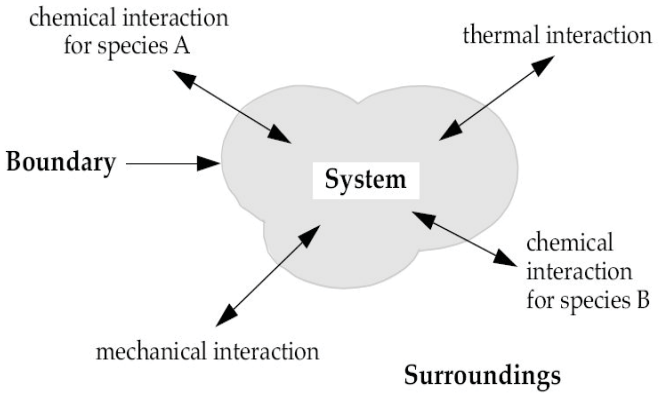
Lecture 2.1
Foundations of Properties & Processes

O'Connell & Haile
Chapter 1 & 2

Topics:

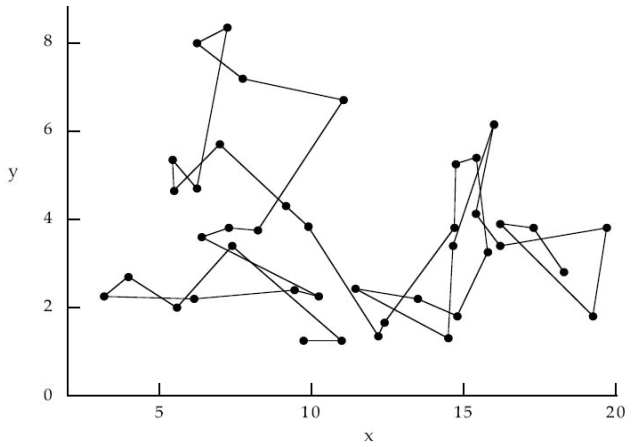
- Primitives
- Work
- 1st & 2nd Laws
- Stuff Equations

System, Surroundings, Boundary, Interactions



Molecular Level Systems

Molecular Structure: Individual, Collective Forms
Molecular Force/Energy: Inter-, intra- forms
Molecular Motion: Molecules never rest though collection of 10^{23} can have no change



PRIMITIVES

Properties - To quantify the senses. "*Variables*"
- Depend only on current condition, not history
- Macroscopic (many different)
- Microscopic (position / momentum of atoms)

Forces - Cause changes by changing coordinates
- Detected by balancing
- Conservative if $\vec{F} = -\vec{\nabla} E$, otherwise dissipative
- Mechanical if *E* in Newton's 2nd law
- Thermodynamic if $E = U \Rightarrow P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$

Equilibrium - Forces balanced -Thermostatics!
- No thermal interaction of system / all parts
- Condition stable to disturbances
  - Not steady state - Not real

State - Fix *Enough* system / boundary properties
Properties = "state functions"
Differences $\Delta F = F_2 - F_1$ independence of path
Mathematically continuous & differentiable

Extensive Properties - Depend on size(mass) of system to 1st order

Intensive Properties - Unaffected by change

Measurables - Instruments yield property values $T, P, V, \{x\}$, etc.

Conceptuals - Not directly measurable
Devised for organizing & simplifying relations
$E, H, S, A, G, \overline{G}_i, f_i$, etc.

Changes: Complicated = Thermodynamics!

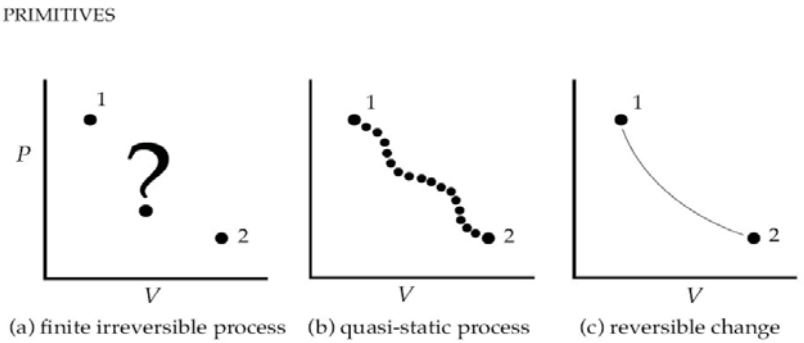
Static Limit - All forces balanced (no net force)
May be equilibrium state but not necessarily
Can occur for differential approaches

