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Mech 222
Thermodynamics

Reference Handbook

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Spring 2018

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PART I: PROBLEM SOLVING

1 PROBLEM SOLVING APPROACH

Step 0: Draw one or more diagrams

- Sketch of the physical system
- Process curve on property diagram
    - P-v, T-v, P-T, T-s...

Step 1: Identify constraints which are specific to this problem

- Givens ("External Constraints")
    - Values [record these directly on diagrams!], thermodynamic keywords
- Property Models ("Internal Constraints"), one per component:
    - Ideal Gas, Incompressible, Empirical (Tables)

    These constraints connect properties at some point to different properties at the *same* point in space and time

Step 2: Combine the problem-specific constraints with universal constraints (listed below) to relate the required back to the givens. In harder problems, you will generally have to chain several constraints together. Perform the manipulations symbolically (avoid substituting values) for as long as possible.

The universal constraints which may be applied to any problem include:

- "Canned" results which may simplify analysis:
    - The Polytropic Model Process
    - Reversible Steady-Flow Work

    These represent the combination of several constraints which are often encountered together; using the pre-calculated result instead of performing the substitution yourself provides a shortcut
- Thermodynamic Laws (and associated transport equations)
    - Conservation of Mass (Mass Transport)
    - The First Law (Energy Transport)
    - The Second Law (Entropy Transport)

    The transport equations behind these laws connect
    - changes in properties *within* the system
    - fluxes *across the boundary* of the system
    - generation *within* the system

    The engineer must identify the control volume to consider before applying a transport equation; this should be chosen so that

  ○ All property changes of interest are within the system
  ○ All fluxes of interest are across the boundary of the system
  ○ All generation of interest is within the system
  ○ The number of unknown property changes, fluxes, and generations is as small as possible
- Thermodynamic Definitions
  ○ $h = u + Pv$
  ○ Definition of thermal efficiency/coefficient of performance
  ○ Definition of isentropic efficiency
- Non-Thermodynamic Rules: $\vec{F} = m\vec{a}$ (with a Free Body Diagram!), calculus, geometry (with sketch!)...

Step 3: Substitute values *with units* and calculate an answer *with units*

- Unit errors are very common in thermo problems
  ○ They are *so* common that I had a "UNITS" stamp made for marking
- Explicitly tracking your units doesn't just help you avoid being off by a power of 10: it can sometimes help you recognize that you have the wrong formula
  ○ Suppose you were trying to find force using the [wrong] formula $\vec{F} = m\vec{v}$. If you were to plug in values, you'd get $\vec{F}$ in [kgm/s], which is not a unit of force. This would make it obvious that you had the wrong formula.

Step 4: Sanity check

- Did you answer all parts of the question?
- Is the answer appropriate?
  ○ Units [e.g. no distance in kg]
  ○ Sign [e.g. no $\Delta T < 0$ when we know the object is being heated]
  ○ Magnitude [$\Delta T = 1 \times 10^{15}$ K or $\Delta T = 1 \times 10^{-15}$ K is suspicious]

2 IDENTIFYING "GIVENS"

2.1 Interpreting Standard Keywords

1. **Heat Transfer**

   - "Insulated"
     - Unless you're told that there is heat transfer, this should be interpreted as meaning *perfectly* insulated (no heat transfer; $\sum \delta Q = 0$, $\sum \dot{Q} = 0$, $\sum Q = 0$)
     - More rarely, you're told that there is an insulating layer around a system but that heat is flowing through it. In this case, the idea is that heat flows across the system much more quickly than it flows through the insulation, and thus that the system's temperature stays very close to uniform throughout the heating/cooling process
       - This implies that the heat transfer occurring *within the system* is reversible (as it does not flow down a temperature gradient); all entropy generation is in the insulation, where heat flows down a temperature gradient
   - "Adiabatic": No heat transfer ($\sum \delta Q = 0$, $\sum \dot{Q} = 0$, $\sum Q = 0$)
   - "In a water bath": Extremely rapid heat transfer, to the point that the system T is constant (at the temperature of the water bath)

2. **Physical Restraint**

   - "Rigid" Container: V is constant ($\mathrm{d}V = 0$, $\frac{\mathrm{d}}{\mathrm{d}t}V = 0$, $\Delta V = 0$)
     - This means no boundary work can be done
   - Compressed by a piston, which is held down by its own weight, external pressure, and . . .
     - No other forces: P is constant
       - This means the boundary work integral simplifies to $\int P \, \mathrm{d}V = P \Delta V$
     - A spring: P increases linearly with V, with slope $\mathrm{d}P/\mathrm{d}V = k/A^2$, where
       - k is the spring constant
       - A is the area of the piston

3. **System-Wide Properties**

   - Speaking of "*the*" value of an intensive property (T, P, v, etc.) in some region indicates that that property is *uniform* (discussed below as its own keyword) throughout that region

4. **Time / Space Derivatives**

- "Constant" can refer to one of two ideas:
    - "Steady": constant over *time*
        - for properties, Φ: change/rate of change is *zero*

$$\mathrm{d}\Phi = 0 \qquad \frac{\mathrm{d}}{\mathrm{d}t}\Phi = 0 \qquad \Delta\Phi = 0$$

        - for fluxes, Ψ: rate of transfer is the same at all times

$$\dot{\Psi} \neq f(t)$$

    - "Uniform": constant over *space*. If this is true for all intensive properties (T, P, v, etc.), then:
        - It makes sense to assign a single T, P, v, etc. to the entire system
        - There no irreversibilities associated with gradient self-smoothing
- Non-constancy also has its own keywords:
    - "Un-Steady" / "Transient": not constant over time. This implies the negation of everything that *steady* implies
    - "Non-Uniform": not constant over space. This implies the negation of everything that *uniform* implies
- "Slow": the rate at which system properties are changed is low enough relative to the rate at which the system properties naturally equilibrate that the contents of the system are effectively at equilibrium throughout the process. This implies that:
    - The system properties are *uniform* (discussed above as its own keyword) throughout the process
    - Unless the system is *perfectly insulated* (discussed above as its own keyword), it has plenty of time to establish thermal equilibrium with its surroundings throughout the process, and thus remains at the temperature of the surroundings.

    This is a *very* common assumption in thermodynamics
- "Fast": There is no time for significant heat transfer: $\sum Q \approx 0$.
    - This does *not* imply that $\sum \dot{Q} = 0$; the idea is that $\Delta t \approx 0$, so regardless of the value of $\sum \dot{Q}$, the total heat transferred ($\sum Q = \Delta t \sum \dot{Q}$) is small.

