Engineering Thermodynamics

Summary of topics from University of Washington course
ME323: Engineering Thermodynamics
taught Winter 2016 by Prof. Dayong Gao (DXG)
compiled by Michael C. McGoodwin (MCM). Content last updated 6/19/2016

Table of Contents

(Applicable primary textbook chapters and sections are shown in parentheses)

Introduction

Catalog Course Description

"Engineering thermodynamics, including thermodynamic concepts and properties, the first and second laws of thermodynamics, energy conversion, refrigeration, humidification, and combustion. Engineering design applications."

Instructor

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Ph.D. Department of Mechanical Engineering, Concordia University, Canada, 1990
B. Sc. Dept. of Modern Mechanics, University of Science and Technology of China (USTC), 1983
Research Interests:
(1) Cryo-biomedical engineering and cryobiology;
(2) Artificial organs
(3) Bio-instrument and biosensors for rapid and accurate diagnosis and detection of diseases

I am grateful to Professor Gao for his warm welcome to me as an auditing student, and for his excellent and thorough classroom instruction. He does a fine job of putting across the importance of this wide-ranging subject matter, and repeats key points sufficiently to assure that each student had a fair chance to learn them.

I also enjoyed the participation of retired electrical engineer David Morgan, a fellow auditor who shared notes with me from missed lectures as well as zestful enthusiasm for the learning process.

Textbook

A summary such as this can only attempt to hit the high points for the copious material presented in the textbook: *Thermodynamics: An Engineering Approach*, by Yunus Çengel and Michael A. Boles, 7th Edition. McGraw Hill, 2011, hereafter termed *TAEA7*. This is an excellent, self-instructing, and unusually detailed textbook (now in its 8th edition) with many hundreds of illustrations and graphs, copious sample problems (only a few of which have I summarized), and an extensive collection of tables. It takes little for granted regarding the student's prior knowledge of relevant physics and chemistry etc., and reviews many of the underlying science concepts. It emphasizes precise communication of basic principles and real-world examples. It hopes to foster intuitive understanding, creative thinking, a deeper understanding of principles, and a strong interest and enthusiasm for the subject matter. It takes a practical approach to sign conventions, preferring terms such as Q_{in} and Q_{out}. The website resources are quite extensive (see below). The print textbook version includes a free limited academic version of *Engineering Equation Solver* (EES) software.[1] Freestanding designations like (5-2) indicate that the material is derived from section 2 of Chapter 5. A designation preceding an equation such as (2-35) signifies equation number 35 from chapter 2. Altogether, this book gives outstanding value for its moderate price, and it is highly recommended—you should buy it!

Note that although this summary makes considerable use of the textbook materials, including its organization into chapters and sections, I have greatly diversified the sources of materials included, drawing on many other resources found on the web.

Units

Because of the mixed usage of units systems prevailing in the US, the textbook presents examples and tables in both

- the **SI system** of units ("**metric**", "MKS") &
  employing base units of m—kg—s—A—K—mol—cd
- the "**English Engineering**" system of units, aka "**US Customary System**" of units ("**USCS**", "FPS") &
  employing units including s—ft—lb_{mass}—lb_{force}—°F—°R

Although USCS units are clearly essential still for many real-world US calculations, I have elected to use only SI units in this summary.

Labs

I did not attend these. The visit to the UW power plant and central HVAC system was especially informative. However, I recommend an especially well-done UW Power Plant video[2] prepared by MFA student "Tina".

Author of this summary

I am a retired physician who only audited this course, thus I have limited expertise. I prepare summaries such as this primarily as a personal study aid for assisting in learning and bonding with such voluminous material. I will be gratified if other persons find this in any way useful. In this purely not-for-profit project, I

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[1] http://fchart.com/ees/ees_app.php

[2] https://www.washington.edu/facilities/ops/video

have included some copyrighted material, hopefully falling within fair usage and always credited in the footnotes. Please observe prudence in what you copy from this summary, buy the textbook, and go to the original sources which I have referenced. If you are an author who wishes to have removed certain copyrighted materials that I have included here, please advise. These materials and references were reasonably current in 2016, but I will not be updating this document and expect that it will in part gradually go out of date.

Suggestions and corrections would be graciously accepted. Send email to this address (reformatted):
MCM at McGoodwin period NET

Web Resources for Engineering Thermodynamics

Most of the web resources I have used appear in the footnotes, but the following are broad in their application.

Course Textbook Thermodynamics Web Resources[3]

- Student Study Guide PPTs (each chapter as a PPT, includes nomenclature, abbreviations, and definitions)
- Glossary (each chapter has separate HTML glossary page: select chapter in combo box, then click on *Glossary*)
- Other: Photo Gallery; Errata
- 8th Edition Student Materials

Other Thermodynamics-Related Web Resources

- Engineering Thermodynamics (Web course by Israel Urieli)
- Zittau's Online Fluid Property Calculator (extensive & excellent)
- NIST Chemistry WebBook (tables of TD-related data)
- *Dictionary of Physics 7 ed.* , editors Law and Rennie.
  Access at UW Library > Search on Encyclopedias > Oxford Reference Online >
  Browse and Search Titles > refine terms > Book Title "A Dictionary of Physics"
  or ISBN: "eISBN: 9780191783036" Useful for basic definitions

Book chapters included in the course and/or discussed in this summary

Bold = substantial partial course coverage by instructor

Items in parentheses indicate state of summarization by MCM

Chap 1: (MCM: selective summary completed)

Chap 2: (MCM: selective summary thru 2-6; also did partial 2-8 [radiation heat transfer]; omitted efficiencies 2-7 & balance of 2-8.)

Chap 3-7: (MCM: selective summary completed)

Chap 8: (MCM: mostly omitted)

Chap 9-14: (MCM: selective summary completed)

Chap 15-17: (MCM: omitted)

Tables: (MCM: Studied and used extensively, important but not summarized)

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[3] http://highered.mheducation.com/sites/007352932x/information_center_view0/index.html

History, Units, Symbols, and Some Basics (1)

(text Chapter 1 & other sources)

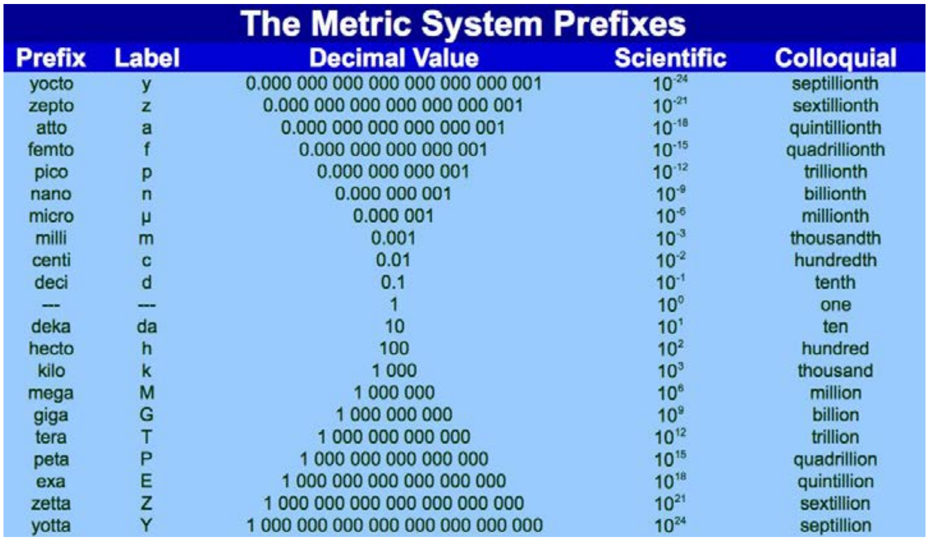
Notable Persons in the History of Thermodynamics

See

http://www.eoht.info/page/Thermodynamics+pioneers
http://www.eoht.info/page/Thermodynamics+founders
http://www.eoht.info/page/thermodynamics

Prefixes in the SI System (Système international d'unités)

Here, the "colloquial name" is from the American "short scale" in which
10^9 = giga = billion (not milliard), and
10^{-9} = nano = billionth (not milliardth).[4]



The Metric System Prefixes

Prefix	Label	Decimal Value	Scientific	Colloquial
yocto	y	0.000 000 000 000 000 000 000 001	10^{-24}	septillionth
zepto	z	0.000 000 000 000 000 000 001	10^{-21}	sextillionth
atto	a	0.000 000 000 000 000 001	10^{-18}	quintillionth
femto	f	0.000 000 000 000 001	10^{-15}	quadrillionth
pico	p	0.000 000 000 001	10^{-12}	trillionth
nano	n	0.000 000 001	10^{-9}	billionth
micro	µ	0.000 001	10^{-6}	millionth
milli	m	0.001	10^{-3}	thousandth
centi	c	0.01	10^{-2}	hundredth
deci	d	0.1	10^{-1}	tenth
---	---	1	10^{0}	one
deka	da	10	10^{1}	ten
hecto	h	100	10^{2}	hundred
kilo	k	1 000	10^{3}	thousand
mega	M	1 000 000	10^{6}	million
giga	G	1 000 000 000	10^{9}	billion
tera	T	1 000 000 000 000	10^{12}	trillion
peta	P	1 000 000 000 000 000	10^{15}	quadrillion
exa	E	1 000 000 000 000 000 000	10^{18}	quintillion
zetta	Z	1 000 000 000 000 000 000 000	10^{21}	sextillion
yotta	Y	1 000 000 000 000 000 000 000 000	10^{24}	septillion

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[4] http://forum.allaboutcircuits.com/threads/rules-for-creating-neat-schematics.112294/ and
http://www.unitarium.com/si-prefixes

Some Recurrent Abbreviations Used in the Textbook[5]

A	area (m^2)
C_P	specific heat at constant pressure (kJ/(kg·K))
C_V	specific heat at constant volume (kJ/(kg·K))
COP	coefficient of performance
d	exact differential
E	stored energy (kJ)
e	stored energy per unit mass (kJ/kg)
F	force (N)
g	acceleration of gravity (9.807 m/s^2)
H	enthalpy (H= U + PV) (kJ)
h	specific enthalpy (h= u + Pv) (kJ/kg)
h	convective heat transfer coefficient (W/(m^2·K)

K	Kelvin degrees
k	specific heat ratio, C_P/C_V
k	10^3
k_t	thermal conductivity (W/(m-°C))
M	molecular weight or molar mass (kg/kmol)
M	10^6
m	mass (kg)
N	moles (kmol)
n	polytropic exponent (isentropic process, ideal gas n = k)
η	isentropic efficiency for turbines, compressors, nozzles
η_{th}	thermal efficiency (net work done/heat added)
P	pressure (kPa, MPa, psia, psig)
Pa	Pascal (N/m^2)

Q_{net}	net heat transfer ($\sum Q_{in} - \sum Q_{out}$) (kJ)
q_{net}	Q_{net} /m, net heat transfer per unit mass (kJ/kg)
R	particular gas constant (kJ/(kg·K))
R_u	universal gas constant (= 8.314 kJ/(kmol·K))
S	entropy (kJ/K)
s	specific entropy (kJ/(kg·K))
T	temperature (°C, K, °F, R)
U	internal energy (kJ)
u	specific internal energy (kJ/(kg ·K))
V	volume (m^3)
V&	volume flow rate (m^3/s)
$\overset{\rho}{V}$	velocity (m/s)
v	specific volume (m^3/kg)
$\bar{v}$	molar specific volume (m^3/kmol)

X	distance (m)
X	exergy (kJ)
x	quality
Z	elevation (m)
W_{net}	net work done [($\sum W_{out} - \sum W_{in})_{other} + W_b$] (kJ) where W_b = for closed systems and 0 for control volumes
w_{net}	W_{net} /m, net work done per unit mass (kJ/kg)
W_t	weight (N)
δ	inexact differential
ε	regenerator effectiveness
ϕ	relative humidity
ρ	density (kg/m^3)
ω	humidity ratio

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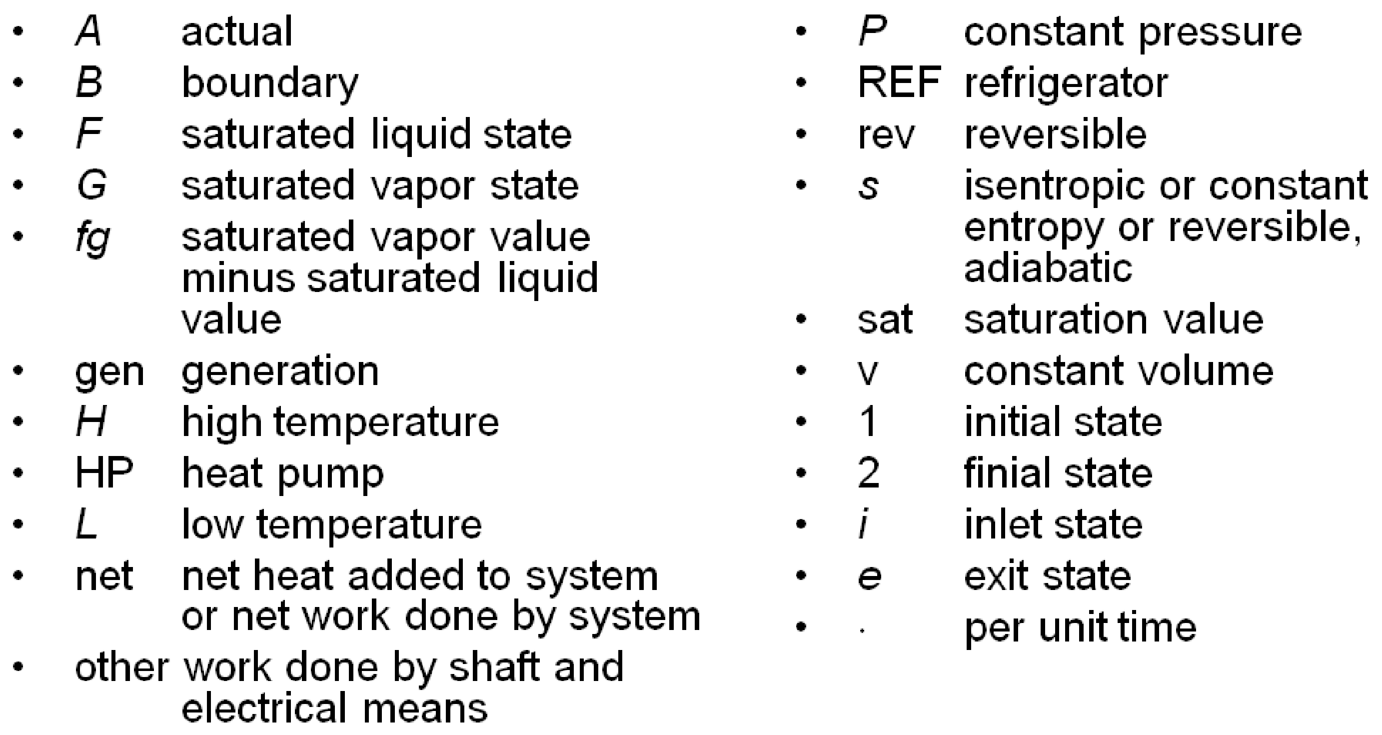
[5] Table assembled from textbook website chapter_01.ppt. Symbols for volume flow $\dot{V}$ rate and velocity V display incorrectly here. The textbook uses a different glyph for the V of total volume versus voltage **V** or velocity V [here shown in Algerian]. A more detailed list of symbols is found inside the textbook front cover.

Subscripts and Superscripts[6]



A	actual
B	boundary
F	saturated liquid state
G	saturated vapor state
fg	saturated vapor value minus saturated liquid value
gen	generation
H	high temperature
HP	heat pump
L	low temperature
net	net heat added to system or net work done by system
other	work done by shaft and electrical means
P	constant pressure
REF	refrigerator
rev	reversible
s	isentropic or constant entropy or reversible, adiabatic
sat	saturation value
v	constant volume
1	initial state
2	finial state
i	inlet state
e	exit state
˙	per unit time

Basic Terminology and Selected Concepts

(text Chapter 1 & other sources)

The subject of this course is **classical macroscopic thermodynamics TD** (i.e., not microscopic *statistical*[7] *thermodynamics*). According to the text website paraphrased, **Thermodynamics** is concerned with the ways energy is stored within a body or system and how energy transformations, including those which involve heat flow and work done on or by the system, may take place. Another partial definition: "The study of the laws that govern the conversion of energy from one form to another, the direction in which heat will flow, and the availability of energy to do work..."[8] Also,

> "**Thermodynamics** is a branch of physics concerned with heat and temperature and their relation to energy and work. It defines macroscopic variables, such as internal energy, entropy, and pressure, that partly describe a body of matter or radiation. It states that the behavior of those variables is subject to general constraints, that are common to all materials, beyond the peculiar properties of particular materials. These general constraints are expressed in the four laws of thermodynamics [including the Zeroth Law]. Thermodynamics describes the bulk behavior of the body, not the microscopic behaviors of the very large numbers of its microscopic constituents, such as molecules. The basic results of thermodynamics rely on the

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[6] assembled from textbook website chapter_01.ppt (symbols for volume flow $\dot{V}$ rate and velocity v incorrect)

[7] https://en.wikipedia.org/wiki/Statistical_mechanics , see also
http://plato.stanford.edu/entries/statphys-statmech/

[8] "thermodynamics." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

> existence of idealized states of thermodynamic equilibrium. Its laws are explained by statistical mechanics, in terms of the microscopic constituents."[9]

The following topic summaries are taken from the text website and text, with supplementation as needed.

Units conversions may be made by multiplying a quantity in specified units with **Unity Conversion Ratios**, which have a value of 1 and include such expressions as lbf / (32.174 lbm-ft-s^{-2}) or N / (kg m s^{-2}).

In many of the discussions, the words *atoms* or *molecules* are sometimes used when the other term might be more appropriate.

Mass

Mass is a measure of a body's inertia, i.e. its resistance to acceleration, but may also be measured by the gravitational force it produces (because gravitational and inertial mass are indistinguishable).[10] It is measured in kilograms **kg**, a base SI unit. In USCS units, mass is expressed in **avoirdupois pounds** (**lb** or **lbm**, where 1 lbm = 16 avoirdupois **ounce oz** exactly = 0.45359237 kilograms exactly).

Force

Force is, "The agency that tends to change the momentum of a massive body, defined as being proportional to the rate of increase of momentum. For a body of mass m traveling at a velocity $\mathbb{V}$, the momentum is m$\mathbb{V}$. In any coherent system of units, the force is therefore given by F=d(m$\mathbb{V}$)/dt. If the mass is constant F=m(d$\mathbb{V}$/dt)=ma, where a is the acceleration… Forces occur always in equal and opposite action–reaction pairs between bodies, though it is often convenient to think of one body being in a force field."[11] Force is measured in **Newtons N**, where F = ma and 1 N produces on a 1 kg of mass an acceleration of 1 m s^{-2}. A 1 kg mass experiences a downward force from gravity—this is a variable force called its **weight**, and is given by f = ma = 9.807 N when local gravitational acceleration g = 9.807 m s^{-2}. The **standard gravitational acceleration g_0** is defined as 9.80665 m s^{-2}, and was originally intended to be an average value for g at sea level at 45° degrees latitude. A force of 1 **kg-force** (kgf) is defined as the force which will accelerate a 1 kg mass by 9.80665 m s^{-2} exactly.[12] In USCS, a 1 **pound-force** (1 lbf) is the force which will accelerate 1 lbm by approximately 32.174049 ft s^{-2}:

$$1 \text{ lbf} = 1 \text{ lbm} \times (9.80665 \text{ m s}^{-2}) \,/\, (\text{exactly } 0.3048 \text{ m/ft}) \approx 32.174049 \text{ lbm-ft s}^{-2}$$

In other words, 1 lbf is the weight force exerted by standard gravity on 1 lbm.

Temperature

Temperature is scalar intensive property, "The property of a body or region of space that determines whether or not there will be a net flow of heat into it or out of it from a neighboring body or region and in which direction (if any) the heat will flow. If there is no heat flow the bodies or regions are said to be in thermodynamic equilibrium and at the same temperature. If there is a flow of heat, the direction of the flow is from the body or region of higher temperature."[13] Temperature is expressed in **Kelvin K** in the SI system, or the derived units **°C Celsius**, where absolute zero 0 K = -273.15 °C, thus T(K) = T(°C) - 273.15. The **thermodynamic temperature scale TTS** (absolute temperature scale) is a linear scale with units of Kelvins,

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[9] https://en.wikipedia.org/wiki/Thermodynamics

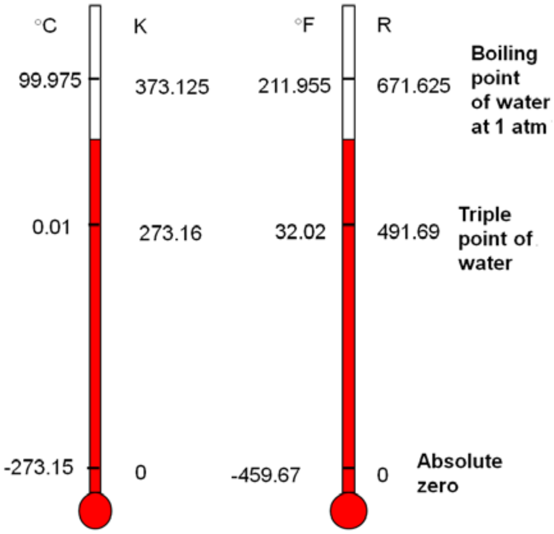
[10] "mass." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016 7th Edition,
eISBN: 9780191783036
http://www.oxfordreference.com.offcampus.lib.washington.edu/view/10.1093/acref/9780198714743.001.0001/acref-9780198714743

[11] "force." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

[12] https://en.wikipedia.org/wiki/Standard_gravity

[13] "temperature." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

and Kelvins are one of the SI base units. This scale uses absolute zero[14] as 0 K and originally used the freezing point of water as the only defining fixed point (said to be 0 °C at 237.15 K). There were 100 divisions from freezing to boiling of water, thus its increments were called centigrade, a now obsolete historical name. In 1954, the triple point of water[15] was adopted as the sole fixed point other than absolute zero for K (at 237.16 K) and Celsius scales (0.01°C). A temperature increment of 1 °C is the fraction 1/273.16 of the thermodynamic temperature difference between absolute zero and the triple point of water. (The TTS is further discussed below in the chapter 6 summary.)



The **International Temperature Scale of 1990** (ITS-90)[16] defines the K and C scales by absolute zero and the triple point of water as before, but also uses 16 other fixed points.[17] These added fixed points, along with precisely defined measuring techniques, are used to optimize actual measurement or calibration of the thermodynamic temperatures over a wide range, from 0 K to more than 1000 °C. The triple point of water is defined as before as exactly 273.16 K or 0.01 °C. ITS-90 and the SI no longer make primary use of the freezing point of water as a fixed point. The effect of this revised scale is that water at 1 atm now boils at about 99.975 °C. A change in Kelvin T, ΔT(K), is identical to a change in Celsius T, ΔT(°C), but K should always be used for TD calculations involving single temperatures rather than involving a change. The USCS temperature scales and units are **Rankine °R** and **Fahrenheit °F**, which are redefined in ITS-90 as shown in the diagram,[18] and water at 1 atm now boils at about 211.955 °F or 671.625 °R. Exact conversions between these 4 scales may be performed with the following formulas:[19] Note that 9/5 = 1.8 exactly.

To	From °Celsius	From Kelvin	From °Fahrenheit	From Rankine
°C	—	[°C] = [K] − 273.15	[°C] = ([°F]−32) × (5/9)	[°C] = ([°R] − 491.67) × (5/9)
K	[K] = [°C] + 273.15	—	[K] = ([°F] + 459.67) × (5/9)	[K] = [°R] × (5/9)
°F	[°F] = [°C] × (9/5) + 32	[°F] = ([K] × (9/5)) − 459.67	—	[°F] = [°R] − 459.67
R	[°R] = ([°C] + 273.15) × (9/5)	[°R] = [K] × (9/5)	[°R] = [°F] + 459.67	—

Two bodies are in **thermal equilibrium** when they have reached the same temperature. According to the “**Zeroth Law of TD**”, “if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.”[20]

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[14] The lowest temperature attained in the lab so far is said to be 100 picokelvins (pK). The lowest temp observed in nature is ~1 K (in the Boomerang Nebula). https://en.wikipedia.org/wiki/Absolute_zero

[15] Vienna Standard Mean Ocean Water (VSMOW), is pure water with a defined H and O isotopic composition, originally consisting of a mixture of distilled ocean waters collected from different spots around the globe. https://en.wikipedia.org/wiki/Vienna_Standard_Mean_Ocean_Water

[16] http://www.its-90.com/its-90.html

[17] ITS-90’s 17 defining fixed points are listed in this order: He–V, equilibrium H_2–T, equilibrium H_2 (or He)–V x2, Ne–T, O_2–T, Ar–T, Hg–T, H_2O–T, Ga–M, In–F, Sn–F, Zn–F, Al–F, Ag–F, Au–F, and Cu–F. Here V = vapor pressure, T = triple point, M = melting point, F = freezing point. (http://www.its-90.com/table1.html)

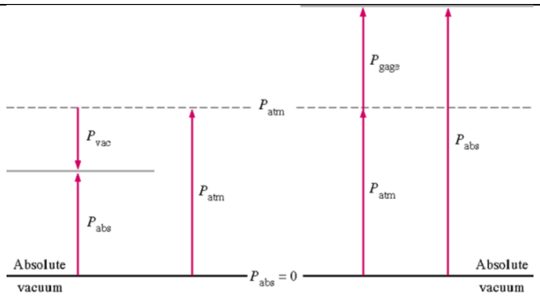
[18] adapted from Image from textbook website chapter_01.ppt

[19] https://en.wikipedia.org/wiki/Rankine_scale , https://en.wikipedia.org/wiki/Celsius , https://en.wikipedia.org/wiki/Kelvin , and https://en.wikipedia.org/wiki/Fahrenheit

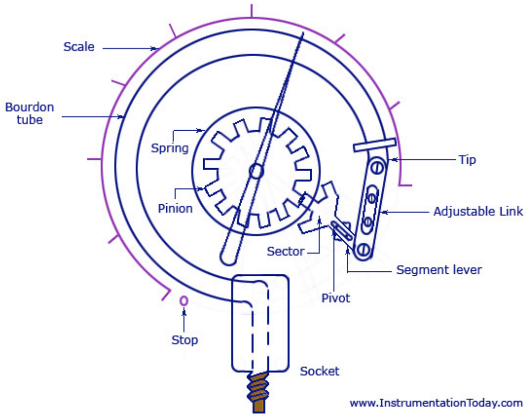
[20] *TAEA7* p. 17, per R. H. Fowler 1931, and https://en.wikipedia.org/wiki/Zeroth_law_of_thermodynamics

Pressure

Pressure is a scalar intensive quantity expressing the force exerted perpendicular (normal) to the surface of an object per unit area over which that force is distributed.[21] (When solids exert a similar perpendicular force on a surface, it is called a **normal stress**.) Its unit is **pascals Pa**, where 1 Pa = 1 N/m^2. The pressure force arises from random collisions of molecules due to their kinetic energy. **Absolute pressure** is the true pressure on the surface relative to absolute vacuum zero pressure. **Gage pressure** (**gauge pressure**) is the difference between absolute pressure and atmospheric pressure where the measurement is being made. When $P_{abs} > P_{atm}$, $P_{gage} = P_{abs} - P_{atm}$. When $P_{abs} < P_{atm}$, a partial vacuum exists and P_{gage} is often expressed as a positive vacuum pressure P_{vac}, where $P_{vac} = P_{atm} - P_{abs}$ (see diagram to follow on left).[22] In USCS, pressure is given by **lbf/in²** or **psi**, but absolute and gage pressures may be shown as **psia** and **psig**, respectively. A tire pressure of 32 psi is actually psig, the absolute amount above P_{atm}.



Absolute vs. Gage Pressure and Vacuum



Bourdon Tube Pressure Gauge

Pressure may be measured by manometers (suitable for small to moderate differences), Bourdon tube devices (diagram above to right),[23] and electronic pressure transducers (useful over a wide range, including strain-gage and piezoelectric transducers), etc.

Pressure units and quantities of interest include:

1 Pa = 1 N/m^2
1 bar ≡ 10^5 Pa
1 atm ≡ 101,325 Pa ≡ 1.01325 x 10^5 Pa ≡ 101.325 kPa = 1.01325 bars = 1013.25 millibar (mbar, mb)
≈ 14.696 psi ≈ 760 mm Hg (or Torr) ≈ 29.92 in Hg ≈
1 kgf/cm^2 = 9.807 N/cm^2 = 9.807 x 10^4 N/m^2 = 9.807 x 10^4 Pa = 0.9807 bar = 0.9679 atm
1 mm Hg ≈ 1 Torr = 1/760 atm [units of Hg subject to revision based on density revision]

Note that 1 bar, 1 atm, and 1 kgf/cm^2 are almost equal in value.

Pressure increases in a fluid with depth h, given simply by $\Delta P = \rho g h$ provided ρ and g are uniform. (ρ variation with depth is often negligible for virtually incompressible fluids over small height differences.) If density varies with height or depth z, the differential $dP = -\rho g\, dz$ may be integrated to obtain ΔP, which reduces to $\Delta P = \rho g h$ for constant ρ.

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[21] Pressure is a scalar quantity, a magnitude: "It relates the vector surface element **A** (a vector normal to the surface) with the normal force $\mathbf{F}_{\mathbf{normal}}$ acting on it. The pressure is the scalar proportionality constant that relates the two normal vectors $d\mathbf{F}_{\mathbf{normal}} = -P\, d\mathbf{A}$, where the force $\mathbf{F}_{\mathbf{normal}}$ is toward the surface but the surface element normal vector **A** points outward. https://en.wikipedia.org/wiki/Pressure w MCM modifications

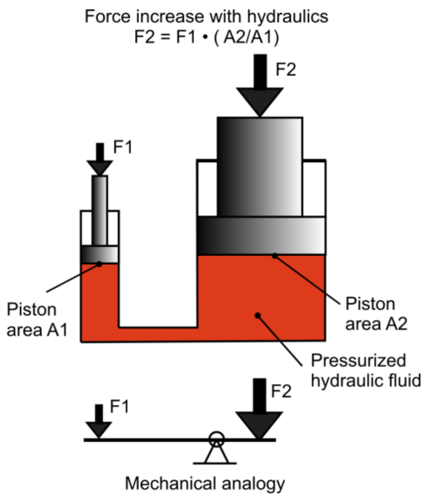
[22] Image from textbook website chapter_01.ppt

[23] http://www.instrumentationtoday.com/bourdon-tube/2011/09/

Hydrostatic Paradox and Hydraulic Pressure

A stable fluid at rest has equal pressure at points all at the same depth h, regardless of the amount or shape of fluid above it, provided the density ρ and g are uniform (i.e., for 2 points compared, the points are interconnected by the same static fluid). This is called the *hydrostatic paradox* (noted by Pascal).[24] It becomes the basis for Pascal's law ($\Delta P = \rho g \Delta h$) and *hydraulic pressure* devices. This law simplifies solving manometer problems involving more than one fluid in the tube.

As an example, for two connected cylinders having pistons of differing cross sectional area but positioned at about the same height (see diagram),[25]



$F_1 = PA_1$ and $F_2 = PA_2$, P is constant across the horizontal dimension, so
$F_2 / F_1 = A_2 / A_1$
The linear excursion of the larger piston will be correspondingly smaller than that of the smaller piston.

US Standard Atmosphere Model

Air pressure, density, cooling capacity, and airfoil lift all decrease with increasing altitude. The U.S. Standard Atmosphere Air model[26] specifies in part these Geopotential altitudes (m) and corresponding pressures (in Pa = N/m^2 when each value shown is multiplied by 10^4):

-1000 m: 11.39 0 m: 10.13 1000 m: 8.988 2000 m: 7.950 5000 m: 5.405,
10000 m: 2.65 20000 m: 0.5529 30000 m: 0.1197 50000 m: 0.008

Energy, Work, and Power

Energy originally denoted the capacity of acting or being active, but in modern physical science it is the capacity to do physical work. (In reality, its exact forms are not always easy to define and encompass.)[27]

Work is, per OED, "The operation of a force in producing movement or other physical change, esp. as a measurable quantity; the result of a force operating through a distance; energy transferred from one system to another that causes changes in the macroscopic properties of the latter (such as volume, height, or speed)."[28] In a physics dictionary, a more restrictive definition is found: "The work done by a force acting on a body is the product of the force and the distance moved by its point of application in the direction of the force. If a force F acts in such a way that the displacement s is in a direction that makes an angle θ with the direction of the force, the work done is given by: $W = F\,s\cos\theta$. Work is the scalar product of the force and displacement vectors."[29] Work is usually mechanical in nature, but the textbook and TD in general also refer to electrical work (done by electrical force on charged particles like electrons), rotational shaft work, etc.

It takes energy to do work, and they are closely related.[30] **Work** and **Energy** are expressed in the derived quantity **Joules J** or **kilojoules kJ**. The following are equivalent unit expressions for 1 J:

$$1\,\mathrm{J} = 1\,\frac{\mathrm{kg\,m^2}}{\mathrm{s^2}} = 1\,\mathrm{N\,m} = 1\,\mathrm{Pa\,m^3} = 1\,\mathrm{W\,s} = 1\,\mathrm{C\,V}$$

where Pa = pressure in pascals, W = Watts, C = coulombs, V = volts.[31]

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[24] http://scubageek.com/articles/wwwparad.html

[25] Image from https://upload.wikimedia.org/wikipedia/commons/e/e7/Hydraulic_Force_Torque_275px.png

[26] http://www.engineeringtoolbox.com/standard-atmosphere-d_604.html

[27] Robert & Samuel. "Energy." *Encyclopedia of Science, Technology, and Ethics*. Ed. Carl Mitcham. Vol. 2. Detroit: Macmillan Reference USA, 2005. 619-622. Gale Virtual Reference Library. Web. 26 Jan. 2016

[28] "work, n.": *OED Online*. Oxford University Press, December 2015. Web. 26 January 2016.

[29] "work." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

[30] https://en.wikipedia.org/wiki/Work_%28physics%29#Work_and_energy

Work = force × distance, and 1 J = 1 N m = 1 k m^2 s^{-2}. Rotational work is given by W = F θ r = T θ, where F = tangential force N, θ is angle of rotation in radians, r is radius m, and T is **torque** (**moment**) in N m. Although the units of torque are N-m = kg m^2 s^{-2}, torque is not a form of energy (for which the units are J = kg m^2 s^{-2}).

Heat energy is expressed in J or kJ. Heat may also be expressed in calories, where 1 cal = 4.1868 J exactly (but definitions vary). In USCS, energy is given by **British thermal unit Btu**, where 1 Btu ≈ 1.0551 kJ depending on definitions. (The value shown is given by the textbook, and represents the energy required to raise the temperature of 1 lbm of liquid water starting at T = 68°F by 1 °F at constant P = 1 atm.)[32] Human food "calories" are actually **kilocalories**. In TD, Heat is energy in transition as it crosses a boundary, thus it might best be termed **Heat Transfer**.[33] Its symbols are Q, q, and $\dot{Q}$, etc. Further details about forms of energy follow below.

Power is, "The rate at which work is done or energy is transferred [or used]."[34] It is given as energy per unit time with units **Watts**, where 1 W = 1 J/s and 1 kW = 1 kJ/s.

Thermodynamics Systems, States, Properties, Processes, and Equilibria

A **Thermodynamic (TD) System** is a quantity of matter or region in space chosen for study. It is bounded by a real or imaginary surface called the **boundary**, which separates the system from its **surroundings**.

A system with no movement of mass into or out of it (such as a sealed tank) is called a **closed system** with **fixed mass** (aka **control mass**). Energy in the form of heat or work may move in and out, and the real or imagined boundary and enclosed volume may move.

If energy as well as mass is not allowed to move in or out, the closed system is also **isolated**. [Apparently the volume of an isolated system can change.] An **isolated system** is a general system of fixed mass (thus a closed system) where no heat or work may cross the boundary. It is a closed system with fixed mass and also with no energy crossing its boundary. An isolated system is often a collection of systems (aka **subsystems**) contained within an overall boundary, including a main system and surrounding systems all within the overall boundary that are exchanging mass and energy among themselves but none exchange mass or energy outside the overall boundary.

A system with fixed volume which allows mass (and energy) to enter or exit is called an **open system** with a **fixed volume** (aka **control volume**) — it is enclosed within a real or imagined control surface. Energy and mass may move in and out and the boundary, which is usually fixed (but may move in some systems). Examples of control volume devices include compressors and turbines. Under steady-flow conditions, instantaneous mass and energy contained in the volume are often constant.

A system at **equilibrium** has various stable characteristics called **thermodynamic properties**, including pressure P, temperature T, volume V, entropy S, enthalpy H, internal energy U, etc.

The **state postulate** asserts, "The thermodynamic state [in equilibrium] of a simple compressible system is completely specified by two independent, intensive properties." **Simple** means that electrical, magnetic, gravitational, motion, surface tension, viscosity, fluid shear, capillarity, anisotropic stress, external force fields or other such effects are absent or negligible.[35] The intensive properties (for single-phase systems) may include T, v, P, h, s, u, etc. (where lower case denotes specific property per unit mass, see further below). Gravity will not be negligible if significant elevation differences are involved. *Compressible* means that V is not fixed, and may vary for instance with P or T. Certain extensive properties such as total mass must also be specified to completely characterize a system, in addition to the requisite 2 intensive properties.

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[31] https://en.wikipedia.org/wiki/Joule
[32] https://en.wikipedia.org/wiki/British_thermal_unit
[33] *TAEA7* p. 60
[34] "power." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016
[35] textbook website chapter_03.ppt

Intensive properties in a system are those properties that are independent of size or mass, and are usually shown in lower case. These include the *specific* forms b of normally extensive properties B, obtained by expressing b = units of B / units of mass. Intensive properties include: Temperature T, Pressure P, [Age], [Color], Density ρ, v, h, s, u, g, a, e, pe, ke, x, and any other mass independent property (see below).[36]

In contrast, **Extensive properties** are those that vary directly with size, extent, or mass etc. of the system, and are (often) shown in upper case. These include: mass m, total volume V, total energy E, or other mass-dependent properties.

One may test for intensive vs. extensive: Dividing the system in half does not change the value of an intensive property.

A **specific volume** v is the total volume V divided by the mass m it contains (thus v is inverse **density**, which is mass per unit volume).

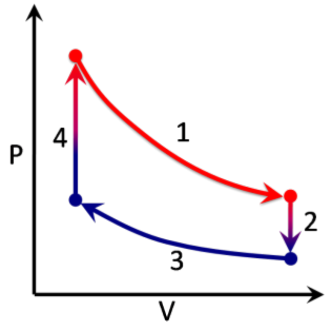
Other specific quantities, signifying the amount per unit mass, include
specific Gibbs function (or free energy) g
specific Helmholtz function (or free energy) a
specific total energy e
specific enthalpy h
specific KE or **PE (**symbols: **ke or pe)**
specific entropy s
specific internal energy u, and
specific exergy x.

For a substance with density ρ, the ratio between ρ and the density of water is called a **specific gravity SG** or **relative density**. Typically, both substances being compared are measured at T = 4 °C (where water is the densest) and at 1 atm = 101.325 kPa pressure.[37]

At **thermodynamic equilibrium**, a system maintains thermal equilibrium (uniform temperature), mechanical equilibrium (uniform pressure), phase equilibrium (the mass of two or more phases, e.g., ice and liquid water, are in equilibrium) and chemical equilibrium.

A **process** is a change in a system from one state to another. If the system remains nearly in equilibrium during this change, it is a **quasi-equilibrium process** or **quasi-static process**. The process often is graphed as following a **process path** (e.g., a process path on a P-V diagram for a system undergoing compression is illustrated in the diagram to right as process 3).

A process (or a series of connected processes) with identical starting and ending states is called a **cycle**. The example shown here is for an idealized Stirling cycle having 4 processes.[38]



Often, one state variable is held constant during a process:

Isobaric = constant P
Isothermal = constant T
Isentropic = constant s
Isochoric (aka **Isometric** or **Isovolumetric**) = constant v

Path Function and Differentials

According to the state postulate (above), the thermodynamic state and (intensive) properties such as v, P, and T are determined when 2 intensive state properties are known. Because state variables may be more or less exactly known and their changes between states are independent of path, their differentials can be denoted with exact differentials dV, dv, dP, etc. and the change in a property between 2 states can be obtained by integrating over the variable. Thus

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[36] https://en.wikipedia.org/wiki/List_of_thermodynamic_properties
[37] https://en.wikipedia.org/wiki/Specific_gravity
[38] https://en.wikipedia.org/wiki/Stirling_cycle#/media/File:Stirling_Cycle_color.png

$\int_1^2 dV = V_2 - V_1 = \Delta V$, regardless of path taken

However, changes in heat or work are path dependent, there is no corresponding exact integral for work or heat transfer, and their differentials are therefore shown as inexact differentials. Work and Heat are not properties, and there is no meaning to such terms as W_1, W_2, Q_1, Q_2 , $\Delta W = W_2 - W_1$, or $\Delta Q = Q_2 - Q_1$ (any of which would imply values for W or Q at particular states). We can only determine net transfers in or out of heat, and work in or work out:

$\int_1^2 \delta W = W_{12}$ a net work transfer having values which vary by path taken, there is no fixed ΔW and no meaning to W_1 or W_2

$\int_1^2 \delta Q = Q_{12}$ a net heat transfer having values which vary by path taken, there is no fixed ΔQ and no meaning to Q_1 or Q_2

Energy and Work (2)

(text Chapter 2 & other sources)

A TD system with mass m has a **Total Energy E** and **specific energy e** = E/m. There are many forms of energy, many of which are typically ignored or negligible in TD analyses. In TD, the absolute value of E is not known and we may assign E = 0 at some arbitrary reference point. We are primarily interested in changes in E between states (ΔE), and these ΔE's are independent of the arbitrary reference point for E chosen. Total energy E is contained or stored in a system, thus may be regarded as **static** [?intrinsic], whereas **dynamic energy interactions** are performed on or by a system (by **Work**, **Heat transfer**, and/or **Mass transfer**) and are not stored in the system. An energy interaction is **Heat transfer** if its driving force is a temperature difference, otherwise it is **Work transfer** (and/or **Mass transfer** for open systems).[39] In a science dictionary, **heat** is defined as, "The process of energy transfer from one body or system to another as a result of a difference in temperature. The energy in the body or system before or after transfer is also sometimes called heat but this leads to confusion, especially in thermodynamics."[40]

Forms of Energy

The following tabular summary of physical energies is assembled from the textbook, Wikipedia, and other sources, and includes many forms of energy that are not particularly relevant to TD. Many of the items listed overlap and are not meant to be mutually exclusive.[41] Forms of energy include **Macroscopic** (applying to an entire body relative to a reference point, plane, direction, etc.) and **Microscopic** (applying to individual microscopic atoms, molecules, etc.) Energy forms are abbreviated in upper case for the total system value and in lower case for the specific energy per unit mass. Forms of Work are separately listed (further below)

Total Energy **E/e**	In TD, the sum of internal, potential, and kinetic energies (U, PE, and KE). This differs from **dynamic energy interactions** performed on a system (by Work, Heat transfer, and/or Mass transfer). Zero value may be arbitrarily set.
Kinetic Energy **KE/ke**	Energy of (usually) macroscopic organized matter due to translation in a particular direction with respect to a frame of reference (or due to rotation about a particular axis of rotation again with a frame of reference). (In TD, KE does not include the KE of random and highly disorganized motions of microscopic entities such as atoms and molecules, which is considered part of Internal Energy.) It is the work required to accelerate an object to a given speed or rotation. Always positive (≥0), it is given by $mV^2/2$ or $I\omega^2/2$, where v = translational velocity magnitude, I is moment of inertia and ω = angular velocity magnitude in radians /s (for non-relativistic speeds). Energy flow is a special type of KE in systems arising from flowing mass, expressed as $\dot{E} = \dot{m}e$ (in J/s), where e is specific energy and mass flow rate $\dot{m} = \rho\dot{V}$ (in m/s).

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[39] *TAEA7* p. 56

[40] "heat." *A Dictionary of Physics*. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

[41] https://en.wikipedia.org/wiki/Forms_of_energy and *TAEA7* p. 53 etc.

Potential Energy **PE/pe**	The work done against a given force in changing the position of a (usually) macroscopic object with respect to a reference position or its position relative to other bodies. Applies to many forms in this list. (In TD, it does not include the PE of individual atoms and molecules, which is considered part of Internal Energy.) For uniform gravity, PE = mg Δh, where g is local gravitational acceleration, and Δh is height difference with respect to the reference level. May be positive or negative.
Internal Energy **U/u**	A quantity defined for a TD system consisting of the sum of all microscopic forms of energy (including the KE and PE of the individual atoms and molecules moving randomly, etc.) The portion of U associated with random [thermal] kinetic energies of molecules and atoms and that (approximately)[42] determines the temperature is called **sensible energy**.[43] (This term is preferred over **sensible heat**.) T is not directly proportional to U because T only measures the KE part of U. The absolute internal energy is usually not known, and TD analyses typically define arbitrary state values where U is set to zero. (Because of this, states of lower internal energy may have negative U). Components of U can include: **I. SENSIBLE ENERGY** or **SENSIBLE HEAT** (this contributes to T): • translation and rotation of individual atoms and molecules • vibration within molecules • vibration of atoms and/or molecules in crystal lattices **II. LATENT ENERGY** (a term preferred in TD over **latent heat**) • change of phase (phase transition) of a substance in a system at constant temperature and without chemical change.[44] “Latent heat [latent energy] is the quantity of heat absorbed or released when a substance changes its physical phase at constant temperature (e.g., from solid to liquid at the melting point or from liquid to gas at the boiling point).”[45] **III. OTHER ENERGIES** (all of these are usually not considered in TD): • chemical bond energy between atoms and molecules. (i.e., atomic orbital and molecular orbital energy; • electron spin • nuclear binding, spin, and excitation energy • Other stable microscopic energies.
Mechanical Energy	The sum of (usually only macroscopic) KE and PE (and internal energy is not included). The textbook states that mechanical energy applies to energy that can be converted to mechanical work completely and directly by ideal mechanical devices such as turbines (thus excluding thermal energy). The term is often associated with pumps and turbines operating under pressure, and the units of **flow work** are those of pressure, Pa = N/m^2 = $N\text{-}m/m^3$ = J/m^3. The mechanical energy flow rate per unit time of a flowing fluid (in total and in [mass] specific forms) is[46] $\dot{E}_{\text{mechanical}} = \dot{m}\left(\frac{P}{\rho} + \frac{V^2}{2} + gz\right)$ and $\dot{e}_{\text{mechanical}} = \frac{P}{\rho} + \frac{V^2}{2} + gz$ where $\dot{m}$= mass flow rate per unit time, P = pressure, ρ=density, V=fluid velocity, and gz = gravitational PE of the fluid. Note that flow work/energy P/ρ = P v.

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[42] http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/temper.html#c1

[43] *TAEA7* p. 55 , also http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/inteng.html

[44] https://en.wikipedia.org/wiki/Latent_heat

[45] "latent heat." *A Dictionary of Physics.* Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016

[46] *TAEA7* p. 59

Mechanical Wave Energy	A form of usually macroscopic mechanical energy propagated by a material's oscillations, (always ≥0). Includes ocean and water waves, sound waves, seismic waves, surface waves, perhaps gravitational waves, etc. "A wave that is an oscillation of matter, and therefore transfers energy through a medium. While waves can move over long distances, the movement of the medium of transmission—the material—is limited. Therefore, oscillating material does not move far from its initial equilibrium position. Mechanical waves transport energy. This energy propagates in the same direction as the wave...Mechanical waves can be produced only in media which possess elasticity and inertia."[47] Not studied in this course.
Chemical Energy	PE contained in chemical atoms and molecules and stored in chemical bonds. It is, "the potential of a chemical substance to undergo a transformation through a chemical reaction to transform other chemical substances... Breaking or making of chemical bonds involves energy, which may be either absorbed or evolved from a chemical system".[48] Bonds (intermolecular forces) tend to be strongest in solids, weaker in liquids, weakest in gases. Not studied in this course.
Electric Energy	PE from the electric field force, usually at a macroscopic level. Electrochemical energy is also a kind of PE found in batteries. Can also result from torque arising from atomic or molecular electric dipole moments. Not studied in this course except for electrical work (such as resistive heating).
Magnetic Energy	PE from the magnetic field force, usually at a macroscopic level. Can also result from torque arising from atomic or molecular magnetic dipole moments. Not studied in this course.
Surface Tension Energy (Surface Energy)	PE from surface tension effects, usually at a macroscopic level. Not studied in this course.
Radiant Energy	Energy of electromagnetic radiation including light and other photon radiations, always positive (≥0). Potentially relevant to TD. Not studied in this course. Subatomic particles such as neutrinos and muons also carry energy and beta rays are electrons, but all radiations except photons have mass. These emanations were not studied in this course.
Nuclear Binding Energy	Nuclear binding energy is the energy that would be required to disassemble the nucleus of an atom into its component parts, thus it is positive (≥0). It is the PE from binding forces of nucleons that are associated with the formation of the atomic nucleus. "The nuclear [strong] force is separate from what historically was known as the weak nuclear force. The weak interaction is one of the four fundamental interactions, and it refers to such processes as beta decay. The weak force plays no role in the interaction of nucleons, though it is responsible for the decay of neutrons to protons and vice versa."[49] Not usually relevant to TD systems analysis and not studied in this course.
Ionization Energy	PE of binding an electron to its atom or molecule. It is, "qualitatively defined as the amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated gaseous atom to form a cation."[50] Thus it is always positive (≥0). This is a variant of chemical energy. Not usually relevant to TD systems analysis and not studied in this course.

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[47] https://en.wikipedia.org/wiki/Mechanical_wave

[48] https://en.wikipedia.org/wiki/Chemical_energy modified MCM,
http://chemwiki.ucdavis.edu/Physical_Chemistry/Thermodynamics/State_Functions/Internal_Energy

[49] https://en.wikipedia.org/wiki/Nuclear_force

[50] https://en.wikipedia.org/wiki/Ionization_energy

Elastic Energy	PE arising from deformation of a material (or its container) that exhibits a restorative force (as with a spring or rubber balloon). Not studied in this course.
Gravitational Energy	PE from gravitational field force, usually at a macroscopic level. May be relevant when substantial differences in height (elevation) are involved.
Rest and Relativistic Energy	Rest energy arising from Einstein's mass energy equivalence is given by $E_0=m_0c^2$, where m_0 is ordinary mass of a substance at rest and c is the speed of light in vacuum. Relativistic energy of a particle or of an object moving at a velocity near c and with magnitude V, namely rest + kinetic energy, but ignoring other types of energy which are usually negligible, is given by $\mathrm{E}_{\mathrm{KE+Rest}} = \gamma \mathrm{m}_0 \mathrm{c}^2$ where the Lorentz factor $\gamma = 1/\sqrt{1-\frac{\mathrm{V}^2}{\mathrm{c}^2}}$ Not usually relevant to TD systems analysis, and not studied in this course.
Thermal Energy and Heat Transfer	Thermal energy is microscopic energy due to disordered random motions of atoms, molecules, etc. In our TD textbook, thermal energy in considered part of Internal Energy, and we observe the transfer of thermal energy (aka heat transfer) only when energy moves across a boundary in a process driven by a difference in temperature.

Note that "Mechanical Work Energy" is discussed below under Work Energy Transfer.

Thermal Energy Transfer Across a System Boundary (Heat Energy Transfer)

From text chap. 1, 2-3, 2-8 & others

Heat was regarded by Lavoisier as a transferrable substance of finite quantity called **caloric**. However, this theory was discredited, in part because heat can be continuously generated by friction, and heat now is regarded as a form of energy that is transferred. Heat transfer is the transfer of thermal energy from one body or system to another as a result of a difference in temperature. According to TD definitions, a **system does not possess intrinsic heat (or work)**—there is only transfer of heat in or out of the system during a process. Heat is transferred by **thermal conduction**, **convection**, and/or **radiation**.

A well-insulated system containing a burning candle has no transfer of heat (adiabatic process), and the conversion of chemical potential energy to sensible thermal energy is not associated with a change in total internal energy. In contrast, if a potato is the system and it is heating up in an oven, there is a heat energy transfer into the potato driven by the temperature difference.[51]

Consider an insulated oven with an electrical heating element:
- if the element is considered part of the system inside the oven, then the internal heating of the oven is due to a work energy transfer achieved by the electrons in the element's circuit crossing the boundary to do electrical work inside. Alternatively,
- if the element is considered outside of the system inside the oven, then the internal heating of the interior air is due to a heat energy transfer achieved by heat crossing the boundary between the element and interior air and driven by a temperature difference.[52]

Thermal/Heat energy transfers occur only at system boundaries, they are associated with processes between states and not states themselves, and they are path functions (for which the magnitudes depend on the path followed and not merely on the starting and ending states).

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[51] *TAEA7* p. 64

[52] *TAEA7* p. 64-5

Thermal Conduction Heat Transfer

This is, "The transmission of heat through a substance from a region of high temperature to a region of lower temperature. In gases and most liquids, the energy is transmitted mainly by collisions between atoms and molecules with those possessing lower kinetic energy. In solid and liquid metals, heat conduction is predominantly by migration of fast-moving electrons, followed by collisions between these electrons and ions. In solid insulators, the absence of free electrons restricts heat transfer to the vibrations of atoms and molecules within crystal lattices."[53]

Heat conduction in solids takes place via transmitted molecular/atomic vibrations in the lattice and by motions of free electrons (the latter predominates in metals, the former tends to predominates in nonmetals). Heat conduction rate in the direction of a temperature gradient through a homogeneous substances is, according to Fourier's Law, proportional to the thermal conductivity k_t (in W/m-K), the cross sectional area A, and the thermal gradient:[54]

$$\dot{Q}_{cond} = -k_t A \frac{dT}{dx} \text{ (Watts)}$$

The minus sign allows heat conduction to be positive in the positive x direction (along which temperature is decreasing). The thermal conductivity is highest for certain exotic materials (Helium II >100,000; graphene ~5000; diamond ~2300), less high for metals (Ag 429; Cu 401; Au 314; Al 237; Fe ~80; Carbon steel ~40; Stainless steel ~18; Hg 8.5), and often much lower for non-metals and insulators (water 0.613; oak wood 0.17; air 0.026).

Thermal Convection Heat Transfer

This is, "A process by which heat is transferred from one part of a fluid to another by movement of the fluid itself. In **natural convection** the movement occurs as a result of gravity; the hot part of the fluid expands, becomes less dense, and is displaced by the colder denser part of the fluid as this drops below it…" The textbook states that convection is between a solid surface and an adjacent liquid or gas, and involves the combined effects of conduction and fluid motion. If there is no fluid motion, there is conduction but not convection.[55] The faster the fluid/gas movement, the greater the heat transfer rate. In **forced convection**, a typically hot fluid is transferred from one region to another by a pump or fan. In **natural or free convection**, the fluid/gas moves by buoyancy arising from differences in density under the effect of gravity.

If heat transfer causes a **change of phase** of a fluid (such as with **boiling** with rising vapor bubbles coming off a heated surface, or condensation with falling droplets), this is also considered a type of convection (after all, there are motions of the fluid). The rate of heat transfer, by Newton's law of cooling, is proportional to the convection heat transfer coefficient h (in W/m-K), the cross sectional area A, and the change of temperature from solid surface to the fluid:[56]

$$\dot{Q}_{convection} = hA\,(T_{surface} - T_{fluid}) \text{ (Watts)}$$

Here the convection heat transfer coefficient h (in W/m^2-K) is empirical and depends on surface geometry, type of fluid motion, fluid properties, bulk fluid velocity, etc.

Bulk motion of fluids or gases (**advection**) by wind or other mechanisms (besides buoyancy) can also bring about heat transfer.

Radiation Heat Transfer (aka radiant heat or heat radiation)

This is, "Energy in the form of electromagnetic waves [photons] emitted by a solid, liquid, or gas as a result of its temperature. It can be transmitted through space; if there is a material medium, this is not warmed by

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[53] "conduction." A Dictionary of Physics. Eds. Law, Jonathan, and Richard Rennie. : Oxford University Press, 2015. Oxford Reference. 2015. Date Accessed 26 Jan. 2016 Similarly for convection and radiation.

[54] *TAEA7* p. 92, including data on thermal conductivity See also https://en.wikipedia.org/wiki/List_of_thermal_conductivities

[55] *TAEA7* p. 93

[56] *TAEA7* p. 93-4

the radiation except to the extent that it is absorbed. Although it covers the whole electromagnetic spectrum, the highest proportion of this radiation lies in the infrared portion of the spectrum at normal temperatures."[57]

A process in which no heat is transferred into or out of the system is **adiabatic**—these occur in well insulated systems or systems that have the same temperature as the surroundings. Adiabatic processes are not necessarily isothermal. Heat energy has units of J or kJ. Heat transfers are symbolized by Q_{12} [heat transferred from state 1 to state 2] and q_{34} [heat transferred per unit mass from state 3 to state 4]. Heat transfer rates are given by $\dot{Q}$ and $\dot{q}$, representing heat transfer per unit time and heat transfer per unit mass and per unit time.

By convention, net heat transferred into a system from its surroundings is considered positive and termed Q_{in}. Heat energy transferred in during a process in which the system goes from state 1 to state 2 may be termed Q_{12}. If the net transfer of heat energy is zero or inward for the system, $Q_{12} = Q_{in} \geq 0$, but otherwise Q_{in} is negative (and Q_{out} is positive). When working solutions, the direction of net heat transfer may be assumed to be inward with $Q_{in} \geq 0$. If the calculated Q_{in} proves to be negative, the direction of net heat transfer has been found instead to be outward and $Q_{out} > 0$.

Thermal radiation is emitted maximally from an idealized black body according to the Stefan-Boltzmann law:

$$\dot{Q}_{\text{emission,max. black body}} = \sigma A T^4 \quad \text{(Watts)}$$

where σ is the Stefan-Boltzmann constant, A is the emitting surface area, and T is in K.

Real substances ("grey bodies") have reduced emission, expressed as an emissivity factor ε, where $0 \leq \varepsilon \leq 1$, so that actual thermal emission at the surface is:

$$\dot{Q}_{\text{emission,real}} = \varepsilon \sigma A T^4 \quad \text{(Watts)}$$

The ideal black body has emissivity = 1.

The absorptivity of a substance $0 \leq \alpha \leq 1$ is the fraction of radiant energy absorbed at a surface. The emissivity and absorptivity depends on T and wavelength, and according to Kirchhoff's Law of radiation,[58] they are equal at the same T and wavelength.

For an opaque surface (no transmission), radiation incident on the surface, radiation absorbed by the surface, and radiation reflected by the surface are related as follows:

$$\dot{Q}_{\text{incident}} = \dot{Q}_{\text{absorbed}} + \dot{Q}_{\text{reflected}} = \alpha \dot{Q}_{\text{incident}} + (1-\alpha)\dot{Q}_{\text{incident}} \quad \text{(Watts)}$$

The net radiation heat transfer at a surface is the difference between radiation emitted and radiation absorbed. If radiation absorbed > radiation emitted, the surface is gaining energy by radiation, otherwise it is losing energy or unchanged (for 0 difference).

Work Energy Transfer Across a System Boundary

Heat and Work represent energy interactions between a system and its surroundings. Energy crossing a closed boundary (no mass transfer) is either heat or work. Heat transfer is always driven by temperature differences between the system and the surroundings, and proceeds in the direction of decreasing temperature. Any other energy transfer is **work energy transfer** (according to the expanded definition of work in TD as exemplified in the OED definition above), and involves forces acting through a distance. (For example, the transfer can be via a shaft's rotation, a piston's oscillatory movement, or an electrical current crossing the boundary arising from a voltage **V**). The units of work are those of energy: J or kJ. According to TD definitions, the **system does not possess intrinsic work (or heat)**—there is only transfer of work in or out of a system during a process. This transfer may be expressed per unit mass as $w = W/m$, where m is the system mass. As always, the work done by or on the system per unit time is Power = $\dot{W}$, in units of kW or kJ/s.

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[57] *A Dictionary of Science*, by Elizabeth A. Martin, 2010, Oxford U Press

[58] https://en.wikipedia.org/wiki/Kirchhoff's_law_of_thermal_radiation

By convention, net work done by a system on its surroundings is considered positive and termed W_{out}. Work done during a process for which the system changes from state 1 to state 2 may be termed W_{12}. If the net transfer of work energy is zero or is out from the system, $W_{12} = W_{out} \geq 0$, but otherwise W_{out} is negative (and W_{in} is positive). When working solutions, the direction of net work may be assumed to be outward $W_{out} \geq 0$. If the calculated W_{out} proves to be negative, the direction of net work has been found instead to be inward and $W_{in} > 0$.

Work energy transfers occur only at boundaries, they are associated with processes between states and not states themselves, and they are path functions (for which the magnitudes depend on the path followed and not merely on the starting and ending states).

There are several types of **Work Energy Transfers** beyond the traditional Force • distance. Recall the OED definition, which states in part, "The operation of a force in producing movement *or other physical change...*" , Some of the types of work are summarized to follow.

Mechanical Work Types

Displacement work: We are most familiar with the traditional definition of work by **displacement**, W = Force x distance. There must be a force exerted by the system (or surroundings) against a boundary, and the boundary must move in response to and in the direction of the force. The magnitude of work is given by

$$W = \int_1^2 F\,ds$$

where W = Mechanical work (J = N-m)
F = force in N
ds = displacement along which force is exerted (m)

Mechanical Work and energy are closely related, energy is required to do mechanical work, but they are not identical.

Lifting work: Mechanical work by displacement can be performed against the opposing force of gravity. In this case, the object acquires increasing gravitational PE while work is done on it (expended) to lift it up. There are typically some frictional losses and other inefficiency losses in the equipment doing the lifting.

Acceleration work: When an object is **accelerated** under a force (applied, gravitational, etc.), work is done against the object (i.e., expended) equaling the difference in KE (KE_{end} - KE_{start}) + frictional losses + other inefficiency losses.

Mechanical work may be performed by **expansion or compression of a gas against a moving boundary** (not discussed here, see summary of chapter 4-1).

Rotational work: Mechanical work also is transmitted by **torque** on rotating shafts.[59] For constant rotational torque τ,

$$W_{shaft} = 2\pi n F r = 2\pi n \tau$$
$$\dot{W}_{shaft} = 2\pi \dot{n} \tau$$

where W_{shaft} is work done in n revolutions (J)
$\dot{W}_{shaft}$ is work done per second (Power in W)
r = shaft radius (m)
F = tangential force (N) exerted at rim of shaft at radius r = τ/r
τ = constant torque exerted = Fr (N-m)

---

[59] *TAEA7* p. 66

n = total revolutions

$\dot{n}$ = revolutions/s (rpm/60)

Elastic Spring work: Mechanical work can be done acting on a **spring**. Assuming x is an elongation from the rest position of the spring, the work done in lengthening the spring from position x_1 to x_2 is:

$$W_{spring} = \frac{1}{2}k(x_2^2 - x_1^2)$$

where W_{spring} is work done (kJ)
x_1 to x_2 are starting and ending positions, resp. (m)
k = spring constant (kN/m)

Elastic Bar work: Mechanical Work is also performed when contracting or elongating an **elastic bar** (not so much as to induce a plastic deformation).[60] (The amount of contraction or elongation is proportional to the normal force F and the bar length L, and inversely proportion to the modulus of elasticity E and the cross sectional area A.[61]) The work in elastic deformation is given by:

$$W_{elastic} = \int_1^2 \sigma_n A \, dx \quad \text{(Watts)}$$

where $W_{Elastic}$ = Elastic mechanical work (J)
F = Force in the direction of the elongation or compression (N)
A = cross sectional area of bar (m^2)
σ_n = normal stress = F/A (N/m^2)
dx = displacement along which the normal stress force is exerted (m)

Surface tension work: The textbook also illustrates mechanical work performed in stretching a liquid film against the force of surface tension.

Non-Mechanical Work Types

This includes forms of work other than those that are obviously mechanical. A generalized force F must be identified that acts in the direction of a generalized displacement dx, so that the path dependent inexact differential $\delta W = F\,dx$.

Some of these are summarized to follow:

Electrical Work

Here, the force is the **Electromotive force EMF** or voltage **V**. This forces electrons to flow in the circuit against resistance or a back EMF (thus a displacement against a force). For a pure resistance R, heating results at a rate of $P = VI = I^2R$, and this is therefore a type of heat energy transfer. In the following example, I assume a simple DC fixed voltage and pure resistance R:[62]

$$W_{electrical} = \mathbf{V}N = \mathbf{V}I\,\Delta t$$
$$\dot{W}_{electrical} = \mathbf{V}I = I^2R$$

where $W_{electrical}$ = Electrical Work transferred in J
$\dot{W}_{electrical}$ = Electrical power in Watts
N = charge (coulombs), $\mathbf{V}$ = DC Voltage (Volts), I = Current (Amperes)

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[60] *TAEA7* p. 67-8

[61] https://en.wikipedia.org/wiki/Hooke's_law#Tensional_stiffness_of_a_uniform_bar

[62] *TAEA7* p. 65

If **V** varies (as occurs with AC current), $W_e = \int_1^2 \mathbf{V}I\,dt$ etc.

Magnetic Work

The force is the external magnetic field strength, the displacement is the total magnetic dipole moment. Topic not studied.[63]

Electrical Polarization Work

The force is the external electric field strength, the displacement is the polarization of the medium, i.e., the sum of the molecular electric dipole rotation moments. Topic not studied.[64]

The First Law of Thermodynamics (1LTD; Conservation of Energy; Energy Balance)

(from text Chapter 2 & other sources)

These terms arise from the same empiric considerations first studied by Joule, and are equivalent: "**The First Law of Thermodynamics**" (abbreviated here as **1LTD**), "**Conservation of Energy**", and "**Energy Balance**". This empirical but consistently observed "law" states, "Energy cannot be created or destroyed during a process, but only change forms". (The mass-energy equivalence does not usually arise in TD but would have to be factored in for nuclear reactions.) As previously stated, in TD the absolute value of E is not known and we may assign E = 0 at some arbitrary reference point. We are interested primarily in changes in E, thus ΔE, and not in its absolute value E. As to the origins of the 1LTD,

> "The first full statements of the law came in 1850 from Rudolf Clausius and from William Rankine; Rankine's statement was perhaps not quite as clear and distinct as was Clausius's."[65]

Forms of Energy Balance Equations

The Energy Balance formulation, which applies to any system and any process, states that the net change in E of the system during a process (ΔE) is equal to the difference between the total energy entering the systems and the total energy leaving the system during a process. Expressed as an equation, the following is applicable to all systems undergoing any process:

Amount Forms

(2-35) **AMOUNT FORM** $E_{in} - E_{out} = \Delta E_{system}$ (kJ or J)

For simple compressible systems (with no electric, magnetic, or surface tension effects):

(2-33) $\Delta E = \Delta U + \Delta KE + \Delta PE$

or

$$\Delta E = m(u_2 - u_1) + \frac{1}{2}m(V_2^2 - V_1^2) + mg(z_2 - z_1)$$

---

[63] https://en.wikipedia.org/wiki/Magnetic_moment

[64] https://en.wikipedia.org/wiki/Polarization_density

[65] https://en.wikipedia.org/wiki/First_law_of_thermodynamics includes much discussion of sign conventions and various formulations of how to express this for varying systems. See also,
http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node15.html and
https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter3a.html

For stationary systems, KE and PE are 0 and $\Delta E = \Delta U$ (for example, if thermal energy transfer enters a closed stationary system).