Quasistatic Process - Steps have differential net force - Not necessarily nondissipative

Reversible Change - No dissipative forces
Must have differential net force
An idealization only - not a "process"

Irreversible Process - All real processes with finite + dissipative forces

Property Changes of Systems



No intermediate "states"

Many intermediate "states"

Continuous & differentiable path of states

WORK

Work: integral of force causing coordinate change

$$W = \int \vec{F} \bullet d\vec{r}$$

Sign convention: $W > 0$ if work done ON system (in)
$W < 0$ if work done BY system (out)

Potential Energy: work to move mass in gravity (state property) (g_c converts units)

$$W_p = \int_{z_1}^{z_2} \frac{mg}{g_c} dz = \frac{Mg}{g_c}(z_2 - z_1) \equiv \Delta E_p$$

Kinetic Energy - work to change velocity

$$W_k = \int_{x_1}^{x_2} \frac{m}{g_c}\frac{du}{dt} dx = \int_{u_1}^{u_2} \frac{m}{g_c}\frac{dx}{dt} du = \frac{m}{2g_c}(u_2^2 - u_1^2) \equiv \Delta E_k$$

PV WORK

Pressure-Volume work - is <u>not</u> a state property

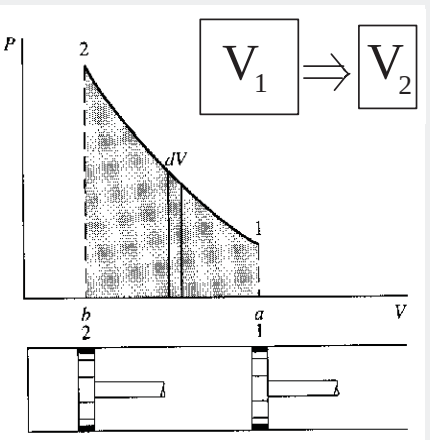
Surroundings at pressure, P_{ext}, changes boundary to give volume change

$$W = -\int_{V_1}^{V_2} P_{ext} dV$$

= area under curve

$W > 0$ for $V_2 < V_1$

$W < 0$ for $V_1 < V_2$



Examples - Piston-Cylinder Paths

Case:

a. $P_{2a} = P_1$

$W_a = P_1 (V_e - V_f)$

Areas show that

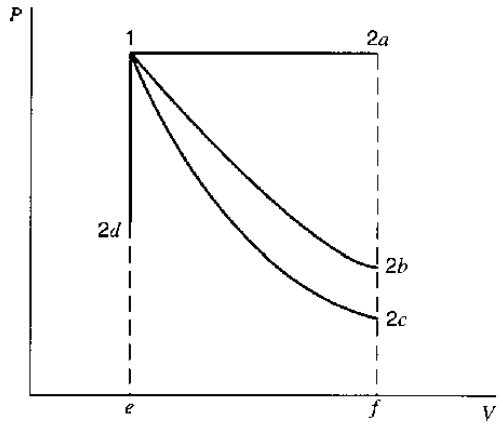
$|W_a| > |W_b| >$

$> |W_c| > |W_d|$

d. $V_1 = V_{2d}$

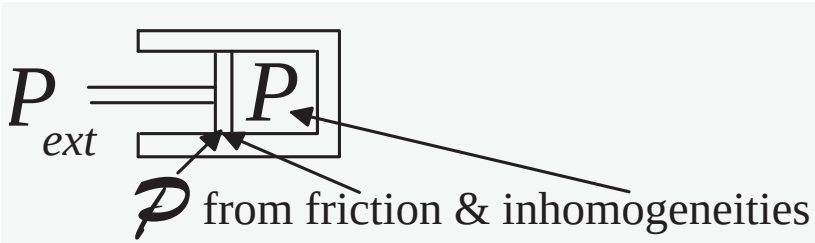
$W_d = 0$

Note: No *real* path is continuous



LOST WORK FROM DISSIPATION

Dissipative part of pressure, $\mathcal{P} \geq 0$, from difference across boundary $P_{ext} = P \pm \mathcal{P}$