5. **Mass Transfer**

- "Sealed" / "Closed": No mass transfer
- "Small" leak emptying/filling the system:
  - system loses/gains mass, but the process is *slow* (discussed above as its own keyword)
  - the process occurring *at and in a tiny vicinity around* the leak is irreversible (due to un-restrained expansion), but the process occurring *within the system* (far from the leak) does not have any irreversibilities associated with the spreading of gradients

6. **Reversibility**

- "Reversible": the process associated with a given system may be described as. . .
  - *Internally* Reversible, meaning that the sub-component of the process which occurs within the *system* is reversible
  - *Externally* Reversible, meaning that the sub-component of the process which occurs within the *surroundings* is reversible
  - *Totally* Reversible, meaning that the overall process is reversible. This is true if and only if the process is both internally and externally reversible
- "Frictionless" / "Inviscid": there are no irreversibilities associated with viscous friction because. . .
  - There is no friction at the wall, and thus nothing to create velocity gradients within the fluid ["frictionless" case]
  - There is no viscosity ["inviscid" case]

2.2 Standard Assumptions for Steady-Flow Devices

(1) First Law Analysis

Device	Pipe Assumption				
	1 $\Delta P = 0$	2(a) $\dot{W}_{P,\vec{g}}^{\text{fluid}\leftrightarrow\text{surr}} = 0$	2(b) $\dot{Q}^{\text{fluid}\leftrightarrow\text{surr}} = 0$	3 $\Delta\vec{v} = 0$	4 $\Delta z = 0$
Single-Stream Devices					
Pipe	✓	✓	✓	✓	✓
Throttling Valve	✗	✓	✓	✓	✓
Nozzle	✗	✓	✓	✗	✓
Diffuser	✗	✓	✓	✗	✓
Pump	✗	✗	✓	✓	✓
Compressor	✗	✗	~	✓	✓
Turbine	✗	✗	~	✓	✓
Condenser	~	✓	✗	✓	✓
Boiler/Evaporator	✓	✓	✗	✓	✓
Multi-Stream Devices					
Heat Exchanger	~	✓	✓	✓	✓
Mixing Chamber	~	✓	✓	✓	✓
Flash Evaporator	✗	✓	✓	✓	✓

✓ $\implies$ valid   ~ $\implies$ common, though not strictly valid   ✗ $\implies$ invalid

Additionally, it is standard practice to assume that all of these these devices operate *at steady state* unless it is specifically stated that they do not.

(2)   Second Law Analysis

Device	Reversible?	Reversibility requires...
Single-Stream Devices		
Pipe	✓	all pipe assumptions hold
Throttling Valve	✗	$\Delta P = 0$ (no throttling)
Nozzle	∼	$\eta_s = 1$
Diffuser	∼	$\eta_s = 1$
Pump	∼	$\eta_s = 1$
Compressor	∼	$\eta_s = 1$
Turbine	∼	$\eta_s = 1$
Condenser	∼	all heat flows down ΔT of 0; $\Delta P = 0$
Boiler/Evaporator	∼	all heat flows down ΔT of 0; $\Delta P = 0$
Multi-Stream Devices		
Heat Exchanger	∼	all heat flows down ΔT of 0; no pressure drops
Mixing Chamber	✗	mixing streams identical (no mixing); $\Delta P = 0$
Flash Evaporator	✗	$\Delta P = 0$ (no evaporation)

<div align="center">✓ ⟹ Always   ∼ ⟹ Sometimes   ✗ ⟹ Never</div>

3   SELECTING PROPERTY MODELS

The three property models used in Mech 2 Thermodynamics are:

1. **Ideal Gas**

   Appropriate for:

   - Any gas at $T_R \equiv \frac{T}{T_{\text{crit}}} \gtrsim 2$ and $P_R \equiv \frac{P}{P_{\text{crit}}} \lesssim 0.8$
   - Air, N_2, O_2, CO_2, CO, He, He, Ar at all but the most extreme conditions
   - Water vapour in the atmosphere (Mech 327)

   Inappropriate for:

   - Any two-phase mixture
   - Steam in industrial processes
   - Refrigerants (R-12, R-134a)

2. **Incompressible**

   Appropriate for:

   - Liquids at all but the most extreme conditions
   - Solids at all but the most extreme conditions

   Inappropriate for:

   - Anything else

3. **Empirical (Property Tables)**

   Appropriate for anything in range, but only necessary for:

   - Saturated Mixtures
   - Vapours/Gases which aren't ideal

   Note that tables are *not* the best approach for liquids; assuming incompressibility is faster and introduces negligible error
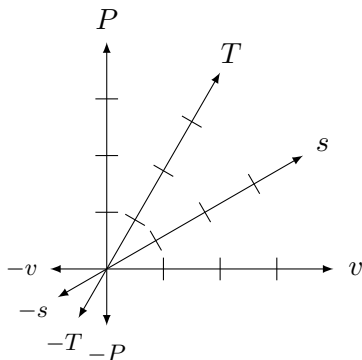
PART II: PROPERTIES OF SUBSTANCES

4 PROPERTY DIAGRAMS

4.1 Relative alignment of T, s, P, and v axes

For any two-dimensional diagram in which the axes are two of (T, s, P, v), the relative alignment of those four property axes is represented by the "P-T-s-v rosette":

Potential Initialisms	
Post	**P**rince
Thermodynamic	**T**iberius
Stress	**S**neezed
Visorder (??)	**V**iolently
Please	**P**iss
Take	**T**astes
Some	**S**omewhat
Venom	**V**ile

...with the following caveats:

- In two-phase regions, the T and P axes become parallel

- (*Beyond scope of course*) At states where constant-pressure heating would cause *contraction*, the T and s axes are both mirrored through the origin. This includes:
  - Single-phase states with negative coefficients of thermal expansion (e.g., liquid water at $P = 1\,\text{atm}$ and $T < 3.98\,°\text{C}$)
  - Two-phase states corresponding to a "quirky" phase equilibrium, for which heat addition leads to contraction (e.g. at familiar pressures, water's solid-liquid equilibrium is "quirky" because melting *increases* density)

A rough version of any two-axes property diagram can be created as follows:

1. Shear the "P-T-s-v rosette" until the axes of interest are aligned horizontally and vertically (shear transformations preserve the ordering of the axes)

2. Erase the other two axes, but do not erase their cross-lines; instead, extend them to mark iso-lines of the two other properties

This rough version will correctly illustrate how the slopes of the two iso-lines compare

- To *zero* (i.e., whether they slope upwards or downwards)

- To *one another* (i.e., which one slopes more steeply)

...but will *not* include fine details such as how the iso-lines curve over the diagram.