Energy can be transferred by **heat transfer**, **work transfer**, and/or **mass flow**. In the latter, mass entering a system arrives carries energy and may leave the system with that energy altered (e.g., the mass may have decreased in T).

Therefore, the energy balance can be written,

(2-34) $E_{in} - E_{out} = (Q_{in} - Q_{out}) + (W_{in} - W_{out}) + \left(E_{mass,in} - E_{mass,out}\right) = \Delta E_{system}$ (kJ)

All of the quantities in the middle expression have positive values and directions are noted by *in* and *out*.

$(Q_{in} - Q_{out}) = 0$ for adiabatic processes.

$(W_{in} - W_{out}) = 0$ in processes having no work interactions.

$\left(E_{mass,in} - E_{mass,out}\right) = 0$ in closed processes with no mass flow across system boundaries.

Energy balance for any process in **amount per unit mass** form is given by:

(2-38) $e_{in} - e_{out} = \Delta e_{system}$ (kJ/kg)

Rate Forms

As noted above, the amount form of energy balance for any system for any process can be expressed as

(2-35) $E_{in} - E_{out} = \Delta E_{system}$ (kJ/s)

The equivalent **RATE FORM** of equation 2-35 for any process is:

(2-36) $\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{system}}{dt}$ (kJ/s)

Simplifications may be made when any of the following rates are constant:

(2-37) $Q = \dot{Q}\Delta t \qquad W = \dot{W}\Delta t \qquad \Delta E = \frac{dE}{dt}\Delta t$

Differential forms

The **differential forms** of Energy balance are:

(2-39) $\delta E_{in} - \delta E_{out} = dE_{system}$ (kJ) or $\delta e_{in} - \delta e_{out} = de_{system}$ (kJ/kg)

Another statement of 1LTD in differential form, assuming the only form of energy entering or leaving a system are via heat transfer and work transfer, is:[66]

$dU = \delta Q - \delta W$

where dU = infinitesimal increase in internal energy,
δQ = inexact path-dependent differential heat transfer into a system, and
δW = inexact path-dependent differential work of all forms done by the system.

For open systems in which mass is not constant during a process, the **conservation of mass** (chap. 5) also applies, to be discussed later (especially for steady-fluid-flow systems and for systems with unsteady but uniform flow (chap. 5)

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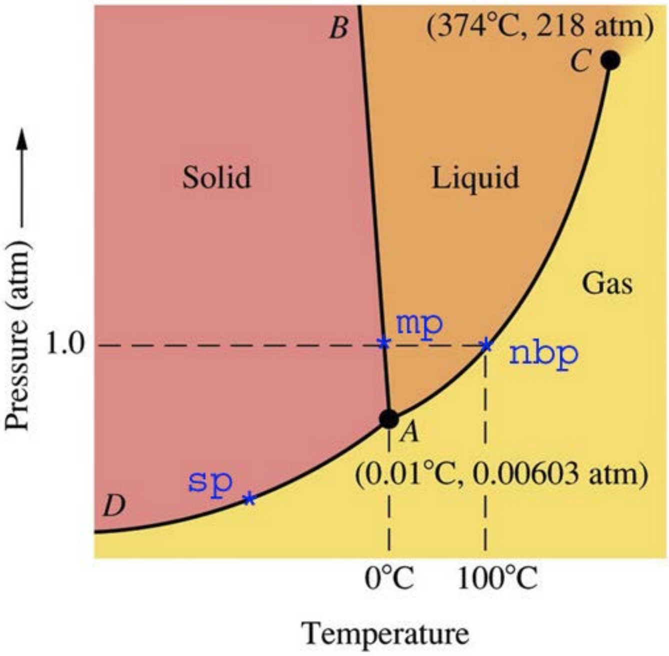
[66] https://en.wikipedia.org/wiki/Thermodynamic_equations

Properties of Pure Substances (3)

(from text Chapter 3 & other sources)

Phases and Phase Changes



A **pure substance** has a homogeneous and invariant chemical composition in all its phases—solid, liquid, or gas/vapor. Provided it meets this definition, it may be a mixture of chemical species. **Air** is often included, but it qualifies only in a limited range that does not include the liquid or solid phases of air or water vapor.

Solids (of atoms or molecules) are arranged in compact 3D fixed patterns with strong interatomic attractive forces, and atomic motions are confined to vibrations (oscillations). If a solid is heated, the increasing motion of the constituent atoms increases until bonds are broken and the solid melts into a **liquid** (or **sublimates**). The resulting liquid is similar in density and volume, but the atoms/molecules can now rotate and translate freely. With further heating, the liquid vaporizes or evaporates into a **gas/vapor**, with lower density, greater intermolecular distances and volume, higher energy per atom/molecule (which must be released for the gas to condense back to a liquid). As noted above, some phase changes associated with fluids in motion (such as boiling) are considered to be a type of thermal convective energy transfer.

Phases of water are shown in the adjacent P-T diagram.[67] Annotations include: mp = melting point, nbp = normal boiling point, sp = sublimation ?points (which occurs along D-A), A = triple point, C = Critical Point.

Property and Phase Diagrams

TD Relationships for containers holding only pure water (in various mixtures of liquid and vapor states)

If we know the amount (mass m) and temperature T_{sat} of saturated liquid water, we may derive the pressure P_{sat} and specific volume v from table A-4, then calculate the total volume V = mv.

If we know the volume of saturated water vapor V at a stated pressure P_{sat}, we may determine the T_{sat} and v from table A-5, then compute mass m = V/v.

If we know the mass m of saturated water at T_{sat}, and it is completely vaporized at constant P, we can derive the volume change ΔV and heat energy transfer required to effect the vaporization (this is the enthalpy of evaporation mh_{fg}, see below) from table A-5.

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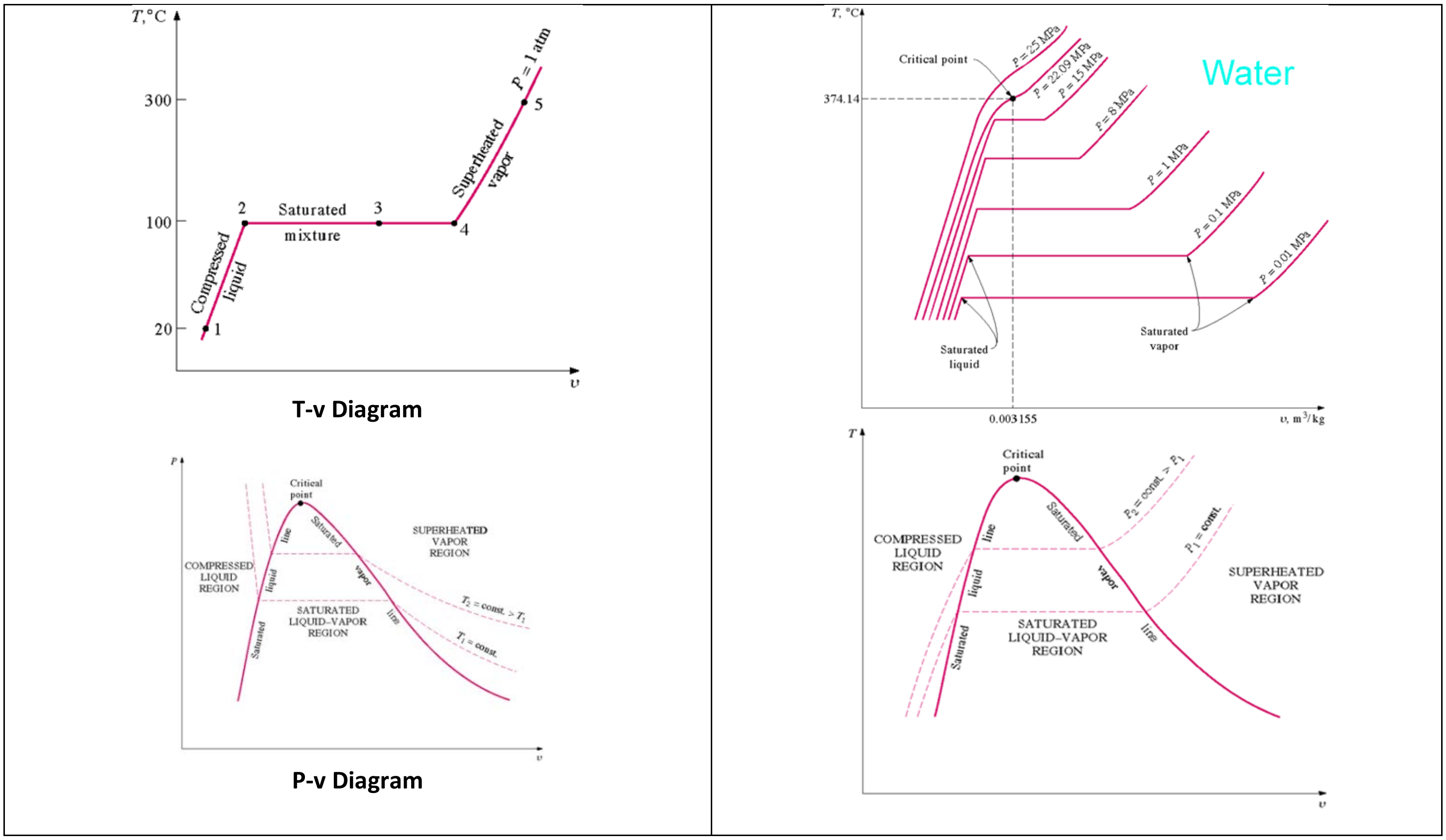
[67] https://stevengoddard.files.wordpress.com/2010/09/water-phase-diagram1.jpg

2D T-v and P-v phase diagrams

The 3 basic phases (solids, liquids, and gases) are summarized in the following three 2D T-v line diagrams (and a single 2D P-v diagram, lower left).[68]

A solid when heated (see 3D diagrams further below) builds up thermal energy until it is at its melting T for the given pressure, so that any further heating would cause a partial **liquefaction** (or in some cases **sublimation**). For ice, the saturated specific volume symbol commonly used is v_i. With further heating, the solid continues to melt at a constant melting T until it becomes completely melted. It is then termed a called a **compressed liquid** (a somewhat peculiar name) or **subcooled liquid** (meaning that it is not yet hot enough for it to start to vaporize). Most solids increase in volume when they melt, but water decreases in volume as it melts (as shown in the 3D diagrams to follow).

As the compressed liquid is heated, its temperature rises until it can receive no more heat while fully remaining a liquid (see 2D diagrams). This temperature is shown as T_{sat}, with onset at a specific volume v_f at which point the liquid is termed a **saturated liquid** (so named because it was "saturated with caloric" in the archaic model). Any further heat addition results in partial **vaporization**, so that the system becomes (though still a pure substance) a **mixture** of **saturated liquid** and **saturated vapor** with varying specific volume v, remaining at a fixed temperature T_{sat} while vaporization proceeds and v rises. Once the liquid is fully vaporized, the resulting vapor with specific volume v_g is termed a **saturated vapor**, in that any removal of heat from it would cause a partial condensation. Addition of further heat causes the gas to increase in temperature above T_{sat}, and to increase further in v, and it is now termed a **superheated vapor** or **gas**. The change in specific volume that occurs during the saturated mixture phase (moving from state 2 to state 4 in the diagram upper left) is labeled $v_{fg} = v_g - v_f$. The term *vapor* applies when the gas is near the saturated vapor line (thus having a potential to re-condense), whereas the term *gas* is preferred when the state is well into the superheated region.


T-v Diagram

P-v Diagram

Sample T-v and P-v Phase Diagrams

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[68] Image from textbook website chapter_03.ppt

If similar plots for water, as in the upper left image, are made of T v curves for various constant pressures as parameters, the graph upper right obtains (with numerical values for water shown in the upper right diagram).[69] Note that the value of v_f at which T_{sat} begins is seen to increase with increasing P, and the width of the specific volume change $\Delta v = v_{fg} = (v_g - v_f)$ occurring in the saturation mixture phase decreases with increasing P. If the values, for rising P, of T and v are plotted—including specifically, the values where saturated liquid begins and saturated vapor begins—the lower right curve above obtains. The pure substance is shown to exist in phases: a **compressed liquid** region (on the left), a **saturated liquid-vapor mixture** region (in the center), and a **superheated vapor/gas** region (to the right). (Freezing is not depicted in the 2D images above, but is in the 3D images to follow.) The lower right 2D graph also show the existence of a **critical point**, where the distinction between gas/vapor and liquid disappears. The critical point lies at the junction of the **saturated liquid line** on the left and the **saturated vapor line** on the right. The latter two lines together comprise the **saturation dome**.

A set of graphs can also be made of P-v diagrams similar to T-v diagrams—here, T becomes the parameter that is held constant for the various curves (lower left diagram). Note that the P-v curves rise steeply on the left outside the saturation dome, because the liquid is relatively incompressible and high pressures are needed to reduce v even slightly. The T-v curves (above right) also show that a sharp falloff of T to the left of the saturation dome is needed to reduce v even slightly.

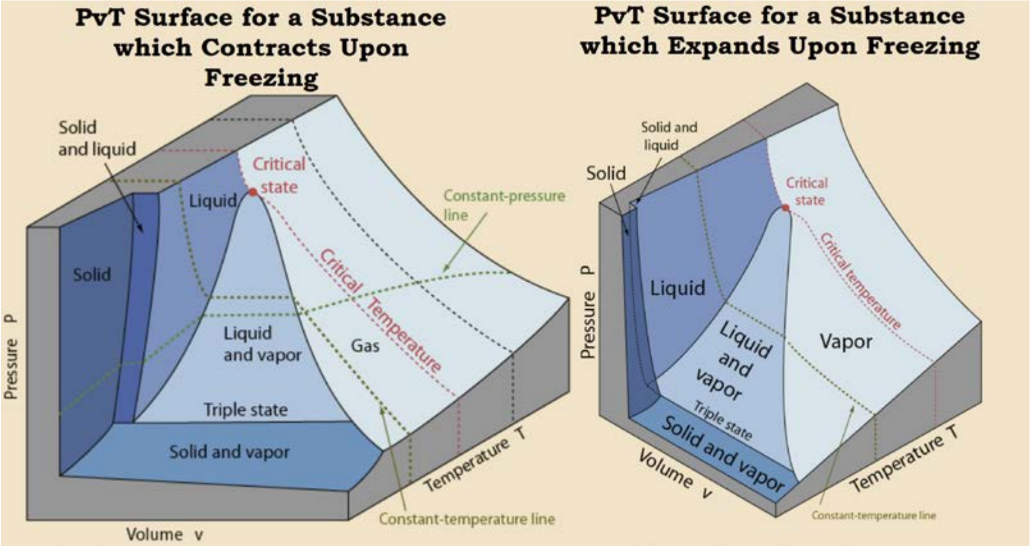
Calculating TD relationships for closed simple systems of water

If we know the amount (mass m) and temperature T_{sat} of saturated liquid water, we may derive the pressure P_{sat} and specific volume v from table A-4, then calculate the total volume V = mv.

If we know the volume of saturated water vapor V at a stated pressure P_{sat}, we may determine the T_{sat} and v from table A-5, then compute mass m = V/v.

If we know the mass m of saturated water at T_{sat}, and it is completely vaporized at constant P, we can derive the volume change ΔV and heat energy transfer required to effect the vaporization (this is the enthalpy of evaporation mh_{fg}, see below) from table A-5.

3D P-v-T phase diagrams



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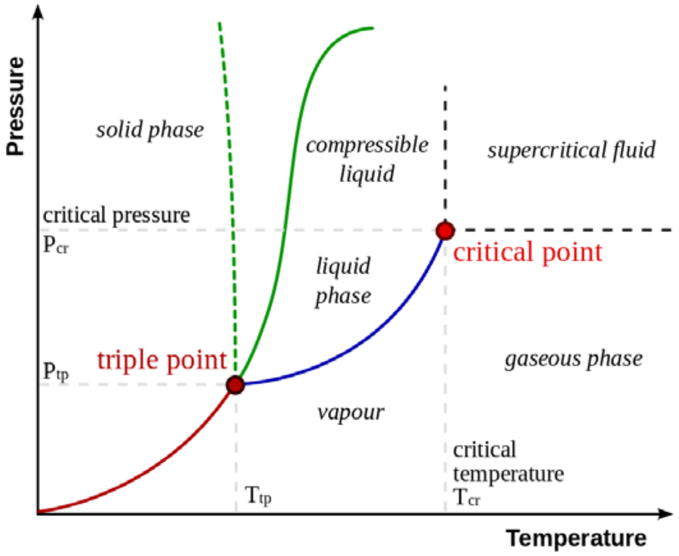
[69] T-v and P-v images are adapted from textbook website chapter_03.ppt

In the 3D P-v-T surface phase diagrams above,[70] the behavior of substances that expand on freezing (like water) and those that contract on freezing is contrasted.[71] On the left, a constant pressure line is illustrated similar to the 2D above graphs. The status of the Critical point (critical state) is more apparent. These graphs also depict the solid state, the state where a mixture of solid and liquid exists, the state where a mixture of solid and vapor exists, and the **triple line** (**triple state** or **triple point**) where solid, liquid, and vapor coexist. It is apparent that the triple point is defined at a particular P and T, but values of v vary over a range.

2D P-T phase diagrams

When P is plotted against T (i.e., the 3D surface above is projected onto the P-T plane), the triple state or line appears as a single **Triple Point** (see diagram below).[72] The triple point occurs typically at a very precise and sharply defined combination of T and P (though at variable v). Because of this, triple points play an important role in precisely defining and calibrating the ITS-90 temperature scale.

The following diagram also nicely depicts the **critical point** as defined by a **critical pressure P_{cr}** and the **critical temperature T_{cr}**. (This point also exists at a **critical specific volume v_{cr}**.)[73]



The dotted green line (aka **coexistence curve**) is for water. “For most substances [represented by the solid green line above] the gas–liquid–solid triple point is also the minimum temperature at which the liquid can exist. For water, however, this is not true because the melting point of ordinary ice decreases as a function of pressure, as shown by the dotted green line in the phase diagram. At temperatures just below the triple point, compression of water vapor at constant temperature transforms water vapor first to solid and then to liquid (water ice has lower density than liquid water, so increasing pressure leads to a liquefaction).”

“The Clausius–Clapeyron relation can be used to find the relationship between pressure and temperature along phase boundaries…”[74] It gives the slope of the tangent to the coexistence curve dP/dT for a given T, P:

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[70] http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/pvtsur.html , with minor MCM modifications

[71] The 3-D surface diagrams in the textbook p. 123 are more difficult to understand regarding freezing.

[72] https://en.wikipedia.org/wiki/Triple_point including quoted text and diagram

[73] http://aerostudents.com/files/thermodynamics/pureSubstances.pdf

[74] https://en.wikipedia.org/wiki/Clausius%E2%80%93Clapeyron_relation quoted & paraphrased text+image

The textbook gives this relationship simplified for liquid-vapor and solid-vapor phases changes:[75]

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{Ph_{fg}}{RT^2} \qquad \text{or} \qquad \left(\frac{dP}{P}\right)_{sat} = \frac{h_{fg}}{R}\left(\frac{dT}{T^2}\right)_{sat} \qquad \text{or} \qquad \ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

Boiling vs. Evaporation

"Liquids may change to a vapor at temperatures below their boiling points through the process of **evaporation**. Evaporation is a surface phenomenon in which molecules located near the liquid's edge, not contained by enough liquid pressure on that side, escape into the surroundings as vapor... On the other hand, **boiling** is a process in which molecules anywhere in the liquid escape, resulting in the formation of vapor bubbles within the liquid"[76] According to the textbook, **evaporation** occurs when the vapor pressure is less than the saturation pressure of the liquid $P_{sat@T}$. Evaporation involves no bubble formation or bubble motion. The term **boiling** is reserved for the following conditions: there is a solid-liquid interface [ignoring the special case of direct liquid heating by microwave cooking], the solid is maintained at a temperature substantially above the liquid's T_{sat} for the given pressure, and there is rapid motion of vapor bubbles in the liquid and arising from the surface.[77]

Vapor Pressure and Boiling

A liquid boils when its **saturated vapor pressure** (**saturation vapour pressure**) becomes equal to the external pressure (i.e., atmospheric pressure for an open container) on the liquid. If the liquid is exposed to normal atmospheric pressure at sea level, the liquid boils when its saturated vapor pressure becomes equal to 1 atmosphere (or 101325 Pa or 101.325 kPa or 760 mmHg). At sea level, this happens for pure water when the temperature reaches approximately 100°C.[78] But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.[79] Saturated vapor pressure is a function of T and has an empirical formula[80]

$$e_s = 6.11 \bullet 10^{\left(\frac{7.5T}{237.3+T}\right)} \qquad \text{(T in °C, } e_s \text{ millibars mb)}$$

The boiling point of water rises only slightly if the water is salty or otherwise diluted by a non-volatile solute. The following formula gives the boiling point elevation by a solute[81]

$$\Delta T_b = K_b \cdot b_B$$

where ΔTb = the boiling point elevation = T_b (solution) - T_b (pure solvent)
K_b = the **ebullioscopic constant**, which is dependent on the properties of the solvent...
b_B = is the molality of the solution ...

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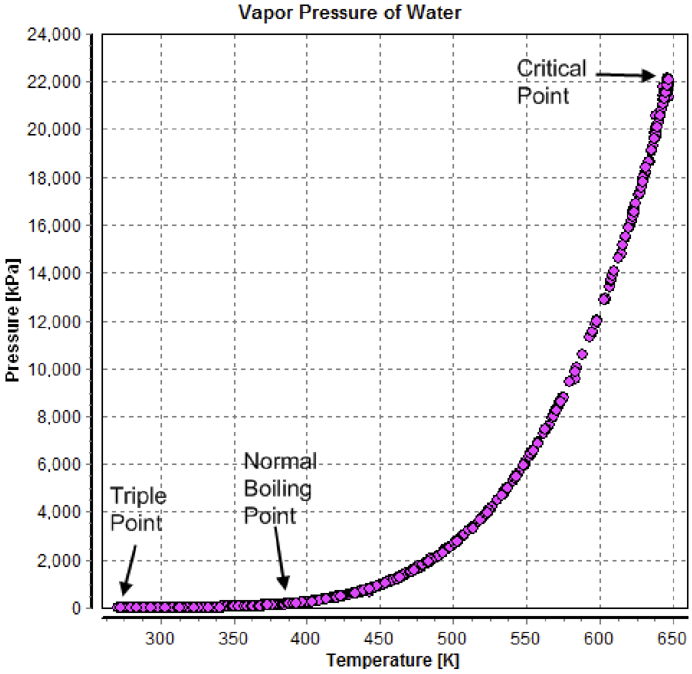
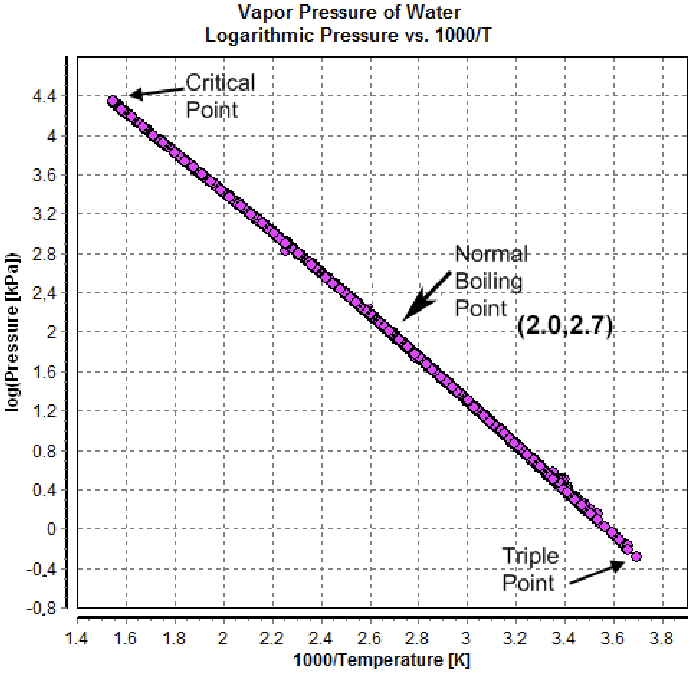
[75] *TAEA7* p. 670
[76] https://en.wikipedia.org/wiki/Boiling_point
[77] *TAEA7* p. 148
[78] Actually, 99.975 °C. The boiling point of water rises only slightly if the water is salty or otherwise diluted by a non-volatile solute.
[79] http://www.chemguide.co.uk/physical/phaseeqia/vapourpress.html paraphrased by MCM
[80] http://www.srh.noaa.gov/epz/?n=wxcalc_vaporpressure
[81] https://en.wikipedia.org/wiki/Boiling-point_elevation

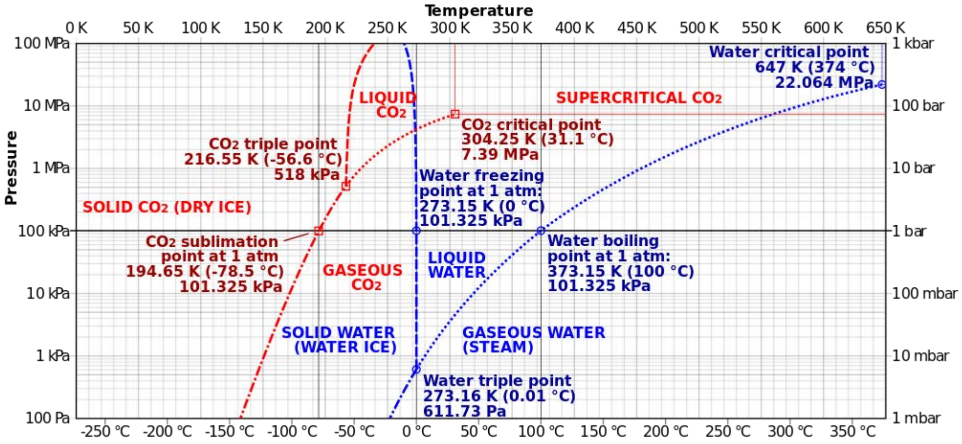
An empiric relationship of vapor pressure P of pure water versus T is shown graphically as follows:[82]





Dry Ice

Below the triple point, liquid cannot exist in stable equilibrium, only solid or vapor.[83] For substances such as dry ice (CO_2), which have triple point T_{tp} = 216.55 K and P_{tp} = 518 kPa (thus greater than 1 atm or 101.315 kPa), solid to vapor sublimation is the only possible phase change, because a stable liquid component cannot exist at 1 atm.[84]



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[82] https://en.wikipedia.org/wiki/Vapour_pressure_of_water indication of normal boiling point modified by MCM, data from Dortmund Data Bank

[83] *TAEA7* p. 121

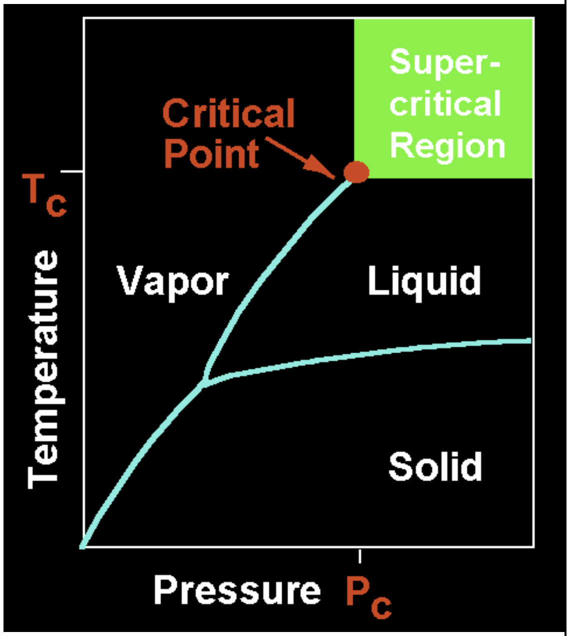
[84] https://en.wikipedia.org/wiki/Dry_ice incl. diagram

Freeze drying (aka lyophilization or cryodesiccation)

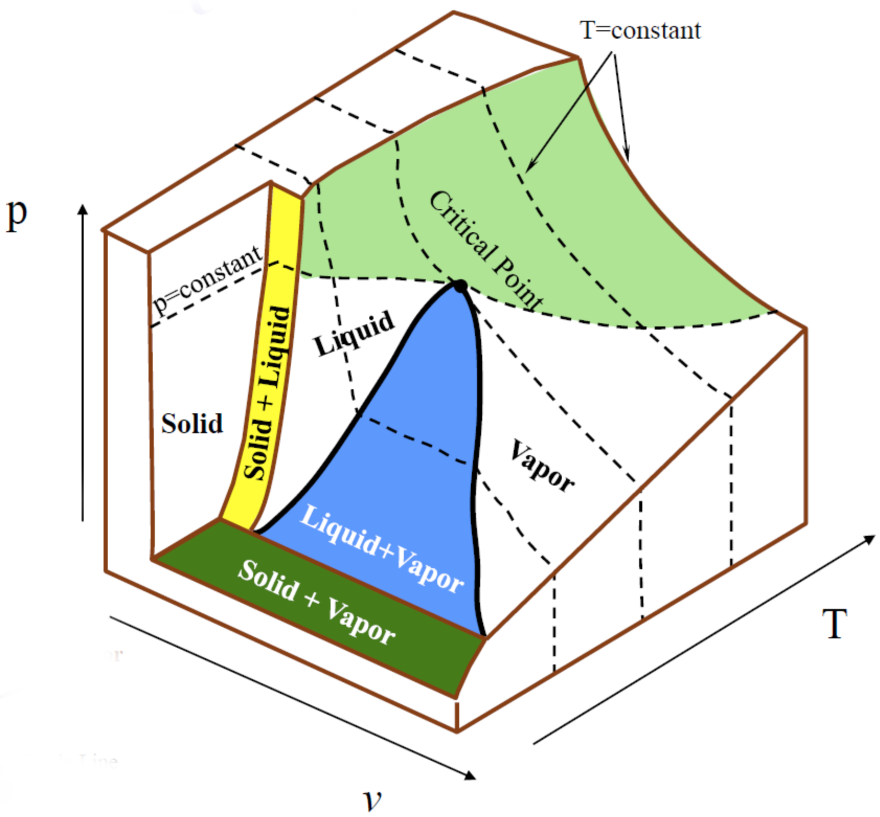
In this process for drying vegetables, fruits, and other substances (steps are only briefly described here):[85]

(1) T is dropped rapidly to −50 °C and −80 °C (after various pretreatments) until all is frozen, then
(2) P is markedly lowered (so that T and P are both below the triple point), then
(3) heat is slowly added to induce **sublimation** while still at very low $P < P_{tp}$ for **primary drying**, then
(4) **secondary drying** to remove unfrozen water continues over hours to days.

Supercritical Fluid SCF



SUPERCRITICAL FLUID T-P PHASE DIAGRAM



SUPERCRITICAL FLUID P v T PHASE DIAGRAM

A supercritical fluid SCF[86] is a substance in a thermodynamic state where temperature and pressure are both above the substance's critical point (T_c, P_c). According to this definition for supercritical fluids, T is never $< T_c$ and P is never $< P_c$ (thus, the bounds are rectangular on a T-P diagram, see left diagram above). However, this simplification is not always the case at extremes of pressure (see the following diagram,[87] showing solid CO_2 (red) existing above T_c and P_c). The SCF state is depicted in green in the P-v-T diagram above on the right.[88]

> "Supercritical fluids are highly compressed gases which combine properties of gases and liquids in an intriguing manner. Fluids such as supercritical xenon, ethane and carbon dioxide [the latter if exceeding T_{cr} = 31.10 °C and P_{cr} 7.39 MPa] offer a range of unusual chemical possibilities in both synthetic and analytical chemistry… Supercritical fluids have

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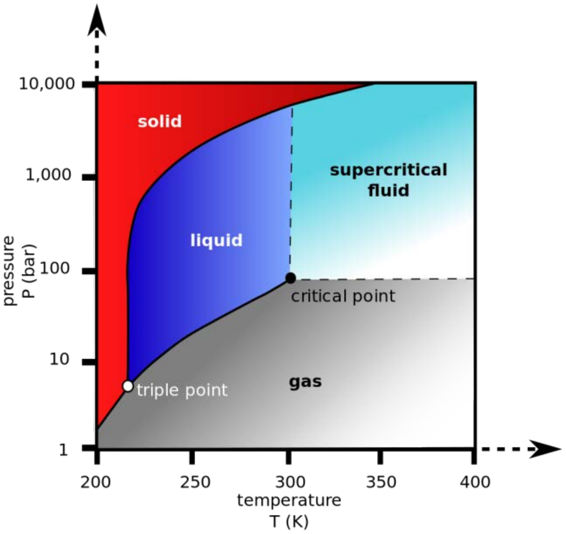
[85] https://en.wikipedia.org/wiki/Freeze-drying (not the same example as in the textbook)
[86] These are not usually termed supercritical gas or supercritical liquid
[87] https://en.wikipedia.org/wiki/Supercritical_fluid
[88] http://soliton.ae.gatech.edu/people/jseitzma/classes/ae3450/phases.pdf

solvent power similar to a light hydrocarbon for most solutes. However, fluorinated compounds are often more soluble in $scCO_2$ than in hydrocarbons; this increased solubility is important for polymerization... Solubility increases with increasing density (i.e. with increasing pressure). Rapid expansion of supercritical solutions leads to precipitation of a finely divided solid... The fluids are completely miscible with permanent gases (e.g. N_2 or H_2) and this leads to much higher concentrations of dissolved gases than can be achieved in conventional solvents."[89]

"A supercritical fluid is a state where matter is compressible and behaves like a gas (i.e. it fills and takes the shape of its container), which is not the case when it is in a liquid state (an incompressible fluid that occupies the bottom of its container). However, a supercritical fluid has the typical density of a liquid and hence its characteristic dissolving power. That is why we cannot define the supercritical fluid as a liquid or as a gas... [For CO_2,] once the critical temperature and pressure have been reached, the two distinct phases of liquid and gas are no longer visible. The meniscus [in a demonstration window] can no longer be seen. [SCF's] typically have density of 0.2 - 0.9 g/ml, low viscosity comparable to gases, and diffusivity intermediate between usual gases vs. liquids."[90]



Carbon Dioxide Phase Diagram

SCF's can be used in supercritical fluid chromatography SFC, biocatalysis, biomass gasification, water oxidation (of toxic waste) and water hydrolysis (e.g., polysaccharides and lignin), nano- and micro-particle formation, cleaning (including dry cleaning, where CO_2 replaces perchloroethylene PERC), extraction of or from thermally labile materials (caffeine, Vit. E, essential oils), dispersion, polymer manufacturing, fractionation, impregnation and dyeing, various other chemical reactions, SC reactors, biodiesel production, and many other applications. We will be hearing much more about this innovative technology.

Property Tables and Selected Derived Properties

(3-5)

The property tables in the back of the textbook (presented in SI and USCS units) are very useful for solving problems to a high degree of accuracy. Some of the tables and tabulated values (including derived and combination properties such as s, h, u, etc.) are discussed below.

Water Tables

For **saturated water** by T_{sat}, values of: P_{sat}, v_f, v_g, u_f, u_{fg}, u_g, h_f, h_{fg}, h_g, s_f, s_{fg}, and s_g (Table A-4)
For **saturated water** by P_{sat}, values of: T_{sat}, v_f, v_g, u_f, u_{fg}, u_g, h_f, h_{fg}, h_g, s_f, s_{fg}, and s_g (Table A-5)
For **superheated water** by T and P, values: of v, u, h, and s (Table A-6)
For **compressed liquid water** by T and P, values of: v, u, h, and s (Table A-7)
For **saturated ice-water vapor** by T, values of: P_{sat}, v_i, v_g, u_i, u_g, h_i, h_{ig}, h_g, s_i, s_{ig}, and s_g, (Table A-8)
(Symbols and subscripts are clarified below.)

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[89] http://www.nottingham.ac.uk/supercritical/scintro.html incl. image (edited MCM)
[90] https://www.uni-leipzig.de/~pore/files/3rd_irtg_workshop/dvoyashkin.pdf and
http://chemeng.iisc.ernet.in/giridhar/rect.html and
https://en.wikipedia.org/wiki/Supercritical_fluid

Enthalpy

Total Enthalpy (fr. Greek *To Heat*) is a convenient combination property recognized by Richard Mollier and defined as

$$H = U + PV \quad (\text{kJ})$$

Specific enthalpy is

$$h = u + Pv \quad (\text{kJ/kg})$$

The units of PV are kPa m^3 = kJ (because 1 kN m^{-2} m^3 = 1 kN m = 1 kJ). See **Mollier chart** of h vs. s for water, textbook chart Figure A-10.

Symbols (as in the water tables) are described as follows :

v_f = specific volume of saturated liquid (i.e., along the saturated liquid line),
(f = German flüssigkeit = liquid)

v_g = specific volume of saturated vapor (i.e., along the saturated vapor line)
g = gas (vapor)

$v_{fg} = (v_g - v_f)$ (specific volume change when changing from saturated liquid to saturated vapor)

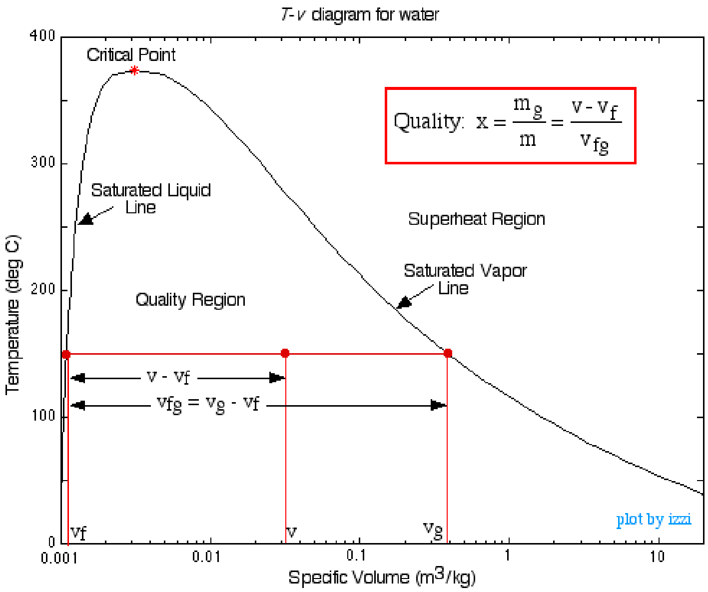
h_f = specific enthalpy of saturated liquid (along the saturated liquid line)

h_g = specific enthalpy of saturated vapor (along the saturated vapor line)

$h_{fg} = (h_g - h_f)$ = **enthalpy of vaporization**

The enthalpy of vaporization h_{fg} is also called the **latent heat of vaporization**, the amount of energy needed to vaporize a unit mass of saturated liquid to saturated vapor starting at a given pressure P and corresponding T_{sat} (table A-5, Saturated Water).[91]

Saturated Liquid-Vapor mixtures of a pure substance and Quality:



The relative proportion of a mixture of saturated liquid and saturated vapor (inside the saturation dome) of a system consisting of only a pure substance is expressed by the **quality x**:

$$x = \frac{m_{vapor}}{m_{total}}$$

where x is defined only for pure substance saturated mixtures, and $0 \leq x \leq 1$, and

where $m_{total} = m_{liquid} + m_{vapor} = m_f + m_g$

(x is diagrammed to right.[92])

x is 0 when all of the substance is saturated liquid, and 1 when all of the substance is saturated vapor. Quality can serve as one of two intensive properties that can describe a state. The process of vaporization produces a change in relative amounts of liquid and vapor, not their other properties such as P and T. The substance is said to be in a mixture and thus mixed together in an averaged volume (the actual volume), although the gas and liquid phases are usually physically separated due to gravity. The quantity x is the relative horizontal distance in the P-v or T-v diagram along the **saturated liquid-vapor mixture line**, as determined by values of specific volume. (For instance, 25% is 1/4 the way along this line starting at v_f). The value is x is calculated from table values by:

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[91] *TAEA7* p. 125

[92] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2a.html

$$x = \frac{v_{avg} - v_f}{v_{fg}}$$

We can express average properties of v, u, h, and (generically) y for saturated Liquid-Vapor mixtures:

$v = v_{avg} = v_f + xv_{fg}$

$u = u_{avg} = u_f + xu_{fg}$

$h = h_{avg} = h_f + xh_{fg}$

$y = y_{avg} = y_f + xy_{fg}$ where y can represent v, u, or h and $y_f \le y \le y_g$

The use of quality x can simplify certain calculations for saturated liquid-vapor mixtures. Given a mass of m pure water, the T, and the mass of liquid water, we can calculate the P and V. Given a volume and mass of **refrigerant 134a** (**R-134a**, **1,1,1,2-Tetrafluoroethane**)[93] at pressure P, we can determine v, v_f, v_g, (from table A-12), T, x, h_f, h_g (table 12), and therefore h, m_g, V_g and V_f.

Superheated Vapor/Gas of a pure substance

This phase exists to the right of the saturated vapor line on the T-v diagram of P-v diagram, or above the critical temperature. T and P are now independent. The properties P and T determine v, u, and h. Superheated vapor compared to saturated vapor has:[94]

$P < P_{sat}$ (lower pressure) for same T

$T > T_{sat}$ (higher temperature) for same P

$v > v_g$ (higher specific volume) for same P or same T

$u > u_g$ (higher specific internal energy) for same P or same T

$h > h_g$ (higher specific enthalpy) for same P or same T

Given the P and T, we can determine the u of water from table A-6 (superheated water). Given P and h, we can determine T (table A-6), etc.

Compressed Liquid (aka Subcooled Liquid) of a pure substance

These are less commonly represented in table form (e.g., Table 7 Compressed Liquid water) because properties are strongly dependent on T but nearly independent of P. They are often approximated by the Saturated Liquid data for a given T. For a compressed liquid, if tabular values are lacking, we use

$h \approx (h_f @ T) + (v_f @ T) \bullet (P - P_{sat} @ T)$

Compressed liquids have:

$P > P_{sat}$ (higher pressure) for same T

$T < T_{sat}$ (lower temperature) for same P

$v < v_f$ (lower specific volume) for same P or same T

$u < u_f$ (lower specific internal energy) for same P or same T

$h < h_f$ (lower specific enthalpy) for same P or same T

Given T and P for a compressed liquid water, u may be obtained from Table A-7 (compressed liquid water) or estimated from table A-4 (Saturated liquid) with minimal error.

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[93] https://en.wikipedia.org/wiki/1,1,1,2-Tetrafluoroethane

[94] *TAEA7* p. 131

Reference States and Reference Values

We are usually concerned with changes in h, u, m and s rather than absolute values. Therefore, the tables typically select a particular state (the **reference state**), such as saturated liquid water at 0.01 °C and assign **reference property values** like $u = 0$ and $s = 0$. As a result, some of the properties may take on negative values.

To determine what state a pure substance is in so that the proper table can be selected: If T and u are known, then for that T,

if $u < u_f$	compressed liquid
if $u_f \leq u \leq u_g$	saturated mixture
of $u > u_g$	superheated vapor

Then using the proper table, determine other properties such as P.

A similar decision process may be used if we know T and v or h.

Or, if we know T and P, then for that P

if $T < T_{sat}$	compressed liquid
if $T = T_{sat}$	saturated mixture
if $T > T_{sat}$	superheated vapor

Also, given x and P, we can infer T_{sat} from table 5 (saturated water), then obtain u_f, u_{fg}, and u.

Equations of State EOS: The Ideal Gas EOS, Compressibility Factor Z, Other EOS

(3-6) (3-7)

Gas and *vapor* are nearly synonymous, but *vapor* is more commonly used to describe a gaseous substance not far from the saturated vapor line (and therefore potentially close to the point of condensation).

An Ideal Gas is an idealized (imaginary) gas that obeys the relationship

$PV = nR_uT$ (Ideal gas relation, equation, or "law")

where

P = Pa

$V = m^3$

n = Number of moles

R_u = universal gas constant (aka ideal gas constant, see below)

T = Kelvin

This is a relationship first stated by Émile Clapeyron in 1834[95] as a combination of

Boyle's law:	$P_1/P_2 = V_1/V_2$	at constant T
Charles's law:	$T_1/T_2 = V_1/V_2$	at constant P
Avogadro's Law:	$V \propto n$	at constant P

R_u in SI is

$R_u = 8.3144598(48)\ \text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ [these are units of PV/nT]

$R_u = 8.3144598(48)\ \text{kPa m}^3\ \text{K}^{-1}\ \text{kmol}^{-1}$

$R_u = 8.3144598(48)\ \text{J K}^{-1}\ \text{mol}^{-1}$

Avogadro's number or **constant** is a pure number which equals the number of atoms present in exactly 12 grams of pure ^{12}C, or $\sim 6.023 \bullet 10^{23}$ units. It can also be said to be the number of constituent chemical units (usually atoms or molecules) per mole of substance, given more precisely[96] as $6.022140857(74) \times 10^{23}\ \text{mol}^{-1}$.

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[95] https://en.wikipedia.org/wiki/Ideal_gas_law

[96] https://en.wikipedia.org/wiki/Avogadro_constant

Mean molecular mass[97] (or more precisely the **relative atomic mass RAM**[98] or **relative molecular mass**) is a ratio relative to the mass of an atom of ^{12}C. It is therefore g/g or unitless, but may be expressed in "units" of **Daltons** (formerly **atomic mass units** or **amu**). The **mean molecular mass** of natural water is about 18.015 Daltons (relative to ^{12}C = 1, reflecting a small fraction of ^{2}H present). Methane CH_4 has a mean molecular mass of 16.043 Daltons (see table). The relative atomic mass of Cl (also a weighted average) is 35.45 while the mass in Daltons of the most common isotope of Cl is 34.99 (see table).

1 mole (aka **gram-mole**, symbol **mol or gmol**) is the amount of pure substance containing the same number of chemical units as there are atoms in exactly 12 grams of ^{12}C (i.e., **Avogadro's number** of units, shown above). (The older term *gram molecular weight* has been deprecated.) Molar mass has also been given in **kg-moles** or **kmol** (where 1 kmol = the amount of pure substance containing the same number of chemical units as there are atoms in exactly 1 kg of ^{12}C). 1 mole of water molecules has a **molar mass M** of 18.0152 g/mol or 18.0152 kg/kmol. Alternatively stated, the number of molecules in a mole (known as Avogadro's constant) is defined such that the mass of one mole of a substance, expressed in grams, is numerically equal to the **mean molecular mass** of the substance (in Daltons). One mole of CH_4 has a mean molecular mass of 16.043 Daltons.[99]

Precise calculations involve the added complexity of considering the naturally occurring and somewhat variable isotopic mix of elements, such as for H, C, O, Na, etc. (see table). Molecules differing only by differing isotopic content of one or more of the constituent elements are called **isotopologues**.[100] Some of these relationships are summarized in the following table:[101]

Atom or Molecule	**Relative Atomic Mass (Daltons or amu)**	**Exact Monoisotopic Mass (Using Most Abundant Isotope for Each Element, in Daltons or amu)**	**Most Common Stable Isotopes for Elements**
H	1.007941	^{1}H → 1.00783	^{1}H and ^{2}H
C	12.010736	^{12}C → 12.00000 (by definition)	^{12}C and ^{13}C
O	15.999405	^{16}O → 5.99491	^{16}O, ^{17}O, and ^{18}O
Na	22.989769	^{23}Na → 22.98977	^{23}Na
Cl	35.452938	^{35}Cl → 34.96885	^{35}Cl and ^{37}Cl
CH_4	16.042499	^{1}H, ^{12}C → 16.03130	
H_2O	18.015286	^{1}H, ^{16}O → 18.01056	
NaCl	58.442707	^{23}Na, ^{35}Cl → 57.95862	
R-134a **CH_2FCF_3**	102.030966	^{1}H, ^{12}C, ^{19}F → 102.00926	

When properties are expressed per unit mole, their symbols are shown with a bar on top: $\bar{v}, \bar{u}, \bar{h}$ with units such as m^3/kmol, J/mol, etc.

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[97] https://en.wikipedia.org/wiki/Molecular_mass

[98] https://en.wikipedia.org/wiki/Relative_atomic_mass

[99] https://en.wikipedia.org/wiki/Molecular_mass

[100] https://en.wikipedia.org/wiki/Mass_%28mass_spectrometry%29

[101] http://www.chemcalc.org/ Statistically weighted molecular mass MW vs. exact (monoisotopic) mass EM

Ideal Gas Relation

The ideal gas relation $PV = nR_uT$ may also be expressed for a particular pure substance as

$$Pv = RT$$

where v = specific volume
R (gas constant for the particular gas) = R_u / M
where M =- molar mass (*molecular weight*)
R_u = universal gas constant

There are several other convenient forms of the ideal-gas equation.

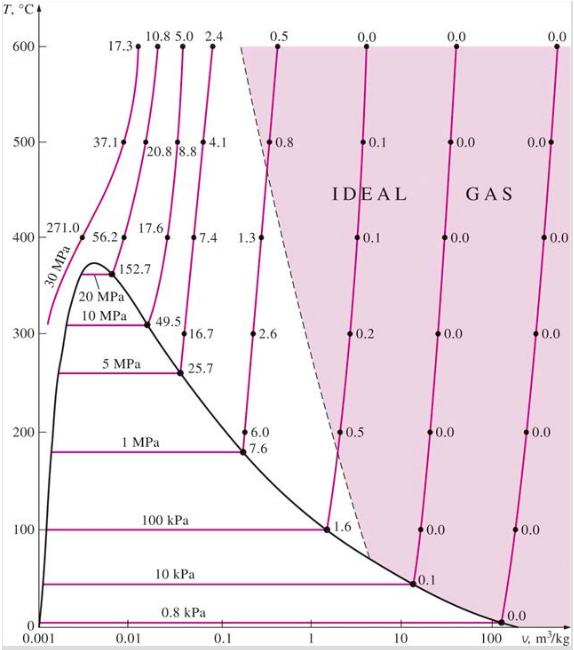
$$PV = mRT \qquad PV = nR_uT \qquad P\bar{v} = R_uT \qquad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where m = mass of gas
$\bar{v}$ = volume per mole

The last form expresses ideal gas states 1 and state 2 for which m is the same.

Deviation from Ideal Gas Relation Behavior

Real gases obey the ideal gas equation closest at low densities and at high temperatures, far to the right of the critical point on the T-v diagram (color region in the following diagram). Dense gases such as water vapor near saturation and refrigerants should not be treated as ideal gases. The deviation from “ideal” for water as superheated steam may be seen in a percentage error diagram derived from the textbook:



Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

Here we may see that the region for superheated water in the color shaded area (well to the right of the critical point and to the right of the saturated vapor line) yields an error of < 1% in the use of the ideal gas equation. In the region close to the critical point, there is a very high error, up to 330%.[102]

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[102] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2b.html and http://www.kostic.niu.edu/350/_350-posted/350LecturePPT-Cengel7th/Chapter_3_lecture.ppt (diagram, modified MCM)

Compressibility Factor Z

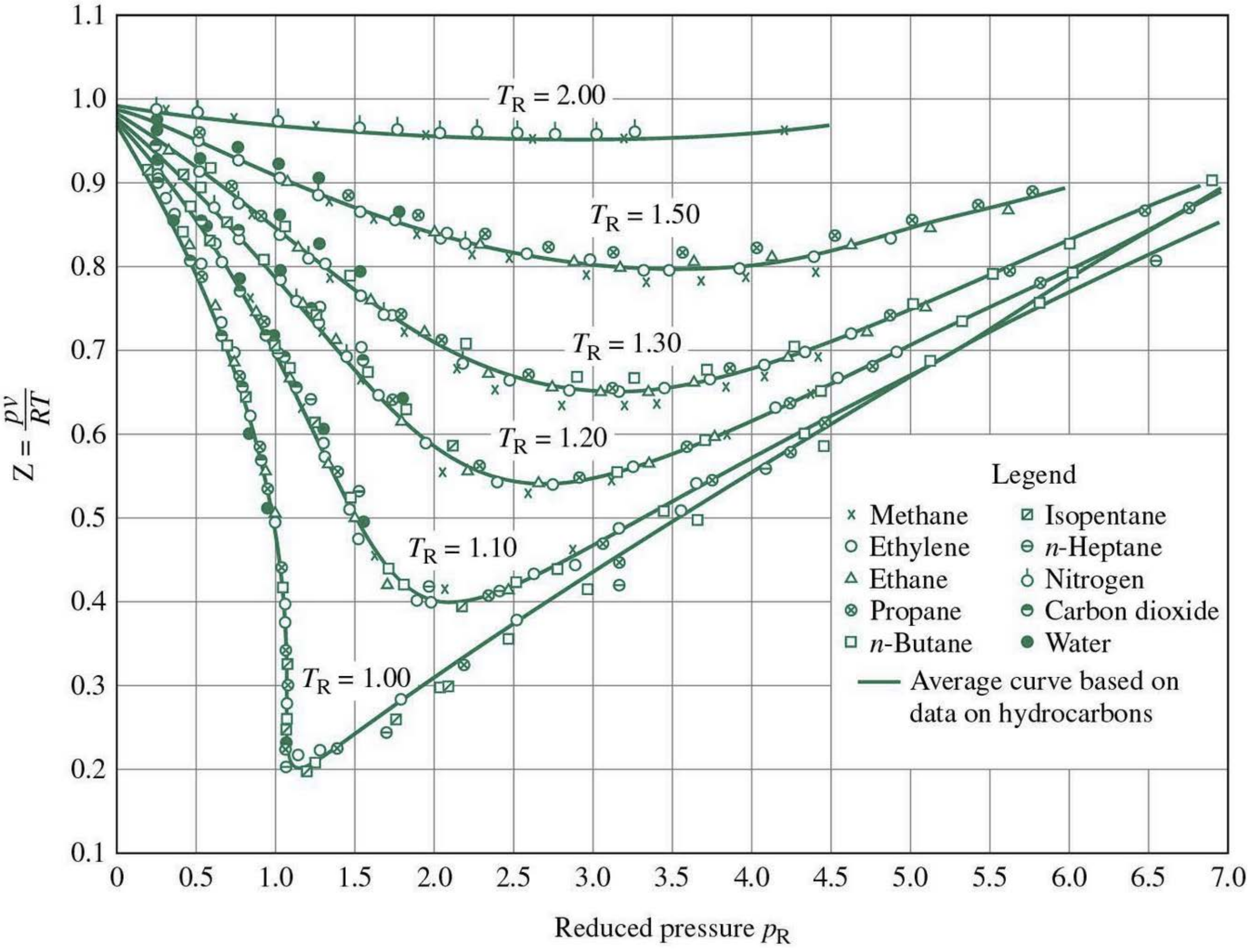
The **compressibility factor Z** , defined as $Pv = ZRT$ or $Z = Pv/RT$ or $Z = v_{actual}/v_{ideal}$, gives a more exact estimate of the deviation from ideal gas behavior. Although the curves would be different for each gas molecular species, the use of **Reduced Pressure** $P_R = P/P_{cr}$ and **Reduced Temperature** $T_R = T/T_{cr}$ provides normalized curves which closely approximate the true empirically determined Z for a variety of gases (see first diagram).[103] Exact correspondence to the ideal gas law corresponds to a horizontal line with Z = 1 in the graphs below. As T_R and P_R approach 1 (T nears T_{cr}, P nears P_{cr}, the value of Z is smallest in order to correct for the greatest error. These diagrams demonstrate that,[104]

(1) At very low P ($P_R \ll 1$), gases behave close to ideal regardless of T.

(2) At high T ($T_R > 2$), gases behave close to ideal regardless of P (unless $P_R \gg 1$)

(3) At high P_R = 10 to 40, gases have $Z > 1$, and Z is larger for T_R values closer to 1[105]

(4) The greatest deviation from ideal is in the region of the critical point,
where $P_R = T_R = 1$.



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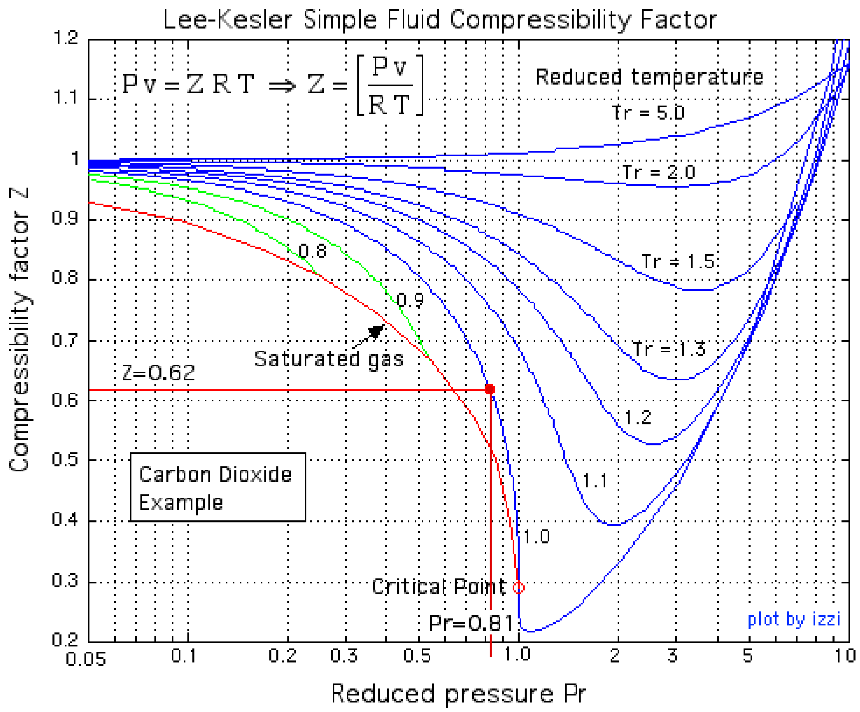
[103] http://www.mae.wvu.edu/~smirnov/mae320/figs/F3-12.jpg

[104] *TAEA7* p. 137-9

[105] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2b.html and expanded Nelson-Obert Generalized Compressibility Chart extending to P_R = 40 as shown in http://entropy.sdsu.edu/testhome/Test/solve/basics/tables/tablesRG/zNO.html



Other Equations of State EOS (3-8)

There are other empirical formulas which attempt to better model the PvT relationship. Of these, the **van der Waals EOS** is the simplest and a favorite of students:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where a/v^2 attempts to adjust for the intermolecular forces and b accounts for the volume occupied by gas molecules.[106] Some empirical values of these coefficients are given here.[107]

The **Beattie-Bridgeman EOS** has 5 experimentally determined constants and gives reasonable values for $\rho < 0.8\ \rho_{cr}$. Other more complex empiric formulas such as the **Virial EOS** [having many terms] and the **Benedict–Webb–Rubin EOS** [having 8 constants], are best reserved for computer implementations.

Vapor Pressure, Evaporation, Drying

The vapor pressure of water in air is the partial pressure of the water vapor in air, P_v. The sum of the partial pressures of individual gas species in a container yields the resultant actual pressure P. For each species, the partial pressure is proportional to the number of moles. When air is saturated with water (relative humidity $\varphi = 100\%$, where otherwise $0 \le \varphi \le 100\%$), the vapor pressure P_v of water is the saturation pressure of water P_{sat} at that temperature. For example, at 25 °C, the vapor pressure P_v at humidity $\varphi = 100\%$ is P_{sat} of saturated air, thus 3.17 kPa (compared to 1 atm = 101.325 kPa).[108] For dry air at 100 °C and $\varphi = 100\%$, the P_v is 101.42 kPa.[109] Air may be regarded as comprised of dry air with partial pressure P_a plus water vapor with partial pressure = vapor pressure = P_v, so total air $P = P_a + P_v$. Here, $P_v = \varphi P_{sat@T}$ for all φ and T. Humans prefer $40\% < \varphi < 60\%$ for maximal comfort.

Hotter air can obviously hold much more water vapor (thus nasal passages dry out more in cold winters because relatively dry outside air has very low φ when heated up inside). Colder air can hold less of the water

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[106] *TAEA7* p. 141-

[107] http://www2.ucdsb.on.ca/tiss/stretton/database/van_der_waals_constants.html

[108] Table A-4 (for saturated water)

[109] *TAEA7* p. 146

vapor held at higher temperatures, and condensation (fog, dew, other precipitation) may result when air is chilled. Drying of wet clothes proceeds faster if the air has low humidity, because the **diffusion gradient** for water vapor is greater. If φ = 100%, there is no diffusion gradient and the clothes do not dry—the water in the clothes is said to be in **phase equilibrium** with the water vapor in the air. This equilibrium occurs when $P_v = P_{sat@T.}$ With low φ, the diffusion gradient is higher and drying proceeds more rapidly. When $P_v < P_{sat@T}$, phase equilibrium has not been attained, and net water evaporation will continue to occur at the liquid-gas interface. Water wants to achieve phase equilibrium by evaporating until $P_v = P_{sat@T}$.

Comment: Don't confuse mixtures of pure substance liquid & vapor states (such as pure water as liquid and/or steam) with liquid/vapor states of water in air. The latter is no longer a pure substance because the liquid and vapor phases do not have identical compositions and behave differently.

Energy Analysis of Closed Systems (Having No Mass Transfer) (4)

(from text Chapter 4 & other sources)

Moving Boundary Work (4-1)

Here we consider closed systems which have constant mass in the system during a process or processes. The boundary may move however, and **moving boundary work** can be performed at the moving boundary, either by (W_{out}) or on (W_{in}) the system. This work is quantitated by integrating P dV or P dv (dV or dv is the volume differential). One familiar example is the expansion of the combustion chamber which causes the piston to move in the internal combustion engine (see later discussion).

An expanding gas does boundary work, which transfers work energy between the system and its surroundings. For quasi-equilibrium changes, $\delta W_b = F\,ds = P\,A\,ds = P\,dV$ (where dV is a volume differential, A = piston cross-sectional area, and P to be precise is absolute pressure at the inner surface of the piston). The **inexact differential δW_b**, as previously noted, is used in general because this quantity may be path dependent and is not determined only by the starting and ending state. However, with gas expansion and contraction (probably for any gas), the boundary work is given by an exact integral:

$$W_b = \int_1^2 \delta W = \int_1^2 P\,dV = W_{12}.$$

Thus the work is given by the integral "process area" under the P V curve (in units of $Pa\ m^3 = N\ m^{-2}\ m^3 = N\ m = J$). Boundary $work_{out}$ with gases is positive when the volume is increasing ($dV > 0$, expansion of the system) and negative when the volume is decreasing ($dV < 0$, compression). Such work is often termed "P dV" work. The integral of P dV can be evaluated only if a relationship $P = f(V)$ is known, such as that of an ideal gas. For different functional relationships, such as $P = f_1(V)$, $f_2(V)$, etc., the integral of P dV will vary.

Sometimes, we have discrete values at which P and V are known rather than a $P = f(V)$ relationship, and the integrals can be estimated by interpolation accordingly. **For complete cycles, the path in P V space encloses a P V space "area" (in units of $Pa\ m^3 = J$) which represents the net boundary work performed.**[110] This "area" is the sum of the areas of multiple processes along the path, where work on the system (during compression) is negative, and work by the system (during expansion) is positive. This work will vary with the process paths taken. This "area" is also shown as dA in the textbook, easily confused with piston area A in m^2. For P-v diagrams, the cyclical area enclosed represents the boundary work done per unit mass.

Boundary work in a car engine transfers energy to the surroundings in order to overcome friction ($W_{friction}$) (piston, crankshaft, etc.), to push air out of the way by opposing the atmospheric pressure (W_{atm}), and to turn the crankshaft which ultimately will turn the wheels (W_{crank}). $Work_{out}$ must equal energy received, thus

$$W_b = W_{friction} + W_{atm} + W_{crank} = \int_1^2 (F_{friction} + P_{atm}A + F_{crank})\,ds$$

Isometric Process

Boundary work for which the volume is constant (termed **isometric**, **isochoric**, or **isovolumetric**) has $dV = 0$ and therefore $W_b = 0$. This is represented by a vertical line on the P V or P v diagram.

Isobaric Process

Boundary work for which the pressure is constant (termed **isobaric**) has

$$W_b = \int_1^2 P\,dV = P\int_1^2 dV = P\Delta V = mP\Delta v$$

and this is a horizontal line on the P V or P v diagram.

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[110] *TAEA7* p. 165

Isothermal Process

When a process has constant temperature (termed **isothermal**), we have for ideal gases PV = mRT_0 = C (a constant) and P = C/V. Therefore, the P-V curve is a hyperbola, and the W_b is given by

$$W_b = \int_1^2 P\,dV = C\int_1^2 \frac{dV}{V}dV = C\ln\frac{V_2}{V_1} = P_1V_1\ln\frac{V_2}{V_1} = P_1V_1\ln\frac{P_1}{P_2} \text{ etc. , since } P_1V_1 = P_2V_2.$$

For example, if pressure increases and volume decreases due to compression, work W_b is done on the system and is negative.

W_b can be calculated for an expanding gas due to the combined effects of moving a piston against the force of a spring being compressed as well as against the force of the opposing atmospheric pressure.[111]

Polytropic processes

Polytropic processes are those with properties which are found to satisfy an empirically derived formula of the form

$$P = CV^{-n}$$

where n is a positive integer that may be 1. The boundary work is given by

$$W_b = \int_1^2 P\,dV = C\int_1^2 V^{-n}\,dV = C\frac{V_2{}^{-n+1} - V_1{}^{-n+1}}{-n+1} = \frac{P_2V_2 - P_1V_1}{1-n}$$

where $C = P_1V_1^n = P_2V_2^n$

Energy Balance for Closed Systems (4-2)

Recall the equation discussed earlier for conservation of energy and energy balance (2-23 to 2-39, etc.). As noted, $Q_{net,in}$ is considered positive and $W_{net,out}$ is considered positive. If the calculations show $Q_{net,in}$ to be negative, then this means that $Q_{net,out}$ is actually positive, etc.

For a cycle in a closed system, the 1LTD dictates that

$$Q_{net,in} - W_{net,out} = \Delta U$$

but $\Delta U = 0$ for a cycle, so

$$Q_{net,in} = W_{net,out}$$

Constant Pressure Heating

When providing electric heating work $W_{e,in}$ to a closed system maintained at constant pressure by a piston under gravity, the P V diagram shows a horizontal line from state 1 (on the saturated vapor line) to 2 (superheated steam) since P holds constant as V rises. Here, the energy balance leads to

$$Q - W = U_2 - U_1 = \Delta U$$

$$Q - W_{other} - W_b = U_2 - U_1$$

The boundary work is

$$W_b = P_0(V_2 - V_1)$$

$$Q - W_{other} - P_0(V_2 - V_1) = U_2 - U_1$$

$$Q - W_{other} = P_0V_2 - P_0V_1 + U_2 - U_1$$

---

[111] *TAEA7* p.169

Because $H \equiv U + PV$, the final form is

$$Q - W_{other} = H_2 - H_1 = \Delta H$$

Thus, for isobaric (constant P) closed system quasi-equilibrium processes, the boundary work is included in the enthalpy term ΔH.

