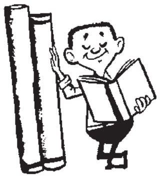
Review of First and Second Law of Thermodynamics



Reading	**Problems**
4-1 → 4-4	4-32, 4-36, 4-87, 4-246
5-2 → 5-4, 5.7	
6-1 → 6-13	6-122, 6-127, 6-130

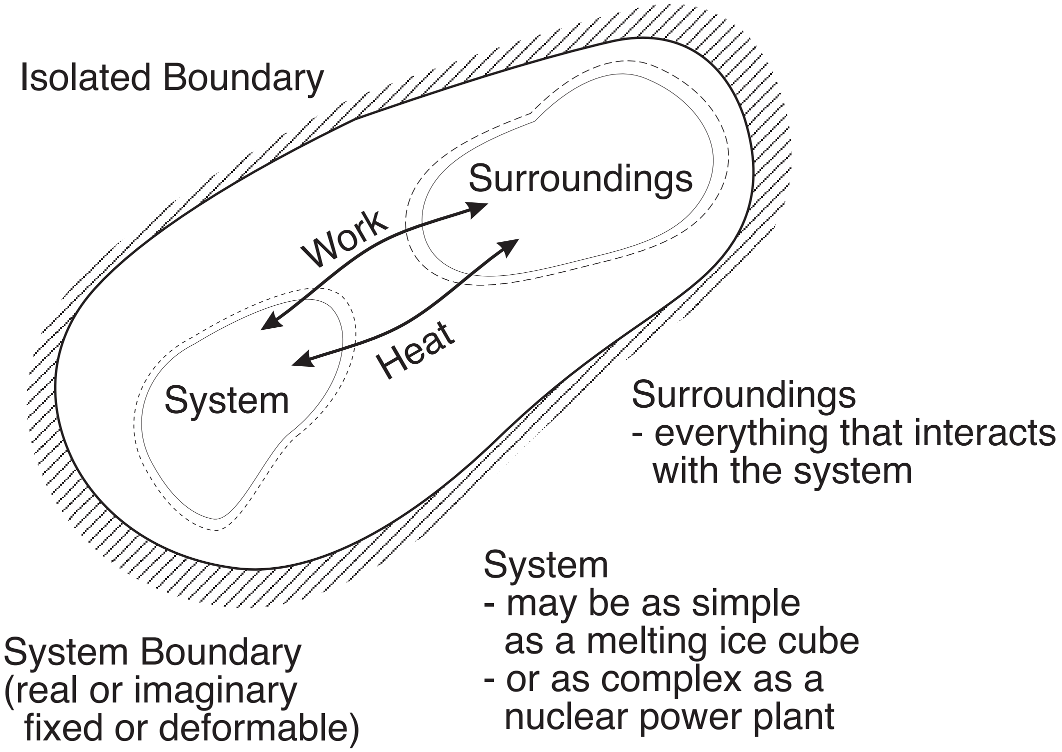
Definitions

SYSTEM:

- any specified collection of matter under study.
- all systems possess properties like mass, energy, entropy, volume, pressure, temperature, etc.

WORK & HEAT TRANSFER:

- thermodynamics deals with these properties of matter as a system interacts with its surroundings through work and heat transfer
- work and heat transfer are NOT properties → they are the forms that energy takes to cross the system boundary



First Law of Thermodynamics

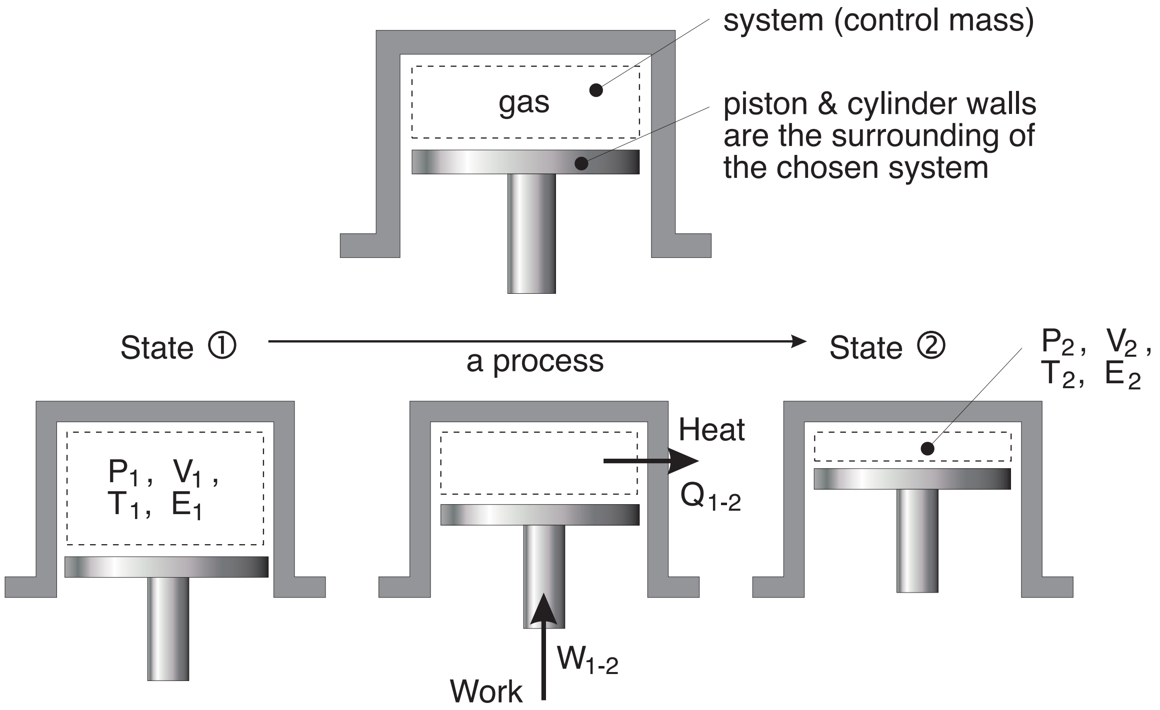
Control Mass (Closed System)

CONSERVATION OF ENERGY:

- the energy content of an isolated system is constant

$$\textit{\textbf{energy entering}} - \textit{\textbf{energy leaving}} = \textit{\textbf{change of energy within the system}}$$

Example: A Gas Compressor



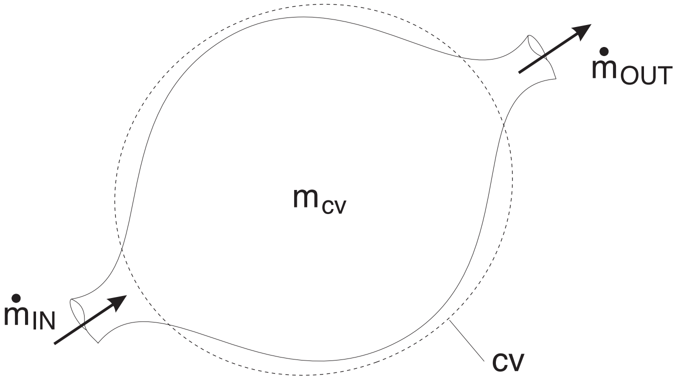
Performing a 1st law energy balance:

$$\left\{\begin{matrix} Initial \\ Energy \\ E_1 \end{matrix}\right\} \begin{matrix} + \\ - \end{matrix} \left\{\begin{matrix} Energy\ gain\ W_{1-2} \\ Energy\ loss\ Q_{1-2} \end{matrix}\right\} = \left\{\begin{matrix} Final \\ Energy \\ E_2 \end{matrix}\right\}$$

$$\boxed{E_1 + W_{1-2} - Q_{1-2} = E_2}$$

Control Volume Analysis (Open System)

CONSERVATION OF MASS:



$$\left\{\begin{array}{c}\boldsymbol{rate\ of\ increase}\\ \boldsymbol{of\ mass\ within}\\ \boldsymbol{the\ CV}\end{array}\right\} = \left\{\begin{array}{c}\boldsymbol{net\ rate\ of}\\ \boldsymbol{mass\ flow}\\ \boldsymbol{IN}\end{array}\right\} - \left\{\begin{array}{c}\boldsymbol{net\ rate\ of}\\ \boldsymbol{mass\ flow}\\ \boldsymbol{OUT}\end{array}\right\}$$

$$\frac{d}{dt}(m_{CV}) = \dot{m}_{IN} - \dot{m}_{OUT}$$

where:

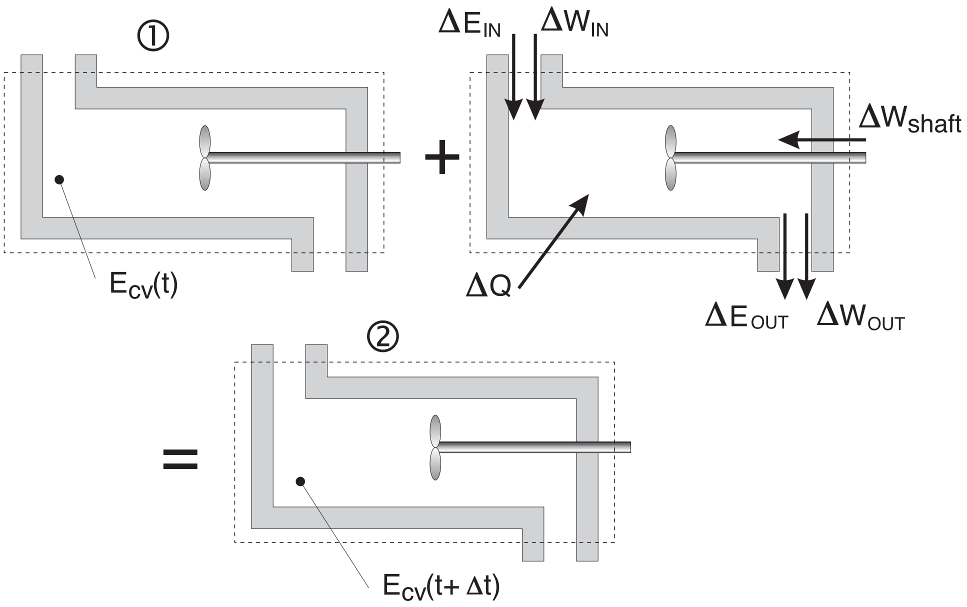
$$\begin{aligned} m_{CV} &= \int_V \rho\, dV \\ \dot{m}_{IN} &= (\rho\, v^*\, A)_{IN} \\ \dot{m}_{OUT} &= (\rho\, v^*\, A)_{OUT} \end{aligned}$$

with v^* = average velocity

CONSERVATION OF ENERGY:

The 1st law states:

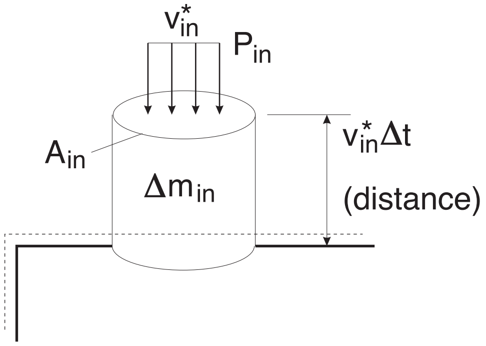
$$E_{CV}(t) + \Delta Q + \Delta W_{shaft} + (\Delta E_{IN} - \Delta E_{OUT}) + (\Delta W_{IN} - \Delta W_{OUT}) = E_{CV}(t + \Delta t) \quad (1)$$



where:

$$\begin{aligned}\Delta E_{IN} &= e_{IN} \Delta m_{IN} \\ \Delta E_{OUT} &= e_{OUT} \Delta m_{OUT} \\ \Delta W &= \text{flow work} \\ e &= \frac{E}{m} = \underbrace{u}_{internal} + \underbrace{\frac{(v^*)^2}{2}}_{kinetic} + \underbrace{gz}_{potential}\end{aligned}$$

What is flow work?



$$\Delta m_{IN} = \rho_{IN} \overbrace{A_{IN}\, v^*_{IN}\, \Delta t}^{volume}$$

$$\begin{aligned}\Delta W_{IN} &= F \cdot distance \\ &= \underbrace{P_{IN}\; A_{IN}}_{F} \;\cdot\; \underbrace{v^*_{IN}\; \Delta t}_{\Delta s} \\ &= \frac{P_{IN}\; \Delta m_{IN}}{\rho_{IN}}\end{aligned}$$

with

$$v = \frac{1}{\rho}$$

$$\Delta W_{IN} = (P\; v\; \Delta m)_{IN} \quad \longrightarrow \text{flow work} \tag{2}$$

Similarly

$$\Delta W_{OUT} = (P\; v\; \Delta m)_{OUT} \tag{3}$$

Substituting Eqs. 2 and 3 into Eq. 1 gives the 1st law for a control volume

$$\begin{aligned}E_{CV}(t+\Delta t) - E_{CV}(t) &= \Delta Q + \Delta W_{shaft} + \Delta m_{IN}(e+Pv)_{IN} \\ &\quad - \Delta m_{OUT}(e+Pv)_{OUT}\end{aligned} \tag{4}$$

Equation 4 can also be written as a rate equation $\longrightarrow$ divide through by Δt and take the limit as $\Delta t \longrightarrow 0$

$$\frac{d}{dt}E_{CV} = \dot{Q} + \dot{W}_{shaft} + [\dot{m}(e+Pv)]_{IN} - [\dot{m}(e+Pv)]_{OUT}$$

where:

$$\dot{m} = \rho\; v^*\; A$$

Note that:

$$\begin{aligned}e + Pv &= \underbrace{u + Pv} + \frac{(v^*)^2}{2} \;+\; gz \\ &= h(enthalpy) \;+\; KE \;+\; PE\end{aligned}$$

Second Law of Thermodynamics

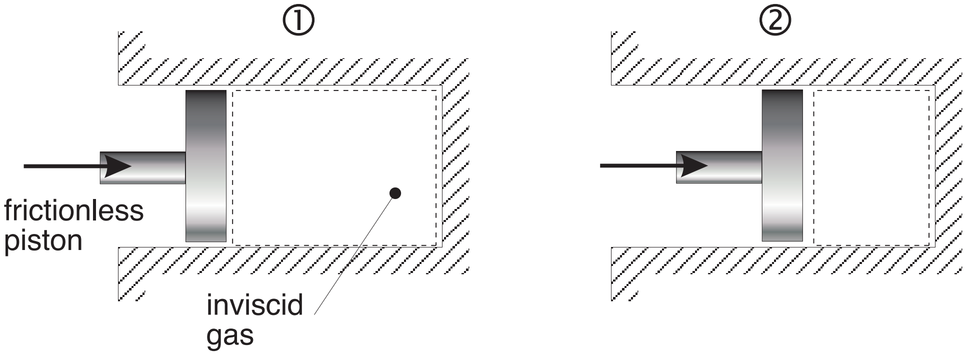
1. *Entropy is a measure of the degree of* <u>*microscopic disorder*</u> *and represents our* <u>*uncertainty*</u> *about the microscopic state.*

2. The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

   The second law states:

$$(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0 \qquad \text{where } \Delta \equiv final - initial$$

<u>Example: Slow adiabatic compression of a gas</u>



Idealization - which makes the process completely reversible

A process $\mathbf{1} \rightarrow \mathbf{2}$ is said to be reversible if the reverse process $\mathbf{2} \rightarrow \mathbf{1}$ restores the system to its original state without leaving any change in either the system or its surroundings.

$\rightarrow$ idealization where $S_2 = S_1 \quad \Rightarrow \mathcal{P}_S = 0$

$T_2 > T_1 \quad \Rightarrow$ increased microscopic disorder

$V_2 < V_1 \quad \Rightarrow$ reduced uncertainty about the whereabouts of molecules

$$\underbrace{Reversible}_{\mathcal{P}_S=0} + \underbrace{Adiabatic\ Process}_{Q=0} \Rightarrow \underbrace{Isentropic\ Process}_{S_1=S_2}$$

The 2nd law states:

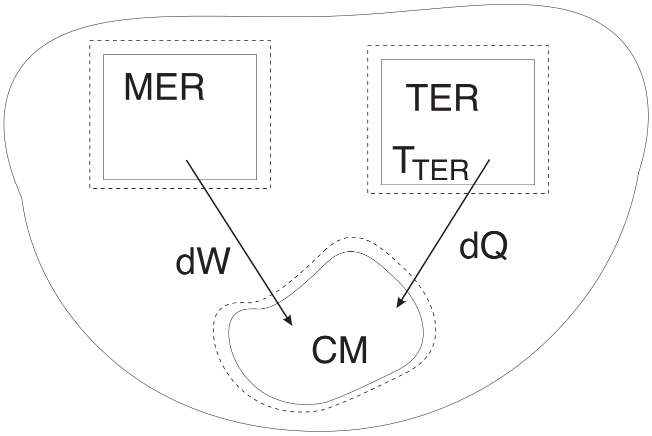
$$\mathcal{P}_S = (\Delta S)_{system} + (\Delta S)_{surr} \geq 0$$

where:

$> \mathbf{0}$ irreversible (real world)

$= \mathbf{0}$ reversible (frictionless, perfectly elastic, inviscid fluid)

How do we determine entropy in a system?



For an isolated system $\boldsymbol{\mathcal{P}} \geq \mathbf{0}$.

$$\overbrace{(dS)_{CM}}^{storage} + \overbrace{\underbrace{(dS)_{TER}}_{-\frac{dQ}{T_{TER}}} + (d\cancel{S}^{\,0})_{MER}}^{net\ transfer\ out} = \overbrace{d\mathcal{P}_S}^{production}$$

Therefore

$$(dS)_{CM} = \frac{dQ}{T_{TER}} + d\mathcal{P}_S$$

Integrating gives

$$(S_2 - S_1)_{CM} = \frac{Q_{1-2}}{T_{TER}} + \underbrace{\mathcal{P}_{S_{1-2}}}_{\geq 0}$$

where

$\frac{Q_{1-2}}{T_{TER}}$ - the entropy associated with heat transfer across a finite temperature difference

Gibb's Equation for a Simple Compressible Substance

simple	→	has only one work mode
compressible	→	the work mode is $\boldsymbol{Pdv}$ work

$$\begin{aligned} S &= S(U, V) \\ dS &= \underbrace{\left(\frac{\partial S}{\partial U}\right)_V}_{=\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_U}_{=\frac{P}{T}} dV \end{aligned}$$

$$\boxed{T\,dS = dU \;+\; PdV}$$

This form of Gibb's equation is very general and very useful.

The general derivation of Gibb's equation:

from the 1st law ⇒ $dq = du + Pdv \qquad (1)$

from the 2nd law ⇒ $ds = \dfrac{dq}{T} \qquad (2)$

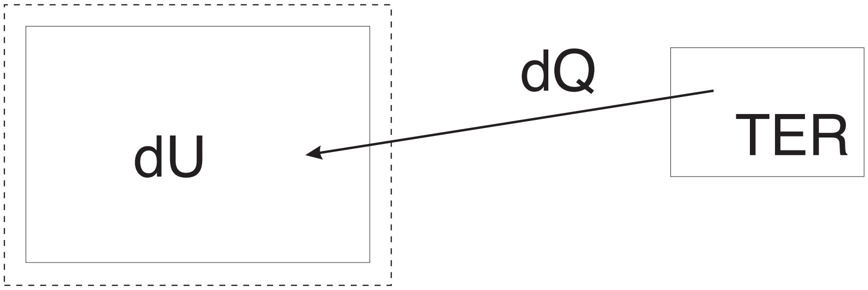
Combining (1) and (2) gives

$$ds = \frac{du}{T} + P\frac{dv}{T}$$

or

$$\begin{aligned} T\,ds &= du + P\,dv \\ T\,dS &= dU + P\,dV \end{aligned}$$

Second Law Analysis for a Control Mass



- control mass is uniformly at $\boldsymbol{T_{TER}}$ at all times
- control mass has a fixed size ($\boldsymbol{V = constant}$)

From Gibb's equation

$$\boldsymbol{T_{TER}\, dS = dU + P\, d\cancel{V}^{0}}$$

From the 1st law

$$\boldsymbol{dU = dQ}$$

Therefore for a reversible process

$$\boldsymbol{dS = \frac{dQ}{T_{TER}}}$$

We integrate to give

$$\boldsymbol{S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}}}$$

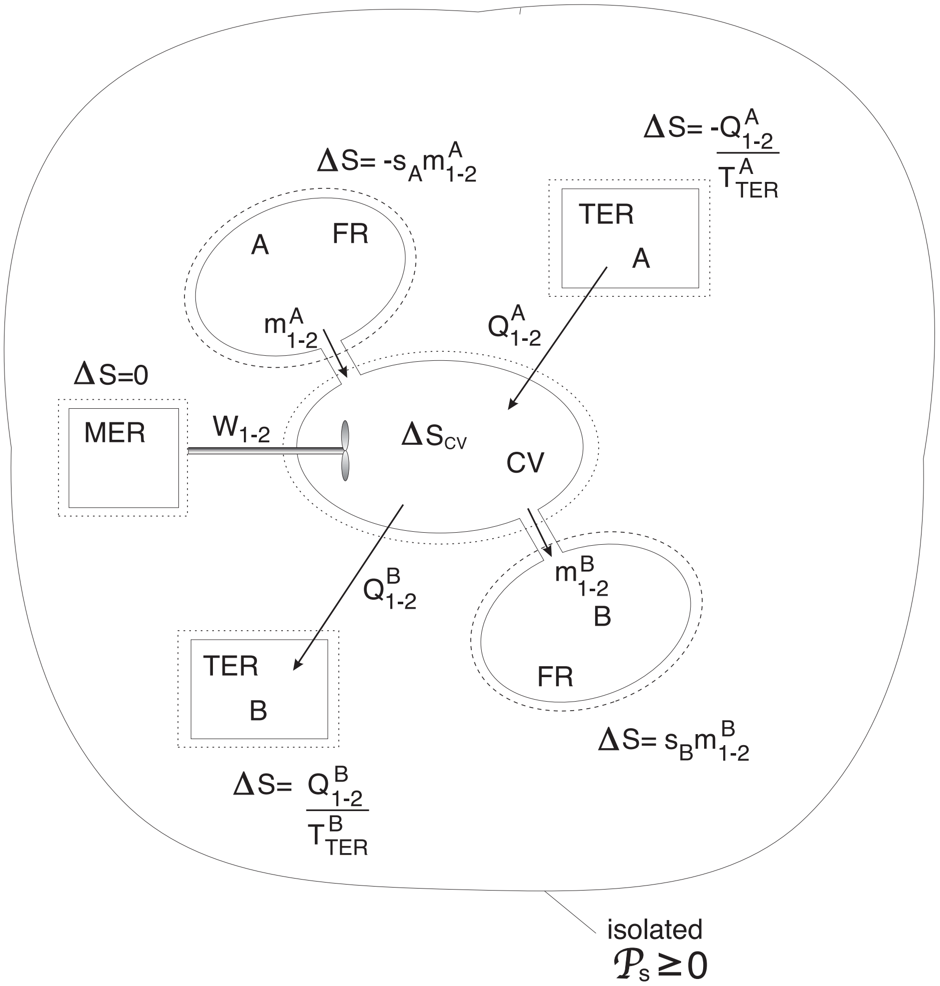
and for a non-reversible process

$$\boldsymbol{dS = \frac{dQ}{T_{TER}} + d\mathcal{P}_S}$$

We integrate to give

$$\boldsymbol{S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}} + \mathcal{P}_{S_{1-2}}}$$

Second Law Analysis for a Control Volume



For the isolated system

$$(\boldsymbol{\Delta S})_{sys} + (\boldsymbol{\Delta S})_{sur} = \mathcal{P}_{S_{1-2}} \geq 0$$

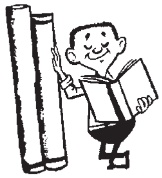
$$\Delta S_{CV} - s_A m^A_{1-2} + s_B m^B_{1-2} - \frac{Q^A_{1-2}}{T^A_{TER}} + \frac{Q^B_{1-2}}{T^B_{TER}} = \mathcal{P}_{S_{1-2}}$$

or as a rate equation

$$\left(\frac{dS}{dt}\right)_{CV} = \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{IN} - \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{OUT} + \dot{\mathcal{P}}_S$$

This can be thought of as $\boldsymbol{accumulation = IN - OUT + generation}$

State Equations



Reading	**Problems**
6-4 ⟶ 6-12	

An Isentropic Process for an Ideal Gas

Given:

- constant specific heats over a wide range of temperature
- $ds = 0$
- $du = c_v dT \equiv c_v = \left(\frac{\partial u}{\partial T}\right)_V$
- $dh = c_p dT \equiv c_p = \left(\frac{\partial h}{\partial T}\right)_P$

Gibb's equation can be written as

$$Tds = du + Pdv = c_v dT + Pdv = 0 \qquad (1)$$

where $ds = 0$ because we have assumed an isentropic process.