4.2   *P-v Diagrams*

On a P-v Diagram,

- Isotherms and isentropes always have non-positive slopes

  - Isotherms have negative slopes except under the vapour dome, where they have slopes of zero
  - Isentropes always have negative slopes

- At each point, the local isentrope has a more negative slope than the local isotherm

- The area below/left of the process curve has physical significance in some cases:

  - **Closed System:** area below curve, $\int P \mathrm{d}v$, is the (outward) specific boundary work (see Section 8)
  - **Open System, Steady, Internally Reversible Process:** area left of curve, $\int v \mathrm{d}P$ is a component of the net (outward) specific work (see Section 14)

An example P-v diagram, for water, is presented below:
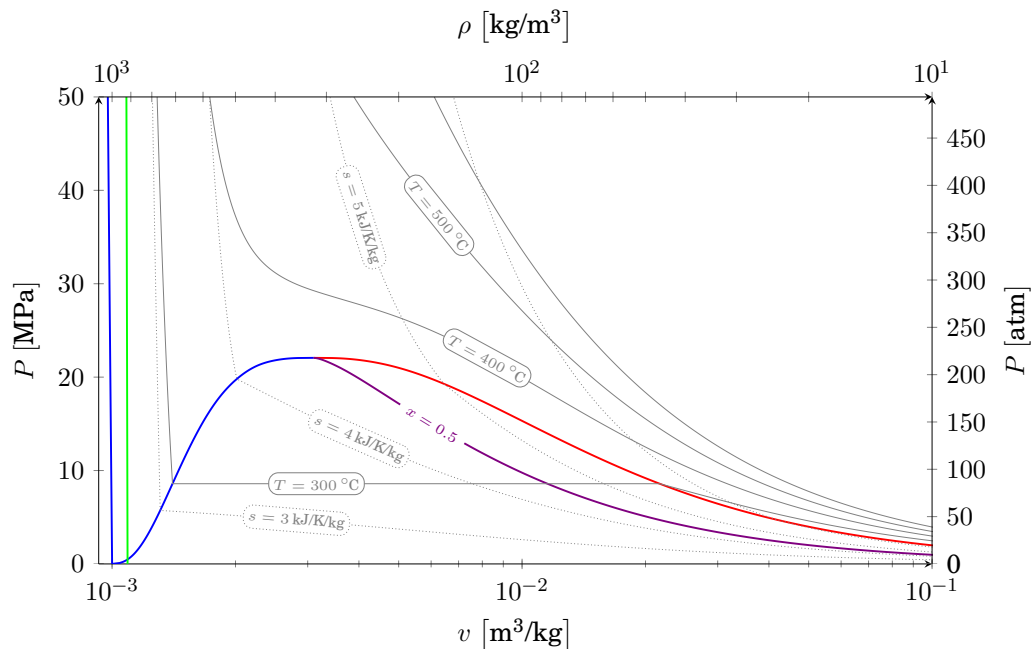
4.3 T-s Diagrams

On a T-s Diagram,

- Isochors and isobars always have non-negative slopes

  ○ Isochors always have positive slopes
  ○ Isochors have positive slopes except under the vapour dome, where they have slopes of zero

- At each point, the local isochor has a more positive slope than the local isobar

- The area under a process curve, $\int T \mathrm{d}s$, has physical significance in some cases:

  ○ **Closed System, Internally Reversible Process:**

  $$Q_{\text{in}}^{\text{net}} = m \int_1^2 T \, \mathrm{d}s$$

  ○ **Open System, Steady, Internally Reversible Process:**

  $$\dot{Q}_{\text{in}}^{\text{net}} = \dot{m} \int_{\text{in}}^{\text{out}} T \, \mathrm{d}s$$

An example T-s diagram, for water, is presented below:
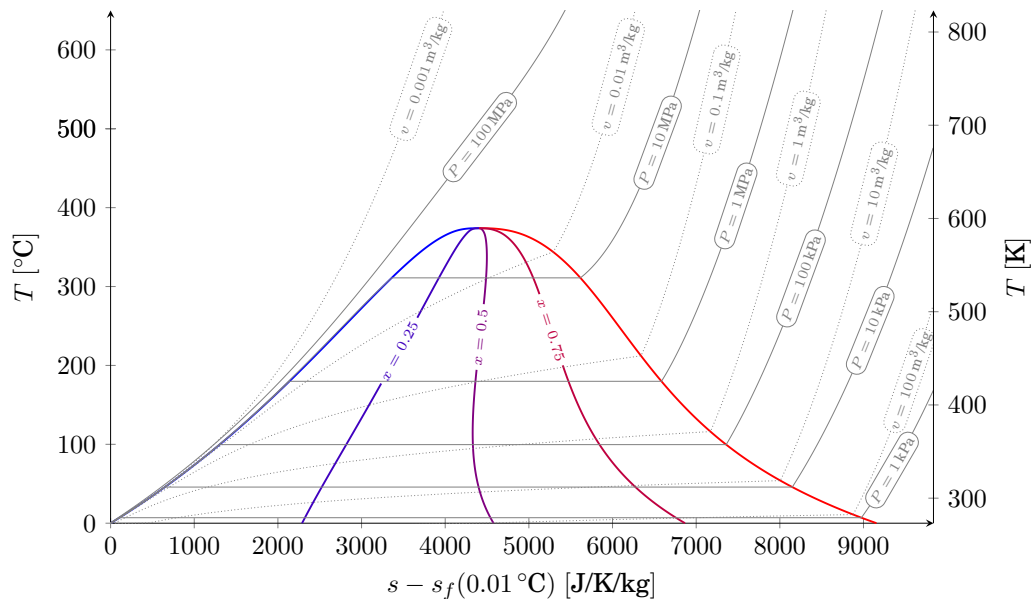
5   PROPERTY EVALUATION

5.1   State, Extent, and Degrees of Freedom (Gibbs' Phase Rule)

We can separate the qualities of a system into three distinct categories:

1. **Kinematic State:** position and its time derivatives (velocity, acceleration...)