Given an amount of electrical energy in $W_{e,in}$, and heat out Q_{out} for constant P, we have

$$W_{e,in} - Q_{out} - W_b = \Delta U = U_2 - U_1$$

or

$$W_{e,in} - Q_{out} = \Delta H = m(h_2 - h_1) \quad \text{(constant P)}$$

Thus we can determine the final specific enthalpy h_2. Knowing h_2 and P, we can find the final temperature T_2 from table A-6 (superheated water). The work exerted on the piston during expansion at constant P is included in the H or h term.

Unrestrained Expansion into an Evacuated Space at Constant T

Here we consider a sample process wherein 5 kg of compressed liquid water at P = 200 kPa is allowed to expand into an evacuated space of the same size (so the overall volume doubles). The process is held at constant T = 25°C. The $\Delta KE = \Delta PE = 0$. There is no energy transfer and no work is done on the surroundings (the system encloses both the water and the evacuated space, so there is no moving boundary work), so $\Delta E = \Delta U$. The final specific volume v_2 is double the starting v_1. Using Table 4 (sat. water) for the given T = 25°C, we find that the water becomes a saturated liquid-vapor mixture for which $v_f < v_2 < v_g$, and we can determine the final P_2 from the same table. The final internal energy can be found:

$$u_1 \approx u_f @ 25°C$$

$$u_2 = u_f + x_2 u_{fg}$$

From this, we may compute the $Q_{in} = \Delta U = m(u_2 - u_1) = 0.25$ kJ of heat transfer into the system.

Specific Heats Defined (4-3)

Specific heat in general is the amount of heat required to raise the temperature of a unit mass by 1 degree. This is process dependent. Two forms are useful in TD:

Specific Heat at Constant Volume c_v

Specific Heat at Constant Pressure c_p

c_p is always greater than c_v because at constant pressure, the system is allowed to expand against a boundary, and the energy for this expansion work must be supplied to the system. They are formally defined:

Specific Heat at Constant Volume $c_v = \left(\frac{\partial u}{\partial T}\right)_v$, i.e., the change in specific internal energy per unit ΔT at constant v

Specific Heat at Constant Pressure $c_p = \left(\frac{\partial h}{\partial T}\right)_p$, i.e., the change in specific enthalpy per unit ΔT at constant p

Units of specific heats are kJ/(kg °C) or equivalently kJ/(kg K).

These relations apply to all processes for any substance. The internal energy and enthalpy can change by any means, not just by heat, so the term *specific energy* might have been more appropriate.

When specified on a molar basis, specific heats are given instead as

$\bar{c}_v$ in (kJ/(kmol °C) or kJ/(kmol K)

$\bar{c}_p$ in (kJ/(kmol °C) or kJ/(kmol K)

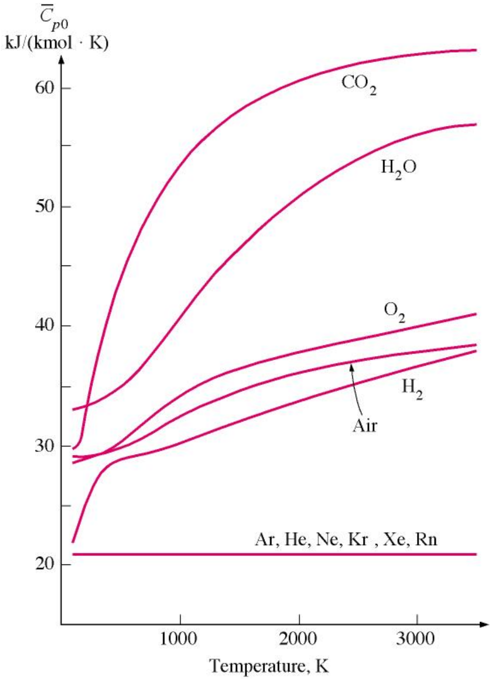
Internal Energy, Enthalpy, and Specific Heats of Ideal Gases (4-4)

Recall Pv = RT for ideal gas, where R is specific for the particular gas.

Specific Internal energy u of an ideal gas is only a function of t, so u = u(T)

Specific enthalpy of an ideal gas is a function also only of T: h = u + Pv =u + RT = u(T) + RT = h(T). Therefore, the specific heats can only depend on T. At a given T, u, h, c_v, and c_p are fixed in value.

Specific heats for ideal gases depend on T, but the function may be complex, and the values are often obtained from a table (A-2b), aided if necessary by interpolation and (for relatively small temperature intervals) by averaging. All gases approach ideal gas behavior at low pressures... Note that monoatomic gas molecules (He, Ar, Ne, Kr, Xe, Rn) have constant and lower molar specific heats compared to molecules of more than one atom , because they lack rotational and vibrational degrees of freedom.



Molar specific heats for ideal gases at low fixed P[112]

Summarizing techniques for determining how internal energy and enthalpy change for ideal gases:

(1) Use tabulated u and h data and

$u_2-u_1 = c_{v,avg} (T_2-T_1)$

$h_2-h_1 = c_{p,avg} (T_2-T_1)$

(2) Integrate c_v and c_p relations as a function of T

(3) Use average specific heats.

The specific heat relations to ideal gases are given by

$c_p = c_v + R$

$\bar{c}_p = \bar{c}_v + R_u$

The **specific heat ratio k** is defined:

$k = c_p / c_v$

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[112] Image from textbook website chapter_04.ppt

It varies with T, and has a value of 1.667 for monoatomic gases but for most diatomic molecules is about 1.4 at room T.

Sample problems omitted.

Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids (4-5)

Solids and liquids are essentially incompressible, specific volumes remain nearly constant during processes. Therefore, the specific heats c_v and c_p are virtually identical for incompressible substances, and they may be said to have a single specific heat c (table A-3).

Internal energy changes for incompressible substances depend on T only. Exact differentials may be used for du. For small T changes, an average T may be used in

$$\Delta \mathrm{u} \cong \mathrm{c}_{\mathrm{avg}}(\mathrm{T}_2 - \mathrm{T}_1)$$

Enthalpy changes for incompressible substances, P dv is nil and

$$\Delta \mathrm{h} = \Delta \mathrm{u} + \mathrm{v}\,\mathrm{dP} + \mathrm{P}\,\mathrm{dv} = \Delta \mathrm{u} + \mathrm{v}\,\Delta \mathrm{P} \;\cong\; \mathrm{c}_{\mathrm{avg}}(\mathrm{T}_2 - \mathrm{T}_1) + \mathrm{v}\,\Delta \mathrm{P}$$

For constant P processes where $\Delta P = 0$, $\Delta \mathrm{h} = \Delta \mathrm{u} \cong \mathrm{c}_{\mathrm{avg}} \Delta \mathrm{T}$

For constant T processes where $\Delta T = 0$, $\Delta \mathrm{h} = \mathrm{v}\Delta \mathrm{P}$

Sample problems omitted.

TD Aspects of Biological Systems

Interesting, familiar, and omitted.

Mass and Energy Analysis of Control Volume Systems With Mass Transfer (5)

(from text Chapter 5 & other sources)

TD problem analysis often focuses on the conservation of mass and of energy during a process, or equivalently, the utilization of mass balance equations and energy balance equations (mass and energy at START and END states, IN and OUT states, INLET and EXIT states, state 1 and 2, etc.)

Conservation of Mass

(5-1)

Mass-Energy Equivalence

Mass and energy are both conserved in everyday circumstances. However, they can be interconvertible as **mass-energy** according to Einstein's Mass–energy equivalence $E=m_0c^2$, but this essentially applies only in certain high energy situations and is not relevant to this course. The m_0c^2 energy in mass is very high. When 1 kg of water is formed chemically from O_2 and H_2, 15.8 MJ of energy per kg of reactants is released by the chemical reaction. This is the amount of $E=m_0c^2$ energy contained in only 1.76×10^{-10} kg of mass (assuming total conversion to energy). Annihilation of matter, with complete conversion to energy (which apparently occurs only with particle-antiparticle collisions) can release more than 10^{10} times the energy released by chemical reactions involving the same mass of particles.

Mass Flow Rate and Volume Flow Rate for Control Volume (CV) Systems

Such systems have a changing amount of mass within a defined boundary (which may be moveable, see 5-5). Often, we refer to a **mass flow rate** $\dot{m}$ (kg/s) flowing into the control volume (CV) through a fixed cross section A_c. The differential mass flow rate $\delta\dot{m}$ is given by

$\delta\dot{m} = \rho\, V_n\, dA_c$ (kg/s) where

$\delta\dot{m}$ is the inexact differential corresponding to the path-dependent mass transfer (kg/s)

dA_c is the cross sectional differential element

V_n is the flow velocity magnitude normal to the cross section element

ρ = density

For a CV system in a pipe with flowing mass, the integrated flow rate across the entire cross section of the pipe is given by

$$\dot{m} = \int_{A_c} \rho V_n \, dA_c$$

Although mass flow rates are usually non-uniform across a cross-section (typically with laminar flow,[113] faster away from wall friction, fastest in the center), an average velocity V_{avg} across the full cross-section often serves adequately:

$$V_{avg} = \frac{1}{A_c}\int_{A_c} V_n \, dA_c \qquad \text{(m/s)}$$

Thus the mass flow rate for averaged velocity and for constant density across a pipe cross-section becomes

$\dot{m} = \rho\, V_{avg}\, A_c = \rho\, V\, A_c$ where V_{avg} is shown as V (average velocity, not volume)

If the fluid is incompressible, ρ can be simplified to the bulk average density.

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[113] https://en.wikipedia.org/wiki/Laminar_flow

The **volume flow rate** of a fluid flowing across a cross-section A_c is given by

$\dot{V} = \int_{A_c} V_n \ dA_c$ where V_n is the normal velocity at element dA_c. (m/s)

(Differing glyphs reduce confusion resulting from the use of the V symbol for velocity V, volume V, and voltage **V**.)

For average flow velocity V_{avg} , the integral yields a volume flow rate $\dot{V} = V_{avg}A_c = VA_c$, where V is the average velocity.

Using this averaged volume flow rate $\dot{V}$, mass flow rate becomes:

$\dot{m} = \rho\ \dot{V}$ = (mass/vol) $\dot{V} = \dot{V}$ / (vol /mass) = $\dot{V} / v$ (kg/s)

Mass balance

Mass is of course conserved in a control volume CV system, so mass balance is expressed by

$m_{in} - m_{out} = \Delta m_{CV}$ and

$\dot{m}_{in} - \dot{m}_{out} = dm_{CV}/dt$

Total mass in CV:

$m_{CV} = \int_{CV} \rho\ dV$ here, dV is the volume differential.

and rate of change of mass within the CV is:

$\dot{m}_{CV} = \frac{d}{dt}\int_{CV} \rho\ dV$

For closed control volume systems, $\dot{m}_{CV} = 0$.

The general conservation of mass requires that the time rate of change of mass in the CV plus the net mass flow rate through the control surface CS surrounding the CV is equal to zero. This leads to one of several ways of expressing the conservation of mass for a CV system (valid for moving or deforming CV boundaries, if necessary allowing for relative velocity of low magnitude and normal to the CS of the CV):

$\frac{dm_{CV}}{dt} = \sum_{in} \dot{m} - \sum_{out} \dot{m}$ (kg/s)

(This formula does not specifically consider the starting value of m_{CV} in the system.)

For **steady flow CV systems**, the mass entering equals the mass exiting the system, so

$m_{CV} = \int_{CV} \rho\ dV = \text{constant}$ and $\frac{dm_{CV}}{dt} = 0$ and $\sum_{in} \dot{m} = \sum_{out} \dot{m}$

where dV is the volume differential.

Many devices operating at a steady flow have only one inlet (subscripted as 1 or in or i) and one outlet (subscripted as 2 or exit or e). These include steady-flow turbines, nozzles, diffusers, compressors, and pumps.

For steady flow of a single stream,

$\dot{m}_1 = \dot{m}_2$ so $\rho_1 V_1 A_1 = \rho_2 V_2 A_2$ (Density x Velocity V x Cross Section Area are same)

For a **steady-flow of an incompressible fluid**, density is constant and using averaged velocities, volume flow rates are given by

$\sum_{in} \dot{V} = \sum_{out} \dot{V}$ (sums of fluid volume rates of flow are the same) and for a **steady-flow of incompressible fluid in a single stream** (one entry, one exit)

$\dot{V}_1 = \dot{V}_2$ (Volume flow rates are the same)

so

$V_1 A_1 = V_2 A_2$ (Velocity V_{avg} x Cross Section Area are the same)

Flow Work and the Energy of a Flowing Fluid

(5-2)

The **flow work** (**flow energy**) is the amount of energy needed to push a fluid into or out of a control volume. We may envision an imaginary piston at the CV inlet with cross sectional area A exerting pressure P on a fluid volume element with volume V having length L and just ready to enter the CV system. The force exerted across the cross section of the inlet is F = PA. If the fluid volume is pushed into the CV through distance L, the flow work performed to do this displacement is

$W_{flow} = F\ L = (P\ A)\ L = P\ (A\ L) = P\ V$ (kJ) (V = Total Volume)

$w_{flow} = P\ v$ (kJ/kg) (v = Specific Volume, w = specific flow work)

Although there is apparently some controversy regarding the status of PV or Pv as work versus energy, the textbook prefers to regard the PV flow quantity as **flow energy**, thus one of the energy components of the flowing fluid CV system.

Total Energy of a Flowing Fluid

On a unit mass basis, the total specific energy e of a simple compressible non-flowing system is the sum of internal energy u, KE, and PE:

$e = u + \frac{V^2}{2} + gz$ (kJ/kg) where V is velocity of ke and z is elevation (z is often constant).

Flowing fluids also have flow energy Pv, so total specific energy θ of a flowing fluid is given by

$\theta = Pv + u + \frac{V^2}{2} + gz = (Pv + u) + \frac{V^2}{2} + gz$ (kJ/kg)

where v is specific volume, V of ke is flow velocity

$\theta = h + \frac{V^2}{2} + gz$ (kJ/kg) where h is specific enthalpy = Pv + u (V in ke is velocity)

Enthalpy in TD was introduced in part because of the simplification in evaluating flowing fluids: if h is used, it is no longer necessary to consider flow energy or flow work of the system. The θ term (h + ke + pe) is also called **methalpy** (a rarely used term).[114]

Energy Transport by Mass

Under the assumption that the properties of mass are uniform, total energy E_{mass} of a flowing fluid of mass m is $E_{mass} = m\theta$. For a uniform single stream, the total energy transported by mass m and the energy flow (transport) rate carried by $\dot{m}$ are given by

$E_{mass} = m\theta = m(h + \frac{V^2}{2} + gz)$ (kJ) (V of ke is Velocity)

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[114] http://www.sfu.ca/~mbahrami/ENSC%2520388/Notes/First%2520Law%2520of%2520Thermodynamics_Control%2520Volumes.pdf

$$\dot{E}_{mass} = \dot{m}\theta = \dot{m}(h + \frac{V^2}{2} + gz) \qquad (kW) \quad (V \text{ of ke is Velocity})$$

Although these simplified relationships (which assume steady single stream flow) are useful approximations, more complex equations may be needed in cases where mass at inlet or exit or across the cross-section may be changing.

Energy Analysis of Steady-Flow CV Systems

(5-3)

Steady-flow conditions are achieved in many CV systems after startup transients have ceased. In a steady-flow system, the fluid properties may vary from point to point, but by the definition of "steady", the extensive and intensive properties remain constant over time *at any particular point*. Moreover, the boundaries do not change. Therefore, the overall mass flow rates at an opening are constant. (For simplicity, mass flow rate is often assumed to be constant across the cross-section of the opening, see further discussion regarding *uniform* flow below.) The system is also assumed to have heat and work interactions with the surroundings which are not changing with time. The total energy content of the CV system E_{CV} is assumed to be constant. Thus,

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{system}}{dt} = 0 \qquad \text{or} \qquad \dot{E}_{in} = \dot{E}_{out} \qquad (kW)$$

Energy balance for steady-flow systems (considering all forms of energy transfer, including work and heat, and where summations are over all inlets and exits), are given equations as follows:[115] Some of the quantities used are here defined:

$\dot{Q}$ = Rate of heat transfer in/out of CV system across boundary with its surroundings (kJ/s = kW)

$\dot{W}$ = Power (kJ/s = kW)

When the boundary is fixed, boundary work is zero, otherwise it must be accounted for. The work to push mass into or out of the system is included in the enthalpy term (kJ/kg). $\dot{W}$ represents the remaining work done on/by the system by/to the surroundings, such as shaft power or electrical power.

$h_2 - h_1$ = Change of specific enthalpy (kJ/kg)

V_1, V_2 = average fluid velocity magnitudes (m/s)

Δke and Δpe = change in specific ke (m^2/s^2 = J/kg) and in pe (kJ/kg), use units conversions PRN.

For general steady-flow CV systems, the energy balance of heat, work, and energy carried by mass is

(5-36) $$\dot{Q}_{in} + \dot{W}_{in} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right) = \dot{Q}_{out} + \dot{W}_{out} + \sum_{out} \dot{m}(h + \frac{V^2}{2} + gz) \qquad (kW)$$

where V of ke is Velocity

For single streams, and assuming that net heat in is positive and net work out is positive, the energy balance may be rewritten as

(5-38) $$\dot{Q} - \dot{W} = \dot{m}\,[h_2 - h_1 + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)\ ] \qquad \text{Steady-Flow overall energy balance (kW)}$$

where V_n of ke is Velocity

Dividing by $\dot{m}$, and noting that $q = \frac{\dot{Q}}{\dot{m}}$ and $w = \frac{\dot{W}}{\dot{m}}$ where q and w are heat and work flow per unit mass of the working fluid:

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[115] First stated by Gustav Zeuner 1828 – 1907 in 1859

(5-39) $q - w = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$ Steady-Flow energy balance per unit mass (kJ/kg)

where $\mathbb{V}_n$ of ke is Velocity

When Δke and Δpe are negligible and/or ke and pe do not change significantly within a CV system, as with very low velocities and small height differences, the energy balance on per unit mass basis simplifies to:

(5-40) $q - w = h_2 - h_1$ (kJ/kg)

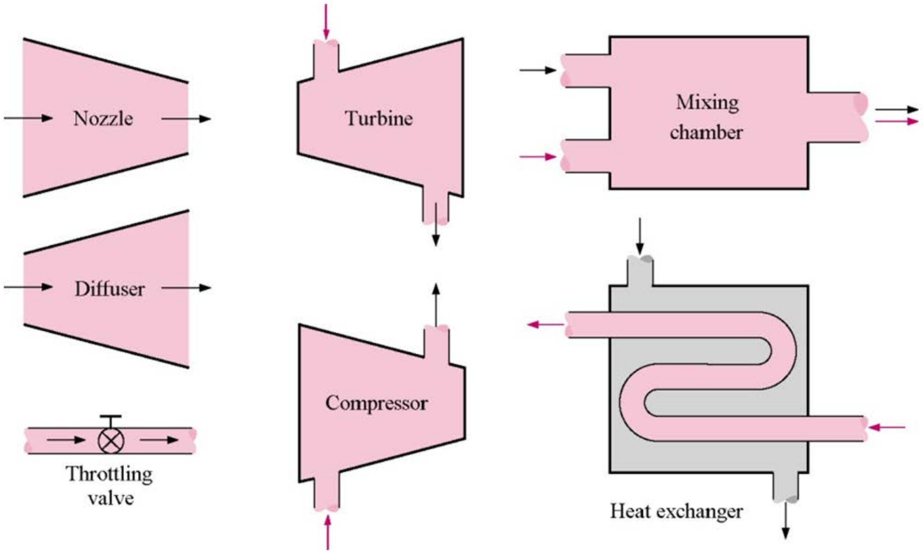
[Exceptions: high velocity streams; pumping fluid to high elevation; hydroelectric plants]

Steady-Flow Engineering Devices: Nozzles, Diffusers, etc.

(5-4)

The focus here is on **steady-flow** devices with no change in properties over extended periods. Startup transients are ignored.

Diagrams from the textbook[116] for common devices are as follows:



Nozzles and Diffusers

(5-4.1)

Subsonic nozzles accelerate or speed up fluid velocity. They have, and are often depicted in diagrams as having, a larger wider inlet region XS-area where P is higher and fluid flow velocity lower, and a smaller narrower outlet region XS-area where P is lower and fluid flow velocity $\mathbb{V}$ is higher.

Subsonic diffusers decelerate or slow fluid velocity. They have, and are often depicted in diagrams as having, a smaller narrower inlet region XS-area where P is lower and fluid flow velocity is higher, and a larger wider outlet XS-area where P is higher and fluid flow velocity $\mathbb{V}$ is lower.

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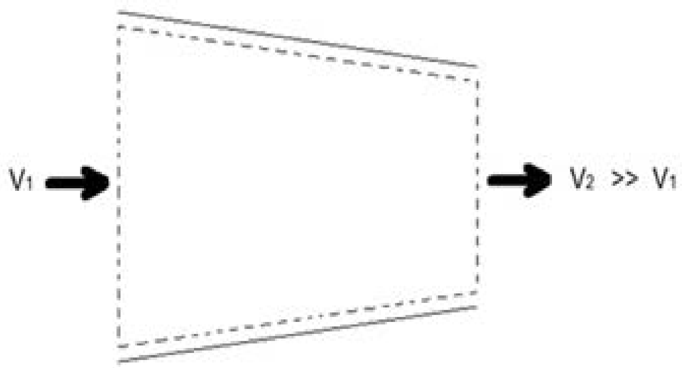
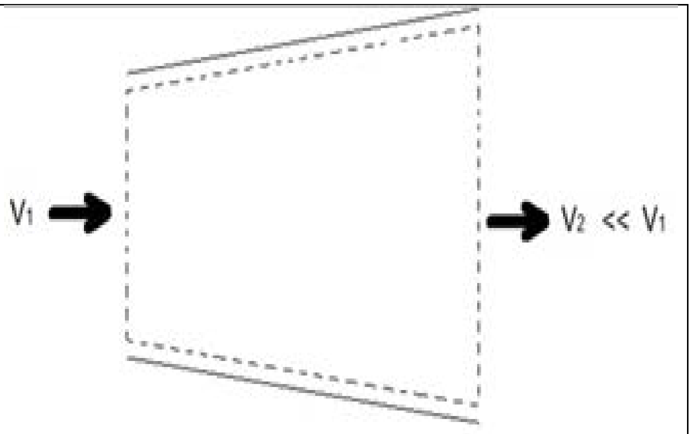
[116] *TAEA7* Chapter 07_1.ppt



Subsonic Nozzle[117]



Diffuser (Subsonic)

For nozzles and diffusers, fluids passing rapidly through these devices typically have at most a very small amount of heat transfer, and pe does not change, nor is any work done. Although nozzles and diffusers may discharge freely to the environment (air), this is often not the case for typical TD situations.

Subsonic Nozzle

A nozzle increases the velocity magnitude ($\mathbb{V}_{exit} \gg \mathbb{V}_{in}$) and increases specific kinetic energy ke ($ke_{exit} > ke_{in}$) of a flowing fluid at the expense of pressure. For **subsonic** flow devices with relatively small velocity changes, such as lawn sprinkler nozzles, they have larger cross-sectional (XS) entry area than XS exit area (i.e., they are **converging**). A purely converging nozzle will not have a supersonic exit velocity.[118]

For subsonic adiabatic flow in a smooth nozzle with convergence and no change in pe or work, analysis is made using the rate form of the energy balance equation:[119]

$$\dot{m}\left(h_1 + \frac{V_1^2}{2}\right) = \dot{Q}_{out} + \dot{m}\left(h_2 + \frac{V_2^2}{2}\right)$$ (kW) ($\mathbb{V}_n$ of ke is velocity)

The mass flow rate $\dot{m}$ is constant from inlet to exit. Temperature decreases mainly because internal energy is converted to ke.

Supersonic nozzle

Supersonic nozzle behavior is discussed in Chapter 17, a topic which we did not study, and I will offer only limited comments. For supersonic nozzles, found in rockets and supersonic jets, the nozzle is typically **converging/diverging** (termed a **de Laval nozzle**) or in some cases is purely **diverging**[120] from the high pressure combustion chamber.[121] It is stated that a purely converging nozzle cannot have a supersonic exhaust exit velocity.[122] Rocket engines attain the following typical nozzle exit velocities:[123]

1.7 to 2.9 km/s for liquid monopropellants (such as hydrazine N_2H_4 or H_2O_2)
2.9 to 4.5 km/s for liquid bipropellants (usually a fuel such as RP-1 or H_2 and oxidizer like O_2)
2.1 to 3.2 km/s for solid propellants

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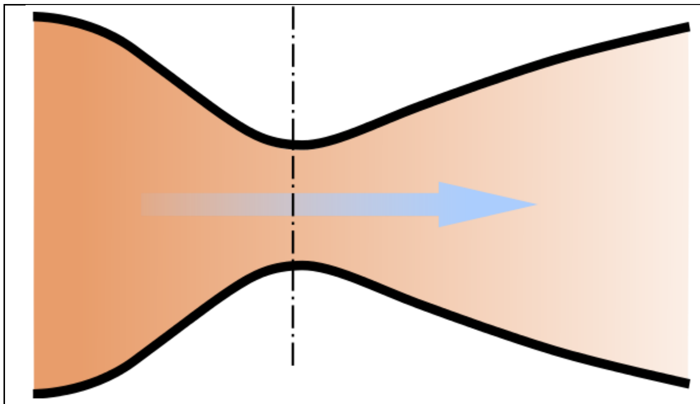
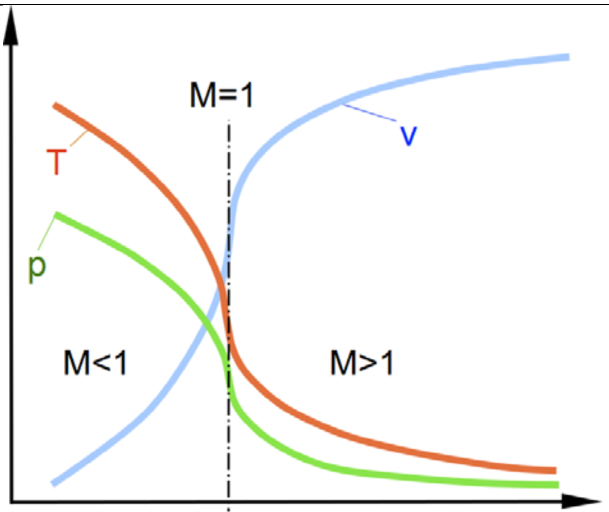
[117] http://engineering-references.sbainvent.com/thermodynamics/nozzle-diffusers.php both diagrams
[118] https://www.grc.nasa.gov/www/k-12/airplane/nozzleh.html
[119] *TAEA7* p. 232
[120] https://wiki.ucl.ac.uk/display/MechEngThermodyn/First+law+applied+to+flow+processes
[121] https://wiki.ucl.ac.uk/display/MechEngThermodyn/First+law+applied+to+flow+processes and http://www.engapplets.vt.edu/fluids/CDnozzle/cdinfo.html
[122] *TAEA7* p. 857
[123] https://en.wikipedia.org/wiki/Rocket_engine_nozzle



de Laval Nozzle Supersonic nozzle[124]



de Laval Nozzle Properties[125]
(Blue = velocity $\mathbb{V}$, Red = Temp, Green = pressure
M = Mach number = 1.0 (“sonic”) at throat minimum

Diffuser

A diffuser is the opposite of a nozzle, decreasing the velocity ($\mathbb{V}_{exit} \ll \mathbb{V}_{in}$) and specific kinetic energy ($ke_{exit} < ke_{in}$) of a fluid while (?unless freely discharging to air) increasing the pressure. Subsonic flow diffusers are diverging, with smaller entry cross-sectional XS-area than exit XS-area. For subsonic adiabatic flow in a smooth diffuser with divergence and no change in pe or work, analysis may be made again using the rate form of the energy balance equation:

$$\dot{m}\left(h_1+\frac{\mathbb{V}_1^2}{2}\right)=\dot{Q}_{out}+\dot{m}\left(h_2+\frac{\mathbb{V}_2^2}{2}\right) \qquad \text{(kW)} \quad (\mathbb{V}_n \text{ of ke is velocity})$$

The T rises mainly because ke is converted to internal energy.

Turbines and Compressors

(5-4.2)

These are typically single stream devices. For both types of devices, PE is often unchanged and therefore can be ignored. KE changes may be small relative to enthalpy changes.

Turbines

These convert kinetic or flow energy of a stream of gas of fluid into rotating shaft work (via work done against the blades), for the purpose of providing power output to drive an external generator, vehicle drive wheels, etc. Typical diagrams depict a smaller inlet end where fluid enters typically at higher P, higher T, lower velocity $\mathbb{V}$, and lower specific volume v. At the larger outlet end, the fluid exits at lower P, lower T, higher velocity $\mathbb{V}$, and higher specific volume v.

Heat transfer is often negligible. Although fluid or gas velocities and velocity changes can be high, the KE change is often negligible compared to the change (decrease) in enthalpy.

For single stream steady-state ($\dot{m}$ = constant) adiabatic turbines, and when pe and ke can be ignored:

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[124] https://en.wikipedia.org/wiki/De_Laval_nozzle and
https://en.wikipedia.org/wiki/Rocket_engine_nozzle (both diagram and graphs)

[125] https://en.wikipedia.org/wiki/Rocket_engine_nozzle

The enthalpy decrease may be calculated from input and output P plus input T. In some cases, the gas (typically superheated steam) is converted to a saturated liquid-vapor mixture, so the determination of final enthalpy h_2 requires determining the quality x (ratio of liquid to vapor), i.e., $h_2 = h_1 + xh_{fg}$ as previously discussed. The energy balance becomes:

$$\dot{Q}_{\mathrm{in,net}} - \dot{W}_{\mathrm{out,net}} = \dot{m}\left(h_1 + \frac{V_1^2}{2} + gz_1\right) - \dot{m}\left(h_2 + \frac{V_2^2}{2} + gz_2\right) \qquad \text{(kW)} \quad \text{(}V_n\text{ of ke is velocity)}$$

and when the turbine operates adiabatically,[126]

$$\dot{m}\left(h_1 + \frac{V_1^2}{2} + gz_1\right) = \dot{W}_{\mathrm{out,net}} + \dot{m}\left(h_2 + \frac{V_2^2}{2} + gz_2\right) \qquad \text{(kW)} \quad \text{(}V_n\text{ of ke is velocity)}$$

$$w_{\mathrm{out,net}} = -\left((h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_2)\right) \qquad \text{(kJ/kg)} \quad \text{(}V_n\text{ of ke is velocity)}$$

Compressors, Pumps, and Fans

These utilize power input (typically as shaft work driven by electrical power), and convert this to increased gas or fluid pressure. Typical diagrams for compressors depict a larger inlet region XS-area where fluid enters typically at lower P, lower T, higher velocity V, and higher specific volume v rate. At the larger outlet end, the fluid exits at higher P, higher T, lower velocity V, and lower specific volume v.

By convention, *pumps* usually pump liquids (possibly to high pressures), whereas *compressors* typically compress gases (possibly to high pressures). Heat transfer is often negligible unless there is intentional cooling or intercooling. *Fans* typically operate at ambient pressure in the open, increase air pressure only slightly, and move a relatively large volume of air often at relatively high velocity.

For single stream steady-state devices, and when pe and ke can be ignored, we have as energy balance:[127]

$$\dot{W}_{\mathrm{in}} = \dot{m}q_{\mathrm{out}} + \dot{m}(h_2 - h_1) = \qquad \text{(kW)}$$

$$\text{where } \dot{Q}_{\mathrm{out}}\left(\frac{\mathrm{kJ}}{\mathrm{s}} \text{ or kW}\right) = \dot{m}q_{\mathrm{out}}\left(\frac{\mathrm{kg}}{\mathrm{s}}\frac{\mathrm{kJ}}{\mathrm{kg}} \text{ or } \frac{\mathrm{kJ}}{\mathrm{s}} \text{ or kW}\right)$$

Compression converts electrical and/or mechanical input power to increased enthalpy (u + Pv) and therefore increased T. Compression typically generates heat transfer out (i.e., heat loss), which may substantial, and intentional cooling or intercooling may be necessary). If the fluid compressed behaves as an ideal gas, the enthalpy depends only on the T and can be found in a table (e.g., Table A-17 for air).

Throttling Valves or Devices

(5-4.3)

These are flow-restricting devices that cause a significant pressure drop in the fluid, and usually (but not always) a substantial drop in T. They do no work, so $\dot{w} = 0$. In some cases, the valve presents sufficient exposed surface area that the process is not adiabatic, but many devices are considered adiabatic. The throttling process is irreversible due to entropy increase (see for instance, the T-s diagrams for the throttling process in the Ideal Vapor-Compression Refrigeration Cycle below).

Exit velocities and therefore ke are increased, but it is commonly assumed that the ke change may be ignored, so that the throttling process is **isenthalpic**, therefore

$h_2 \approx h_1$ (kJ/kg)

$u_1 + P_1v_1 \approx u_2 + P_2v_2$ (kJ/kg)

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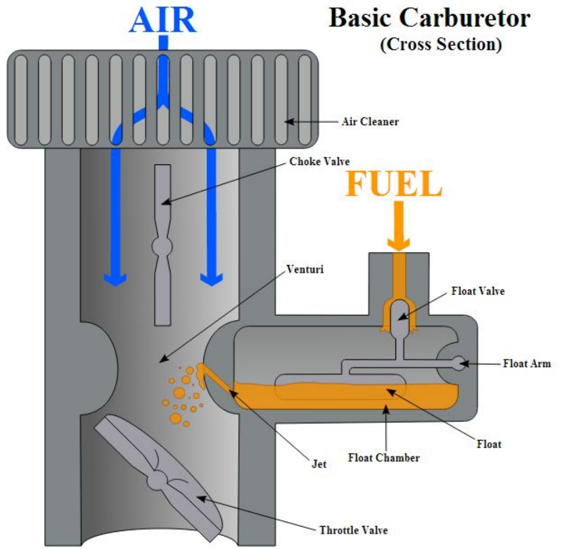
[126] *TAEA7* p. 235

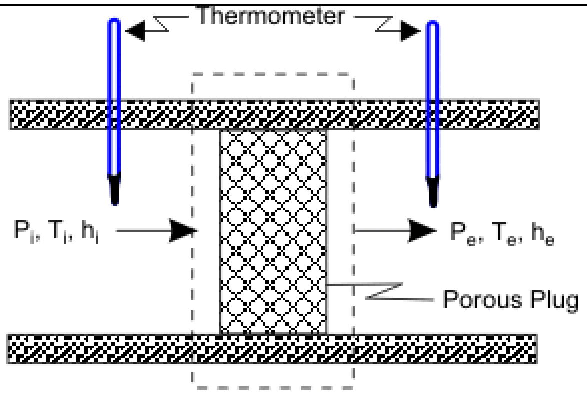
[127] *TAEA7* p. 233

Under these assumptions, if flow energy Pv increases from throttling ($P_2v_2 > P_1v_1$), internal energy decreases and T drops. If flow energy decreases from throttling ($P_2v_2 < P_1v_1$), internal energy increases and T rises (see T-s diagram below). For ideal gases, for which h = h(T), T does not change with throttling. In some systems, such as in vapor compressor refrigeration systems, the drop in T and P at the throttle (expansion valve) is associated with a phase change in the refrigerant—from a liquid to a saturated liquid + vapor mixture —and the energy required to vaporize some of the fluid is absorbed from the refrigerant itself (contributing to its T drop).

Throttles can consist of a simple porous plug,[128] an orifice plate, an adjustable valve or butterfly valve (such as are found in gasoline engine carburetor throttles), an abrupt narrowing, a capillary tube, or any type of flow or pressure control valve.



Gasoline Engine Carburetor with Throttle[129]



Joule and Thomson's (Kelvin's) experimental porous plug throttle

The temperature change with respect to P of **adiabatic isenthalpic throttling** (**Joule-Thomson expansion**) is expressed by the **Joule-Thomson (Kelvin) coefficient**, given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]$$

(Text equations 12-51 & 52, v is specific volume; see also here[130])

Some of the features of the thermodynamics of adiabatic isenthalpic throttling (Joule-Thomson expansion) are depicted in the following T-s diagram for N_2. (Note that in this T-s diagram, the behavior of N_2 is shown in regions for which it is far from an ideal gas and T is not constant.)

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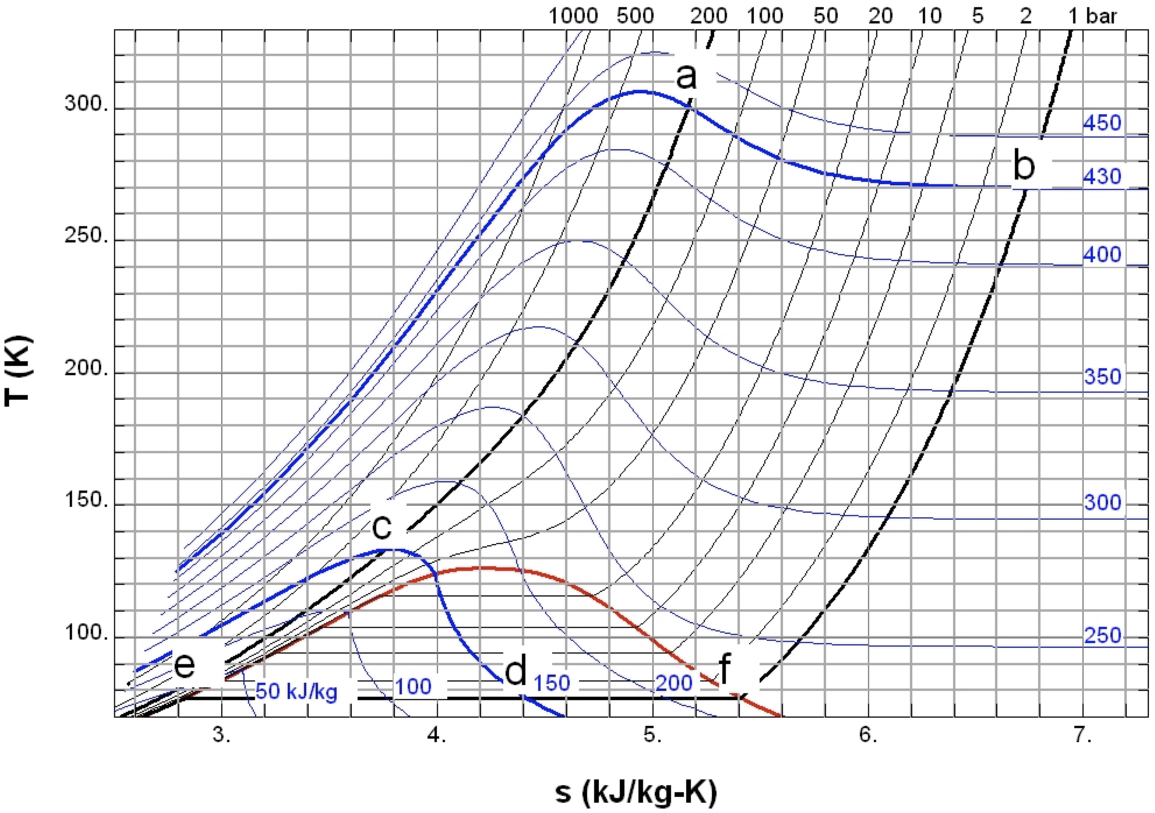
[128] http://www.nptel.ac.in/courses/112104113/14 including diagram of porous plug throttle

[129] http://jalopnik.com/how-a-carburetor-works-496394819

[130] https://en.wikipedia.org/wiki/Joule%E2%80%93Thomson_effect including T-s diagram. The effect is named after James P. Joule 1818-1889 and William Thomson aka Lord Kelvin 1824-1907.



T-s diagram for Isenthalpic Throttling of Nitrogen N_2

The curves that arc upward to the right (on roughly the right half of the diagram) are isobaric curves (constant pressure, expressed in bars). The curves resembling the blue ones (rising to a peak and then falling) are isenthalpic curves (in kJ/kg) along which throttling takes place. (The red curve is the saturation dome for N_2 and is not an isenthalp.) Throttling from state a to b or from state c to d causes P to decrease and T also to decrease—the example from c to d ends in the saturated mixture region. This is the familiar cooling we are accustomed to with throttling. However, throttling on either of the dark blue isenthalps starting and finishing to the left of the peak for this T-s curve will be associated with a fall in P but a rise in T.

How T changes with small increments of P, i.e. $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$, from Joule-Thomson expansion is summarized as follows:

Temperature Increases for $\mu_{JT} < 0$

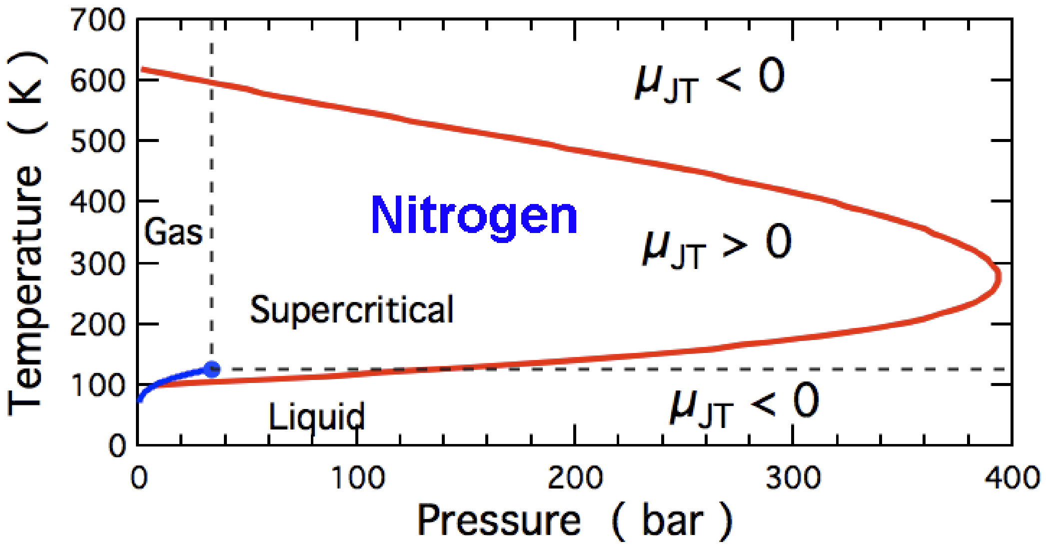
Temperature is Constant for $\mu_{JT} = 0$

(This is true for an ideal gas. Thus, ideal gases neither warm nor cool
upon being expanded at constant enthalpy.)

Temperature Decreases for $\mu_{JT} > 0$

On a T-P diagram (see below), most of the constant enthalpy curves (not depicted in the diagram) attain a peak value where $\mu_{JT} = 0$ at a particular T and P. The locus of these peak h values (the so-called **inversion temperatures**) define an **inversion line** or **inversion curve** which separates the region where $\mu_{JT} > 0$ from the region where $\mu_{JT} < 0$. The point where the upper part of the inversion line intersects the T axis defines a value of T termed the **maximum inversion temperature**—above this temperature no inversion occurs and $\mu_{JT} < 0$.

The following T-P diagram depicts the behavior of Nitrogen N_2 and its inversion line. The red line (inversion line) defines where $\mu_{JT} = 0$ and exhibits a maximum inversion temperature of about 610 K. Within the multi-phasic region to the left and enclosed by the red line, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h > 0$. In this region, a Joule-Thomson expansion (for which P decreases) produces cooling (decreased T). Outside that region (i.e., to the right of the inversion line where $\mu_{JT} < 0$), a Joule-Thomson expansion with decreased P produces heating (increased T).[131]



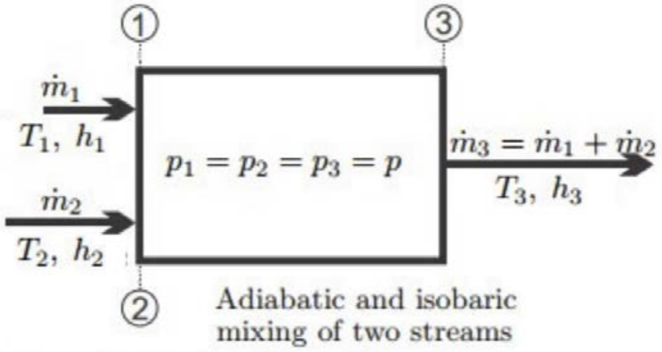
T-P diagram for Nitrogen N_2, showing status of Joule-Thomson (Kelvin) coefficients versus Inversion Line (shown in red). The gas-liquid coexistence curve (blue line), terminates at the critical point (solid blue dot).

Mixing Chambers

(5-4.4a)

These are where two streams of fluids mix. In the most general case, the input streams and the output stream may differ in phase and the mass flow rates might not be steady.

A typical and simpler example would be a T-elbow or Y-elbow mixing chamber where steady flows of cold ① and hot ② liquid water for a shower are mixed to form the final warm mixture ③—the following example proceeds on these all-liquid steady state assumptions.



From conservation of mass, the mass flow rates of the individual input streams are additive in forming the output stream, thus

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 \qquad \text{(kg/s)}$$

The effects of ke and pe are usually negligible, there is no work performed, and we assume no significant heat transfer occurs (the process is assumed to be adiabatic).

Thus,

$$\dot{Q} = 0 \quad \text{and} \quad \dot{W} = 0$$

Assuming also that the two streams and the final stream all have the same pressure (a reasonable assumption needed to prevent backflow), the diagram to the right applies.[132]

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[131] https://en.wikipedia.org/wiki/Joule%E2%80%93Thomson_effect including T-P diagram, image modified MCM

[132] http://machineryequipmentonline.com/hvac-machinery/open-systemsclosed-heat-exchangers-and-open-heat-exchangersadiabatic-mixing/ image slightly modified by MCM

Because we have assumed that all three fluids ① ② and ③ are liquids, we may approximate the enthalpies by $h_1 = h_f$ @ T_1, etc. Energy balance for an adiabatic process with $\dot{w} = 0$ and with no change in pe or ke reduces to the following:

$$\dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3 \qquad (\mathrm{kg/s}) \times (\mathrm{kJ/kg}) = (\mathrm{kW})$$

Dividing by $\dot{m}_3$, we obtain final stream specific enthalpy:

$$h_3 = (\dot{m}_1 h_1 + \dot{m}_2 h_2)/\dot{m}_3 \qquad (\mathrm{kJ/kg})$$

To attain a particular desired T for the mixed fluid, we solve for a suitable proportion y of input streams of hot T_1 and cold T_2:

$$y = \frac{\dot{m}_1}{\dot{m}_2} \quad \text{or} \quad \dot{m}_1 = y\dot{m}_2$$

Dividing the original energy balance equation above by $\dot{m}_2$:

$$yh_1 + h_2 = (y+1)h_3 \qquad \text{since} \qquad y + 1 = \frac{\dot{m}_1}{\dot{m}_2} + 1 = \frac{\dot{m}_1}{\dot{m}_2} + \frac{\dot{m}_2}{\dot{m}_2} = \frac{\dot{m}_3}{\dot{m}_2}$$

Solve for y:

$$y = \frac{h_3 - h_2}{h_1 - h_3}$$

Of course, this process is irreversible and entropy increases from the uncontrolled mixing.

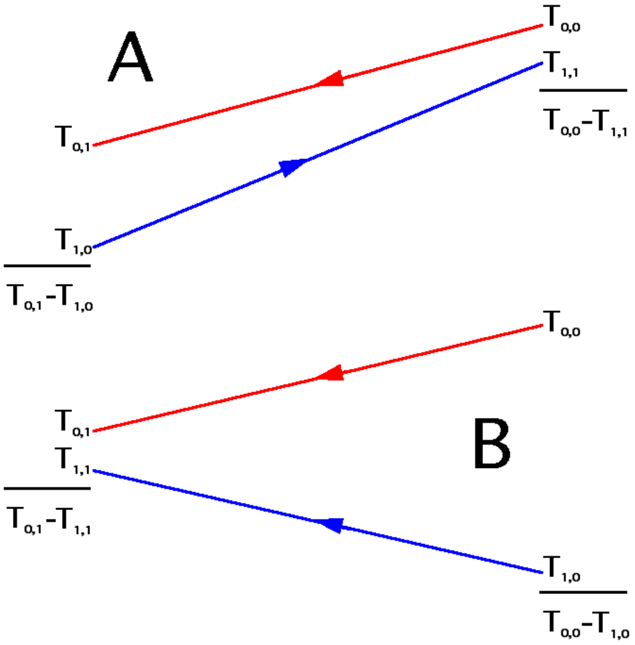
(Note: An example of Adiabatic Mixing of Two Air Streams is discussed in the Gas Mixtures section.)

Heat Exchangers

(5-4.4b) In these devices, two moving fluid streams exchange heat without mixing—this typically occurs within a constant volume. These may be a straight tube within a shell, a coiled tube within a shell, two concentric or annular tubes, etc. We often assume for simplicity that for a control volume consisting of the entire well-insulated exchanger at steady flow, $\dot{Q}_{CV} = 0$ (heat is not exchanged to the surroundings), though of course heat is exchanged between the fluid streams. The mass flow rate of each fluid stream in steady flow conditions is assumed to be constant.

In **Countercurrent heat exchangers**, the direction of fluid flow in one stream is in the opposite direction from that in the other. "The counter-current exchange system can maintain a nearly constant gradient between the two flows over their entire length of contact. With a sufficiently long length and a sufficiently low flow rate this can result in almost all of the [heat being] transferred… "[133]

For example, in the upper image A illustrating temps in a **Countercurrent flow heat exchanger**, the final temperature $T_{1,1}$ of the initially colder fluid is nearly as high as the initial temperature $T_{0,0}$ of the initially warmer fluid. Their temperature difference at the final state of the colder fluid, namely ($T_{0.0}$ - $T_{1,1}$) is fairly small, but most of the heat in the initially warmer tube has been transferred to the initially colder tube, and $T_{0.1}$ may be less than $T_{1,1}$. In contrast, the lower diagram B is for a **Concurrent flow heat**



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[133] https://en.wikipedia.org/wiki/Countercurrent_exchange

exchanger, in which the flow direction is the same in each tube. It can be seen that here that the final temperatures of the two tubes is also close, but $T_{0.1} > T_{1,1}$. If the goal is to transfer the most heat from the warmer to the colder tube, the countercurrent mechanism is more effective.

Countercurrent flow heat exchange occurs in mammalian extremities between the arterial and venous sides, helping to reduce heat losses from the extremity.[134] **Countercurrent flow exchangers** of a variety of types play important biological roles. These are used for example in exchanging solutes such as O_2 by fish, and in concentrating urine waste products in the Loop of Henle of the kidney.

Pipe and Duct Flow

(5-5) These often satisfy steady-flow conditions. Heat transfer can be significant especially for longer pipes, and may be intentional (e.g., for steam pipes in a boiler), or can be minimized with insulation. Within the pipe or duct, a wire may be used to add heating via I^2R electrical work, or pump/fan shaft work may be performed on the stream. KE is rarely significant (except when cross-sections vary or compressibility effects are prominent). PE may vary significantly for long runs with substantial elevation change.

Energy Analysis of Unsteady-Flow (or Transient-Flow) Processes

(5-5)

These involve systems in which changes occur in the control volume: the mass in the system does not remain constant, and/or they have changing (moving) boundaries. Examples include

- filling an expanding reservoir (such as a tire)
- charging up a fixed vessel with pressurized gas using a supply line
- discharging a fluid from a pressurized vessel
- driving a turbine with pressurized gas from a container
- using a pressure cooker.

The processes under consideration here have definite start and end points extending over a time interval Δt. These systems are usually fixed in position (stationary) but if there are moving boundaries, boundary work must be considered.

Some of these unsteady flow processes can be adequately represented by **uniform-flow**, an idealization which assumes that, "the fluid flow at any inlet or exit is uniform and steady, and thus the fluid properties do not change with time or position over the cross section of an inlet or exit. If they do, they are averaged and treated as constants for the entire process [presumably at the inlet or exit]."[135] I am still a bit unclear if this means that the cross-sectionally averaged flow can be expressed by a single average constant velocity throughout the entire system and process and across the entire cross-section of interest.[136] Exact definition and clarification of the assumed conditions will be needed.

Mass balance is as usual given by

(5-42 etc.) $$m_{in} - m_{out} = \Delta m_{system} = (m_{final} - m_{initial})$$

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[134] https://en.wikipedia.org/wiki/Thermoregulation

[135] *TAEA7* p. 244

[136] MCM note: The text is a bit ambiguous. If the unsteady but uniform flow is considered to have a constant average velocity magnitude throughout the process (not just across the cross section), this might seem to be an oversimplification. Other authors state,
(1) "A truly uniform flow is one in which the velocity is [the] same at a given instant at every point in the fluid." http://www.civilengineeringterms.com/fluid-mechanics-1/steady-flow/
(2) "Unsteady uniform flow. At a given instant in time the conditions at every point are the same, but will change with time." http://www.efm.leeds.ac.uk/CIVE/CIVE1400/Section3/dynamics.htm
(3) Unsteady is changing in time. Uniform is not changing in space or position.
http://www.cah.sdu.edu.cn/article/pdf/fluid/Ch4%2520%2520Basics%2520of%2520Fluid%2520Flow%2520.pdf

Energy balance is given by

$$\dot{E}_{in} - \dot{E}_{out} = \Delta E_{system} \qquad \text{(kW)}$$

where the total energy content of the system is changing during the process (due to heat or work transfers, boundary work, mass energy transport, etc.)

$$\text{(5-45)} \quad (Q_{in} + W_{in} + \textstyle\sum_{in} m\theta) - (Q_{out} + W_{out} + \sum_{out} m\theta) = (m_2e_2 - m_1e_1)_{system} \qquad \text{(kJ)}$$

Thus, when changes in KE and PE are negligible, and again assuming Q_{in} and W_{out} are positive,

$$\text{(5-46, mod.)} \quad Q_{net,in} - W_{net,out} = \textstyle\sum_{out} mh - \sum_{in} mh + (m_2u_2 - m_1u_1)_{system} \qquad - \qquad \text{(kJ)}$$

If no mass enters of leaves, $m_{in} = m_{exit} = 0$ and $m_1 = m_2 = m$, this reduced to a closed system.

An interesting example in the text[137] of unsteady uniform flow describes the charging of a rigid evacuated vessel with steam at 300 °C and at 1 MPa from a fixed pressure line fitted with a shutoff valve. Here, the final T of 456 °C in the vessel was surprisingly high compared to that of the entering steam. This arises because the flow energy (flow work) part (Pv) of the enthalpy of line steam ($h_1 = u_1 + Pv = 3051$ kJ/kg) is converted to sensible internal energy ($u_1 = 2794 \rightarrow u_2 = 3051$ kJ/kg) when flow ceases in the vessel, causing an elevation of temperature of its steam.

A More General Energy Equation

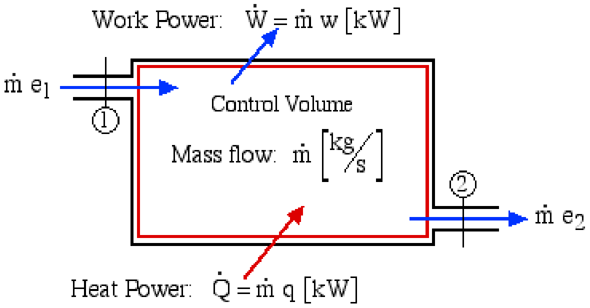
(Chap 5 p. 247)

This section, which I did not master, provides a somewhat more general expression of the 1LTD, conservation of energy for uniform flow CV systems. Other forms of energy are mentioned, such as $W_{viscous}$, and work done by pressure forces is detailed (applying the Reynolds transport theorem). One of the final equations obtained (limited to a control volume with uniform flow at inlets and outlets, and negligible work from viscous and other effects) is:

$$\text{(5-59)} \quad \dot{Q}_{net,in} - \dot{W}_{shaft,net\ out} = \frac{d}{dt}\int_{CV} e\rho\, dV + \textstyle\sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right) - \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right) \qquad \text{(kW)}$$

Here, e is as before the total energy per unit mass for the CV, V = volume, and flow streams enter (in) and leave (out) the control surface.

The following control volume diagram for steady flow conditions illustrates some of these concepts[138]



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[137] *TAEA7* p. 244

[138] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter4a.html (on left) and https://wiki.ucl.ac.uk/display/MechEngThermodyn/First+law+applied+to+flow+processes (on right)

The Second Law of Thermodynamics 2LTD (6)

(from text Chapter 6 & other sources)

The Second Law of Thermodynamics (**2LTD**) is an empirical finding which imposes an additional condition over the 1LTD on what heat energy can be made to do. The 2LTD holds that energy has a *quality* (as well as the *quantity* assessed in the 1LTD).[139] The 2LTD is useful in determining the theoretical limits of how much heat can be converted to work, electricity, or other useful forms of energy. Ultimately it is expressed in terms of entropy (see Entropy chapter summary), but it can also be discussed in certain contexts without specific reference to entropy.

In TD, we must consider the availability of thermal energy (heat) **reservoirs**, specifically thermal energy (heat) **sources** and thermal energy (heat) **sinks**. These are often environmental resources such as rivers, oceans, the atmosphere, etc. They are considered to have very large thermal energy (heat) capacity (typically expressed as mc or mc_p, where c = specific heat), such that adding or removing heat has little effect on the reservoir's temperature.

In actuality, discharging of waste heat from power plants into environmental reservoirs such as rivers can cause heating with definitely detrimental effects and is termed **thermal pollution.** Thermal pollution of environmental reservoirs can be made apparent by infrared remote sensing, as shown in the following images:

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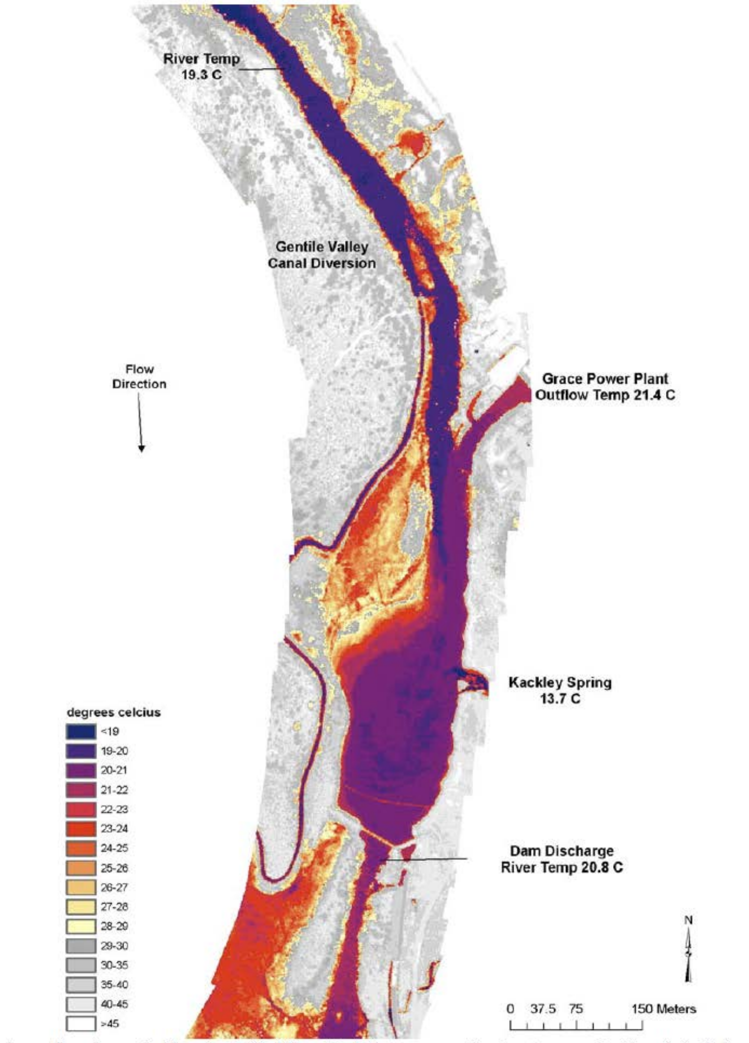
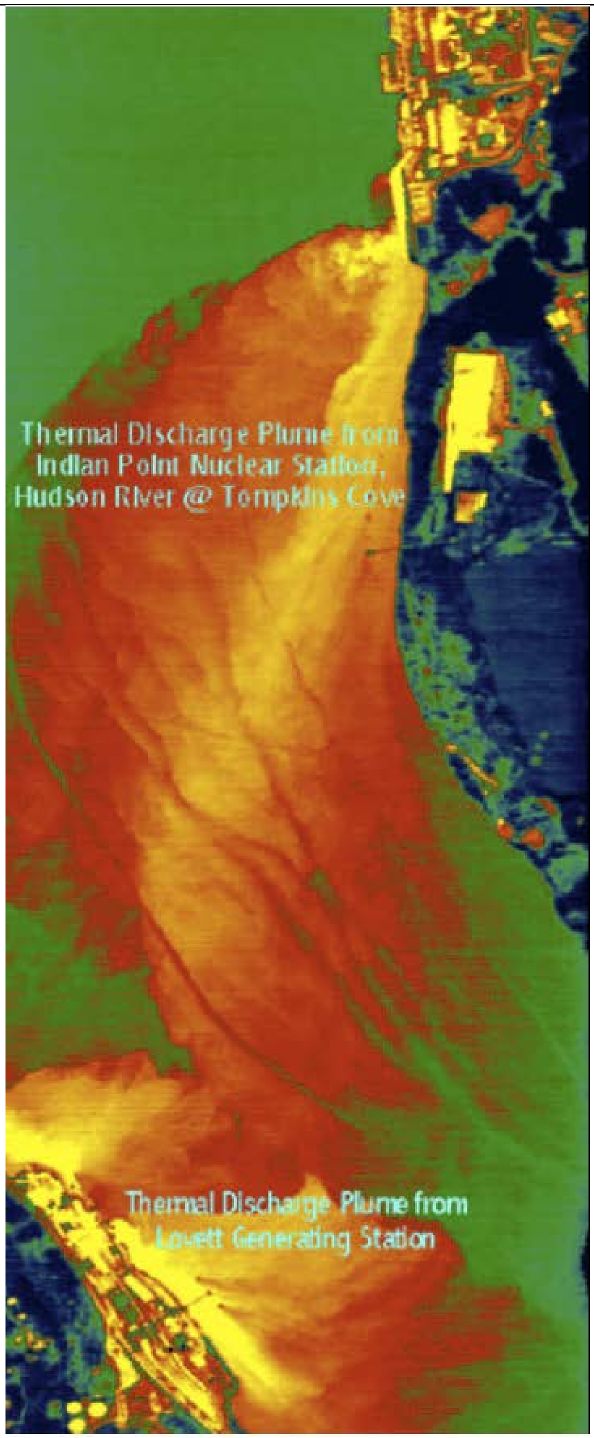
[139] *TAEA7* p. 278



Lower Bear Image 3. Near river mile 100, multiple factors cause the river to warm significantly including a large canal diversion and the Grace Power Plant outflow. Even with a significant cold inflow at Kackley Spring and an impoundment below the power plant, the river warms 1.5°C over a ½-mile distance.

This infrared remote sensing image nicely displays river temperature changes associated with water discharge from a hydroelectric HE plant. Upstream colder Bear River water is on the right, mildly heated river water associated with the Grace hydroelectric HE power plant (in ID) is on the left. This example shows temperature differences but is not necessarily a demonstration of power plant heat pollution, because the HE plant receives its water via penstocks from a distant higher elevation dammed reservoir. The heating may be caused simply by the diversion of water from a warmer distant source reservoir rather than by the actual power generation process.[140]



The extent of the thermal plume from the cooling water discharge of Indian Point Unit 3, and the Lovett generating station.

Hudson River (NY) thermal pollution from nuclear and coal fired power plants (T color scale not available)[141]

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[140] http://www.pacificorp.com/content/dam/pacificorp/doc/Energy_Sources/Hydro/Hydro_Licensing/Bear_River/Bear_River_Thermal_Imaging_Report.pdf

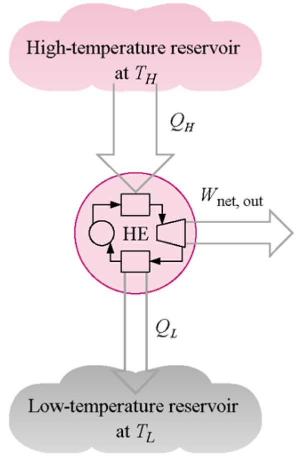
[141] https://www.riverkeeper.org/wp-content/uploads/2010/03/1397-PH-Henderson-Attachment-3-Expert-Report-Cont-EC-1.pdf
this image minimally modified by MCM

Heat Engines Versus Refrigeration Systems

Heat engines are physical devices that utilize a cyclical process to convert transfers of heat (thermal energy) into mechanical energy or work. (In contrast, refrigerators and heat pumps are like cyclical heat engines that run in reverse, thus converting work into heat transfers.)

Characteristics of an ideal Heat Engine include the following:

- A **pump** is usually present to pump the **working fluid** into the **boiler** (or similar).
- The heat engine working fluid receives heat (**Q_{in}** or **Q_H**) in the boiler from a relatively high temperature heat source (at temperature **T_H**)
- Part of this thermal energy Q_{in} is converted to net work out **$W_{net,out}$**, often in the form of rotation of a shaft that does external work. The amount of work **W_{in}** to operate the pump reduces **$W_{net,out}$** (modestly for pumped liquid, more so for compression of a gas).
- The unused remainder of **Q_{in}** is rejected as **waste heat** (**Q_{out}** or **Q_L**) to a lower temperature sink or reservoir (at temperature **T_L**).
- The engine operates in a **cycle**, so that the final state is the same as the starting state (but see exceptions below).



$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

Diagram of a Heat Engine
and Its Thermal Efficiency[142]

Energy is conserved per 1LTD, so that (simplified and ignoring various losses[143])

$$W_{net,out} = W_{out} - W_{in} = Q_{in} - Q_{out}$$

(where all quantities are shown as positive magnitudes, and W_{in} is the work for the pump to pump or compress the working fluid).[144]

The textbook expands the definition of heat engine to also include other work-producing devices such as the internal combustion engines, noting that these operate in a mechanical cycle but not in a TD cycle (because the working fluid is discharged as exhaust along with the waste heat, and does not return to its initial state). The textbook does not use *heat engine* to describe refrigerators or heat pumps per se. However, it does refer to refrigerator cycles and heat pumps as like heat engines operated *in reverse* (i.e., they take work and convert it to heat transfers).[145] It seems to me that the term should be reserved for devices which convert heat to work.