The definition of enthalpy is

$$h = u + Pv$$

Taking the derivative yields

$$dh = \underbrace{du + Pdv}_{\equiv Tds} + vdP$$

$$dh = Tds + vdP \quad \Rightarrow \quad Tds = 0 = dh - vdP$$

$$\boxed{c_p dT - vdP = 0} \qquad (2)$$

Equating Eqs. (1) and (2) through the $\boldsymbol{dT}$ term gives

$$\boldsymbol{\frac{dP}{P} = -\frac{c_p}{c_v}\frac{dv}{v}} \qquad \textbf{(3)}$$

Integrating (3) from its initial state to a final state

$$\boldsymbol{P_1 v_1^k = P_2 v_2^k = constant = P v^k}$$

where

$$\boldsymbol{k = \frac{c_p}{c_v}}$$

The product of $\boldsymbol{P \cdot v^k}$ remains constant for an ideal gas when:

- specific heats are constant
- the gas undergoes an isentropic process ⟶ reversible + adiabatic

Combining this result with the ideal gas equation of state

$$\boxed{\boldsymbol{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}}}$$

The isentropic process is a special case of a more general process known as a <u>polytropic process</u>

where ⟶ $\boldsymbol{Pv^n = constant}$ and $\boldsymbol{n}$ is any number.

Special Cases

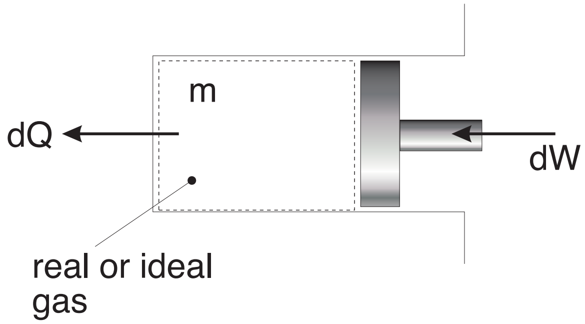
$\boldsymbol{n = 1}$ $\boldsymbol{Pv = RT = constant}$ ⇒ isothermal process

$\boldsymbol{n = 0}$ $\boldsymbol{Pv^0 = constant = P}$ ⇒ isobaric process (constant pressure)

$\boldsymbol{n = k}$ $\boldsymbol{Pv^k = constant}$ ⇒ isentropic process ($\boldsymbol{k = c_p/c_v}$)

$\boldsymbol{n = \infty}$ $\boldsymbol{Pv^\infty = constant}$ ⇒ isochoric process (constant volume)

Reversible Compression/Expansion for a Fixed Mass



$$\begin{aligned} dU &= dW - dQ \\ mdu &= dW - dQ \qquad (1) \end{aligned}$$

$$dS = -\frac{dQ}{T} + \mathcal{P}_S$$

where $\mathcal{P}_S = 0$ for a reversible process.

$$mds = -\frac{dQ}{T} \qquad (2)$$

Combining (1) and (2) through the $-dQ$ term gives

$$mdu = dW + mTds \qquad (3)$$

From Gibb's Eq., $Tds = du + Pdv$

$$mdu = mTds - mPdv \qquad (4)$$

Combining Eqs. (3) and (4)

$$\begin{aligned} mTds - mPdv &= dW + mTds \\ dW &= -mPdv \end{aligned}$$

$$W_{1-2} = -m\int_1^2 Pdv \qquad \Rightarrow \qquad w_{1-2} = \frac{W_{1-2}}{m} = -\int_1^2 Pdv$$

Reversible Isothermal Process for an Ideal Gas

We know for an ideal gas

$$\boldsymbol{Pv = constant = RT}$$

or

$$\boldsymbol{P = \frac{constant}{v}} \qquad (1)$$

$$\boldsymbol{Pv = constant = P_1 v_1 = P_2 v_2} \qquad (2)$$

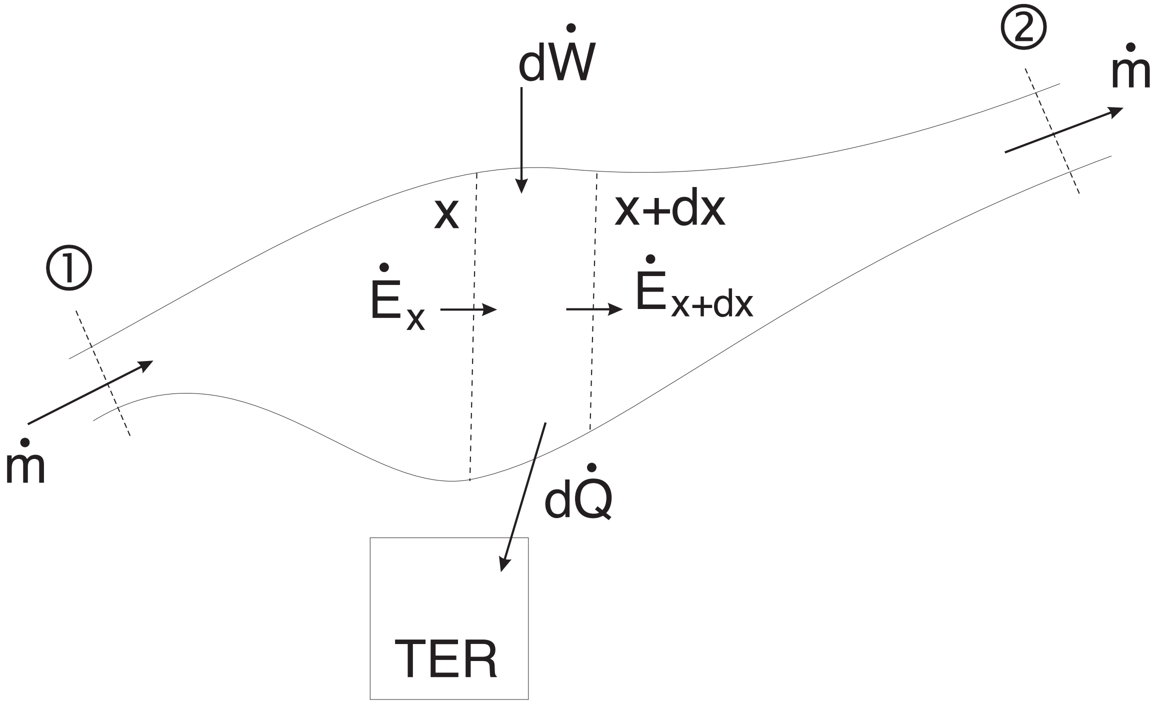
The work done at the boundary of a simple, compressible substance (S.C.S.) during a reversible process

$$\begin{aligned} \boldsymbol{w_{1-2} = -\int_1^2 P dv} &= \boldsymbol{-constant \int_1^2 \frac{dv}{v}} \\ &= \boldsymbol{-P_1 v_1 \ln \frac{v_2}{v_1}} \\ &= \boldsymbol{P_1 v_1 \ln \frac{v_1}{v_2}} \end{aligned}$$

$$\begin{aligned} \boldsymbol{W_{1-2} = mRT \ln \frac{v_1}{v_2}} &= \boldsymbol{mRT \ln \frac{V_1}{V_2}} \\ &= \boldsymbol{mRT \ln \frac{P_2}{P_1}} \end{aligned}$$

A General Formulation

Steady State, Steady Flow in a Flow Channel of Arbitrary Cross-section with Work and Heat Transfer



$$\begin{aligned} d\dot{E} &= \dot{E}_{final} - \dot{E}_{initial} \\ &= \dot{E}_{x+dx} - \dot{E}_x \end{aligned}$$

where

$$\begin{aligned} \dot{E} &= \dot{m}(e + Pv) \\ &= \dot{m}(u + \frac{(v^*)^2}{2} + gz + Pv) \end{aligned}$$

From the 1st law

$$\begin{matrix} \textit{rate of energy} \\ \textit{storage} \end{matrix} = \begin{matrix} \textit{rate of} \\ \textit{work} \end{matrix} + \begin{matrix} \textit{rate of} \\ \textit{heat transfer} \end{matrix} + \begin{matrix} \textit{net rate of energy} \\ \textit{leaving the system} \end{matrix}$$

$$\frac{dE_{CV}}{dt} = d\dot{W} - d\dot{Q} - d\dot{E} \qquad (1)$$

where $\frac{dE_{CV}}{dt} = 0$ for steady state.

Equation (1) becomes

$$0 = d\dot{W} - d\dot{Q} - \dot{m}\ d\left[u + Pv + \frac{(v^*)^2}{2} + gz\right] \qquad (2)$$

From the 2nd law

$$\begin{matrix} rate\ of \\ entropy \\ storage \end{matrix} = \left\{ \begin{matrix} rate\ of \\ entropy \\ inflow \end{matrix} - \begin{matrix} rate\ of \\ entropy \\ outflow \end{matrix} \right\} + \begin{matrix} rate\ of \\ entropy \\ production \end{matrix}$$

$$\frac{dS_{CV}}{dt} = [\dot{m}s]_x - [\dot{m}s]_{x+dx} - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

where $\frac{dS_{CV}}{dt} = 0$ for steady state.

$$0 = -\dot{m}ds - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

or

$$d\dot{Q} = T_{TER}\dot{\mathcal{P}}_S - T_{TER}\dot{m}ds \qquad (3)$$

Combining (2) and (3) through $d\dot{Q}$

$$\boxed{T_{TER}\ \dot{\mathcal{P}}_S - T_{TER}\ \dot{m}ds = d\dot{W} - \dot{m}\ d\left(u + Pv + \frac{(v^*)^2}{2} + gz\right)} \qquad (4)$$

Equation (4) can be used for any SS-SF process.

Special Cases

1. Reversible, SS-SF Process

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP$$

2. Incompressible Substance

$$\frac{\dot{W}}{\dot{m}} = v_{in}(P_{out} - P_{in})$$

3. Incompressible Substance and $d\dot{W} = 0$

$$\frac{P}{\rho} + \frac{(v^*)^2}{2} + gz = constant$$

4. Isothermal Ideal Gas, Compression/Expansion

$$\frac{\dot{W}}{\dot{m}} = P_{in} v_{in} \ln\left(\frac{P_{out}}{P_{in}}\right)$$

5. Isentropic Ideal Gas, Compression/Expansion

$$\frac{\dot{W}}{\dot{m}} = \left(\frac{k}{k-1}\right)(Pv)_{in}\left[\left(\frac{P_{out}}{P_{in}}\right)^{(k-1)/k} - 1\right] = c_p(T_{out} - T_{in})$$

Incompressible Liquids

- a substance whose volume cannot be changed
- no substance is truly incompressible, but this model is good for most liquids and solids

State Postulate

- the number of independent intensive thermodynamic properties is equal to the number of relevant <u>reversible</u> work modes <u>plus one</u>.
- the “plus one” is for the independent control on energy through heat transfer
- we know that for a *simple* (has only one work mode), *compressible* (the work model is Pdv work) substance
  - 2 thermodynamic properties will fix the rest
    - list of intensive properties includes, T, u, P, v, s
    - state postulate says two will fix the rest, i.e. if u and v are known, the equations of state are

$$\begin{aligned} T &= T(u, v) \\ P &= P(u, v) \\ s &= s(u, v) \end{aligned}$$

Hence, if the substance is assumed to be incompressible, then its internal energy, for example, cannot be varied independently by work transfer $\longrightarrow$ but it can be varied by heat transfer at constant volume, i.e. $Pdv = 0$ since $dv = constant$. There are no reversible work modes.

i.e.

$$u = u(T) \ \ only$$

$$dh = du + Pd\cancelto{0}{v} + vdP$$

where $Pdv = 0$ for an incompressible substance.

For an incompressible substance

$$c_p = c_v = \overline{c}$$

Gibb's Equation. states

$$Tds = du + P\cancelto{0}{dv}$$

therefore

$$ds = \frac{du}{T} = \overline{c}\,\frac{dT}{T}$$

Integrating from the initial state to the final state

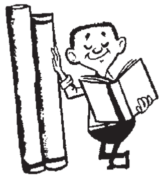
$$s_2 - s_1 = \overline{c}\ln\left(\frac{T_2}{T_1}\right)$$

as $T_2 \longrightarrow T_1$, i.e. isothermal condition $\Rightarrow$ $s_2 \longrightarrow s_1$, i.e. isentropic.

In summary

$$\begin{aligned}
u_2 - u_1 &= \overline{c}\,(T_2 - T_1) \\
h_2 - h_1 &= (u_2 - u_1) + v(P_2 - P_1) \\
s_2 - s_1 &= \overline{c}\ \ln(T_2/T_1)
\end{aligned}$$

Availability



Reading	**Problems**
7.1 - 7.8	7-29, 7-37, 7-40, 7-48, 7-60, 7-68, 7-107

Second Law Analysis of Systems

AVAILABILITY:

- the theoretical maximum amount of work that can be obtained from a system at a given state $\boldsymbol{P_1}$ and $\boldsymbol{T_1}$ when interacting with a reference atmosphere at the constant pressure and temperature $\boldsymbol{P_0}$ and $\boldsymbol{T_0}$.
- describes the work potential of a given system.
- also referred to as "exergy".

The following observations can be made about availability:

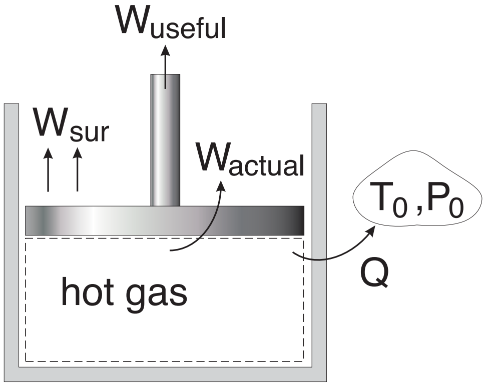
1. Availability is a **property** - since any quantity that is fixed when the state is fixed is a property. For a system at state 1 and specified values of the atmosphere of $\boldsymbol{T_0}$ and $\boldsymbol{P_0}$, the maximum useful work that can be produced is fixed.
2. Availability is a **composite property** - since its value depends upon an external datum - the temperature and pressure of the dead state.
3. Availability of a system is **0** at its **dead state** when $\boldsymbol{T = T_0}$ and $\boldsymbol{P = P_0}$. It is not possible for the system to interact with the reference atmosphere at the dead state. The system is said to be in thermodynamic equilibrium with its surroundings.
4. Unless otherwise stated, assume the dead state to be:

$$\begin{aligned} \boldsymbol{P_0} &= \boldsymbol{1\ atm} \\ \boldsymbol{T_0} &= \boldsymbol{25^\circ C} \end{aligned}$$

5. The maximum work is obtained through a reversible process to the dead state.

$$\underbrace{\boldsymbol{REVERSIBLE\ WORK}}_{\boldsymbol{W_{rev}}} = \underbrace{\boldsymbol{USEFUL\ WORK}}_{\boldsymbol{W_{useful}}} + \underbrace{\boldsymbol{IRREVERSIBILITY}}_{\boldsymbol{I}}$$

Control Mass Analysis



$$\boldsymbol{W_{rev} = W_{useful} \ + \ I}$$

where

$$\begin{aligned} \boldsymbol{W_{actual}} &= \boldsymbol{W_{useful} + W_{sur}} \\ \boldsymbol{W_{sur}} &= \boldsymbol{P_0(V_2 - V_1) = -P_0(V_1 - V_2)} \end{aligned}$$

To find $\boldsymbol{W_{actual}}$, incorporate the 1st and 2nd laws to get

$$\boldsymbol{W_{actual} = (E_1 - E_2) - T_0(S_1 - S_2) - T_0\mathcal{P}_s}$$

and

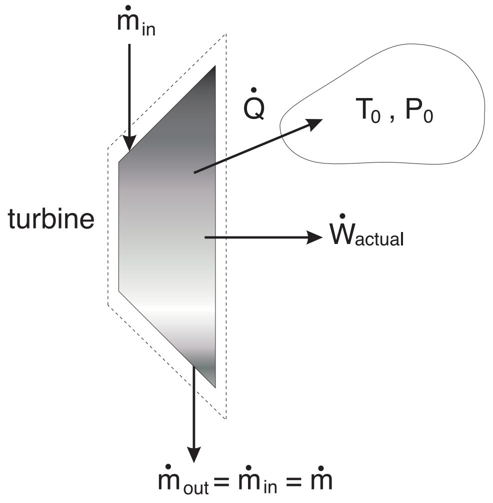
$$\begin{aligned} \boldsymbol{W_{useful}} &= \boldsymbol{(E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2) - T_0\mathcal{P}_s} \\ \boldsymbol{W_{rev}} &= \boldsymbol{(E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)} \end{aligned}$$

$$\begin{aligned} \boldsymbol{X = \Phi} &= \boldsymbol{CONTROL\ MASS\ AVAILABILITY} \\ &= \boldsymbol{W_{rev}\ (in\ going\ to\ the\ dead\ state)} \\ &= \boldsymbol{(E - E_0) - T_0(S - S_0) + P_0(V - V_0)} \end{aligned}$$

The availability destroyed is $\boldsymbol{X_{des} = I = W_{rev} - W_{useful} = T_0\mathcal{P}_s}$

This can be referred to as: irreversibilities, availability destruction or loss of availability.

Control Volume Analysis



From the 1st law

$$\cancelto{0}{\frac{dE_{cv}}{dt}} = -\dot{W}_{actual} - \dot{Q} + \left[\dot{m}\left(h + \frac{(v^*)^2}{2} + gz\right)\right]_{in} - \left[\dot{m}\left(h + \frac{(v^*)^2}{2} + gz\right)\right]_{out} \qquad (1)$$

From the 2nd law

$$\cancelto{0}{\frac{dS_{cv}}{dt}} = \left(\dot{m}s + \frac{\cancelto{0}{\dot{Q}}}{T_{TER}}\right)_{in} - \left(\dot{m}s + \frac{\dot{Q}}{T_0}\right)_{out} + \dot{\mathcal{P}}_s \qquad (2)$$

Combining (1) and (2) through the $\dot{Q}$ term,

$$\begin{aligned}
\dot{W}_{actual} &= \left[\dot{m}\left(h + \frac{(v^*)^2}{2} + gz - T_0 s\right)\right]_{in} - \left[\dot{m}\left(h + \frac{(v^*)^2}{2} + gz - T_0 s\right)\right]_{out} - T_0\dot{\mathcal{P}}_S \\
&= \dot{m}\left[-T_0\Delta s + \Delta h + \Delta KE + \Delta PE\right] - (T_0\dot{\mathcal{P}}_s) \qquad (3)
\end{aligned}$$

The specific flow availability, ψ, is given as

$$\psi = -T_0(s - s_0) + (h - h_0) + \left(\frac{(v^*)^2}{2} - \frac{(\cancelto{0}{v_0^*})^2}{2}\right) + g(z - \cancelto{0}{z_0}) \qquad (4)$$

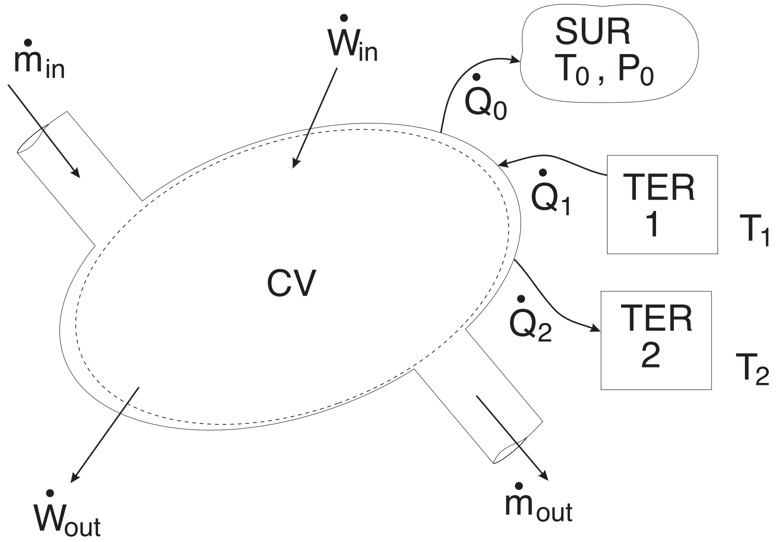
For a steady state, steady flow process where we assume KE=PE=0

$$\dot{W}_{rev} = (\dot{m}\psi)_{in} - (\dot{m}\psi)_{out} \tag{5}$$

$$\dot{X}_{des} = \dot{I} = \dot{W}_{rev} - \dot{W}_{actual} = T_0\dot{\mathcal{P}}_s \tag{6}$$

$$\psi = (h - h_0) - T_0(s - s_0) \tag{7}$$

The General Exergy Equation



From the 1st law

$$\frac{dE_{cv}}{dt} = \dot{W}_{in} - \dot{W}_{out} - \dot{Q}_0 + \dot{Q}_1 - \dot{Q}_2 + [\dot{m}(e + Pv)]_{in} - [\dot{m}(e + Pv)]_{out} \tag{1}$$

From the 2nd law

$$\frac{dS_{cv}}{dt} = \left(\dot{m}s - \frac{\dot{Q}_0}{T_0} + \frac{\dot{Q}_1}{T_1}\right)_{in} - \left(\dot{m}s + \frac{\dot{Q}_2}{T_2}\right)_{out} + \dot{\mathcal{P}}_s \tag{2}$$

Multiply (2) by $\boldsymbol{T_0}$ and subtract from (1) to eliminate $\boldsymbol{Q_0}$, which leads to the generalized exergy equation

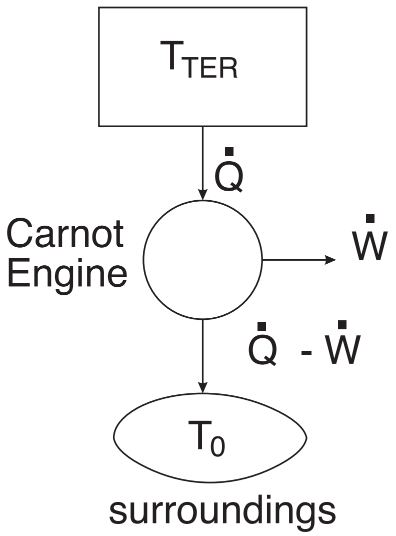
$$\begin{aligned}\frac{d}{dt}(E - T_0 S)_{CV} &= \dot{W}_{in} - \dot{W}_{out} + [\dot{m}(e + Pv - T_0 s)]_{in} \\ &\quad -[\dot{m}(e + Pv - T_0 s)]_{out} + \left(\dot{Q}_1 - \frac{T_0 \dot{Q}_1}{T_1}\right)_{in} \\ &\quad - \left(\dot{Q}_2 - \frac{T_0 \dot{Q}_2}{T_2}\right)_{out} - T_0 \dot{\mathcal{P}}_S \qquad (3)\end{aligned}$$

We can rewrite Eq. (3) in a generalized form by introducing the definitions of $\boldsymbol{\Phi}$ and $\boldsymbol{\psi}$.

$$\begin{aligned}\frac{d\Phi}{dt} &= P_0 \frac{dV_{CV}}{dt} + \left[\dot{W} + \dot{m}\psi + \dot{Q}\left(1 - \frac{T_0}{T_{TER}}\right)\right]_{in} \\ &\quad - \left[\dot{W} + \dot{m}\psi + \dot{Q}\left(1 - \frac{T_0}{T_{TER}}\right)\right]_{out} - \dot{I}\end{aligned}$$

where

$$\begin{aligned}\dot{I} = \dot{X}_{des} &= T_0 \dot{\mathcal{P}}_s \\ &= exergy\ destruction\ rate \\ \Phi &= [(E - E_0) + P_0(V - V_0) - T_0(S - S_0)]_{CV} \\ &= non - flow\ exergy \\ \psi &= (h - h_0) - T_0(s - s_0) + \frac{1}{2}\left[(v^*)^2 - (v_0^*)^2\right] + g(z - z_0) \\ &= flow\ exergy \\ \dot{W}_{useful} &= \underbrace{(\dot{W}_{in} - \dot{W}_{out})}_{\dot{W}_{actual}} - \left(\underbrace{P_0 \frac{dV_{CV}}{dt}}_{W_{sur}}\right)\end{aligned}$$



Notice that:

$$\boldsymbol{\eta = \frac{\dot{W}}{\dot{Q}} = 1 - \frac{T_0}{T_{TER}}}$$

Therefore

$$\boldsymbol{\dot{W}} = \underbrace{\boldsymbol{\dot{Q}\left(1 - \frac{T_0}{T_{TER}}\right)}}_{\substack{\text{appears in the} \\ \text{general exergy equation}}}$$

This term represents the work potential (exergy) of a given TER with respect to the surroundings (dead state) at $\boldsymbol{T_0}$.