2. **Extent:** size (typically quantified by mass)

3. **Thermodynamic State:** everything else (temperature, pressure, density... any intensive property)

   $\implies$ Samples have the same thermodynamic state *if and only if* (after discarding information about the kinematic state and the extent) there is no test which can differentiate between them

Gibbs' Phase Rule postulates that, for a system which

- contains a fixed number of independent chemical components, C ($C \geq 1$)

- is at equilibrium

The total number of degrees of freedom (independent variables) required to define the extent and the thermodynamic state is always the same, but the way that those degreees of freedom are partitioned between the state and the extent varies with the number of phases, to wit:

$$\overbrace{\underbrace{S}_{\substack{\text{DoF} \\ \text{in} \\ \text{state}}} + \underbrace{X}_{\substack{\text{DoF} \\ \text{in} \\ \text{extent} \\ \underbrace{= P}_{\text{Phases}}}}}^{\overbrace{N}^{\substack{\text{Total} \\ \text{DoF}}}} = \underbrace{C}_{\substack{\text{Indep.} \\ \text{chem} \\ \text{comp.}}} + 2$$

5.2   Identifying the Appropriate Approximation
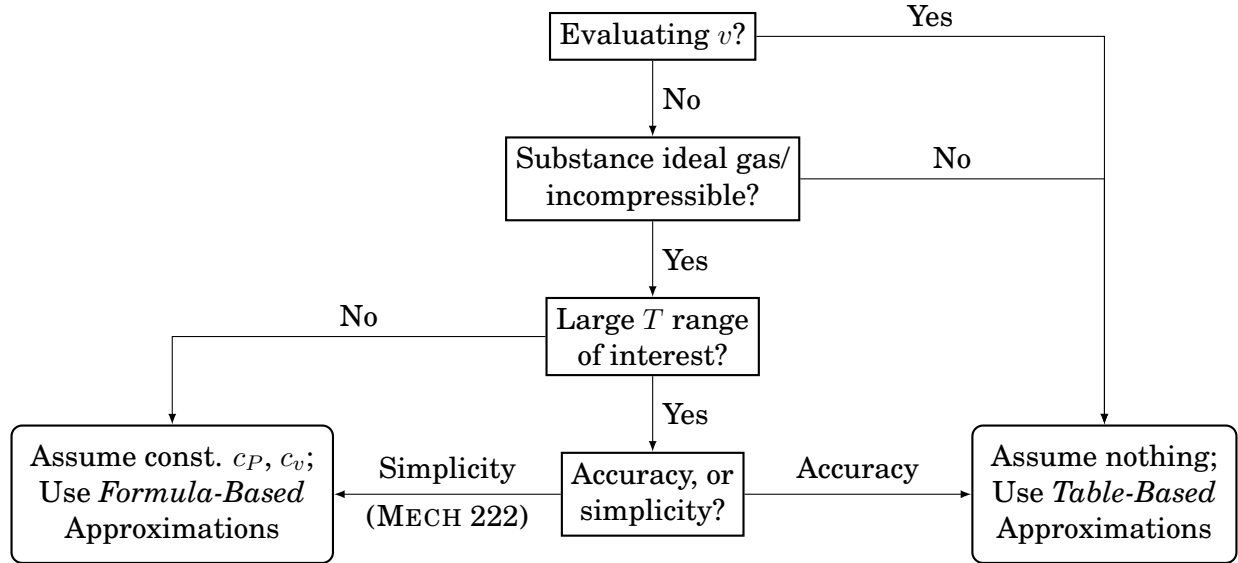
5.3   Formula-Based Approximations for Property Changes

Phase	Identities	Δu	Δh	Δs
			Constant-(c_P, c_v) approximation of...	
Incompressible Solid / Liquid	$c_P = c_v \equiv c$	$c\Delta T$	$c\Delta T + v\Delta P$ (often $\approx c\Delta T)^\dagger$	$c\ln\left(\dfrac{T_2^*}{T_1^*}\right)$
Ideal Gas	$c_P = c_v + R$	$c_v\Delta T$	$c_P\Delta T$	$c_P\ln\left(\dfrac{T_2^*}{T_1^*}\right) - R\ln\left(\dfrac{P_2^*}{P_1^*}\right)$ or $c_v\ln\left(\dfrac{T_2^*}{T_1^*}\right) + R\ln\left(\dfrac{v_2}{v_1}\right)$ or $c_v\ln\left(\dfrac{P_2^*}{P_1^*}\right) + c_P\ln\left(\dfrac{v_2}{v_1}\right)$

* The superscript in T^* or P^* indicates that an *absolute* scale must be used

† The approximation $\Delta h \approx c\Delta T$ is generally valid unless ΔP is much larger relative to the scale of everyday processes than ΔT is (which typically only comes up when $\Delta T = 0$ and $\Delta P \neq 0$)

5.4 Table-Based Approximations

Phase	v	$(u - u_{\text{ref}})$	$(h - h_{\text{ref}})$	$(s - s_{\text{ref}})$
Liquid	$v(P,T)$ or † $v_f(T)^\ddagger$	$u(P,T)$ or † $u_f(T)$	$h(P,T)$ or † $v_f(T)^\ddagger \cdot (P - P_{\text{sat}}(T)) + h_f(T)$	$s(P,T)$ or † $s_f(T)$
Saturated Mixture	$\phi_f(T \text{ or } P) + x \cdot \phi_{fg}(T \text{ or } P)$ (where ϕ represents v, u, h, or s)			
Vapour (Non-Ideal Gas)	$\phi(P,T)$ (where ϕ represents v, u, h, or s)			
[Ideal] Gas	$\dfrac{RT^*}{P^*}$	$u(T)$	$h(T)$	$s^\circ(T) - R\ln\left(\dfrac{P^*}{P^*_{\text{ref}}}\right)^{\S}$

* The superscript in T^* or P^* indicates indicates that an *absolute* scale must be used

† The first option is more precise, but requires interpolation in a compressed solid/compressed liquid table, which may be unavailable or sparsely populated. The second approximation is generally acceptable; the implied assumption is that the substance is *incompressible*, i.e., that all properties are independent of P

‡ Although the T used when evaluating $v_f(T)$ should nominally be the system T, v is very close to constant for a solid or liquid, so using a nearby T instead of the precise T often introduces a negligible error

§ The user is free to choose the reference pressure; entropy values then become relative to the T_{ref} satisfying $s^\circ(T_{\text{ref}}) = 0$ and the chosen reference pressure. Tables which present s° may label it as "entropy at [pressure]"; *even when this is the case*, the remains user remains free to select another reference pressure.