Comparison of Heat Engine, Refrigerator/Air-Conditioning/HP-Cooling-Mode, and HP-Heating-Mode Cycles	
Heat engine	Boiler/Steam Gen. (Q_{in}) → Turbine (W_{out}) → Condenser (Q_{out}) → Feedwater Pump (W_{in})
Refrigerator or Heat Pump in Cooling Mode (Air Conditioner)	Compressor (W_{in}) → Condenser ($Q_{H,out\ rejected}$ at T_H) → Expansion (Throttle) → Evaporator ($Q_{L,in\ from\ cooled\ space}$ at T_L).
Heat Pump in Heating Mode	Compressor (W_{in}) → Condenser ($Q_{H\ to\ room}$ at T_H) → Expansion (Throttle) → Evaporator ($Q_{L\ in\ from\ outside}$ at T_L).

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[142] Image from textbook website chapter_06.ppt

[143] https://www.researchgate.net/publication/227421394_Energy_and_Exergy_Analysis_of_Thermal_Power_Plants_A_Review

[144] The term *working fluid* applies to a gas, a liquid, a mixture of saturated liquid and vapor, or even a supercritical fluid.

[145] *Heat Engine*: The term is used more loosely by others. For instance, Wikipedia lists a variety of heat engines, and includes the Earth itself, heat pumps, and refrigerators (which are again said to be heat engines operated in reverse). https://en.wikipedia.org/wiki/Heat_engine

For heat engines, Q_{out} is never zero, and the amount of Q_H that produces work is less than 100%.

The thermal efficiency η_{th} of a heat engine is defined as

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_L}{Q_H}$$

The character is η is Greek eta, thus transliterated starts with the same letter E as *efficiency*.

Ideal and real thermal efficiencies η_{th} are always less than 1 and can be, in real applications, 25% for automobile spark-ignition internal combustion engines, 40% for diesel internal combustion engines and large gas-turbine plants, and more than 60% for large combined cycle gas and steam turbine power plants (CCGT plants), which use more than one TD cycle, see diagram lower right in the table below of 4 diagrams].[146]

Heat engines are further discussed in Chap 9 Gas Power Cycles summary and Chap 10 Vapor and Combined Power Cycles summaries, but some aspects are included to follow.

External Combustion Steam Power Plant (a Heat Engine)

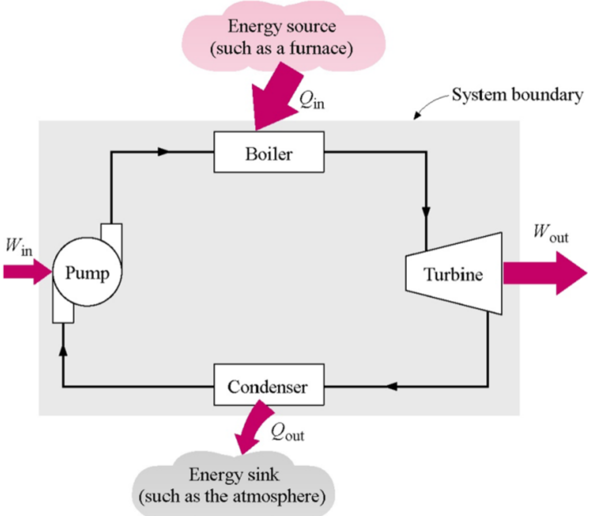

Diagram of a Steam Power Plant (a Heat Engine) [147]

One of the classic heat engines is the **external combustion steam power plant** (depicted above). The cycle consists of:

Boiler/Steam Gen. (Q_{in}) → Turbine (W_{out}) →

Condenser (Q_{out}) → Feedwater Pump (W_{in})

A diagram of a steam power plant is shown below, using water as the working fluid (in liquid, saturated mixture, vapor, or supercritical fluid phases) and rate symbols for steady-state operation. On the top left is a general diagram; the top right is a practical design for a coal-fired supercritical steam power plant at Athens, Ohio.[148] The former's cycle, as depicted in its Pressure - Enthalpy P-h diagram (bottom left), is as follows:

- The rate of heat input in the **Boiler** or **Steam Generator** (heat derived from fossil fuel combustion, nuclear fission, solar thermal heating, etc.) is shown as $\dot{Q}_{boiler/steam} = \dot{Q}_{in}$
- The working fluid (as high pressure steam ①) turns a **Turbine** converting some of the input heat to

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[146] https://en.wikipedia.org/wiki/Combined_cycle and https://powergen.gepower.com/resources/knowledge-base/combined-cycle-power-plant-how-it-works.html

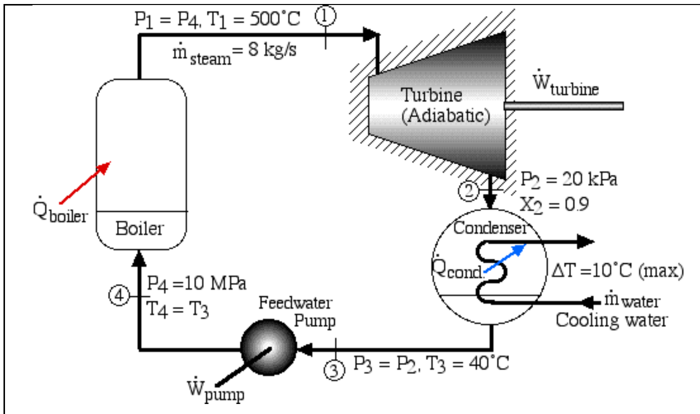
[147] Image from textbook website chapter_06.ppt

[148] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter4b.html images and quoted text

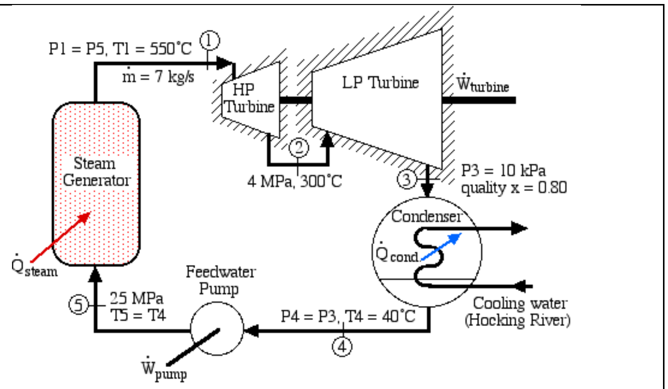
useful work $\dot{W}_{turbine} = \dot{W}_{out}$ in the form of mechanical shaft power. In the process, the pressure of the steam falls and it becomes a saturated mixture ②.

- The saturated mixture is then cooled to compressed liquid water ③ in the **Condenser**
- The **Feedwater pump** uses a relatively small amount of input work $\dot{W}_{pump}=\dot{W}_{in}$ to pressurize and return the working fluid (liquid water) to the starting point (④ in the upper left diagram) before the fluid enters the boiler/steam generator.

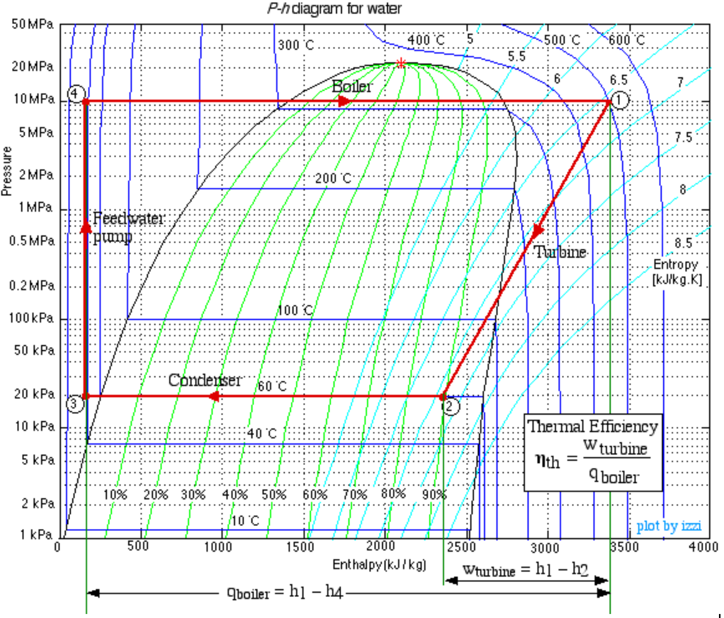
The cycle by which the upper left power plant operates is depicted in the lower left P-h diagram. Its author states, "Notice from the P-h diagram plot how we can get an instant visual appreciation of the system performance, in particular the thermal efficiency of the system by comparing the enthalpy difference of the turbine (1)-(2) to that of the boiler (4)-(1). We also notice that the power required by the feedwater pump (3)-(4) is negligible compared to any other component in the system."



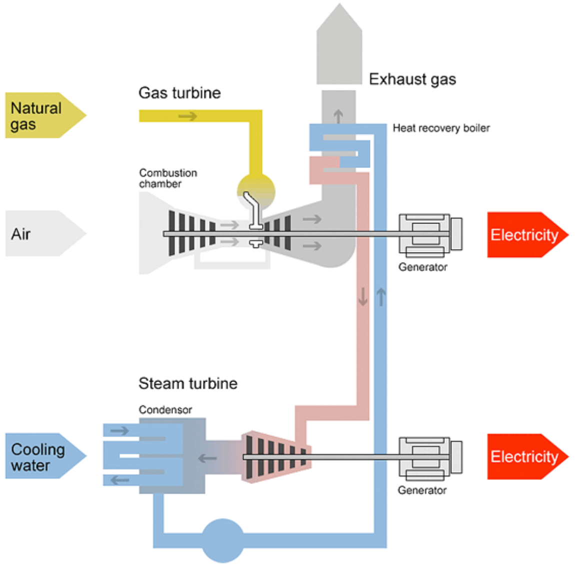
General simplified design of a steam power plant (non-supercritical)



Simplified design of a supercritical steam power plant, in which peak P and T are above the critical point (and omitting reheating in the turbine, feedwater heating, various losses)



P-h diagram for the basic steam power plant (top left above)



Combined Cycle Gas Turbine (CCGT) Plant pairing a gas internal combution turbine with a steam turbine operated by its exhaust[149]

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[149] http://www.eon.com/en/business-areas/power-generation/natural-gas-and-oil/combined-cycle-gas-turbine-how-it-works.html

Refrigeration Systems and Air-Conditioning

Summary of **vapor compression refrigeration cycle**:

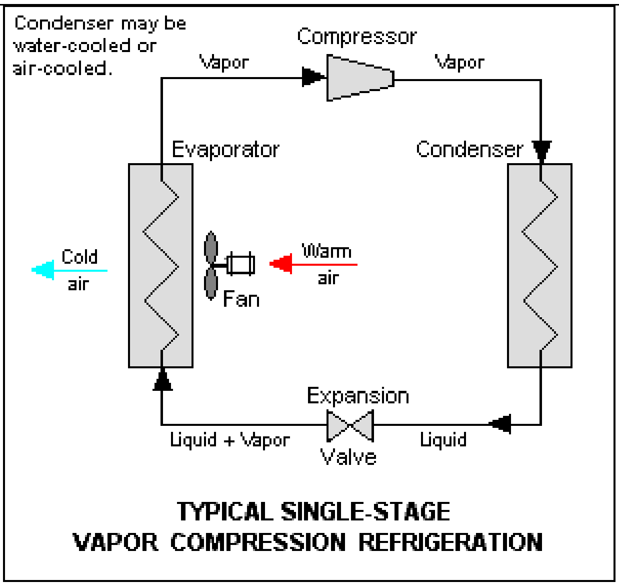
Compressor	(W_{in})
Condenser	($Q_{H,out}$)
Expansion	(Throttle)
Evaporator	($Q_{L,in}$)

These topics are more extensively covered in summaries of Chapter 11 and 13.

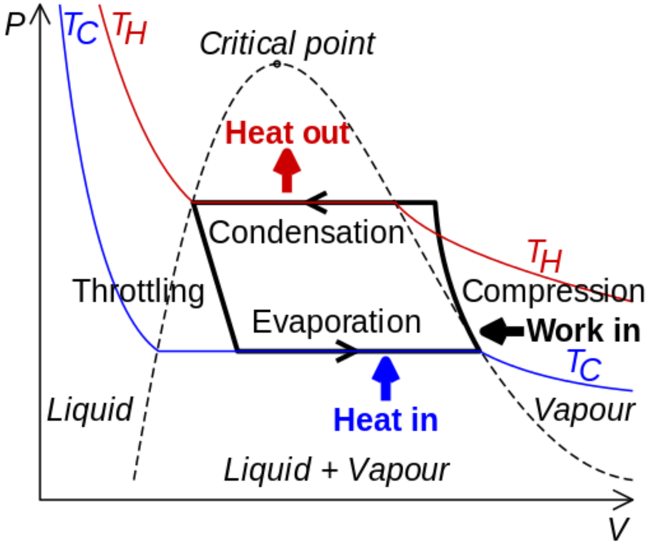
"An **air conditioner** requires work to cool a living space, moving heat from the cooler interior (the heat source) to the warmer outdoors (the heat sink). Similarly, a **refrigerator** moves heat from inside the cold icebox (the heat source) to the warmer room-temperature air of the kitchen (the heat sink). The operating principle of the refrigeration cycle was described mathematically by Sadi Carnot in 1824… The **vapor-compression cycle** is used in most household refrigerators as well as in many large commercial and industrial refrigeration systems."[150] The following left image is a schematic diagram of the components of a typical vapor-compression refrigeration system". The right image is a P-V [probably P-v] diagram for same. This refrigeration cycle is further discussed in the Chap. 11 summary.

Household refrigerators have improved much in **efficiency** in recent decades, due to more efficient motors and compressors, better insulation (urethane foam expanded in place) and seals, and larger coil surface areas, even though the basic vapor-compression cycle (with typical COP_R = 1.3) is unchanged.

Refrigerators maintain the **freezer** typically at -18 °C (0 °F) and the **main compartment** at 3 °C (37.4 °F). Special refrigerator sections are used to keep (1) leafy vegetables and fresh fruits moist to prevent drying, (2) eggs from drying, (3) butter warmer and isolated from odors, and (4) meat compartment maintained at -0.5 °C (31.1 °F), etc. Refrigerators consume 90 to 600 W but run only 30% of the time on the average. For minimizing power consumption, open doors as seldom as possible and for the shortest time possible, cool down hot foods before placing in the frig (but stay within food/bacteria safety limits), clean condenser coils and don't block air flow to them, check door gasket for leaks, avoid unnecessarily low temperature settings, avoid excessive ice buildup, and turn off heating coils w power-saver switch (these heaters are used to reduce condensation on outside surfaces in humid environments).



Components of a typical vapor-compression refrigeration system



Idealized Pressure-volume P-v diagram for a typical refrigeration cycle

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[150] https://en.wikipedia.org/wiki/Vapor-compression_refrigeration quoted text & both images

Environmental concerns: **Refrigerants** pose environmental concerns because they destroy the stratospheric ozone layer that absorbs UV light, and some are also greenhouse gases. Refrigerants, listed in order from the highest to the lowest potential of ozone depletion, include Bromochlorofluorocarbons, CFCs, then HCFCs. "Though HFCs [Hydrofluorocarbons] and PFCs [Perfluorocarbons] are non-ozone depleting, many have global warming potentials that are thousands of times greater than CO_2. Some other refrigerants such as propane and ammonia are not inert, and are flammable or toxic if released. New refrigerants were developed in the early 21st century that are safer for the environment, but their application has been held up due to concerns over [local] toxicity and flammability.[151] Refrigerants are discussed in greater detail in the Chapter 11 summary.

Heat Pump Systems

Summary of heating mode HP cycle:

Compressor (W_{in})
Condenser ($Q_{H\text{ to room}}$)
Expansion (Throttle)
Evaporator ($Q_{L\text{ from outside}}$)

See Chapter 11 summary for further details.

These are energy-efficient devices which are not heat engines (i.e., they do not convert thermal energy to work, though they resemble a heat engine run in reverse). They use electrical energy/work ($W_{net,in}$) to pump heat from T_L to T_H. When the goal is to release Q_H into a heated interior space, the heat pump is operating in **Heating Mode** (and the device is often termed a **Heat Pump**). When the goal is to release Q_H to the outside, drawing heat Q_L from a chilled inhabited room or refrigerator box, it is operating as a Heat Pump in **Cooling Mode** or as a **Refrigerator** or **Air Conditioner**.[152]

For a **Heat Pump operated in heating mode**, "high pressure HP vapor refrigerant is sent [from the compressor] to the indoor heat exchanger coil [serving as the condenser]. The refrigerant [vapor] gives up its energy [enthalpy of vaporization] to the inside air [heating it] and condenses to a [high pressure HP] liquid. The liquid is throttled to a low pressure LP and low temperature [liquid or liquid+vapor mixture, which is delivered] to the outdoor coil [serving as the evaporator, which receives thermal energy] from the outside air. The refrigerant vaporizes [substantially or completely in the evaporator], enters the compressor to be compressed to the high pressure [HP vapor], and the cycle is completed."[153]

For a **heat pump operated in cooling mode**, the compressor sends high-pressure HP vapor refrigerant to the outdoor coil heat exchanger (condenser). The refrigerant gives up its heat energy [enthalpy of vaporization] to the outside air [heating it] and condenses to a high pressure HP liquid. The liquid is then throttled to a low pressure LP and low temperature [liquid-vapor mixture], and delivered to the indoor coil heat exchanger (evaporator), where a fan blows the resulting cooled air into the room. The LP vapor then enters the compressor to complete the cycle.

The following is a diagram of a representative home heat pump operated in heating mode.[154] Low pressure saturated vapor enters the compressor, and electrical work is expended to produce high pressure vapor exiting the compressor. This enters the condenser section where enthalpy of vaporization (heat) is given up into a duct for heating the interior space that is in need of heating, and the refrigerant condenses to a liquid. Still at high pressure, the liquid refrigerant is throttled to a low pressure and low T liquid [or saturated liquid-vapor mixture]. In the evaporator, located outside, heat is extracted to provide the heat of vaporization so the liquid becomes a saturated LP vapor and returns to the compressor, completing the cycle.

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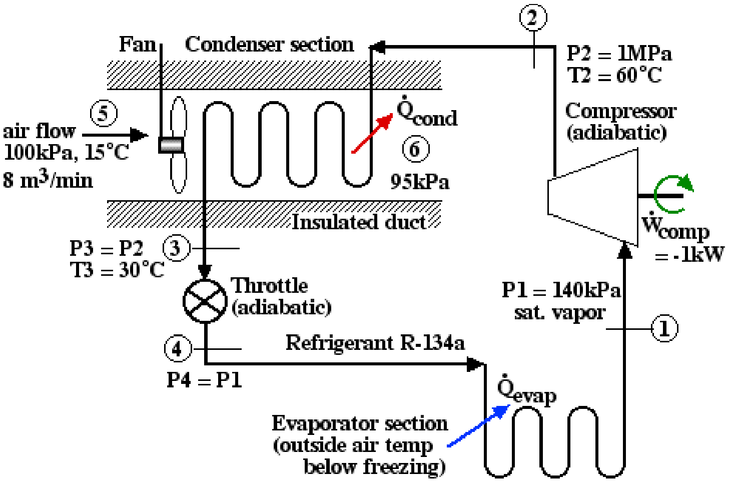
[151] https://en.wikipedia.org/wiki/List_of_refrigerants

[152] http://energy.gov/energysaver/heat-pump-systems , see also https://www.refrigerationbasics.com/RBIII/heat_pumps1.htm

[153] *TAEA7* Chapter11.ppt

[154] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/refrigerator/heatpump.html



Home heat pump operated in heating mode

By usual definitions, thermal efficiency can never be greater than 100%.

But the performance of a heat pump is expressed by a different index, its **Coefficient of Performance**.

The performance of a Heat Pump operated in **Heating Mode** is expressed by:

$$\textbf{Coefficient of Performance COP}_{\textbf{HPH}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} /$$

(Note that I have chosen to abbreviate the quantity as COP_{HPH} rather than the more customary COP_{HP} or COP_h to eliminate ambiguity about which heat pump mode of operation applies.)

The performance of a Heat Pump operated in **Cooling Mode** (including as a Refrigerator) is expressed by

$$\textbf{Coefficient of Performance COP}_{\textbf{R}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

When operating under the same conditions, $COP_{HPH} = COP_R + 1$ or $COP_R = COP_{HPH} - 1$.

Heat Pumps are discussed in detail in Chapter 11 summary.

The Second Law of Thermodynamics

There are a variety of statements and formulations that express, in one form or another, this empirical but consistently observed “law”. Nicolas Léonard Sadi Carnot (1824) provided the historical beginnings.[155]

(1) The **Kelvin-Planck Statement** (William Thomson—Lord Kelvin, c. 1851 and Karl Ernst Ludwig Planck c. 1897), is as follows:

> A. It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.[156]

Alternatively stated:

> B. It is impossible to construct a device which operates on a cycle and produces no other effect than the transfer of heat from a single body in order to produce work.”[157]

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[155] https://en.wikipedia.org/wiki/Second_law_of_thermodynamics

[156] *TAEA7* p. 284

[157] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter5.html

(2) The **Clausius statement** (Rudolf Julius Emanuel Clausius 1822-1888, published 1854):

> A. It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.[158]

Alternatively stated:

> B. Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.[159]

The Clausius statement can be shown to be equivalent to the Kelvin-Planck Statement. (See chapter 7 summary for Clausius Inequality.)

Perpetual Motion Machines

These are any devices, proposed or envisioned, that violate either the 1LTD or the 2LTD. Those that violate the 1LTD are termed "**Perpetual Motion Machines of the First Kind PMM1**" whereas those that violate the 2LTD are termed "**Perpetual Motion Machines of the Second Kind PMM2**". Numerous failed PPM1 and PPM2 devices have been proposed throughout history.

There is also a **PMM3**:

> "A perpetual motion machine of the third kind, usually (but not always) defined as one that completely eliminates friction and other dissipative forces, to maintain motion forever (due to its mass inertia)... Although it is impossible to make such a machine, as dissipation can never be 100% eliminated in a mechanical system, it is nevertheless possible to get very close to this ideal... Such a machine would not serve as a source of energy but would have utility as a perpetual energy storage device."[160]

The concept of a PMM is further clarified:

> A perpetual motion is a motion of enduring physical objects that are **very large compared with atoms**, that continues indefinitely. This is impossible because of friction and other modes of degradation or disruption of form. A perpetual motion machine is a hypothetical machine that can do work indefinitely without an energy source. This kind of machine is impossible, as it would violate the first or second law of thermodynamics... These laws of thermodynamics apply even at very grand scales. For example, the motions and rotations of **celestial bodies** such as planets may appear perpetual, but are actually subject to many processes that degrade or disrupt their form, such as solar winds, interstellar medium resistance, gravitation [including tidal interactions], thermal radiation and electromagnetic radiation... Thus, machines which extract energy from finite sources will not operate indefinitely, because they are driven by the energy stored in the source, which will eventually be exhausted. A common example is devices powered by ocean currents, whose energy is ultimately derived from the Sun, which itself will eventually burn out. Machines powered by more obscure sources have been proposed, but are subject to the same inescapable laws, and will eventually wind down.[161]

An atom's orbiting electron might be regarded as in perpetual motion, a PMM3, according to some atomic models and definitions. Some would say a machine is not a PP *machine* unless it **delivers work or energy**. "Energy cannot be extracted from motion of such electrons if they are in the *ground state* (and most atoms are) because there are no lower-lying energy states allowed by quantum mechanics. If the electrons are not in

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[158] *TAEA7* p. 290

[159] https://en.wikipedia.org/wiki/Second_law_of_thermodynamics

[160] https://en.wikipedia.org/wiki/Perpetual_motion

[161] ibid.

the ground state, you can extract useful energy, but then the atoms go into lower energy states until they reach their ground state, from which no further energy can be extracted."[162]

Regarding perpetual motion at the **atomic or subatomic level** without transfer of energy—such as electrons orbiting in their ground state, or nucleons bound and moving in their nucleus—some contend (without proof as yet) that protons, neutrons, and other baryons (and therefore even the most stable of atoms), will decay away someday.[163] This is currently hypothetical, and half-lives for most bound nucleons are at the least extremely long. Effectively perpetual motion might conceivably exist at the atomic scale for some atomic species, thus the need to state that PPMs are forbidden at least for 'objects that are very large compared with atoms'. "

Reversible and Irreversible Processes

Certain processes can go in only one direction, for instance transfers from hot to cold. A cold cup of coffee will not spontaneously heat up from room temperature heat.

A reversible process RP is one which can be reversed without leaving any trace on its surroundings.[164] Otherwise, it is irreversible. No heat engine can have thermal efficiency = 100%, but how high is possible? Reversible processes do not occur in nature, they are simply idealized concepts. RPs are useful however in that they simplify mathematical analysis through a series of equilibrium states, and they provide useful models to compare with actual processes. It is the case that reversible (typically slow) processes deliver the most work output and/or consume the least work when compared to irreversible (typically fast) processes

RPs give the theoretical limits of device efficiency based on the 2LTD. **Second Law Efficiency** η_{II} can be defined as:

$\eta_{II} = w_{actual} / w_{reversible}$ for work producing device, thus < 1

$\eta_{II} = w_{reversible} / w_{actual}$ for work absorbing device, thus < 1

Here, II is Roman numeral 2.

Irreversible processes include:

- **Friction** and **shear forces** (in which work become heat),
- **Unrestrained expansion of a gas** into a lower P space (input of work for compression and heat transfer would be required to restore the product to the original state),
- **Mixing of dissimilar fluids**
- **Heat transfer across a finite temperature difference** (input of work for refrigeration would be required to restore the original temp difference, can never be near reversible unless conceptually at infinitesimal T difference),
- **Electric resistance heating**
- **Inelastic (plastic) deformation of solids**
- **Chemical reactions** (other than dynamic equilibrium reactions[165] proceeding in both directions equally and simultaneously).

Reversible reactions have no irreversible components. A process is **internally reversible** if there are no irreversible internal components (i.e., in the system)—this applies also to quasi-equilibrium processes. It is **externally reversible** if there are no irreversible external components outside the system boundary but associated with the process. It is totally reversible, aka simply **reversible**, if it is both internally and externally reversible.

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[162] https://van.physics.illinois.edu/qa/listing.php?id=154

[163] http://futurism.com/science-explained-atoms-last-forever/ and https://en.wikipedia.org/wiki/Proton_decay

[164] *TAEA7* p. 294

[165] http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Chemical_Equilibria/Reversible_vs._Irreversible_Reactions

The Carnot Heat Engine Cycle, Carnot Refrigeration Cycle, & Carnot Principles

(6-7, 6-8)

This cycle was proposed by Sadi Carnot in 1824. The **Carnot heat engine** is a theoretical idealized one which operates on the Carnot cycle. There are two isothermal processes and two adiabatic processes. The following diagrams illustrate the Carnot cycle on a closed system heat engine (though it can also be executed in a steady flow system). (Text descriptions below use work designations as given in the textbook and apply to the lower left diagram. The work signage differs in the remaining diagrams, which were taken from another source.[166]) The Carnot cycle is an idealized cycle in which each process is reversible, and work is delivered by the heat engine. The cylinder is intermittently insulated but this can be removed to allow heat transfer. The idealized steps are:

> (Process 1 or I) **Reversible Isothermal Expansion** from state 1 → 2, T_H = constant. This is achieved by removing insulation and allowing heat q_{in} or Q_H from reservoir T_H to enter the system, raising the volume v while maintaining $T = T_H$ in the system. The expanding gas inside the system does $work_{out}$ on its surroundings (such as the piston in upper left diagram). The volume expansion would reduce T but any infinitesimal drop dT is countered by the inflow of heat. Total heat in is $q_{in} = Q_H$.
>
> (Process 2 or II) **Reversible Adiabatic Isentropic Expansion** from state 2 → 3, $T_H \rightarrow T_L$. This is achieved by applying insulation to the cylinder head to prevent heat transfer. Further expansion of the gas volume v inside the system does further $work_{out}$ on its surroundings (such as by the piston in upper left diagram). T drops from $T_H \rightarrow T_L$. No heat enters during this adiabatic reversible isentropic process.
>
> (Process 3 or III) **Reversible Isothermal Compression** from state 3 → 4, T_L = constant. This is achieved by again removing insulation from the cylinder and allowing heat q_{out} or Q_L to flow from the system into reservoir T_L while compressing the system, decreasing the volume v while maintaining $T = T_L$ in the system. The compression of the gas inside the system and diminishing volume v is caused by work done on the system by its surroundings ($work_{in}$). The compression would increase T but any infinitesimal rise dT is countered by outflow of heat. Total heat out (or rejected) is $q_{out} = Q_L$.
>
> (Process 4 or IV) **Reversible Adiabatic Isentropic Compression** from state 4 → 1, $T_H \rightarrow T_L$. This is achieved by reapplying insulation to the cylinder head. Further $work_{in}$ is done by the surroundings on the system, causing the piston to move inward and to further compress the gas decreasing v. The T rises from $T_L \rightarrow T_H$ No heat enters during this adiabatic reversible isentropic process. This completes the cycle.

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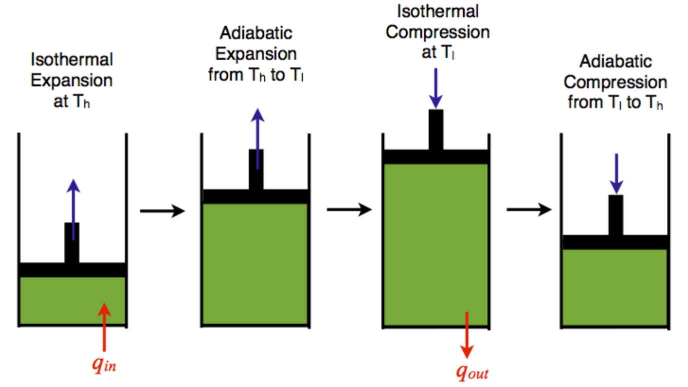
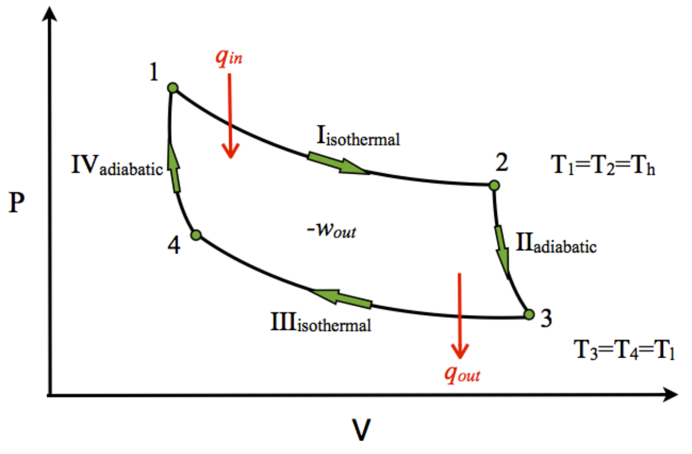
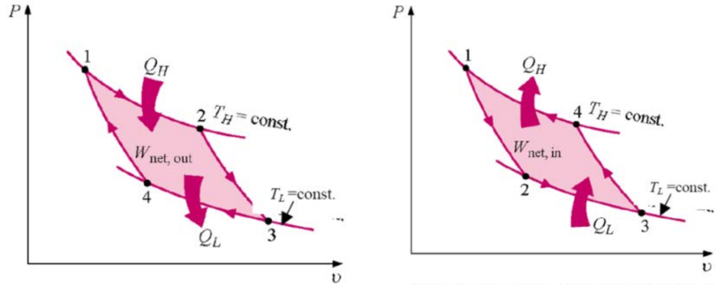
[166] http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Thermodynamics/Thermodynamic_Cycles/Carnot_Cycle



An ideal gas-piston model of the Carnot cycle. The piston positions shown are at 1, 2, 3, and 4, the starts of each process I, II, III, and IV. This piston is not passive: it conveys work$_{out}$ in 1-2 and 2-3, while receiving work$_{in}$ in 3-4 and 4-1



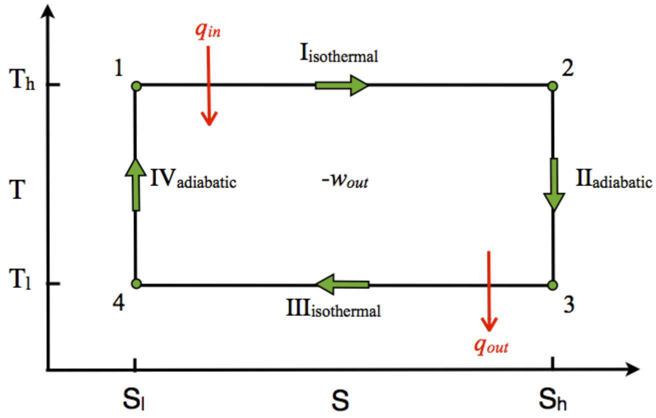
Carnot Cycle P-V diagram



P-v diagram for Carnot heat engine

P-v diagram for Carnot refrigerator

LEFT: Carnot Cycle Heat Engine
RIGHT: Reversed Carnot Cycle operated as a Refrigerator[167]



Carnot Cycle T-S diagram

The path 1 → 2 → 3 on the P V or T-S diagram defines an area representing work done **by** the system on its surroundings.

The path 3 → 4 → 1 on the P V or T-S diagram defines an area representing work done **on** the system by its surroundings.

The area enclosed by the full path of the Carnot cycle on either the P V or T-S diagram (for the sequence of states 1-2-3-4-1) is the net work done **by** the system on its surroundings.[168] This is a positive amount and in textbook usage, W_{out} is considered positive and thus **$W_{net,out}$ is positive**. With the Carnot heat engine, the system has done net work on its environment, fueled by two heat transfers Q_H and Q_L. (With the Carnot refrigerator, refrigeration is achieved via **$W_{net,out}$ being negative**, i.e., work on the system is required.)

The Carnot cycle is the most efficient way possible to move between the 4 designated states in this order, in the sense that thermal efficiency

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_L}{Q_H}$$

is maximal.

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[167] Image from textbook website chapter_06.ppt

[168] *TAEA7* p. 489

Carnot Refrigeration Cycle

If the Carnot heat engine cycle is run in reverse (sequence of states 1-4-3-2-1 as depicted in the right half of the image on lower left), the device becomes a **refrigerator** operating on the **Carnot Refrigeration Cycle**.[169]

Referring again to the right half of the image on lower left (which differs in numbering from the Carnot heat engine numbering), the path 1 → 2 → 3 on the P v diagram covers an area representing P v work done **by** the system on its surroundings.

The path 3 → 4 → 1 covers an area representing P v work done **on** the system by the surroundings.

The area enclosed by the full path of the reverse Carnot cycle on the P v diagram (for 1-2-3-4-1) is the net work done on the system by its surroundings. This is a positive amount and in textbook usage, W_{in} is considered negative and thus **$W_{net,out}$ is negative** or **$W_{net,in}$ is positive.** Heat Q_L is absorbed from T_L and rejected as Q_H to T_H, as a result of net work input into the system.

The Carnot Principles (Carnot Theorem)

These are proven from the 2LTD:[170]

(1) The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.
[or, All heat engines [operating] between two heat reservoirs are less efficient than a Carnot heat engine operating between the same two reservoirs.]

(2) The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.
[or, Every Carnot heat engine between a pair of heat reservoirs is equally efficient, regardless of the working substance employed or the operation details.]

The Thermodynamic Temperature Scale TTS (Kelvin scale)

The efficiency of reversible heat engines is given by a function of T_H and T_L only, or $Q_H/Q_L = f(T_H, T_L) = \varphi(T_H)/\varphi(T_L)$. Kelvin proposed that the function φ can be simply a temperature T, thus defining a thermodynamic temperature scale (aka the Kelvin scale) in terms of ratios of temperatures. The temperature ratios on this scale are simply the ratio of heat transfers for a reversible heat engine operating between T_H and T_L. The scale is defined and calibrated by assigning two points

- $T=0$ K , the first point needed to define the linear scale, the position of absolute zero
- $T_{tp,water} = 273.16$ K, the second point needed to define the linear scale, the **triple point of water**

An increment of 1 K becomes 1/273.16 of the temperature interval between absolute zero and the triple point of water. Celsius and Kelvin are converted by °C = K - 273.15 and K = °C + 273.15). An increment of 1 K = an increment of 1 °C precisely.

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[169] *TAEA7* p. 299

[170] *TAEA7* p. 300 and [https://en.wikipedia.org/wiki/Carnot's_theorem_%28thermodynamics%29]

The precisely defined key temperatures for the thermodynamic temperature scale (Kelvin scale) along with certain approximate points for water are as follows:

Exact Definitions and Approximations of Temperatures	**K**	**°C**
Conversion of K to °C (precise, by definition)	—	Add 273.15 to K
Absolute Zero (precise, by definition)	0	-273.15
Melting point of Water at 1 atm (approx.)[171]	273.1499	−0.0001
Triple point of Water (precise, by definition)	273.16	0.01
Boiling point of Water at 1 atm (approx.)[172]	373.1339 (or 373.124)	99.9839 (or 99.974)

Measurements of Kelvin (TTS) temperatures can be made approximately with constant volume ideal gas thermometers and other precision instruments.

The **thermodynamic temperature scale** and the **International Temperature Scale of 1990** (ITS-90) are also discussed earlier in this summary.

Carnot Efficiency

Carnot Heat Engine Efficiency is defined in terms of the TTS:[173]

$\eta_{th} = W_{net,out} / Q_{in}$ [for all cycles]

$\eta_{max} = \eta_{Carnot} = 1 - T_L/T_H$ [for all reversible cycles including Carnot cycles]

This is the highest efficiency possible for a reversible heat engine operating between T_H and T_L. For irreversible cycles, the efficiency $\eta_{th,irrev} < 1 - T_L/T_H$, and it is never possible to have a heat engine operate with a higher efficiency than a Carnot heat engine operating between the same given temperatures T_H and T_L. When η_{Carnot} = 70% (for instance a steam power plant operating between 1000 K and 300K), the actual (real) efficiency attained of the power plant is always substantially less.

Note that $Q_{L,rev} = (T_L/T_H)\, Q_{H,rev.}$

Compared to the **Carnot Refrigerator** (reversible Carnot cycle operated "in reverse"),[174] the performance of an actual heat pump operated in **Cooling Mode** has limitations as follows (due to friction, losses, etc.):

Coefficient of Performance $\mathbf{COP_{R,rev}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} = \frac{1}{\frac{T_H}{T_L} - 1}$

$\mathbf{COP_{R,rev} \geq COP_{R,actual}}$ for actual and therefore irreversible cycles

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[171] https://en.wikipedia.org/wiki/Celsius: "The ice point of purified water has been measured to be 0.000089(10) degrees Celsius – see Magnum, B.W. (June 1995). "Reproducibility of the Temperature of the Ice Point ..." (PDF). NIST Technical Note 1411. Archived from the original (PDF) on 7 March 2007

[172] https://en.wikipedia.org/wiki/Celsius: "For [distilled] Vienna Standard Mean Ocean Water at one standard atmosphere (101.325 kPa) when calibrated solely per the two-point definition of thermodynamic temperature... There is a different approximation using ITS-90 which approximates the temperature to 99.974 °C

[173] *TAEA7* p. 303

[174] *TAEA7* p. 613

Compared to the **Carnot Heat Pump** (reversible Carnot cycle operated "in reverse"),[175] the performance of an actual heat pump operated in **Heating Mode** has similar limitations as follows (due to friction, losses, etc.):

Coefficient of Performance $COP_{HP,rev}$ $= \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1-\frac{Q_L}{Q_H}} = \frac{1}{1-\frac{T_L}{T_H}}$

$COP_{HP,rev} \geq COP_{HPH,actual}$ for actual and therefore irreversible cycles (due to friction, losses, etc.)

Quality of Energy

In the Carnot engine cycle, efficiency is higher when T_H is higher, thus thermal energy has higher quality when higher in temperature because more of it can be converted to useful work. Work is a more valuable form of energy compared to heat because all of it can be utilized (though ultimately it results in conversion to heat), whereas only a part of thermal (heat) energy can be converted to useful work. Thus, it can be more useful to have a smaller amount of Q_{in} at a higher temperature T_H rather than a larger amount of Q_{in} at a lower temperature T_H. Although energy is always conserved, energy quality is not.

The textbook gives a sample problem in which a Carnot refrigerator operates inside the saturation dome of R-134a between 20 °C and -8 °C, where state 3 is on the saturated vapor line and state 4 is on the saturated liquid line. The specific enthalpy of vaporization h_{fg} between 3 and 4 is obtained from the table A-11, and with this information the mass of refrigerant vaporized can be calculated as well as the P at state 4.

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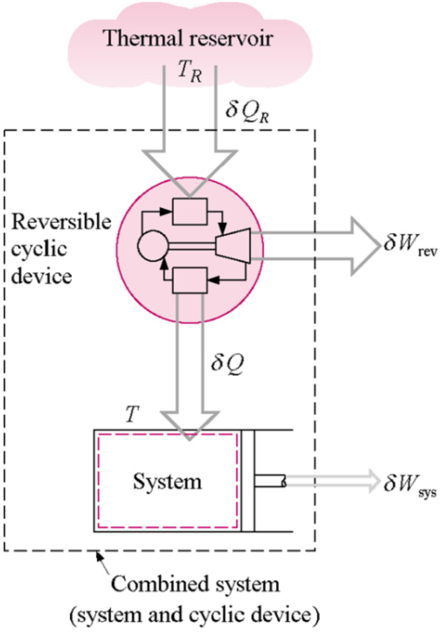
[175] *TAEA7* p. 613

Entropy (7)

(from text Chapter 7 & other sources)

Entropy is a measure of irreversibilities in processes which increase disorder, such as heat transfer through a finite T difference, friction, mixing, unconstrained expansion, non-equilibrium compression and expansion, chemical reactions, etc., any of which can introduce inefficiencies in engineering thermodynamic systems when compared to idealized reversible processes.



The **Second Law of Thermodynamics 2LTD** can be expressed in terms of entropy changes. One statement is, "There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment [surroundings] to increase for an irreversible process and to remain constant for a reversible process."[176] Alternatively, "…all spontaneous processes produce an increase in the entropy of the universe."[177] Details follow.

Clausius Inequality

The Clausius Inequality[178] (formulated in 1855 by Rudolf J. E. Clausius[179] (1822-1888) may be demonstrated by considering a combined system containing a reversible cyclic device RCD and a system with which the RCD exchanges heat δQ at temperature T. The RCD exchanges heat with external reservoirs δQ_R at T_R. The combined system performs Work $\delta W_C = \delta W_{rev} + \delta W_{sys}$ on the surroundings. The inequality states:

$$\oint \frac{\delta Q}{T} \leq 0$$

where δQ is used to indicate that heat differentials are path dependent and thus inexact, and the cyclic integral represents the sum of all heat transfers δQ (from the RCD to the system) divided by T at the separating boundary during the transfers over a full cycle. There can be no net work output as there is only one external thermal reservoir involved (applying the Kelvin-Planck statement).[180] Thus, the Clausius Inequality may be deduced,[181] which is valid for all cycles, reversible or irreversible.

If there are no irreversibilities in the internal system or in the RCD, the combined system has no irreversibilities (so the combined system is said to be internally reversible) and the equal sign applies.

$$\left(\oint \frac{\delta Q}{T} = 0\right)_{\text{int rev.}}$$

Otherwise the inequality applies.

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[176] https://www.grc.nasa.gov/www/k-12/airplane/thermo2.html

[177] http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Thermodynamics/Laws_of_Thermodynamics/Second_Law_of_Thermodynamics

[178] https://en.wikipedia.org/wiki/Clausius_theorem

[179] https://en.wikipedia.org/wiki/Rudolf_Clausius

[180] *TAEA7* p. 323 and Chap 7 PPT, including diagram

[181] *TAEA7* p. 332

Entropy Defined Macroscopically

The quantity dS is the entropy expressed in differential form:

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{int rev.}} \qquad \text{(kJ/K)}$$

Note that the definition of dS requires an internally reversible process.

The second law of thermodynamics **2LTD** requires that for closed actual systems which have irreversible processes,

$$dS > \frac{\delta Q}{T} \qquad \text{(kJ/K)}$$

Entropy S is an extensive property, thus is often described as **total entropy**, whereas specific entropy per unit mass is an intensive property and expressed as s.

We are often interested in changes of total entropy between two states (rather than absolute values of total entropy):

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev.}} \qquad \text{(kJ/K)}$$

where values (usually of s) may be obtained from reference tables. There is no meaning to the integral if it is carried out along an irreversible path (except as shown below). The difference in entropy between the two states 1 and 2 is always given by the ΔS formula for an internally reversible path (if necessary, by using an imaginary path), regardless of the actual path by which the change occurs.

Absolute values of total entropy S are calculated in relation to 0 K according the **3LTD** (see below).

Isothermal Internally Reversible Processes

For these processes,

$$\Delta S = \frac{Q}{T_0} \qquad \text{(kJ/K)}$$

where T_0 is the constant temperature. Q and therefore ΔS may be positive or negative. Entropy in a system may decrease due to heat transfer out of the system—of course the entropy of the surroundings typically increases in such a transfer.

Increase in Entropy Principle (Entropy Generation)

By considering a cycle of two processes, one of which is internally reversible and the other internally reversible or irreversible, it follows that

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev/irrev}} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{\text{int rev.}} \le 0 \qquad \text{(kJ/K) per the Clausius Inequality}$$

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev/irrev}} + S_1 - S_2 \le 0 \qquad \text{(kJ/K)}$$

$$\Delta S_{\text{sys}} = S_2 - S_1 \ge \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev/irrev}} \qquad \text{(kJ/K)} \qquad \text{(7-7)}$$

$$\Delta S_{\text{sys}} - \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev/irrev}} \ge 0 \qquad \text{(kJ/K)}$$

In differential form

$$dS \geq \frac{\delta Q}{T} \qquad \text{(kJ/K)} \qquad \text{(7-8)}$$

where T is measured at the boundary where heat is transferred, and is based on the TTS. Equality applies for internally reversible processes, inequality for processes that are not internally reversible.

We conclude that **entropy increases for a cycle containing an irreversibility**, and remains unchanged only for a fully internally reversible cycle.

Entropy generation S_{gen}

S_{gen} for a closed system is given by

$$\Delta S_{\mathrm{sys}} = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right) + \mathrm{S_{gen}} \qquad \text{(kJ/K)} \qquad \text{(7-9)}$$

or

$$\Delta S_{sys} - \int_1^2 \left(\frac{\delta Q}{T}\right)_{\mathrm{rev/irrev}} = \mathrm{S_{gen}} \qquad \text{(kJ/K)} \qquad \text{(7-9)}$$

and non-zero S_{gen} is due to irreversible processes.

For a reversible process, no entropy is generated and the change in entropy from the integral in such a system represents entropy transfer with heat:

$$\Delta S_{\mathrm{sys}} = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\mathrm{int,rev}}$$

S_{gen} is always a positive or zero quantity and is dependent on the process path (thus not a property).

For a closed system having no transfer of heat or entropy in or out (the integral in 7-9 is zero), the entropy change of a system is equal to the entropy generated S_{gen}, and this is due entirely to irreversibilities, and:

$$\Delta S_{\mathrm{sys,isolated}} = \mathrm{S_{gen}} \geq 0 \qquad \text{(kJ/K)}$$

so that entropy of an isolated system never decreases. Real processes virtually always have some degree of irreversibility and thus nonzero S_{gen}. In fact, entropy generation is a measure of the magnitudes of the irreversibilities present in a process or processes.

For a system and its surroundings considered together as an isolated system (involving no external heat of entropy transfer),

$$S_{\mathrm{gen}} = \Delta \mathrm{S_{total}} = \Delta \mathrm{S_{sys}} + \Delta \mathrm{S_{surr}} \geq 0 \qquad \text{(kJ/K) (7-11)}$$

For multiple subsystems that are part of an enclosing isolated system (no transfer of heat, work, energy, or mass), the sum of the entropy changes for all the combined systems is never less than 0. A system and its immediate surroundings can often be viewed as an isolated system, thus entropy must increase or stay unchanged but cannot decrease. If there is no heat transfer, any entropy change is due to irreversibilities that increase entropy.

A system can have negative entropy change during a process, $\Delta S < 0$, but a system cannot have negative $S_{gen,}$ thus $S_{gen} < 0$ is impossible.

Other Entropy Topics

Spontaneous Reactions and Equilibrium States

Processes proceed spontaneously in a particular direction that satisfies the Increase in Entropy Principle. A system may tend spontaneously toward an **equilibrium state**, but may stop short of completion of, for example, the **chemical reaction** involved in the process. The reaction stops when a maximum value of entropy is attained, and further progress of the reaction would be accompanied by a decrease in entropy from the maximum, which is disallowed by the Increase in Entropy Principle.[182]

The entropy of the universe, and thus its disorder, is always increasing.

Entropy is not “conserved” except for idealized reversible processes.

For the same amount of heat transferred (in kJ) in two systems, one between 800 K and 500 K and the other between 800 K and 750 K, the entropy generated is lower for the system with the smaller temperature difference.

Entropy Changes of Pure Substances

Changes between two states may be determined from tables by comparing intensive entropy s at the two states s_2 and s_1, etc. Typically, such tables arbitrarily set the entropy = 0 for saturated liquid at a defined T_{sat} and P_{sat}. Thus,[183]

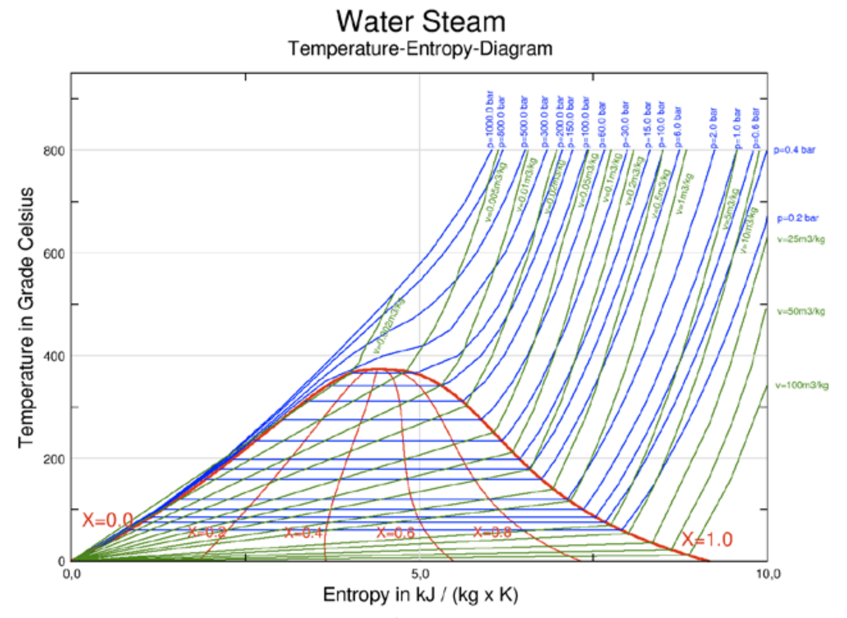
For saturated liquid water at $T_{sat} = 0.01$ °C & $P_{sat} = 0.6117$ kPa , Table A-4 gives $s_f = 0$.
For saturated liquid refrigerant R-134a at $T_{sat} = -40$ °C & $P_{sat} = 51.25$ kPa , Table A-11 gives $s_f = 0$.

These relative values may be used for computing changes in specific entropy, but are not absolute values of s (i.e., they are not expressed relative to absolute zero or 0 K). As with other intensive quantities (u, v, etc.) existing within the saturation dome, the mixed saturated liquid-vapor entropy may be calculated using the quality factor etc. via

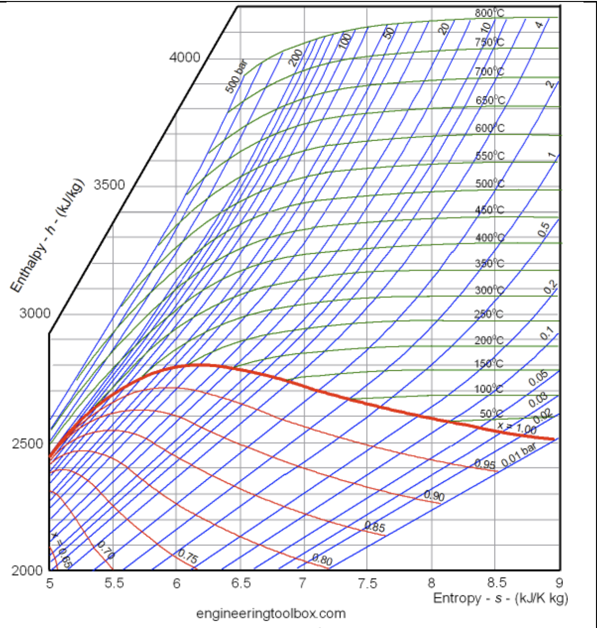
$$s_2 = s_f + x_2 s_{fg}$$

For temperatures below the arbitrary zero point, relative specific entropies in these tables may be negative.

Entropies are often used as the horizontal axis for graphs depicting 2LTD phenomena, such as the T-s diagram[184] or the h-s diagram (**Mollier diagram**)[185] that follow. These diagrams also include isobaric P=const, isovolumetric/isochoric v=const, and/or isothermal T=const lines:



T-s diagram for Water Steam.
blue = const pressures in bar; green = const v;
red = saturation dome and const x



Mollier h-s Diagram for Water-Steam
blue = const pressures in bar; green = const T;
red = saturation dome and const x

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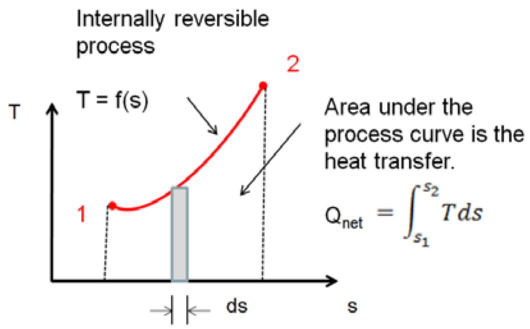
[182] *TAEA7* p. 337
[183] *TAEA7* Table 4 and Table A-11, resp.
[184] https://commons.wikimedia.org/wiki/File:TS-Wasserdampf_engl.png
[185] http://www.engineeringtoolbox.com/mollier-diagram-water-d_308.html

For example, the v=const line (green) for the T-s diagram can be used to envision how entropy changes in a fixed volume container when T is decreased, or the P=const line (blue) for changes that occur at constant pressure.

Significance of heat transfer on the T-s diagram and $W_{net,out}$

Heat transfer is related to the T-s entropy diagram as follows (for an internally reversible process):[186]



In the above figure, the heat transfer in an internally reversible process is shown as the area under the process curve plotted on the T-S diagram.

$$Q_{net} = \int_1^2 TdS$$

This derives from dS = $(\delta Q/T)_{\text{int rev}}$ so $\delta Q_{\text{int rev}}$ = T dS, thus

$$Q_{\text{int.rev}} = \int_1^2 T\,dS$$

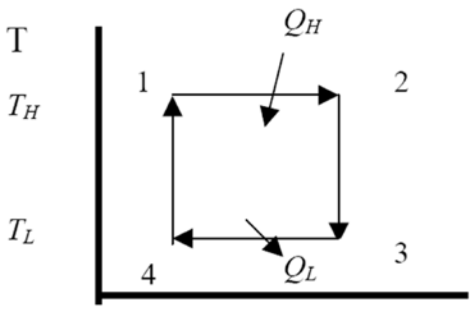
Thus the area under the process curve on a T-s diagram represents the heat transfer during an internally reversible process. (This area is said to be meaningless if the process is not reversible.) For the special case where T is constant,

$$q_{\text{int rev.}} = T_0 \Delta s \quad (\text{kJ/kg})$$

An isentropic process is a vertical line on the T-s diagram.

The Carnot cycle (which is internally reversible) on a T-s diagram becomes as shown in the diagram.

and the area enclosed by the cycle ($W_{net,out} = Q_H - Q_L$) represents the net work performed during the cycle, where W is the net work performed by the cycle operating between T_H and T_C, Q_C is heat leaving the system.[187] Thus, the T-s diagram enclosed area like the P-v diagram enclosed area encloses the $W_{net,out} = Q_H - Q_L$.



Carnot Cycle

1-2, 3-4: Isothermal
2-3, 4-1: Isentropic

Isentropic (Constant Entropy) Processes

Idealized processes that are internally reversible and are adiabatic (involve no heat transfer) are isentropic ($\Delta s = 0$). *Isentropic* is commonly used to refer to **adiabatic reversible** processes. (In some unusual circumstances, a system might have unchanged entropy despite processes that are not strictly reversible and adiabatic, but there would be changes in entropy of the surroundings.)[188] Isentropic processes can serve as ideal models (having no frictional losses or other irreversible losses) to which certain real-life nearly adiabatic processes (e.g., with pumps, turbines, nozzles, and diffusers) may be

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[186] *TAEA7* Chapter_07_1.ppg

[187] *TAEA7* Chapter_07_2.ppt

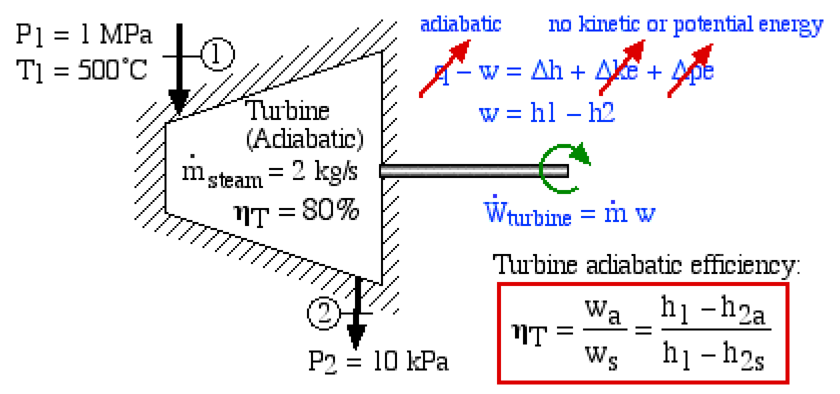
[188] Example: "Work done on the system includes friction internal to the system, and heat is withdrawn from the system, in just the right amount to compensate for the internal friction, so as to leave the entropy [of the system] unchanged." https://en.wikipedia.org/wiki/Isentropic_process

compared. Cycles consisting of such ideal processes may define a maximum efficiency to which the real-life cycles may aspire but never attain.

For an isentropic steam turbine with negligible change in $\dot{E}$, Q, ke, and pe, the rate of work out (power output) is given by[189]

$$\dot{W}_{out} = \dot{m}(h_1 - h_2) \qquad \text{(kW)}$$

$$w_{out} = h_1 - h_2 \qquad \text{(kJ/kg)}$$



Example of Adiabatic steam turbine diagram and calculations for which time rates of change of E, q, ke, and pe are zero.[190]
h_{2a} = actual enthalpy state 2; h_{2s} = isentropic enthalpy state 2, $h_{2a} > h_{2s}$

More on Entropy and the 3LTD

Entropy at the “microscopic” (i.e., atomic/molecular) level represents the degree of molecular disorder or randomness. It is lowest in solids, especially pure crystalline substances with highly ordered atomic arrangement, higher in liquids, higher still in gases.

For pure crystalline (not glassy) substances, vibrations cease at absolute zero, and there are no other possible states (thus there is molecular order and no uncertainty about the state), so that absolute S = 0 at 0 K (ignoring quantum subtleties). This becomes the basis of the **Third Law of Thermodynamics 3LTD**, namely that for pure perfect crystalline substances, absolute entropy S = 0 at 0 K. Other statements of the 3LTD[191] include those of Walter Nernst (developed 1906–12):

> (1) the Nernst-Simon statement, “The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K”,

and

> (2) the Nernst statement 1912, “It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations.”[192]

and

> (3) the Lewis and Randall statement 1923, “If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.”

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[189] *TAEA7* p. 343
[190] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter6a.html
[191] https://en.wikipedia.org/wiki/Third_law_of_thermodynamics
[192] https://en.wikipedia.org/wiki/Third_law_of_thermodynamics

At the atomic/molecular level ("microscopic"), for a system in thermodynamic equilibrium, Boltzmann gave the **total entropy** as

$$S = k \ln p$$

where S is total absolute entropy, k is the Boltzmann constant (1.3806 x 10^{-23} J/K) and p is the "thermodynamic probability" (reflecting the number of possible states or molecular configurations, i.e., the number of microstates consistent with the given macrostate, thus a number > 1).[193] This relationship was developed 1872 to 1875, but put into its current form by Max Planck in about 1900.

Josiah W. Gibbs (1839 – 1903) gave the **Gibbs entropy** (date?) by a more general equation,

$$S = -k_B \sum p_i \ln p_i$$

where p_i are probabilities of various states. If the values of p_i are all equal, the Gibbs formula is said to reduce to the Boltzmann formula. (The values of p_i are probabilities thus less than 1, so their natural logarithms are negative, thus the preceding negative sign.) I have not studied this material in detail.

Useful work cannot be extracted from this disorganized energy, whereas a rotating shaft has organized energy that can be harnessed. No entropy transfer occurs as a result of work energy transfer.[194] Heat is a disorganized form of energy, and some entropy flows with heat transfer. The increase of entropy in a cold body is greater than the decrease in entropy in the hot body giving rise to the heat transfer, thus entropy increases in the combined system.

The T ds Relations

The conservation of energy and definitions of entropy yield the following relationships, valid for reversible and irreversible processes:[195]

First Gibbs	$T\,dS = dU + P\,dV$	
or	$T\,ds = du + P\,dv$	(7-23. 12-10)
or	$du = T ds - P\,dv$	(12-10)
Second Gibbs	$T\,ds = dh - v\,dP$	(7-24)
or	$dh = T\,ds + v\,dP$	(12-11)
	$ds = \frac{du}{T} + \frac{P\,dv}{T}$	(7-25)
and	$ds = \frac{dh}{T} - \frac{v\,dP}{T}$	(7-26)

Changes of Entropy in Liquids and Solids

These are given by

$$s_2 - s_1 = \int_1^2 c(T)\frac{dT}{T} \cong c_{avg} \ln\frac{T_2}{T_1} \qquad \text{(kJ/kg-K)}$$

where $c_p = c_v = c$ and du = c dT for incompressible substances. It follows that the temperature T of incompressible substances remains constant during isentropic processes. In tables for liquids such as CH_4, the entropy for a given T is indeed seen to vary little with P.

The text gives an example where a throttling valve that reduces pressure in liquid methane at 115 K from 5 MPa to 1 MPa at 0.28 m^3/s can be replaced with an isentropic turbine, and this allows capture of wasted work of 1123 kW.[196]

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[193] *TAEA7* p. 346 and https://en.wikipedia.org/wiki/Entropy_%28statistical_thermodynamics%29 This topic is much simplified here.

[194] *TAEA7* p. 347

[195] *TAEA7* p. 350

Changes of Entropy in Ideal Gases (limited summary)

These expressions are given by

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \qquad (7\text{-}30)$$

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \frac{v_1}{v_2} \qquad (\text{kJ/kg-K}) \qquad (7\text{-}31)$$

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1} \qquad (\text{kJ/kg-K}) \qquad (7\text{-}32)$$

The text provides analyses of how to do these calculations with constant specific heats (approximate analysis) and with variable specific heats (exact analysis), using entropy per unit mass or per unit mole basis. The latter makes use of the following quantities:

$$s^\circ = \int_0^T c_p(T) \frac{dT}{T} \qquad (\text{kJ/kg-K}) \text{ integral starting from absolute zero} \qquad (7\text{-}37)$$

$$\int_1^2 c_P(T) \frac{dT}{T} = s_2^o - s_1^o \qquad (\text{kJ/kg-K}) \qquad (7\text{-}38)$$

as well as the following:

relative pressure $P_{r1} = e^{s_1^o/R}$ (dimensionless) p. 358

and

relative specific volume $v_{r2} = \frac{T_2}{P_{r2}}$ (?units, but used in ratios) p. 359

The Ideal gas tables for air (Table A-17) list values of P_r and s° which can be used in these calculations. Other ideal gases list values per unit mole.

Multistage Compression With Intercooling (limited summary)

This important design improvement incorporates 2 or more intermediate constant pressure cooling stages using heat exchangers thereby minimizing work required to achieve the same final high levels of compression and with the least resulting temperature increase. Optimally the successive intercooling stages have equal pressure ratios. In general, there are n stages of compression with n-1 stages of intercooling.