Efficiency and Effectiveness

1. **First law efficiency (thermal efficiency)**

$$\eta = \frac{net\ work\ output}{gross\ heat\ input} = \frac{W_{net}}{Q_{in}}$$

Carnot cycle

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

2. **Second Law Efficiency (effectiveness)**

$$\eta_{2nd} = \frac{net\ work\ output}{maximum\ reversible\ work} = \frac{net\ work\ output}{availability}$$

Turbine → $\eta_{2nd} = \dfrac{\dot{W}/\dot{m}}{\psi_e - \psi_i}$

Compressor → $\eta_{2nd} = \dfrac{\psi_e - \psi_i}{\dot{W}/\dot{m}}$

Heat Source → $\eta_{2nd} = \dfrac{\dot{W}/\dot{m}}{\dfrac{\dot{Q}}{\dot{m}}\left[1 - \dfrac{T_0}{T_{TER}}\right]}$

3. **Isentropic efficiency (process efficiency)**

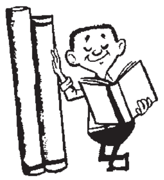
   (a) adiabatic turbine efficiency

$$\eta_T = \frac{work\ of\ actual\ adiabatic\ expansion}{work\ of\ reversible\ adiabatic\ expansion} = \frac{W_{act}}{W_S}$$

   (b) adiabatic compressor efficiency

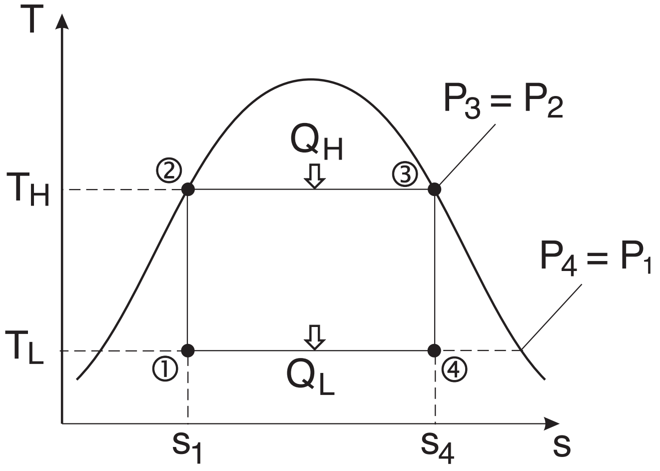
$$\eta_C = \frac{work\ of\ reversible\ adiabatic\ compression}{work\ of\ actual\ adiabatic\ compression} = \frac{W_S}{W_{act}}$$

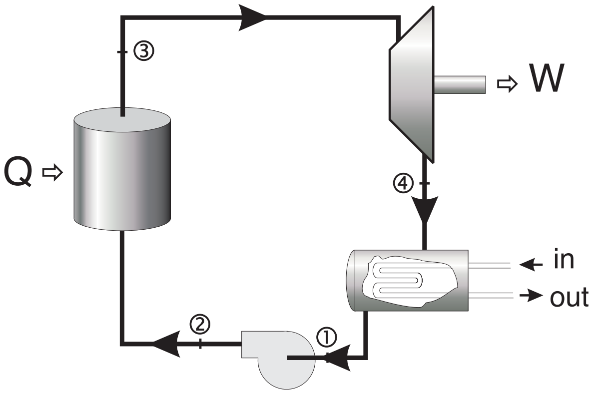
Carnot Cycle



Reading	**Problems**
8-2, 9-1	

- an ideal theoretical cycle that is the most efficient conceivable
- based on a fully reversible heat engine - it does not include any of the irreversibilities associated with friction, viscous flow, etc.
- in practice the thermal efficiency of real world heat engines are about half that of the ideal, Carnot cycle





Process	State Points	Description
Pump	1 ⟶ 2	isentropic compression from $\boldsymbol{T_L} \longrightarrow \boldsymbol{T_H}$ to return vapour to a liquid state
Heat Supply	2 ⟶ 3	heat is supplied at constant temperature and pressure
Work Output	3 ⟶ 4	the vapour expands isentropically from the high pressure and temperature to the low pressure
Condenser	4 ⟶ 1	the vapour which is wet at 4 has to be cooled to state point 1

Cycle Efficiency

- defined as the net work output divided by the gross heat supplied

$$\begin{aligned}\eta &= \frac{W_{net}}{Q_H} \\ &= \frac{Q_H - Q_L}{Q_H} \\ &= 1 - \frac{T_L}{T_H}\end{aligned}$$

From the figure the gross heat supplied is

$$Q_H = area(s_1 \rightarrow s_4 \rightarrow 3 \rightarrow 2 \rightarrow s_1) = T_H(s_4 - s_1)$$

The net work output is

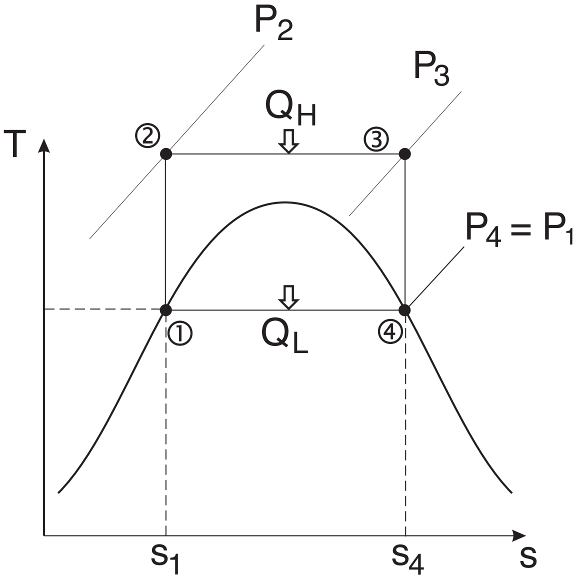
$$Q_H - Q_L = area(1 \rightarrow 4 \rightarrow 3 \rightarrow 2) = (T_H - T_L)(s_4 - s_1)$$

Therefore the Carnot efficiency is

$$\eta = \frac{(T_H - T_L)(s_4 - s_1)}{T_H(s_4 - s_1)} = 1 - \frac{T_L}{T_H}$$

Practical Problems

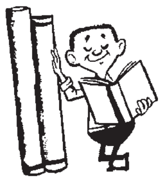
- at state point 1 the steam is wet at $\boldsymbol{T_L}$ and it is difficult to pump water/steam (two phase) to state point 2
- the pump can be sized smaller if the fluid is 100% liquid water
- the pump is smaller, cheaper and more efficient
- can we devise a Carnot cycle to operate outside the wet vapour region



  - between state points 2 and 3 the vapour must be isothermal and at different pressures - this is difficult to achieve
  - the high temperature and pressure at 2 and 3 present metallurgical limitations

The net effect is that the Carnot cycle is <u>not</u> feasible for steam power plants.

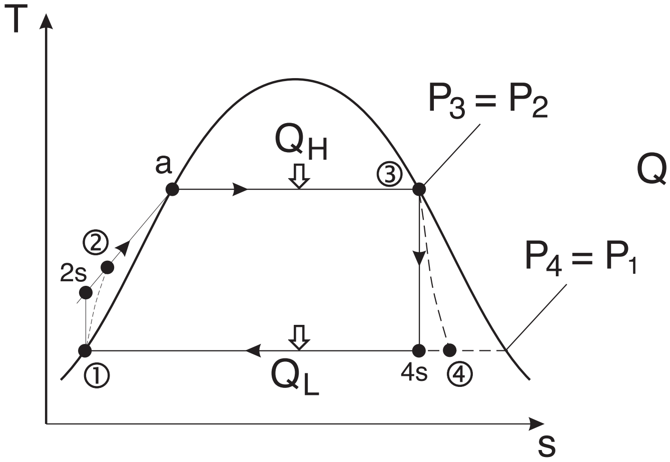
Rankine Cycle

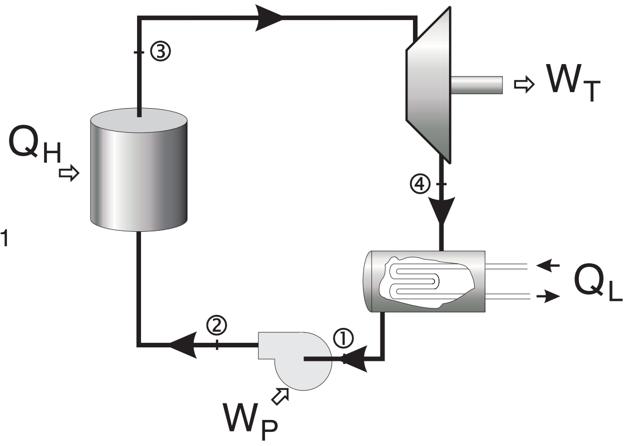


Reading	**Problems**
9-2 ⟶ 9-7	9-16, 9-23, 9-30, 9-38, 9-43, 9-84

Definitions

- working fluid is alternately vaporized and condensed as it recirculates in a closed cycle
- water is typically used as the working fluid because of its low cost and relatively large value of enthalpy of vaporization
- the standard vapour cycle that excludes internal irreversibilities is called the **Ideal Rankine Cycle**





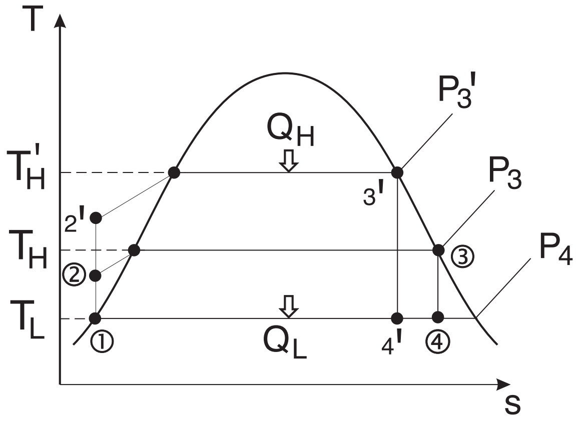
- the condensation process is allowed to proceed to completion between state points **4** ⟶ **1**
  - provides a saturated liquid at 1
- the water at state point 1 can be conveniently pumped to the boiler pressure at state point 2
- but the water is <u>not</u> at the saturation temperature corresponding to the boiler pressure
- heat must be added to change the water at 2 to saturated water at 'a'
- when heat is added at non-constant temperature (between $\mathbf{2} - \boldsymbol{a}$), the cycle efficiency will decrease

Effects of Boiler and Condenser Pressure

We know the efficiency is proportional to $\boldsymbol{\eta \propto 1 - \frac{T_L}{T_H}}$

The question is → how do we increase efficiency $\Rightarrow$ $\boldsymbol{T_L} \downarrow$ and/or $\boldsymbol{T_H} \uparrow$.

1. INCREASED BOILER PRESSURE:



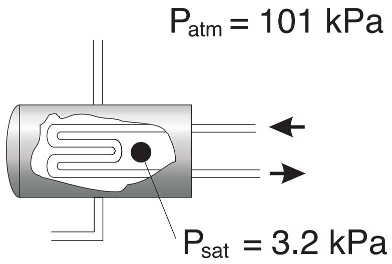
- an increase in boiler pressure results in a higher $\boldsymbol{T_H}$ for the same $\boldsymbol{T_L}$, therefore $\boldsymbol{\eta} \uparrow$.
- but $\mathbf{4'}$ has a lower quality than $\mathbf{4}$
  - wetter steam at the turbine exhaust
  - results in cavitation of the turbine blades
  - $\boldsymbol{\eta} \downarrow$ plus ↑ maintenance
- quality should be $> \mathbf{90\%}$ at the turbine exhaust

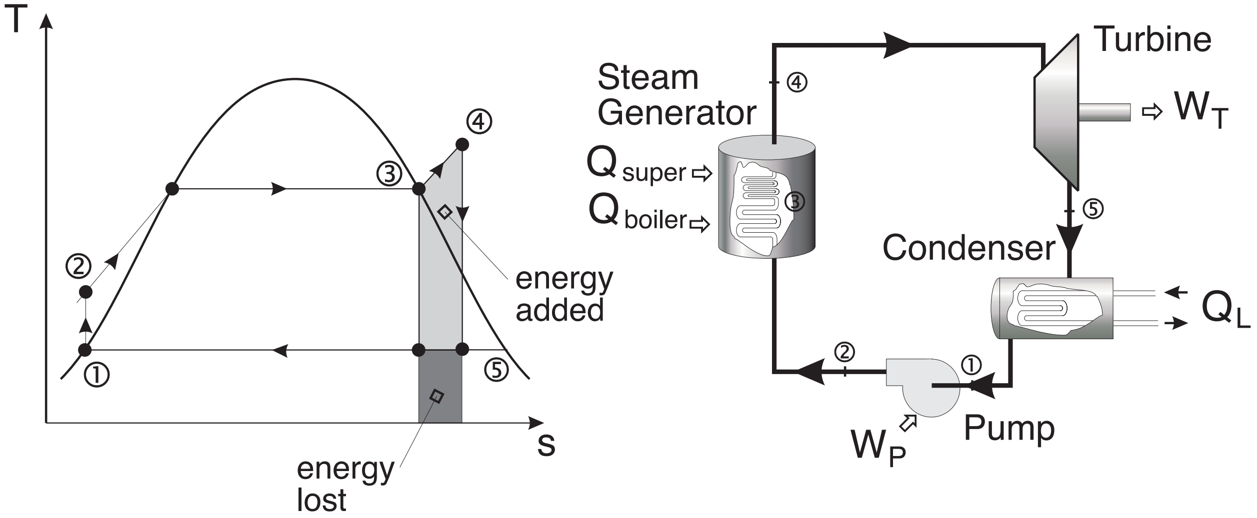
2. LOWER T_L:

- we are generally limited by the ***TER*** (lake, river, etc.)

  eg. lake @ $\mathbf{15\ °C} + \underbrace{\boldsymbol{\Delta T = 10\ °C}}_{\textit{resistance to HT}} = \mathbf{25\ °C}$

  $\Rightarrow$ $\boldsymbol{P_{sat} = 3.2\ kPa}$.
- this is why we have a condenser
  - the pressure at the exit of the turbine can be less than atmospheric pressure
  - the closed loop of the condenser allows us to use treated water on the cycle side
  - but if the pressure is less that atmospheric pressure, air can leak into the condenser, preventing condensation





3. INCREASED T_H BY ADDING SUPERHEAT:

- the average temperature at which heat is supplied in the boiler can be increased by superheating the steam
  - dry saturated steam from the boiler is passed through a second bank of smaller bore tubes within the boiler until the steam reaches the required temperature

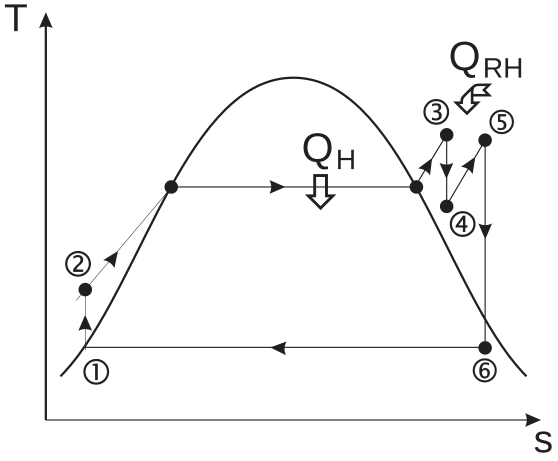
    The advantage is

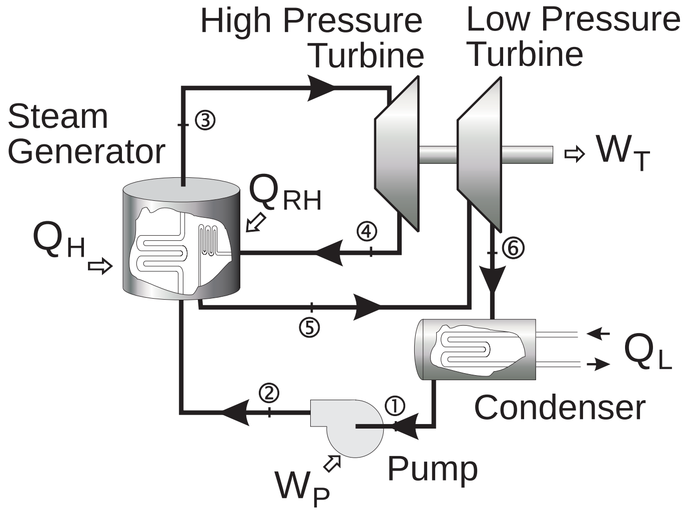
    $$\eta = \frac{W_{net} \uparrow}{Q_H \uparrow} \quad overall \uparrow$$

    The value of $\overline{T}_H$, the mean temperature at which heat is added, increases, while $\overline{T_L}$ remains constant. Therefore the efficiency increases.
  - the quality of the turbine exhaust increases, hopefully where $x > 0.9$
  - with sufficient superheating the turbine exhaust can fall in the superheated region.

Rankine Cycle with Reheat

- the wetness at the exhaust of the turbine should be no greater that 10% - this can result in physical erosion of the turbine blades
- but high boiler pressures are required for high efficiency - tends to lead to a high wetness ratio
- to improve the exhaust steam conditions, the steam can be reheated with the expansion carried out in two steps

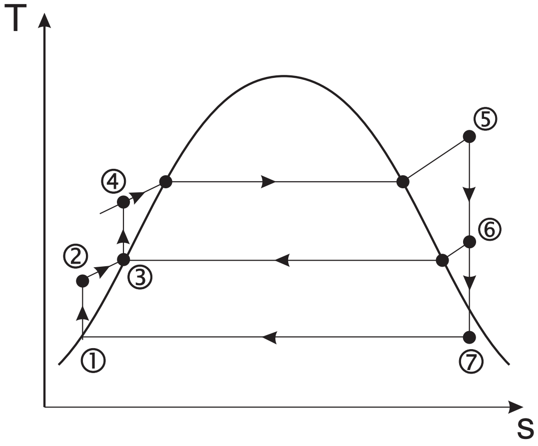


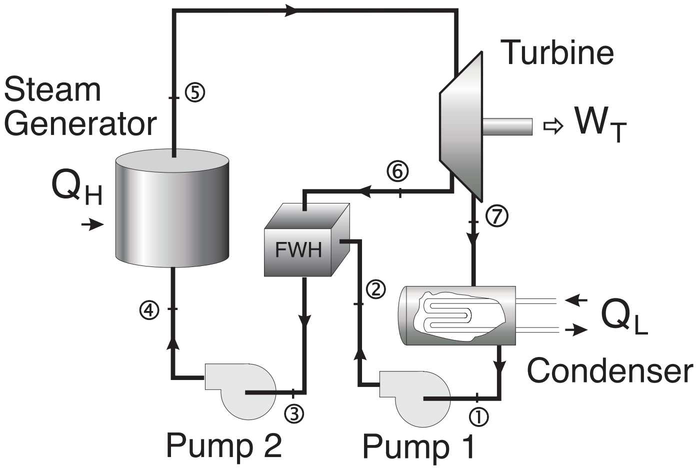


- the temperature of the steam entering the turbine is limited by metallurgical constraints
- modern boilers can handle up to $\boldsymbol{30\ MPa}$ and a maximum temperature of $\boldsymbol{T_{max} \approx 650\ ^{\circ}C}$.
- newer materials, such as ceramic blades can handle temperatures up to $\boldsymbol{750\ ^{\circ}C}$.

Rankine Cycle with Regeneration

- Carnot cycle has efficiency: $\eta = 1 - T_L/T_H$
  - add Q_H at as high a T_H as possible
  - reject Q_L at as low a T_L as possible
- the Rankine cycle can be used with a ***Feedwater Heater*** to heat the high pressure sub-cooled water at the pump exit to the saturation temperature
  - most of the heat addition (Q_H) is done at high temperature





Feedwater Heaters

There are two different types of feedwater heaters

1. ***OPEN FWH:*** the streams mix → high temperature steam with low temperature water at constant pressure
2. ***CLOSED FWH:*** a heat exchanger is used to transfer heat between the two streams but the streams do *not* mix. The two streams can be maintained at different pressures.

1. ***OPEN FWH:***

   - working fluid passes isentropically through the turbine stages and pumps
   - steam enters the first stage turbine at state 1 and expands to state 2 - where a fraction of the total flow is bled off into an open feedwater heater at $\boldsymbol{P_2}$
   - the rest of the steam expands into the second stage turbine at state point 3 - this portion of the fluid is condensed and pumped as a saturated liquid to the FWH at $\boldsymbol{P_2}$
   - a single mixed stream exists the FWH at state point 6

Analysis:

- we must determine the mass flow rates through each of the components.