PART III: THERMODYNAMIC LAWS

6 NOTATION

6.1 Properties vs. Fluxes

A notational distinction is made between properties (such as internal energy and temperature), which are not path-dependent, and fluxes (such as heat, work, and mass transfer[1]) which are path-dependent. Sources (such as entropy generation) can be considered as a form of flux (flux *to* the system *from* nowhere).

	Properties, Φ	Fluxes, X
Differential	$\mathrm{d}\Phi$ (Small change in Φ)	δX (A little bit of X)
Time Derivative	$\dfrac{\mathrm{d}}{\mathrm{d}t}\Phi$ (Rate of change in Φ)	$\dot{X} = \dfrac{\delta X}{\mathrm{d}t}$ (Rate of transfer of X)
Integral	$\displaystyle\int_1^2 \mathrm{d}\Phi = \Delta\Phi$ (Total change is sum of Infinitesimal changes) • Path-independent • Potential function Φ	$\displaystyle\int_1^2 \delta X = X$ (Total transfer is sum of Infinitesimal transfers) • Path-dependent • No potential function

---

[1]*System* mass m_{syst} is a property, but mass transfer in or out ($\delta m_{\mathrm{in/out}}$, $\dot{m}_{\mathrm{in/out}}$) is a flux

6.2   Subscripts

- Index i labels heat fluxes; T_i represents the temperature of the boundary that heat flux i crosses (if T is uniform, this is just the system temperature T)

- Index j labels work interactions

- Index k labels streams; for some intensive property ϕ, ϕ_k represents the ϕ of the matter entering/leaving in stream k

6.3   Sign Conventions for Fluxes

- Heat transfer terms ($\delta Q_i, \dot{Q}_i, Q_i$) are positive if inward and negative if outward

- Work terms ($\delta W_j, \dot{W}_j, W_j$) are positive if outward and negative if inward

- Mass transfer terms ($\delta m_k, \dot{m}_k$) are positive if inward and negative if outward

6.4   Summation

- $\sum_i$ denotes the sum over all heat fluxes

- $\sum_{j \neq P, \vec{g}}$ denotes the sum over all work interactions *except* those associated with pressure and gravity

- $\sum_k$ denotes the sum over all streams

In all cases, inward and outward fluxes are counted in the same sum; direction is accounted for via sign conventions.

7　CONSERVATION OF MASS

7.1　Mass Balance

(1)　Differential Form

$$\overbrace{\mathrm{d}m}^{\substack{\text{Local}\\\text{Change}}} = \sum_k \overbrace{\delta m_k}^{\text{Advection}}$$

(2)　Rate Form

$$\frac{\mathrm{d}}{\mathrm{d}t}m = \sum_k \dot{m}_k$$

(3)　Integrated Form

$$\Delta m = \sum_k \int \delta m_k$$

7.2　Law vs. Transport Equation

Conservation of Mass states that the source term in the mass balance is zero. This has already been accounted for in the transport equations above; we can therefore view the Mass Balance as a statement of Conservation of Mass, and often conflate the two.

8   THE FIRST LAW

8.1   Energy Balance

Defining the of specific flow energy of stream k as

$$\theta_k \equiv \underbrace{u_k + P_k v_k}_{h_k} + ke_k + pe_k$$

where, for each intensive property ϕ, ϕ_k represents the ϕ of the matter entering/leaving in stream k, the energy balance can be written in three forms:

(1)   Differential Form

$$\underbrace{\mathrm{d}(U + KE + PE)}_{\text{Local Change}} = \sum_i \overbrace{\delta Q_i}^{\text{Heat}} - \sum_{j \neq P, \vec{g}} \overbrace{\delta W_j}^{\substack{\text{Work against} \\ \text{forces other} \\ \text{than pressure} \\ \text{and gravity}}} - \overbrace{P \ \mathrm{d}V}^{\substack{\text{Boundary} \\ \text{Work}}} + \sum_k \overbrace{\delta m_k \theta_k}^{\substack{\text{Advection and} \\ \text{Flow Work}}}$$

(2)   Rate Form

$$\frac{\mathrm{d}}{\mathrm{d}t}(U + KE + PE) = \sum_i \dot{Q}_i - \sum_{j \neq P, \vec{g}} \dot{W}_j - P\frac{\mathrm{d}}{\mathrm{d}t}V + \sum_k \dot{m}_k \theta_k$$

(3)   Integrated Form

$$\Delta(U + KE + PE) = \sum_i Q_i - \sum_{j \neq P, \vec{g}} W_j - \int P \ \mathrm{d}V + \sum_k \int \delta m_k \theta_k$$

8.2   Law vs. Transport Equation

The First Law states that the source term in the energy balance is zero. This has already been accounted for in the transport equations above; we can therefore view the Energy Balance as a statement of The First Law, and often conflate the two.

9 THE SECOND LAW

9.1 Entropy Balance

Letting T_i represent the temperature of the boundary across which heat flux i is flowing and s_k represent the specific entropy of the matter entering/leaving in stream k, the entropy balance can be written in three forms:

(1) Differential Form

$$\overbrace{\mathrm{d}\mathbb{S}}^{\substack{\text{Local}\\\text{Change}}} = \sum_i \overbrace{\frac{\delta Q_i}{T_i}}^{\substack{\text{Transport}\\\text{by Heat}}} + \sum_k \overbrace{\delta m_k s_k}^{\text{Advection}} + \overbrace{\delta \mathbb{S}_{\text{gen}}}^{\substack{\text{Local}\\\text{Source}}}$$

(2) Rate Form

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{S} = \sum_i \frac{\dot{Q}_i}{T_i} + \sum_k \dot{m}_k s_k + \dot{\mathbb{S}}_{\text{gen}}$$

(3) Integrated Form

$$\Delta \mathbb{S} = \sum_i \int \frac{\delta Q_i}{T_i} + \sum_k \int \delta m_k s_k + \mathbb{S}_{\text{gen}}$$

9.2 Law vs. Transport Equation

The Second Law implies that the source term in the entropy balance is *non-negative* for any real process. This *in*equality condition has not been (and could not be) incorporated into the transport equations above, so the Entropy Balance and the Second Law are distinct entities. This contrasts with Conservation of Mass and the First Law, where the *equality* conditions that the laws place upon the source terms are routinely incorporated into the associated transport equations, and thus the resulting transport equations are often conflated with the corresponding laws (see Sections 7.2 and 8.2).