The following P-v and h-s diagrams demonstrates the benefits of 3-stage compression intercooling:[197]

h-s diagram: "The effluent from a single-stage compressor ["State 2: 1-stage" in the diagram] has a high enthalpy [specific enthalpy $\hat{h}$]. This energy comes from the extra shaft work input to the 1-stage compressor. A 3-stage compressor with 2 intercoolers [segments along constant pressure lines P_A and P_B] is also more efficient than the 2-stage system because the enthalpy of the fluid leaving a 2-stage compressor ["State 2: 2-stage"] is greater than the effluent from a 3-stage compressor ["State 2: 3-stage"]. But adding stages yields diminishing returns. Adding the 2nd stage boosted the efficiency by more than the 3rd stage did. Adding another stage would move the outlet stream for the multi-stage compressor system closer to state 2T and improve the efficiency, but not by all that much. The isothermal compression [green line] is equivalent to a compression system with an infinite number of stages... So, how many stages should we use in a compression system? ... The outcome is almost always either a 1-stage, 2-stage, or 3-stage compression system... "

P-v diagram: The starting T is T_1, starting P is P_1. HEX A and HEX B= heat exchangers at constant P. The saved work for 3-stage compared to 1-stage is shown in pinkish color. "2T" is idealized isothermal

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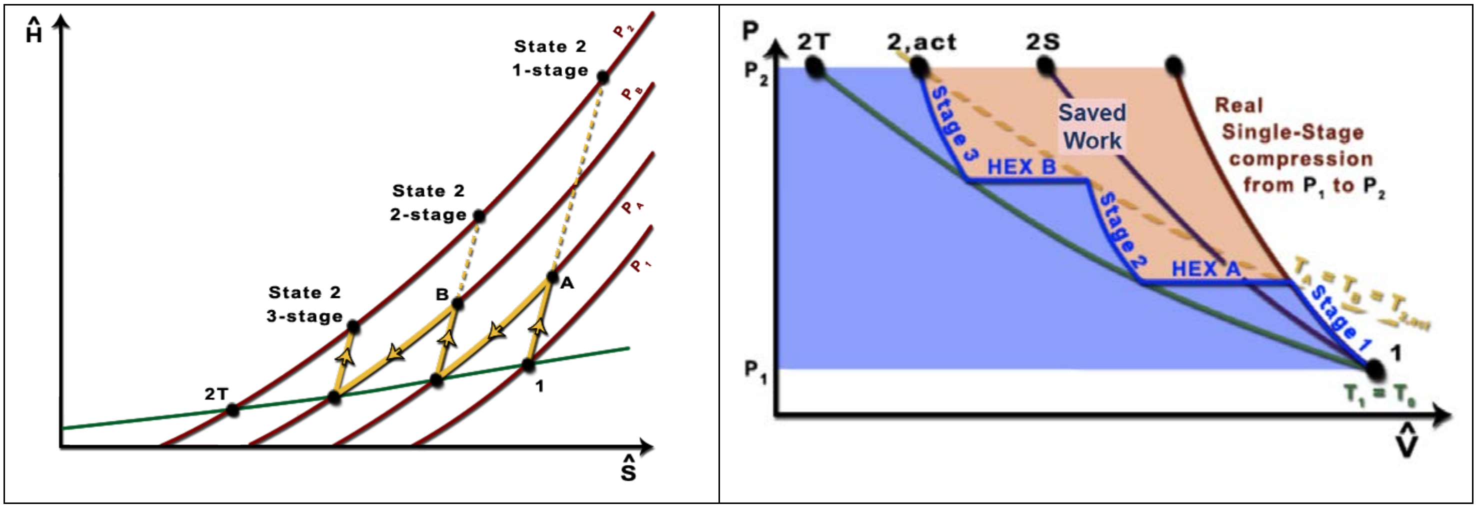
[196] *TAEA7* p. 353

[197] http://www.learnthermo.com/T1-tutorial/ch08/lesson-C/pg16.php quote and both diagram

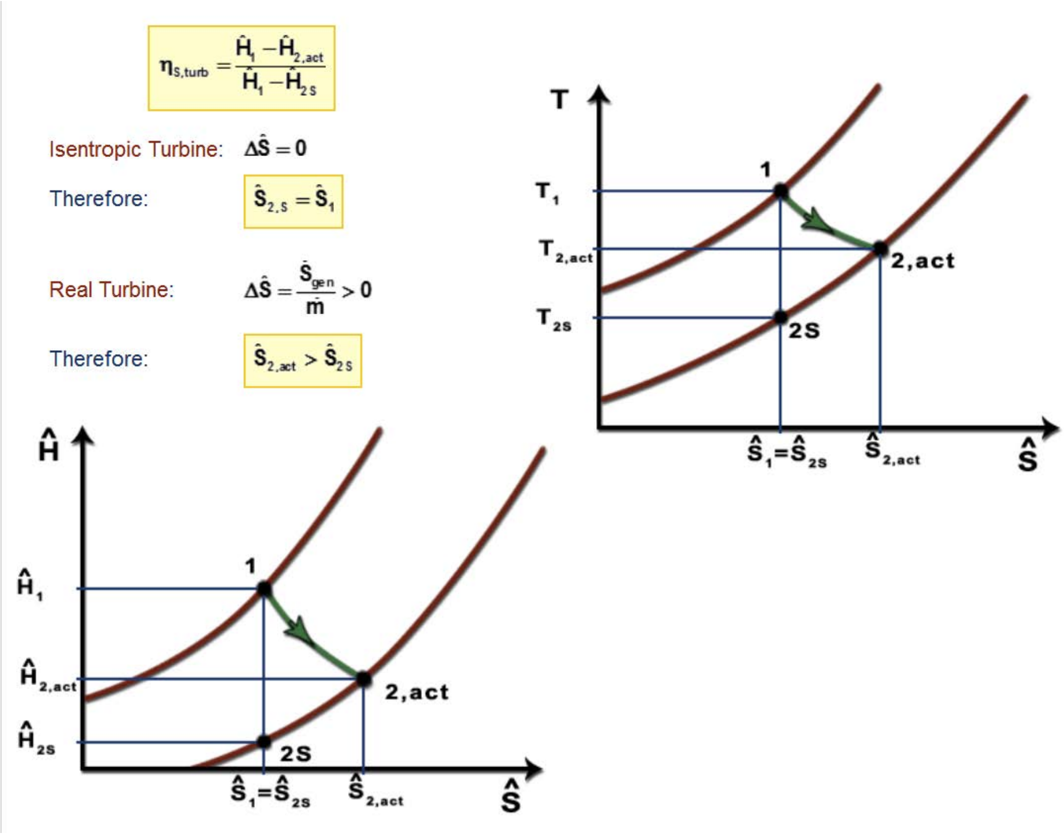
final T. “2,act” is actual final T = $T_A = T_B$ for 3-stage compression. “2S” is idealized isentropic for single stage compression.



Isentropic Efficiencies for Steady-Flow Devices (limited summary)

This type of analysis compares actual Turbine work to Isentropic turbine work, Isentropic Compressor work to actual Compressor work, and actual Nozzle KE to Isentropic Nozzle KE.

A sample analysis is shown in the diagrams below, comparing h-s and T-s diagrams for idealized isentropic and actual turbines. The idealized turbine operates between State 1 and State 2_S. The actual turbine operates between State 1 and State 2_{act}, and State 2_{act} has higher entropy and higher enthalpy compared to 2_S, thus isentropic efficiency $\eta_{S,turb}$ is less than 1.[198]



$$\eta_{S,turb} = \frac{\hat{H}_1 - \hat{H}_{2,act}}{\hat{H}_1 - \hat{H}_{2S}}$$

Isentropic Turbine: $\Delta\hat{S} = 0$

Therefore: $\hat{S}_{2,S} = \hat{S}_1$

Real Turbine: $\Delta\hat{S} = \frac{\dot{S}_{gen}}{\dot{m}} > 0$

Therefore: $\hat{S}_{2,act} > \hat{S}_{2S}$

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[198] http://www.learnthermo.com/T1-tutorial/ch08/lesson-C/pg03.php and pg04.php, including diagrams

Topics Omitted or Simplified For Lack of Time

Steady-Flow Devices that are Reversible deliver the most Work (or consume the least Work)

Bernoulli Equation in Fluid Mechanics

Minimizing Compressor Work (7-11)

Entropy Balance (7-13)

> Entropy Change of a System, Mechanisms of Entropy Transfer (Heat Transfer and Mass Flow), Entropy Generation, Closed Systems, Control Volumes, and Entropy Generation Associated with a Heat Transfer Process.

Optimizing Industrial Plant Efficiencies in the Use of Compressed Air (p. 387)

> Repairing compressed air leaks; Installing High-Efficiency Motors; Using Smaller Motors at High Capacity; Using Cooler Outside Air for Compressor Intake; Reducing Air Pressure Setting

Exergy (8)

(from text Chapter 8 & other sources) Chapter not studied and omitted here.

“In thermodynamics, the exergy of a system is the maximum useful work possible during a process that brings the system into equilibrium with a heat reservoir [usually the environment]. When the surroundings are the reservoir, exergy is the potential of a system to cause a change as it achieves equilibrium with its environment. Exergy is the energy that is available to be used. After the system and surroundings reach equilibrium, the exergy is zero. Determining exergy was also the first goal of thermodynamics. The term *exergy* was coined in 1956 by Zoran Rant (1904–1972) by using the Greek ex and ergon meaning ‘from work’, but the concept was developed by J. Willard Gibbs in 1873.”[199]

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[199] https://en.wikipedia.org/wiki/Exergy

Gas Power Cycles (9)

(from text Chapter 9 & other sources)

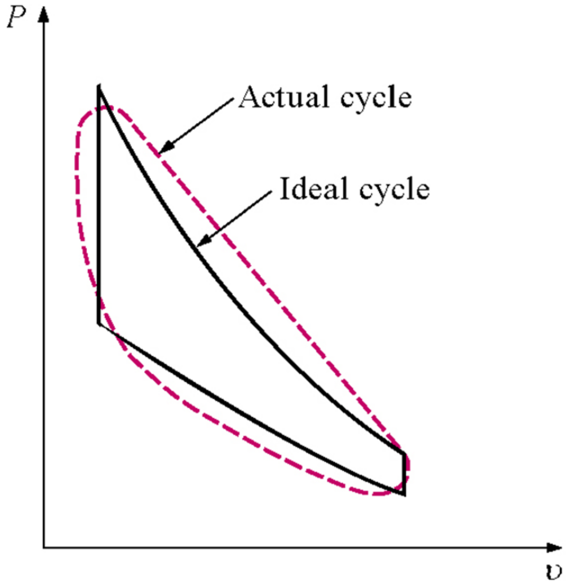
This chapter and Chapter 10 describe some of the real bread and butter devices of mechanical engineering, the technologically advanced and important machines that produce much of our world's energy and make our things go.

Overview of Ideal and Real TD Cycles and Heat Engines

Devices intended to produce net mechanical power out (for example, automotive shaft power or jet propulsion) are often called **engines**. These devices may be said to operate on thermodynamic **Power cycles** (as opposed to **Refrigeration Cycles**). They use heat (thermal energy transfer) as a source of energy, so may be called **heat engines**. TD power cycles operating with a working fluid that remains always in the gas phase—i.e., that never condenses to a saturated mixture or liquid phase—are called **Gas Power Cycles**. (Although a liquid fuel is mixed into and vaporized in the working fluid of most of the internal combustion engines, the TD effect of the liquid phase is apparently negligible, and the idealized and actual cycles of these engines are grouped with the other gas power cycle engines.)

For **closed cycles**, the working fluid is recirculated and returns to the starting place and state. In **open cycles**, such as typical internal combustion engines, the engine operates on a full mechanical cycle, but the working fluid is exhausted to the environment and renewed at the end of each cycle, thus the engine does not go through a complete TD cycle.

In TD analysis of various cycles, we typically start with totally reversible **idealized cycles** (e.g., Carnot, Rankine, Brayton, Diesel, Otto, Stirling, etc.). These theoretical cycles cannot be attained in actual (real) devices—they have performance characteristics that can be approached to some extent but never fully achieved. Nevertheless, the ideal cycles, like the Carnot cycle, present an optimal or best-case scenario. They have the maximum possible thermal efficiency and performance for the conditions and consist of reversible processes with no friction, etc. In the P-v diagram to the right, an ideal but unachievable cycle path with reversible processes is depicted, as well as the cycle path of a real actual device.[200] It appears to be common practice to refer to a real device as operating in one of the named ideal cycles, even though in actuality it deviates substantially from the ideal, with lower efficiency and higher entropy generation, etc.



Thermal efficiency for an ideal reversible heat engine, as mentioned before, can be no better than that of the Carnot cycle:

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_L}{Q_H}$$

Actual cycle efficiency compared to idealized cycle thermal efficiency is reduced by many factors: friction, operation under rapidly changing non-equilibrium conditions, heat losses resulting from inadequate insulation, and other irreversible factors.

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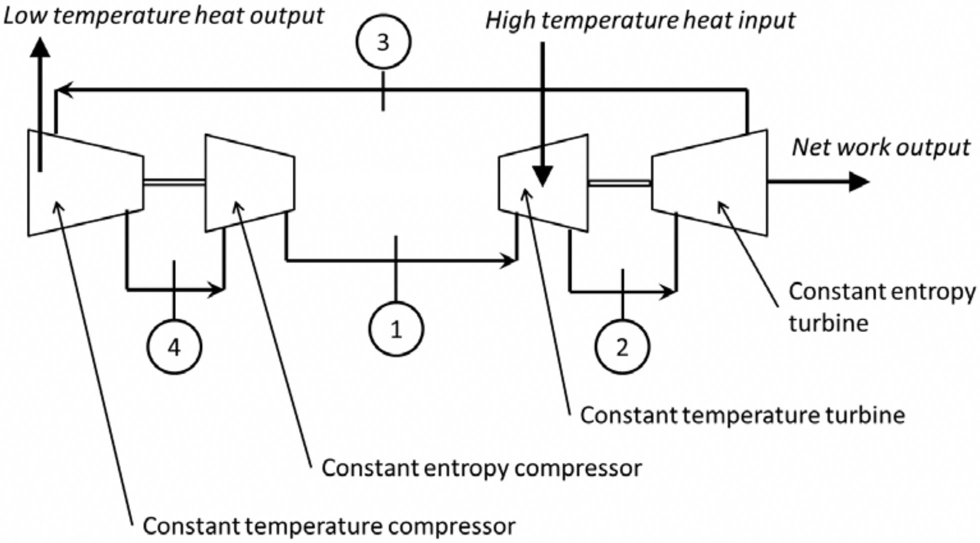
[200] *TAEA7* Chapter_09.ppt

Classic (Standard) and Steady-Flow Carnot Cycles

As discussed, work performed by an ideal cyclical device is given on both P-v and on T-s diagrams by the area enclosed inside the cyclical process curve (path) of the cycle.[201] This work is equal to the net heat transfer into an idealized system, i.e., the heat-addition minus the heat-rejection. In the Carnot cycle, recall that the heat transfers occur at constant T_H and T_L, and that the work transfers are partly isothermal and partly isentropic adiabatic processes.

The ideal classic Carnot cycle may be envisioned alternatively as an ideal steady-flow system, using in sequence an isothermal turbine, an isentropic turbine, an isothermal compressor, and an isentropic compressor:[202]



All processes are reversible for the ideal steady-state Carnot cycle, just as they are with the classic ideal Carnot cycle (discussed earlier):

> Isothermal Q_{in} at 1-2 and adiabatic isentropic expansion at 2-3 produce $Work_{out}$.
>
> $Work_{in}$ (source not shown) along with Q_{out} is needed to produce isothermal compression at 3-4, and further $Work_{in}$ (source not shown) is required to produce adiabatic isentropic compression at 4-1.
>
> Net $Work_{out}$ (shaft work here) = $Work_{out} - Work_{in}$

Although it leads to a simple efficiency calculation, and establishes the principle that the T_H should be maximal (limited by materials heat tolerance) and T_L should be minimal (limited by available cooling), the steady-state ideal Carnot cycle is impractical and unsuitable for actual heat engines.

Simplifying Air-Standard Assumptions

For simplifying analysis of gas power cycles, certain simplifying **air-standard assumptions**[203] are often made to model the so-called **air-standard cycle**:

- The working fluid is air (not the real fuel plus air mixture, nor is it a liquid/gas mixture), which continuously circulates in a closed loop and always behaves as an ideal gas.
- All the processes are internally reversible.
- The combustion chamber process is replaced by a heat addition process which adds heat to a heating section from an external source.

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[201] *TAEA7* p. 489

[202] *TAEA7* p. 491 and (with minor modification by MCM to match *TAEA7* p. 491, http://beyondthisbriefanomaly.org/2012/04/26/accounting-for-a-most-dynamic-universe-part-3/

[203] *TAEA7* p. 492 and http://www.engineersedge.com/thermodynamics.htm

- The exhaust process is replaced by a heat rejection process to an external sink that restores the working fluid to its initial state. The combustion products are also replaced by air.
- If in addition it is also assumed that air has constant specific heats determined at a room T =25 °C, the air-standard assumptions are further called the **cold-air-standard assumptions** adds that .

Otto Cycle

This is the idealized cycle for spark-ignition internal combustion (SI IC) reciprocating engines (used in automobiles, lawn mowers, etc.) The typical larger SI IC engine, such as is found in autos, has a four-process cycle named after Nikolaus A. Otto (1832-1891). The term *Otto Cycle* appears to be applied to the ideal cycle as well as to real actual approximations of the ideal cycle. Otto cycle engines, like many of the other power cycle engine types in this summary, are a highly diverse and mature technology, and here I describe only the thermodynamic basics plus a few interesting details.

Four Stroke Otto Cycle Engine

A **four-stroke engine** (also known as a "**four cycle**" engine) is an internal combustion (IC) engine in which the piston completes four separate strokes while turning a crankshaft through 2 complete rotations. A **stroke** refers to the full travel of the piston along the cylinder in one of the two reciprocal directions. The four separate strokes are termed and described as follows:[204]

1. **Intake stroke**: This stroke of the piston begins at **top dead center** (**T.D.C. or TDC**) and ends at **bottom dead center** (**B.D.C. or BDC**). In this stroke, the intake valve must be in the open position while the piston pulls an air-fuel mixture into the cylinder by producing below-atmospheric (vacuum) pressure inside the cylinder through its downward motion.
2. **Compression stroke**: This stroke begins at BDC, or just at the end of the suction stroke, and ends at TDC. In this stroke the piston compresses the air-fuel mixture in preparation for ignition during the next stroke. Both the intake and exhaust valves are closed during this stage.
3. **Combustion, Expansion, or Power stroke**: This is the start of the second revolution of the four stroke cycle. At this point the crankshaft has completed a full 360 degree revolution. While the piston is at or close to TDC (at the end of the compression stroke), the compressed air-fuel mixture is ignited by a spark plug (in a gasoline engine) or by heat generated by high compression (diesel engines). The hot combustion gases expand and forcefully return the piston to BDC. This stroke is the one and only stroke which produces mechanical work from the engine to turn the crankshaft.
4. **Exhaust stroke**: During the exhaust stroke, the piston once again returns from BDC. to TDC while the exhaust valve is open. This action expels the spent air-fuel mixture through the exhaust valve.

The linear distance between TDC and BDC is the **stroke** and the diameter of the piston is the **bore**. At TDC, the residual gas space in the combustion chamber is called the **clearance volume**. The volume added in moving from TDC to BDC (the volume of a cylinder defined by the stroke height and bore diameter) is the **displacement volume**. The **compression ratio r** is a volume ratio > 1 (e.g., 8:1) defined as

$$r = V_{max} / V_{min} = V_{BDC}/V_{TDC} = \text{(clearance volume + displacement)/(clearance volume)}$$

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[204] https://en.wikipedia.org/wiki/Four-stroke_engine , text paraphrased & modified by MCM

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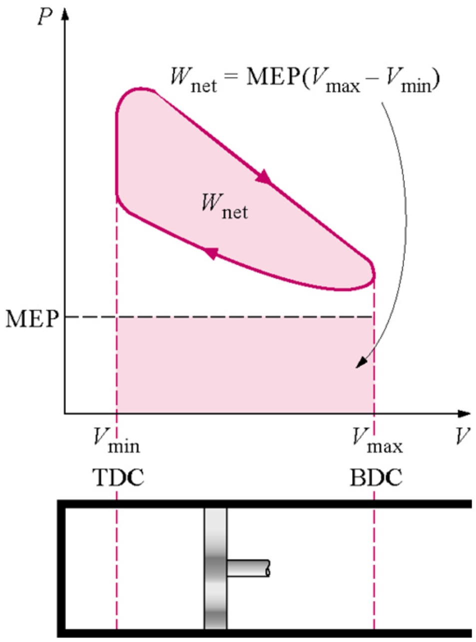
Mean Effective Pressure MEP

The **Mean Effective Pressure MEP** is a fictitious Otto cycle pressure reflecting the concept that Work = P ΔV. "The mean effective pressure (MEP) is a fictitious pressure that, if it operated on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle."[205] Therefore,



$$\begin{aligned} W_{net} &= P_{MEP}\,\Delta V \\ &= MEP \times \text{Piston area} \times \text{Stroke} \\ &= MEP \times \text{Displacement} \end{aligned}$$

or equivalently

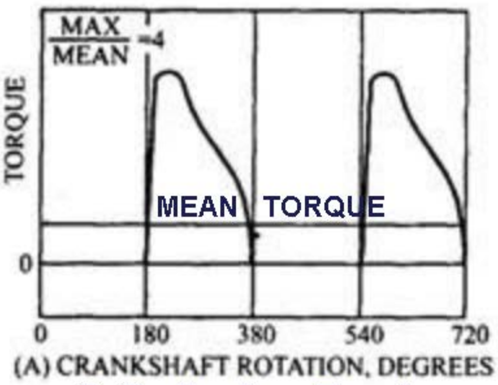
$$MEP = \frac{W_{net}}{\text{Displacement}} = \frac{W_{net}}{V_{max}-V_{min}} = \frac{w_{net}}{v_{max}-v_{min}}$$

Increasing MEP increases net work performed when displacement is unchanged.

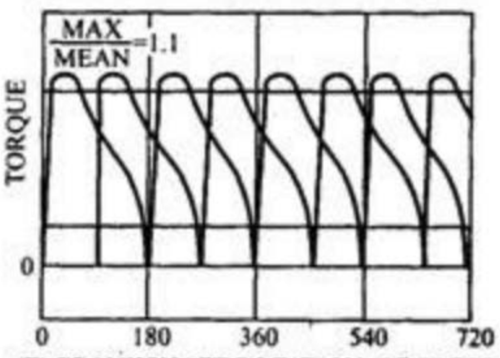
Real Otto Cycle Engines

The color diagram on the next page depicts a Four Stroke ("Four cycle") reciprocating internal combustion engine for which the ideal is the Otto Cycle.[206] The reciprocation of the piston up and down causes and in turn is caused by the rotation of the crankshaft (located below the piston in that diagram, typical of *straight* or *inline* engines such as the "straight six").

For multi-cylinder engines such as the straight-6, V-6, V-8, etc., the pistons fire in a logical and tightly controlled sequence so that the power strokes are evenly spread out in a phased manner and the crankshaft receives more nearly uniform torque. For instance, in a 2-cylinder engine lower left), the ratio of maximum torque (peak of curve) to mean torque (horizontal line near but above 0 torque line) is 4 to 1, whereas for an 8-cylinder engine (lower right), the ratio of maximum torque to mean torque is only 1.1 to 1.[207]



2 Cylinder Engine



8 Cylinder Engine

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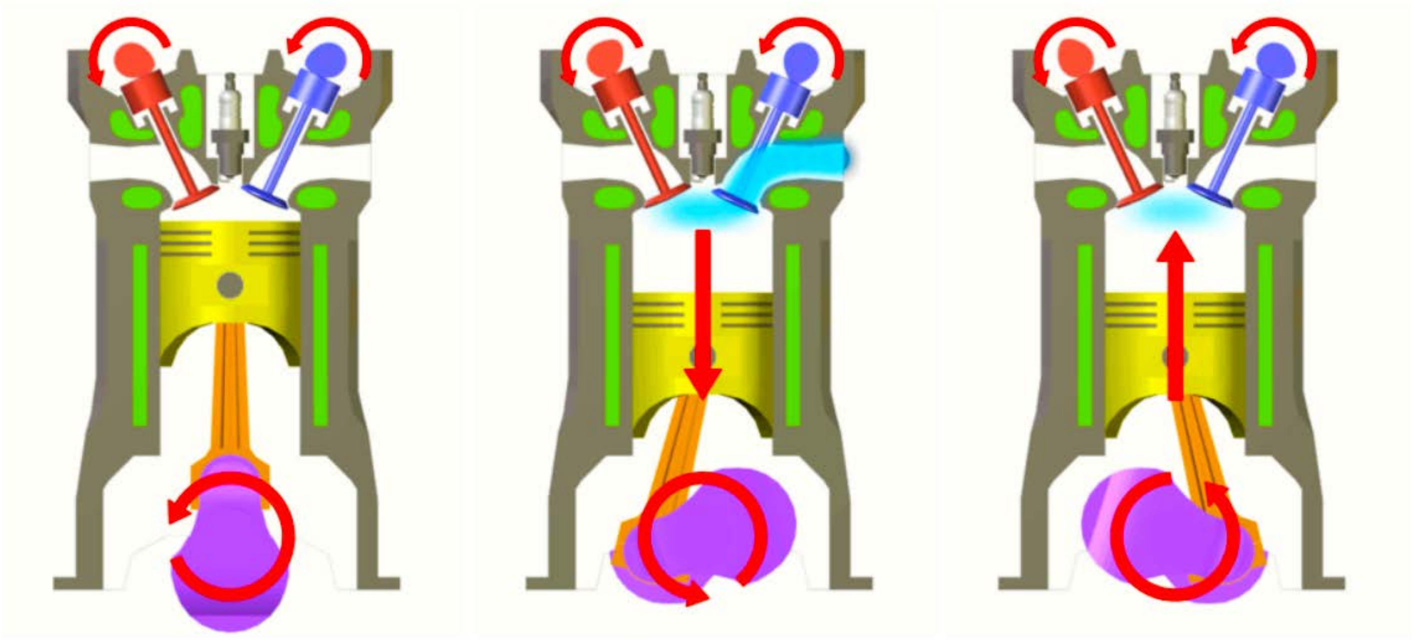
[205] *TAEA7* Chapter_09.ppt

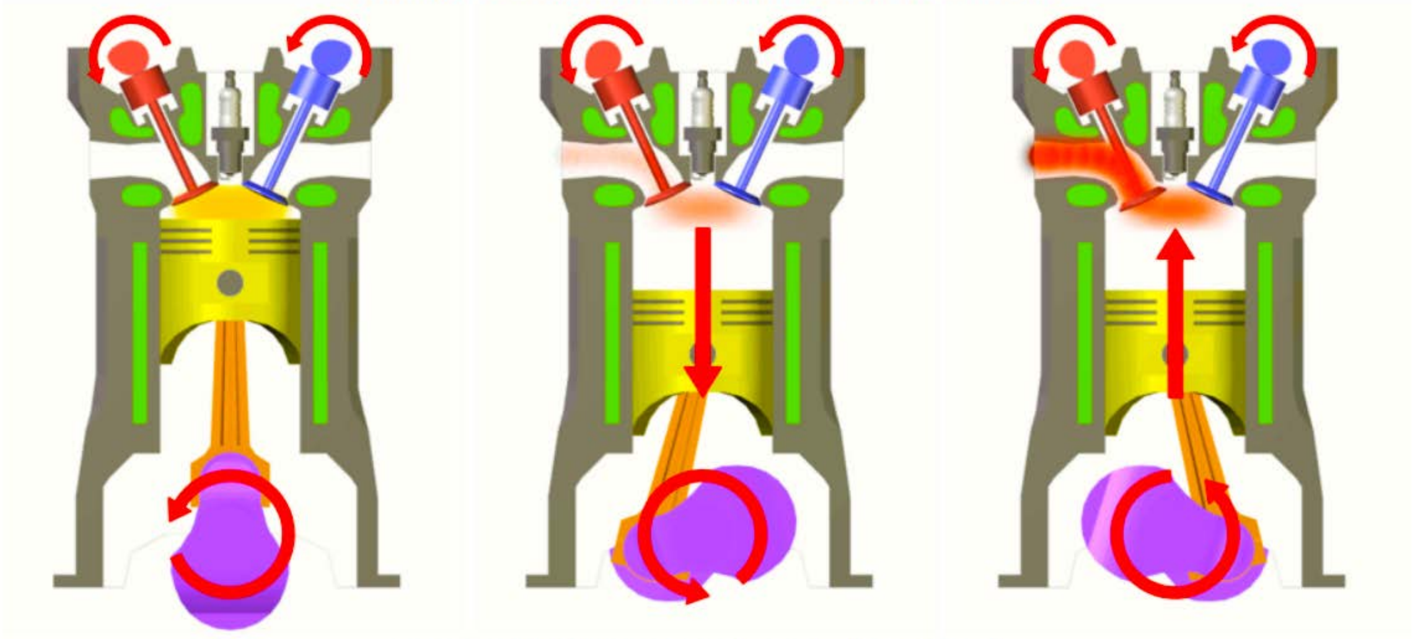
[206] https://en.wikipedia.org/wiki/Four-stroke_engine , image enhanced slightly by MCM

[207] http://what-when-how.com/automobile/multi-cylinder-engines-automobile/ , image adapted by MCM

In the following depiction of a real Otto cycle engine sequence, the crankshaft rotates 720° to complete the 4-process cycle. The *overhead cam shafts* also rotate and produce periodical opening and closing of the intake and exhaust valves. Air/Fuel mixture enters the combustion chamber (blue) and hot exhaust later exits (red).



Starting position, intake stroke, and compression stroke.



Ignition of fuel, power stroke, and exhaust stroke.

Four Stroke ("Four cycle") reciprocating IC engine for which the ideal is the Otto Cycle

In the following P-v diagrams,[208] the actual P-v diagram (upper half) for a real four stroke spark ignition engine is compared to that of the air-standard ideal Otto cycle (lower half). The ideal Otto cycle consists of Isentropic

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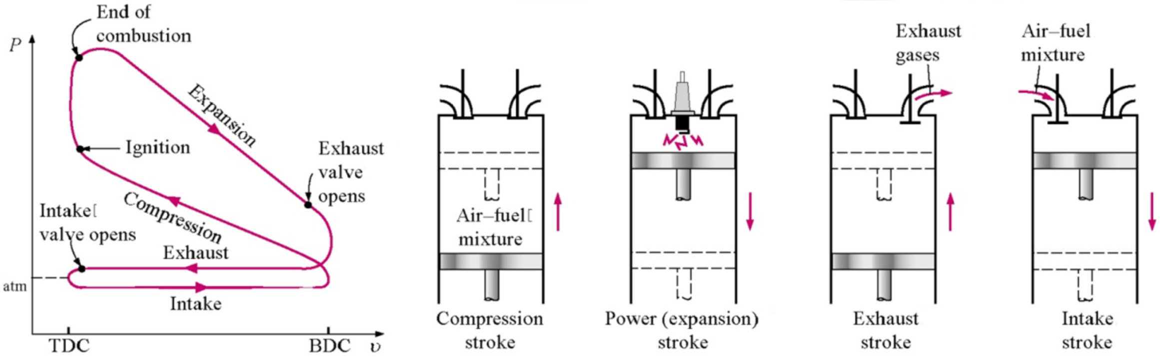
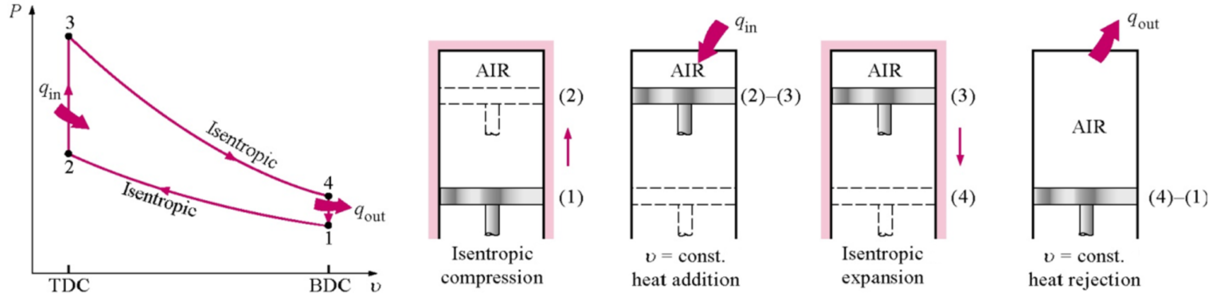
[208] *TAEA7* Chapter_09.ppt, slightly modified MCM

compression (the compression stroke), Heat addition (at constant volume, replacing the combustion process), Isentropic expansion, and Heat rejection (at constant volume, replacing the exhaust stroke).

For the actual cycle, exhaust pressure is slightly above ambient pressure P_{atm} and intake pressure is slightly below ambient pressure. It can be seen that the area enclosed in the actual cycle P-v process curve resembles that of the ideal Otto process curve.



(*a*) Actual four-stroke spark-ignition engine



The air-standard Otto cycle is the ideal cycle that approximates the spark-ignition combustion engine.

Process	Description
1-2	Isentropic compression
2-3	Constant volume heat addition
3-4	Isentropic expansion
4-1	Constant volume heat rejection

There are also **two-stroke ("two-cycle") engines**,[209] which have been extensively used in lawn mowers and other small SI IC engines, but they have generally been more inefficient and more polluting. Their efficiency can be improved by direct fuel injection, stratified charge combustion, and electronic controls.[210] A 2-stroke SI IC engine was first designed in 1878 and patented in 1881 by Dugald Clerk.[211]

Otto Cycle Efficiency (Ideal and Actual)

The ideal Otto cycle efficiency is calculated as

$$\eta_{th,Otto} = 1 - \left({}^{1}/_{r^{k-1}}\right)$$

where r = compression ratio
k = c_p/c_v for air at room T

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[209] https://en.wikipedia.org/wiki/Two-stroke_engine

[210] *TAEA7 p. 495*

[211] https://en.wikipedia.org/wiki/Dugald_Clerk and https://en.wikipedia.org/wiki/History_of_the_internal_combustion_engine

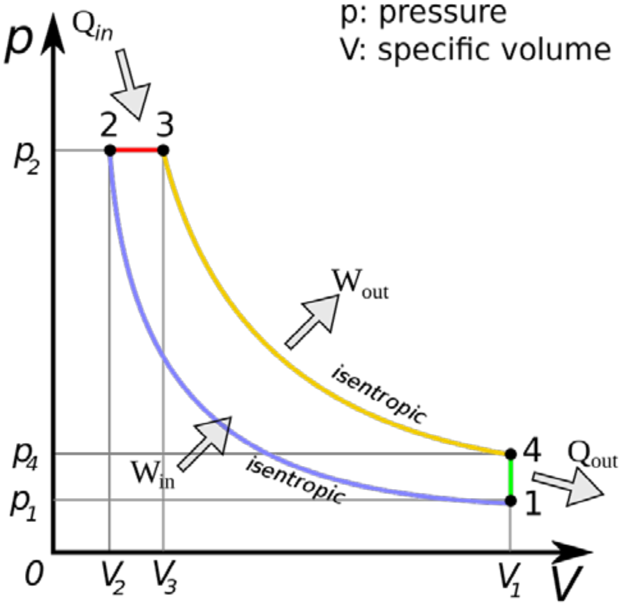
Clearly, the efficiency of the ideal Otto cycle increases by making r larger and/or by increasing k. The value of k increases for air compared to CO_2 and other larger molecules like ethane and octane, but falls as T rises.

The ideal cycle efficiency behaviors are also seen with actual four-cycle engines, so that real engines designs can attempt to improve efficiency by optimization or r and/or k. The value of r for SI IC engines can be increased (from a baseline value of about 6 to 10) to up to about 12 or 13[212] by increasing the compression ratio. However, high r requires gasoline of higher **octane** rating (which is more expensive to produce, and for many years contained polluting tetraethyl lead)—this is needed to prevent **premature autoignition** (**engine knocking**). The engine components including pistons, cylinders, valves, and bearings must also be made stronger to withstand higher r.

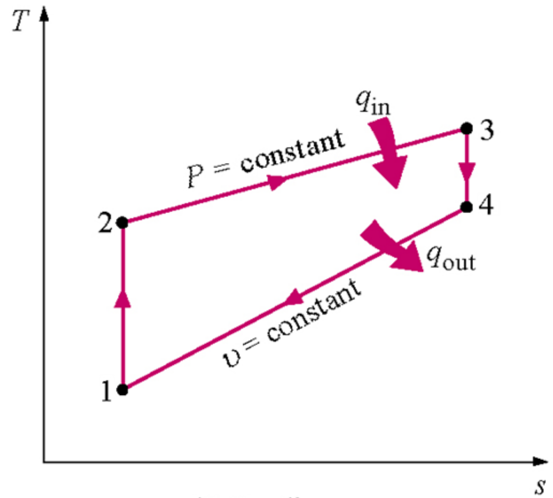
For actual spark-ignition four stroke engines, the actual average thermal efficiency achieved is only η_{th} ≈ 25% to 30% compared to theoretical values for ideal Otto engines of around 52% to 60% (when k = 1.4).

Diesel Cycle

This is the idealized cycle for actual 4-stroke compression ignition internal combustion engines (CI IC engines), and actual CI IC engines are described as operating on the Diesel Cycle. These were first developed by Rudolph Diesel in the 1880s and 1890s.[213] These engines are similar to SI IC engines. However, fuel is injected near TDC at a point where high compression has already raised the T above the autoignition temperature. Thus the fuel air mixture spontaneously ignites and burns as further fuel is injected.



Ideal Diesel Cycle



(b) T-s diagram

Ideal Diesel Cycle

In the ideal Diesel cycle (diagrams immediately above), "The p–V diagram is a simplified and idealized representation of the events involved in a Diesel engine cycle, arranged to illustrate the similarity with a Carnot cycle. Starting at 1, the piston [at V_1] is at bottom dead center and both valves are closed at the start of the compression stroke; the cylinder contains air at atmospheric pressure. Between 1 and 2 the air is compressed adiabatically (isentropically)… by the rising piston. (This is only approximately true since there

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[212] https://en.wikipedia.org/wiki/Compression_ratio

[213] http://www.autoblog.com/2015/10/06/diesel-engine-history-feature/ and https://en.wikipedia.org/wiki/Diesel_engine

will be some heat exchange with the cylinder walls.) During this compression, the volume is reduced [to V_2], the pressure and temperature both rise. At or slightly before 2 (TDC) fuel is injected and burns in the compressed hot air. Chemical energy is released and this constitutes an injection of thermal energy (heat) into the compressed gas. Combustion and heating occur between 2 and 3. In this interval the pressure remains constant since the piston descends, and the volume increases [producing $work_{out}$]; the temperature rises as a consequence of the energy of combustion. At 3 fuel injection and combustion are complete, and the cylinder contains gas at a higher temperature than at 2. Between 3 and 4 this hot gas expands, again approximately adiabatically [and isentropically]. [$Work_{out}$] is done on the system to which the engine is connected [during 3-4]. During this expansion phase the volume of the gas rises [from V_3 to V_4], and its temperature and pressure both fall. At 4 the exhaust valve opens, and the pressure falls abruptly to atmospheric (approximately). This is unresisted expansion and no useful work is done by it. Ideally the adiabatic expansion should continue, extending the line 3–4 to the right until the pressure falls to that of the surrounding air, but the loss of efficiency caused by this unresisted expansion is justified by the practical difficulties involved in recovering it (the engine would have to be much larger).

After the opening of the exhaust valve, the exhaust stroke follows, but this (and the following induction stroke) are not shown on the diagram. If shown, they would be represented by a low-pressure loop at the bottom of the diagram [similar to the actual Otto Cycle above].

At 1 it is assumed that the exhaust and induction strokes have been completed, and the cylinder is again filled with air. The piston-cylinder system absorbs energy [$work_{in}$] between 1 and 2—this is the work needed to compress the air in the cylinder, and is provided by mechanical kinetic energy stored in the flywheel of the engine. Work output [$work_{out}$] is done by the piston-cylinder combination between 2 and 4. The difference between these two increments of work [$work_{out} - work_{in}$] is the indicated work output per cycle [$work_{net,out}$], and is represented by the area enclosed by the p–V loop. The adiabatic expansion [3-4] is in a higher pressure range than that of the compression [1-2] because the gas in the cylinder is hotter during expansion than during compression. It is for this reason that the loop has a finite area, and the net output of work during a cycle is positive.[214]

The T-s diagram[215] for the ideal Diesel cycle is also shown, making clear that 1-2 and 3-4 are isentropic adiabatic processes.

There is also a two-stroke version of the Diesel engine, but I have not studied these.

Diesel Cycle Efficiency (Ideal and Actual)

The ideal Diesel cycle thermal efficiency under cold air standard assumptions is calculated as:

$$\eta_{th,Diesel} = 1 - \left(\frac{1}{r^{k-1}}\right)\left[\frac{(r_c)^k - 1}{k(r_c - 1)}\right]$$

where r = compression ratio,
r_c = cutoff ratio ($r_c = V_3/V_2 = v_3/v_2$)
$k = c_p/c_v$ for air at room T.

The quantity in the square brackets is always > 1. Thus, comparing with the ideal Otto cycle, $\eta_{th,Otto}$ is always greater than $\eta_{th,Diesel}$ for the same values of r and k. However, the much higher compression ratios possible in diesel engines (with r range of approximately $12 \le r \le 23$) substantially improve ideal and actual diesel engine efficiency.

As with the Otto cycle, thermal efficiency also improves with rising k and rising r_c. Real engines improve in efficiency also by relatively slow, more complete combustion, and higher air/fuel mass ratio. Fuels for diesel engines need not be as highly refined as for SI IC engines.

In actual diesel engines, efficiency and fuel consumption (thus mileage) is improved over SI IC engines, with large diesel engines having

$$\eta_{th,Diesel} = 35 \text{ to } 40\%\text{, compared to } \eta_{th,Otto} = 25 \text{ to } 30\%$$

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[214] https://en.wikipedia.org/wiki/Diesel_engine text and P-v graphic

[215] *TAEA7* Chapter_09.ppt

Diesel Cycle Engine Advantages and Disadvantages Compared to Otto Cycle Engines

Advantages

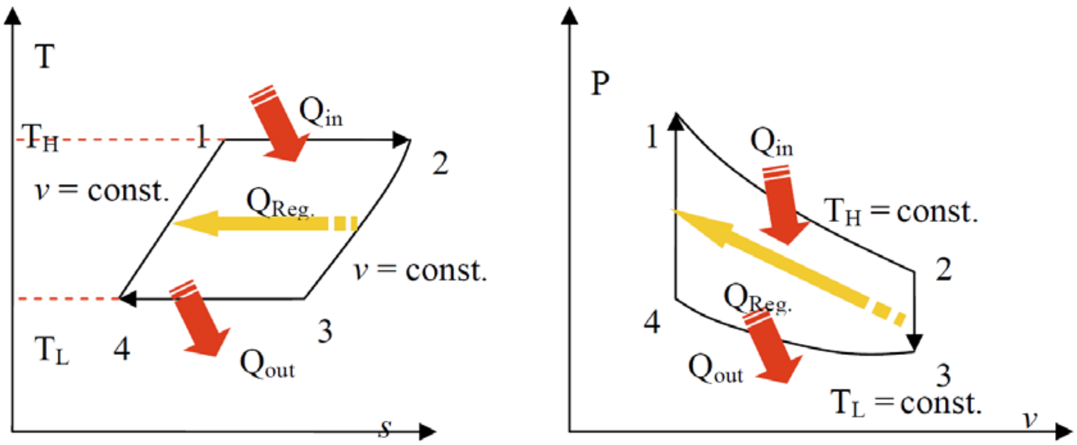
Have higher actual efficiency than Otto cycle (see above)
Scalable to very large size and power output
No high voltage electrical ignition system (improving reliability)
Increased longevity and durability
Fuel is inherently lubricating
Can run on renewable biodiesel fuel
Can accept super-charging or turbo-charging pressures
Generate relatively low CO_2 and CO emissions.

Disadvantages

Must be more rugged to withstand higher compression, thus heavier and more costly to build
More noisy (producing diesel "clatter")
Fuel is no longer cheaper than gasoline
Produce smelly exhaust laden with toxic air contaminants[216] including aerosols of soot and other particles, polycyclic aromatic hydrocarbons (PAHs), various other carcinogens, and greater NO_x.

Stirling and Ericsson Cycles

These are ideal cycles for external combustion engines that incorporate a **regenerator** used to transiently store and release thermal energy. Both incorporate isothermal processes (1 to 2 and 3 to 4), but for (2 to 3 and 4 to 1), the Stirling cycle has isovolumetric processes whereas the similar Ericsson cycle has isobaric processes. Actual implementations have in practice been complex and impractical, but there is rising interest in these cycles because of high thermal efficiency and potential for better emission control.[217]



T-s and P-v diagrams for Stirling cycle.

(Regeneration is shown here as heat flow from the higher volume higher entropy process to the lower volume process.)[218]

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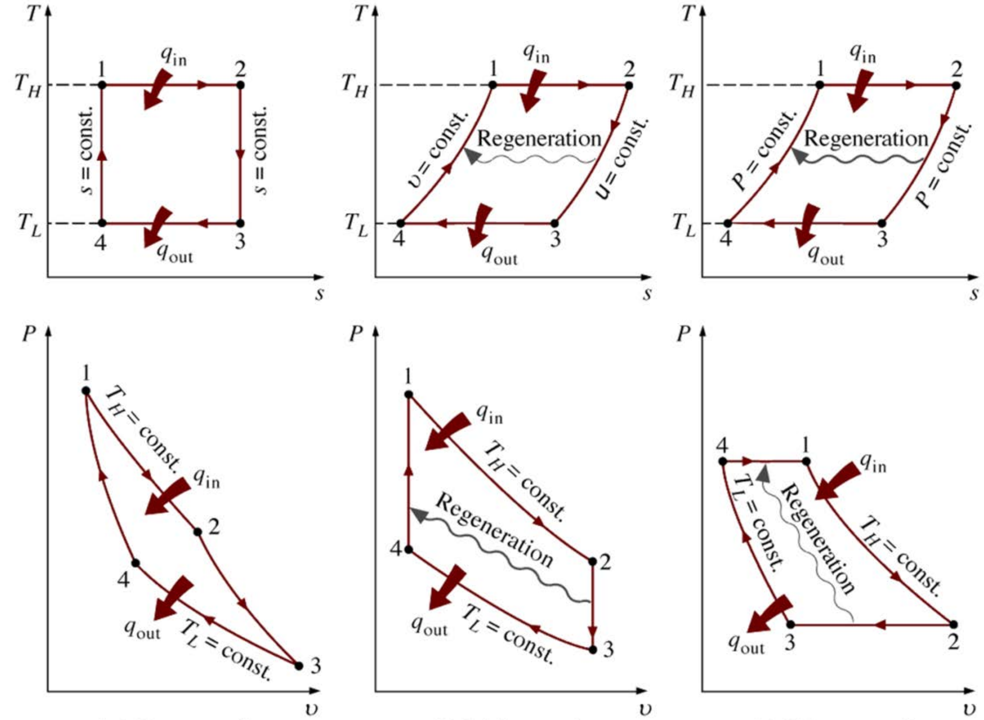
[216] https://en.wikipedia.org/wiki/Diesel_exhaust#Chemical_components and http://www.dummies.com/how-to/content/the-pros-and-cons-of-diesel-engines.html

[217] *TAEA7* p. 507

[218] *Stirling Cycle PDF* by M. Bahrami

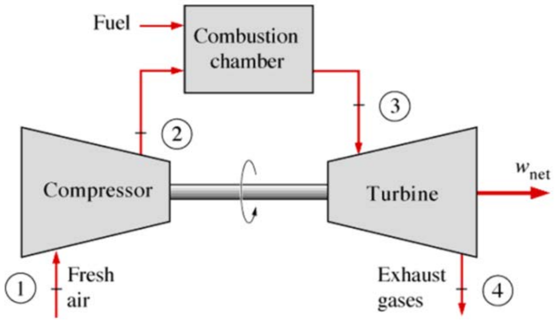


(*a*) Carnot cycle (*b*) Stirling cycle (*c*) Ericsson cycle

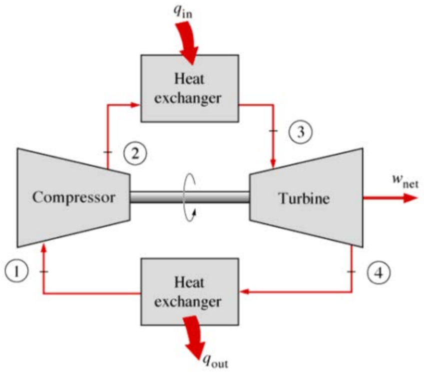
T-s and P-v diagrams comparing Carnot (left), Stirling (middle), and Ericsson (right) ideal cycles[219]

Brayton Cycle (Gas Turbine) Engines

The Brayton cycle is the idealized cycle for gas turbine engines. Most actual Brayton cycle engines are open cycle. Hot gases from a combustion chamber turn the turbine, which produces shaft power to the compressor and net shaft work out. In an open cycle, the gas exiting the turbine is vented as exhaust to air. In the idealized closed model Brayton cycle using air-standard assumptions, the combustion process is replaced with a constant pressure heat addition process from an external source. (The 5 diagrams are from here.[220])



Brayton Open Cycle



Brayton Closed Cycle

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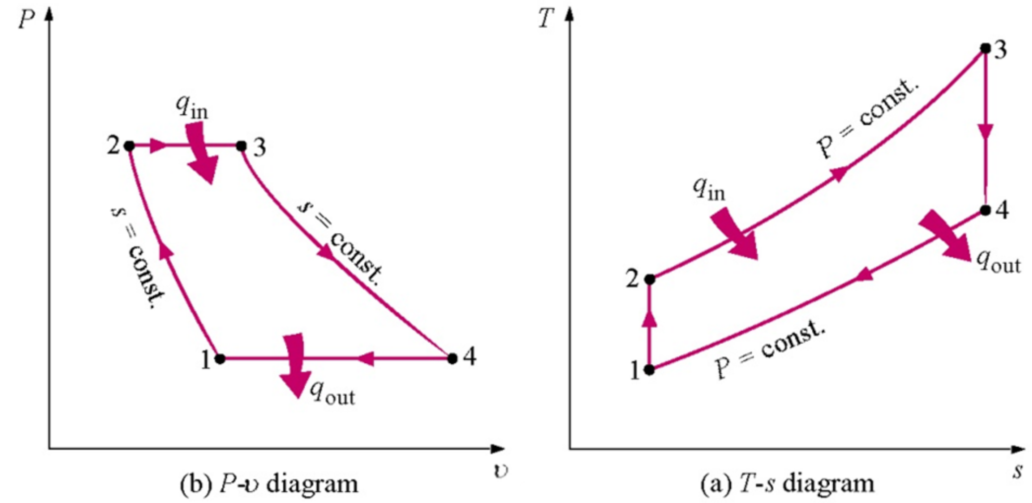
[219] http://www.mhhe.com/engcs/mech/cengel/thermodead/graphics/ppt/pptsource/CHPT08.PPT and https://en.wikipedia.org/wiki/Ericsson_cycle

[220] http://www.mhhe.com/engcs/mech/cengel/thermodead/graphics/ppt/pptsource/CHPT08.PPT , modified MCM



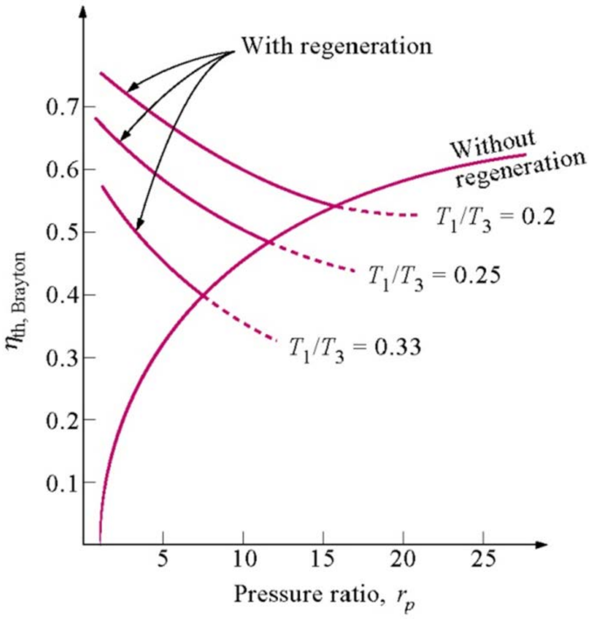
(b) P-v diagram

(a) T-s diagram

Ideal Brayton Closed Cycle: P-v and T-s diagrams

The T-s and P-v diagrams for the Closed Brayton Cycle

Process	Description
1-2	Isentropic compression (in a compressor)
2-3	Constant pressure heat addition
3-4	Isentropic expansion (in a turbine)
4-1	Constant pressure heat rejection



Brayton cycle thermal efficiency, showing effect of pressure ratio r_p, regeneration, and minimum T_1 to maximum T_3 ratios[221]

Basic Brayton Cycle Efficiency (Ideal and Actual)

The thermal efficiency for the ideal Brayton cycle is

$$\eta_{th,Brayton} = 1 - \left(\frac{1}{r_p^{(k-1)k}}\right)$$

where r_p = pressure ratio P_2/P_1
k = specific heat ratio c_p/c_v (apparently for air at room T).

For the ideal cycle as well as for actual gas turbines, thermal efficiency increases for increasing r_p and also for increasing k. Typical values of r_p are $5 \le r_p \le 20$, with most common values of $11 \le r_p \le 16$, the actual design value being selected to optimize $work_{net,out}$.[222]

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[221] *TAEA7* Chapter_09.ppt

The highest temperature attained is state 3, and this is limited by the tolerance of the materials. Gas turbines in power plants operate at a T_{max} of over 1425 °C, which improves thermal efficiency compared to the T_{max} of 620 °C for steam turbines. Unlike steam power plants pumping primarily liquid water (and for which work needed for the pump, called back work, is relatively low), gas turbines consume more than 50% of the turbine $work_{out}$ in compressing the gaseous medium (step 1-2).

The thermal efficiency of the simple ideal Brayton cycle, calculated in a text example[223] using air-standard assumptions, is found to be 43%.

Improving Brayton Cycle Efficiency with Reheating, Regeneration, and Intercooling

By adding
Two-stage Compression with Intercooling, plus
Reheater stage (between the HP and LP turbines), plus
Regeneration (in which some of the hot turbine heats the combustible gases
prior to entering the combustion chamber),
the textbook example 9-8 shows an increase of ideal thermal efficiency to 70% (compared to 43% without these additions).

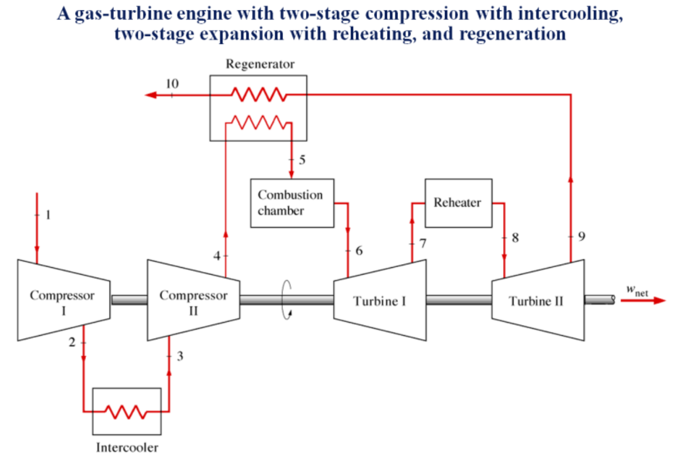
The extent to which an actual regenerator approaches an ideal regenerator is called the **regenerator effectiveness ε**, defined as

$$\in = \frac{q_{regen,actual}}{q_{regen,max.}} = \frac{h_5 - h_{2a}}{h_{4a} - h_{2a}} \approx \frac{T_5 - T_2}{T_4 - T_2}$$

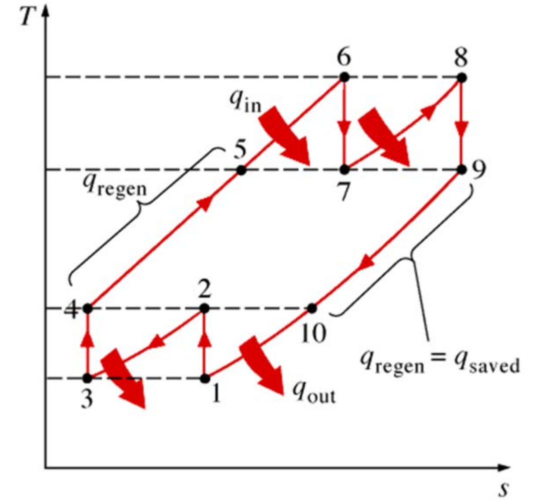
where state 1 is ideal
states 2a and 4a are states of an actual engine rather that isentropic endpoints.

Higher efficiency regenerators can save a great deal of fuel. Most regenerators have ε < 85%.

Actual gas turbines attain thermal efficiencies of > 40% with simple cycle operation, and in **combined cycle** installations [e.g., Brayton gas cycle plus Rankine steam cycle], their **efficiencies can be > 60%** (see examples to follow).[224] In the left diagram that follows, a shaft is depicted which connects the two turbines to the 2 compressors for provision of $work_{in}$ to the compressors from the turbines.



Ideal Brayton cycle with 2-stage compression with intercooling, a reheater stage between turbines, and regeneration[225]



T-s diagram for the Brayton cycle shown to the left

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[222] *TAEA7* p. 509 including fig. 9-33

[223] *TAEA7* p. 511 to 520

[224] https://www.asme.org/engineering-topics/articles/energy/a-new-era-for-natural-gas-turbines &
https://powergen.gepower.com/products/heavy-duty-gas-turbines.html

[225] http://www.mhhe.com/engcs/mech/cengel/thermodead/graphics/ppt/pptsource/CHPT08.PPT, modified MCM

Advantages and Disadvantages of Gas Turbine Engines Over Otto and Diesel Engines[226]

Advantages

very high power to weight ratio
higher power to size ratio
low vibration (because non-reciprocating, single direction of rotation)
fewer moving parts
greater reliability (especially for sustained high power generation)
longer life
high T waste heat in exhaust (useful for combined cycle use or cogeneration)
lower operating P
high operational speed
fuel versatility
low lubricating oil cost and consumption
low emissions of CO and HC
convenient operation with rapid startup compared to steam.

Disadvantages

Higher cost
Less efficient at idle
Longer startup time
Less responsive to changes in power demand
Characteristic whine
Higher NO_x produced at higher temperatures

Applications of Brayton Cycle (Gas Turbine) Engines

Gas turbines are in common use for ships and naval vessels, locomotives, tanks, aircraft (as jet and turboprop propulsion engines, see below), and electric power generation including in nuclear power plants. They even had a brief fling with auto racing in the 1960s, but they were throttled down by the USAC in 1967 and outright banned from the Indianapolis 500 and from other USAC racing venues around 1968.[227]

In ships and power plants, they are often paired with a diesel engine—the diesel supplies efficient steady but lower power (for cruising etc.) while the gas turbine kicks in to provides bursts of higher energy when high speeds are called for. They are so far more expensive than piston engines (for which startup is also faster), and are not as responsive or efficient.[228]

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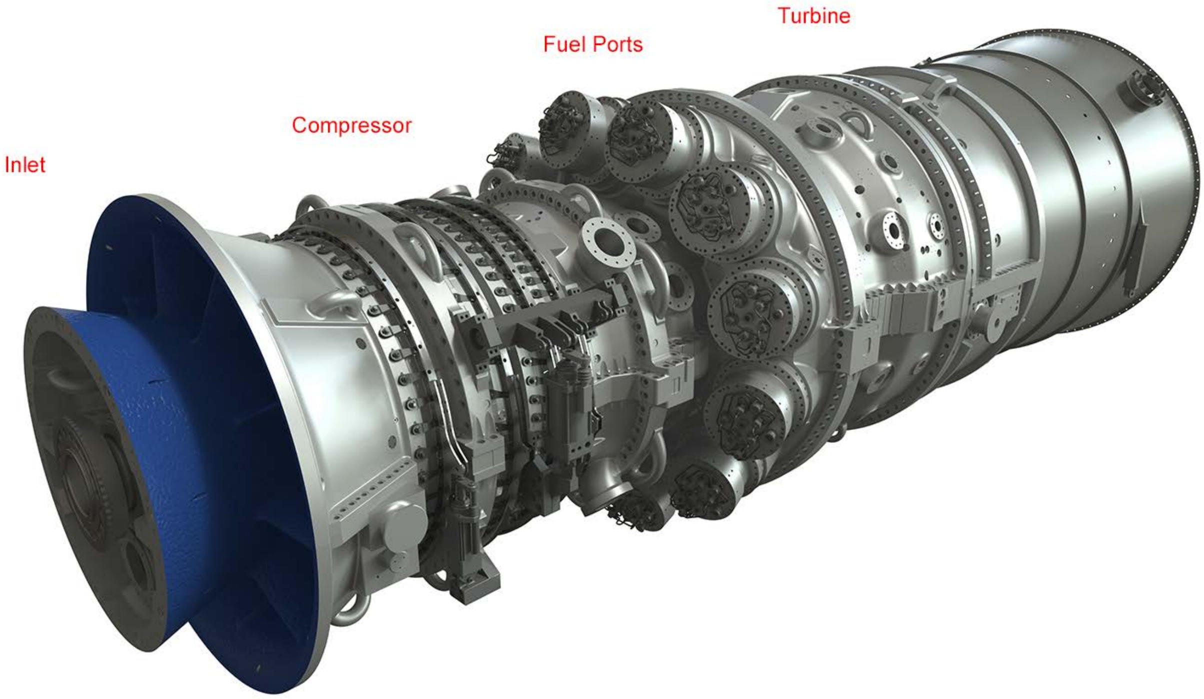
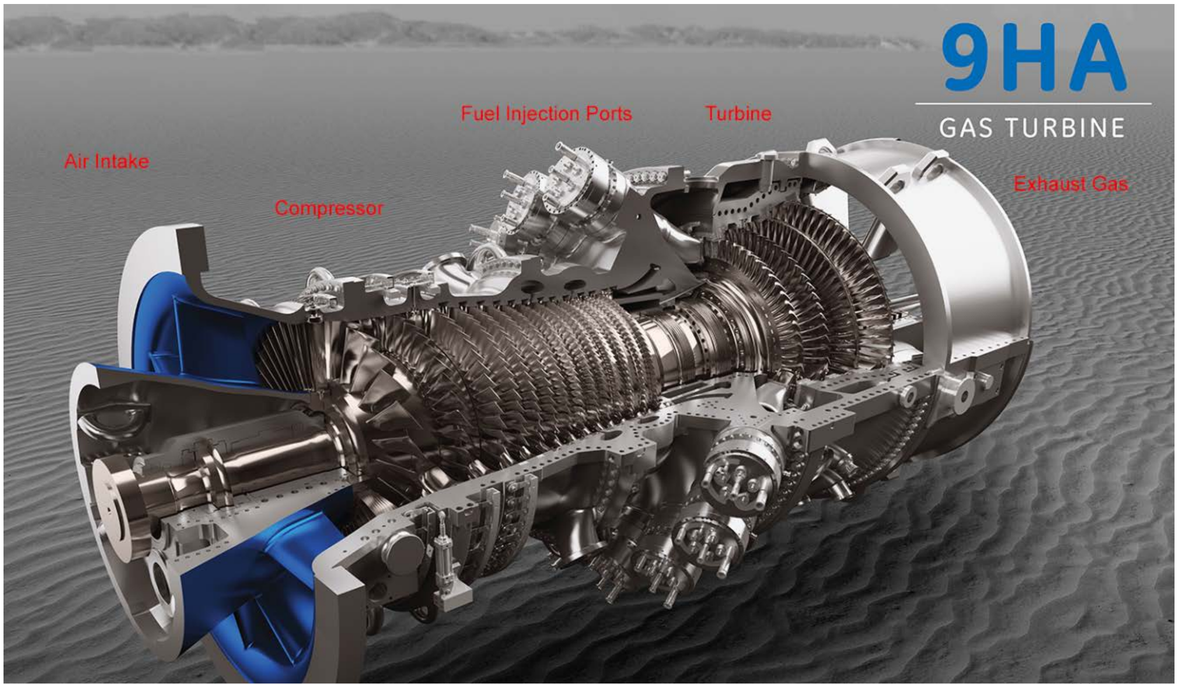
[226] https://en.wikipedia.org/wiki/Gas_turbine
[227] http://www.hotrod.com/features/1506-turbine-cars-past-present-future/ and
http://www.wired.com/2014/10/lotus-turbine-racecar/
[228] https://en.wikipedia.org/wiki/Gas_turbine



GE 7HA Gas Turbine with exterior shells intact[229]



GE 9HA series air-cooled Gas Turbine with shell partly removed, air flows from left to right.[230]

"In simple cycle configuration, the 9HA.01 [50 Hz] is rated 397 MW and the 9HA.02 is rated 470 MW, each at 3000 rpm, offering > 41% [thermal] efficiency. In combined cycle configuration, the 9HA.01 is rated 592 MW and the 9HA.02 is rated 701 MW, each at 3000 rpm, offering >61% efficiency.

In simple cycle configuration, the 7HA.01 [60 Hz] is rated 275 MW and the7HA.02 is rated 330 MW, each at 3600 rpm, offering > 41% efficiency. In combined cycle configuration, the 7HA.01 is rated 813 MW and the 7HA.02 is rated 976 MW, each at 3600 rpm, offering >61% efficiency."

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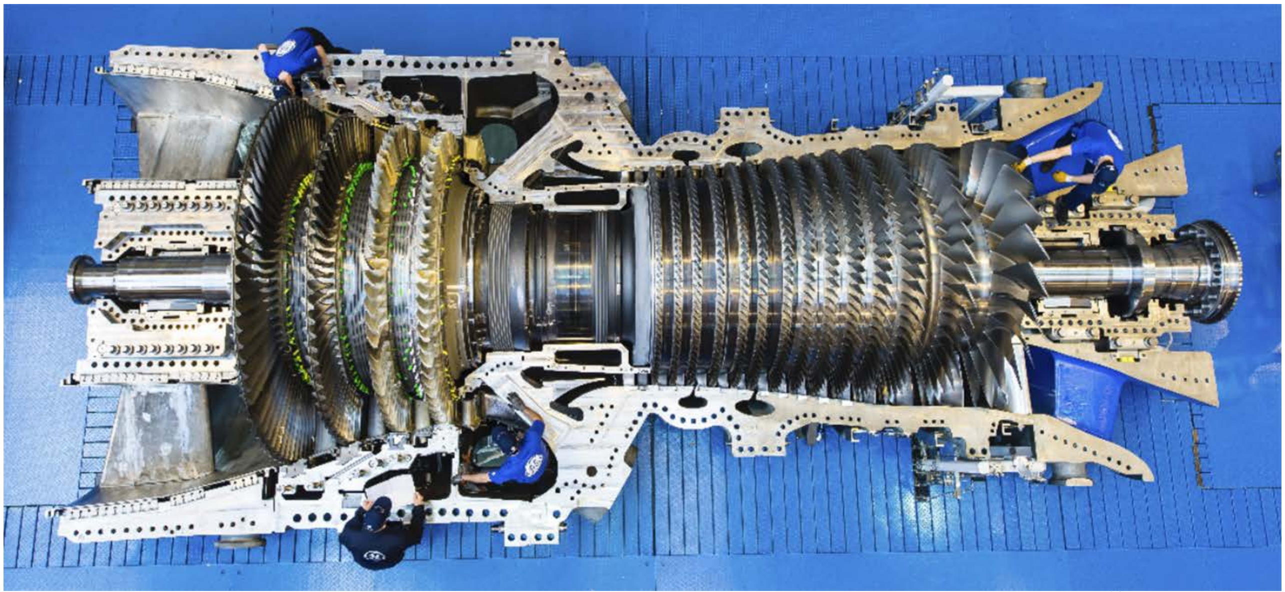
[229] http://mms.businesswire.com/media/20140929006202/en/433956/5/7HA_new.jpg

[230] https://powergen.gepower.com/content/dam/gepower-pgdp/global/en_US/documents/product/gas%20turbines/Posters/9ha-poster-jun15.pdf including image edited and annotated by MCM



GE Gas Turbine 7HA or 9HA series, with half shell removed; air flows from right to left.[231]

Jet Propulsion Cycles

I have briefly reviewed some of the technology of jet and rocket propulsion, but the subject warrants much more study than I have given it. I consider some of the quantitative aspects of thrust and propulsion presented here to be somewhat ambiguous and in need of clarification and refinement.