  By performing an <u>mass balance</u> over the FWH

  $$\dot{m}_2 + \dot{m}_3 = \dot{m}_1 \qquad (1)$$

  If we normalize Eq. (1) with respect the total mass flow rate $\dot{m}_1$

  $$\frac{\dot{m}_2}{\dot{m}_1} + \frac{\dot{m}_3}{\dot{m}_1} = 1 \qquad (2)$$

  Let the flow at state point 2 be

  $$y = \frac{\dot{m}_2}{\dot{m}_1}$$

  Therefore

  $$\frac{\dot{m}_3}{\dot{m}_1} = 1 - y \qquad (3)$$

  Assuming no heat loss at the FWH, establish an <u>energy balance</u> across the FWH

  $$y h_2 + (1 - y) h_5 = 1 \cdot h_6$$

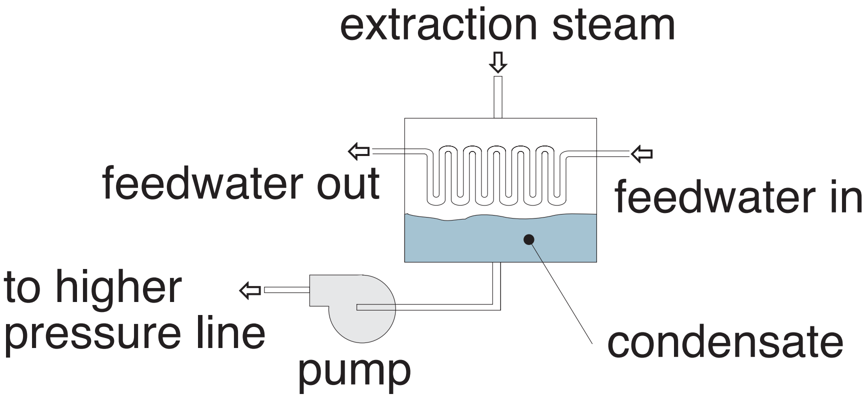
  $$\boxed{y = \frac{h_6 - h_5}{h_2 - h_5} = \frac{\dot{m}_2}{\dot{m}_1}}$$

  and

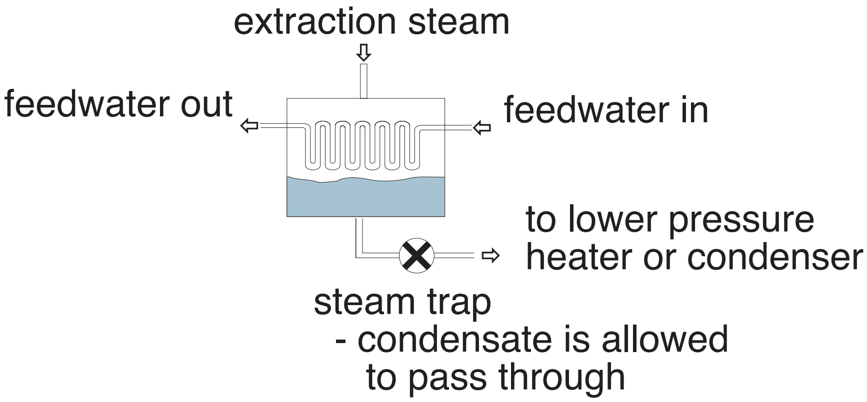
  $$\boxed{1 - y = \frac{\dot{m}_3}{\dot{m}_1}}$$

2. ***CLOSED FWH:***

- two variations exist
  (a) pump the condensate back to the high pressure line



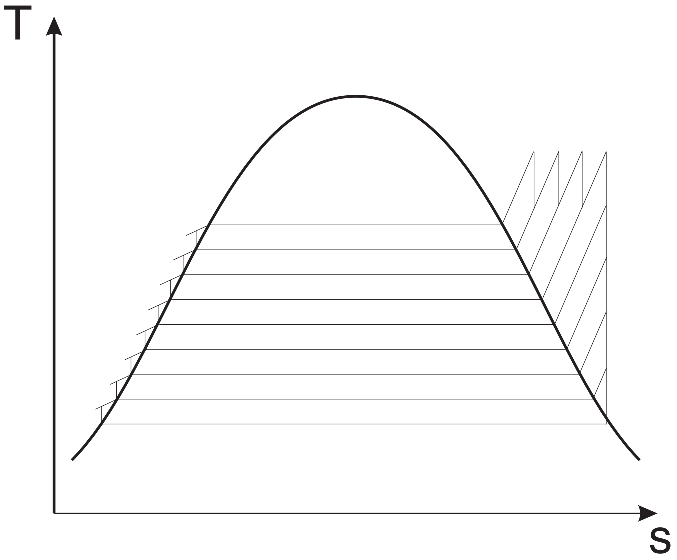
  (b) – a steam trap is inserted in the condensed steam line that allows only liquid to pass
    – liquid is passed to a low pressure region such as the condenser or a low pressure heater



- the incoming feedwater does not mix with the extracted steam
  - both streams flow separately through the heater
  - the two streams can have different pressures

Other Topics

“IDEAL” RANKINE CYCLE:

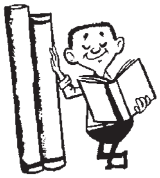


- too expensive to build
- requires multiple reheat and regeneration cycles
- approaches Carnot efficiency

TOPPING CYCLE (BINARY CYCLE):

- involves two Rankine cycles running in tandem with different working fluids such as mercury and water
- why:
  - typically a boiler will supply energy at $\mathbf{1300 - 1400\ ^\circ C}$
  - but $\boldsymbol{T_{critical}}$ for water is $\mathbf{374.14}$
    - most energy is absorbed below this temperature
    - high $\boldsymbol{\Delta T}$ between the boiler source and the water leads to a major source of irreversibilities
  - $\boldsymbol{T_{critical}}$ for mercury is about $\mathbf{1500\ ^\circ C}$
    - no need for superheating
  - combine the large enthalpy of evaporation of water at low temperatures with the advantages of mercury at high temperatures
  - in addition, the mercury dome leads to a high quality at the exit of the turbine

Refrigeration Cycle



Reading	**Problems**
10-1 → 10-5, 10-7, 10-9	10-11, 10-14, 10-39

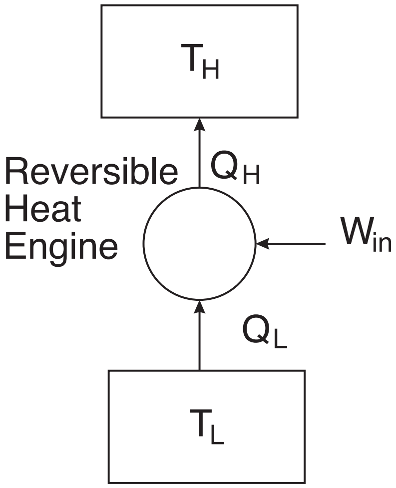
Definitions

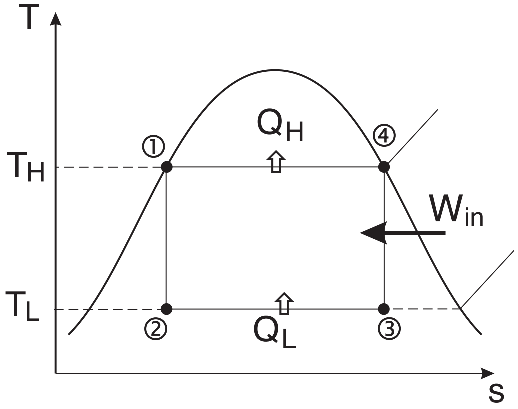
- refrigeration cycles may be classified as
  - vapour compression
  - gas compression
- we will examine only the vapour compression systems
- refrigerators and heat pumps have a great deal in common. The primary difference is in the manner in which heat is utilized.
  - ***Refrigerator*** $\underbrace{\downarrow C}_{takes\ heat\ from} \rightarrow \underbrace{H}_{transfers\ to}$
  - ***Heat Pump*** $\underbrace{C}_{takes\ heat\ from} \rightarrow \underbrace{H \uparrow}_{transfers\ to}$
- the Carnot cycle can serve as the initial model of the ideal refrigeration cycle.
  - operates as a reversed heat engine cycle - transfers a quantity of heat, Q_L, from a cold source at temperature, T_L

$$\begin{aligned} Q_L &= T_L(s_3 - s_2) \\ Q_H &= T_H(s_4 - s_1) \\ W_{in} &= Q_{net} = Q_H - Q_L \\ &= (T_H - T_L)(s_3 - s_2) \end{aligned}$$

The <u>coefficient of performance</u> (COP) is given by

$$COP = \frac{benefit}{cost}$$





$$\boldsymbol{COP_{refrig} = \frac{T_L}{T_H - T_L}}$$

$$\boldsymbol{COP_{heat\ pump} = \frac{T_H}{T_H - T_L}}$$

Note: $\boldsymbol{COP_{heat\ pump} = COP_{refrig} + 1}$, where the "**1**" accounts for the sensible heat addition in going from $\boldsymbol{T_L}$ to $\boldsymbol{T_H}$.

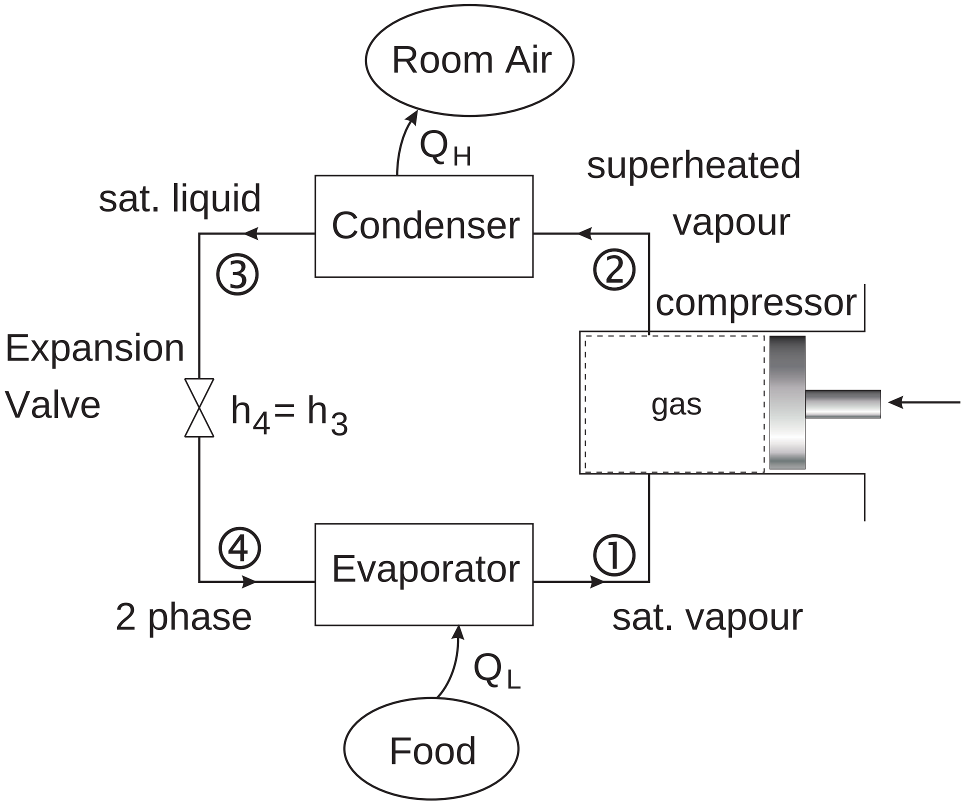
Definition

$$\boldsymbol{Ton\ of\ Cooling = 3517\ W = 12,000\ Btu/hr}$$

Derived from the fact that a ***ton of cooling*** is the energy required to freeze **2000** ***lbm*** of liquid water at **32 °*F*** into ice at **32 °*F*** in 24 hours.

$$\begin{aligned} \boldsymbol{latent\ heat\ of\ fusion} &= \boldsymbol{143.5\ Btu/lbm} \\ \boldsymbol{Ton} &= \boldsymbol{143.5\ \frac{Btu}{lbm} \cdot \frac{2000\ lbm}{24\ hrs}} \\ &= \boldsymbol{11,960\ Btu/hr} \end{aligned}$$

Vapour Compression Refrigeration Cycle

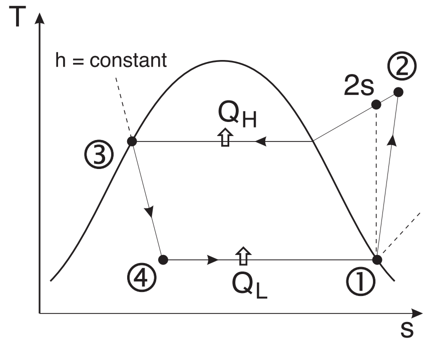


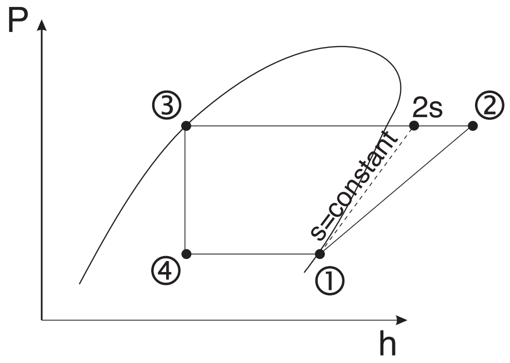
Assumptions for Ideal VCRC

- irreversibilities within the evaporator, condenser and compressor are ignored
- no frictional pressure drops
- refrigerant flows at constant pressure through the two heat exchangers (evaporator and condenser)
- stray heat losses to the surroundings are ignored
- compression process is isentropic

The thermal efficiency of the cycle can be calculated as

$$\boldsymbol{\eta = \frac{q_{evap}}{w_{comp}} = \frac{h_1 - h_4}{h_{2s} - h_1}}$$



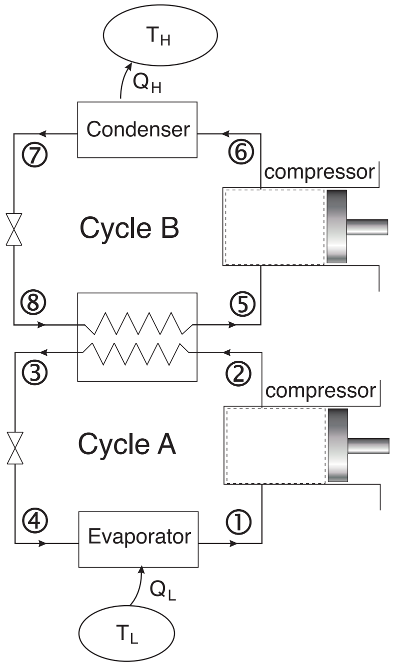


How to Choose a Refrigerant

- the heat of vaporization of the refrigerant should be high. The higher $\boldsymbol{h_{fg}}$, the greater the refrigerating effect per $\boldsymbol{kg}$ of fluid circulated
- the specific heat of the refrigerant should be low. The lower the specific heat, the less heat it will pick up for a given change in temperature during the throttling or in flow through the piping, and consequently the greater the refrigerating effect per $\boldsymbol{kg}$ of refrigerant
- the specific volume of the refrigerant should be low to minimize the work required per $\boldsymbol{kg}$ of refrigerant circulated
- since evaporation and condenser temperatures are fixed by the temperatures of the surroundings - selection is based on operating pressures in the evaporator and the condenser
- selection is based on the suitability of the pressure-temperature relationship of the refrigerant
- other factors include: chemical stability, toxicity, cost, environmental friendliness

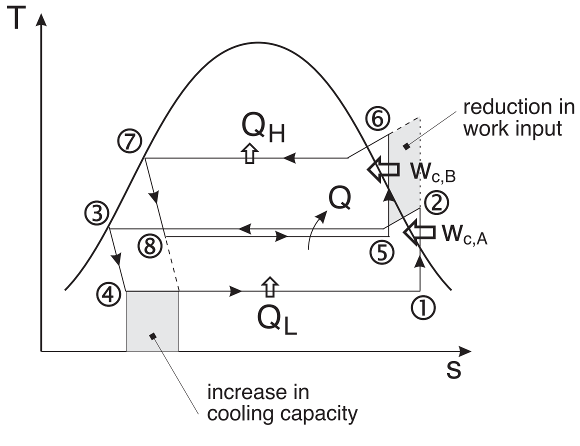
	$\boldsymbol{h_{fg}}$ $(\boldsymbol{kJ/kg})$			
$\boldsymbol{T}(°\boldsymbol{C})$	R12	R134a	Ammonia	H_2O
−20	**160.8**	**213.1**	**1329.3**	–
0	**151.4**	**198.8**	**1262.4**	**2501.3**
20	**140.8**	**182.5**	**1186.7**	**2454.1**
$\boldsymbol{\nu_g}$ **@20** $°\boldsymbol{C}$ $(\boldsymbol{m^3/kg})$	**0.0308**	**0.0356**	**0.1494**	**57.79**
$\boldsymbol{c_p}$ $(\boldsymbol{kJ/kg \cdot K})$	**0.96**	**1.42**	**4.67**	**4.188**

Cascade Refrigeration System



The refrigerants can be selected to have reasonable evaporator and condenser pressures in the two or more temperature ranges

$$\boldsymbol{COP = \frac{Q_L(\uparrow)}{W_{net}(\downarrow)} \quad overall(\uparrow)}$$



Absorption Refrigeration System

Differences between an absorption refrigeration system and a VCRC

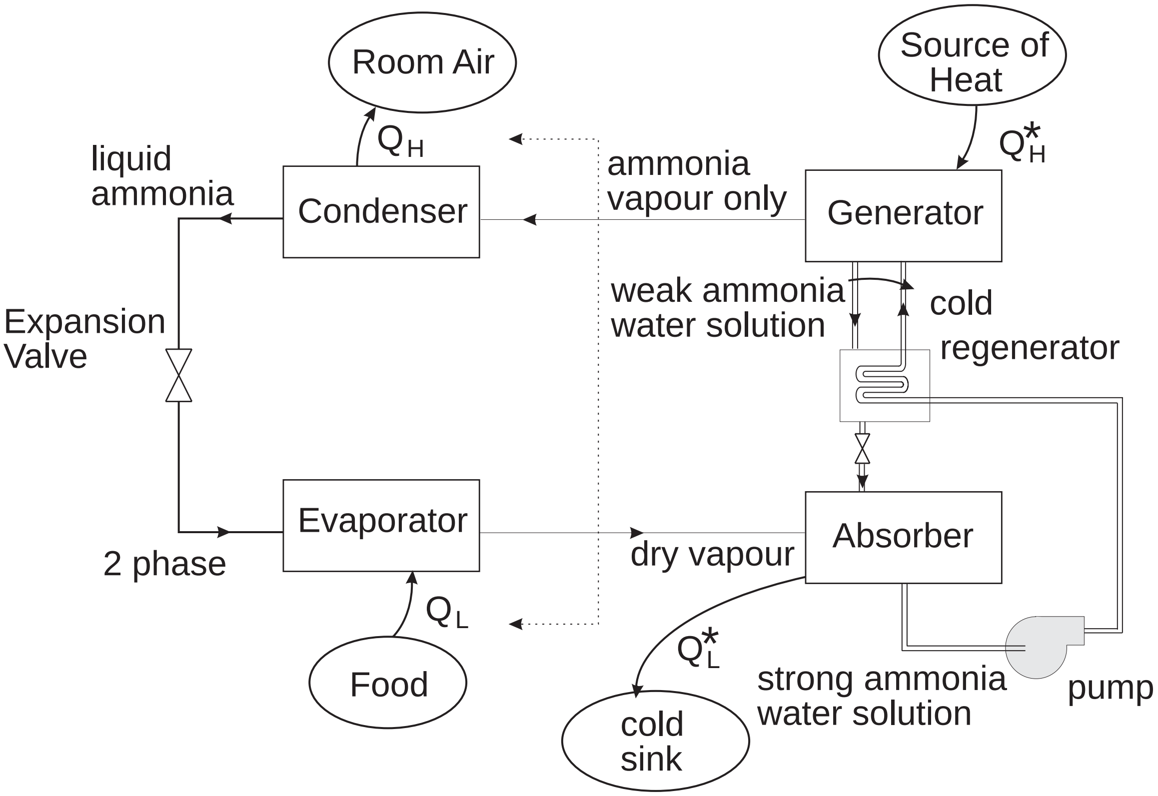
VCRC	Absorption RS
• vapour is compressed between the evaporator and the condenser • process is driven by work	• the refrigerant is absorbed by an absorbent material to form a liquid solution • heat is added to the process to retrieve the refrigerant vapour from the liquid solution • process is driven by heat

Common Refrigerants/Absorber Combinations

	Refrigerant	**Absorber**
1.	ammonia	water
2.	water	lithium bromide

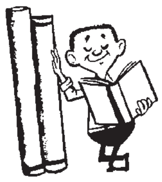
Process

- ammonia circulates through the condenser, expansion valve and evaporator (same as in the VCRC)
- the compressor is replaced by an absorber, pump, generator, regenerator and a valve
- in the absorber, ammonia vapour is absorbed by liquid water
  - the process is exothermic (gives off heat)
  - ammonia vapour is absorbed into the water at low $\boldsymbol{T}$ and $\boldsymbol{P}$ maintained by means of $\boldsymbol{Q_L^*}$
  - absorption is proportional to $\boldsymbol{1/T} \quad \Rightarrow$ the cooler the better
- the pump raises the solution to the pressure of the generator
- in the generator, ammonia is driven out of the solution by the addition of $\boldsymbol{Q_H^*}$, (endothermic reaction)
- ammonia vapour is passed back to the condenser



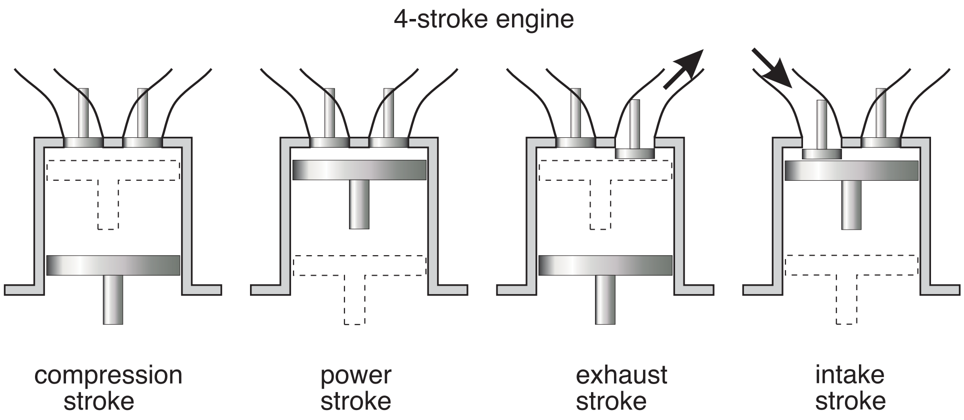
- a regenerator is used to recoup some of the energy from the weak ammonia water solution passed back to the absorber. This energy is transferred to the solution pumped to the generator. This reduces the $\boldsymbol{Q_H^*}$ required to vapourize the solution in the generator. It also reduces the amount of $\boldsymbol{Q_L^*}$ that needs to be removed from the solution in the absorber.

Internal Combustion Engines



Reading	**Problems**
8-3 → 8-7	8-35, 8-45, 8-52

The Gasoline Engine



- conversion of chemical energy to mechanical energy
- can obtain very high temperatures due to the short duration of the power stroke

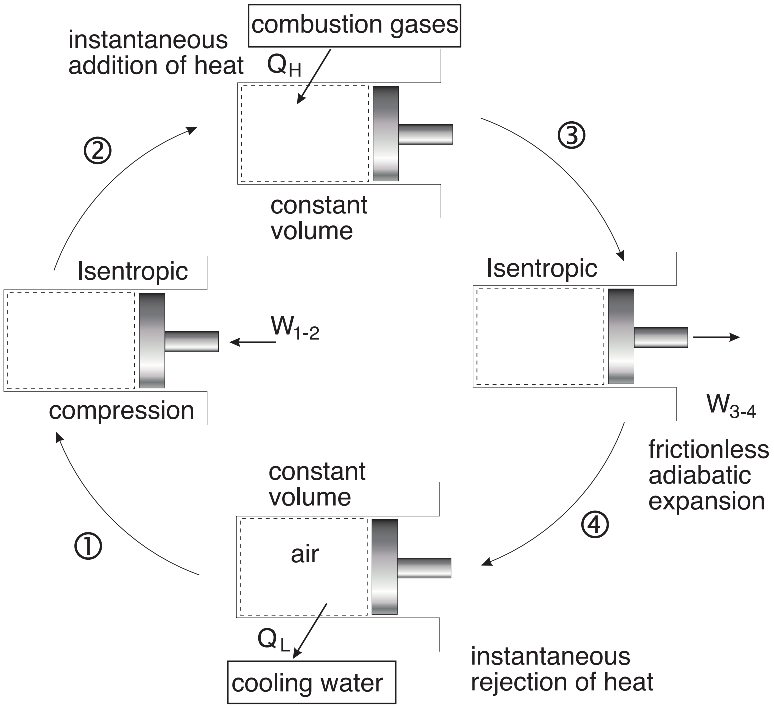
Air Standard Cycle

A closed cycle model for the IC engine, such as the gasoline or diesel cycle. Some assumptions must be made in order to model this complex process.