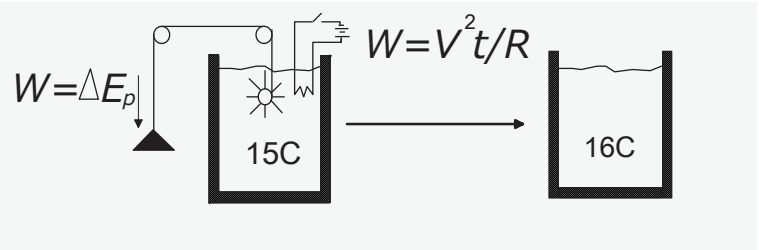


Will get "lost work" from irreversibility,

$$W_{irr} - W_{rev} \equiv W_{lost} = -\int \mathcal{P} dV \geq 0$$

ADIABATIC WORK = PROPERTY CHANGE

Joule (1840's) studied work of changing state; well-insulated(no Q, ΔE_k , Δe_p) = path *independent*



Defined internal energy, U, state property

Proved: 1. No "Caloric" (T changed but no heat)

2. Conversion factor for work units to heat units of 1 hp-h = 2547 BTU

3. Excellent thermometer needed

FIRST LAW OF THERMODYNAMICS

Adiabatic work is a change in energy

(state property) $dE \equiv \delta W_{adiabatic}$

Define ''internal energy'' associated with "thermal state" (*T,P,{x}*) not with kinetic, potential forms

$$dE \equiv dU + dE_k + dE_p$$

Heat is another form of energy change, only seen in nonadiabatic processes

$$\delta Q \equiv \delta W_{adiabatic} - \delta W_{nonadiabatic} = dE - \delta W$$

Note: for work-free process with $\Delta E_k = \Delta E_p = 0$

$$dU = \delta Q_{workfree}$$

Workfree heat is a state property!

Energy Deals with Work and Heat

''Energy'' - *Conceptual* state property dealing with path-dependent, boundary-crossing effect, *W* & *Q*

Not interested in energy itself - is an economizer

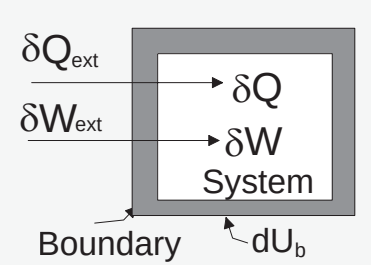
First Law connects some measurable properties to other measurables via a conceptual

Only 1 Equation! ∴Affects # independent variables

$$dE \equiv dU + dE_k + dE_p = \delta Q + \delta W$$

For system+boundary,

$$dU + dU_b = \delta Q + \delta W + dU_b$$
$$= \delta Q_{ext} + \delta W_{ext}$$



Macroscopic (Real) Changes

$$E(T_2, P_2, u_2, z_2) - E(T_1, P_1, u_1, z_1)$$
$$= [U(T_2, P_2) - U(T_1, P_1)] + [E_k(u_2) - E_k(u_1)] +$$
$$+ \left[E_p(z_2) - E_p(z_1)\right] = Q_{1\to 2} + W_{1\to 2}$$

If problem fixes,

***e.g.*, *Q*, initial state (T_1, P_1, u_1, z_1) & final state (T_2, P_2, u_2, z_2), *W* is to be found**

If problem fixes,

***e.g.*, *Q, W,* initial state (T_1, P_1, u_1, z_1) & all but one variable of final state (*e.g.*, P_2, u_2, z_2), rest of final state (*e.g.*, T_2) is to be found**

SECOND LAW

For reversible changes, system measurables give *PV* work: $\delta W_{reversible} = -PdV$

Note: $\delta W_{reversible}/(-P) = dV \Rightarrow$ ***d* (property)**

∴Work becomes state function in 2 ways:

Adiabatic Process (1st Law)

With integrating factor, 1/(-*P*)

How should $\delta Q_{reversible} \Rightarrow$ *d* (property)?