Turbojet Engine

The popular jet of the 1950s was the **turbojet**, a specialized gas turbine with no *fan* or *prop* (propeller). Unlike the open Brayton cycle, in the ideal open jet propulsion cycle of jet engines, the exhaust gases do not expand to atmospheric pressure within the turbine [before passing through the nozzle]. "Instead, they are expanded to a pressure such that the power produced by the turbine is just sufficient to drive the compressor and auxiliary equipment…The net work output of a jet propulsion cycle is zero. [That is, turbine shaft work$_{\text{out}}$ is balanced by compressor and accessory shaft work$_{\text{in}}$.] The gases that exit the turbine at a relatively high pressure are subsequently accelerated in a nozzle to provide the thrust to propel the aircraft…"[232] Moreover, the air entering the diffuser in front is decelerated and pressure increased prior to entry into the compressor. The propulsion comes from an equal and opposite reaction to accelerating the fluid [air plus fuel] in the direction opposite to the aircraft motion. The air of low backward momentum entering the jet engine exits with a much greater backward momentum, and this change in momentum must be balanced by a forward thrust by Newton's 2nd law of motion. The text presents what appears to be a simplified analysis (see for example here[233] for more detailed analyses): Thrust force F is given by the change in momentum with time (simplified, see also here[234]):

$$\mathrm{F} = (\dot{\mathrm{m}}\mathrm{V})_{\text{exit}} - (\dot{\mathrm{m}}\mathrm{V})_{\text{inlet}} = \dot{\mathrm{m}}(\mathrm{V}_{\text{exit}} - \mathrm{V}_{\text{inlet}}) = \dot{\mathrm{m}}(\mathrm{V}_{\text{exit}} - \mathrm{V}_0) \qquad \text{(N)}$$

---

[231] http://www.dieselgasturbine.com/March-2014/GE-Goes-Air-Cooled-With-Its-H-Class/

[232] *TAEA7* p. 521

[233] http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node85.html and http://www.hq.nasa.gov/pao/History/SP-468/ch10-3.htm

[234] https://www.grc.nasa.gov/www/k-12/airplane/thrsteq.html and https://en.wikipedia.org/wiki/Jet_engine

where the V's are gas velocities relative to the engine (not the ground), and the last term applies when the velocity of the air intake = the true airspeed of the aircraft V_0. For still air, V_{inlet} is the aircraft forward velocity V_0 relative to ground. F is used to overcome drag forces including those associated with lift generation.

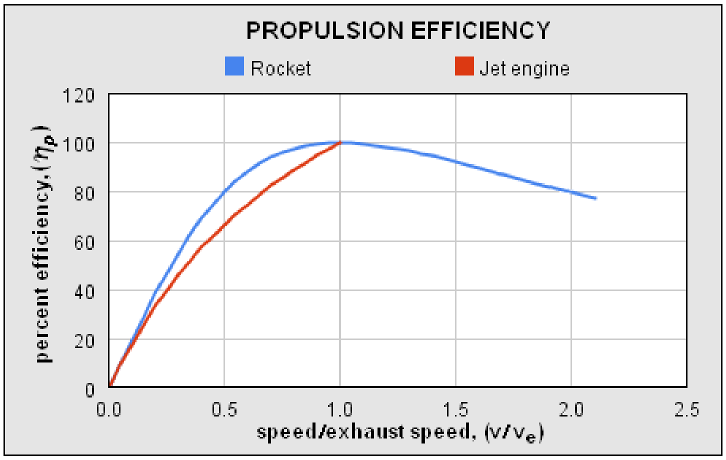
Although no net work is developed by the turbojet engine, the **propulsive power** is the force F multiplied by the distance per unit time over which this force acts, thus
propulsive power = propulsive force × aircraft ground velocity V_0 (as interpreted from textbook figure 9-49):

$$\dot{W}_p = \dot{m}(V_{exit} - V_{inlet})V_{aircraft} \qquad \text{(kW)}$$

The **propulsive efficiency η_p** of turbojet engines is defined in the textbook (p. 522) as

$$\eta_p = \frac{\text{Propulsive Power}}{\text{Energy Input Rate}} = \frac{\dot{W}_p}{\dot{Q}_{in}}$$

and an example is offered in which this quantity is calculated.



However, other sources provide the following formula for propulsive efficiency (symbols adjusted):[235]

$$\eta_p = \frac{2}{1+\frac{V_{exit}}{V_0}}$$

This formula assumes a somewhat different definition of η_p: "The propulsive efficiency is defined as the ratio of the useful power output (the product of thrust and flight velocity, V_0) to the total power output (rate of change of the kinetic energy of gases through the engine)."

Thus, propulsive efficiency is greatest when the jet engine exhaust exits at a speed (V_{exit}) as close as possible to the aircraft velocity V_0. The graph to the right depicts jet engine and rocket η_p. For jet engines, values of η_p range from about 0.2 to nearly 1.

In the ideal turbojet cycle, "the **thermal efficiency** [or **cycle efficiency**] is defined as the ratio of the net power out of the engine to the rate of thermal energy available from the fuel. According to the ideal turbojet engine cycle (see the PDF cited), the thermal efficiency simplifies to (symbols adjusted)

$$\eta_{thermal} = 1 - \frac{T_C}{T_H} = 1 - \frac{T_{\text{at engine inlet}}}{T_{\text{at combustion chamber exit}}}$$

Overall Efficiency (aka **Overall propulsive efficiency**) is given in several sources by

$$\boldsymbol{\eta_{overall} = \eta_p\, \eta_{thermal}}$$

and is therefore lower than the propulsive efficiency. Overall propulsive efficiency is defined as, "the efficiency, in percent, with which the energy contained in a vehicle's propellant is converted into useful energy, to replace losses due to aerodynamic drag, gravity, and acceleration."[236]

The textbook example 9-9 calculates a propulsive efficiency of 22.5%. I am unclear whether or not this is the *overall* efficiency. The remainder of energy input that does not provide propulsion goes into wasted KE in the exhaust gases, increased exhaust gas enthalpy h, and frictional and other losses.

The T-s diagram of the ideal turbojet cycle is shown below (this ideal cycle ignores frictional effects and other irreversibilities).

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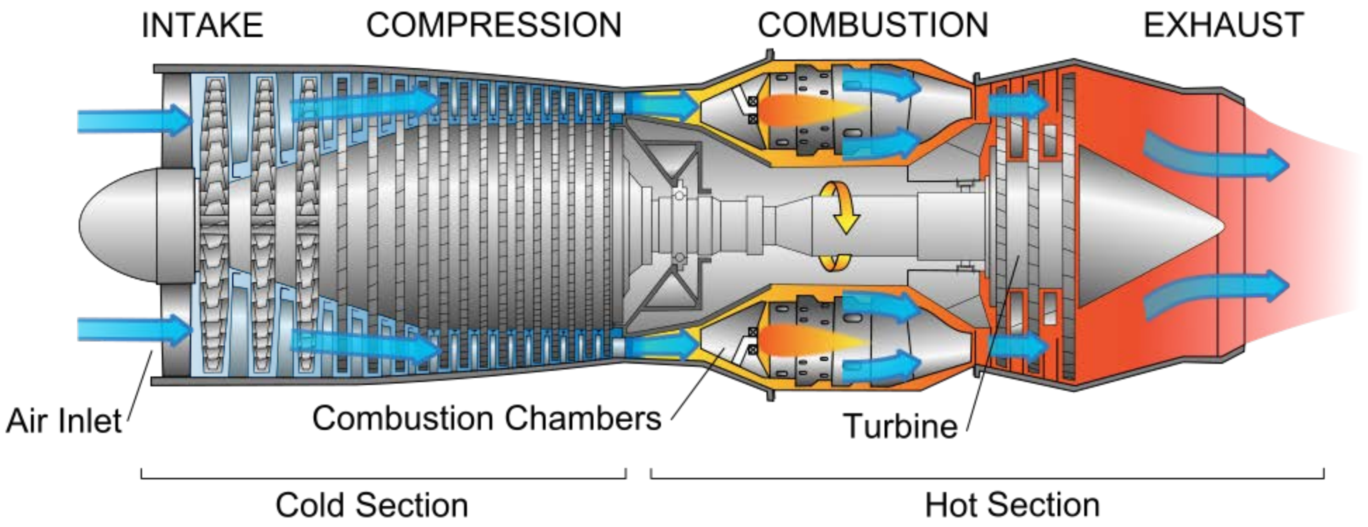
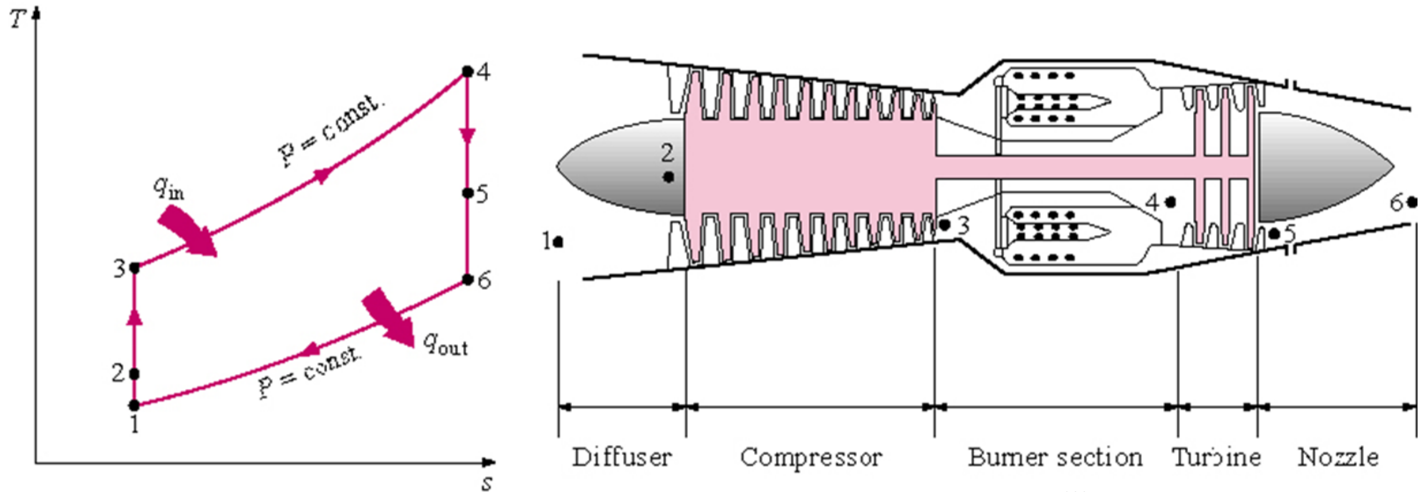
[235] https://en.wikipedia.org/wiki/Propulsive_efficiency formula and graph of propulsion efficiency, and http://www.ltas-cm3.ulg.ac.be/AERO0023-1/ConceptionMecaTurbomachine.pdf formula

[236] https://en.wikipedia.org/wiki/Propulsive_efficiency and http://www.ltas-cm3.ulg.ac.be/AERO0023-1/ConceptionMecaTurbomachine.pdf

1. Air entering the diffuser starts at position 1.
2. In the diffuser, P and T have risen isentropically to state 2 at the front of the compressor.
3. The compressor significantly and isentropically raises P and T to state 3.
4. After the air mixes with fuel in the combustion chamber, it is burned and this heat input is modeled as external heat input while P is constant, attaining the point of maximal T and P at position 4 just in front of the turbine.
5. This hot gas expands in the turbine isentropically, doing work while P and T fall, but the gas leaves the turbine still at moderately high P and T (position 5).
6. P further falls to [close to] ambient by [or close to] the end of the nozzle, and air exits at high velocity.



"Diagram of a typical gas turbine jet engine. Air is compressed by the fan blades as it enters the engine, and it is mixed and burned with fuel in the combustion section. The hot exhaust gases provide forward thrust and turn the turbines which drive the compressor fan blades."[237] "All the thrust of a turbojet engine is due to the exhaust gases leaving the engine at about twice the speed of sound."[238]



T-s diagram for ideal turbojet cycle, and a turbojet in cross section[239]
Air V slows and P rises in the diffuser 1-2.

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[237] https://en.wikipedia.org/wiki/Jet_engine

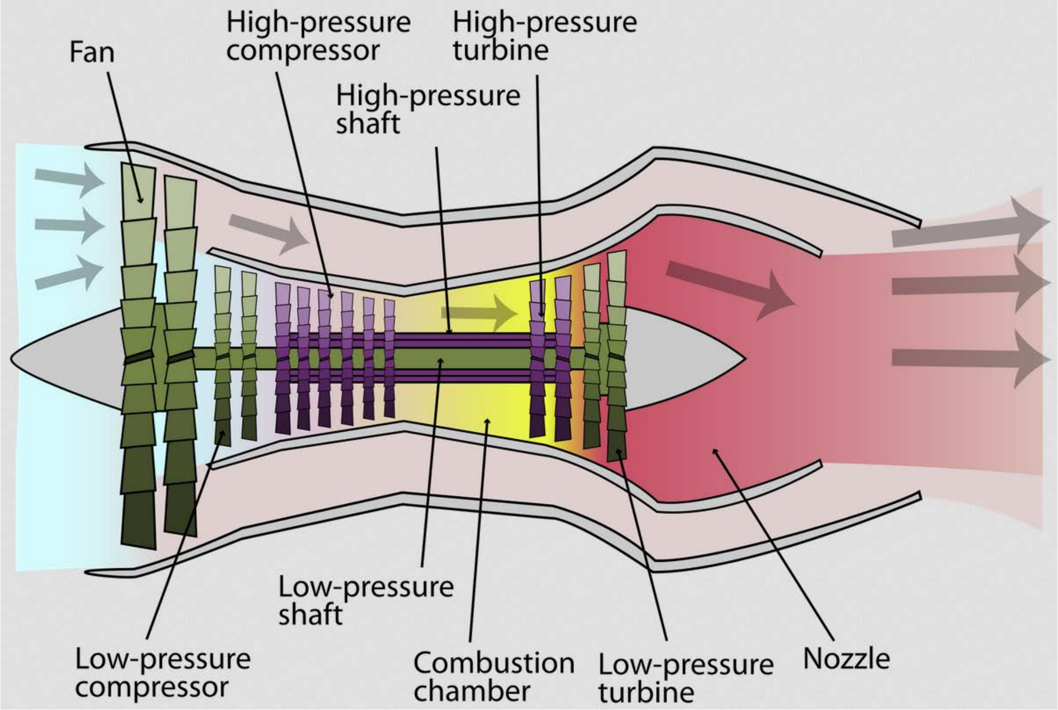
[238] *TAEA7* p. 526. This statement seems to contradict the contention expressed elsewhere that a purely converging nozzle is incapable of putting out supersonic flow.

[239] http://www.mhhe.com/engcs/mech/cengel/thermodead/graphics/ppt/pptsource/CHPT08.PPT, modified MCM

There are a number of variants on the turbojet, some of which follow.

Turbofan Engine (aka Fanjet)

The turbofan, popular especially on large and jumbo jets, combines the words *turbine* and *fan*. It is a gas turbine engine which takes mechanical energy from combustion, and has a ducted fan in front that uses the mechanical energy from the gas turbine to accelerate additional bypass air rearwards. These can range from low-bypass to high-bypass, depending on the bypass ratio, see below. The following diagram illustrates a relatively low-bypass turbofan.



Turbofan diagram showing low-bypass duct and mixing of the exhaust + bypass gas streams providing thrust in final nozzle. The fan is covered by a cowling. Shown is a 2-spool (2 concentric or coaxial shafts) design:
The N1 slower shaft (green, lower RPM) turns the low pressure LP compressor and the LP turbine, as well as the fan.
The N2 faster shaft (purple, faster RPM) turns the high pressure HP compressor and HP turbine.
The fan may have its own planetary reduction gearbox so that its rotation rate may differ from either shaft.

> "…Whereas all the air taken in by a turbojet passes through the turbine (and through the combustion chamber), in a turbofan some of that air bypasses the turbine. A turbofan thus can be thought of as a turbojet being used to drive a ducted fan, with both of those contributing to the thrust. The ratio of the mass-flow of air bypassing the engine core compared to the mass-flow of air passing through the core is referred to as the **bypass ratio**. The engine produces thrust through a combination of these two portions working in concert; engines that use more jet thrust relative to fan thrust are known as **low bypass turbofans**, conversely those that have considerably more fan thrust than jet thrust are known as **high bypass**."[240]

The axial compressor in jet engines (as with many turbines), includes the commonly depicted rotating airfoils (also known as **blades** or **rotors**) which accelerate the fluid, but also stationary airfoils (also known as **stators** or **vanes**). These stator vanes are fixed in place, but in advanced designs may be individually rotated around

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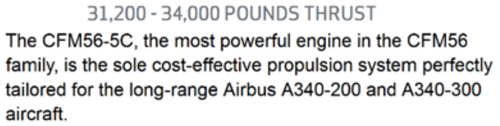
[240] https://en.wikipedia.org/wiki/Turbofan diagram above and quoted text

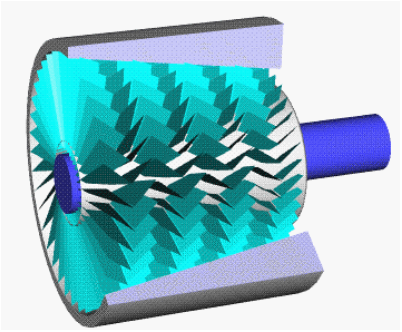
their own axis to adjust for starting conditions and other operational optimizations. The vanes convert the increased rotational kinetic energy into static pressure through diffusion and redirect the flow direction of the fluid, preparing it for the rotor blades of the next stage.[241]



31,200 - 34,000 POUNDS THRUST

The CFM56-5C, the most powerful engine in the CFM56 family, is the sole cost-effective propulsion system perfectly tailored for the long-range Airbus A340-200 and A340-300 aircraft.

Commercial fanjet example (left) used with Airbus jets (CFM International, model CFM56-5C), with removal of inlet and fan cowling and also nacelle over bypass duct (as well as thrust reverser and other components) [242] **Axial compressor (below) with stator vanes & rotor blades**[243]



Rolls-Royce Trent XWB fanjet engine installed under the Airbus A350's wing (compare size to person lower right)[244]

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[241] https://en.wikipedia.org/wiki/Axial_compressor

[242] http://www.cfmaeroengines.com/engines/cfm56-5c

[243] https://www.grc.nasa.gov/www/k-12/airplane/caxial.html animated gif

[244] https://en.wikipedia.org/wiki/Rolls-Royce_Trent_XWB

"Most commercial aviation jet engines in use today are of the high-bypass type, and most modern military fighter engines are low-bypass. Bypass ratios greater than 5:1 are increasingly common with the Rolls-Royce Trent XWB approaching 10:1… [photo above] For reasons of fuel economy, and also of reduced noise, almost all of today's jet airliners are powered by high-bypass turbofans. Turbofans are thus the most efficient engines in the range of speeds from about 500 to 1,000 km/h (310 to 620 mph), the speed at which most commercial aircraft operate."[245]

A gearbox for the fan may be included. For instance, for the Pratt & Whitney PW1000G engine, "By putting a 3:1 gearbox between the fan and the low pressure spool [concentric shaft], each spin at its optimal speed: 4,000-5,000 RPM for the fan and 12,000-15,000 RPM for the spool."[246]

Turboprop Engine (Older Propjets) and Propfan Engine (Newer Propjets)

This design, which removes the cowl from around the fan of a turbofan, provides an effective bypass ratio of up to 100, and outdoes the fuel efficiency of the turbofan, but the older generations operated at relatively low speed (< Mach 0.62) and low-altitude (< 9100 m) where its efficiency is highest. Newer generation **propfans** operate up to Mach 0.82 and altitudes of 12,200 m.[247] The European Aviation Safety Agency EASA defines a propfan as, "A turbine engine featuring **contra rotating fan stages** not enclosed within a casing."[248] The fan may be positioned in front of or behind the engine.

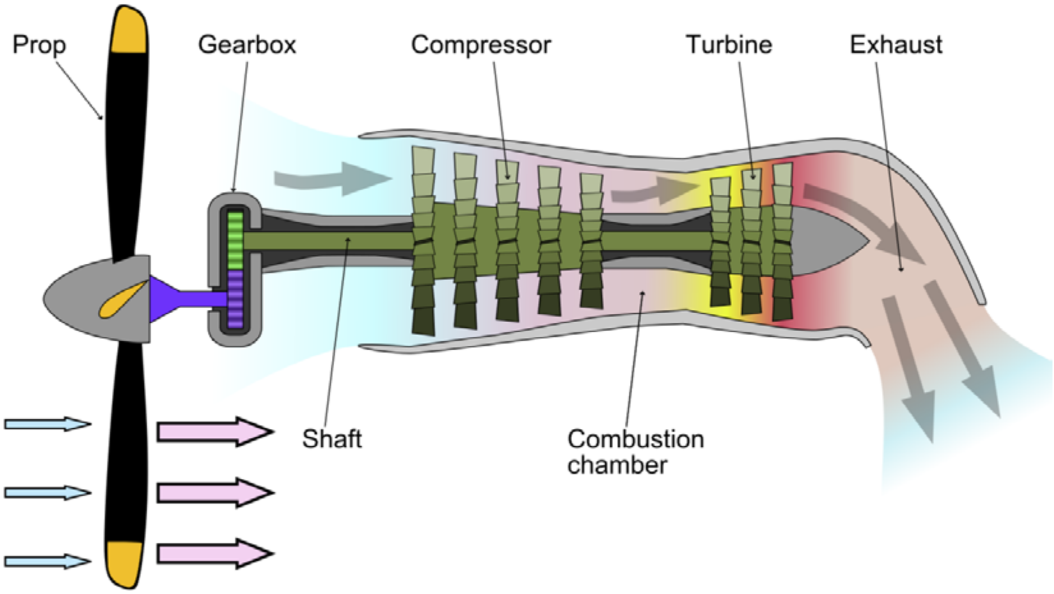

Diagram of Turboprop Engine[249]

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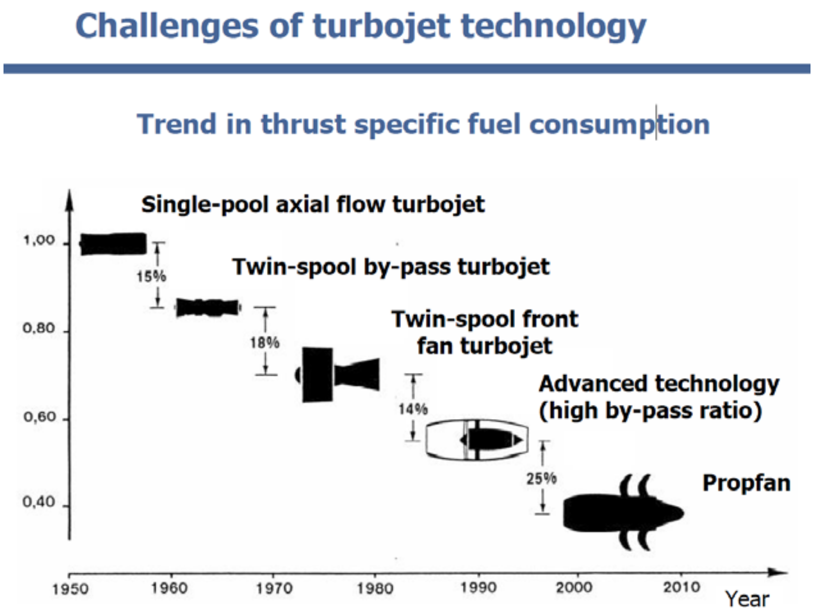
[245] https://en.wikipedia.org/wiki/Turbofan
[246] https://en.wikipedia.org/wiki/Pratt_%26_Whitney_PW1000G
[247] *TAEA7* p. 526
[248] https://en.wikipedia.org/wiki/Propfan
[249] https://en.wikipedia.org/wiki/Turboprop

Other Jet Engine Types and Rocket Engines

There are other forms of jet engines. **Afterburners** can increase thrust at the expense of increased fuel consumption rate (see diagram below). For supersonic velocities, **Ramjets** work best at Mach 2 to 4,[250] whereas **Scramjets** are best for Mach 6 to 8 or higher.[251] Airflow in a scramjet is supersonic throughout the entire engine (whereas it is subsonic before combustion in a ramjet). This allows the scramjet to operate efficiently at extremely high (hypersonic) speeds. **Rocket** engines are also mentioned in the text—they carry both fuel and oxidizer, and create thrust through the acceleration of hot and very high velocity exhaust gases. [I have not attempted a detailed look at the complexities of rocket technology.]

Evolution of thrust specific fuel consumption

The following diagram[252] shows how thrust specific fuel consumption has declined from the original turbojet to high by-pass turbofans and propfans:



Challenges of turbojet technology

Trend in thrust specific fuel consumption

Comparison of Jet Engine and Rocket Propulsion Performance

The propulsive performance of various jet engines is compared as follows:[253] The term **specific impulse I_{sp}** refers to rate of change in momentum per unit of propellant (fuel only for a jet, oxidizer + fuel for a rocket).

For mass units (kg or slug), I_{sp} units are kg-m/s-kg = m/s (velocity units). For weight basis (newton or pounds), I_{sp} units are s (time only, as depicted in the diagram to follow).

> "A propulsion system with a higher specific impulse uses the mass of the propellant more efficiently in creating forward thrust, and in the case of a rocket, less propellant needed for a given ΔV, per the Tsiolkovsky rocket equation. [ΔV is the maximum change of velocity of the vehicle with no external forces acting.] In rockets, this means the engine is more efficient at gaining altitude, distance, and velocity. This is because if an engine burns the propellant faster, the rocket has less weight for a longer period of time, which makes better use of the total force times time that was acquired from the propellant. This is much less of a

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[250] https://en.wikipedia.org/wiki/Ramjet

[251] http://www.nasa.gov/missions/research/f_scramjets.html and https://en.wikipedia.org/wiki/Scramjet

[252] http://www.ltas-cm3.ulg.ac.be/AERO0023-1/ConceptionMecaTurbomachine.pdf

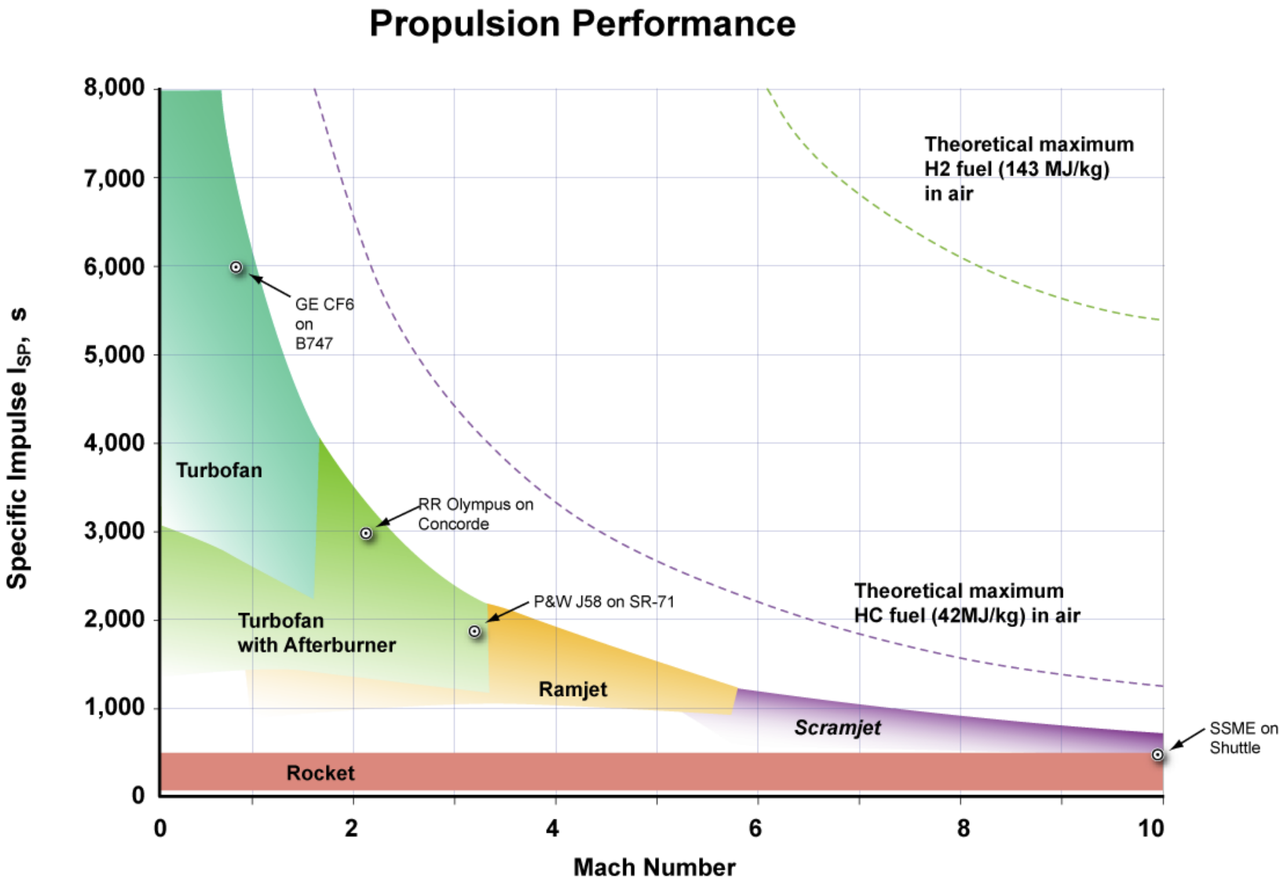
[253] https://en.wikipedia.org/wiki/Scramjet including diagram

consideration in jet engines that employ wings and outside air for combustion to carry payloads that are much heavier than the propellant.

Specific impulse includes the contribution to impulse provided by external air that has been used for combustion and is exhausted with the spent propellant. Jet engines using outside air therefore have a much higher specific impulse than rocket engines. The specific impulse in terms of propellant mass spent (multiplying the weight-based I_{sp} in seconds by g_0) is in units of distance per time which is an artificial velocity called the "**effective exhaust velocity**". [Here, g_0 is standard gravity = 9.8 m/s^2.] This is higher than the actual exhaust velocity because the mass of the combustion air is not being accounted for. Actual and effective exhaust velocity are the same in rocket engines not utilizing air.

Specific impulse is inversely proportional to **specific fuel consumption** by the relationship $I_{sp}=1/(g_o * SFC)$ for SFC in kg/N-s and I_{sp} = 3600/SFC for SFC in lb/lbf-hr."[254]

Jet engines using outside air in general have a much higher specific impulse than rocket engines. The scramjet for instance has a higher specific impulse than a rocket engine because it uses outside oxygen rather than an oxidizer propellant carried onboard.



Comparison of Specific Impulse (weight basis, units of s) for Various Engines including theoretical Hydrogen H_2 and Hydrocarbon HC Fuel maxima (SSME = Space Shuttle Main Engine)

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[254] https://en.wikipedia.org/wiki/Specific_impulse and https://en.wikipedia.org/wiki/Thrust_specific_fuel_consumption and https://en.wikipedia.org/wiki/Tsiolkovsky_rocket_equation

Representative values of Specific Impulses for selected Rocket Engines

- **Saturn V rockets** (Rocketdyne F-1 engine, 1960s and 1970s):

Stage 1 (LOX + RP-1): 265s at sea level / 304s in vacuum
Stage 2 (LOX +LH2): 424s vacuum
Stage 3 (LOX +LH2): 424s vacuum.[255]

- **Space Shuttle main engine** (Aerojet Rocketdyne RS-25 engine, first flight 1981, burning LOX +LH2):

366 seconds (3.59 km/s) at sea level
452 seconds (4.43 km/s) in a vacuum.[256]

- **Space Shuttle Solid Rocket Booster** (ammonium perchlorate 70% (oxidizer), aluminium 16% (fuel), iron oxide 0.4% (catalyst), PBAN polymeric binder 12%, and epoxy curing agent 2%. This propellant is commonly referred to as Ammonium Perchlorate Composite Propellant, or simply APCP. Develops a specific impulse of

242 seconds (2.37 km/s) at sea level
268 seconds (2.63 km/s) in a vacuum.[257]

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[255] http://www.braeunig.us/space/propel.htm including I_{sp} for many fuel/oxidizer combos, and https://en.wikipedia.org/wiki/Rocketdyne_F-1

[256] https://en.wikipedia.org/wiki/Space_Shuttle_main_engine

[257] https://en.wikipedia.org/wiki/Space_Shuttle_Solid_Rocket_Booster

Vapor Power Cycles and Combined Power Cycles (10)

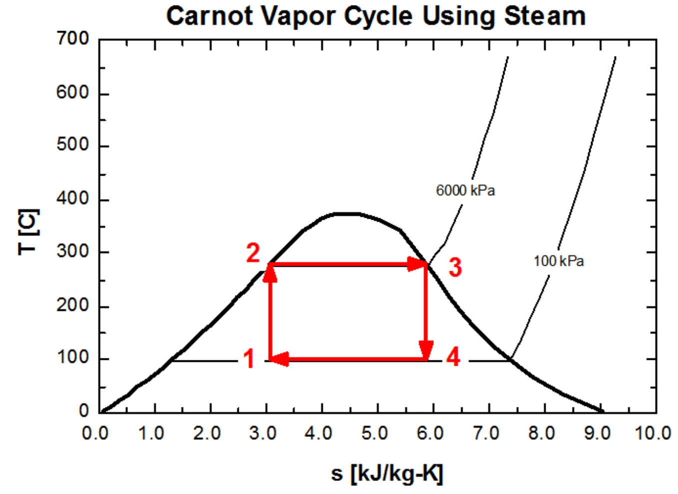
(from text Chapter 10 & other sources)

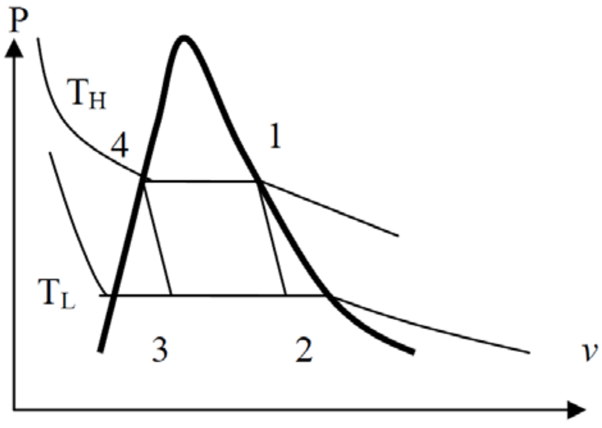
The term *vapor power cycle* implies the working fluid is alternatively vaporized and condensed during the cycle, and that the gaseous phase typically exists near the saturated vapor line.

Steam/water is the most common working fluid used in vapor power cycles. It is cheap, readily available, nontoxic, and has high enthalpy of vaporization. Most vapor power plants are steam power plants, whether powered by coal, natural gas, or nuclear.

Carnot Idealized Vapor Power Cycle

The Carnot vapor cycle operates under the saturation dome (representative versions are shown in the diagrams to follow), and has the usual thermal efficiency $\eta_{max} = \eta_{Carnot} = 1 - T_L/T_H$. However, it is impractical as a model vapor power cycle and cannot be achieved in actual devices.[258]





Carnot Vapor Power Cycle on P-v diagram[259]

The barriers to making a real and successful Carnot vapor power cycle, using state numbers shown on the left, may be summarized:

- For Process 2-3, limiting the heat transfer processes to two-phase (saturated liquid-vapor mixture) systems severely limits the maximum temperature that can be used in the cycle (T_{cr} = 374 C for water).
- For Process 3-4, the turbine cannot handle steam with a high moisture content because of the impingement of liquid droplets on the turbine blades accelerates erosion and wear.
- For Process 1-2, it is not practical to design a compressor that handles two phases.[260]

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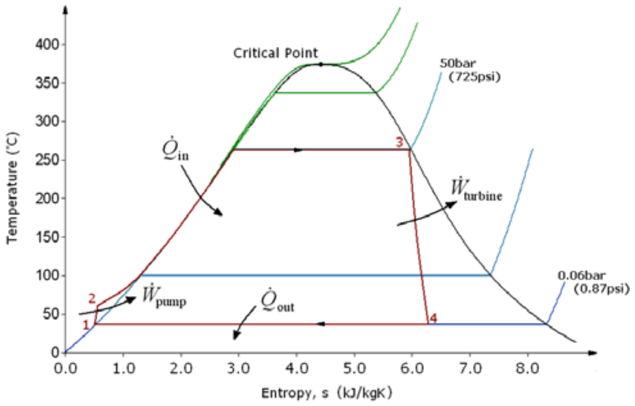
[258] *TAEA7* Chapter_10.ppt including diagram on left

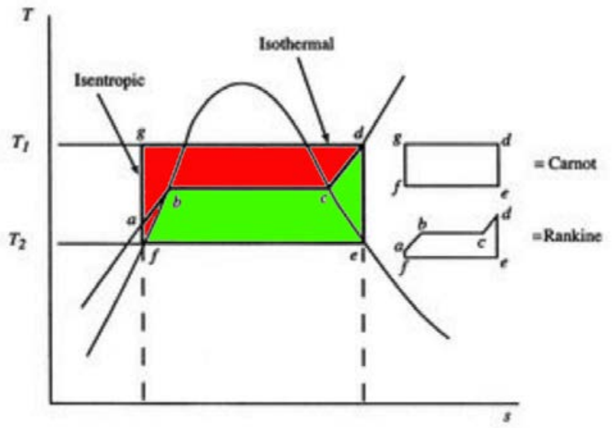
[259] http://www.sfu.ca/~mbahrami/ENSC%20461/Notes/Carnot%20Cycle.pdf

[260] http://www.slideshare.net/upasana_panigrahi/thermodynamics-of-power-plant, numbers adjusted

Rankine Vapor Power Cycle



T-s diagram of a simple Rankine cycle operating at pressures between 0.06bar and 50bar. As depicted, there is no superheating, and the turbine processes a relatively low quality vapor/liquid mixture, both of which are suboptimal[261]



Comparison of Rankine cycle with superheating and Carnot cycle

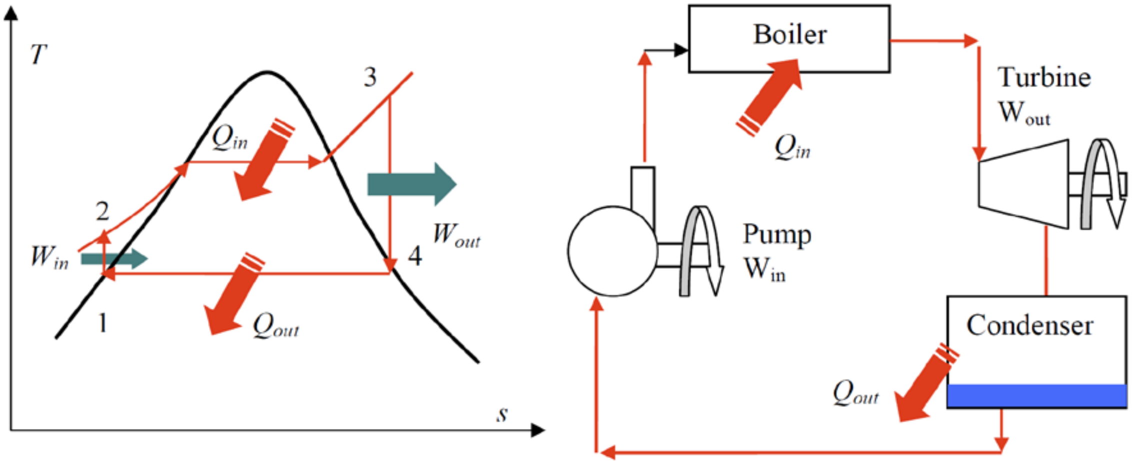


Fig. 2: The ideal Rankine cycle.

An ideal Rankine cycle more suitable for a steam power cycle. The turbine (3-4) operates solely on superheated steam rather than a vapor/liquid mixture, and the pump (1-2) pumps only liquid compressed water.[262]

The **simple Rankine cycle** is an idealized vapor power cycle which can be improved with modifications discussed below. There are four processes in the simple ideal Rankine cycle. (This is summarized from the textbook and Wikipedia. The Wikipedia diagram (upper left above) depicts a basic Rankine cycle without superheating. However, thermal efficiency and durability are improved upon with addition of superheating at 3):[263]

> **Process 1-2, Isentropic compression by a pump:** The working fluid is pumped from low to high pressure (at 2). Because the fluid is a liquid at this stage (it lies to the left of the saturated liquid line in the compressed liquid region), the pump requires relatively little input energy.
>
> **Process 2-3, Constant pressure heat addition in a boiler**: The high pressure compressed liquid enters a boiler where it is heated at constant pressure by an external heat source to

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[261] https://en.wikipedia.org/wiki/Rankine_cycle incl. diagram

[262] http://www.sfu.ca/~mbahrami/ENSC%20461/Notes/Vapor%20Power%20Cycles.pdf

[263] http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node66.html

become first a saturated liquid, then a saturated liquid-vapor mixture, then a superheated vapor (ending at 3, a subcritical state having $T_3 < T_{cr}$). The input energy Q_{in} required to attain this state can be calculated graphically, using an enthalpy-entropy chart (aka h-s or Mollier diagram), or numerically, using steam tables.

Process 3-4, Isentropic expansion in a turbine: The superheated vapor expands through a turbine, generating power. This decreases the temperature and pressure of the vapor, and some condensation may occur (as implied in the diagram lower left), though at state 4, there is and should be at most minimal condensation. The turbine net work output

$W_{net,out} = W_{out} - W_{in}$

for this process (i.e., net after allowing for pump $Work_{in}$) can be easily calculated using the charts or tables.

Process 4-1, Constant pressure heat rejection in a condenser: The slightly wet vapor at 4 then enters a condenser where it is condensed at a constant pressure to become a saturated liquid-vapor mixture, and finally a saturated liquid (at 1). Heat Q_{out} is given off as a result of the enthalpy of vaporization resulting from condensation of the vapor.

The thermal efficiency of the simple idealized Rankine cycle without superheating is given by

$$\eta_{thermal} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_{m2}}{T_{m1}}$$

where T_{m1} is the mean effective temperature defined by (symbols adjusted)

$q_H = Q_{in} = T_{m2}\Delta s_2$ and $q_L = Q_{out} = T_{m1}\Delta s_1$

Because $T_{m1} \approx T_1$ but $T_{m2} < T_2$, the thermal efficiency for the idealized Rankine cycle is less than that of the Carnot cycle operating between T_2 and T_1.

When superheating is added (above: top right and lower left diagrams), the thermal efficiency rises, though still not approaching that of the Carnot cycle. The efficiency of an example of a simple Rankine cycle with superheating is shown in the textbook to be about 26%, compared to 42% for Carnot efficiency between the same T_{min} and T_{max}. The lower efficiency is attributed to the large external irreversibility in the Rankine cycle caused by the large T difference between combustion gases in the furnace and the steam formed.[264]

In the top right T-s diagram above, the lower efficiency of the superheated ideal Rankine cycle (for which work output is proportional to the green area) is compared to the higher efficiency of the Carnot cycle operating between the same $T_{max} = T_{gd}$ and $T_{min} = T_{ef}$ (for which work output is proportional to the green plus red areas).[265]

Some of the inefficiencies encountered in an actual vapor power cycle with superheating are depicted as follows:[266]

- The pump requires greater W_{in}, thus achieving higher entropy at state 2a due to pump irreversibilities rather than ideal Rankine isentropic state 2s.
- Pressure drop (from friction) in the boiler and pipes reduces final pressure P_3 entering the turbine, requiring higher pump pressure in compensation.
- Irreversibilities in the turbine increase entropy (ending at 4a) and reduce the turbine's W_{out}.

The pump and turbine actual versus isentropic ideal efficiencies may be compared by:

$$\eta_{pump} = \frac{w_s}{w_a} = \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

where w_a = actual work w_s = idealized isentropic work

h_{2a} = enthalpy at actual state 2

h_{2s} = enthalpy at idealized isentropic state 2

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[264] *TAEA7* p. 559, 561

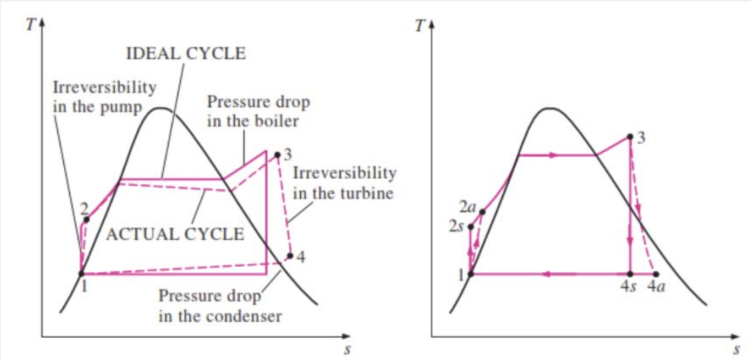
[265] http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node66.html Image modified by MCM

[266] *TAEA7* p. 562, image from http://sounak4u.weebly.com/vapour--combined-power-cycle.html

$$\eta_{turbine} = \frac{w_a}{w_s} = \frac{h_3 - h_{4a}}{h_3 - h_{4s}}$$

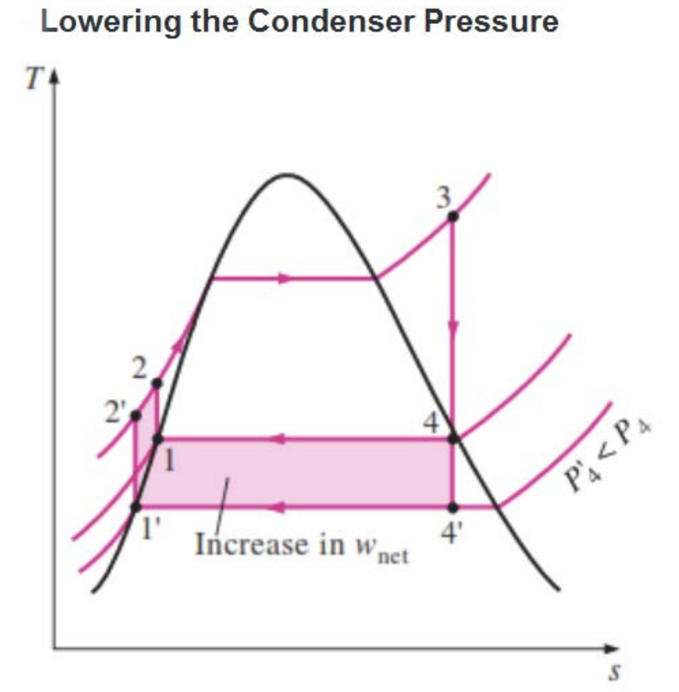
where h_{4a} = enthalpy at actual state 4
h_{4s} = enthalpy at idealized isentropic state 4

DEVIATION OF ACTUAL CYCLE FROM IDEAL CYCLE

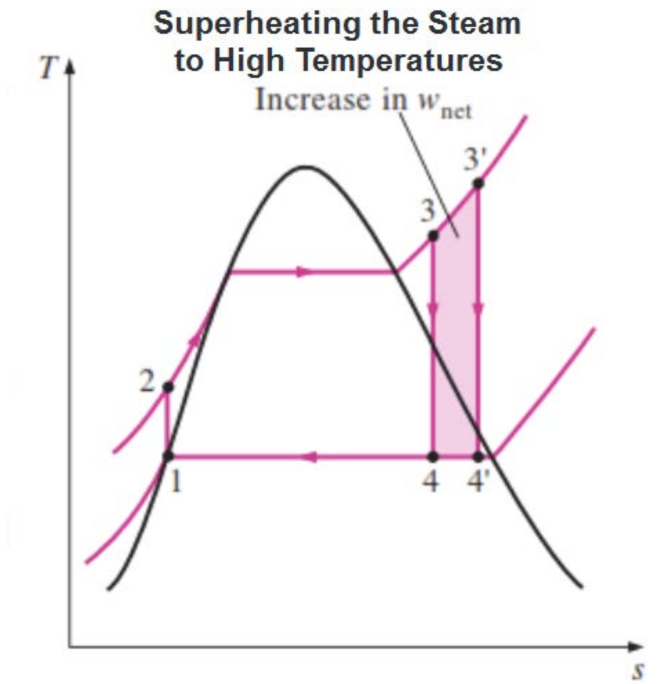


Improving Rankine Efficiency

Actual vapor cycles can be improved substantially in thermal efficiency or otherwise improved with use of many of the following modifications. (The following diagrams[267] illustrate some of their pros and cons):



Lowering Condenser Pressure from 1 to 1’ improves work$_{net}$ (colored area), but may increase air leakage and added turbine erosion from intrusion of moisture



Superheating the steam from 3 to 3’ increases work$_{out}$ and reduces moisture on the turbine blades (desirable). T$_{max}$ is limited to about 620 °C by materials limits.

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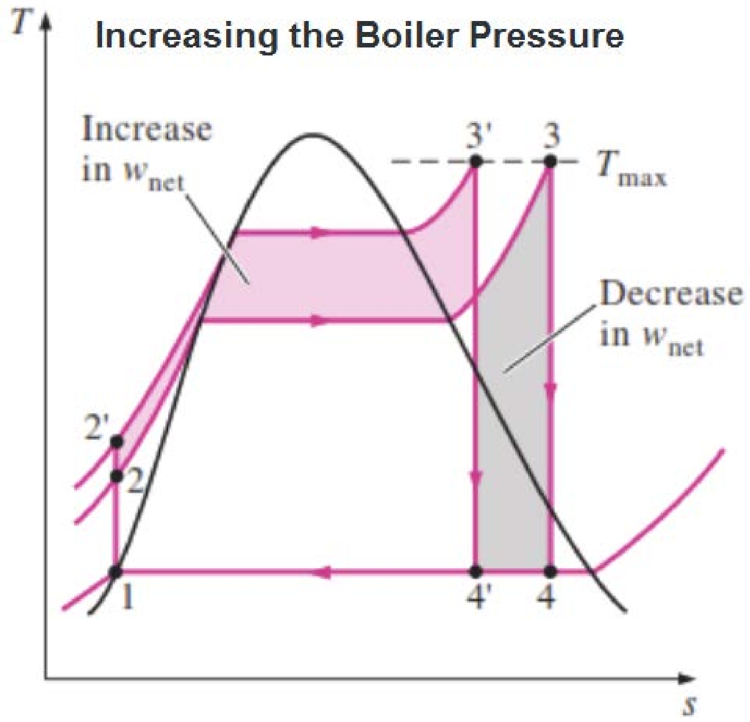
[267] *TAEA7* p. 563-588,
images slightly modified by MCM from http://sounak4u.weebly.com/vapour--combined-power-cycle.html

Lower Condenser Pressure and lower $T_{low,avg}$

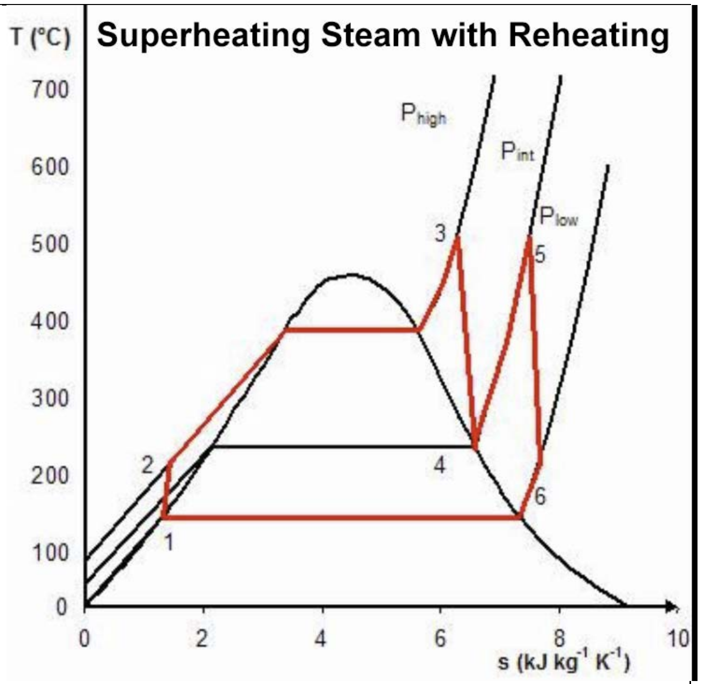
This will increase heat rejection and increase net work (see left diagram above). Condensers usually operate below 1 atm. However, lowering condenser pressure from 4 to 4' will increase the likelihood that air will intrude, and will increase erosion by impact of moisture droplets on the turbine blades. Condenser pressure cannot be lower than the saturation vapor pressure at the T of the cooling medium (otherwise, condensation will not occur).

Superheating the Steam

This heats steam to higher temperature to increase $T_{high,avg}$ and also to reduce moisture at the turbine exit (see 4 to 4' in the above right diagram, and earlier diagrams): Maximal temperature is limited by thermal tolerance of the metals, and currently does not typically exceed 620 °C in steam turbines. **Reheating** may be added to prevent falling into the saturated liquid-vapor mixture region where turbine blade damage from droplets may occur (see right diagram below).



Increasing Boiler Pressure from 3 to 3' can increase condensation in the turbine, necessitating reheating.



By adding reheating stages, high and low pressure turbine stages process only superheated steam, eliminating harmful droplet moisture on the blades.[268]

Supercritical Operation at $P > P_{cr}$ and $T > T_{cr}$

With advances in metallurgy and boiler design, etc., an increasing number of steam power plants operate **supercritically**—that is, for part of the cycle, the P and T exceed the critical point (P_{cr}, T_{cr}) of the working fluid. In the supercritical state, there is no distinction between fluid and gas, and the latent heat of vaporization is zero. Boiler pressures have increased from 2.7 MPa in 1922 to over 30 MPa today. This provides a higher T_{max}, allowing increased cycle efficiency, to >40% for fossil fuel plants (lower for nuclear).

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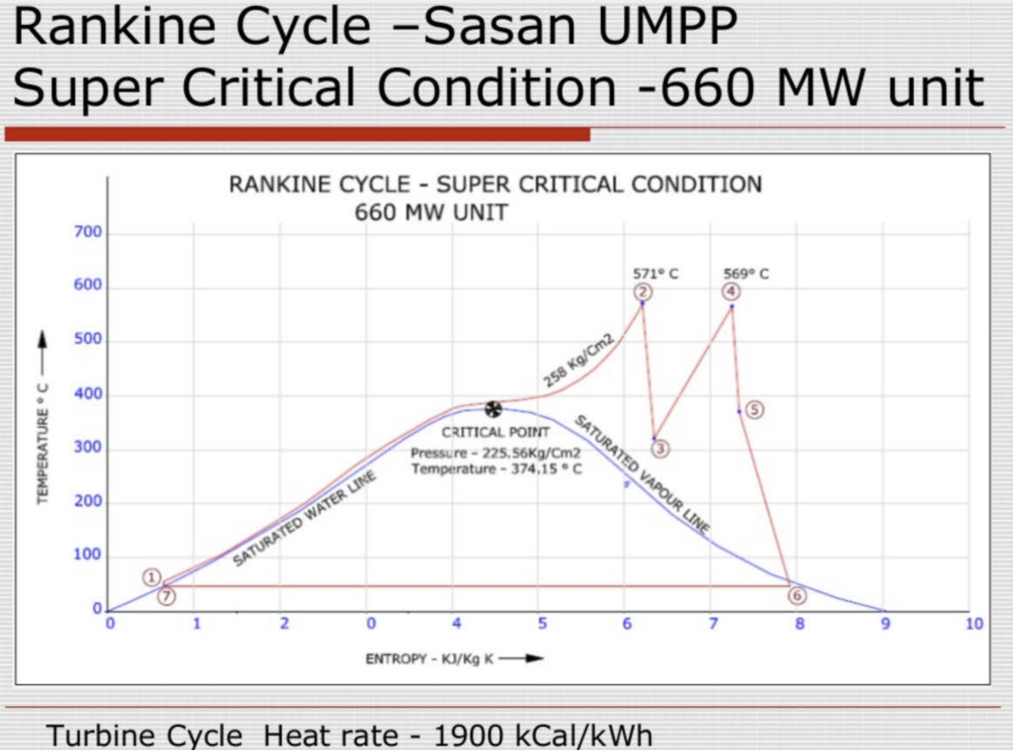
[268] https://en.wikipedia.org/wiki/Rankine_cycle

The following depicts the T-s diagram for a supercritical Rankine cycle device, the Sasan Ultra Mega Power Project in India, which features coal-fired steam generation, authored by Shivaji Choudhury.[269] The diagram shows 2 turbine expansion stages ② to ③ and ④ to ⑤ with reheating at ③ to ④.



Rankine Cycle –Sasan UMPP
Super Critical Condition -660 MW unit

Turbine Cycle Heat rate - 1900 kCal/kWh

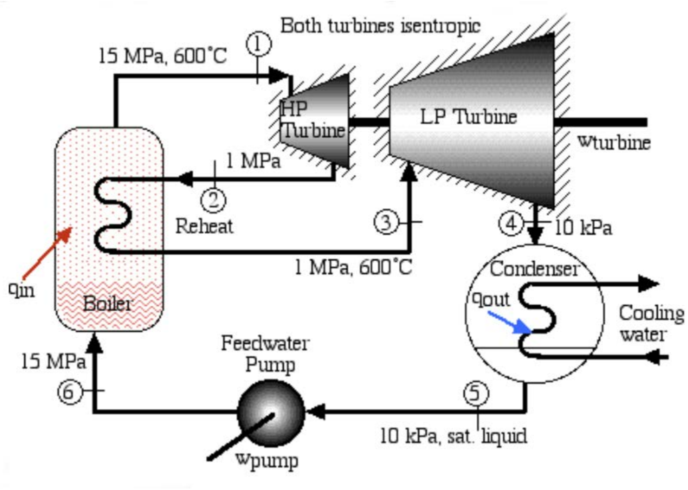
I have also encountered an interesting report studying **supercritical organic Rankine cycles SORC** using R-23, R-32, R-134a, and other common "refrigerants" as the working fluid, for which the critical point is much lower than that of water.[270] The authors concluded, "… R134a would be the best choice for the operating conditions considered. It was found that thermal efficiencies as high as 21% can be obtained for a 200 °C source temperature and a 10 °C sink temperature. However, if the sink is at 25 °C which may be more realistic, an efficiency of 18.5% was obtained." SORC cycles may therefore be impractical for now.

Increase Boiler Pressure

This also increases $T_{high,avg}$. The T_{max} point is shifted to the left, however, which if uncorrected causes too much condensation in the turbine. Reheating may be needed (see diagrams above). Supercriticality resulting from increasing boiler pressure is discussed above.

Reheating in the Turbine Stage(s)

Adding one or more reheating stage allows use of high and low pressure turbines. Steam exiting the high pressure turbine is diverted to the boiler, where it is reheated before being sent to the low pressure turbine



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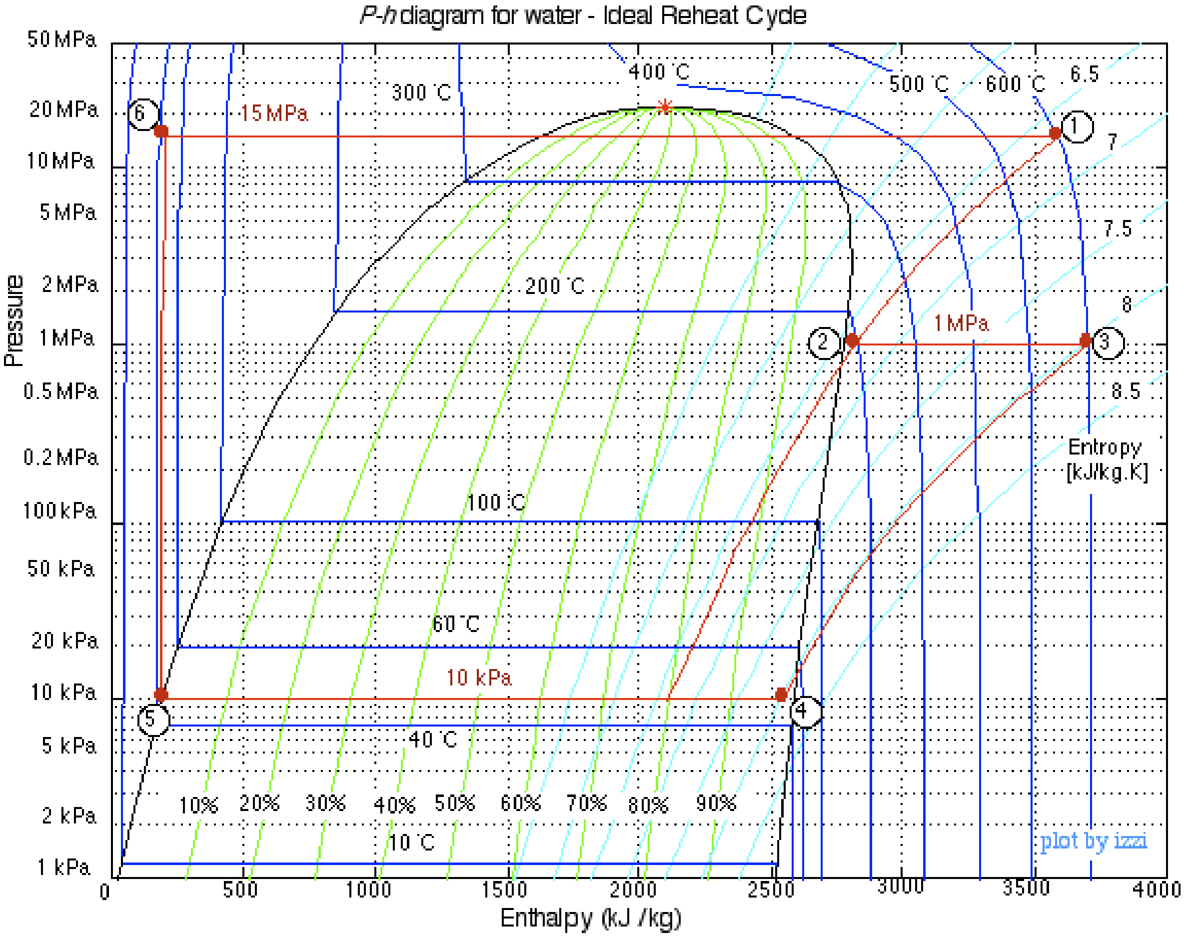
[269] http://www.slideshare.net/SHIVAJICHOUDHURY/super-critical-boiler

[270] R Vidhi, S Kuravi, et al, "Organic Fluids in a Supercritical Rankine Cycle for Low Temperature Power Generation", *J. Energy Resour. Technol* 135(4), 042002 (May 27, 2013)

inlet (see diagram just above[271]). Reheating is commonly used to allow turbine processing only of dry steam lacking moisture droplets that can erode and harm the blades. There can of course be more than 2 turbine stages, with reheating between the stages. If a large number of reheating stages are used, the process is nearly isothermal, but it is rarely practical to have more than two reheat stages.

The following pressure - specific enthalpy (P-h) diagram[272] depicts the operation of an idealized Rankine cycle that operates in subcritical pressures and temperatures, and incorporates superheating [at states 1 and 3] and reheating [in process 2-3]. The cycle depicted also shows that the ending turbine state [4] is associated with only slight condensation under the *saturation dome*, preventing erosion of the turbine blades:



Feedwater Heating FWH (Regeneration)

This is used to raise the average temperature of liquid leaving the pump (called *feedwater*) before it enters the boiler or steam generator. Practical regeneration is accomplished by bleeding off steam from the turbine at an intermediate pressure.

In **open feedwater heating**, this steam is mixed with liquid water from the main feedwater pump (Pump 1), and the combined saturated liquid water is pumped by Pump 2 to attain boiler pressure and sent to the boiler.

In **closed feedwater heating**, diverted steam exchanges heat—in a heat exchanger without mixing—with liquid water from the main feedwater pump (Pump 1), and the combined saturated liquid water is again pumped by Pump 2. (See diagram of Gavin Steam Power Plant, below.)

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[271] https://www.ohio.edu/mechanical/thermo/Applied/Chapt.7_11/Chapter8a.html
[272] https://www.ohio.edu/mechanical/thermo/Applied/Chapt.7_11/Chapter8a.html

Cogeneration

This diverts **process heat** (i.e., otherwise *waste heat*) to provide useful local low quality residential, commercial, and/or industrial heat.

The **utilization factor $\boldsymbol{\varepsilon_u}$** for the plant, which accounts for work output plus usable process heat delivered, is given by[273]

$$\varepsilon_u = \frac{\dot{W}_{net} + \dot{Q}_p}{\dot{Q}_{in}} = 1 - \frac{\dot{Q}_{out}}{\dot{Q}_{in}}$$

Some plants achieve ε_u as high as 80%.

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[273] *TAEA7* p. 583

Summary of Methods and Effects of Improving Efficiency in Ideal Rankine Cycles

The textbook provides a series of worked examples in which features are added to what begins as a simple ideal Rankine cycle plant, and shows how the thermal efficiency can be improved (in all cases neglecting friction and other irreversibilities). Values I have calculated are in parentheses.[274] Blank entries are not specified and are not determined = n.d. Entries for Carnot cycle, Cogeneration plants, and Combined Gas-Vapor Power Cycle are shown for comparison.