ASSUMPTIONS:

- air is an ideal gas with constant c_p and c_v
- no intake or exhaust processes
- the cycle is completed by heat transfer to the surroundings
- the internal combustion process is replaced by a heat transfer process from a TER
- all internal processes are reversible
- heat addition occurs instantaneously while the piston is at TDC

Otto Cycle



Otto Cycle Efficiency

We know the efficiency can be written as the benefit over the cost or in the case of the Otto cycle

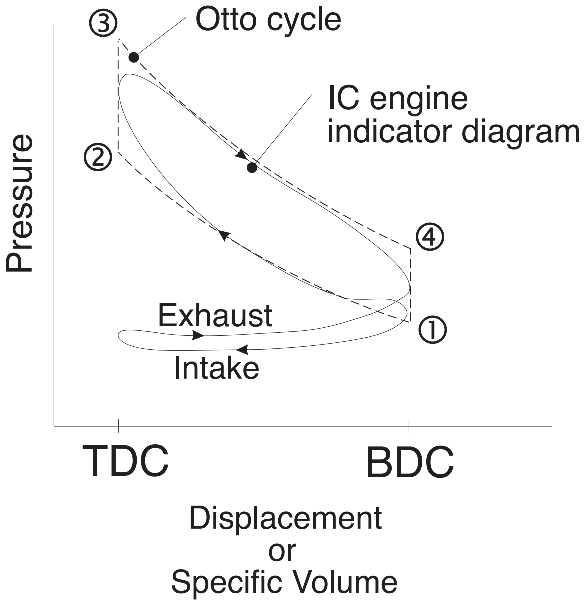
$$\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{Q_{4-1}}{Q_{2-3}}$$

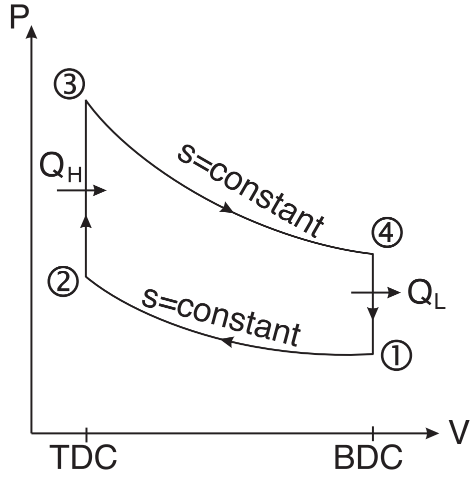
which can be reduced to

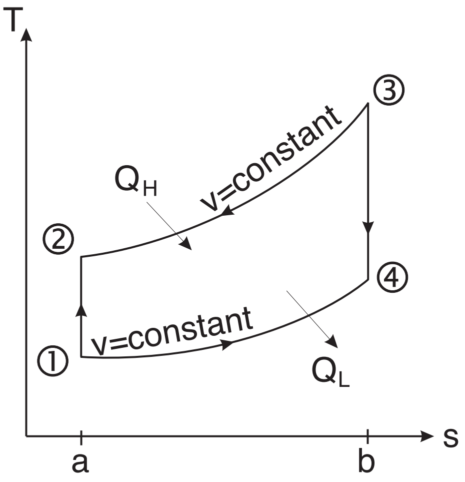
$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1}\right)^{k-1} = 1 - \left(\frac{V_1}{V_2}\right)^{1-k}$$

$$r = \frac{V_1}{V_2} = \frac{V_4}{V_3} = compression\ ratio$$

$$\boxed{\eta_{Otto} = 1 - r^{1-k}}.$$

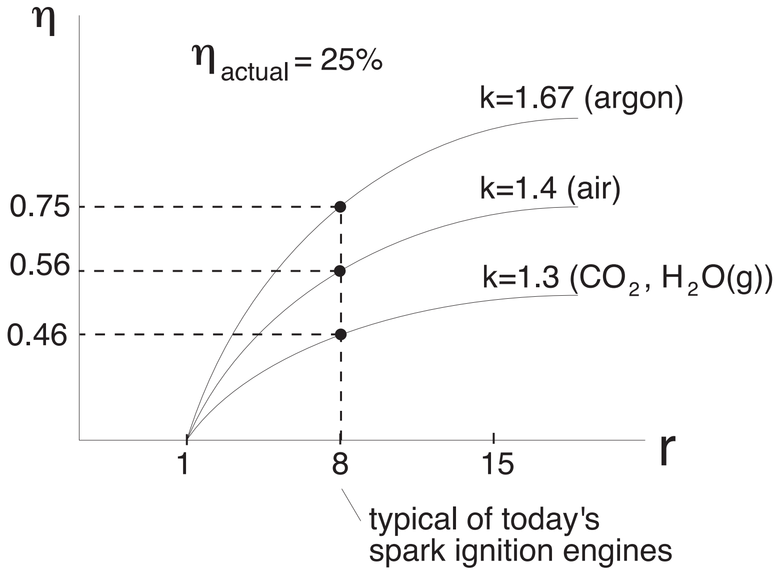






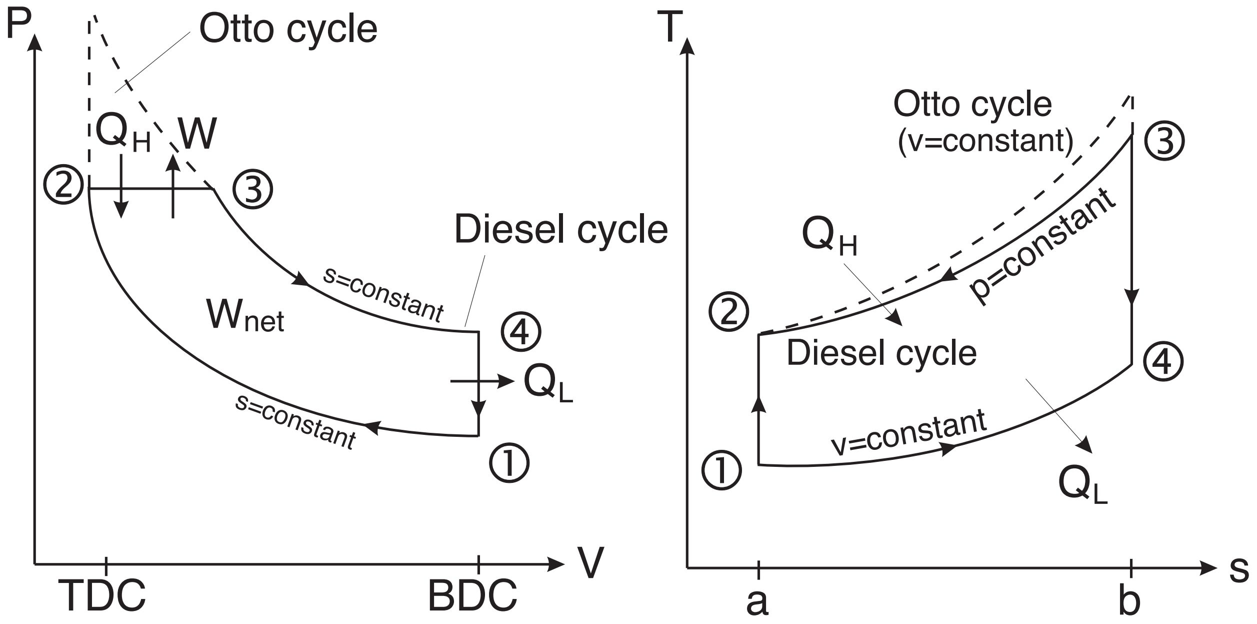
Why not go to higher compression ratios?

- there is an increased tendency for the fuel to detonate as the compression ratio increases
- the pressure wave gives rise to engine knock
- can be reduced by adding tetraethyl lead to the fuel
- not good for the environment



Diesel Cycle

- an ideal cycle for the compression ignition engine (diesel engine)
- all steps in the cycle are reversible
- heat is transferred to the working fluid at constant pressure
- heat transfer must be just sufficient to maintain a constant pressure



Diesel Cycle Efficiency

We know the efficiency can be written as the benefit over the cost or in the case of the Diesel cycle

$$\boldsymbol{\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{Q_{4-1}}{Q_{2-3}}}$$

which leads to

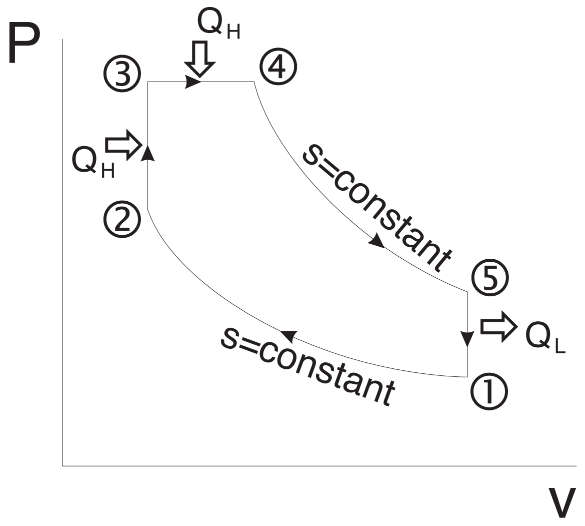
$$\boxed{\boldsymbol{\eta_{Diesel} = 1 - \frac{1}{r^{k-1}}\left(\frac{1}{k}\right)\left(\frac{r_v^k - 1}{r_v - 1}\right)}}$$

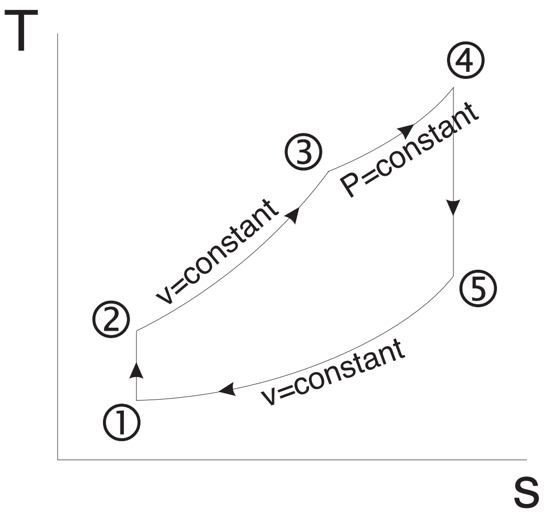
Comparison of the Otto and the Diesel Cycle

- $\boldsymbol{\eta_{Otto} > \eta_{Diesel}}$ for the same compression ratio
- but a diesel engine can tolerate a higher ratio since only air is compressed in a diesel cycle and spark knock is not an issue
- direct comparisons are difficult

Dual Cycle (Limited Pressure Cycle)

- this is a better representation of the combustion process in both the gasoline and the diesel engines
- in a compression ignition engine, combustion occurs at TDC while the piston moves down to maintain a constant pressure





Dual Cycle Efficiency

Given

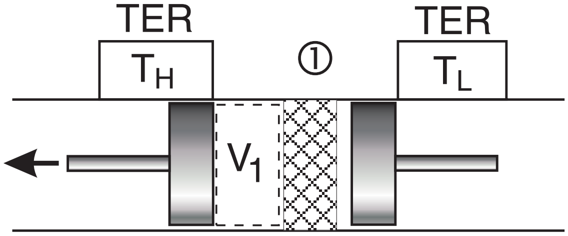
$$\begin{aligned} \boldsymbol{r} &= \frac{\boldsymbol{V_1}}{\boldsymbol{V_2}} = \boldsymbol{compression\ ratio} \\ \boldsymbol{r_v} &= \frac{\boldsymbol{V_4}}{\boldsymbol{V_3}} = \boldsymbol{cutoff\ ratio} \\ \boldsymbol{r_p} &= \frac{\boldsymbol{P_3}}{\boldsymbol{P_2}} = \boldsymbol{pressure\ ratio} \end{aligned}$$

$$\boxed{\boldsymbol{\eta_{Dual} = 1 - \frac{r_p r_v^k - 1}{\left[(r_p - 1) + k r_p (r_v - 1)\right] r^{k-1}}}}$$

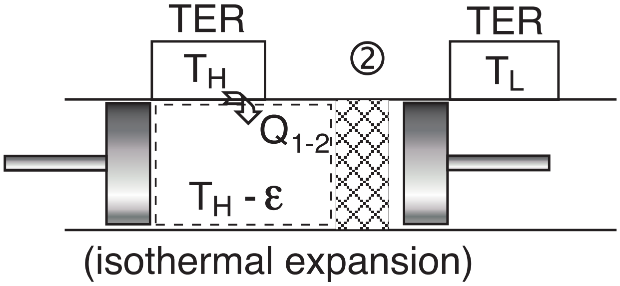
Note: if $\boldsymbol{r_p = 1}$ we get the diesel efficiency.

Stirling Cycle

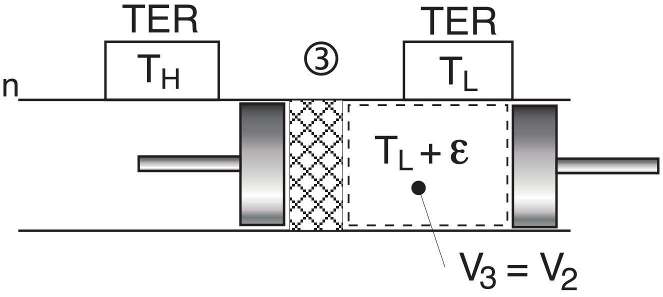
① → ②
isothermal expansion
at high temperature
- heat is added,
  volume expands



② → ③
constant volume
process

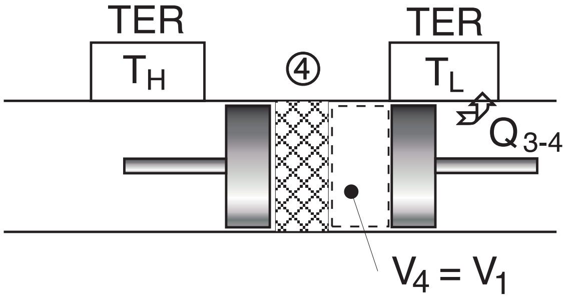


③ → ④
isothermal compression
at low temperature

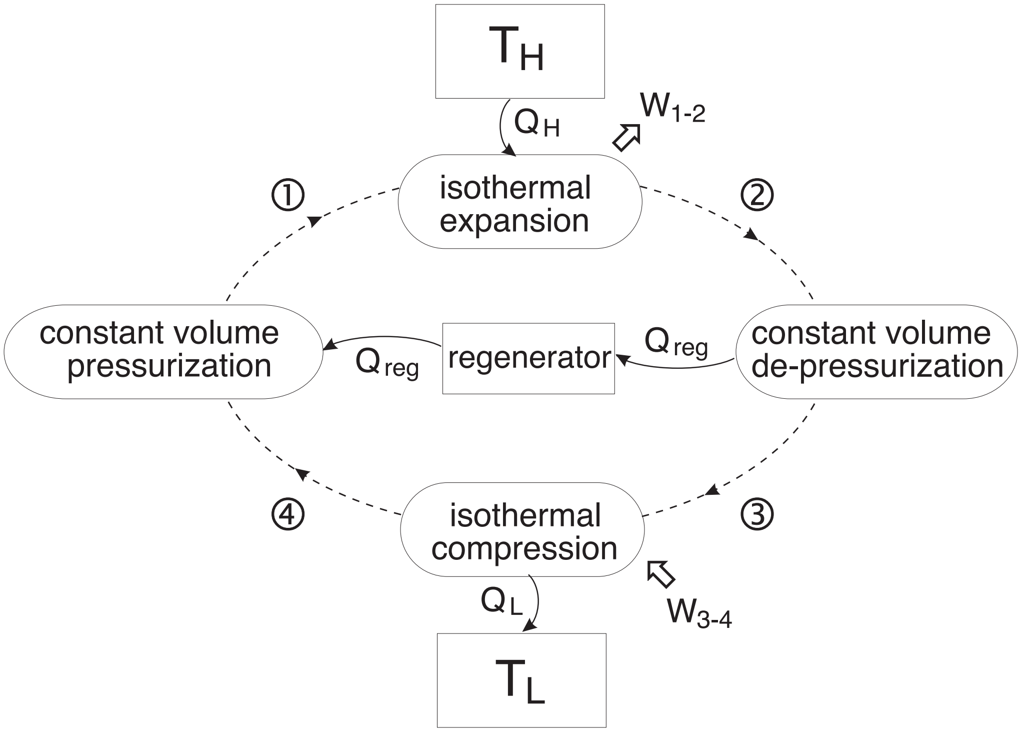


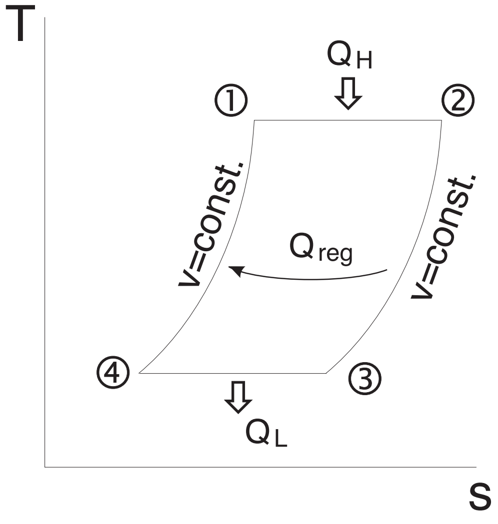
heat the regenerator
by pushing the hot
gas through it

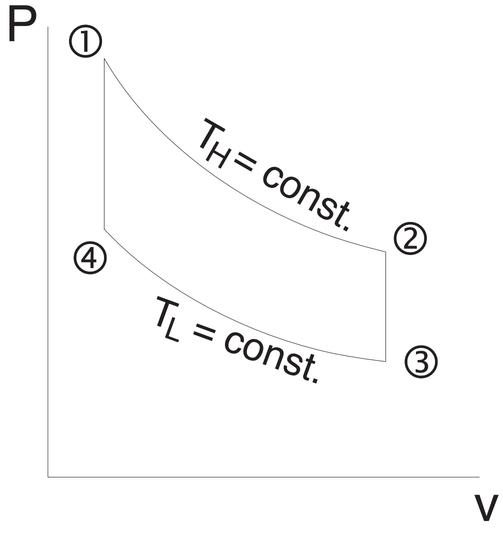
④ → ①
constant volume
process



move both pistons
to the left to get back
to state 1.
During this process the
regenerator cools down
by giving off energy to
the gas

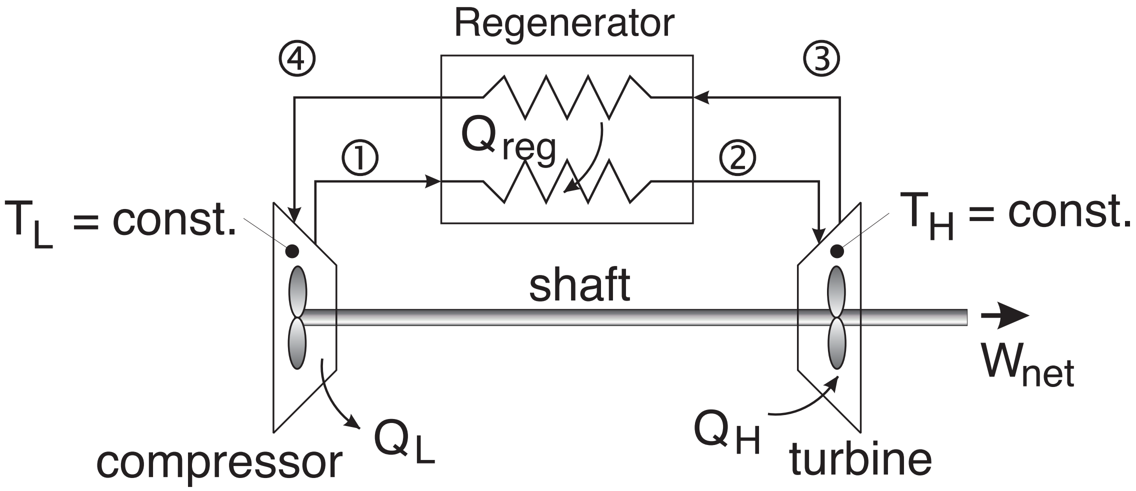






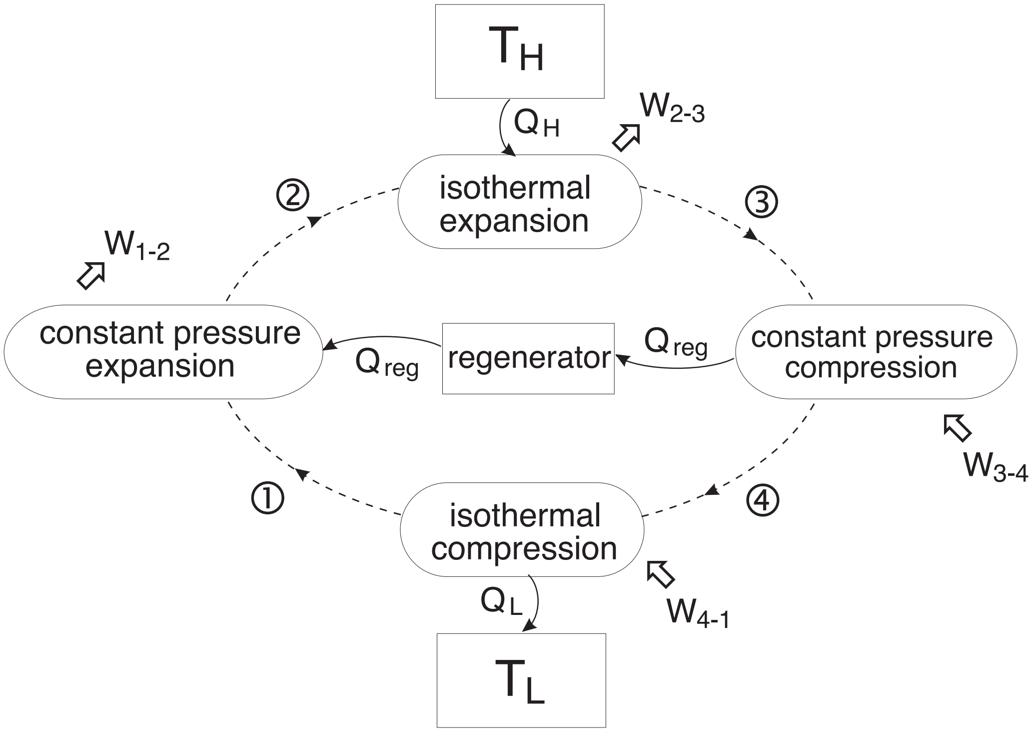
- reversible regenerator used as an energy storage device
- possible to recover all heat given up by the working fluid in the constant volume cooling process
- all the heat received by the cycle is at $\boldsymbol{T_H}$ and all heat rejected at $\boldsymbol{T_L}$
- $\boldsymbol{\eta_{Stirling} = 1 - T_L/T_H}$ (Carnot efficiency)

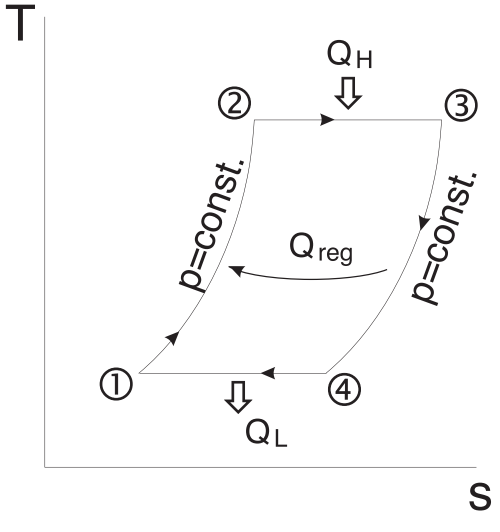
Ericsson Cycle

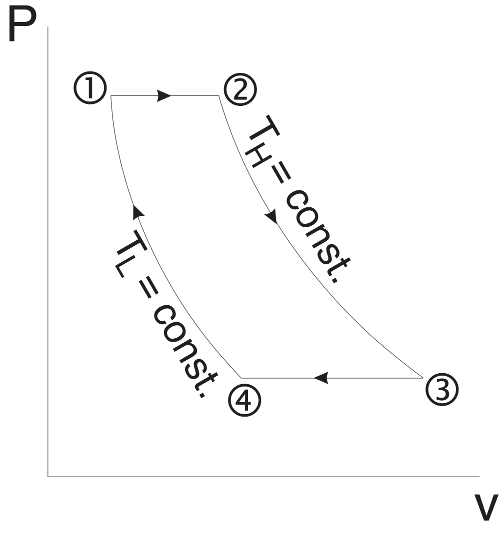


- hardware is not complicated
- but it is very difficult to operate turbines and compressors isothermally
- can approach isothermal conditions by repeated intercooling (compressor) and repeated reheating (turbines)
- $\eta_{Stirling} = 1 - T_L/T_H$ (Carnot efficiency)

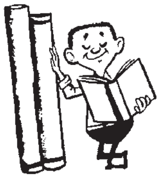
$$\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L(s_4 - s_1)}{T_H(s_3 - s_2)} = 1 - \frac{T_L}{T_H}$$


T_H
Q_H
W_{2-3}
②
isothermal expansion
③
W_{1-2}
constant pressure expansion
regenerator
Q_{reg}
Q_{reg}
constant pressure compression
W_{3-4}
①
④
isothermal compression
W_{4-1}
Q_L
T_L


T
Q_H
②
③
p=const.
p=const.
Q_{reg}
①
④
Q_L
s


P
①
②
T_H= const.
T_L = const.
④
③
v

Brayton Cycle



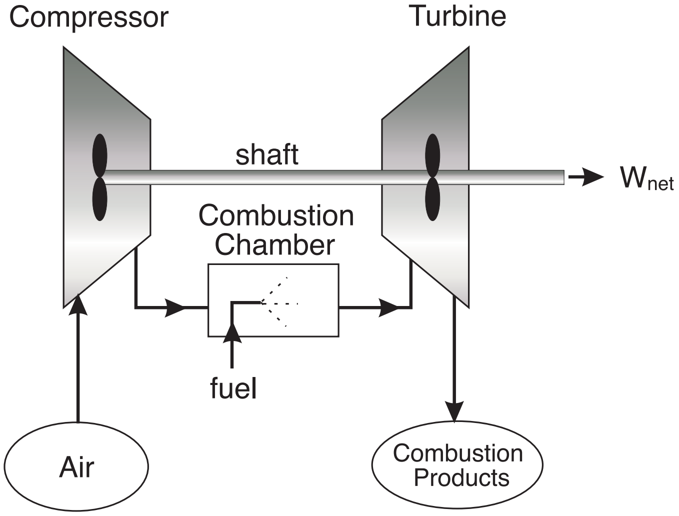
Reading 8-8 → 8-10

Problems 8-76, 8-91, 8-92, 8-107, 8-141

Introduction

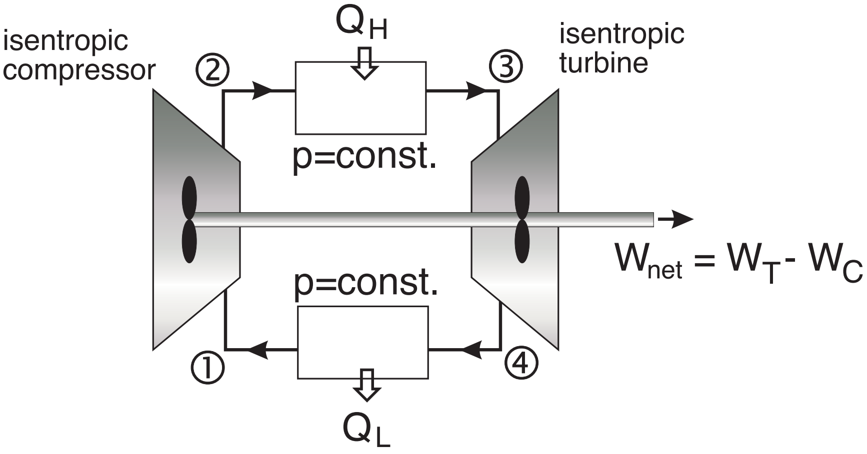
The gas turbine cycle is referred to as the Brayton Cycle or sometimes the Joule Cycle. The actual gas turbine cycle is an open cycle, with the intake and exhaust open to the environment.

