	0		
Nitrogen	kg/hr	0	0	0	0	0	0	0	0				0	0		
Others	kg/hr	954	954	954	859	95	292	4,276	0	136			4,276	0		
Cellulose (S)	kg/hr	28,432	28,432	1,365	1,228	136	136	1,365					1,365			
Xylan (S)	kg/hr	439	439	439	395	44	44	439					439			
Arabinan (S)	kg/hr	61	61	61	55	6	6	61					61			
Other Sugar Polymers (S)	kg/hr	73	73	73	66	7	7	73					73			
Cellulase (S)	kg/hr	81	81	650	585	65	65	650				558	650			
Biomass (S)	kg/hr	0	0	0	0	0	0	0					0			
Zymo (S)	kg/hr	136	136	136	122	14	193	1,068					1,068			
Lignin (S)	kg/hr	14,252	14,252	14,252	12,827	1,425	1,425	14,252					14,252			
Gypsum (S)	kg/hr	28	28	28	25	3	3	28					28			
Ca(OH)2 (S)	kg/hr															
Others (Insoluble Solids)	kg/hr	4,620	4,620	4,620	4,158	462	462	4,620					4,620			
Enthalpy Flow (millions)	Kcal/hr	-1389.4	-1384.5	-1408.7	-1275.5	-141.7	-137.7	-1372.7	-47.5	-0.4	-4.1	-24.2	-1510.9	-136.2	-29.8	-34.7
Average Density	g/ml	1.072	1.059	1.062	1.075	1.075	1.018	1.016	0.002	1.010	0.998	1.040	0.982	0.985	0.002	0.886

Heat Stream No.	MM kcal/hr	Work Stream No.	kW
CP300A	0.09	WP300	545.
CP300	2.40	WP306	119.
CH301	-4.89	WP310	122.
CH302	8.49	WT300	436.
		WT306	113.
		WT310	445.

Eq. No.	Equipment Name	Req	Spare	Equipment Type	Mat Const.
A-300	Ethanol Fermentor Agitator	10		FIXED-PROP	SS304
A-306	Beer Surge Tank Agitator	2		FIXED-PROP	SS304
A-310	Saccharification Tank Agitator	10		FIXED-PROP	SS304
F-300	Ethanol Fermentor	5		FLAT-BTM-STORAG	SS304
H-300	Fermentation Cooler	5	1	PLATE-FRAME	SS304
H-301	Hydrolyzate Heater	1	1	PLATE-FRAME	SS
H-302	Saccharified Slurry Cooler	3		PLATE-FRAME	SS304
H-310	Fermentation Cooler	5	1	PLATE-FRAME	SS304
P-300	Fermentation Recirc/Transfer Pump	5	1	CENTRIFUGAL	SS304
P-306	Beer Transfer Pump	1	1	CENTRIFUGAL	SS304
P-310	Saccharification Recirc/Transfer Pu	5	1	CENTRIFUGAL	SS304
T-306	Beer Storage Tank	1		FLAT-BTM-STORAG	SS304
T-310	Saccharification Tank	5		FLAT-BTM-STORAG	SS304