9.3 Fundamental Irreversibilities

The following processes only occur in the forward direction in nature:

1. Gradient self-smoothing

   $\Rightarrow$ • T gradients spontaneously even out by heat transfer

   $\Rightarrow$ • P gradients spontaneously even out by un-restrained expansion (expansion during which forces are imbalanced)

   • $\vec{v}$ gradients in fluids spontaneously even out due to viscous friction

   • Concentration gradients spontaneously even out by diffusion

2. Micro-scale (point-wise) conversion of work/non-thermal energy into heat/thermal energy

   $\Rightarrow$ • Friction (can also be viewed as self-smoothing of a $\vec{v}$ gradient)

   $\Rightarrow$ • Electrical resistance

3. Metastable $\rightarrow$ stable state transitions

   • Phase Disequilibrium $\rightarrow$ Phase Equilibrium

     ○ Includes: boiling of a *superheated* liquid, precipitation of solute from a *supersaturated* solution

     ○ But not: boiling of a *saturated* liquid, precipitation of solute from a *saturated* solution

   • Chemical Disequilibrium $\rightarrow$ Chemical Equilibrium

     ○ Includes: combustion, cellular respiration

     ○ But not: reactions in ideal fuel cells or batteries, slow shifts in chemical equilibrium

Items marked with "$\Rightarrow$" are those encountered in Mech 2 Thermodynamics.

9.4   The Second Law in Tabular Form

For a thermodynamic system undergoing an arbitrary process, *all statements in the same column are equivalent.*

Criterion	Process Category		
	Irreversible/ Spontaneous	Reversible	Impossible by Second Law
Spontaneous Direction	Forwards	Neither (rate 0)	Backwards
Fundamental Irreversibilities	Present	Not Present	Reversed
Entropy Generation	$(+)$	0	$(-)$
Equilibrium?	Approaching	At	Departing from
Reversed Process	Impossible	Reversible	Irreversible

Note that Spontaneous and Irreversible evoke different emotions, but literally mean *the same thing*:

- Spontaneous: positive vibes (this happens on its own!)

- Irreversible: negative vibes (the reverse process is impossible!)

PART IV: THERMODYNAMIC DEFINITIONS

10 DERIVED PROPERTIES

10.1 Enthalpy

$$h \equiv u + Pv$$

10.2 Specific Heats

(1) Specific Heat at Constant Pressure

$$c_P \equiv \left(\frac{\partial h}{\partial T} \right)_P$$

(2) Specific Heat at Constant Volume

$$c_v \equiv \left(\frac{\partial u}{\partial T} \right)_v$$

(3) Specific Heat Ratio

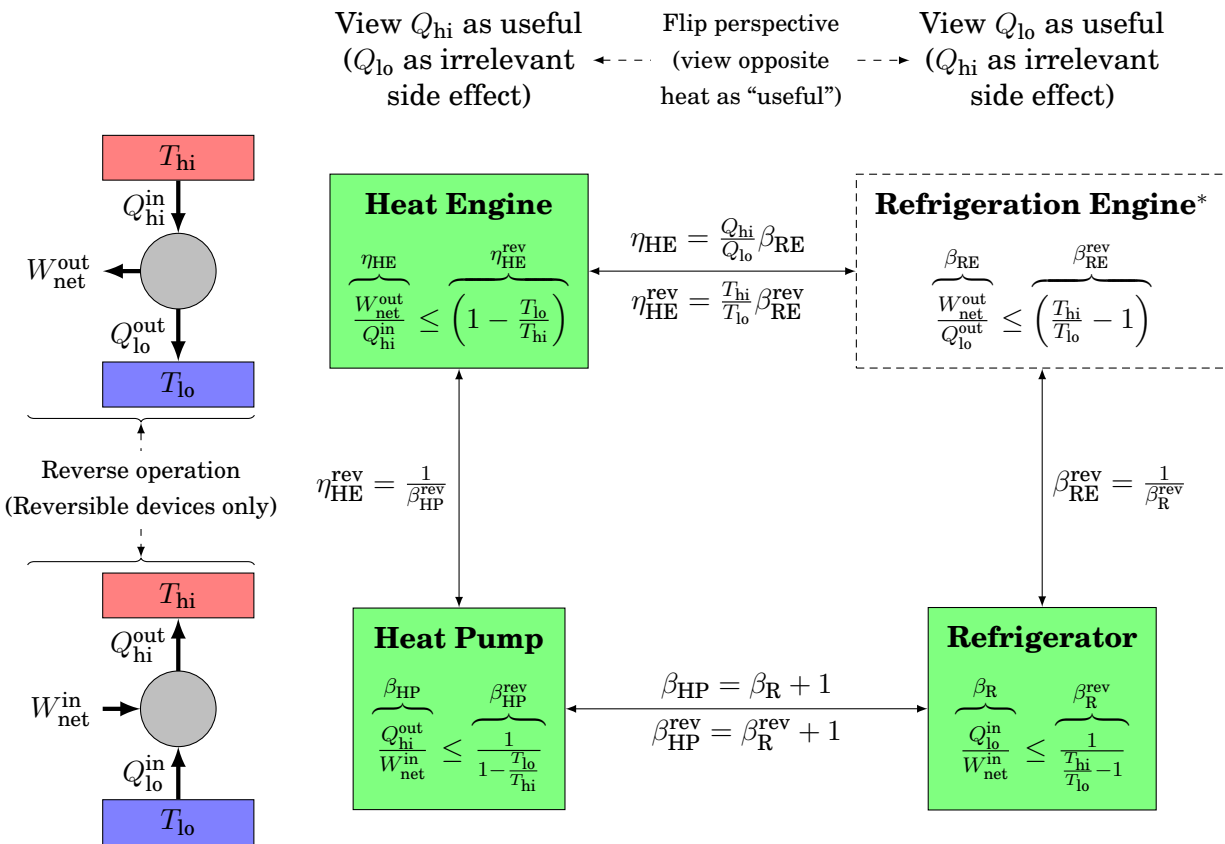$$\gamma \equiv \frac{c_P}{c_v}$$

11　CONVERSION COEFFICIENTS

11.1　General Concept

For a device which accepts heat or work and converts it into a different form of heat or work, the conversion coefficient is defined as

$$\frac{\text{Useful Output}}{\text{Required Input}} \equiv \begin{cases} \text{Thermal Efficiency}, \eta & \text{(Heat Engines)} \\ \text{Coefficient of Performance}, \beta & \text{(Heat Pumps, Refrigerators)} \end{cases}$$

Note that the maximum possible value of the quotient is dictated by the Second Law, and may be greater than, less than, or equal to $100\,\%$.