Open Cycle Gas Turbine Engines

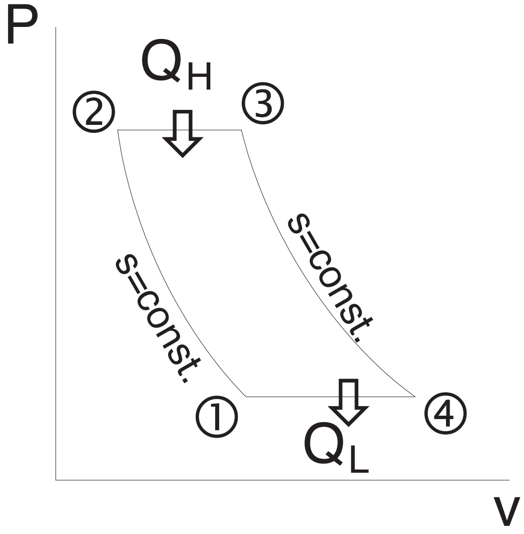


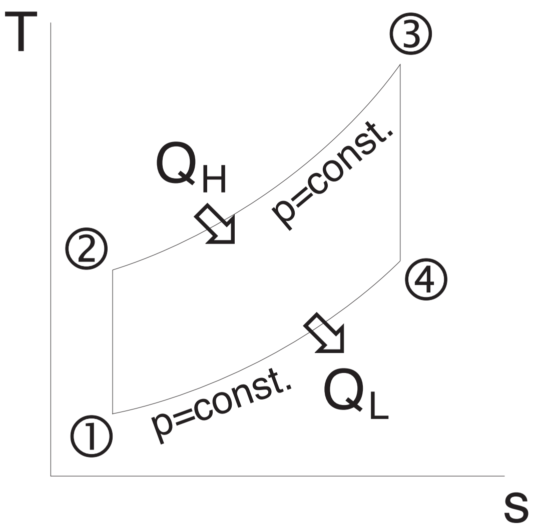
- after compression, air enters a combustion chamber into which fuel is injected
- the resulting products of combustion expand and drive the turbine
- combustion products are discharged to the atmosphere
- compressor power requirements vary from 40-80% of the power output of the turbine (remainder is net power output), i.e. back work ratio = 0.4 → 0.8
- high power requirement is typical when gas is compressed because of the large specific volume of gases in comparison to that of liquids

Idealized Air Standard Brayton Cycle



- closed loop
- constant pressure heat addition and rejection
- ideal gas with constant specific heats

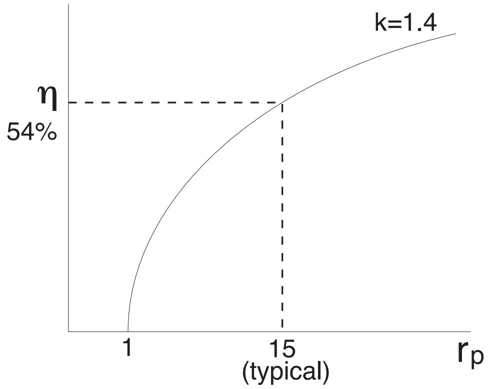




Brayton Cycle Efficiency

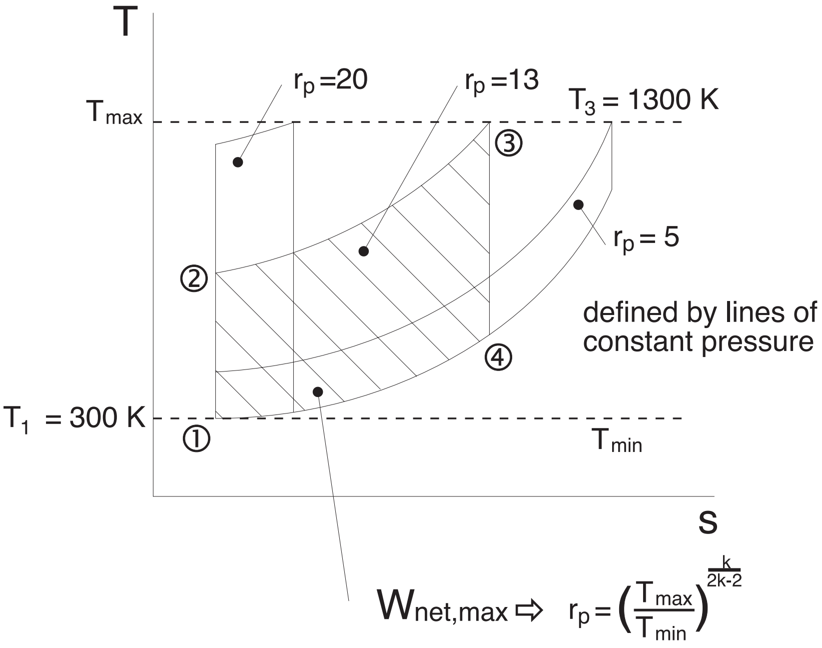
The efficiency of the cycle is given by the benefit over the cost or

$$\boldsymbol{\eta = \frac{W_{net}}{Q_H} = 1 - (r_p)^{(1-k)/k}}$$

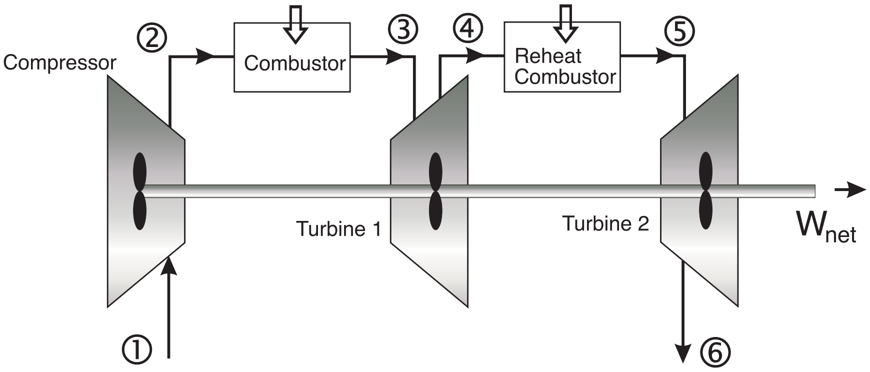


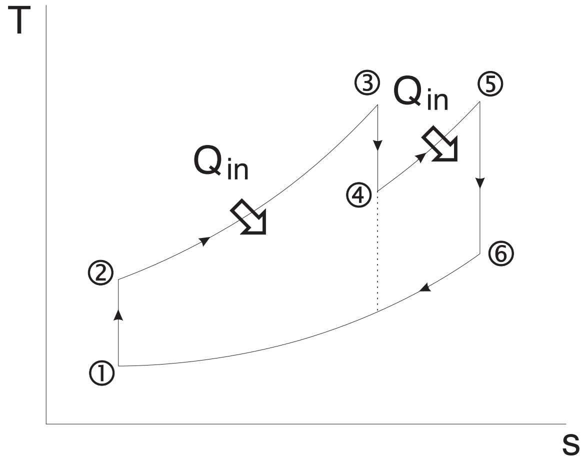
Maximum Pressure Ratio

Given that the maximum and minimum temperature can be prescribed for the Brayton cycle, a change in the pressure ratio can result in a change in the work output from the cycle.



Brayton Cycle with Reheat

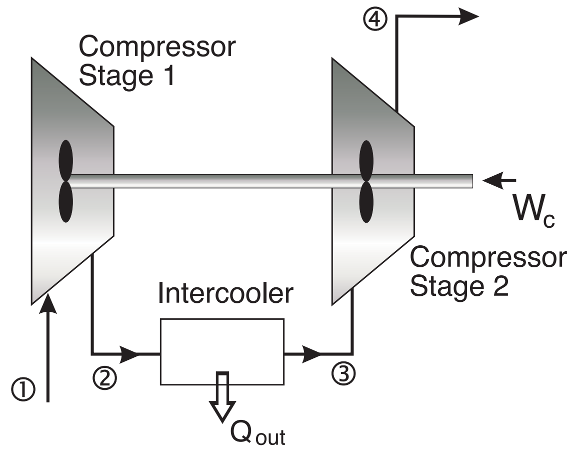


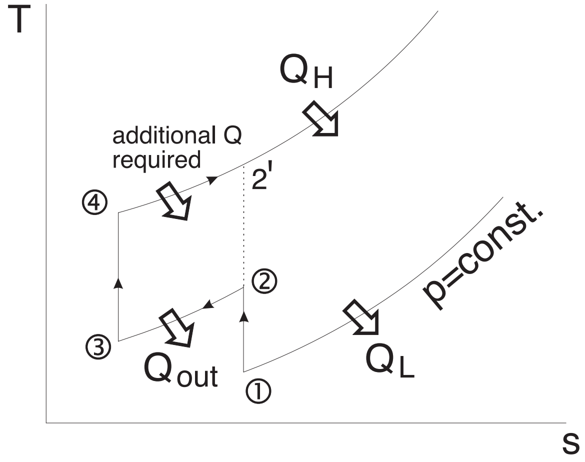


- the maximum temperature at T_3 entering the turbine is limited due to metallurgical constraints
- excess air is extracted and fed into a second stage combustor and turbine
- total work is increased
- but additional heat input is required

Compression with Intercooling

- the work required to compress in a steady flow device can be reduced by compressing in stages
- cooling the gas reduces the specific volume and in turn the work required for compression





How Can We Improve Efficiency?

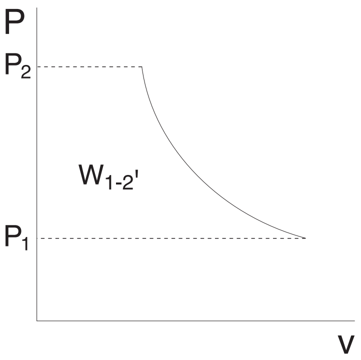
We know the efficiency of a Brayton cycle engine is given as

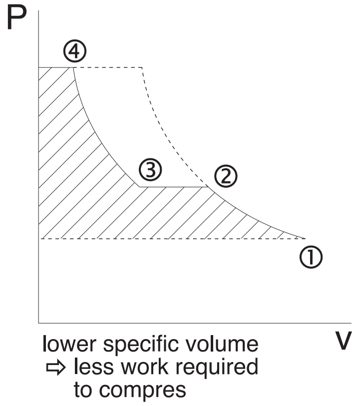
$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_H} = \frac{\dot{W}_{turbine} - \dot{W}_{compressor}}{\dot{Q}_H}$$

There are several possibilities, for instance we could try to increase $\dot{W}_{turbine}$ or decrease $\dot{W}_{compressor}$.

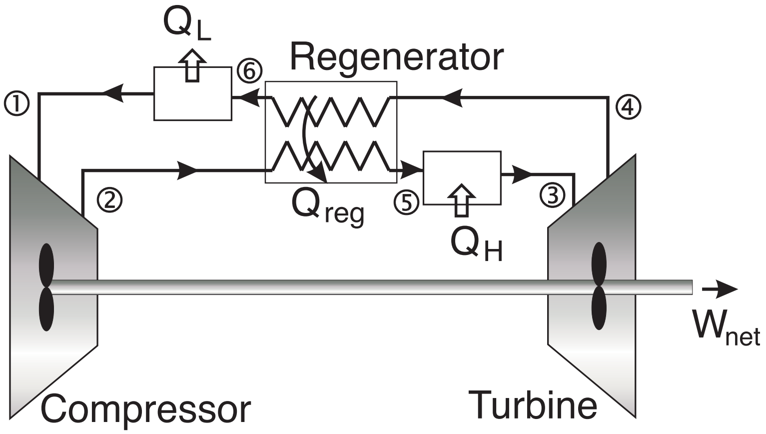
Recall that for a SSSF, reversible compression or expansion

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v \, dP \quad \Rightarrow \quad \textbf{keep } v \uparrow \textbf{ in turbine, keep } v \downarrow \textbf{ in compressor}$$





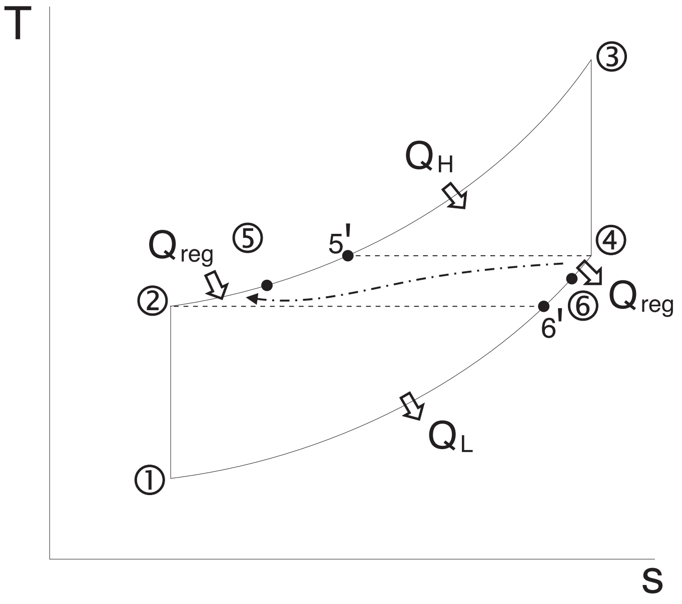
Brayton Cycle with Regeneration



- a regenerator (heat exchanger) is used to reduce the fuel consumption to provide the required $\dot{Q}_H$
- the efficiency with a regenerator can be determined as:

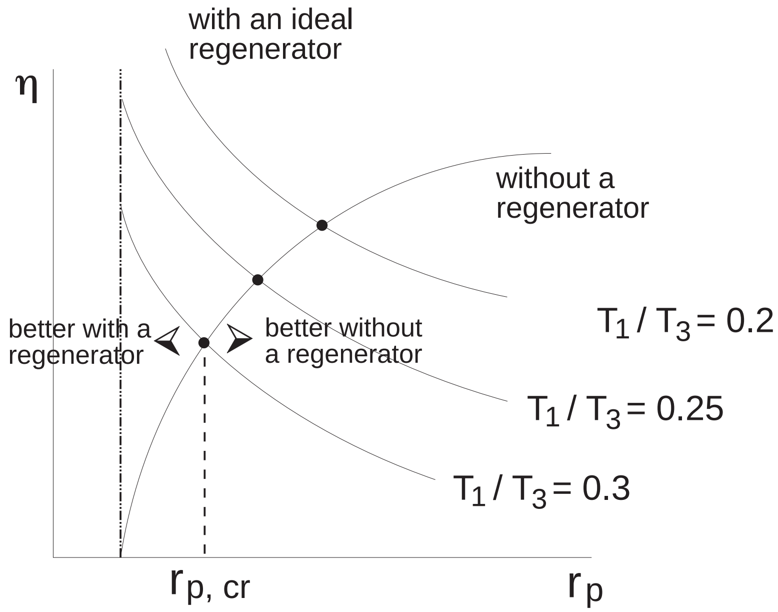
$$\begin{aligned}
\eta = \frac{\dot{W}_{net}}{\dot{Q}_H} &= 1 - \frac{\dot{Q}_L}{\dot{Q}_H} \\
&= 1 - \frac{c_p(T_6 - T_1)}{c_p(T_3 - T_5)} \quad \Rightarrow \quad (for\ a\ real\ regenerator) \\
&= 1 - \frac{c_p(T_6' - T_1)}{c_p(T_3 - T_5')} \quad \Rightarrow \quad (for\ an\ ideal\ regenerator) \\
&= 1 - \frac{c_p(T_2 - T_1)}{c_p(T_3 - T_4)}
\end{aligned}$$

and

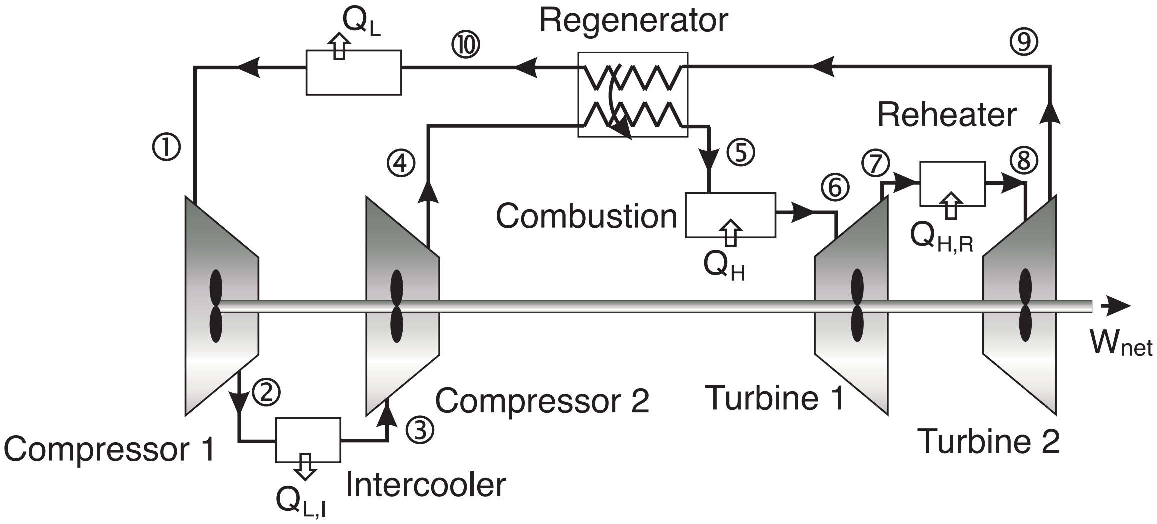


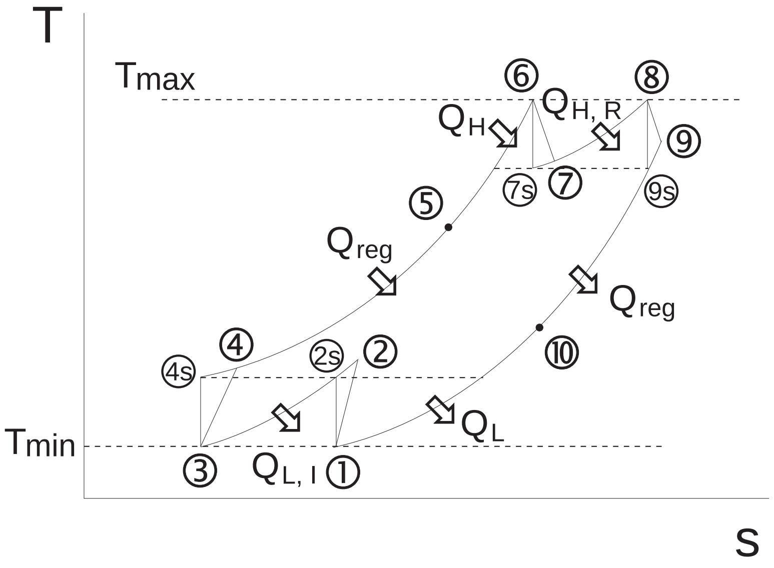
$$\boxed{\eta = 1 - \left(\frac{T_{min}}{T_{max}}\right)(r_p)^{(k-1)/k}}$$

- for a given T_{min}/T_{max}, the use of a regenerator above a certain r_p will result in a reduction of η



Brayton Cycle With Intercooling, Reheating and Regeneration





Compressor and Turbine Efficiencies

Isentropic Efficiencies

(1) $$\eta_{comp} = \frac{h_{2,s} - h_1}{h_2 - h_1} = \frac{c_p(T_{2,s} - T_1)}{c_p(T_2 - T_1)}$$

(2) $$\eta_{turb} = \frac{h_3 - h_4}{h_3 - h_{4,s}} = \frac{c_p(T_3 - T_4)}{c_p(T_3 - T_{4,s})}$$

(3) $$\eta_{cycle} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{c_p(T_4 - T_1)}{c_p(T_3 - T_2)}$$

Given the turbine and compressor efficiencies and the maximum (T_3) and the minimum (T_1) temperatures in the process, find the cycle efficiency (η_{cycle}).

(4) Calculate T_{2s} from the isentropic relationship,

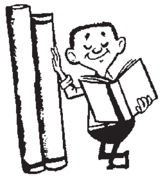
$$\frac{T_{2,s}}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}.$$

Get T_2 from (1).

(5) Do the same for T_4 using (2) and the isentropic relationship.

(6) substitute T_2 and T_4 in (3) to find the cycle efficiency.