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SECTION A300

SACCHARIFICATION & FERMENTATION

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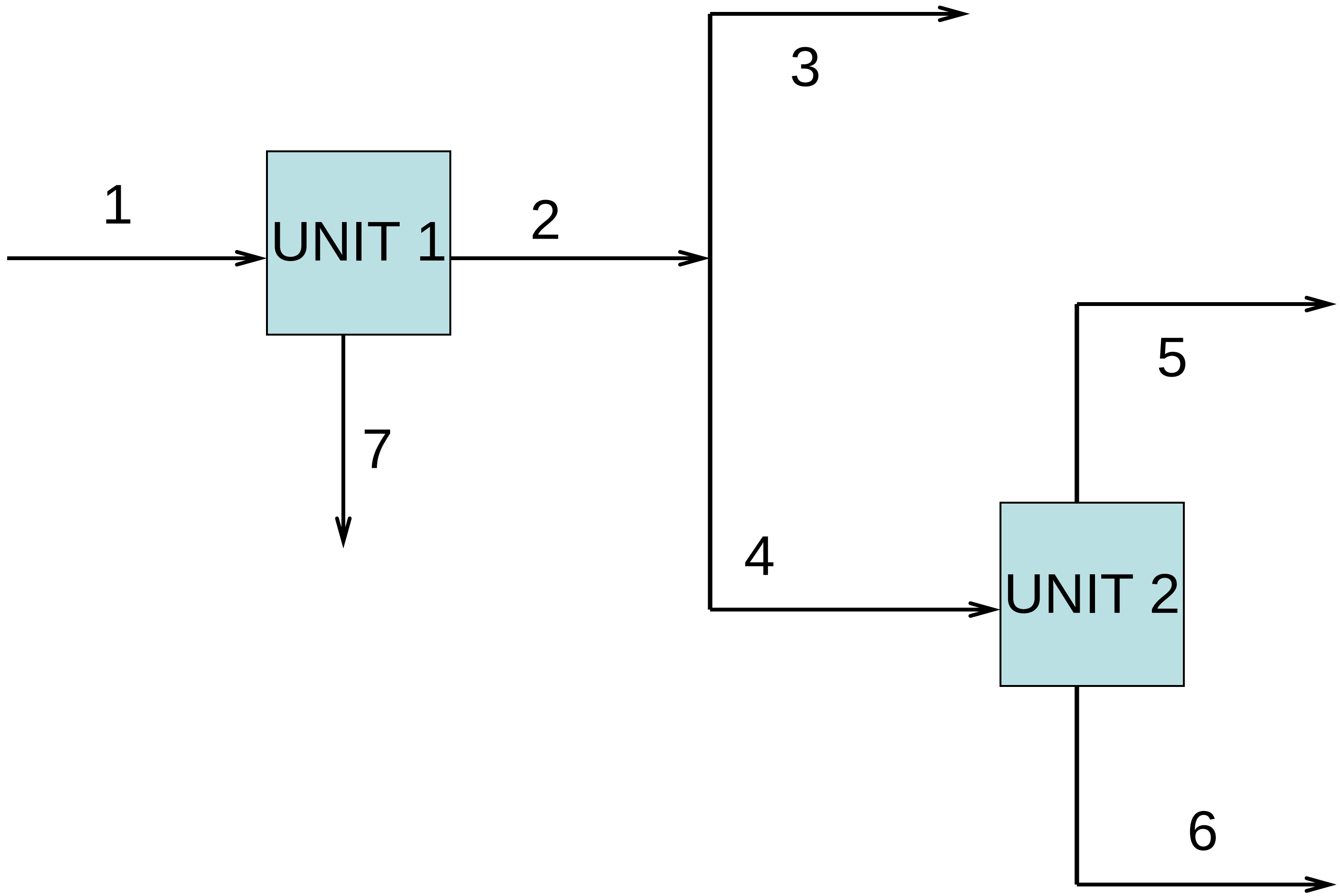