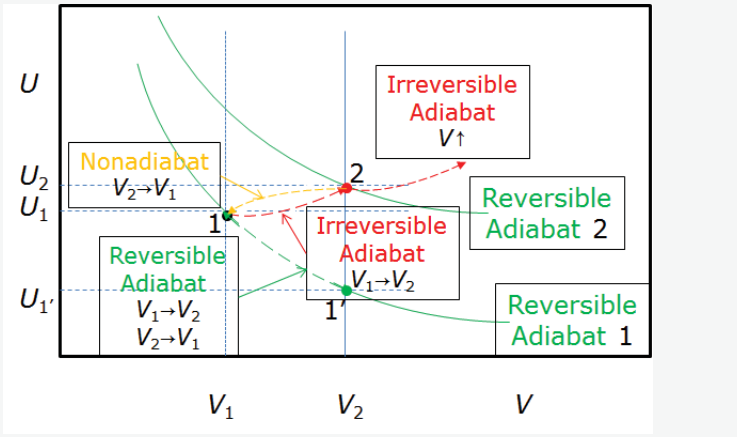
Not from work-free process state function

From integrating factor found by math analysis

HEAT, ENERGY & PROCESSES I.

Empirically, only *some* states possible to get via adiabatic processes from state (U_1,V_1) (Fig. 2.8)

As decrease dissipation, approach limit of fixed relationship, $U = U(V)$ - reversible



Energy Differences from Adiabatic Work

$$\Delta U_{rev} = -\int_{V_1}^{V_2} P dV \; < \Delta U_{irrev} = -\int_{V_1}^{V_2} P_{ext} dV$$

$$\Delta U_{irrev} - \Delta U_{rev} = -\int_{V_1}^{V_2} (P_{ext} - P) dV \; > 0$$

HEAT, ENERGY & PROCESSES II.

Mathematics (Caratheodory, 1909) says that for such a situation there is an integrating factor, λ, for the inexact differential giving, $dS \equiv \delta Q_{rev}/\lambda$

Directionality of irreversible processes as for *U*
Define *dS* > 0 for irreversible adiabats,
***dS* = 0 for reversible adiabat**
***dS* < 0 occurs only in nonadiabats**

Note: Since *S* is a property, Δ*S* found from <u>any</u> convenient process

INTEGRATING FACTOR, ENTROPY, IRREVERSIBILITY

Integrating factor found from heat transfer since heat moves from higher to lower λ
Define $\lambda \equiv T$ (absolute) & $S \equiv$ entropy

Second Law:
Defines entropy & sets its sign: $S \geq 0$
Says *S* is conserved only in reversible processes, otherwise *generated*

Equation 2.3.8 with $\delta S_{gen} \geq 0$

$$dS_{sys} + dS_{boundaries} = \delta Q_{ext}/T_{ext} + \delta S_{gen}$$

S_{gen} is <u>*not*</u> a state property but S_{sys} & $S_{boundaries}$ are

REVERSIBLE / IRREVERSIBLE HEAT & WORK I.

If change of state is same for processes

$$dU = dU_{rev} = dU_{irr}$$

$$dU = \delta Q_{rev} + \delta W_{rev} = \delta Q_{irr} + \delta W_{irr}$$

$$dS = dS_{sys} + dS_{boundaries} = \delta Q_{rev}/T = \delta Q_{irr}/T_{ext} + \delta S_{gen}$$

Left sides are property changes, but right side terms are not; for different ways of changing system state, sum on right same, terms differ

REVERSIBLE / IRREVERSIBLE HEAT & WORK II.

$$\delta W_{lost} = \delta W_{irr} - \delta W_{rev} = \delta Q_{rev} - \delta Q_{irr} \geq 0$$

Work is lost in real (irreversible) processes
Always must put in more, or get out less, real work than for reversible process

Heat effect also changed (as a *consequence*)
Always must put in less, or get out more, real heat than for reversible process

REVERSIBLE / IRREVERSIBLE HEAT & WORK III.

δS_{gen} connected to lost work & heat flow

(Eq. 2.3.10) $T\delta S_{gen} = \delta W_{lost} + (\frac{T_{ext}-T}{T_{ext}})\delta Q_{irr} \geq 0$