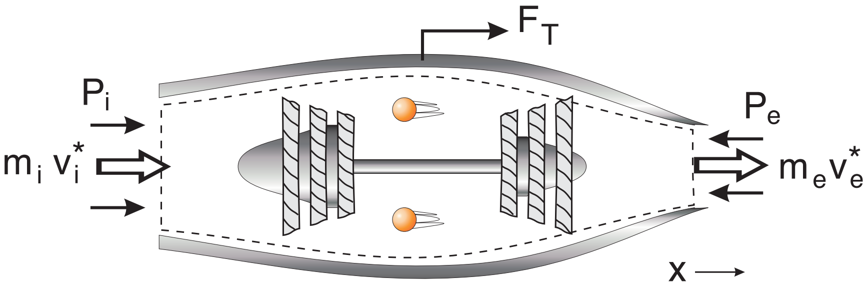
Jet Propulsion



Reading	**Problems**
8-11	8-113, 8-117

Gas Turbines for Aircraft Propulsion

- gas turbines are well suited to aircraft propulsion because of their favorable power-to-weight ratio
- the exhaust pressure of the turbine will be greater than that of the surroundings
- since the gases leave at a high velocity, the change in momentum that the gas undergoes gives a thrust to the aircraft
- gases are expanded in the turbine to a pressure where the turbine work is just equal to the compressor work plus some auxiliary power for pumps and generators i.e. the net work output is zero
- since the gases leave at a high velocity, the change in momentum that the gas undergoes provides a thrust to the aircraft
- typically operate at higher pressure ratios, often in the range of 10 to 25

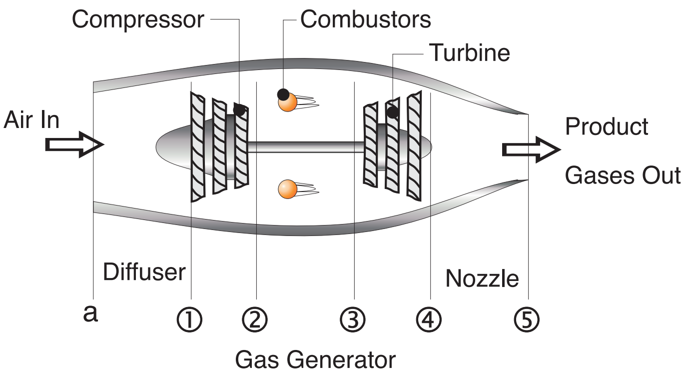


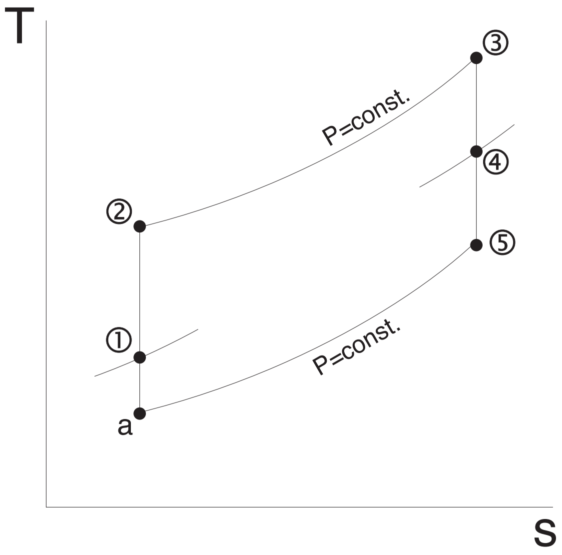
Specific Impulse: $$\boldsymbol{I = \frac{F_T}{\dot{m}_i} = v_e^* - v_i^* = \frac{\text{thrust}}{\text{mass}}}$$

Propulsive Power: $$\boldsymbol{\dot{W}_T = F_T\; v_i^* \approx \dot{m}_i(v_e^* - v_i^*)v_i^*}$$

Propulsive Efficiency: $$\boldsymbol{\eta = \frac{\dot{W}_T}{\dot{Q}_{in}}}$$

Turbojet Engine

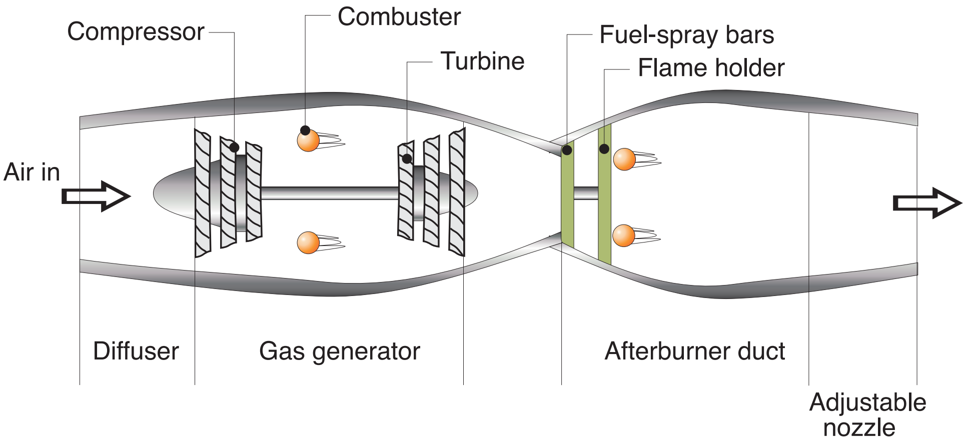




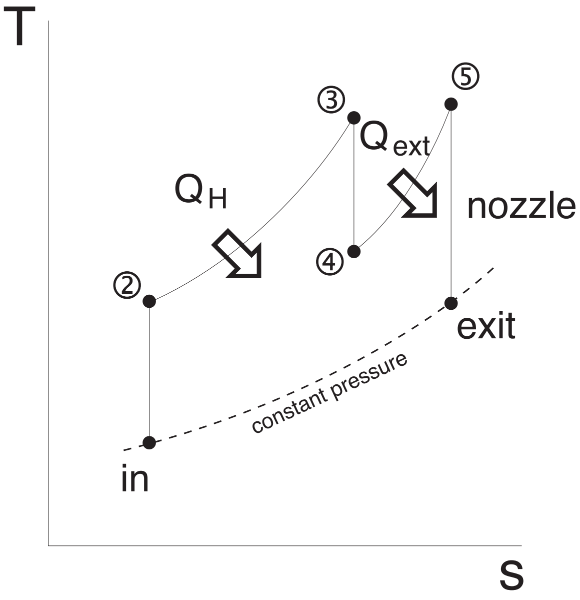
Sections

- **a-1**: **diffuser**
  - decelerates the incoming flow relative to the engine
  - a pressure rise known as a ram effect occurs, $\boldsymbol{v^*}$ (↓), $\boldsymbol{P}$ (↑)
- **1-4**: gas generator
  - compressor, combustor and turbine
    - 1-2: isentropic compression
    - 2-3: constant pressure heat addition
    - 3-4: isentropic expansion through the turbine during which work is developed
  - turbine power just enough to drive the compressor
  - air and fuel are mixed and burned in the combustion chamber at constant pressure
  - $\boldsymbol{P_T >> P_{atm}}$
- **4-5**: nozzle
  - isentropic expansion through the nozzle, air accelerates and the pressure deceases
  - gases leave the turbine significantly higher in pressure than atmospheric pressure
  - gases are expanded to produce a high velocity, $\boldsymbol{v_e^* >> v_i^*}$ results in a thrust
  - $\boldsymbol{v_1^* << v_a^*}$ $\boldsymbol{v_1^*}$ is negligible
  - $\boldsymbol{v_4^* << v_5^*}$ $\boldsymbol{v_4^*}$ is negligible

Afterburner



- similar to a reheat device
- produces a higher temperature at the nozzle inlet, $\boldsymbol{T_5 > T_4}$
- results in an increase in velocity

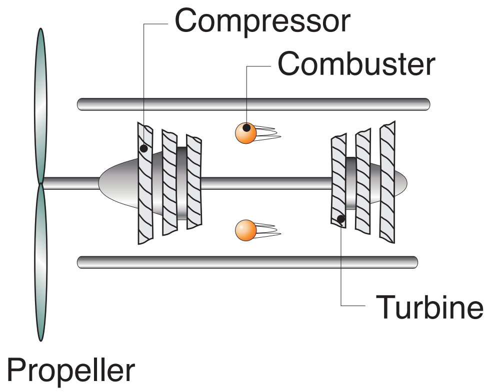


$$\boldsymbol{v_e^* = \sqrt{2(h_4 - h_e)}}$$

$$\boldsymbol{= \sqrt{2c_p(T_4 - T_e)}}$$

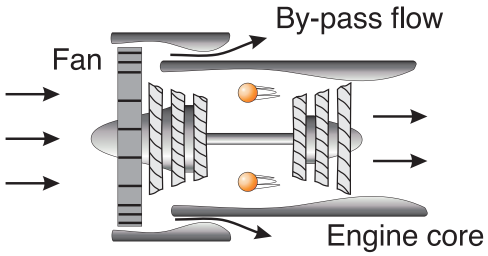
Other Types of Engines

1. Turbo-Prop Engine



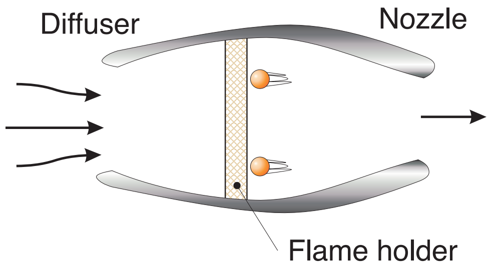
- propellers are best suited for low speed (< 300 mph) flight
- by-pass ratio of 100:1 or more

2. Turbo-Fan Engine (Ducted Turbo-Prop Engine)



- by-pass ratio can be adjusted
- typical by-pass ratios are 5-6

3. Ramjet

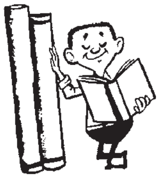


- used in aircraft flying above Mach 1

4. Pulse Jet Engine

- similar to a ram jet but lets in a slug of air at a time and then closes a damper during the combustion stage
- uses a shutter-type valve for damper control
- can be used effectively at low velocities
- used in German V1 missle
- the combustion firing rate was approximately 40 cycles/sec with a maximum flight velocity of 600 mph

Non-Reacting Gas Mixtures



Reading	**Problems**
12-1 → 12-3	12-13, 12-33, 12-36, 12-49
13-1 → 13-7	13-14, 13-15, 13-68, 13-73, 13-77, 13-97, 13-106

Introduction

- homogeneous gas mixtures are frequently treated as a single compound rather than many individual constituents
- the individual properties of inert gases tend to be submerged, such that the gas behaves as a single pure substance
- equations can be derived to express the properties of mixtures in terms of the properties of their individual constituents

Formulations

- the total mass of a mixture, $\boldsymbol{m}$ is the sum of the masses of its components

$$\boldsymbol{m = m_1 + m_2 + \ldots + m_j = \sum_{i=1}^{j} m_i}$$

- the relative amounts of the components present in the mixture can be specified in terms of mass fractions

$$\boldsymbol{Y_i = \frac{m_i}{m} \qquad \Rightarrow \qquad \sum_{i=1}^{j} Y_i = 1}$$

- the total number of moles in a mixture, $\boldsymbol{n}$ is the sum of the number of moles of each of the components

$$\boldsymbol{n = n_1 + n_2 + \ldots + n_j = \sum_{i=1}^{j} n_i}$$

- the relative amounts of the components present in the mixture can be specified in terms of mole fractions

$$\boldsymbol{X_i = \frac{n_i}{n} \qquad \Rightarrow \qquad \sum_{i=1}^{j} X_i = 1}$$

- m_1 and n_i are related by the molecular weight $\tilde{M}_i$

  $$m_i = n_i \tilde{M}_i$$

  Therefore the total mass is

  $$m = \sum_{i=1}^{j} n_i \tilde{M}_i$$

- the mixture molecular weight can be calculated as a mole fraction average of the component molecular weights

  $$\tilde{M} = \frac{m}{n} = \frac{\sum\limits_{i=1}^{j} n_i \tilde{M}_i}{n} = \sum_{i=1}^{j} X_i \tilde{M}_i$$

- X_i and Y_i are also related by the molecular weights

  $$\frac{Y_i}{X_i} = \frac{(m_i/m)}{(n_i/n)} = \left(\frac{m_i}{n_i}\right)\left(\frac{n}{m}\right) = \left(\tilde{M}_i\right)\left(\frac{1}{\tilde{M}}\right)$$

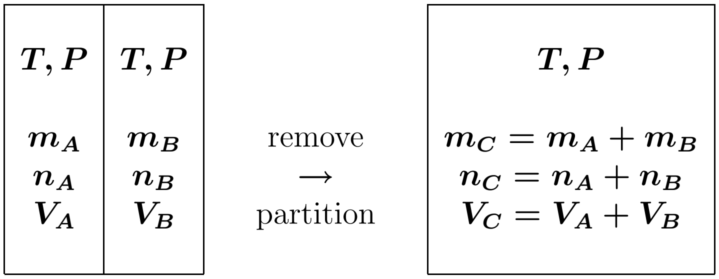
  Therefore

  $$\frac{Y_i}{X_i} = \frac{\tilde{M}_i}{\tilde{M}} \quad \rightarrow \quad Y_i = X_i \left[\frac{\tilde{M}_i}{\sum\limits_{i=1}^{j} X_i \tilde{M}_i}\right]$$

P-V-T Relationships for Ideal Gas Mixtures

Amagat Model (law of additive volumes)

- the volume of a mixture is the sum of the volumes that each constituent gas would occupy if each were at the pressure, P and temperature, T, of the mixture



The volume of the gas mixture is equal to the sum of the volumes each gas would occupy if it existed at the mixture temperature and pressure.

$$\boxed{V = \sum_{i=1}^{j} V_i}$$

Dalton Model (law of additive pressures)

- the pressure of a mixture of gases is the sum of the pressures of its components when each alone occupies the volume of the mixture, V, at the temperature, T, of the mixture

$$\boxed{\begin{array}{c} V, T \\ \\ m_A, n_A, P_A \\ \\ \end{array}} + \boxed{\begin{array}{c} V, T \\ \\ m_B, n_B, P_B \\ \\ \end{array}} = \boxed{\begin{array}{c} V, T \\ \\ m_C = m_A + m_B \\ n_C = n_A + n_B \\ P_C = P_A + P_B \end{array}}$$

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at T and V.

By combining the results of the Amagat and Dalton models i.e. (1) and (2), we obtain for ideal gas mixtures

$$\boxed{\frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n}}$$

Therefore, Amagat's law and Dalton's law are equivalent to each other if the gases and the mixture are ideal gases.

Mixture Properties

Extensive properties such as $\boldsymbol{U, H, c_p, c_v}$ and $\boldsymbol{S}$ can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

$$\begin{aligned} \boldsymbol{U = \sum U_i} &= \boldsymbol{\sum m_i u_i = m \sum Y_i u_i = mu} \\ &= \boldsymbol{\sum n_i \overline{u}_i = n \sum X_i \overline{u}_i = n\overline{u}} \end{aligned}$$

where $\boldsymbol{\overline{u}}$ is the specific internal energy of the mixture per mole of the mixture.

$$\boxed{\begin{aligned} \boldsymbol{u} &= \boldsymbol{\sum Y_i \; u_i} \\ \boldsymbol{h} &= \boldsymbol{\sum Y_i \; h_i} \\ \boldsymbol{c_v} &= \boldsymbol{\sum Y_i \; c_{v_i}} \\ \boldsymbol{c_p} &= \boldsymbol{\sum Y_i \; c_{p_i}} \\ \boldsymbol{s} &= \boldsymbol{\sum Y_i \; s_i} \end{aligned}}$$

Changes in internal energy and enthalpy of mixtures

$$\begin{aligned} \boldsymbol{u_2 - u_1} &= \boldsymbol{\sum Y_i (u_2 - u_1)_i = \int_{T_1}^{T_2} c_v \; dT = c_v (T_2 - T_1)} \\ \boldsymbol{h_2 - h_1} &= \boldsymbol{\sum Y_i (h_2 - h_1)_i = \int_{T_1}^{T_2} c_p \; dT = c_p (T_2 - T_1)} \\ \boldsymbol{s_2 - s_1} &= \boldsymbol{\sum Y_i (s_2 - s_1)_i = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}} \end{aligned}$$

These relationships can also be expressed on a per mole basis.

Entropy Change Due to Mixing of Ideal Gases

- when ideal gases are mixed, a change in entropy occurs as a result of the increase in disorder in the systems
- if the initial temperature of all constituents are the same and the mixing process is adiabatic
  - temperature does not change
  - but entropy does

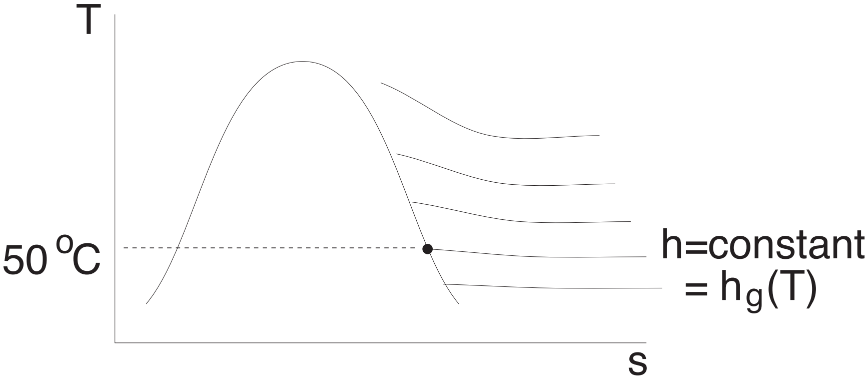
$$\begin{aligned}
\boldsymbol{\Delta S} &= -\left(\boldsymbol{m_A R_A} \ln \frac{\boldsymbol{P_A}}{\boldsymbol{P}} + \boldsymbol{m_B R_B} \ln \frac{\boldsymbol{P_B}}{\boldsymbol{P}} + \cdots\right) \\
&= -\sum_{i=1}^{j} \boldsymbol{m_i R_i} \ln \frac{\boldsymbol{P_i}}{\boldsymbol{P}} \\
&= -\mathcal{R}\sum_{i=1}^{j} \boldsymbol{n_i} \ln \boldsymbol{X_i}
\end{aligned}$$

Notes:

- -ve sign because $\ln \dfrac{Pi}{P} < 0$
- $m_i R_i = m_i \dfrac{\mathcal{R}}{\tilde{M}_i} = n_i \mathcal{R}$

Psychrometrics

- studies involving mixtures of dry air and water vapour
- for $\boldsymbol{T \leq 50^\circ C}$ $\quad (\boldsymbol{P_{sat} \leq 13\ kPa}) \quad \Rightarrow \quad \boldsymbol{h \approx h(T)}$
  - water vapour can be treated as an ideal gas



Definitions

Moist Air

- a mixture of dry air and water vapour where dry air is treated as if it were a pure component
- the overall mixture is given as $\Rightarrow \quad \boldsymbol{P = \frac{mRT}{V}}$

Total Pressure

$$\begin{aligned} \boldsymbol{P} &= \boldsymbol{P_a + P_w} \\ \boldsymbol{P_a} &= \boldsymbol{\frac{m_a R_a T}{V}} \\ \boldsymbol{P_w} &= \boldsymbol{\frac{m_w R_w T}{V}} \end{aligned}$$

where $\boldsymbol{P_a}$ is the partial pressure of air and $\boldsymbol{P_w}$ is the partial pressure of water vapour. Typically $\boldsymbol{m_w << m_a}$.

Relative Humidity - ϕ

$$\phi = \frac{P_w(T)}{P_{sat}(T)} = \frac{\text{vapour pressure at the prevailing T}}{\text{saturation pressure at the prevailing T}}$$

If $P_w = P_{sat}(T)$ the mixture is said to be saturated.

The relative humidity can also be written as

$$\phi = \frac{P_w}{P_{sat}} = \frac{\rho_w}{\rho_s at} = \frac{v_g}{v_w} = \frac{mixture\ volume}{water\ volume}$$

where v_g is the mixture specific volume and v_w is water specific volume.

Specific Humidity (Humidity ratio) - ω

$$\begin{aligned}
\omega &= \frac{m_w}{m_a} = \frac{\text{mass of water vapour}}{\text{mass or air}} \\
&= \frac{\tilde{M}_w n_w}{\tilde{M}_a n_a} = \frac{\tilde{M}_w (P_w V/\mathcal{R}T)}{\tilde{M}_a (P_a V/\mathcal{R}T)} \\
&= \left(\frac{\tilde{M}_w}{\tilde{M}_a}\right)\left(\frac{P_w}{P_a}\right) \\
&= 0.622 \left(\frac{P_w}{P_a}\right)
\end{aligned}$$

In addition ω can be written as

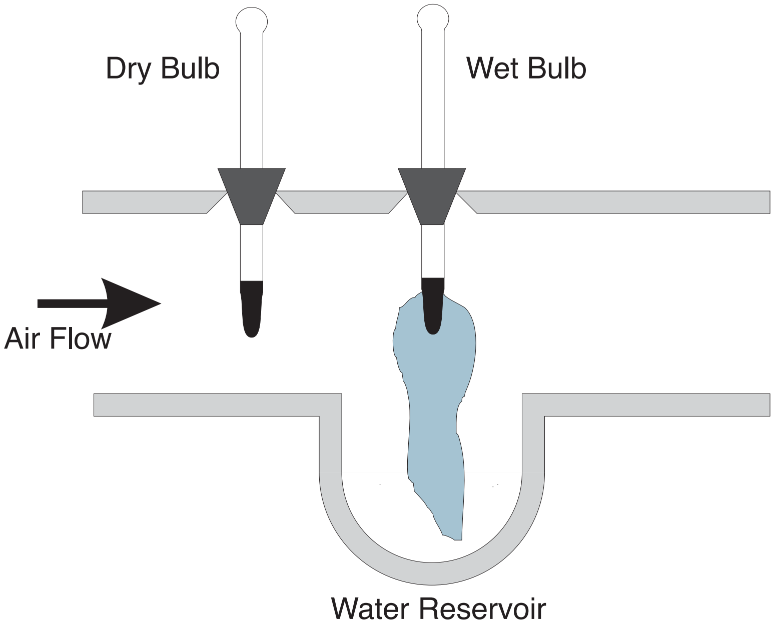
$$\omega = 0.622 \left(\frac{P_w}{P_a}\right) = 0.622 \left(\frac{P_w}{P - P_w}\right) = 0.622 \left(\frac{\phi P_{sat}}{P - \phi P_{sat}}\right)$$

which can be rearranged in terms of relative humidity

$$\phi = \frac{P\gamma}{P_{sat}\left(\omega + \dfrac{\tilde{M}_w}{\tilde{M}_a}\right)} = \frac{P\omega}{P_{sat}(\omega + 0.622)}$$

Dry Bulb Temperature - the temperature measured by a thermometer placed in a mixture of air and water vapour

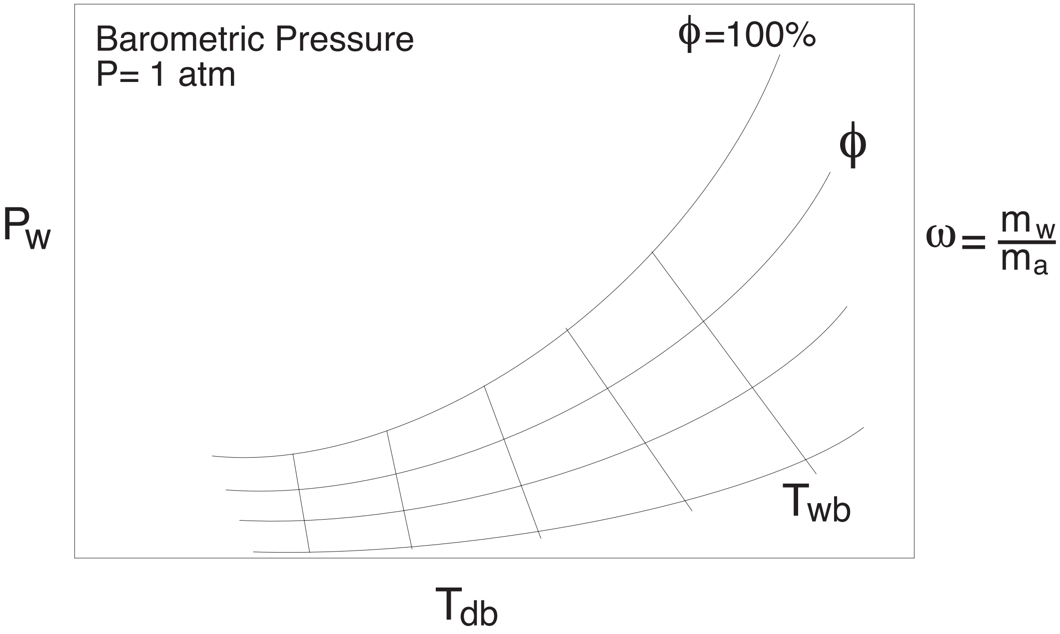
Wet Bulb Temperature



- thermometer surrounded by a saturated wick
- if air/water vapour mixture is not saturated, some water in the wick evaporates and diffuses into the air ⟶ cooling the water in the wick
- at the temperature of the water drops, heat is transferred to the water from both the air and the thermometer
- the steady state temperature is the wet-bulb temperature

Sling Psychrometer - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. $\boldsymbol{T_{DB}}$ and $\boldsymbol{T_{WB}}$ are sufficient to fix the state of the mixture.