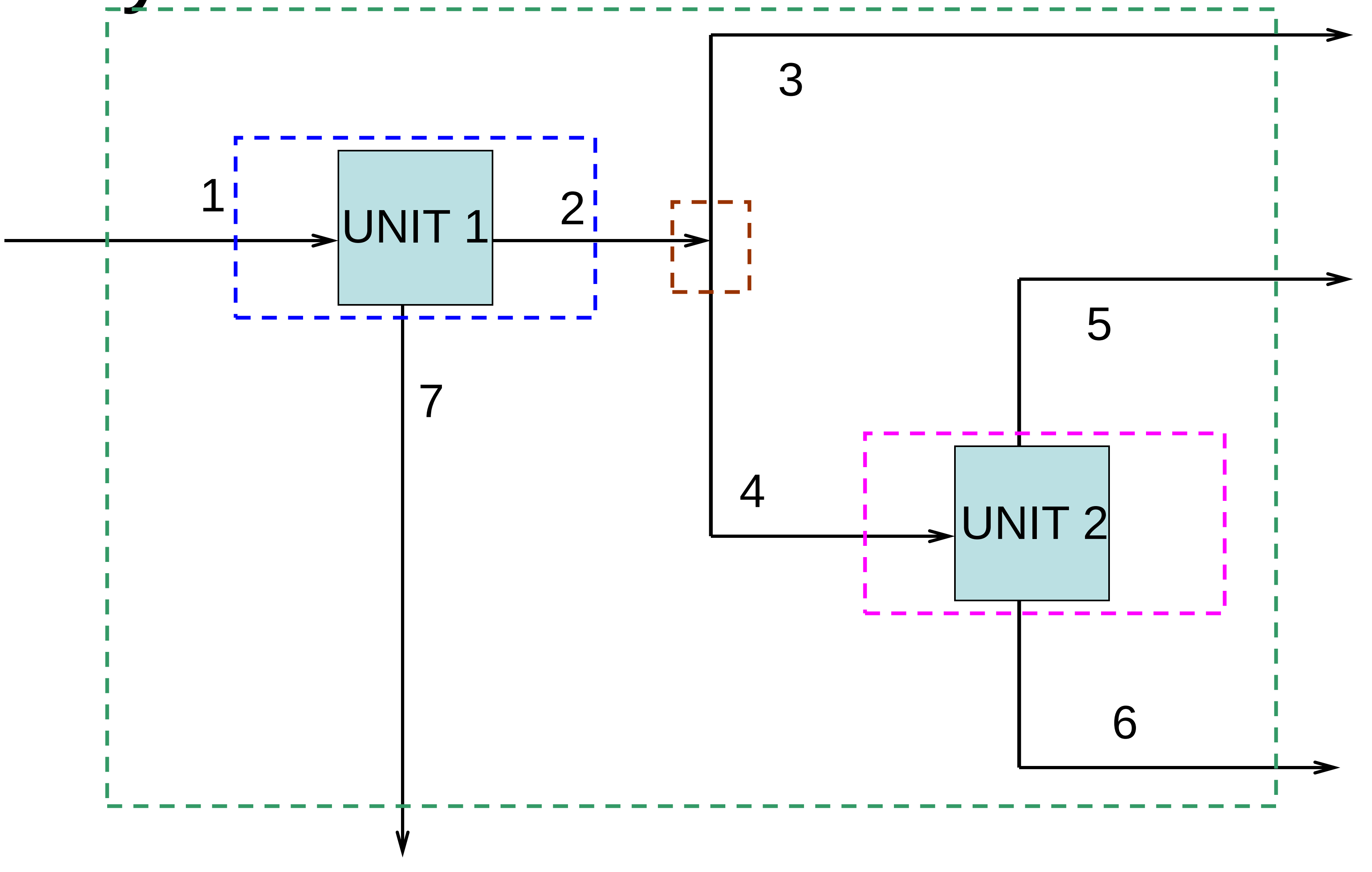
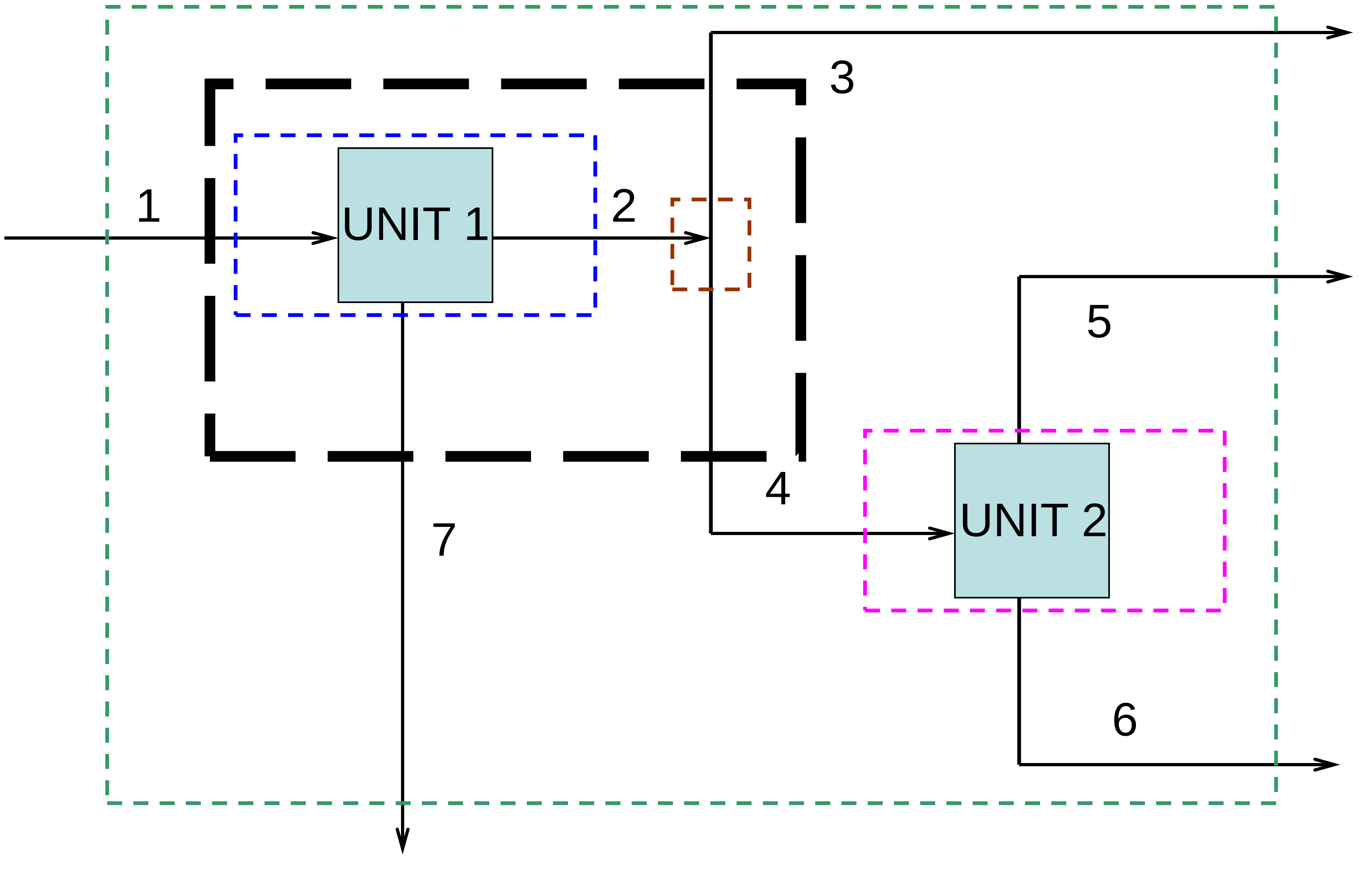
Example:



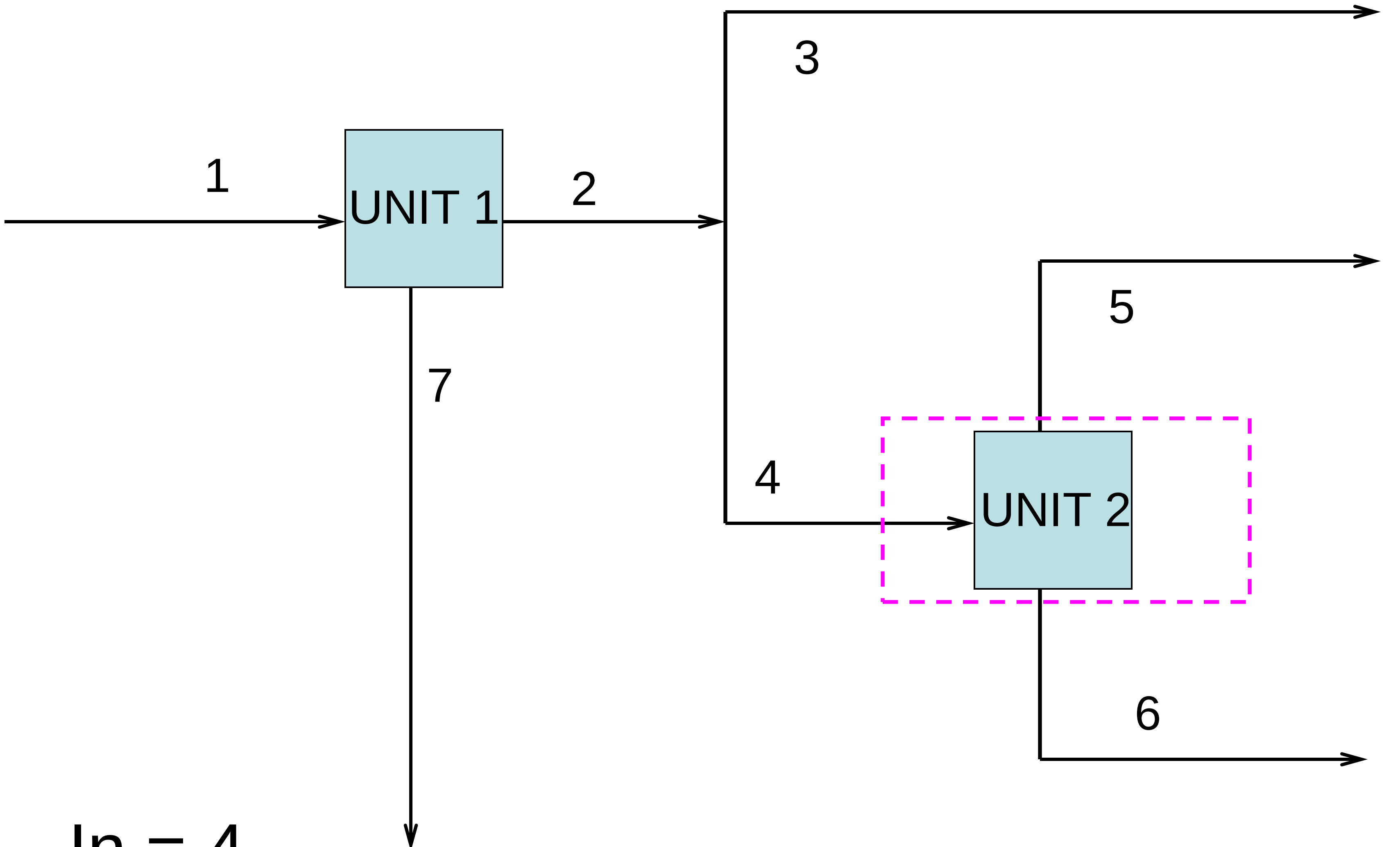
Systems:



Have We Drawn All Systems…

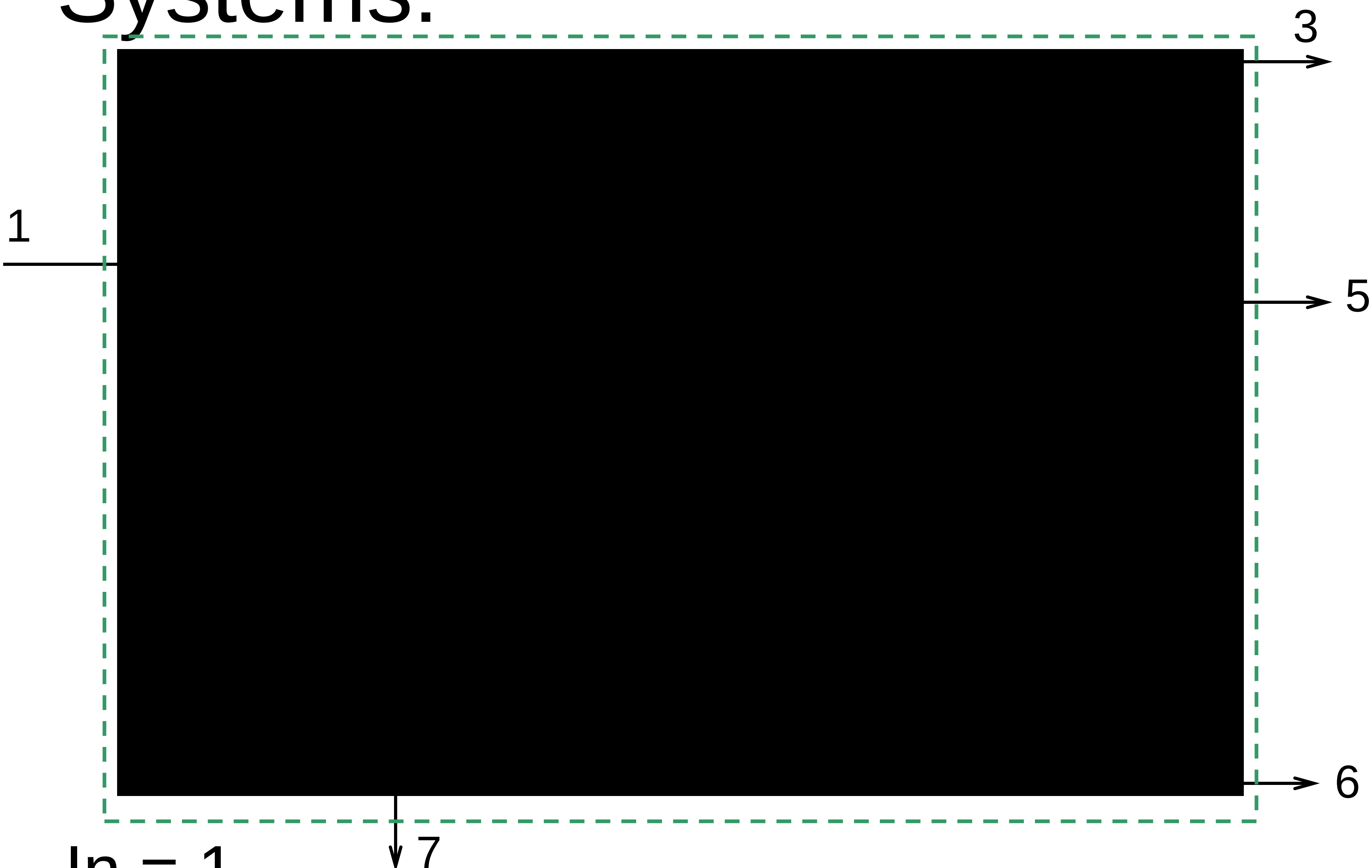


Systems:



In = 4
Out = 5 + 6

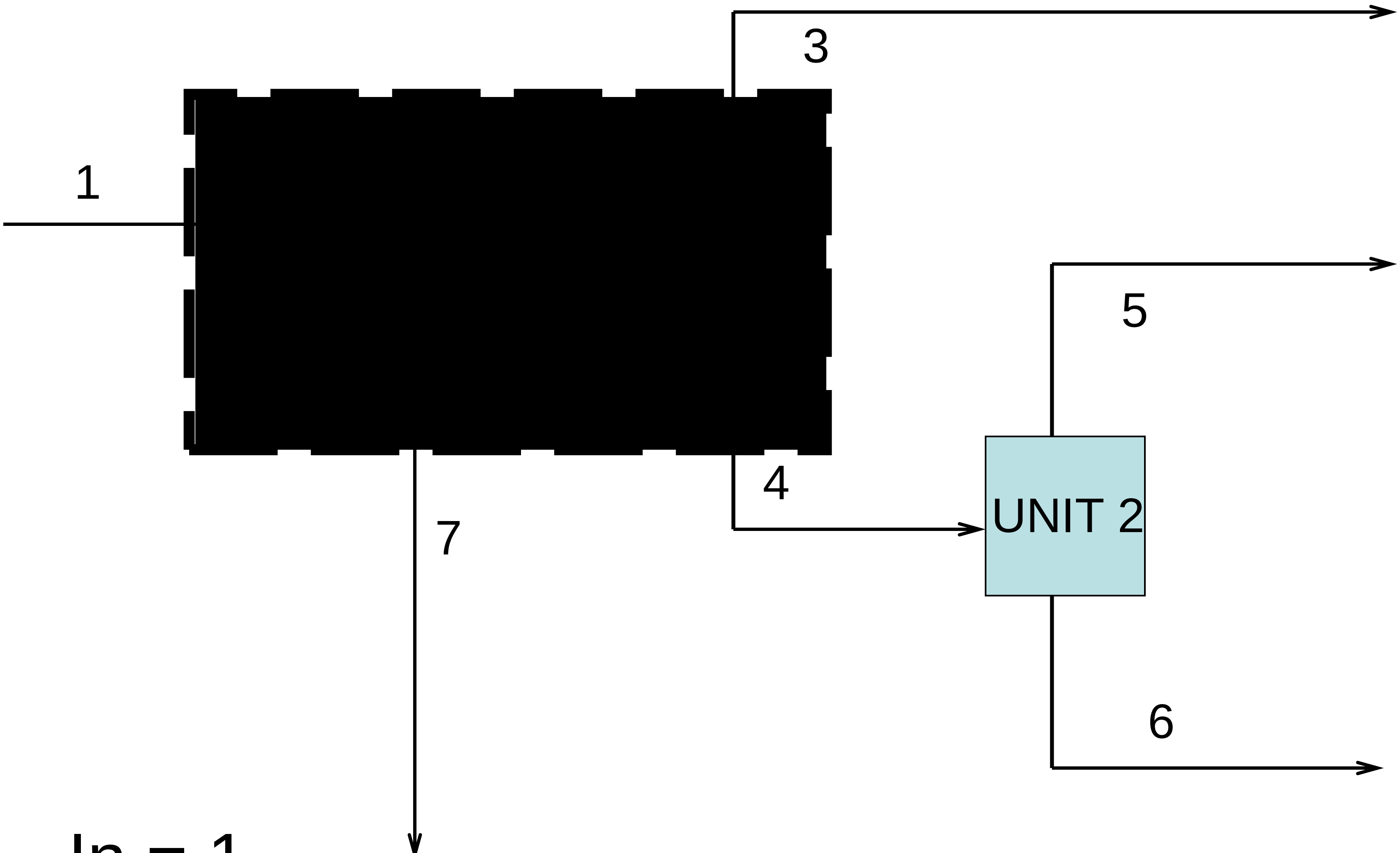
Systems:



In = 1

Out = 3 + 5 + 6 + 7

Systems:



In = 1

Out = 3 + 4 + 7

Solving Complex Processes

- Some systems may have unique solutions
- Some systems may not have unique solutions
- How do we go about deciding how to proceed?

Degree of Freedom Analysis

Variables	Equations	Unique Solution
X	$2X = 16$	$X = 8$
X	$2X + Y = 7$	$X = 2$
Y	$X + 4Y = 14$	$Y = 3$
X	$2X + Y + Z = 7$	$X = 1$
Y	$X + 4Y - 3Z = 0$	$Y = 2$
Z	$3X - Y + 5Z = 16$	$Z = 3$

Degrees of Freedom Cont’d.