$\therefore$ Work, heat $\rightarrow$ contribute separately to δS_{gen}

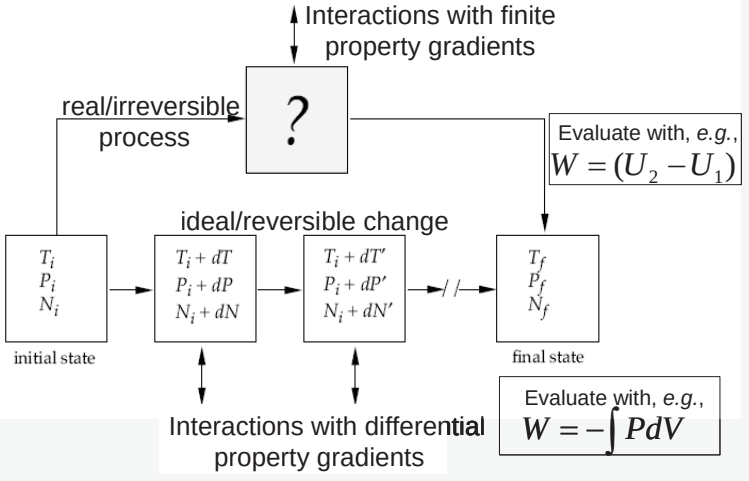
δW_{lost} from inhomogeneities, friction, (*e.g.*, $\mathscr{P}$) > 0

Signs of δQ & (T_{ext} - T) are same, term always > 0

Magnitude of δS_{gen} increases with differences in T, P, $\{x\}$, inhomogeneities, rate of process
T difference has largest impact

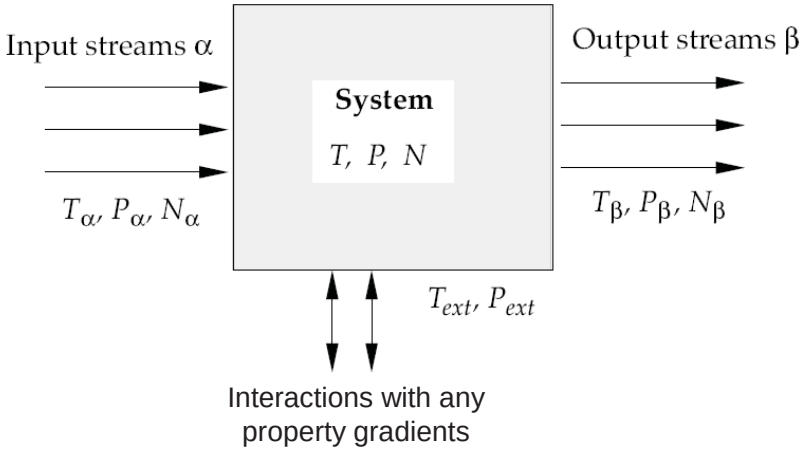
IMAGES OF PROCESSES I.

Two - Picture Processes on Closed Thermodynamic Systems

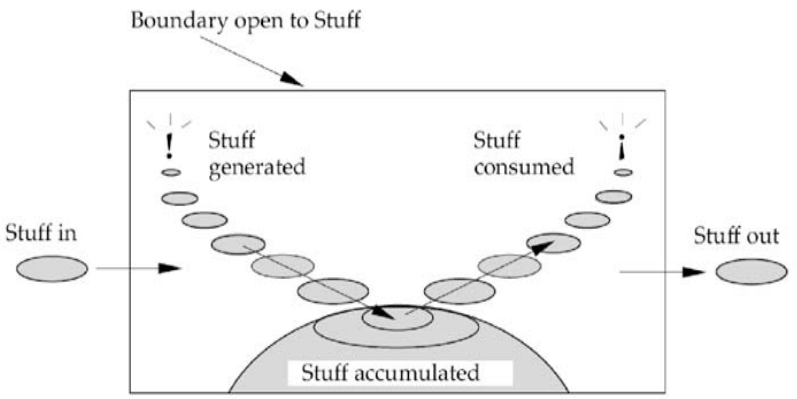


IMAGES OF PROCESSES II.

One-Picture Processes on Open Thermodynamic Systems



THE STUFF Equation



Use for open systems as a 1-picture problem

THERMODYNAMIC STUFF EQUATIONS

ALways true Forms (Differential) - From *Exterior*

Mass / Nonreacting Moles (*Conserved*) - Eq.(2.4.3)

$$dN_{sys} = \sum_{ports} dN_p = \sum_{in\ ports} dN_i - \sum_{out\ ports} dN_o$$

Energy (*Conserved*) - Eq. (2.4.10)

$$d(N_{sys}e_{sys}) + dE_{boundary} = \sum_{in\ ports}(e_i + P_i v_i)dN_i - \sum_{out\ ports}(e_o + P_o v_o)dN_o + \sum_{heat\ flows}\delta(Q_{ext})_f + \delta W_{boundary} + \delta W_{shaft}$$