Rankine Cycle Features & Improvements	**Min. (Cond. Inlet) T °C**	**Max (Turbine Inlet) T °C**	**Min. (Cond. Inlet) P**	**Max (Turbine Inlet) P**	**Comment**	**Thermal Efficiency η_{th}**
10-1: Simple ideal Rankine	(~92)	350	75 kPa	3 MPa	Max P is rather low	**26.0%**
10-3a: Same as 10-1 w lower Minimum T	(~46)	350	10 kPa	3 MPa		**33.4%**
10-3b: Same as 10-3a w higher Maximum T	(~46)	600	10 kPa	3 MPa		**37.3%**
10-3c: Same as 10-3b w higher Boiler P	(~46)	600	10 kPa	15 MPa		**43.0%**
10-4: Same as 10-3c plus Reheat between HP and LP turbines	(~46)	HP: 600 LP: 600	10 kPa	HP: 15 MPa LP: 4 MPa		**45.0%**
10-5: Same as 10-3c plus Open Feedwater Heater (Regeneration) but no Reheat	(~46)	600	10 kPa	15 MPa	Turbine outlet P=1.2 MPa, T=218 °C to FWH	**45.0%**
10-6: Same as 10-5 w Feedwater Heater (Regeneration) plus Reheat	(~46)	HP: 600 LP: 600	10 kPa	HP: 15 MPa LP: 4 MPa	P=4 MPa T=(375) °C to closed FWH P=0.5 MPa T=(276) °C to open FWH	**49.2%**
10-1: Simple ideal Carnot like 10-1 Rankine at same T and P	92	350	75 kPa	3 MPa		**41.5%**
10-8 Ideal Cogeneration Plant: Process heat from 10% steam @ 7 MPa 70% steam @ 500 kPa	(~33)	500	5 kPa	7 MPa	Ideal ε_u = (26 MW +11 MW)/43 = 86.5% Actual Utilization factors ε_u are up to 80%	**NA**
10-9 Ideal Combined Gas-Vapor (Steam) Power Cycle	(~33)	Gas: 1300 Vapor: 500	Gas: n.d. Vapor: 5 kPa	Gas: n.d. Vapor: 7 MPa	9-6 Gas Cycle 10-8b Vapor Cycle (simple Rankine)	**48.7%** **Actual complex CGVPC's are up to 60%**

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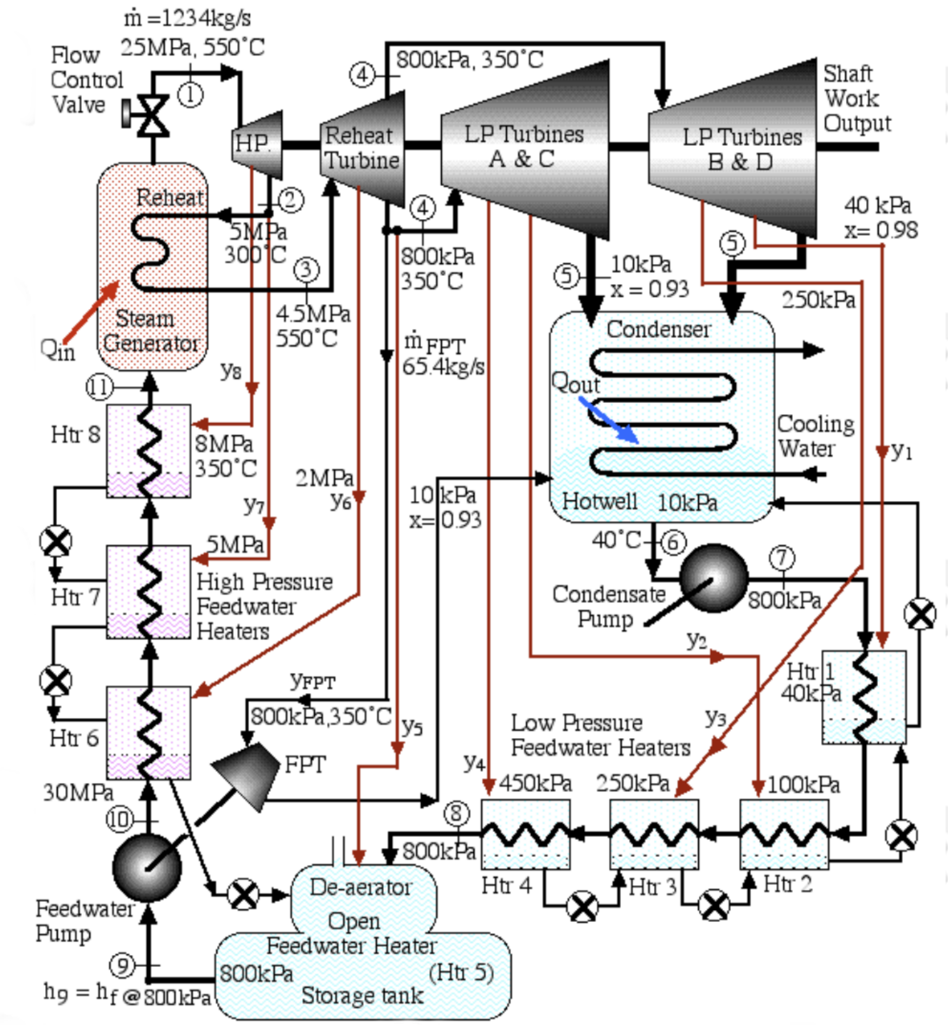
[274] Using online Zittau's Fluid Property Calculator: http://thermodynamik.hszg.de/fpc/index.php

Sample Complex Rankine Cycle Plant

With the many enhancements in efficiency, the Byzantine complexity of a modern stream power plant can be daunting. The following diagram (from an excellent website, *Engineering Thermodynamics*, by Israel Urieli[275]), which I do not pretend to fully understand, depicts a real system that utilizes a HP turbine operating at 25 MPa, a Reheat turbine at 4.5 MPa, and 4 LP turbines all operating at 800 kPa, as well as a feedwater pump turbine at 800 kPa. In addition, it has a steam generator, a condenser, separate condensate and feedwater pumps, and four low pressure closed feedwater heaters, one open feedwater heater / de-aerator, and three high pressure closed feedwater heaters.



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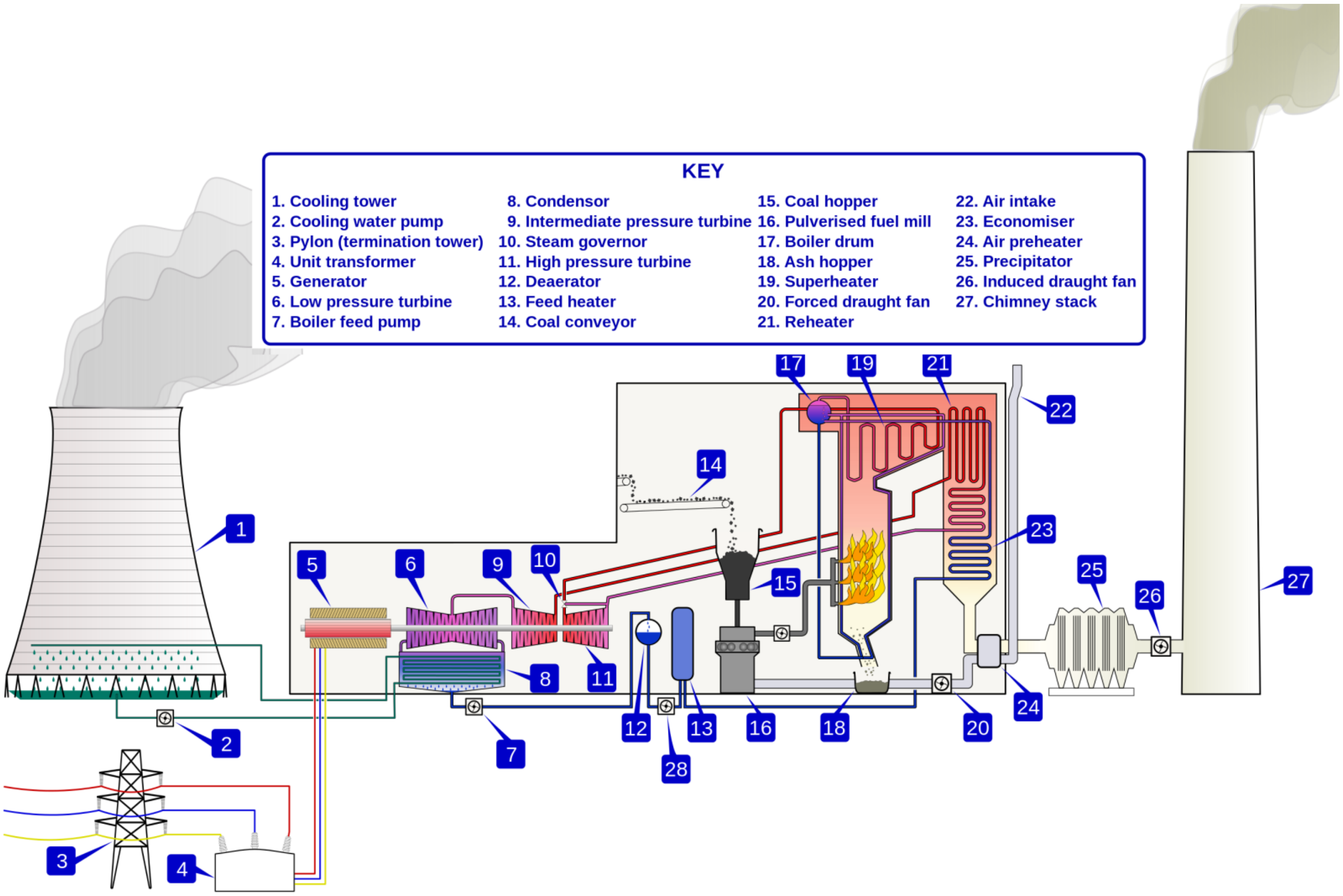
[275] Diagram of the General James M. Gavin Steam Power Plant in Ohio, 1975 https://www.ohio.edu/mechanical/thermo/Applied/Chapt.7_11/SteamPlant/GavinCaseStudy.html

Coal Fired Steam Power Plant (Extended Diagram)

A diagram for a typical modern coal fired steam power plant is illustrated to follow:[276]



The person contributing this image offers the following additional key and explanation [minor alterations by MCM]:

"1. [Hyperboloid wet probably natural draft] cooling tower.
2. Cooling water pump.
3. Transmission line (3-phase).
4. Unit transformer (3-phase).
5. Electric generator (3-phase).
6. Low pressure turbine.
7. Condensate extraction [boiler feed] pump.
8. Condenser.
9. Intermediate pressure turbine.
10. Steam governor valve.
11. High pressure turbine.
12. Deaerator.
13. Feed heater.
14. Coal conveyor.
15. Coal hopper.
16. Pulverized fuel mill.
17. Boiler drum.
18. Ash hopper.
19. Superheater.
20. Forced draught fan.
21. Reheater.
22. Air intake.
23. Economizer.
24. Air preheater.
25. Precipitator.
26. Induced draught fan.
27. Chimney stack.
28. Feed pump between deaerator and feed heater."

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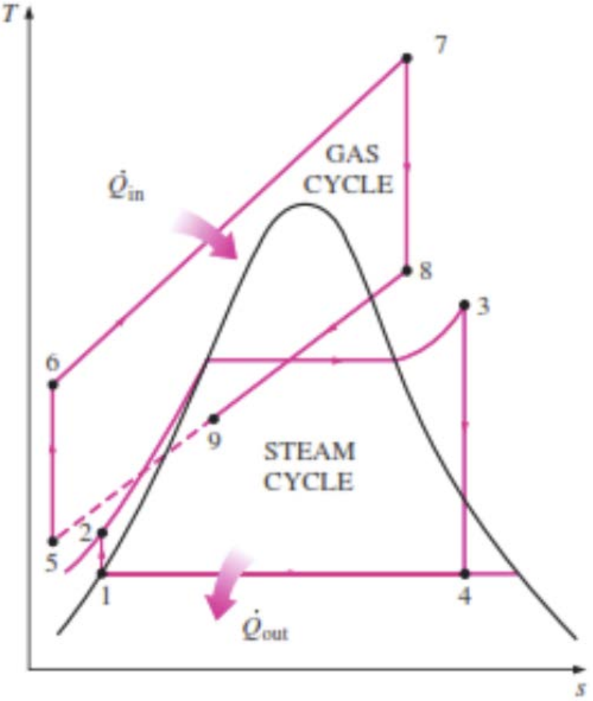
[276] https://en.wikipedia.org/wiki/Thermal_power_station
images by https://en.wikipedia.org/wiki/User:BillC , modified minimally by MCM:
https://commons.wikimedia.org/wiki/File:PowerStation3.svg and
https://en.wikipedia.org/wiki/File:PowerStation2.svg

> “Coal is conveyed (14) from an external stack and ground to a very fine powder by large metal spheres in the pulverized fuel mill (16). There it is mixed with preheated air (24) driven by the forced draught fan (20). The hot air-fuel mixture is forced at high pressure into the boiler where it rapidly ignites. Water of a high purity flows vertically up the tube-lined walls of the boiler, where it turns into steam, and is passed to the boiler drum, where steam is separated from any remaining water. The steam passes through a manifold in the roof of the drum into the pendant superheater (19) where its temperature and pressure increase rapidly to around 200 bar and 570°C, sufficient to make the tube walls glow a dull red. The steam is piped to the high pressure turbine (11), the first of a three-stage turbine process. A steam governor valve (10) allows for both manual control of the turbine and automatic set-point following. The steam is exhausted from the high pressure turbine, and reduced in both pressure and temperature, is returned to the boiler reheater (21). The reheated steam is then passed to the intermediate pressure turbine (9), and from there passed directly to the low pressure turbine set (6). The exiting steam, now a little above its boiling point, is brought into thermal contact with cold water (pumped in from the cooling tower) in the condenser (8), where it condenses rapidly back into water, creating near vacuum-like conditions inside the condenser chest. The condensed water is then passed by a condensate pump (7) to a deaerator (12), then pumped by feedwater pump (28) and pre-warmed, first in a feed heater (13) powered by steam drawn from the high pressure set, and then in the economizer (23), before being returned to the boiler drum. The cooling water from the condenser is sprayed inside a cooling tower (1), creating a highly visible plume of water vapor, before being pumped back to the condenser (8) in cooling water cycle.
>
> The three turbine sets are sometimes coupled on the same shaft as the three-phase electrical generator (5) which generates an intermediate level voltage (typically 20-25 kV). This is stepped up by the unit transformer (4) to a voltage more suitable for transmission (typically 250-500 kV) and is sent out onto the three-phase transmission system (3).
>
> Exhaust gas from the boiler is drawn by the induced draft fan (26) through an electrostatic precipitator (25) and is then vented through the chimney stack (27).”

Combined Gas-Vapor Power Cycle (CGVPC) aka Combined Cycle

Plants employing these cycles combine one or more gas cycles (Brayton gas power cycle) with a steam cycle (Rankine vapor power cycle). Such plants are called **Combined Cycle Gas Turbine (CCGT) Plants** or **Combined Cycle plants**. They employ a **Heat Recovery Steam Generator (HRSG)** which captures exhaust heat from the gas turbine that would otherwise escape through the exhaust stack. Exhaust gas is usually above 500 °C. The HRSG creates steam from the gas turbine exhaust heat and delivers it to the steam turbine.[277] As usual, the steam cycle may involve regeneration, reheating, and other efficiency improvements. Overall thermal efficiencies have exceeded 60% for the best CGVPC/CCGT plants.[278] (These are not the same as Cogeneration plants.)



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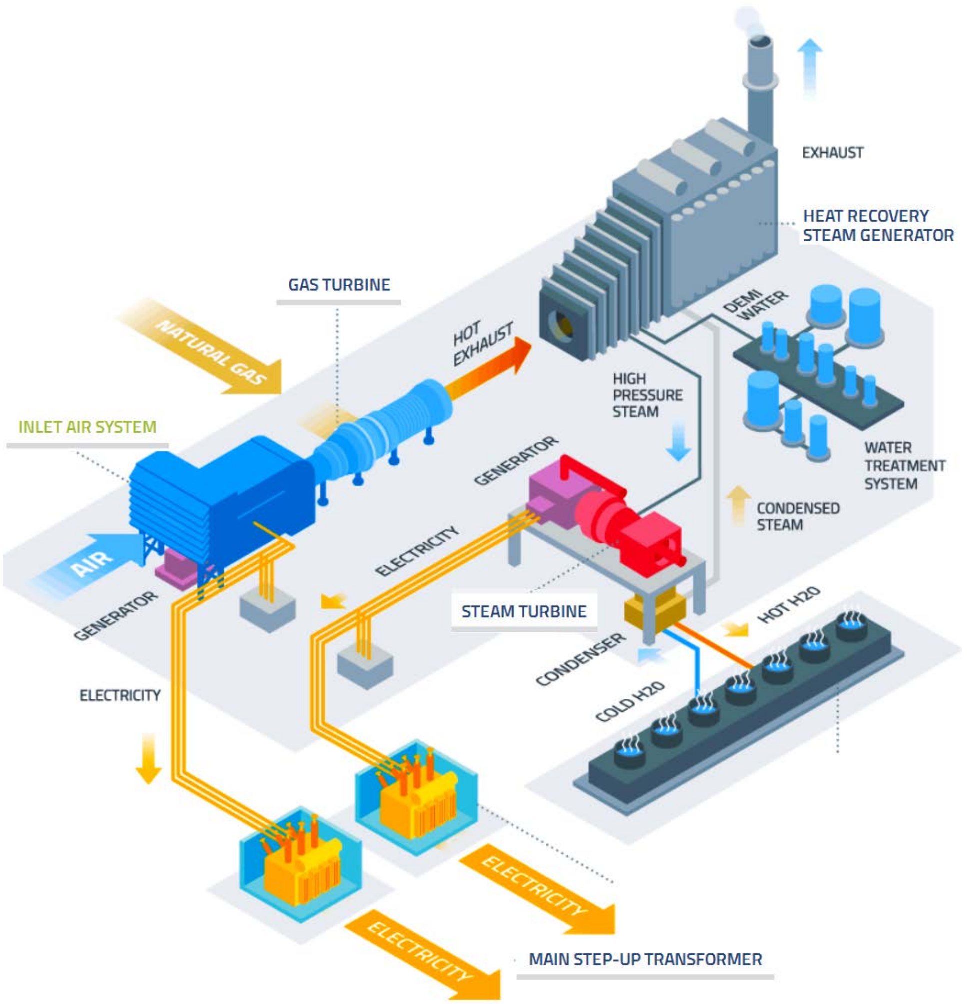
[277] https://powergen.gepower.com/resources/knowledge-base/combined-cycle-power-plant-how-it-works.html and https://en.wikipedia.org/wiki/Combined_cycle

[278] *TAEA7* p. 586

T-s diagram from http://sounak4u.weebly.com/vapour--combined-power-cycle.html

The following diagram by the Italian corporation ERG[279] sketches an actual CCGT plant. Natural gas fires the gas turbine (light blue), which turns a generator (magenta where visible). The generator is cooled by intake air, which presumably also supplies the gas turbine combustion. The hot exhaust from the gas turbine enters a large Heat Recovery Steam Generator HRSG, which transfers the heat to treated water producing HP steam. This enters the Steam Turbine (red), which provides shaft power to a separate generator (also magenta). Thus, both turbines are providing net electrical power out.



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[279] http://www.erg.eu/erg-official-theme/images/infographic/ccgt/ciclo-combinato.gif , image modified and enhanced from animated sequence by MCM

The following depicts a GE **Combined Cycle Gas Turbine (CCGT) Plant**.[280] There are 2 gas turbines (the one exposed in the foreground is blue) and one steam turbine (gold). The turbines drive 3 generators (green). Two large HRSGs on the right capture the exhaust heat and produce steam for the steam turbine. Cooling is to the far right.

Optimal Vapor Power Cycle Working Fluids Compared to Water

In general, the desired properties of an ideal vapor power cycle working fluid include:[281]

1. High critical temperature T_{cr} located above the maximum metallurgically allowed T_{max} (about 620 °C), and a safe maximum pressure P_{max} in the cycle which does not threaten materials strength at the maximal T_{max}.

2. Low triple-point temperature, well below the temperature of the cooling medium, to prevent solidification.

3. A condenser pressure that is not too low. Condensers usually operate below atmospheric pressure P_{atm}, but when condenser pressures are too low, air intrusion is more likely to occur. Condenser pressure also cannot be lower than the saturation vapor pressure P_{sat} at the T_L of the cooling medium. For example, if the low temperature cooling reservoir for the condenser is river water at temperature $T_L = 15$ °C , and the fluid entering the condenser is by design 25 °C, the condenser pressure must be greater than P_{sat} of water at 25 °C, namely 3.2 kPa.

4. A high enthalpy of vaporization (h_{fg}), so that heat transfer to the working fluid is nearly isothermal and large mass flow rates are not needed.

5. A saturation dome that resembles an inverted U rather than an inverted V. This reduces formation of excessive moisture in the turbine from operation ending at quality $x < 100$ % in the saturated liquid-vapor mixture region, and the resultant need for reheating.

6. High thermal conductivity (good heat transfer characteristics)

7. It should also be nontoxic, inert, inexpensive, and readily available.

---

[280] http://electrical-engineering-portal.com/an-overview-of-combined-cycle-power-plant

[281] *TAEA7* p. 589 and https://en.wikipedia.org/wiki/Binary_cycle

Water approaches many of these ideal specifications (especially 2 and 4, probably 6 with a thermal conductivity[282] of 0.6 W·m⁻¹·K⁻¹, which is greater than most common liquids at 300 K), but it is not ideal with respect to several of the criteria:

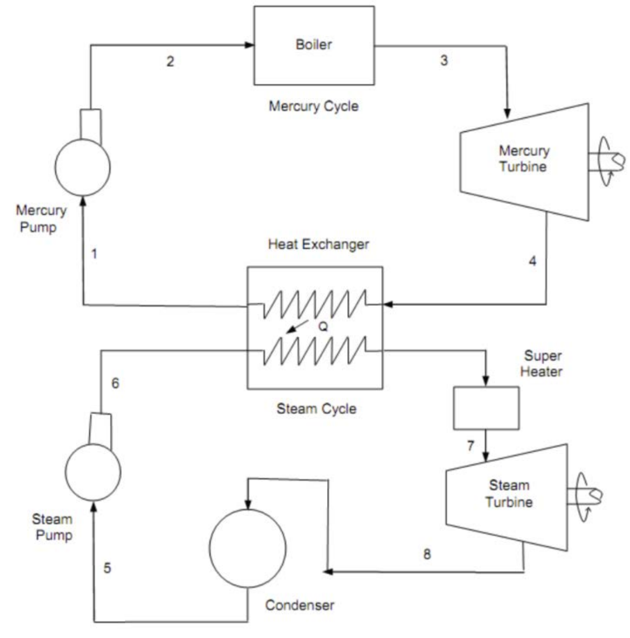
Criterion 1: Water T_{cr} is too low at only 374 °C.
Also, water it has a very high saturation vapor pressure P_{sat} of 16.5 MPa at a T_{max} of 350 °C.

Criterion 3: Water saturation vapor pressure P_{sat} is rather low at 4.2 kPa at 30 °C, 3.2 kPa at 25 °C

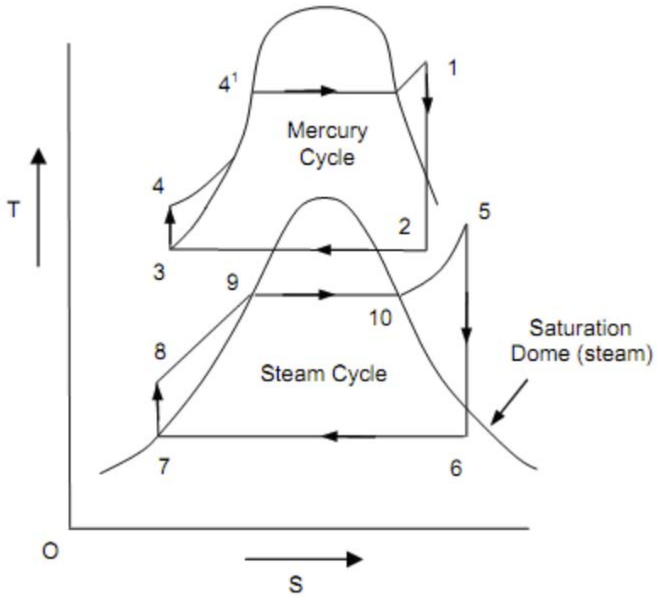
Criterion 5: Water saturation dome has a broad inverted V shape more likely to cause turbine operation ending at quality x <100 % in the saturated liquid-vapor mixture region

Binary Vapor Cycles

Unlike Combined Gas-Vapor Power Cycles (which combine a gas power cycle and a vapor power cycle and are widely deployed), these employ 2 separate vapor cycles and are uncommon. The low temperature vapor cycle usually uses water as the working fluid. However, the high temperature cycle uses such exotic working fluids as liquid/vapor mercury and liquid/vapor Na or K or Na-K mixtures. For Hg, the T_{cr} of Hg is 898 °C, well above metallurgical limits, and its P_{cr} is about 18 MPa, so it is suitable for a high pressure cycle. It more closely approximates the Carnot cycle than the steam/water vapor cycle (apparently because the Hg saturation dome has more of an inverted U shape). However, Hg has a vapor pressure of only 0.07 Pa at a typical condenser T of 32 °C, which is too strong a vacuum for a power plant, so its use is limited to the high pressure cycle. (It is also toxic and costly, and it has a low specific enthalpy of vaporization of 295 kJ/kg at 1 atm compared to 2257 for water.) Binary Vapor Cycles appear currently to be economically infeasible and therefore experimental, though efficiencies as high as 50% are possible.[283] The following diagrams illustrate a binary vapor cycle using Hg and steam:[284]



Mercury Water Binary Vapor Cycle



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[282] http://www.engineeringtoolbox.com/thermal-conductivity-liquids-d_1260.html

[283] *TAEA7* p. 590

[284] http://www.expertsmind.com/topic/vapor-power-cycles/binary-vapor-cycle-97686.aspx

Refrigeration Cycles (11)

(from text Chapter 11 & other sources)

Certain aspects of refrigeration and heat pumps—diagrams, P-v and T-s diagrams, refrigerants, and pumps—are discussed in the Chap. 6 summary.

Refrigeration cycles require input power or work W_{in} (usually electrical) to produce refrigeration by causing a non-spontaneous heat (thermal energy) transfer from lower to higher T ($T_L \rightarrow T_H$). In contrast, heat engines use input heat (thermal energy) transfer ($T_H \rightarrow T_L$) to produce useful mechanical work $W_{net,out}$, such as shaft power, and ultimately electrical generation, propulsion, or other uses.

The most important and widely used method of refrigeration is the **vapor-compression refrigeration cycle**. It is employed in refrigerators and heat pumps (operated in either mode). In both types of devices, heat is effectively pumped from a lower temperature T_L to a higher T_H.

The Reversed Carnot Cycle (a theoretical refrigeration cycle discussed in Chap. 6) is impractical for actual refrigeration use.

In the heat pump operated in heating mode, the heat Q_L is extracted at T_L from the cold environment (outside air or an underground reservoir, etc.) and released into the heated interior space at T_H as Q_H. In the refrigerator, the T_L is found in the freezer or main compartment, which is chilled by the extraction of heat at a lower temperature T_L, and the release of waste heat into the room at T_H.

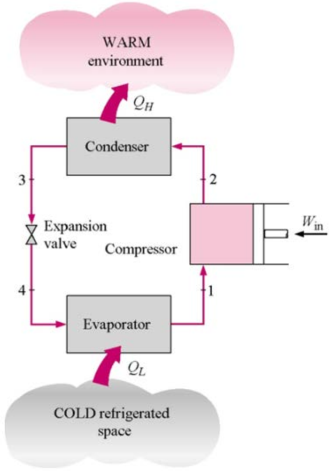
Vapor-Compression Refrigeration Cycle Overview

(11-3, 11-4,11-5)

The **vapor-compression refrigeration cycle** is the most widely used refrigeration cycle both for refrigeration systems and for heat pumps. Apparently, there is no eponym strongly associated with this cycle (in contrast to Rankine, Brayton, Diesel, etc.) In 1834, "an American expatriate to Great Britain, Jacob Perkins [1766-1849], built the first working vapor-compression refrigeration system" and received a patent on it.[285]

This cycle has four components: **Evaporator**, **Compressor**, **Condenser**, and **Expansion/throttling** [or optionally, passage in an isentropic turbine]. (see diagram on right)

Process	Description
1-2	Isentropic Compression
2-3	Constant pressure heat rejection in the Condenser
3-4	Throttling in an Expansion valve (non-isentropic)
4-1	Constant pressure heat addition in the Evaporator



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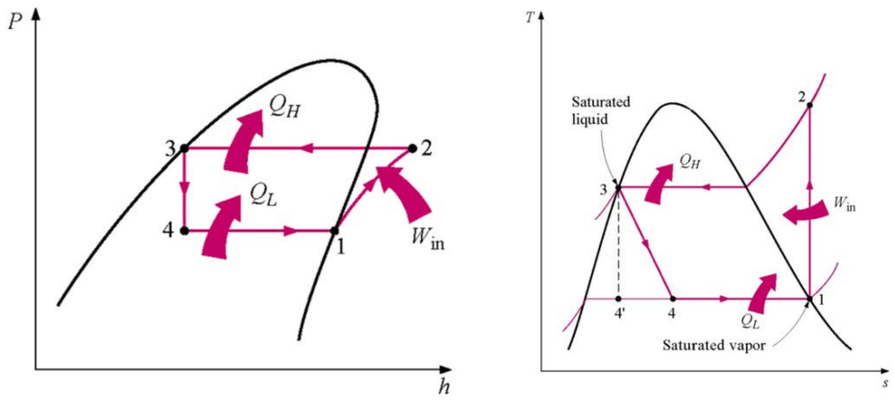
[285] https://en.wikipedia.org/wiki/Vapor-compression_refrigeration

To summarize, the refrigerant enters the Compressor as a saturated vapor and as it is compressed its P and T increase, so that it exits the compressor in a superheated state. This vapor condenses at constant P in the Condenser (T is constant while the refrigerant is a saturated mixture), giving up its enthalpy of vaporization to form a HP saturated liquid. It is then Throttled down to the low evaporator pressure and low T, and vaporizes in the Evaporator as it absorbs heat from the refrigerated space. These four processes are summarized as follows (with reference to the P-h and T-s diagrams that follow):[286]



P-h diagram (left) and T-s diagram (right) of the Ideal Vapor-Compression Refrigeration Cycle

Process 1-2: Starts with saturated vapor, Compressor using W_{in} performs isentropic compression
(P, T, and h increase substantially to a superheated state.)
Process 2-3: Rejects heat Q_H (Enthalpy of vaporization) in the Condenser at constant high P
(h and s decrease; T decreases but is constant while saturated is mixture present.)
No work is performed.
Process 3-4: Throttling via an expansion valve at constant h
(P and T decrease; s increases in this irreversible step.)
(Alternatively, an isentropic turbine could be used ending at 4' instead of 4, improving the COP_R.)
Process 4-1: Heat Q_L is absorbed by the refrigerant at constant low P and constant low T in the Evaporator.
The liquid/vapor mixture evaporates to a saturated vapor. (h and s increase.)
The refrigerated space providing the Q_L is chilled.

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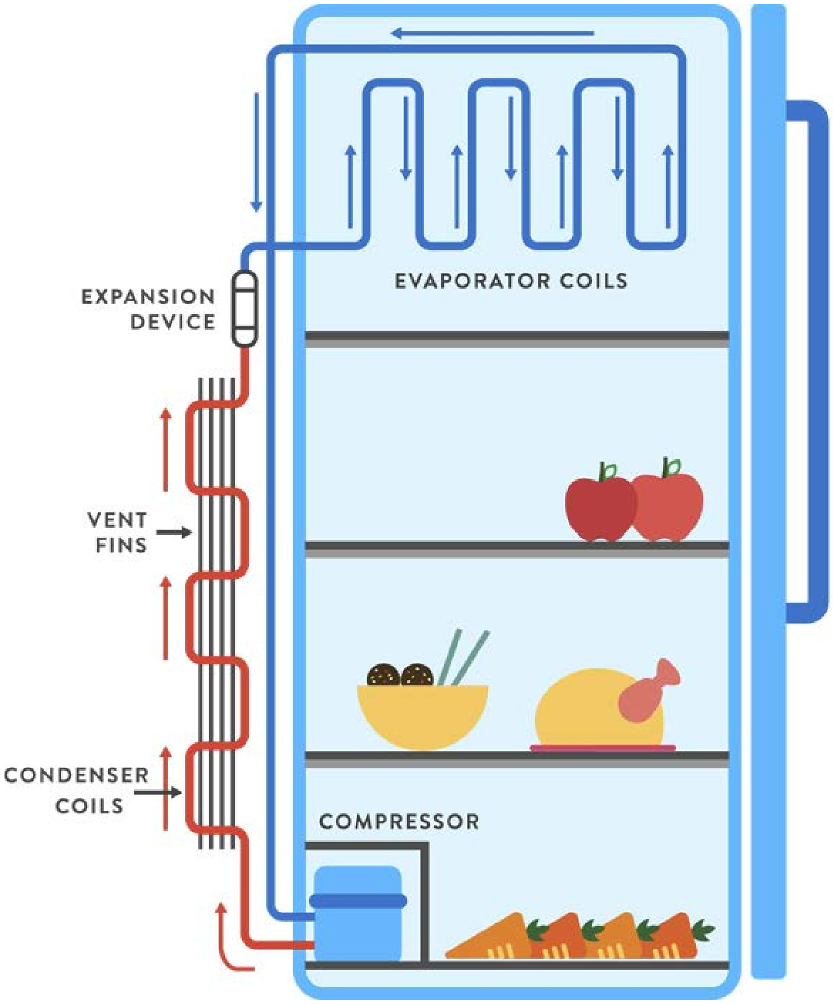
[286] *TAEA7* Chap_11.ppt, modified by MCM

Components of a Home Refrigerator



In a typical actual home refrigerator (see simplified diagram[287] to the right) the compressor is located typically at the bottom near floor level. (In this diagram, red refrigerant lines and components are hotter, whereas blue are colder.)

The Condenser coils, where waste heat is rejected to the room air, are often positioned behind the refrigerator.

The Expansion throttle valve or capillary tube is near the condenser.

The Evaporator coils are located in the freezer and possibly also the main compartment, where they extract Q_L from the refrigerated space. This added thermal energy (heat) provides the enthalpy of vaporization to the refrigerant needed to cause it to vaporize (evaporate).

According to the textbook example,[288] for an ideal vapor-compression refrigeration cycle refrigerator operating with R-134a between 0.14 MPa (in the Evaporator) and 0.8 MPa (in the Compressor) and with a refrigerant mass flow rate of 0.05 kg/s, the COP_R for a refrigerator using a throttle valve is found to be 4.0, whereas with an isentropic turbine, the COP_R is found to be 5.1, a significant improvement in performance but at the cost of added complexity.

Second Law Efficiency η_{II} of an idealized Vapor-Compression Refrigeration Cycle

The second law efficiency η_{II} of an idealized Vapor-Compression Refrigeration Cycle, as calculated in an example[289] in the textbook using R-134a, is found to be η_{II} = 35%. Recall that η_{II} is the ratio of COP_R to $COP_{R,rev}$ (not the ratio of Q_L to W_{in}).

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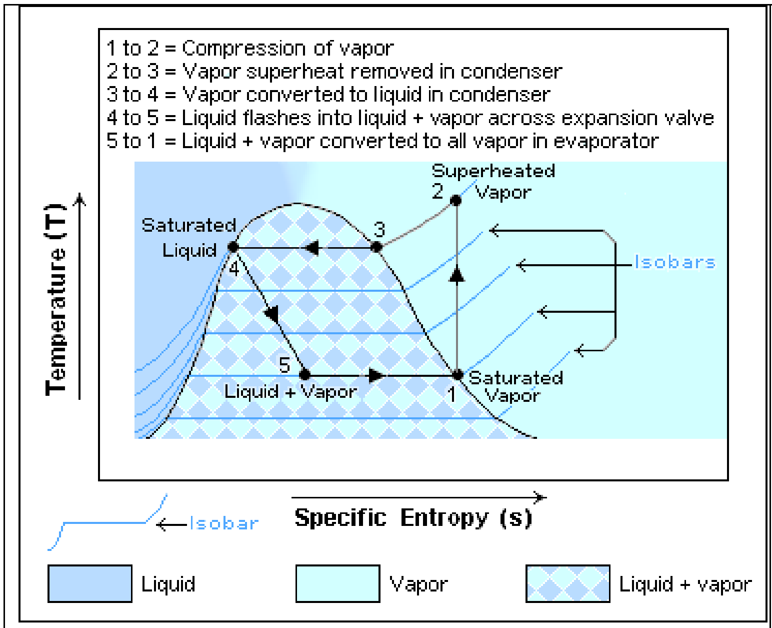
[287] https://www.fantasticfridges.com/YoungLearners/HowdoesaFridgeWork

[288] *TAEA7* p. 616

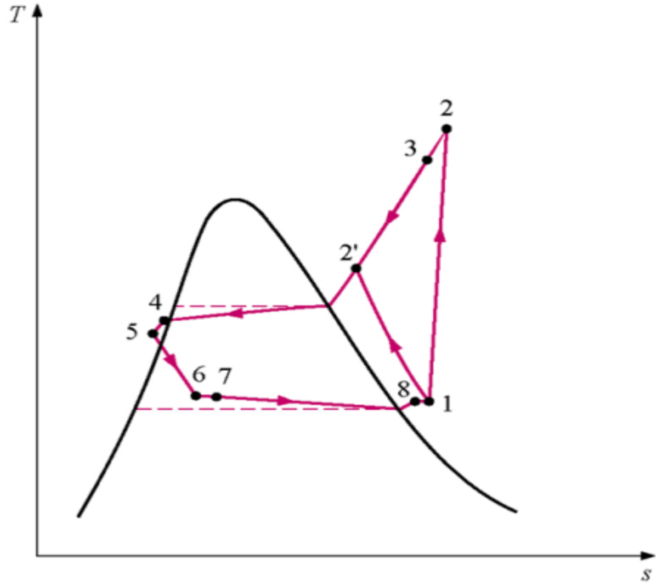
[289] *TAEA7* p. 622

A T-s diagram[290] for an Ideal Vapor-Compression refrigeration system (with no irreversibilities or frictional losses) is shown on the left below.

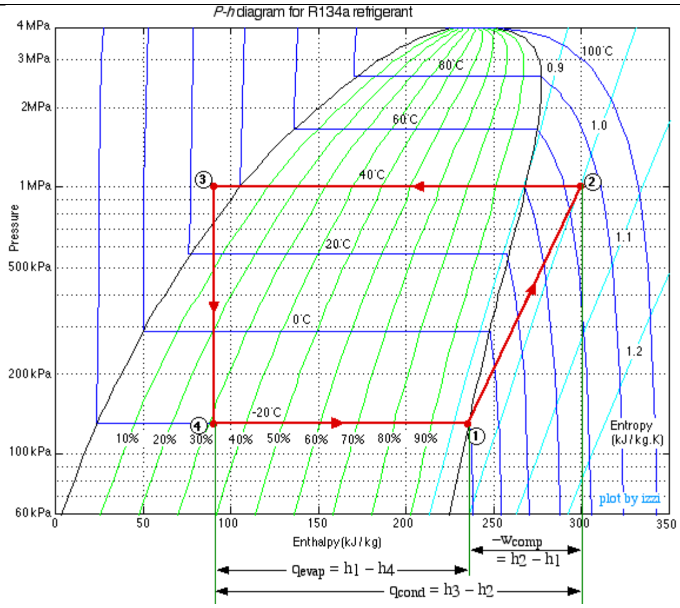
An actual vapor-compression refrigerator cycle exhibits various frictional losses, pressure drops, heat losses, and other irreversibilities cause a drop of COP_R. (The decrease in COP_R is found to be is rather slight in the textbook example, p. 617-619. The T-s diagram below on the right derives from this source).



T-s Diagram for
an Ideal Vapor-Compression refrigeration system



T-s diagram for an actual refrigeration cycle
with irreversibilities.



P-h diagram for a Basic R134a
Vapor-Compression Refrigeration System
showing Isenthalpic Expansion by throttling at ③ ④

To the left is a P-h diagram[291] for a basic R134a Idealized Vapor-Compression Refrigeration System.

Note that the throttle valve expansion process is modeled as isenthalpic, and the condenser stage ② ③ and evaporator stage ④ ① are modeled as isothermal. However, the compression process ①-② does not appear to be modeled as isentropic (in contrast to the idealized example top left). The isentropic (light blue) lines resemble but are not parallel to the ①-② process path (red line).

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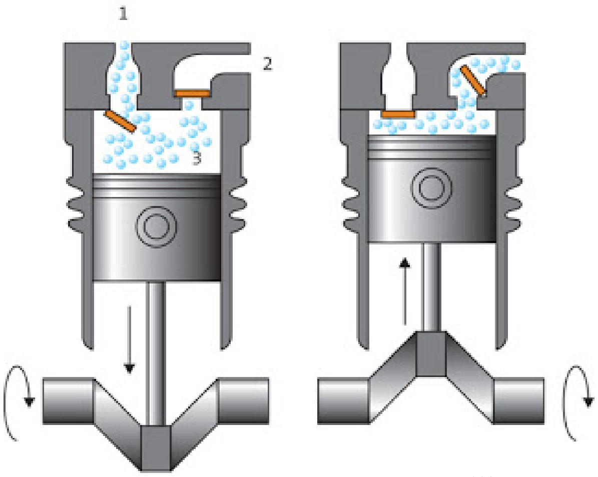
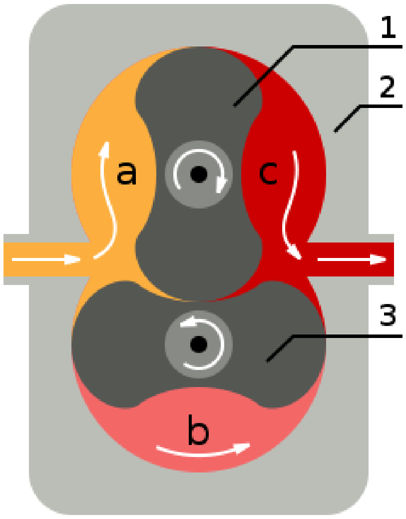
[290] https://en.wikipedia.org/wiki/Vapor-compression_refrigeration
[291] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter4c.html

Compressor Types

Compressor types include **Reciprocating piston compressors** (having inlet and outlet valves, widely used, produce high pressure, require high maintenance), **Rotary Screw compressor** (widely used, including Lysholm types and Roots blowers with lobed rotors, see diagram), **Centrifugal (radial) compressors** (using rotating impeller, produce low pressures, few moving parts), **Scroll compressors**[292] (which use two interleaving spiral scrolls to compress fluids discharging in the center), and others.



Reciprocating Piston Compressor[293]



Roots blower compressor mechanism[294]

Centrifugal compressor impeller[296]

Lysholm screw compressor mechanism[295]

Some refrigeration units may have multiple stages which require the use of multiple compressors (see later discussion). The gas motor/compressors unit types include motors which are hermetic (hermetically sealed) or open, and compressors which are hermetic or semi-hermetic, the choice of which pertains to the ease of making repairs and the likelihood of loss of refrigerant when seals fail. Compressors cannot be replaced by amateur DIYers, due to EPA regulations.

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[292] https://en.wikipedia.org/wiki/Scroll_compressor
[293] http://topcompressorhjtypes.blogspot.com/
[294] https://en.wikipedia.org/wiki/Roots-type_supercharger
[295] https://en.wikipedia.org/wiki/Vapor-compression_refrigeration
[296] http://www.conceptsnrec.com/Resources/Photo-Gallery/Compressors.aspx

Refrigerant Properties and Selection Criteria

(text 11-6)

Refrigerant working fluids include Chlorofluorocarbons CFC's, ammonia, hydrocarbons (such as propane and isobutane), CO_2, and many others. The choice must be based on situation and design requirements. Ethyl ether was formerly used but is highly flammable and toxic. Typical **refrigerants** for commercial and household refrigerators have included R-11, R-12, R-134a (an HFC), R-22 (an HCFC), R-502, and R-600a (isobutane, an HC).[297] Hyphens in the refrigerant R classification abbreviations are included in ASHRAE Numbers,[298] National Refrigerants, Inc., and Wikipedia, but are omitted on some other sites.

Ammonia

Ammonia (R-171) is toxic but widely used in large commercial or industrial applications, such as food refrigeration, dairy and meat processing, ice cream, ice production, and other low-temperature manufacturing.

Advantages: "As a refrigerant, ammonia has four major advantages over CFCs and HCFCs:

> • An ammonia-based refrigeration systems costs 10-20% less to build than one that uses CFCs because narrower-diameter piping can be used.
>
> • Ammonia is a 3-10% more efficient refrigerant than CFCs [higher COP_R and enthalpy of vaporization], so an ammonia-based system requires less electricity, resulting in lower operating costs. [It has lower energy cost, more favorable thermodynamic and transport properties, and higher heat transfer coefficients.]
>
> • Ammonia is safe for the environment, with an Ozone Depletion Potential (ODP) rating of 0 and a Global Warming Potential (GWP) rating of 0.
>
> • Ammonia is substantially less expensive than CFCs or HCFCs"[299]

Disadvantages: There are two key disadvantages to using ammonia as a refrigerant:

> • It is not compatible with copper, so it cannot be used in any system with copper pipes.
>
> • Ammonia is poisonous in high concentrations. Two factors, however, mitigate this risk: ammonia's distinctive smell is detectable at concentrations well below those considered to be dangerous, and ammonia is lighter than air, so if any does leak, it will rise and dissipate in the atmosphere."[300]

Halogenated Refrigerants

These began in the 1920s and 1930s with R-21, R-12 "Freon", and R-11. They are quite diverse and characterized by generally less toxicity (than ammonia for instance), greater expense, and greater environmental impact (mainly, the depletion of stratospheric ozone).[301]

R-11 (a chlorofluorocarbon or CFC: trichlorofluoromethane) was used in large capacity water chillers for A/C of buildings, but is being phased out. U.S. production was ended in January 1, 1996.

R-12 ("Freon", a CFC, dichlorodifluoromethane) was formerly extensively used in home refrigerators, freezers, and automobile A/C. But, like other fully halogenated CFC's, these are being phased out for environmental

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[297] https://en.wikipedia.org/wiki/List_of_refrigerants

[298] American Society of Heating, Refrigerating, and Air-Conditioning Engineers: https://www.ashrae.org/standards-research--technology/standards--guidelines/standards-activities/ashrae-refrigerant-designations

[299] http://www.goodway.com/hvac-blog/2009/08/ammonia-as-a-refrigerant-pros-and-cons/

[300] ibid. and *TAEA7* p. 624

[301] Detailed info including phaseout schedules available for refrigerants via links from http://www.refrigerants.com as well as various Wikipedia pages specific for the refrigerant.

reasons. R-12 manufacture was banned in 1996. The CFCs are being replaced by such compounds as R-134a (a haloalkane: 1,1,1,2-Tetrafluoroethane) which lacks chlorine.

R-22 (a hydrochlorofluorocarbon HCFC: Chlorodifluoromethane), is used in window A/C's, heat pumps, large refrigerators, etc., and is somewhat more ozone friendly than the CFC's, but is scheduled for near-total end of US production by 2020.

R-502 (a blended refrigerant of Chlorodifluoromethane (HCFC-22) and Chloropentafluoroethane (CFC-115)), was the dominant refrigerant in commercial refrigeration such as supermarkets and was used for low temperature refrigeration, but it is being phased out as of 1995.

R-404A (blend of HFC's: R-125, R-143a, and R-134a) is used for low and medium temperature refrigeration applications and is replacing R-502, although it has slightly higher saturation pressures than R-502:

R-404A	liquid sat pressure	19.9 psia at -40 °F	31.9 psia at -20 °F
R-502	liquid sat pressure	18.7 psia at -40 °F	29.8 psia at -40 °F.

The Saturation pressures versus low to medium T for some of the refrigerants are shown in a diagram further below.

Other Refrigerants

These include many common compounds though formulated and packaged specifically for use as refrigerants, including various hydrocarbons (isobutane R-600A, propane R-290, ethane, ethylene, etc.), CO_2 (R-744), H_2, He, N_2, O_2, Ar, SO_2, water/steam, air, and many others.

Selecting the Optimal Refrigerant

Important general categories to consider include **thermodynamic cycle** (**thermophysical**) properties, **technological** issues, **economic costs**, **safety**, **environmental issues**, and **other** criteria.[302] Here are some of the specifics:

T versus Saturation Vapor Pressure P_{sat} in the Evaporator

For adequate heat transfer, the refrigerant in the evaporator should be 5 to 10 °C below the lowest T desired in the refrigerated space (e.g., -20 °C refrigerant for -10 °C chilled space). In the evaporator is the lowest pressure in the cycle, and this should be above atmospheric pressure to prevent intrusion of air.[303] Thus, at sea level, it should have a saturation pressure of > 1 atm at -20 °C to chill a space at -10 °C. (Indeed R-134a has P_{sat} @ -20 °C = 132.8 kPa; ammonia R-171 has P_{sat} @ -20 °C = 1.90 bar = 190 kPa[304], thus both exceed 101.3 kPa.

A chart of P_{sat} vs. T in °C for several refrigerants is shown to follow.[305]

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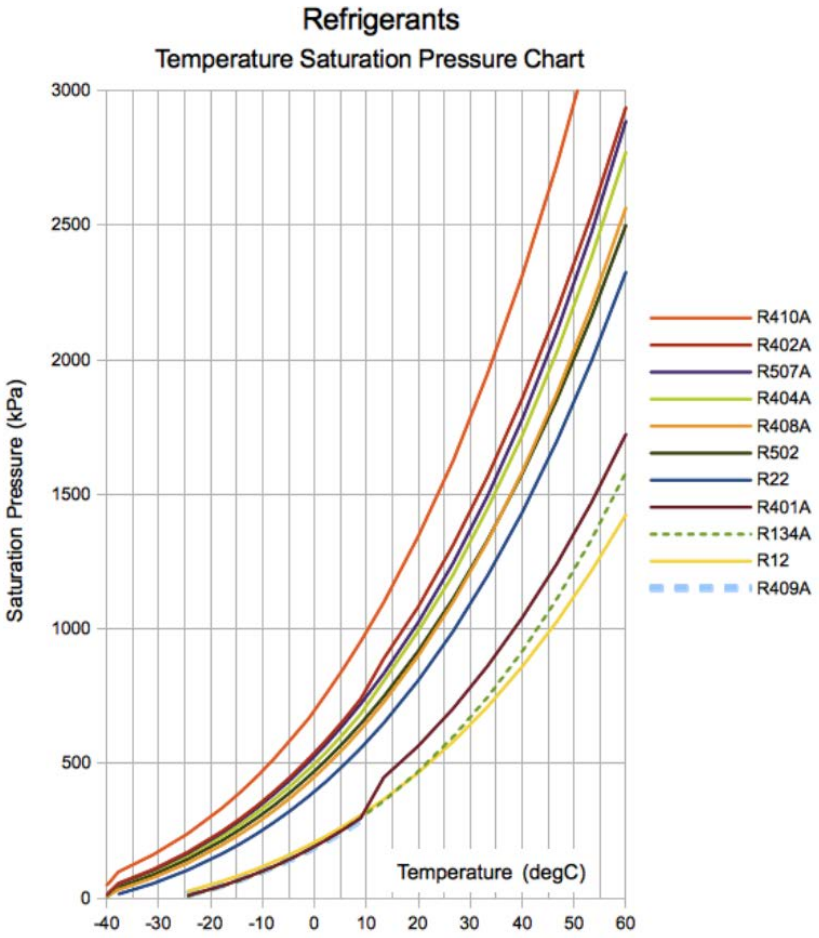
[302] http://www.achrnews.com/articles/94354-criteria-for-refrigerant-selection and https://www.bsria.co.uk/news/article/choosing-wisely-the-selection-for-refrigerants-must-take-into-account-the-latest-f-gas-legislation/

[303] *TAEA7* p. 625

[304] https://engineering.purdue.edu/ME200/Thermodynamic_tables_SI_units.pdf

[305] http://www.engineeringtoolbox.com/refrigerant-temperature-pressure-chart-d_1683.html, adapted MCM



P_{sat} vs. T in °C for several refrigerants

T_H and P in the Condenser

For optimal heat rejection at T_H in the condenser, the refrigerant T must be above the temperature of the cooling medium (which typically is ambient air at about +20 °C).[306] Also the P_{sat} of the refrigerant should be well below the P_{cr} at the temperature of the cooling medium of about +20 °C (to maintain isothermal transfer).[307] For example with R-134a, P_{sat} @ +20 °C = 572 kPa versus P_{cr} = 4.059 MPa (and T_{cr} = 101.06 °C).[308]

High Specific Enthalpy of Vaporization (h_{fg})

This should be maximal to minimize required mass flow rate, and thus reduce compressor power usage. Some h_{fg} values are:

R-134a	h_{fg} = **212.9** kJ/kg @ -20 °C	**182.3** kJ/kg @ +20 °C.[309]
Ammonia R-171	h_{fg} is **1329.1** kJ/kg @ -20 °C	**1185.6** kJ/kg @ +20 °C.[310]
Water R-718	[water is frozen @ -20 °C]	**2453.5** kJ/kg @ +20 °C.[311]

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[306] *TAEA7* p. 625

[307] *TAEA7* p. 626

[308] https://www.ohio.edu/mechanical/thermo/property_tables/R134a/ and *TAEA7* Table A-11 for R-134a

[309] *TAEA7* Table A-11 for R-134a

[310] https://engineering.purdue.edu/ME200/Thermodynamic_tables_SI_units.pdf

[311] *TAEA7* Table A-4 for Saturated water

Thus ammonia is far superior to R-134a in this criterion.

Other Important Refrigerant Factors To Optimize[312]

Toxicity	(minimize)	**Detectability if leaking**	(optimize)
Corrosiveness	(minimize)	**Materials Compatibility**	(optimize)
Flammability	(avoid if possible)	**Chemical Stability**	(maximize)
Lubricant properties	(optimize)	**Cost**	(minimize)
Recyclability	(recycle if possible)		
Refrigerant mixtures	(optimize **azeotropic** property so components fractions in liquid refrigerant are the same as in the vapor)		
Environmental impact	(minimize if accidental or routine venting, especially pertaining to ozone depletion and global warming potential GWP)		

For heat pumps, the minimum T and P at which they operate may be higher than for other refrigeration systems, and refrigerant choices might therefore be different.

Heat Pumps Used For Heating and Cooling

(11-1,11-7, 6-4)

See also comments in Chapter 6, including cycle summaries.

Heat pumps, though more expensive to purchase and install, are growing in popularity in the US because of their potential for energy efficiency and for dual heating/cooling function. They are most cost-effective in areas that have strong cooling needs and modest heating needs (such as the southern US), and less effective in areas with very low winter temperatures (such as the northern US).

In the diagram on the left to follow, heat pump operation in heating mode and in cooling mode are depicted. Most heat pumps have a **reversing valve** that allows operation in heating or cooling mode. (This reverses the roles of the indoor and outdoor heat exchanging coils, changing roles between condenser versus evaporator.)

The diagram to follow on right includes typical values of liquid/vapor properties for a heat pump in cooling mode using R-134a.

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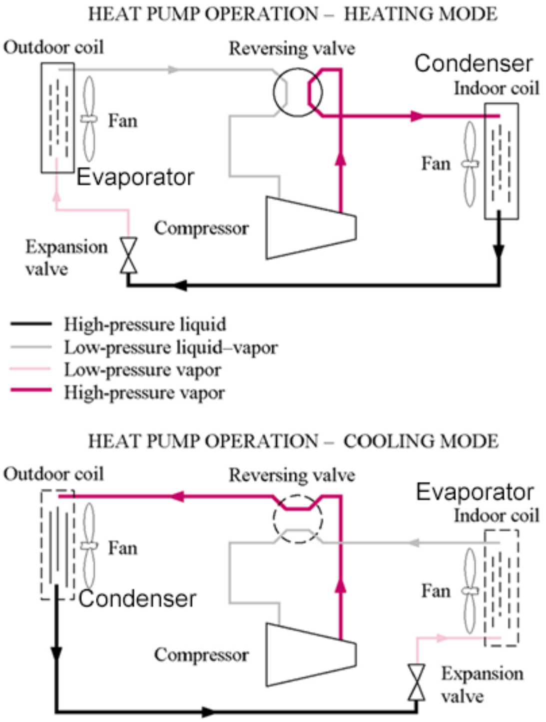
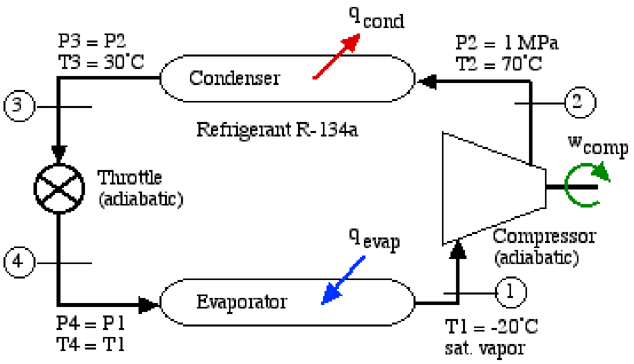
[312] *TAEA7 p. 626*



Heat pump diagrams for heating and cooling modes[313]



Basic refrigeration or heat pump system in cooling mode with typical property values[314]

Heat Pump Performance COP

The performance of a heat pump operated in Heating Mode is expressed by:

$$\textbf{Coefficient of Performance COP}_{\textbf{HPH}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

The performance of a heat pump operated in Cooling Mode (including as a Refrigerator) is expressed by

$$\textbf{Coefficient of Performance COP}_{\textbf{R}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

Under the same operating conditions, $COP_{HPH} = COP_R + 1$ or $COP_R = COP_{HPH} - 1$.

Typical COP values for Heat Pumps are:[315]

For Heating Mode: $1 < COP_{HPH} < 3$ to 4 (compared to 1 for electrical resistance heating).
COP can be higher, 2.5 to 5.0, if a ground source of heat is used, higher if geothermal heat.

For Cooling Mode: $3 < COP_R < 6$ (Refrigerating Heat Pump Mode, or Refrigerator)

Heat pump and Refrigeration/Air Conditioner systems are often rated by their **Energy Efficiency Ratio EER** or **Seasonal Energy Efficiency Ratio SEER** (see discussion further below).

For a heat pump in heating mode, a COP_{HPH} value of 4 means that the addition of 1 kW of electric energy is needed to have the beneficial release of 4 kW of heat at the condenser [into the interior room]. At the

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[313] Image and quoted text from textbook website chapter_06.ppt, image annotated MCM

[314] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter4c.html

[315] https://en.wikipedia.org/wiki/Heat_pump

evaporator side 3.0-3.5 kW of heat is extracted [from outside]. The additional heat is generated by the electrical energy used by the compressor.

For a heat pump in cooling mode, or for a refrigeration system, a COP_R of 4 indicates that 1 kW of electricity is needed for the evaporator to extract 4 kW of heat (from the chilled space).[316]

Heat pumps in heating mode that draw heat from the air, especially if humidity is high, are subject to **frosting**, which can reduce efficiency or disrupt heat transfer, and they are ineffective if outdoor T is too low.

Heat may also be drawn from water well or ground (geothermal) sources, which are not subject to frosting. The latter systems are more expensive and complex but have higher COP's.

In the Seattle area, "the temperature 6 feet underground is a constant 49.5 degrees Fahrenheit [9.7 °C] year round, warmer than the average air temperature in the winter and cooler than normal air temperatures in the summer."[317]

Performance and Efficiency of Refrigerators and Heat Pumps

(11-2, 11-3, 6-4)

The performance of refrigerators and heat pumps are mentioned in Chap. 6 summary, and presented in greater detail here:

Coefficients of Performance COP_R and COP_{HPH}

The performance of a **Heat Pump** operated in **Heating Mode** is expressed by:

$$\textbf{Coefficient of Performance } \mathbf{COP_{HPH}} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

The performance of a **Heat Pump** operated in **Cooling Mode** (including as a Refrigerator) is expressed by

$$\textbf{Coefficient of Performance } \mathbf{COP_R} = \frac{\text{Desired Ouput}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

When operating under the same conditions, $COP_{HPH} = COP_R + 1$ or $COP_R = COP_{HPH} - 1$.

Typical performance and COP values for Refrigerators and Heat Pumps are summarized as follows:[318]

Performance of a Refrigerator or a Heat Pump in Cooling Mode (COP_R)

$3 < COP_R < 6$ (Heat Pump in Cooling Mode or Refrigerator).

For a **refrigeration** system, a COP_R of 4 indicates that 1 kW of electricity is needed for 4 kW of heat to be extracted at the **Evaporator** from the **refrigerated/chilled space**.[319] COP_R is higher for smaller differences between T_H (at external **Condenser**) and T_L (at Evaporator), i.e., for lower $T_H - T_L$. COP_R is higher for higher Evaporator T_H in the refrigerated space.

The following left graph[320] depicts the effect of T_L on COP_R (Heat Pump in Refrigeration Mode): Higher Evaporator (chilled space) temperatures increase COP_R.

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[316] http://www.industrialheatpumps.nl/en/how_it_works/cop_heat_pump/ text edited and corrected MCM

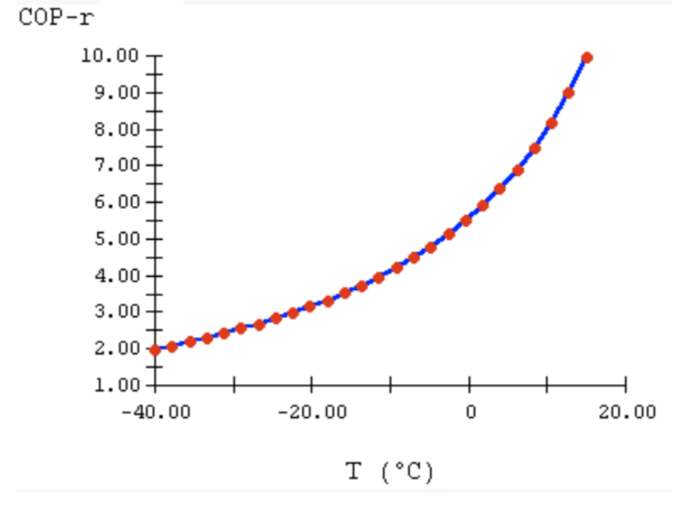
[317] http://www.seattletimes.com/seattle-news/high-fuel-costs-have-more-homeowners-eying-geothermal-heat/

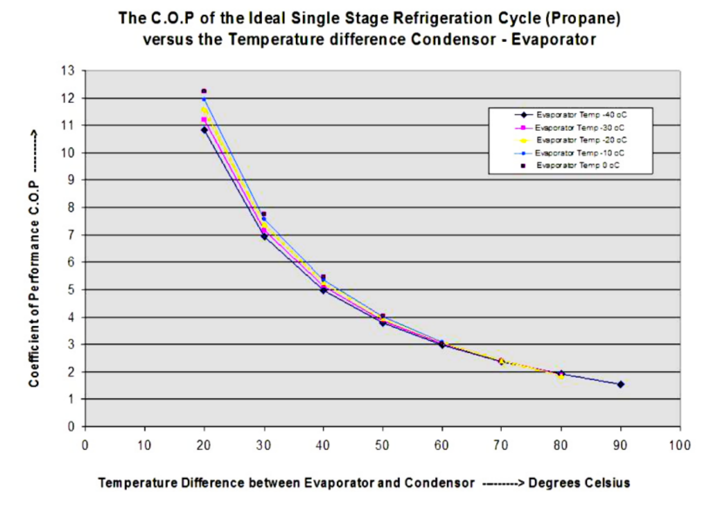
[318] https://en.wikipedia.org/wiki/Heat_pump and *TAEA7* p. 612

[319] http://www.industrialheatpumps.nl/en/how_it_works/cop_heat_pump/ text edited and corrected MCM

[320] http://www.qrg.northwestern.edu/thermo/design-library/refrig/refrig.html image enhanced MCM; and http://www.achrnews.com/articles/94191-putting-propane-into-the-refrigerant-loop , use of propane as a refrigerant

The right graph (for a modeled ideal propane refrigerant vapor compression refrigeration cycle) shows that the COP_R is higher for smaller differences between T_H (at external Condenser) and T_L (at Evaporator), whereas COP_R modeled in the Evaporator T range shown is barely affected by Evaporator T.



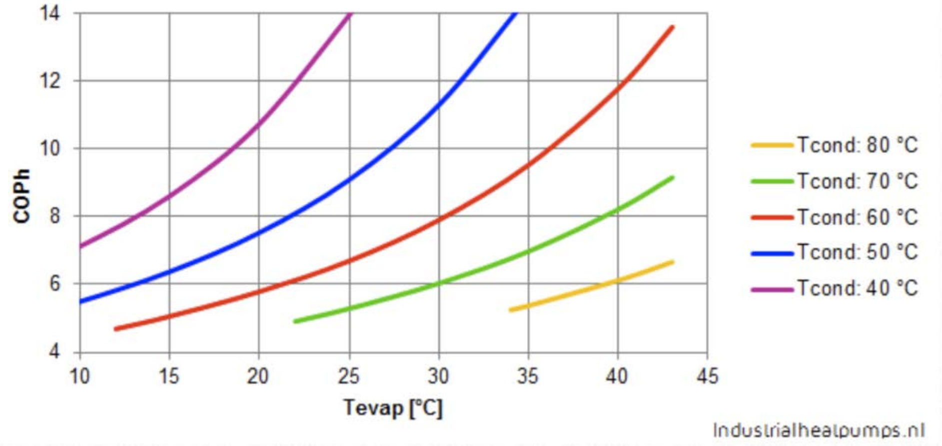


Performance of a Heat Pump in Heating Mode (COP_{HPH})

1 < COP_{HPH} < 3 to 4 for **air source** heat pumps ASHP (compare this to 1 for electrical resistance heating), COP_{HPH} is lower and sometimes < 1 for very cold outside temperatures (if COP_{HPH} < 1, resistive heating is typically substituted). COP_{HPH} can be 2.5 < COP_{HPH} < 5.0 or higher for **ground source** heat pumps GSHP. In general, COP_{HPH} is higher for smaller differences between T_H (at Evaporator) and T_L (at Condenser), i.e., for lower T_H - T_L.

For a heat pump operating in **heating mode**, a COP_{HPH} value of 4 means that the addition of 1 kW of electric energy is needed to produce a release of 4 kW of heat at the **condenser** into the **heated interior space**. At the **evaporator** side, ~3.0 kW of heat is extracted from the cold environment (outside air or an underground reservoir, etc.) The additional heat released at the condenser (4 - 3 = 1 kW in this example) is provided by the electrical energy operating the compressor. COP_H is higher for lower outside T_L at the evaporator.

The following graph[321] depicts these effect on COP_{HPH} (Heat Pump in Heating Mode): Higher condenser (heated space) temperatures reduce COP_{HPH} and higher evaporator temperatures increase COP_{HPH}.



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[321] http://www.industrialheatpumps.nl/en/how_it_works/cop_heat_pump/ image modified slightly

Energy Efficiency Ratio EER, Seasonal Energy Efficiency Ratio SEER, and IEER

(6-2 and outside sources, not discussed in Chapter 11)

Refrigeration/Air Conditioner systems and Heat pumps are often rated by their **energy efficiency ratio EER** or **seasonal energy efficiency ratio SEER**. SEER usually has a higher numeric value than EER for the same equipment and seems to be the preferred index. "Typical EER for residential central cooling units = 0.875 × SEER."[322]

The following discussion touches on some of the highlights of these complex and evolving standards.