11.2　Heat Engines, Heat Pumps, and Refrigerators

View Q_{hi} as useful (Q_{lo} as irrelevant side effect) ← - - Flip perspective (view opposite heat as "useful") - - → View Q_{lo} as useful (Q_{hi} as irrelevant side effect)

Heat Engine

$$\underbrace{\frac{W^{\text{out}}_{\text{net}}}{Q^{\text{in}}_{\text{hi}}}}_{\eta_{\text{HE}}} \leq \underbrace{\left(1 - \frac{T_{\text{lo}}}{T_{\text{hi}}}\right)}_{\eta^{\text{rev}}_{\text{HE}}}$$

$$\eta_{\text{HE}} = \frac{Q_{\text{hi}}}{Q_{\text{lo}}} \beta_{\text{RE}}$$
$$\eta^{\text{rev}}_{\text{HE}} = \frac{T_{\text{hi}}}{T_{\text{lo}}} \beta^{\text{rev}}_{\text{RE}}$$

Refrigeration Engine[*]

$$\underbrace{\frac{W^{\text{out}}_{\text{net}}}{Q^{\text{out}}_{\text{lo}}}}_{\beta_{\text{RE}}} \leq \underbrace{\left(\frac{T_{\text{hi}}}{T_{\text{lo}}} - 1\right)}_{\beta^{\text{rev}}_{\text{RE}}}$$

$$\eta^{\text{rev}}_{\text{HE}} = \frac{1}{\beta^{\text{rev}}_{\text{HP}}}$$

$$\beta^{\text{rev}}_{\text{RE}} = \frac{1}{\beta^{\text{rev}}_{\text{R}}}$$

Reverse operation (Reversible devices only)

Heat Pump

$$\underbrace{\frac{Q^{\text{out}}_{\text{hi}}}{W^{\text{in}}_{\text{net}}}}_{\beta_{\text{HP}}} \leq \underbrace{\frac{1}{1 - \frac{T_{\text{lo}}}{T_{\text{hi}}}}}_{\beta^{\text{rev}}_{\text{HP}}}$$

$$\beta_{\text{HP}} = \beta_{\text{R}} + 1$$
$$\beta^{\text{rev}}_{\text{HP}} = \beta^{\text{rev}}_{\text{R}} + 1$$

Refrigerator

$$\underbrace{\frac{Q^{\text{in}}_{\text{lo}}}{W^{\text{in}}_{\text{net}}}}_{\beta_{\text{R}}} \leq \underbrace{\frac{1}{\frac{T_{\text{hi}}}{T_{\text{lo}}} - 1}}_{\beta^{\text{rev}}_{\text{R}}}$$

Left-side reservoir diagram: T_{hi}, $Q^{\text{in}}_{\text{hi}}$, $W^{\text{out}}_{\text{net}}$, $Q^{\text{out}}_{\text{lo}}$, T_{lo}; reversed: T_{hi}, $Q^{\text{out}}_{\text{hi}}$, $W^{\text{in}}_{\text{net}}$, $Q^{\text{in}}_{\text{lo}}$, T_{lo}.

[*] The concept of a "Refrigeration Engine" is non-standard; it is included here to complete patterns only

12   ISENTROPIC EFFICIENCY

12.1   Applicability

The isentropic efficiency is defined for

- Pumps

- Compressors

- Turbines

- Nozzles

- Diffusers

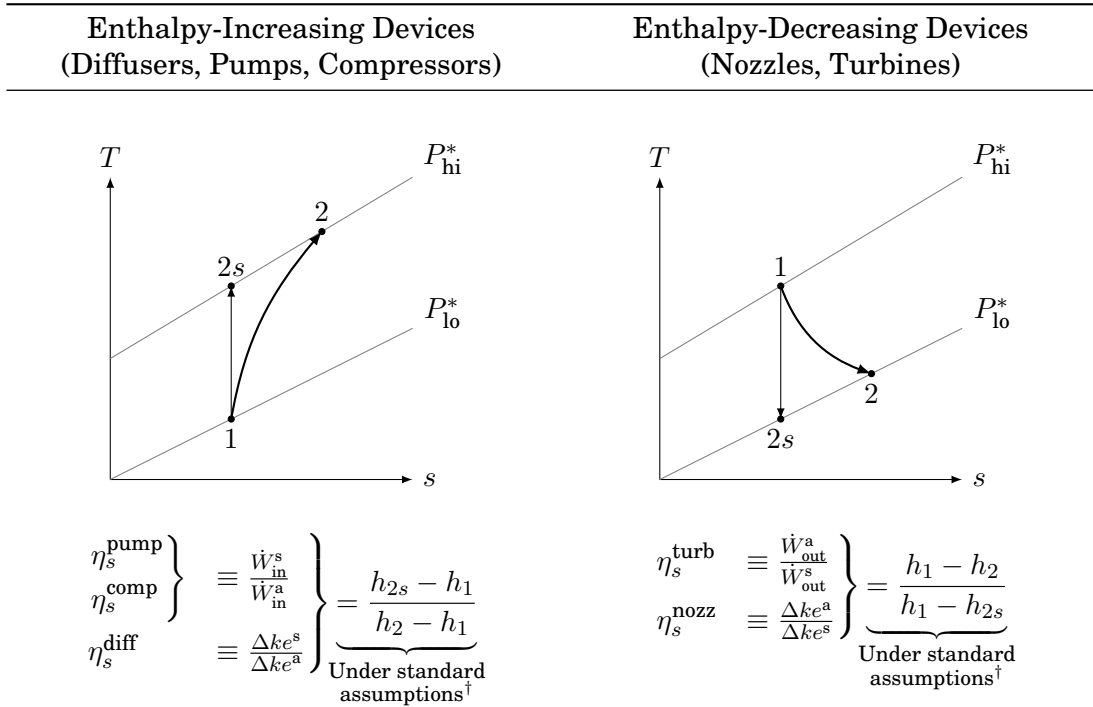which operate *adiabatically* and at *steady state*.