Entropy (*Generated*) - Eq. (2.4.21)

$$d(N_{sys}s_{sys}) + dS_{boundary} = \sum_{in\ ports} s_i dN_i - \sum_{out\ ports} s_o dN_o + \sum_{heat\ flows}\delta\left(\frac{Q_{ext}}{T_{ext}}\right)_f + \delta S_{gen}$$

Notation

e = molar energy =

$$e = u + e_{kinetic} + e_{potential} = u + \frac{m}{Mg_c}\{\tfrac{1}{2}u_v^2 + gz\}$$

u, s = molar internal energy, entropy as, *e.g.*,

$$u_i = u(T_{in}, P_{in}, \{x\}_{in})$$

N = moles, m = mass, M = mol. wt., $N = m/M$

g_c = conv. factor(= 1 for MKS, 32.17 lb_m-ft)

u_v = velocity, z = elevation, $_{sys}$= in system, dS_{gen} in system & boundary

Cases

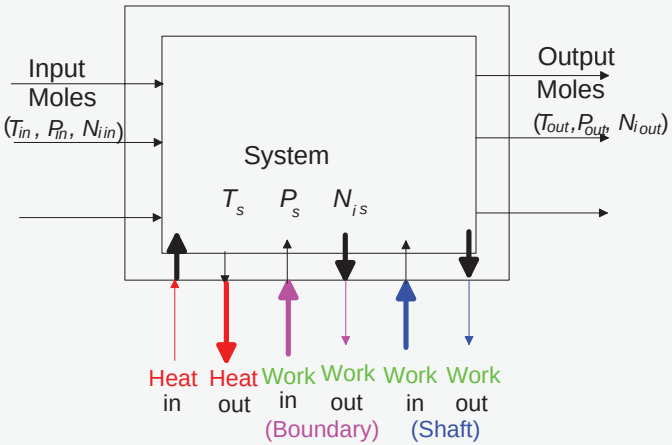
If *system closed*, $dN_i = dN_o = 0$

If *process adiabatic*, $\delta Q = 0$

If *boundaries rigid*, etc., $\delta W_{boundary} = 0$

If *process reversible*, $\delta S_{gen} = 0$

IMAGE OF STUFF EQUATIONS



INTEGRATED STUFF EQUATIONS

Fixed Environment & State of Port Streams

Mass / Nonreacting Moles (Conserved)

$$(N_{sys})_2 - (N_{sys})_1 = \sum_{in\ ports} N_i - \sum_{out\ ports} N_o$$

Energy (Conserved)

$$(N_{sys}e_{sys})_2 - (N_{sys}e_{sys})_1 + \Delta E_{boundary} = \sum_{in\ ports}(e_i + P_i v_i)N_i - \sum_{out\ ports}(e_o + P_o v_o)N_o + \sum_{heat\ flows}(Q_{ext})_f + W_{boundary} + W_{shaft}$$

Entropy (Generated)

$$(N_{sys}s_{sys})_2 - (N_{sys}s_{sys})_1 = \sum_{in\ ports} s_i N_i - \sum_{out\ ports} s_o N_o + \sum_{heat\ flows}\left(\frac{Q_{ext}}{T_{ext}}\right)_f + S_{gen}$$

CASES

For <u>steady state</u>, can use rate form, *e.g.*, $\dot{N}_i = \frac{dN_i}{dt}$

MB

$$(N_{sys})_2 - (N_{sys})_1 = 0 = (s_{sys})_2 - (s_{sys})_1 = (e_{sys})_2 - (e_{sys})_1$$

EB

$$0 = \sum_{in\ ports} \dot{N}_i - \sum_{out\ ports} \dot{N}_o$$

$$0 = \sum_{in\ ports}(e_i + P_i v_i)\,\dot{N}_i - \sum_{out\ ports}(e_o + P_o v_o)\,\dot{N}_o + \sum_{heat\ flows}(\dot{Q}_{ext})_f + \dot{W}_{boundary} + \dot{W}_{shaft}$$

NB

$$0 = \sum_{in\ ports} s_i\,\dot{N}_i - \sum_{out\ ports} s_o\,\dot{N}_o + \sum_{heat\ flows}\left(\frac{\dot{Q}_{ext}}{T_{ext}}\right)_f + \dot{S}_{gen}$$