- Once your system is defined and knowns & unknowns identified:
  - Count unknown variables (V)
  - Count independent eqns.
    - **Material balances (B)** on individual components or the total system, note: maximum number of eqns. Is equal to the number of chemical species for a non reactive system.
    - **Physical property eqns. (P):** (ie. relations of mass, volume, density, specific gravity etc..)
    - **Physical constraints (C):** fractions of moles or mass must add to one because they are fractions.

Degrees of Freedom Cont'd.

DF = # Unknowns - # Independent Eqns.

DF = V-B-P-C

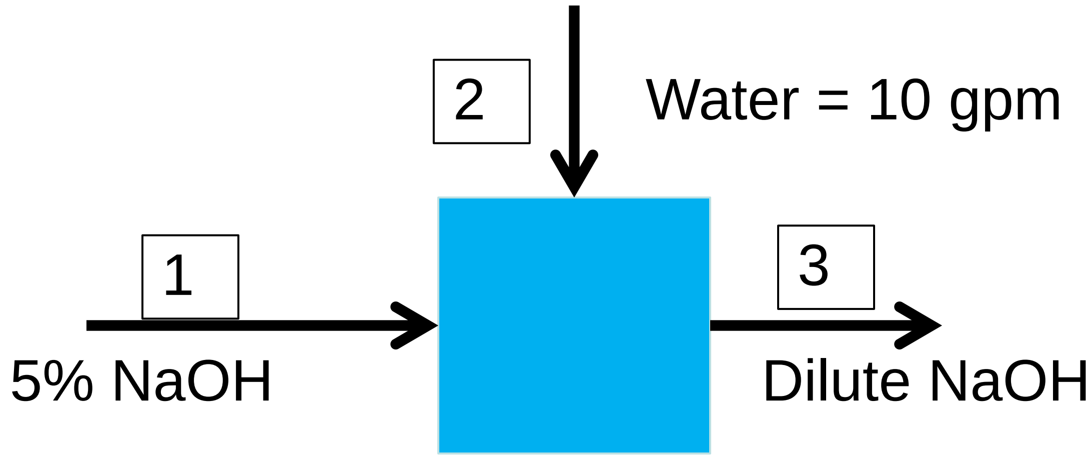
DF > 0 - underspecified problem, infinite solns.

DF = 0 - problem can be solved exactly

DF < 0 - overspecified, contains redundancy, and possibly an erroneous relationship if indeed all of your equations are "independent".

Sodium Hydroxide Example

- A 5.00% wt solution of sodium hydroxide is being diluted by a 10.0 gpm stream of pure water.
- What is the weight percent of sodium hydroxide in the stream exiting the system at 2.00×10^2 lbm/min?
- Assume steady-state conditions.



Composition	1	2	3
NaOH	0.05	0	?
Water	x1w	1	?

Mass	1	2	3
NaOH	?	0	?
Water	?	?	?
Total	?	?	200 lbm

Mass Balance	1	2	3
NaOH	0.05 * m1	0	X3n * 200
Water	0.95 * m1	83.4 lbm	X3w * 200
Total	m1	83.4 lbm	200 lbm

Variables (V) = **m1** **X3n** **X3w** **= 3**

Balances (B) = **NaOH** **Water** **= 2**

Physical Properties (P) = ρ_{water} = 8.34 lbm/gal **= 0**

Constraints (C) = **X3n + X3w = 1** **= 1**

DF = V-B-P-C = 3 - 2 - 0 - 1 = 0

System is solvable

Tips for DOF Analysis

- Solve what you can without complex algebra!
- If you have a **physical property** that allows you to calculate mass or energy, use it to eliminate a variable!

- Remember that fractions must sum to 1 **(physical constraint).** If you can solve missing fractions based on what you're given, do so! Eliminate a variable!

Summary

- Defining Systems in Complex Processes
  - Boundaries must be contiguous
  - Boundaries define what’s in and what’s out!
  - Careful selection of system boundaries can be used to solve complex problems
- Degree of Freedom Analysis
  - Determine if a unique solution is possible for the system as you have defined it.
  - The number of equations must equal or exceed the number of unknown variables