12.2   Notation

Given a real process 1–2. . .

- Label the real process 1–2 as process "a" ("actual")

- Define a new state $2s$ such that $P_{2s} = P_2$ and $s_{2s} = s_1$

- Label reference process 1–$2s$ as process "s" ("constant s," i.e., isentropic)

It is generally convenient to visualize the states and processes using a T-s diagram.

12.3 Diagrams and Formulae

Enthalpy-Increasing Devices (Diffusers, Pumps, Compressors)	Enthalpy-Decreasing Devices (Nozzles, Turbines)

$$\left.\begin{array}{c}\eta_s^{\text{pump}} \\ \eta_s^{\text{comp}}\end{array}\right\} \equiv \dfrac{\dot{W}_{\text{in}}^{\text{s}}}{\dot{W}_{\text{in}}^{\text{a}}} \left.\begin{array}{c}\\ \\ \end{array}\right\}$$

$$\eta_s^{\text{diff}} \equiv \dfrac{\Delta ke^{\text{s}}}{\Delta ke^{\text{a}}} \left.\right\} = \underbrace{\dfrac{h_{2s} - h_1}{h_2 - h_1}}_{\substack{\text{Under standard} \\ \text{assumptions}^{\dagger}}}$$

$$\eta_s^{\text{turb}} \equiv \dfrac{\dot{W}_{\text{out}}^{\text{a}}}{\dot{W}_{\text{out}}^{\text{s}}}$$

$$\eta_s^{\text{nozz}} \equiv \dfrac{\Delta ke^{\text{a}}}{\Delta ke^{\text{s}}} \left.\right\} = \underbrace{\dfrac{h_1 - h_2}{h_1 - h_{2s}}}_{\substack{\text{Under standard} \\ \text{assumptions}^{\dagger}}}$$

[*] The illustrated isobars do not cross the vapour dome; if the relevant isobars *do* cross the dome, they run perfectly horizontally while under it

[†] Listed in Section 2.2. The isentropic efficiency of nozzles can also be defined as $ke_{\text{out}}^{\text{a}}/ke_{\text{out}}^{\text{s}}$; this is essentially equivalent to the definition above so long as $ke_1 \ll (ke_2, ke_{2s})$

12.4 Typical Values

- For devices which have moving parts (compressors, pumps, turbines): $70\,\% \lesssim \eta_s \lesssim 88\,\%$ (typically higher for larger devices)

- For devices which do not have moving parts (diffusers, nozzles): $90\,\% \lesssim \eta_s \lesssim 97\,\%$

13   THE POLYTROPIC MODEL PROCESS

13.1   Definition and Applicability

A process can be described as "polytropic with index n" if and only if

$$Pv^n = \text{const.}$$

Any value of n may be selected; several common choices are tabulated below:

	Process	
Substance	Conditions	n
Any	Isobaric (const. P)	0
Ideal Gas	Isothermal (const. T)	1
Ideal Gas	Adiabatic, only boundary work *or* Isentropic (const. s)	$\gamma \equiv \frac{c_p}{c_v}$
Any	Isochoric (const. V)	∞

13.2   Property Ratios

If a process is polytropic with index n, then temperature, specific volume, and pressure ratios can be quickly inter-converted starting from the equation:

$$\left(\frac{P_2}{P_1}\right)^{\frac{1}{n}} = \left(\frac{v_2}{v_1}\right)^{\frac{1}{-1}} = \underbrace{\left(\frac{T_2}{T_1}\right)^{\frac{1}{n-1}}}_{\text{Ideal gas only}}$$

These equations will give indeterminate forms ($1^{\pm\infty}$) if you try to use the same piece of information twice:

- Using a formula involving P_2/P_1 for isobaric: $P_2/P_1 = 1$ and $n = 0$ gives $1^{-\infty}$

- Using a formula involving T_2/T_1 for isothermal: $T_2/T_1 = 1$ and $n = 1$ gives 1^{∞}

- Using a formula involving V_2/V_1 for isochoric: $V_2/V_1 = 1$ and $n = \infty$ gives $1^{-\infty}$

Mathematically, the problem is that n describes the shape of the curve through state space and the "given" property ratio is *supposed* to define the endpoint. In the examples above, n and the given property ratio *both* describe the shape of the curve — some other ratio is required to define the endpoint.

13.3   Work Integrals

If a process is polytropic with index n, then the two integrals which one might care about when evaluating work can be evaluated as:

$$\int_1^2 P\mathrm{d}v = \begin{cases} \dfrac{1}{1-n}\left(P_2 v_2 - P_1 v_1\right) = \underbrace{\dfrac{R}{1-n}\left(T_2 - T_1\right)}_{\text{Ideal gas only}} & (n \neq 1) \\[3em] -Pv\ln\left(\dfrac{P_2}{P_1}\right) = Pv\ln\left(\dfrac{v_2}{v_1}\right) & (n = 1) \end{cases}$$

$$\int_{\text{out}}^{\text{in}} v\mathrm{d}P = \begin{cases} \dfrac{n}{1-n}\left(P_{\text{out}}v_{\text{out}} - P_{\text{in}}v_{\text{in}}\right) = \underbrace{\dfrac{nR}{1-n}\left(T_{\text{out}} - T_{\text{in}}\right)}_{\text{Ideal gas only}} & (n \neq 1) \\[3em] -Pv\ln\left(\dfrac{P_{\text{out}}}{P_{\text{in}}}\right) = Pv\ln\left(\dfrac{v_{\text{out}}}{v_{\text{in}}}\right) & (n = 1) \end{cases}$$

Where, when $n = 1$,

$$Pv = P_1 v_1 = P_2 v_2 \underbrace{= RT_1 = RT_2}_{\text{Ideal gas only}}$$

14   REVERSIBLE STEADY-FLOW WORK

For a steady-flow device, the best-case performance (most work out/least work in) is realized when the process occurring inside the device is *reversible*, and this maximum performance can be evaluated in terms of the inlet and outlet states as:

$$\dot{W}_{\text{net}}^{\text{rev}} = \dot{m}\left[\int_{\text{out}}^{\text{in}} v\mathrm{d}P + (ke_{\text{in}} - ke_{\text{out}}) + (pe_{\text{in}} - pe_{\text{out}})\right]$$

If the process is, additionally, polytropic with index n, then $\int v\mathrm{d}P$ can be evaluated using previously-introduced formulae.