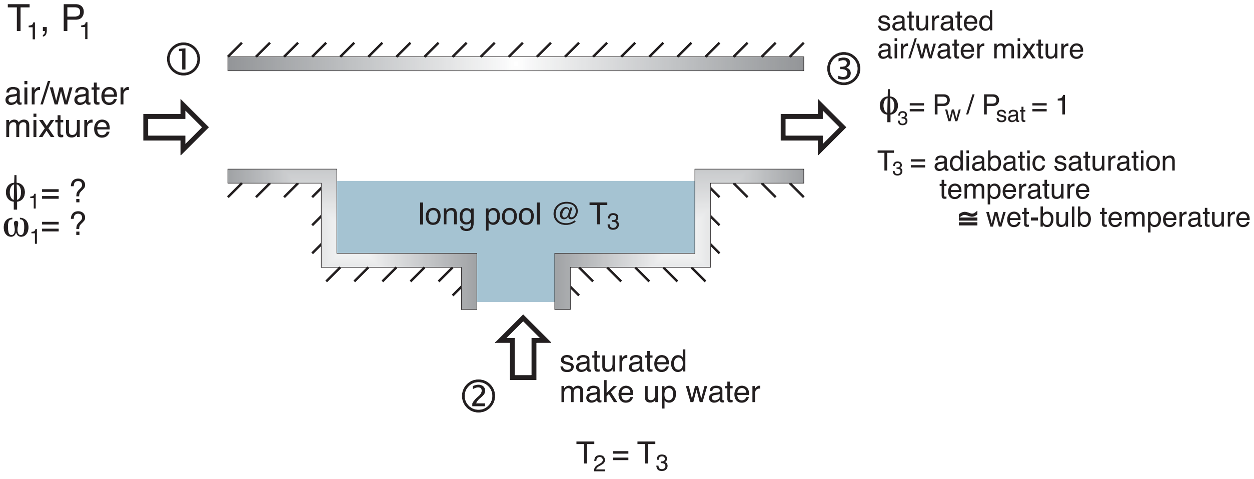
The Psychrometric Chart



where the **dry bulb** temperature is the temperature measured by a thermometer place in the mixture and the **wet bulb** temperature is the adiabatic saturation temperature.

An Adiabatic Saturator

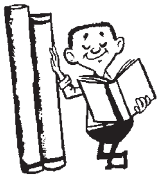
How can we measure humidity?



- the adiabatic saturator is used to measure humidity

- two inlets, single exit device through which moist air passes
- air-water mixture of unknown humidity enters at a known pressure and temperature
- if air/water mixture is not saturated, ($\boldsymbol{\phi < 100\%}$), some water from the pool will evaporate
- the energy required to evaporate the water comes from the moist air $\longrightarrow$ mixture temperature decreases
- for a sufficiently long duct, the moisture exits with $\boldsymbol{\phi_3 = 1}$
- the temperature of the exiting mixture is called the adiabatic saturation temperature

Reacting Gas Mixtures



Reading	**Problems**
14-1 → 14-7	14-16, 14-22, 14-42, 14-48, 14-68, 14-77, 14-91, 14-93

Definitions

Combustion Process:

- a fuel made up of hydrocarbons is said to have burned completely if:
  - all the carbon present in the fuel is burned to carbon dioxide
  - all the hydrogen is burned to water
- if the conditions are not fulfilled the combustion process is incomplete

Combustion Reactions:

reactants → products

or

fuel + oxidizer → products

- in all cases the mass is conserved
  mass of products = mass of reactants

Fuels:

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
  - liquids → gasoline - octane, C_8H_{18}
  - gases → methane, CH_4
  - solids → coal

Combustion Air:

- dry air is considered to be

$$\left.\begin{array}{l}\textbf{21\% oxygen}\\ \textbf{79\% nitrogen}\end{array}\right\}\text{ on a molar basis}$$

$$\boldsymbol{molar\ ratio} = \frac{n_{N_2}}{n_{O_2}} = \frac{0.79}{0.21} = 3.76$$

1 *mole* of air can then be written as $[0.21\ O_2\ +\ 0.79\ N_2]$

Air-Fuel Ratio:

$$\frac{mass\ of\ air}{mass\ of\ fuel} = \frac{moles\ of\ air \times \tilde{M}_{air}}{moles\ of\ fuel \times \tilde{M}_{fuel}}$$

$$AF = \bar{AF}\left(\frac{\tilde{M}_{air}}{\tilde{M}_{fuel}}\right)$$

where:

AF - air fuel ratio on a mass basis

$\overline{AF}$ - air fuel ratio on a molar basis

$\tilde{M}_{air}$ = 28.97 kg/kmole

Theoretical or Stoichiometric Air:

- the minimum amount of air that supplies sufficient oxygen for complete combustion of all carbon and hydrogen in the fuel - referred to as stoichiometric, 100% stoichiometric or theoretical
- no free oxygen would appear in the products

Equivalence Ratio:

- defined as

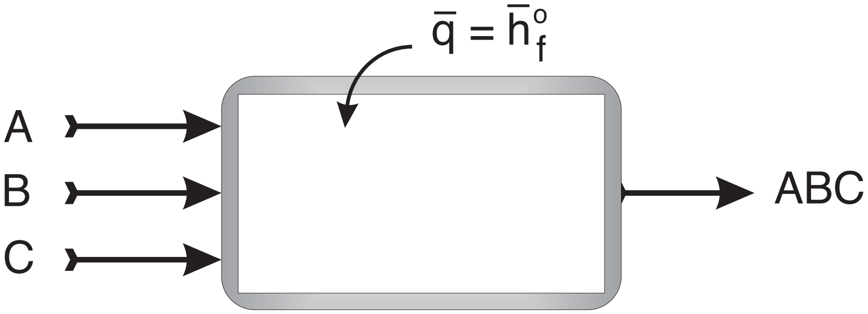
$$\boldsymbol{equivalence\ ratio} = \frac{AF_{actual}}{AF_{theoretical}}$$

- if the equivalence ratio is:
  - > 1 → lean mixture (excess air)
  - < 1 → rich mixture (not enough air)

Conservation of Energy for Reacting Systems

Enthalpy of Formation

- when chemical reactions occur, reactants disappear and products are formed
  → differences cannot be calculated for all substances involved
- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure
  - $T_{ref} = 25°C \rightarrow 298\ K$
  - $P_{ref} = 1\ atm$
- $h = 0$ assigned to elements in their most stable form i.e. $O_2, N_2, C, etc.$
- **Enthalpy of Formation:** *the energy released or absorbed when a compound is formed from its stable elements at STP*



where $\bar{h}_f^o$ is the enthalpy of formation.

Effects of Non-Standard Temperature

$$\bar{h}(T,P) = \bar{h}_f^o + \underbrace{(\bar{h}_{T,P} - \bar{h}_{T=25\ °C,\ P=1\ atm})}_{\Delta\bar{h}\ at\ known\ temperatures}$$

where

$\bar{h}_f^o$ is the heat resulting from a chemical change at $T = 25\ °C$ and $P = 1\ atm$

$\Delta\bar{h}$ is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $T_{ref} = 25\ °C$

Enthalpy of Combustion

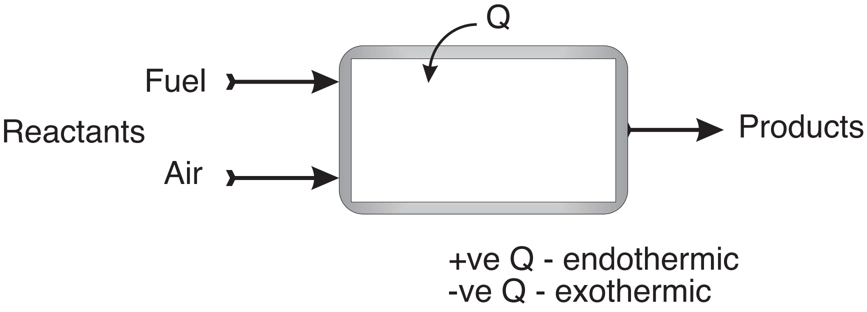
- **Enthalpy of Combustion:** *the difference between the enthalpy of the products and the enthalpy of the reactants where complete combustion occurs at a given temperature and pressure*

$$Q = \sum (mh)_P - \sum (mh)_R = \underbrace{H_P(T_P) - H_R(T_R)}_{H_{RP}}$$

$$Q = \sum (n\overline{h})_P - \sum (n\overline{h})_R = \underbrace{\overline{H}_P(T_P) - \overline{H}_R(T_R)}_{\overline{H}_{RP}}$$

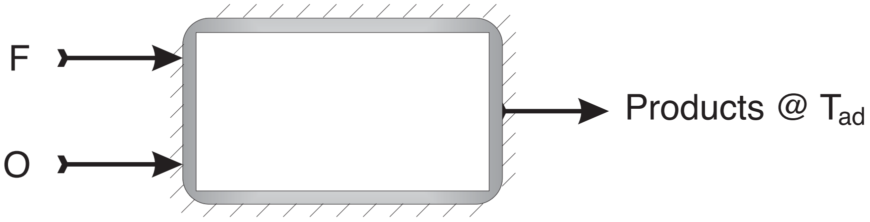
where

$$\overline{h}_c = H_{RP}/kmole\ of\ fuel$$



Heating Value

- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion when products are returned to the state of the reactants
- two values are used
  - **HHV**: higher heating value - obtained when all the water formed by combustion is a liquid at the reference temperature
  - **LHV**: lower heating value - obtained when all the water formed by combustion is a vapour as an ideal gas in the mixture of the products



Adiabatic Flame Temperature

- under adiabatic conditions, the maximum temperature attained by the products when combustion is complete is called the adiabatic flame or adiabatic combustion temperature

$$H_P(T_{ad}) = H_R(T_R)$$

$$\sum_P n_P\,(\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta\overline{h}})_P = \sum_R n_R\,(\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta\overline{h}})_R$$

We need to collect terms based on what we know or can readily calculate and what we do not know, i.e. terms that are a function of T_{ad}.

$$\sum_P \underbrace{n_P\,(\overline{h})_P}_{\substack{sensible\ heat \\ function\ of\ T_{ad}}} = \underbrace{\sum_R n_R\,(\overline{h} - \overline{h}^o)_R - \left(-\sum_P n_P\,(\overline{h}^o)_P\right)}_{\substack{sensible\ heat \\ function\ of\ T_R\ or\ T_{ref}}}$$

$$+\underbrace{\sum_R n_R\,(\overline{h}_f^o)_R - \sum_P n_P\,(\overline{h}_f^o)_P}_{\substack{chemical\ heat \\ function\ of\ T_R\ or\ T_{ref}}}$$

Fuel	Oxidizer Oxygen (K)	Air (K)
H_2	3079	2384
CH_4 (methane)	3054	2227
C_3H_8 (propane)	3095	2268
C_8H_{18} (octane)	3108	2277

Dew Point

- since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapour in the form of gaseous products can be significant
- if the gaseous products of combustion are cooled at constant mixture pressure the dew point temperature is reached when water vapour begins to condense
- since corrosion of duct work, mufflers etc. can occur, the knowledge of dew point temperature is important

Example:

The pressure of the water vapour is given as

$$P_w = X_w \; P$$

where the mole fraction is

$$X_w = \frac{n_w}{n}$$

As an example

$$CH_4 + 2(O_2 + 3.76 N_2) \longrightarrow 1 \; CO_2 + 2 \; H_2O + 7.52 \; N_2$$

$$X_w = \frac{c}{b + c + d} = \frac{2}{10.52} = 0.190$$

Knowing that the overall pressure of the products is $1 \; atm$, we can find P_w as

$$P_w = X_w \; P = 0.190 \;\times\; 1 \; atm = 0.190 \; atm$$

From the saturate water tables, we can find the temperature that corresponds to a vapour pressure of $0.190 \; atm$ or $19.25 \; kPa$.

The dew point temperature is approximately $T_{DP} \approx 60 \; °C$.

Evaluation of Entropy for Reacting Systems

The 2nd law entropy equation can be written as

$$\underbrace{S_{in} - S_{out}}_{due\ to\ heat\ \&\ mass\ transfer} + \underbrace{S_{gen}}_{generation} = \underbrace{\Delta S_{system}}_{change\ in\ entropy}$$

For a closed system, such as a combustion process, the entropy balance on the system can be written as

$$\sum \frac{Q_i}{T_i} + S_{gen} = S_P - S_R$$

- a common datum must be used to assign entropy values for each substance involved in the reaction
- an entropy of 0 for pure crystalline substances is obtained at absolute zero
- the entropy relative to this datum is called absolute entropy
- absolute entropy at 1 atm and temperature T is denoted as $s^o(T)$ or $\overline{s}^o(T)$ for a per unit mass or per mole basis
- while $\overline{h}$ was only a function of temperature for ideal gases, we must account for the effects of both T and P in entropy
- the entropy at any value of T and P can be calculated as

  $$\overline{s}(T,P) = \underbrace{\overline{s}^o(T)}_{tables} - \mathcal{R} \ln\left(\frac{P_i}{P_{ref}}\right)$$

  where

  $$\begin{aligned} P_{ref} &= 1\ atm \\ P_i &= partial\ pressure\ of\ i'th\ component \\ \mathcal{R} &= 8.31434\ kJ/kmole \cdot K \end{aligned}$$

- the partial pressure P_i can also be written as

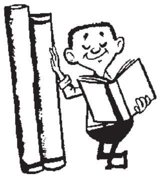
  $$P_i = X_i P$$

  and

  $$\overline{s}(T,P_i) = \overline{s}_i^o(T) - \mathcal{R} \ln\left(\frac{X_i P}{P_{ref}}\right)$$

  where P is the mixture pressure and X_i is the mole fraction of the $i'th$ component.

Thermal Equilibrium



Reading	**Problems**
15-1 → 15-6	

Criterion for a Reacting Mixture

In general, the thermodynamic state of any mixture capable of heat transfer, expansion work and chemical reaction can be fixed by the specification of its internal energy, volume and composition.

$$S = S(U, V, n_1, n_2, \ldots n_k)$$

Recalling the fundamental definition of T, P and $\overline{\mu}_i$, where $\overline{mu}_i$ is the molar electro chemical potential of the $i'th$ component per mole of the $i'th$ component.

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,n_i}}_{\equiv \frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,n_i}}_{\equiv \frac{P}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial n_1}\right)_{U,V,n_j,j\neq 1}}_{\equiv -\frac{\overline{\mu}_1}{T}} dn_1 + \cdots + \underbrace{\left(\frac{\partial S}{\partial n_k}\right)_{U,V,n_j,j\neq k}}_{\equiv -\frac{\overline{\mu}_k}{T}} dn_k$$

Using the above relation, the Gibb's function for a mixture can be written as

$$TdS = dU + PdV - \sum_{i=1}^{k} \overline{\mu}_i dn_i \qquad (1)$$

Noting the Gibb's function (free energy used to predict the spontaneity of a chemical reaction) is defined as

$$\begin{aligned} G &= H - tdS = U + PV - TS \\ dG &= dU + PdV + vdP - TdS - SdT \end{aligned}$$

or when combined with Eq. (1)

$$dG = VdP - SdT + \sum_{i=1}^{k} \overline{\mu}_i dn_i \qquad (2)$$

For the general equilibrium condition, consider the reacting mixture as the system

From a 1st law balance

$$dU = dQ - dW = dQ - PdV \qquad (3)$$

From a 2nd law balance

$$dS \frac{dQ}{T} \geq 0 \qquad (4)$$

Combining (1), (3) and (4)

$$\sum_{i=1}^{k} \overline{\mu}_i \, dn_i \leq 0 \qquad (5)$$

This is the product of the chemical potential and the change in composition.

As the reactions continue, some species will be formed ($dn_i > 0$) and others will be depleted ($dn_i < 0$), such that

$$\sum \overline{\mu_i} \, dn_i < 0$$

Eventually the reactions will be completed and there will be no further change in the composition of the mixture

$$\sum \overline{\mu_i} \, dn_i = 0$$

This is the *Equilibrium criterion.*

Notice that for the common case of combustion at constant T and P, Eq. (5) yields

$$dG_{T,P} \leq 0$$

When equilibrium is finally obtained

$$dG_{T,P} = 0$$

A reaction can take place spontaneously as long as Gibb's function decreases.

Examining the mixture more closely

$$\begin{array}{c} \boldsymbol{n_1} \text{ moles of } \boldsymbol{A_1} \\ \boldsymbol{n_2} \text{ moles of } \boldsymbol{A_2} \\ \vdots \\ \boldsymbol{n_k} \text{ moles of } \boldsymbol{A_k} \end{array}$$

where

$$\begin{aligned} \boldsymbol{A_1} &= \boldsymbol{chemical\ constituents} \\ \boldsymbol{\nu_i} &= \boldsymbol{stoichiometric\ coefficients} \end{aligned}$$

Therefore a chemical equation of reactants and products can be written as

$$\boldsymbol{\nu_1 A_1 \ + \ \nu_2 A_2 \leftrightarrow \nu_3 A_3 \ + \ \nu_4 A_4} \qquad \textbf{(6)}$$

For example:

$$\boldsymbol{H_2 + CO_2 \leftrightarrow CO + H_2O}$$

$$\boldsymbol{\nu_{H_2} = 1, \quad ; \quad \nu_{CO_2} = 1, \quad ; \quad \nu_{CO} = 1, \quad ; \quad \nu_{H_2O} = 1}$$

As a result of reaction (6), the composition of the mixture will change by

$$\begin{aligned} \boldsymbol{dn_2} &= \boldsymbol{\frac{\nu_2}{nu_1} dn_1} \quad \Rightarrow \quad \boldsymbol{\frac{dn_2}{\nu_2} = \frac{dn_1}{\nu_1}} \\ \boldsymbol{dn_3} &= \boldsymbol{-\frac{\nu_3}{nu_1} dn_1} \quad \Rightarrow \quad \boldsymbol{\frac{dn_1}{\nu_1} = -\frac{dn_3}{\nu_3}} \\ \boldsymbol{dn_4} &= \boldsymbol{-\frac{\nu_4}{nu_1} dn_1} \quad \Rightarrow \quad \boldsymbol{\frac{dn_1}{\nu_1} = -\frac{dn_4}{\nu_4}} \end{aligned}$$

From Eq. (5)

$$\boldsymbol{\sum \overline{\mu}_i \, dn_i \leq 0}$$

we obtain

$$\boldsymbol{\left[\underbrace{(\overline{\mu}_1 \nu_1 + \overline{\mu}_2 \nu_2)}_{EP_{LHS}} - \underbrace{(\overline{\mu}_3 \nu_3 + \overline{\mu}_4 \nu_4)}_{EP_{RHS}} \right] \ dn_1 \leq 0}$$

If $EP_{LHS} > EP_{RHS}$ then $dn_1 < 0$ and A_1 is being depleted, i.e. the reaction proceeds to the right.

If $EP_{LHS} < EP_{RHS}$ then $dn_1 > 0$ and the reaction proceeds to the left.

Hence equilibrium is attained when

$$(\overline{\mu}_1\nu_1 + \overline{\mu}_2\nu_2) - (\overline{\mu}_3\nu_3 + \overline{\mu}_4\nu_4) = 0 \qquad (7)$$

or in general

$$\sum_{R\ (LHS)} \overline{\mu}_i\nu_i = \sum_{P\ (RHS)} \overline{\mu}_i\nu_i \qquad (8)$$

In a perfect gas, $\overline{\mu}$ for the $i'th$ species is given by

$$\overline{g}_i = \overline{\mu}_i = \overline{g}_i^o(T, P_0) + \mathcal{R}T \ln\left(\frac{P_i}{P_0}\right) \qquad (9)$$

where $P_0 = 1\ atm$ is the reference pressure and $\overline{g}_i^o$ is Gibb;s function of components i evaluated at T and $P = 1\ atm$.

Note that

$$\frac{P_i}{P} = \frac{n_i}{n}$$

The molal Gibb's function is

$$\overline{g}_i^o = \overline{g}_i(T, P_0) = \text{function of } T \text{ only}$$

$$\overline{g}_i^o = \overline{h}_{f_i}^o - T\ \overline{s}_i^o$$

Substitute Eq. (9) into (7), noting that the products and the reactants must be at a constant T.

$$\begin{aligned}(\mu_1\overline{g}_1^o + \mu_2\overline{g}_2^o) - (\mu_3\overline{g}_3^o + \mu_3\overline{g}_3^o) &= \mathcal{R}T \ln\left[\frac{\left(\frac{P_3}{P_0}\right)^{\nu_3}\left(\frac{P_4}{P_0}\right)^{\nu_4}}{\left(\frac{P_1}{P_0}\right)^{\nu_1}\left(\frac{P_2}{P_0}\right)^{\nu_2}}\right] \\ &= -\Delta G^o = -\Delta G(T, P_0)\end{aligned}$$

Therefore

$$\underbrace{\left(\frac{P_3^{\nu_3}P_4^{\nu_4}}{P_1^{\nu_1}P_2^{\nu_2}}\right)\left(\frac{1}{P_0}\right)^{\nu_3+\nu_4-\nu_1-\nu_2}}_{\equiv K(T)} = \exp\left[-\frac{\Delta G^o}{\mathcal{R}T}\right] \qquad (10)$$

where $K(T)$ is the equilibrium constant for reactions.

The JANAF tables list $\ln K$ with $P_0 = 1\ atm$ for various reactions fo substances.

Note that

$$P_i = P\left(\frac{n_i}{n}\right)$$

Therefore

$$K(T) = \left(\frac{n_3^{\nu_3}\ n_4^{\nu_4}}{n_1^{\nu_1}\ n_2^{\nu_2}}\right)\left(\frac{P}{nP_0}\right)^{\nu_3+\nu_4-\nu_1-\nu_2}$$

Example:

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \qquad (12)$$

$$K_{12} = \left(\frac{n_{H_2O}}{n_{H_2}\ n_{O_2}^{1/2}}\right)\left(\frac{P}{nP_0}\right)^{1-1-1/2}$$

Note that K depends on the way the equation is written

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \qquad (13)$$

Then

$$K_{13} = \frac{1}{K_{12}} \Rightarrow \ln K_{13} = -\ln K_{12}$$

The $\boldsymbol{K's}$ can be combined when the reactions are combined

$$\boldsymbol{C + \frac{1}{2}O_2 \leftrightarrow CO \qquad (14) \quad \rightarrow K_{14}}$$

$$\boldsymbol{H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \qquad (15) \quad \rightarrow K_{15}}$$

$$\boldsymbol{C + O_2 \leftrightarrow CO_2 \qquad (16) \quad \rightarrow K_{16}}$$

Equations (14) + (15) - (16) gives

$$\boldsymbol{H_2 + cO_2 \leftrightarrow CO + H_2O \qquad (17)}$$

$$\boldsymbol{K_{17} = \frac{n_{CO}\; n_{H_2O}}{n_{H_2}\; n_{CO_2}} = \frac{K_{14}\; K_{15}}{K_{16}}}$$