Energy Efficiency Ratio (EER)

"The **Energy Efficiency Ratio (EER)** of a particular cooling device is the ratio of output cooling energy (in BTU) to input electrical energy (in W-h) at a given operating point. EER is generally calculated using a 95 °F outside temp and an inside (actually return air) temp of 80 °F and 50% relative humidity. The EER is related to the coefficient of performance [COP_R] … with the primary difference being that the COP of a cooling device is unit-less, because the numerator and denominator are expressed in the same units [whereas EER is expressed in (BTU/h)/W]…" [323]

The EER is defined by

$$EER \equiv 3.41214 \times COP_R \quad \text{with units of} \quad (BTU/h)/W \text{ or } BTU/W\text{-}h]$$

where the conversion uses 3.412 BTU/W-h.[324] But in addition, "EER is generally calculated using a 95 °F outside temp and an inside (actually return air) temp of 80 °F and 50% relative humidity…"[325]

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[322] https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio

[323] https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio and
http://www.engineeringtoolbox.com/heat-pump-efficiency-ratings-d_1117.html

[324] *TAEA7* p. 288 and https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio

[325] https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio

Seasonal Energy Efficiency Ratio (SEER)

"The Seasonal Energy Efficiency Ratio (SEER) … is defined by the 'Air-Conditioning, Heating, and Refrigeration Institute in its 2008 standard AHRI 210/240'."[326]

"The SEER is also … expressed in (BTU/h)/W but instead of being evaluated at a single operating condition [like the EER], it represents the expected overall performance for a typical year's weather in a given location. The SEER is thus calculated with the same indoor temperature [80 °F], but over a range of outside temperatures from 65 °F (18 °C) to 104 °F (40 °C), with a certain specified percentage of time in each of 8 bins spanning 5 °F (2.8 °C). There is no allowance for different climates in this rating, which is intended to give an indication of how the EER is affected by a range of outside temperatures over the course of a cooling season… Typical EER for residential central cooling units =

$$\text{EER} = 0.875 \times \text{SEER}$$

[Thus] SEER is a higher value than EER for the same equipment… A more detailed method for converting SEER to EER uses this [approximate] formula:

$$\text{EER} = -0.02 \times \text{SEER}^2 + 1.12 \times \text{SEER}$$

Note that this method is used for benchmark modeling only and is not appropriate for all climate conditions… A SEER of 13 is approximately equivalent to an EER of 11, and a COP of 3.2, which means that 3.2 units of heat are removed from indoors per unit of energy used to run the air conditioner… Typical EER for residential central cooling units = 0.875 × SEER. SEER is a higher value than EER for the same equipment…"[327]

"… The higher the unit's SEER rating the more energy efficient it is… For example, consider a 5,000-British-thermal-unit-per-hour (1,500 W) air-conditioning unit, with a SEER of 10 (BTU/h)/W, operating for a total of 1000 hours during an annual cooling season (e.g., 8 hours per day for 125 days)… The annual total cooling output would be 5000 BTU/h x 8 h/day x 125 days/yr = 5,000,000 BTU/year. With a SEER of 10 BTU/W·h, the annual electrical energy usage would be about … 500,000 W·h/year…

… The United States requires that residential systems manufactured after 2005 have a minimum SEER rating of 13. ENERGY STAR qualified Central Air Conditioners must have a SEER of at least 14.5. Window units are exempt from this law so their SEERs are still around 10… Substantial energy savings can be obtained from more efficient systems. For example by upgrading from SEER 9 to SEER 13, the power consumption is reduced by 30% (equal to 1 minus 9/13)…."[328]

The Integrated Energy Efficiency Ratio IEER

This is a newer seasonal efficiency rating method: "A newly developed measurement that evaluates the efficiency of a unitary air-conditioning or heat pump system on a seasonal basis is the IEER [integrated energy efficiency ratio]… IEER is best suited for chillers and VRF [variable-refrigerant flow] systems because these systems generally utilize multiple air handlers (or fan coils) as part of the system…"[329]

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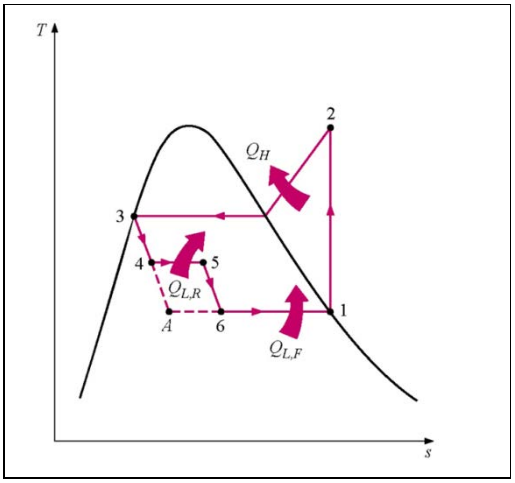
[326] "AHRI 210/240 Standard: Performance Rating of Unitary Air-Conditioning and Air-Source Heat Pump Equipment"

[327] https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio

[328] https://en.wikipedia.org/wiki/Seasonal_energy_efficiency_ratio

[329] http://www.achrnews.com/articles/125139-the-science-of-hvac-efficiency-ratings

Multipurpose Refrigeration Systems Using a Single Compressor



In some refrigeration systems, it is desirable to have more than one throttling valve but only one compressor. In such a system, for example, part of the fluid is throttled only partially to an intermediate pressure and attains an intermediate temperature (such as one optimal for the refrigerator compartment), whereas the remainder of the fluid bypasses the warmer refrigerator section, is throttled to a lower pressure, and produces a colder temperature needed for the freezer section.

See T-s diagram to right, in which path 3-4 represents partial throttling and path 3-4-A represents full throttling. The warmer Q_{LR} is shunted to the refrigerator compartment, whereas the colder Q_{LF} is shunted to the freezer compartmen.t[330]

Multistage System with Two Compressors and a Heat Exchanger

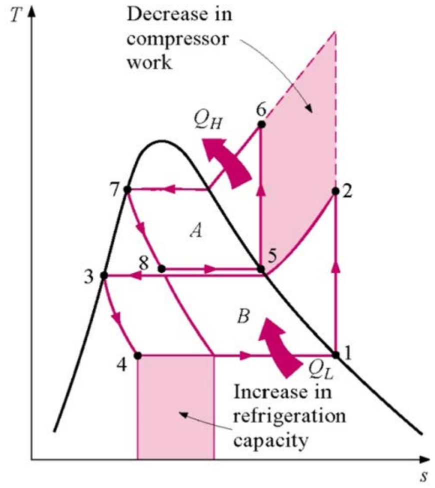
If a single refrigerant is not optimal at both the evaporator and condenser T and P, it may be necessary to employ two or more sequential (**cascaded**) cycles (stages) having differing refrigerants and/or compressors. These are called Cascade Refrigeration Systems. In a two stage system, Q_{in} for the evaporator of the top cycle is furnished by Q_{out} from the condenser of the bottom cycle.

Idealized System

The diagram to the right from the textbook shows an idealized cascading system with two vapor-compression systems in series.

"The COP of a refrigeration system also increases as a result of cascading."[331] The diagram shows that a cascade refrigeration system can reduce compressor work (by excluding the colored area upper right enclosed with dotted lines) and can increase refrigeration capacity (by adding in the extra color region lower left where there is an increased amount of heat absorbed from the refrigerated space).

Despite the way this diagram is drawn, the condensation process of the lower stage that occurs in the HEX (the horizontal part of process 2-3 within the saturation dome) must proceed at a $T_H = T_3$ somewhat hotter than the $T_L = T_8$ of the evaporator process (8-5) of the upper stage occurring within the same HEX and saturation dome.



T-s diagram of Multi-Stage (Cascade) Refrigeration Systems (see text to left about process 5-8 versus process 2-3)

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[330] *TAEA7* Chapter_11.ppt

[331] *TAEA7* Chapter_11.ppt and *TAEA7* p. 629 text and diagram

Actual System

The diagram on the right shows a cascading 2-stage system (apparently an actual system) which achieves a low final temperature of -50 °C in the lower stage. Operation of the 2 stages is as follows:

Upper Stage (Higher Temperature HT stage): The upper stage uses R-134a refrigerant. Low Pressure (LP) vapor is presented to and compressed by the upper stage (High T) compressor, producing HP vapor. Heat is rejected in the upper stage condenser, and condensation to HP liquid occurs. In the throttle expansion valve, P and T drop and the fluid becomes a LP "liquid" (more likely a saturated mixture). In the closed heat exchanger (HEX), the evaporator of the upper stage receives heat via proximity with the condenser of the lower stage, and the evaporator liquid is vaporized drawing off enthalpy of vaporization. As before, the lower stage condenser fluid in the HEX must be hotter than the upper stage evaporator fluid for desired heat exchange to proceed. The LP vapor from the evaporator completes the upper stage cycle by returning to the inlet of the upper stage compressor.

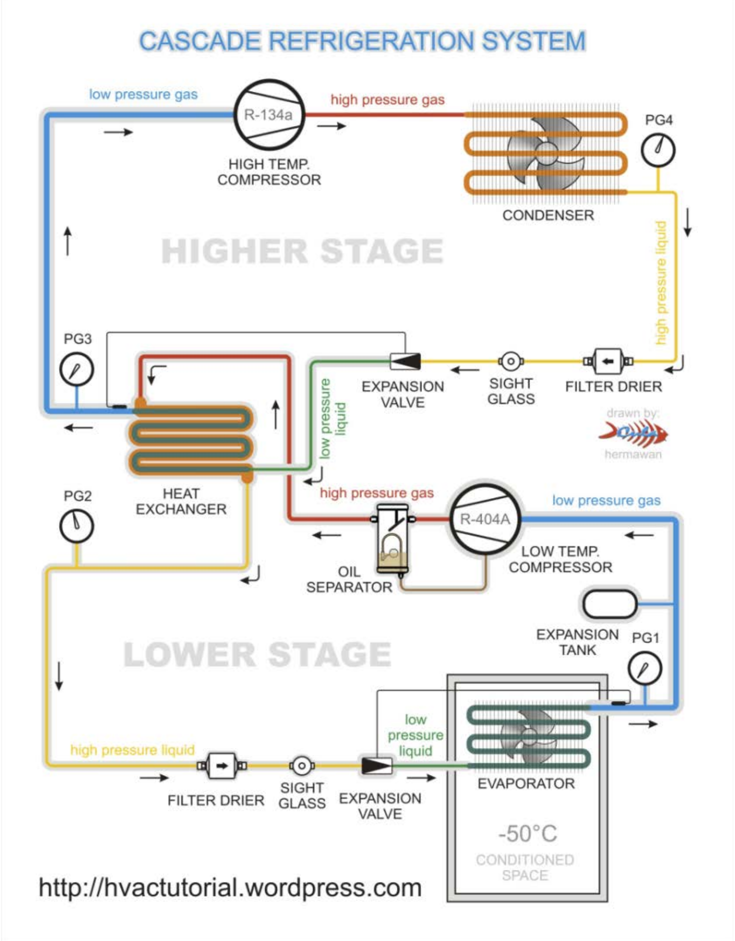


Diagram illustrating components of what appears to be an actual multistage system.[332]

Lower Stage (Lower Temperature LT stage): The lower stage uses R-404a refrigerant. Low Pressure (LP) vapor is presented to and compressed by the lower stage LT compressor, producing HP vapor. Heat is rejected in the lower stage condenser located in the HEX, and condensation to HP liquid occurs. In the throttle expansion valve, P and T drop and the fluid becomes a LP liquid (more likely a saturated mixture). In the evaporator of the lower stage, heat is extracted from the refrigerated space to provide enthalpy of vaporization, and the fluid becomes a LP vapor. The LP vapor completes the lower stage cycle by returning to the inlet of the lower stage compressor.

Analysis of Refrigerants in this example: The lower stage uses R-404a refrigerant (a mixture of R-125, R-143a, and R-134a). It is intended here to refrigerate a chilled space down to -50 °C. The refrigerant should therefore attain a minimum T of -60 °C. At that temperature, P_{sat} = **49.8** kPa.[333] This does not exceed 1 atm (101.3 kPa), so the refrigerant does not fully meet the criterion that minimizes likelihood of air intrusion. However, by comparison, P_{sat} for R-134a at -60 °C = **15.9** kPa.[334] Therefore, R-404a appears superior to R-134a for use in the lower stage at least by this criterion.

---

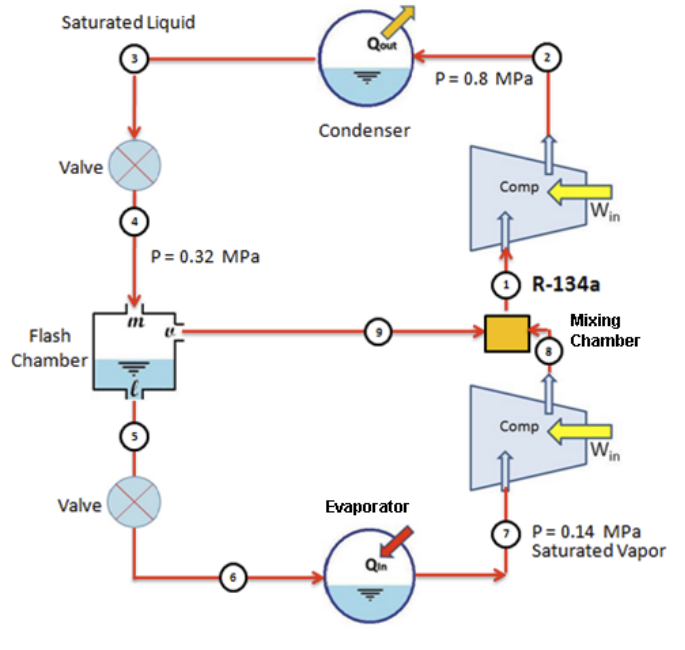
[332] https://hvactutorial.wordpress.com/refrigeration-system/special-refrigeration-system/cascade-refrigeration-system/ , by blogger Hermawan

[333] http://www.linde-gas.ro/internet.lg.lg.rou/ro/images/R404A54_138670.pdf

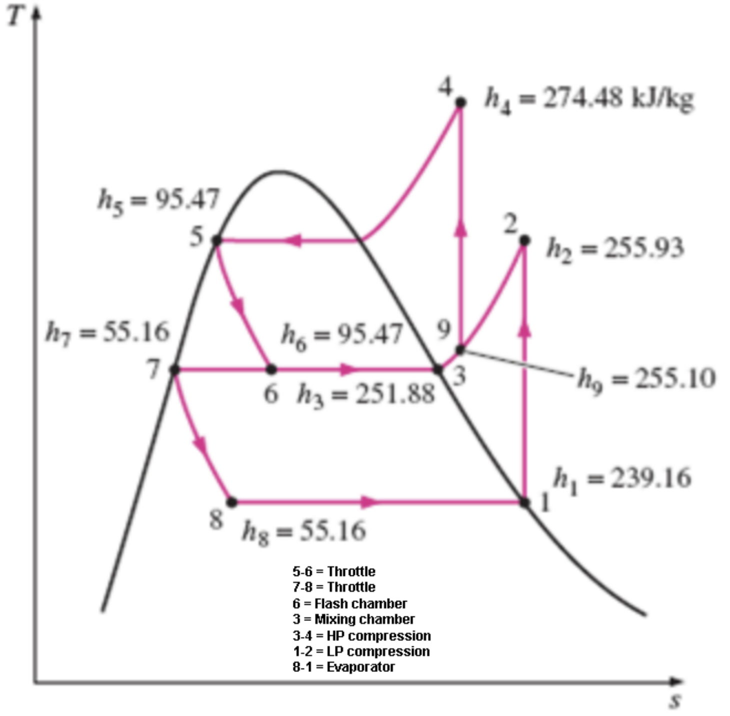
[334] Huber, M. L. and McLinden, M. O., "Thermodynamic Properties of R134a (1,1,1,2-tetrafluoroethane)" (1992). International Refrigeration and Air Conditioning Conference. Paper 184. http://docs.lib.purdue.edu/iracc/184. Calculation via MBWR equation of state.

Multistage Compression Systems Using a Flash Chamber

In Multistage Compression Systems Using a Flash Chamber, more than one compressor is used and the higher and lower pressure systems may exchange heat not with a heat exchanger but instead mix the shared refrigerant in a **flash chamber**. These are illustrated in the following diagrams.



Multi-Stage Refrigeration System employing a flash (mixing) chamber[335]



T-s diagram (from textbook)[336]

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[335] http://tesint.com/thermoflo/help/multi-stage-refrigeration-system/, added annotation by MCM

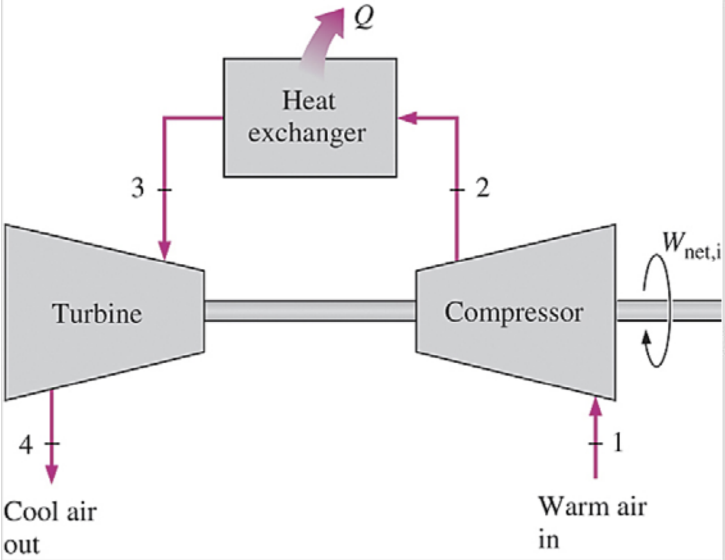
[336] http://www.transtutors.com/questions/a-two-stage-refrigeration-cycle-with-a-flash-chamber-consider-a-two-stage-compressio-708518.htm and *TAEA7* p. 632, annotated by MCM

Gas Refrigeration Cycles

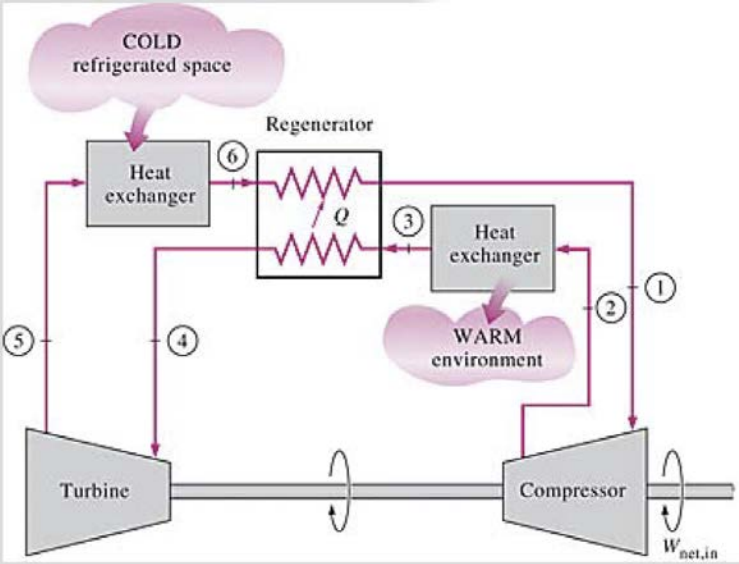
These use what is effectively a reversed Brayton cycle rather than a vapor compression cycle. The refrigerant remains gaseous at all times. Expansion occurs in a turbine, which provides some of the input power to the compressor. The COP_R's are lower than for vapor compression cycles. Their advantages are simple lighter components, so they are found on aircraft cooling systems.

Diagrams for Gas Refrigeration Cycles follow (derived from the text):[337]

> on the left is an open-cycle aircraft cooling system
>
> on the right is a closed system with two heat exchangers and regeneration.



An open-cycle aircraft cooling system.



Gas refrigeration cycle with regeneration

Gas Refrigeration Cycles are further described as follows:

> "When the working fluid is a gas that is compressed and expanded but doesn't change phase, the refrigeration cycle is called a gas cycle. **Air** is most often this working fluid. As there is no condensation and evaporation intended in a gas cycle, components corresponding to the condenser and evaporator in a vapor compression cycle are the **hot and cold gas-to-gas heat exchangers** in gas cycles.
>
> The gas [refrigeration] cycle is less efficient than the vapor compression cycle because the gas cycle works on the reverse Brayton cycle instead of the reverse Rankine cycle. As such the working fluid does not receive and reject heat at constant temperature. In the gas cycle, the refrigeration effect is equal to the product of the specific heat of the gas and the rise in temperature of the gas in the low temperature side. Therefore, for the same cooling load, a gas refrigeration cycle needs a large mass flow rate and is bulky.

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[337] http://www.kostic.niu.edu/350/_350-posted/350lectureppt-cengel7th/chapter_11_lecture.pdf , modified by MCM

> Because of their lower efficiency and larger bulk, **air cycle** coolers are not often used nowadays in terrestrial cooling devices. However, the air cycle machine is very common on **gas turbine-powered jet aircraft** as cooling and ventilation units, because compressed air is readily available from the engines' compressor sections."[338]

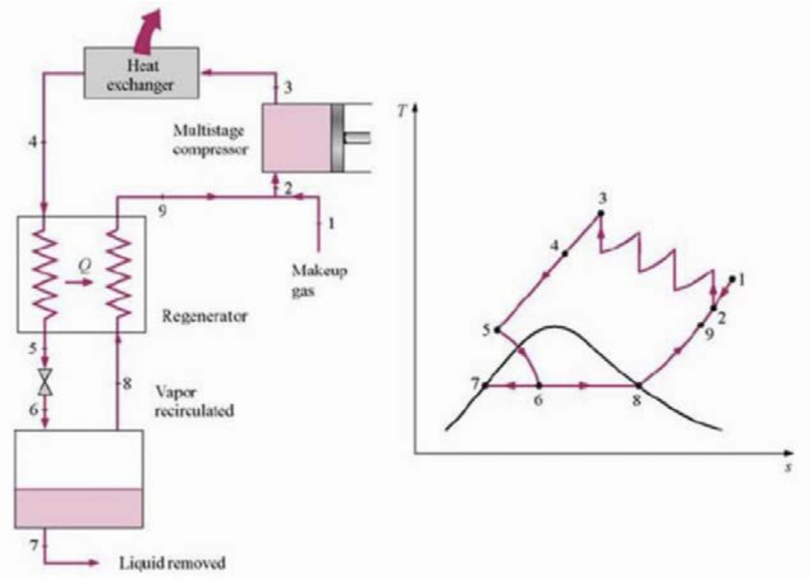
Passenger jet engine compressors also contribute *bleed air* from low, intermediate, or high pressure stages, which is sent to the environmental control system for the purpose of pressurizing the aircraft.[339]

Gas Liquefaction Systems

The preferred term is *liquefaction. Fluidification* is also found in the OED, but *liquification* is not—the latter appears to be non-standard though occasionally encountered term.

These are complex systems based on the Linde-Hampson and other cycles, which typically involve multistage compression, expansion, and regeneration. I have not taken the opportunity to study these systems and processes carefully.

A diagram derived from the text[340] shows a simplified schematic of the Linde-Hampson system on the left, and a T-s diagram on the right. Makeup gas is mixed with uncondensed vapor from the regenerator. This gas enters multiple compression and intercooling stages which raise the pressure nearly isothermally in passing from state 2 to state 3. The HP gas is cooled in an aftercooler or other cooling system to state 4, and further cooled in a regenerative counter-flow heat exchanger to state 5. It then undergoes throttling which by the Joule-Thomson effect produces a saturated mixture of vapor and liquid (state 6). This is collected in a reservoir, and saturated liquid (liquefied gas) is drawn off, while the vapor is recirculated. Details are omitted here on this important but highly technical subject.[341]



The following illustrates an example of a commercial system for producing **Liquefied Natural Gas LNG**, taken from an informative PDF brochure produced by MT LNG = Marine Technology Liquefied Natural Gas. [342]

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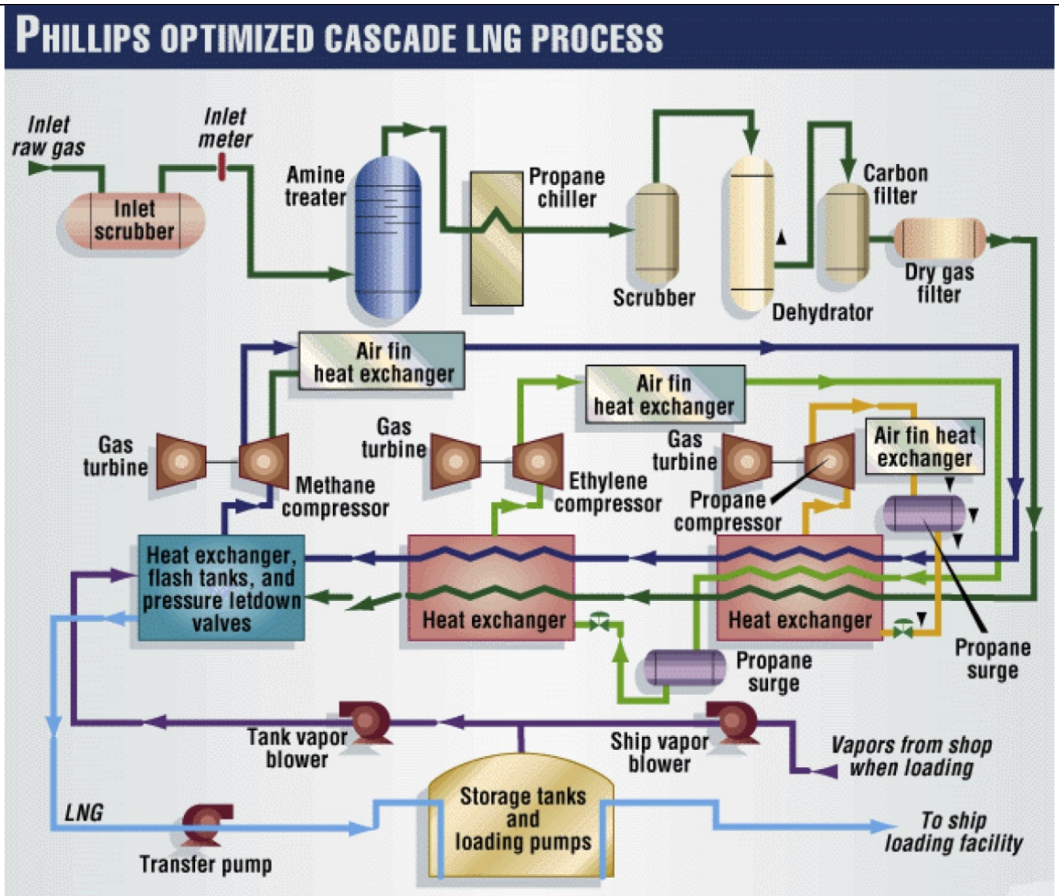
[338] https://en.wikipedia.org/wiki/Refrigeration

[339] and https://en.wikipedia.org/wiki/Cabin_pressurization

[340] http://coolingdevice.net/4.html

[341] http://encyclopedia2.thefreedictionary.com/Liquefaction+of+Gases and http://energy.gov/sites/prod/files/2013/04/f0/LNG_primerupd.pdf

[342] http://www.golng.eu/files/Main/news_presentations/rostock/Liquefied%20Natural%20Gas%20General%20Knowledge.pdf


PHILLIPS OPTIMIZED CASCADE LNG PROCESS
Inlet raw gas
Inlet meter
Inlet scrubber
Amine treater
Propane chiller
Scrubber
Dehydrator
Carbon filter
Dry gas filter
Air fin heat exchanger
Air fin heat exchanger
Air fin heat exchanger
Gas turbine
Methane compressor
Gas turbine
Ethylene compressor
Gas turbine
Propane compressor
Heat exchanger, flash tanks, and pressure letdown valves
Heat exchanger
Heat exchanger
Propane surge
Propane surge
Tank vapor blower
Ship vapor blower
Vapors from shop when loading
LNG
Transfer pump
Storage tanks and loading pumps
To ship loading facility

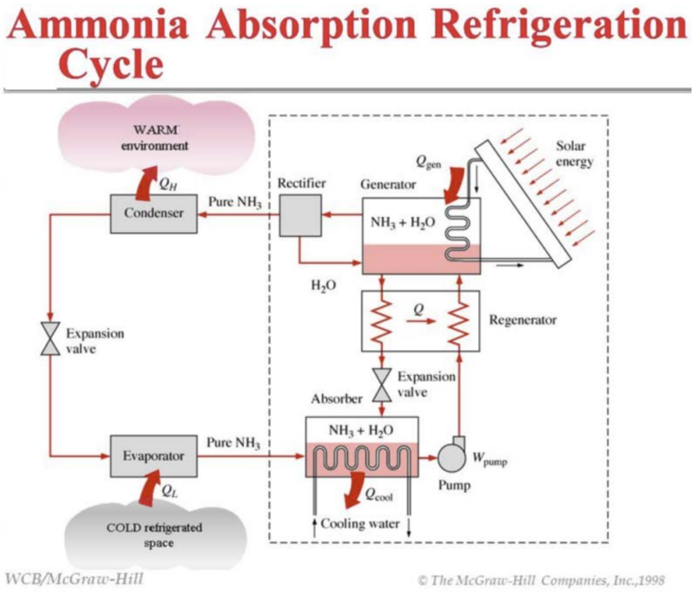
Other Refrigeration Systems

Other refrigeration systems include **Absorption Refrigeration** (which has low COP_R but can use low quality renewable energy)[343] and **Thermoelectric Refrigeration** (which uses the Peltier effect with no moving parts but has very low COP).[344]

Absorption Refrigeration Systems

These are economically attractive only when inexpensive renewable heat power is available (geothermal, solar, cogeneration waste heat, etc.) They involve absorption of a refrigerant by a transport medium. The ammonia-water system is most widely used (invented 1859), but others include water-Lithium Bromide and water-Lithium Chloride. In the latter, water is the refrigerant, and must operate above the freezing point of water.

Absorption refrigeration systems are heat-driven systems. Compared to vapor-compression systems, they are much more complex, much bulkier, less efficient, and require larger cooling systems to reject waste heat. However, they have the major advantage that compression acts on a liquid rather than a vapor, so work input is very small. They are found only in large commercial and industrial installations, but also in RV refrigerators.[345] The actual COP_R is usually less than 1.[346]



In the **ammonia-water system** (diagram to right),[347] the compressor of a vapor-compression system is replaced by a complex absorption mechanism, and the system includes an absorber, a pump, a generator, a regenerator, a valve, and a rectifier. This diagram depicts solar energy as the source of low grade heat that powers the generator, but other sources are also used.

Wikipedia describes absorption refrigeration systems as follows:

> "Both absorption and [vapor-compression] refrigerators use a refrigerant with a very low boiling point (less than 0 °F (−18 °C)). In both types, when this refrigerant evaporates (boils), it takes some heat away with it, providing the cooling effect. The main difference between the two systems is the way the refrigerant is changed from a gas back into a liquid so that the cycle can repeat. An absorption refrigerator changes the gas back into a liquid using a method that needs only heat, and has no moving parts other than the refrigerant itself.
>
> The absorption cooling cycle can be described in three phases:
>
> **Evaporation [Vaporization]**: A liquid refrigerant evaporates in a low partial pressure environment, thus extracting heat from its surroundings (e.g. the refrigerator's compartment). Because of the low partial pressure, the temperature needed for evaporation is also low.

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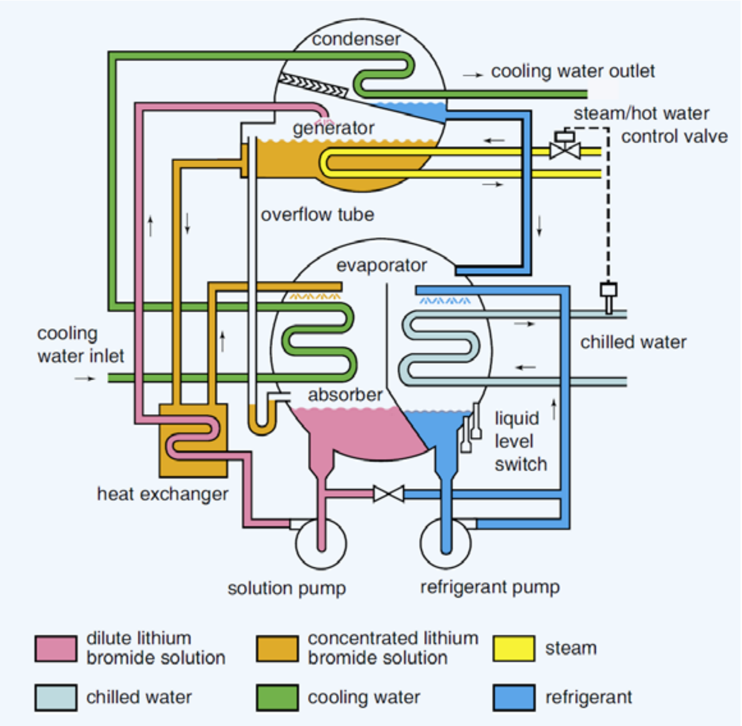
[343] www.scirp.org/journal/PaperDownload.aspx?paperID=47541
[344] https://en.wikipedia.org/wiki/Thermoelectric_cooling and www.ijeit.com/vol%202/Issue%207/IJEIT1412201301_03.pdf
[345] http://home.howstuffworks.com/refrigerator5.htm and https://en.wikipedia.org/wiki/Absorption_refrigerator
[346] *TAEA7* p. 637-639
[347] Image from earlier edition of *TAEA7*, found at: http://images.slideplayer.com/10/2682232/slides/slide_12.jpg

> **Absorption**: The now gaseous refrigerant is absorbed by another liquid (e.g. a salt solution).
>
> **Regeneration**: The refrigerant-saturated liquid is heated, causing the refrigerant to evaporate out. The hot gaseous refrigerant passes through a heat exchanger, transferring its heat outside the system (such as to surrounding ambient-temperature air), and condenses. The condensed (liquid) refrigerant supplies the evaporation phase.
>
> In comparison, a compressor refrigerator uses an electrically powered compressor to increase the pressure on the gaseous refrigerant…”[348]

An example of a commercially available **Lithium Bromide Absorption Chiller** (Carrier models 16JL/16JLR) is shown in the following schematic diagram.[349] The system does not use CFCs or other compounds destructive to the ozone. It is powered by low pressure steam or hot water or waste heat (yellow in the diagram).



> “The 16JL/JLR consists of evaporator, absorber, condenser, generator, solution heat exchanger, solution pump, refrigerant pump, control system and other auxiliary system, etc. The operating principle of the chiller is [as follows]:
>
> In a highly vacuum state, refrigerant water [dark blue] evaporates at a low temperature (4.4°C), which cools down chilled water [light blue] circulating in the evaporator tube. Refrigerant vapor generated in evaporator is absorbed by lithium bromide solution in the absorber [mauve], which makes the solution become dilute [with respect to the LiBr salt]. Such dilute solution [mauve] is fed into the heat exchanger by the solution pump, where the temperature rises. After that, it enters the generator, in which it is further heated and concentrated [with respect to the LiBr salt] by steam or hot water [yellow]. The concentrated solution returns to the absorber [gold spray] after passing through the heat exchanger [gold] for repeated use. In the absorber and evaporator, lithium bromide solution and refrigerant water spray onto tubes of the heat exchangers to enhance the heat exchange effect.”

The diagram also depicts cooling water [green] which apparently (1) cools the water in the condenser before it passes to the evaporator, and (2) cools the concentrated solution that returns to the absorber.

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[348] https://en.wikipedia.org/wiki/Absorption_refrigerator

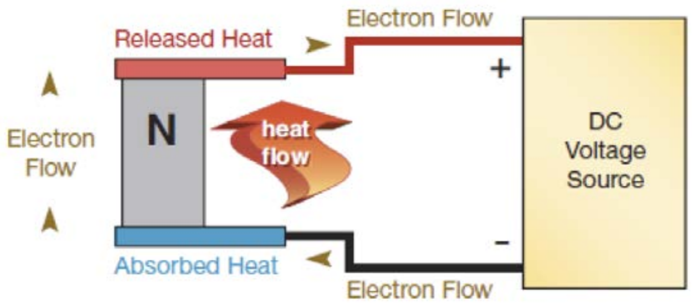
[349] http://www.carrier.com.hk/comm/comm_new2010/2013%20Cat/Absorption%20Chiller/16JLR%20CN%20(C).pdf including diagram and quoted text edited by MCM

Thermoelectric Refrigeration Systems

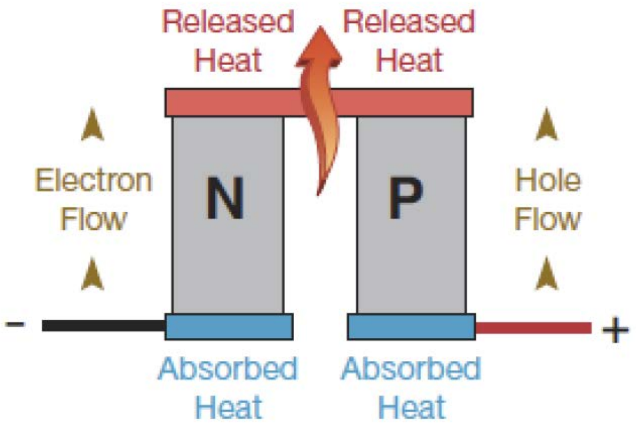
These use the Peltier effect and have no moving parts but have very low COP_R.

> "The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices can be used as temperature controllers.
>
> The term *thermoelectric effect* encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect. Textbooks may refer to it as the Peltier–Seebeck effect. This separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Baltic German physicist Thomas Johann Seebeck. Joule heating, the heat that is generated whenever a current is passed through a resistive material, is related, though it is not generally termed as thermoelectric effect. The Peltier–Seebeck and Thomson effects are thermodynamically reversible, whereas Joule heating is not."[350]

It was Peltier who discovered in 1834 that a reversed current can cool a junction. In the following diagrams, N- and P-type semiconductors are combined with DC power to produce a current leading to a cooled surface. "Thermoelectric coolers operate by the Peltier effect (which also goes by the more general name thermoelectric effect). The device has two sides, and when DC electricity flows through the device, it brings heat from one side to the other, so that one side gets cooler while the other gets hotter. The "hot" side is attached to a heat sink so that it remains at ambient temperature, while the cool side goes below room temperature. In some applications, multiple coolers can be cascaded together for lower temperature."[351]



Peltier Effect showing cooling of N-type semiconductor at end connected to negative polarity.[352]



Peltier Effect showing cooling of N-type semiconductor where connected to negative terminal, and cooling of P-type semiconductor where connected to positive terminal.[353]

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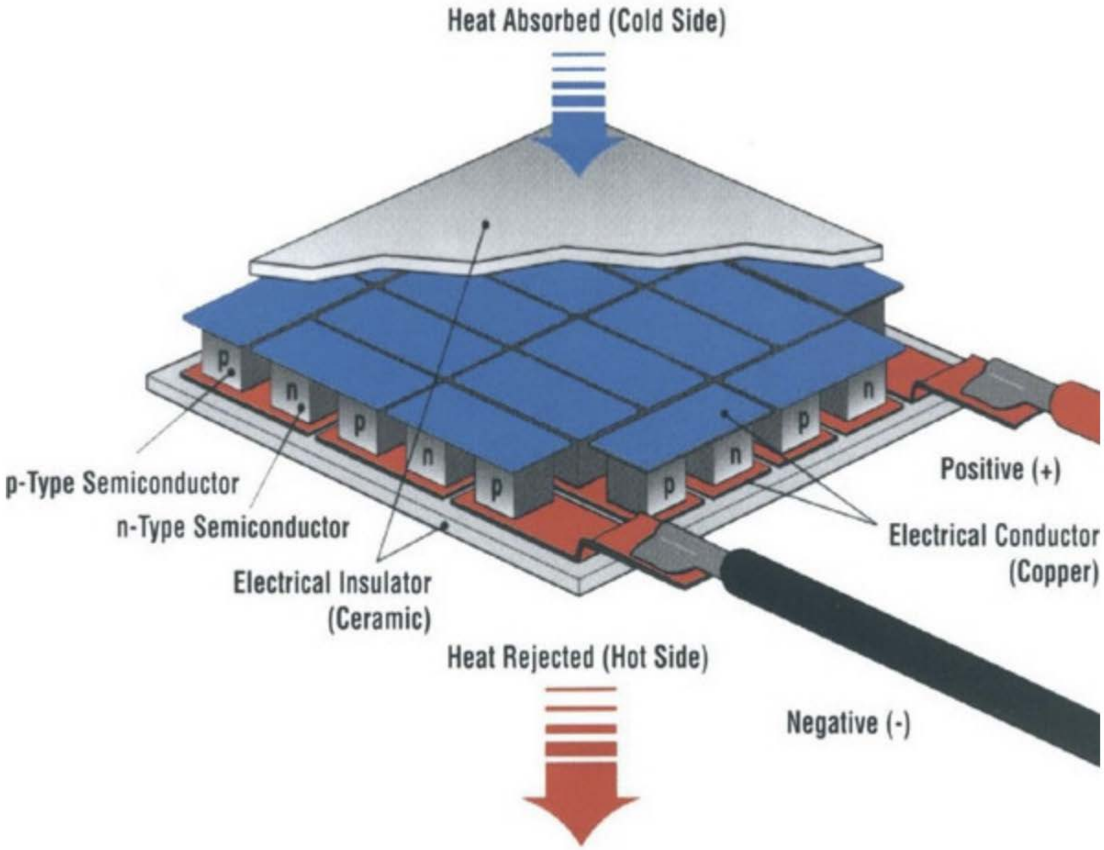
[350] https://en.wikipedia.org/wiki/Thermoelectric_effect
[351] https://en.wikipedia.org/wiki/Thermoelectric_cooling
[352] http://www.pnl.gov/main/publications/external/technical_reports/PNNL-19259.pdf (upper diagrams)
[353] ibid.

By connecting n-type and p-type semiconductors in series, it is possible to produce a module that is large enough to provide a useful amount of heating/cooling or electrical power and still achieve a configuration that is thermally in parallel so that the heat flows in one direction. This works because the holes are repelled by positive charge and the electrons are repelled from negative charge. In the n-type material, the charge carriers (electrons) flow with the electrical current, and in the p-type material, the charge carriers (holes) flow against the current.



Peltier Effect showing cooling (blue) of multiple N-type and P-type semiconductors attached electrically in series and thermally in parallel[354]

As in the right diagram further above (if I understand the current drawing correctly), the negative DC terminal connects to the thermally hot side of the P-type conductor (in series), and the positive DC terminal connects to the hot side of the N-type conductor.

In a commercial catalog of industrial single stage thermoelectric coolers, units having a maximum of 199 thermocouples (398 thermoelectric elements) consume electricity up to 21 A at 24.6 V (thus 517 W), have heat transfer (cooling) Q_{max} = 310 W, and achieve temperature differentials $\Delta T = 70$ °C.[355]

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[354] http://edge.rit.edu/content/P09451/public/thermo_module.jpeg

[355] http://www.amstechnologies.com/fileadmin/amsmedia/downloads/4121_thermoelectriccoolersforindustrialapplications.pdf

TD Property Relations (12)

(condensed from text Chapter 12 & other sources)

This chapter provides techniques and formulas used in determining quantities for simple compressible systems that cannot be measured directly.

Using Partial Derivatives and Partial Differentials

(12-1)

The text includes a convenient review of partial derivatives and partial differentials, which use the symbol ∂ and are determined while holding one or more quantities constant. Use is made of the following relations that apply to partials for TD properties with exact differentials:

Given

$$\mathrm{M} = \left(\frac{\partial z}{\partial x}\right)_y \text{ and } \mathrm{N} = \left(\frac{\partial z}{\partial y}\right)_x$$

then

$$\left(\frac{\partial \mathrm{M}}{\partial y}\right)_x = \left(\frac{\partial \mathrm{N}}{\partial x}\right)_y$$ for properties that have exact differentials.

The text also derives the reciprocity relation

$$\left(\frac{\partial x}{\partial z}\right)_y = 1/\left(\frac{\partial z}{\partial x}\right)_y$$

and the cyclic relation

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Among the many available TD-related equations provided are the following:

The Gibbs Function, Helmholtz Function, and Gibbs Relations

(12-2)

These make possible derivation, under specified conditions, of non-measurable properties based on measurable ones.

Gibbs function $g \equiv h - T\,s$

Helmholtz function $a \equiv u - T\,s$
(a is also called the **Helmholtz free [specific] energy**)

> "The **Helmholtz free energy** [symbol A/a or F/f] is a thermodynamic potential that measures the 'useful' work obtainable from a closed thermodynamic system at a constant temperature. The negative of the difference in the Helmholtz energy is equal to the maximum amount of work that the system can perform in a thermodynamic process in which volume is held constant. If the volume is not held constant, part of this work will be performed as boundary work. The Helmholtz energy is commonly used for systems held at constant volume. Since in this case no

> work is performed on the environment, the drop in the Helmholtz energy is equal to the maximum amount of useful work that can be extracted from the system. For a system at constant temperature and volume, the Helmholtz energy is minimized at equilibrium… It is usually denoted by the letter A (from the German “Arbeit” or work), or the letter F.”[356]

Gibbs Relations for Simple Compressible Systems

First Gibbs Relation	$T\,dS = dU + P\,dV$
or	$T\,ds = du + P\,dv$
or	$du = T\,ds - P\,dv$
Second Gibbs Relation	$T\,ds = dh - v\,dP$
or	$dh = T\,ds + v\,dP$
Third Gibbs Relation	$da = -s\,dT - P\,dv$
Fourth Gibbs Relation	$dg = -s\,dT + v\,dP$

Maxwell Relations

Text 12-2

The Maxwell relations (for Simple Compressible Systems) follow from Gibbs (for which the numbering is arbitrary; second derivatives adapted from here[357]):

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{v}}\right)_{\mathrm{s}} = -\left(\frac{\partial \mathrm{P}}{\partial \mathrm{s}}\right)_{\mathrm{v}} = \frac{\partial^2 \mathrm{u}}{\partial \mathrm{s}\,\partial \mathrm{v}}$$

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{s}} = +\left(\frac{\partial \mathrm{v}}{\partial \mathrm{s}}\right)_{\mathrm{P}} = \frac{\partial^2 \mathrm{h}}{\partial \mathrm{s}\,\partial \mathrm{P}}$$

$$\left(\frac{\partial \mathrm{s}}{\partial \mathrm{v}}\right)_{\mathrm{T}} = +\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = -\frac{\partial^2 \mathrm{a}}{\partial \mathrm{T}\,\partial \mathrm{v}}$$

$$\left(\frac{\partial s}{\partial P}\right)_{T} = -\left(\frac{\partial v}{\partial T}\right)_{p} = -\frac{\partial^2 \mathrm{g}}{\partial \mathrm{T}\,\partial \mathrm{P}}$$

These allow determination of entropy s changes (which cannot be measured) from changes in P, v, and T.

Clapeyron equation and Clapeyron-Clausius equation

Text 12-3

The Clapeyron equation, named after Benoît Paul Émile Clapeyron (1799 - 1864), is applicable to any phase-change process at constant P and T. It allows determination of **enthalpy of vaporization h_{fg}** at a given T by measuring the slope of the saturation curve on a P-T diagram along with the specific volume of saturated liquid and saturated vapor at the given temperature:[358]

$$\left(\frac{\mathrm{dP}}{\mathrm{dT}}\right)_{\mathrm{sat}} = \frac{\mathrm{h_{fg}}}{\mathrm{T\,v_{fg}}} \qquad (12\text{-}22)$$

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[356] https://en.wikipedia.org/wiki/Helmholtz_free_energy

[357] https://en.wikipedia.org/wiki/Maxwell_relations and https://en.wikipedia.org/wiki/Table_of_thermodynamic_equations

[358] *TAEA7* p. 668

or more generally for any phase-change process, changing from phase 1 to phase 2 at constant T and P:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T\,v_{12}} \qquad (12\text{-}23)$$

The **Clapeyron-Clausius equation** makes use of several simplifying approximations (ideal gas, etc.) and is used to determine the variation of saturation pressure with T, and other uses:

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

This chapter also provides general relations involving du, dh, ds, c_v, and c_p. (section 12-4)

The Joule-Thomson Coefficient

(12-5)

This gives the behavior of T with P of a fluid during a throttling (P decreases) and with h = constant:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] \qquad (12\text{-}51 \text{ and } 52)$$

For a throttling process, in which P decreases ($\partial P < 0$):

Temperature Increases ($\partial T > 0$) for $\mu_{JT} < 0$

Temperature constant ($\partial T = 0$) for $\mu_{JT} = 0$ (This is true for an ideal gas.)

Temperature decreases ($\partial T < 0$) for $\mu_{JT} > 0$

See further discussion of Joule-Thomson Coefficient, along with T-P and T-s diagrams, under Throttling Valves of Devices. See also Figure 12-14.

The Δh, Δu, and Δs of Real Gases

This text section 12-6[359] deals with real gases departing from ideal gases. It derives equations for **enthalpy departure** (from ideal gas enthalpy h*, see text Figure A-29), internal energy changes of real gases, and **entropy departure** (text Figure A-30).

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[359] *TAEA7* p. 680

Gas Mixtures (13)

(from text Chapter 13 & other sources)

These are mixtures of pure non-reactive substances which, by common TD usage for the term *gas*, are in P and T ranges where they remain fully gaseous throughout the processes involved. This chapter (13-1) reviews definitions and expressions—for a given volume, sample, etc., as apparent by the context:

1 mole (mol) = 6.022×10^{23} elementary entities[360]
(molecules, atoms, etc. of a substance or mix of substances)
1 kmol = 1000 mol
mole number (number of moles in a mixture, etc.) = N **(mol)**
moles in a gas mixture of a mixture component or species i = N_i **(mol)**
molar mass of a substance M = mass per mole of a substance
= (formerly termed the **Gram Molecular Weight)** **(g/mol or kg/kmol)**
mass of a single substance m = NM **(g)**
mass of a gas mixture component i = m_i **(g)**
mass of a total mixture $m_m = \Sigma m_i$ **(g)**
moles in a mixture $N_m = \Sigma N_i$ **(mol)**
mole fraction (mole ratio) for substance i : $y_i = N_i/N_m$ where $\Sigma y_i = 1$ **(unitless)**
apparent (average) molar mass of a mixture $M_m = m_m / N_m$
= $\Sigma m_i/N_m$
= $\Sigma N_i M_i/N_m = \Sigma y_i M_i$ **(g)**
(this is the average mass (g) of 1 mole of the mixture's mix of components = 6.022×10^{23} entities)
mass fraction $mf_i = m_i/m_m = y_i\,(M_i/M_m)$ where $\Sigma mf_i = 1$ **(unitless)**
average gas constant R_m for a mixture = R_u / M_m **[Pa m^3 K^{-1} mol^{-1}]**

The **partial pressure of any component** in a gas mixture is the pressure (Pa, N/m^2, etc.) that the current quantity of the substance (g, kg, mol, etc.) present would exert at that T and in its current Volume if present alone

The following "laws" hold exactly for ideal gases (in which the molecules are sufficiently far apart that they do not interact), and only approximately for real gases:

Dalton's law of additive partial pressures: the total pressure of a gas mixture is equal to the sum of the [partial] pressures each gas would exert if it existed alone at the mixture's T and total volume.

Amagat's law of additive partial volumes: the total volume of a gas mixture is equal to the sum of the [partial] volumes each gas would occupy if it existed alone at the mixture's T and total pressure.

A component partial pressure $P_i = y_i P_m$, where y_i is the mole fraction or ratio of component i moles (N_i) to the total moles (N_m). A component partial volume $V_i = y_i V_m$.

Analysis of mixtures of ideal gases is presented (13-2), as is **Kay's rule** for P-v-T behavior of non-ideal (real) gas mixtures. Section (3-3) analyzes extensive and intensive properties of ideal and real gas mixtures (U, u, H, h, S, s, and specific heats $c_{v,m}$ and $c_{p,m}$). These sections are not summarized here.

Ideal Gas Mixtures, useful relationships:[361]

$$\frac{P_i(T_m,V_m)}{P_m} = \frac{N_i R_u T_m/V_m}{N_m R_u T_m/V_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{V_i(T_m,V_m)}{V_m} = \frac{N_i R_u T_m/P_m}{N_m R_u T_m/P_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

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[360] https://en.wikipedia.org/wiki/Mole_%28unit%29
[361] *TAEA7* p. 697

Gas-Vapor Mixtures and Air-Conditioning (14)

(from text Chapter 14 & other sources)

The term *gas-vapor*, in the TD context and usage of air-conditioning terminology, refers to mixtures of pure non-reactive substances which are in P and T ranges for which at most one of the substances (usually water vapor) is found during part of a cycle to be in a state near or on the saturated vapor line or even in the partly condensed state.

This chapter deals with air-water-vapor mixtures, which are at the heart of **air-conditioning** (abbreviated **AC** or **A/C**, and applying to both **heating** and **cooling**).[362] Air-conditioning according to the textbook is the technology which adjusts air temperature, humidity, and even velocity for optimization of human comfort (or by extension, for the comfort of other sheltered animals or plants). This is in contrast to **refrigeration**, in which the medium of interest is a pure substance (the refrigerant), and the goal is primarily to chill a space.

Dry Air versus Atmospheric Air

Actual atmospheric air in TD is regarded as a mixture of **dry air** (without water vapor) and **water vapor**. Dry air properties are represented by subscript *a*, such as P_a. Water vapor properties are shown with subscript *v*, such as P_v. A mixture property (averaged, composite) is shown with a subscript *m*. (Of course these subscripts are also used in other TD contexts for *actual*, *specific volume*, and *mass*, etc., so one must carefully note the context and hope to avoid confusion.)

At T below 50 °C, the P_{sat} of water vapor is less than 12.3 kPa (compared to 1 atm = 101.325 kPa), and water vapor behaves effectively as an ideal gas, so that its partial pressure $P_{\text{water vapor}}$ is given by

$$P_{\text{water vapor}}V_{\text{total}} = N_{\text{water vapor}}R_{U}T$$

or

$$P_{\text{water vapor}}v = R_{\text{water vapor}}T \qquad \text{where } R_{\text{water vapor}} = R_u/M_{\text{water vapor}} \qquad \text{and} \qquad v = \text{specific volume.}$$

Thus, actual air is comprised of a sum of partial pressures consisting of

$$P_m = P_a + P_v \quad \text{(kPa)}$$

where the actual air mixture is shown as P_m or as P without a subscript.

The partial pressure of water P_v is also called the **vapor pressure**. (See earlier discussion *Vapor Pressure and Boiling*.) When air is **saturated** with water vapor, the amount of water vapor in air is at the maximum that the air can hold for the given T (and the vapor is in TD equilibrium with any condensed water present, see right diagram to follow). The partial pressure of water vapor P_v for this state is called the **saturated vapor pressure** or **saturation vapor pressure** or **equilibrium vapor pressure** for that T, and is symbolized variously and inconsistently as P_g (using the g subscript for states on the saturated vapor line) and other symbols:

$$\mathbf{P_g \equiv P_{v,sat} \equiv P_{sat} \equiv P_{WS} \equiv e_S}$$

In T ranges fully encompassing air-conditioning conditions (-10 to +50 °C), dry air is nearly an ideal gas, so c_p is nearly constant and

$$c_p \approx 1.005 \text{ kJ/kg-K}$$

For water vapor in these T conditions (-10 to +50 °C), even to the point of saturation, enthalpy of water vapor h_v is effectively a function only of T (i.e., constant for constant T), thus

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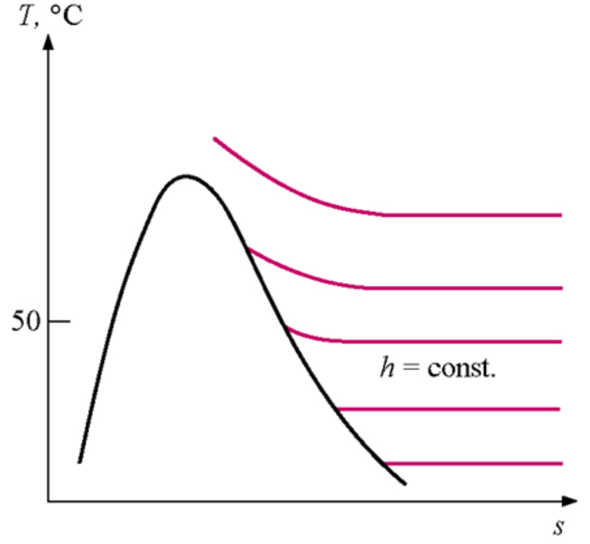
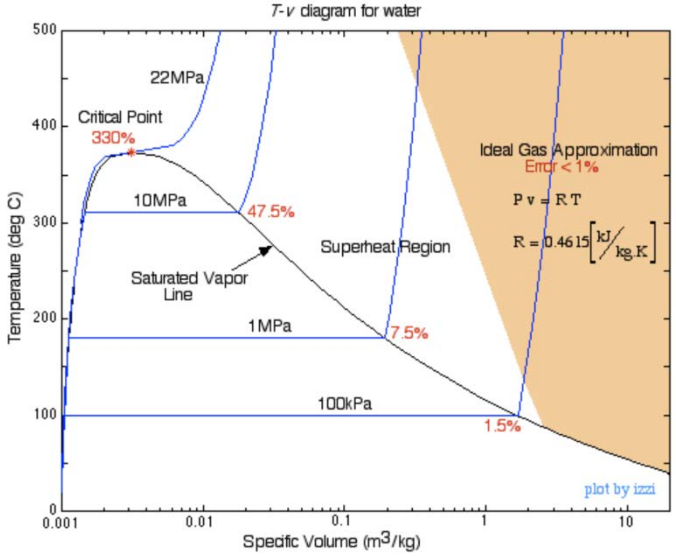
[362] Alternatively: "In the most general sense, air conditioning can refer to any form of technology that modifies the condition of air (heating, cooling, (de-)humidification, cleaning, ventilation, or air movement). However, in construction, such a complete system of heating, ventilation, and air conditioning is referred to as **heating, ventilation, and air conditioning** (**HVAC**), as opposed to AC. https://en.wikipedia.org/wiki/Air_conditioning

$$h_v(T, \text{low } P) \approx h_g(T) \approx 2.500.9 + 1.82T \qquad \text{(kJ/kg for T in °C)}$$

where h_g is enthalpy of saturated water vapor as shown on the saturation dome for pure water (see graph on right to follow).



For Dry air, h is constant for constant T [363]



T-v diagram for water liquid, liquid-vapor mixture, and vapor. The quantity $m_g = 1 / v_g$ is determined along the saturated vapor line for a given T (see discussion below). AC temperatures are -10 to 50 °C, for which water vapor pressure is well below 1 atm. Blue lines are constant P.[364]

Specific (Absolute) Humidity and Relative Humidity

The **absolute humidity** = **specific humidity** = **humidity ratio** = **ω** (i.e., the mass of water vapor in air per unit mass of dry air) is given by

$$\omega = \frac{m_v}{m_a} = \frac{P_v/R_v}{P_a/R_a} = 0.622\frac{P_v}{P_a} = 0.622\frac{P_v}{P - P_v} = \qquad \text{(kg water vapor / kg dry air , thus unitless)}$$

where $P = P_m$ = Total Pressure and T does not enter directly into the computation.

When water is added to dry air, water vapor content and humidity increases to a maximum at which point the air is **saturated** and the water vapor pressure P_v is at the **saturation pressure P_{sat}** for water at that T (e.g., for 25 °C, P_{sat} = 3.16 kPa per Table A-4). Once saturated, further water added to the air will condense to liquid (unless **supersaturation** occurs).[365] If P_v < 3.16 kPa at 25 °C, the air is not saturated with water vapor.

Human comfort depends in part on the **relative humidity φ**, defined for a given T as

$$\varphi = \frac{m_v}{m_g} = \frac{P_v V/R_v T}{P_g V/R_v T} = \frac{P_v}{P_g} \qquad \text{(unitless)}$$

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[363] *TAEA7* Chapter_14.ppt

[364] https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2b.html

[365] Clouds and other systems can become **supersaturated** with water vapor. **Supersaturation** is a temporary state which occurs when there is an absence of condensation nuclei or surfaces on which water can condense. http://www.met.sjsu.edu/~clements/met60_lecture/lecture_6.ppt

where m_g = the maximal water vapor content (kg/m^3) which air can hold at temperature T. We use the familiar g subscript to denote a point on the saturation vapor curve on the right side of the saturation dome (see graph above right).

Given v_g, we can compute m_g.

$m_g = 1 / v_g$. (kg/m^3)

Relative humidity φ and absolute humidity ω are related for a given T by

$$\varphi = \frac{\omega\, P}{(0.622 + \omega)\, P_g} \qquad \text{and} \qquad \omega = \frac{0.622\, \varphi\, P_g}{P - \varphi\, P_g} \qquad \text{(unitless)}$$

where P_g = the pressure for the given T at which the water vapor is saturated.

Note that relative humidity φ is inversely proportional to P_g for constant ω.

Mnemonic: abs**o**lute humidity ω **o**mega relat**i**ve humidity φ ph**i**

Relationship of Relative to Absolute Humidity

When T goes up with ω constant, v_g decreases (because a smaller volume of warmer air can hold the same mass of water at equilibrium), so m_g (the inverse of v_g) increases, thus the air can hold more moisture per unit volume, and RH = φ decreases.

In a system that is isobarically heated (raising T at constant P) and keeping ω constant, the RH = φ decreases because the equilibrium vapor pressure of water ($P_g = P_{sat}$) increases with increasing temperature.

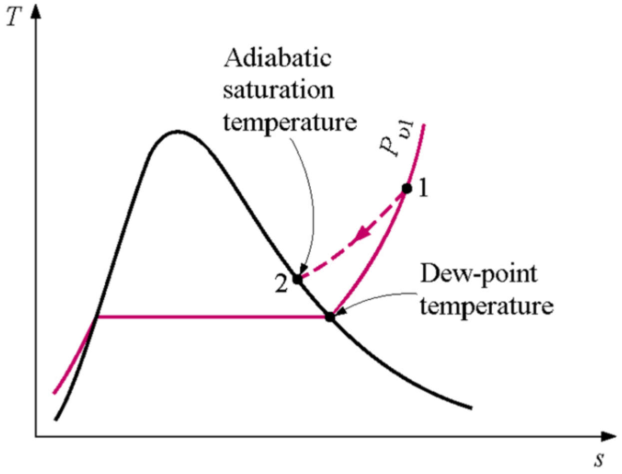
In a system is isothermally compressed (raising P at constant T) and keeping ω constant, the RH = φ increases because the partial pressure of water in the system increases with the resulting volume reduction. If the RH = φ would exceed 100%, water condensation will occur (unless supersaturation conditions arise).

If the pressure of a system is changed by simply adding more dry air, without changing the volume, the relative humidity φ would not change (but absolute humidity $\omega = {}^{m_v}/_{m_a}$ would decrease).

For a given system, a change in relative humidity can be caused by any or all of the following:[366]

a change in P
a change in T
a change in volume V
a change in absolute humidity (water vapor content) ω

Dew Point Temperature T_{DP}



The dew point T_{DP} (dew point temperature or dewpoint) is the T at which condensation begins when air is cooled at constant P and P_v [absolute humidity]. It is given by $T_{DP} = T_{sat,\ water}$ @ constant P (and constant P_v).

The dew point T_{DP} is a measure of atmospheric moisture. It is the temperature to which air must be cooled at constant pressure and water content [absolute humidity ω] to reach saturation and onset of condensation. A higher dew point indicates more moisture in the air; a dew point greater than 20 °C (68 °F) is considered uncomfortable and greater than 22 °C (72 °F) is considered to be extremely humid.[367]

In the T-s graph to the right, the red solid line is a

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[366] https://en.wikipedia.org/wiki/Relative_humidity
[367] https://en.wikipedia.org/wiki/Dew_point , paraphrased MCM

constant P curve. Starting at point 1 with T = T_1, if one cools the system maintaining constant $P_v = P_{v1}$ (as well as constant total P), the solid line intersects the saturation vapor line at the dew-point temperature T_{DP}. This is T_{sat} for water @ P_{v1}. At this point, any further attempt to cool the system causes condensation to a saturated water vapor mixture consisting of condensed liquid plus vapor, while T does not drop further until all water has condensed out. (This is because latent heat of vaporization is released to the system and opposes the cooling as long as condensation is continuing.) During this stage of condensation, the absolute humidity ω of water vapor is decreasing, relative humidity φ remains constant at 100%, and T_{DP} = actual T.

Wikipedia states, "OSHA recommends indoor air be maintained at 20 to 24.5 °C (68.0 to 76.1 °F) with a 20 to 60% relative humidity (a dew point of −4.5 to 15.5 °C (23.9 to 59.9 °F))." The relationship of T_{DP} to human comfort at higher temperatures is summarized in the accompanying table:[368]

Dew point		Human perception	Relative humidity at 32 °C (90 °F)
Over 26 °C	Over 80 °F	Severely high...	73% and higher
24–26 °C	75–80 °F	Extremely uncomfortable, fairly oppressive	62–72%
21–24 °C	70–74 °F	Very humid, quite uncomfortable	52–61%
18–21 °C	65–69 °F	Somewhat uncomfortable for most people at upper edge	44–51%
16–18 °C	60–64 °F	OK for most, but all perceive the humidity at upper edge	37–43%
13–16 °C	55–59 °F	Comfortable	31–36%
10–12 °C	50–54 °F	Very comfortable	26–30%
Under 10 °C	Under 50 °F	A bit dry for some	25% and lower

Elaborate approximate formulas relating Dew Point to Relative Humidity are given here[369] and the psychrometric chart is also quite useful for estimating it (see below).

Measures of Absolute and Relative Humidity Using Adiabatic Saturation T_{AST}, Wet Bulb T_{WB}, and Electronic Humidity Devices

Adiabatic Saturation T (T_{AST}) is a measure used to estimate the absolute and relative humidity φ. This somewhat cumbersome method involves blowing ambient air across the surface of a pool of water inside an insulated device, measuring the entering temperature T_1 and the exiting T_2 from the water pool apparatus. Depending on the starting relative humidity φ_1, the water pool will cool the air down to varying degrees while saturating it with water vapor (φ_2=100%). Of course, the higher the starting humidity φ_1, the less the T drop (cooling). The exiting temp T_2 is **the adiabatic saturation temperature T_{AST}**. (There is no heat or work transfer.) The incoming relative humidity φ_1 (which is unknown) is calculated from the measurable and table-derived quantities as (assuming constant $P_1 = P_2 = P$):[370]

$$\omega_1 = \frac{c_p(T_2 - T_1) + \omega_2 h_{fg2}}{h_{g1} - h_{f2}} \qquad (14\text{-}14)$$

where

$$\omega_2 = \frac{0.662\, P_{g2}}{P - P_{g2}} \qquad (14\text{-}15)$$

and applying a previous formula

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[368] https://en.wikipedia.org/wiki/Dew_point , adapted MCM, quote and table.

[369] https://en.wikipedia.org/wiki/Dew_point#Calculating_the_dew_point

[370] *TAEA7* p. 738 and https://www.chegg.com/homework-help/definitions/adiabatic-saturation-and-wet-build-temperatures-5

$$\varphi_1 = \frac{\omega_1 \, P}{(0.622 + \omega_1)\, P_{g1}}$$

where P_{g1} for the given P and T_1 and other quantities in these equations can be determined from the tables.

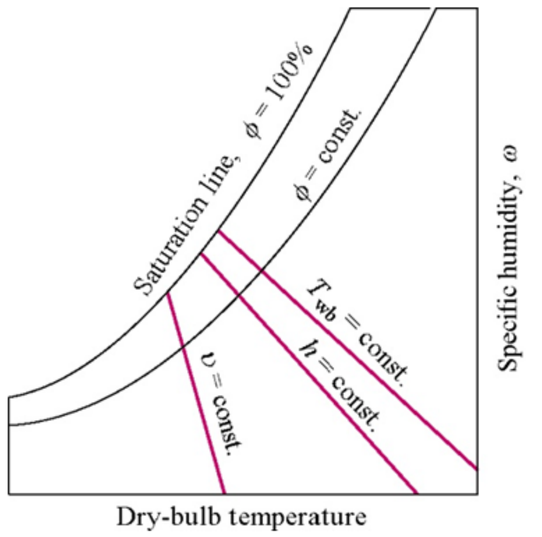
The T-s diagram curve for this device is also depicted in the diagram immediately above: point 2, where the dashed cooling curve intersects with the saturation vapor curve, is the adiabatic saturation temperature T_{AST}. It is a warmer T than the T_{DP}, which is understandable because evaporative cooling is involved but not to the point of inducing condensation.

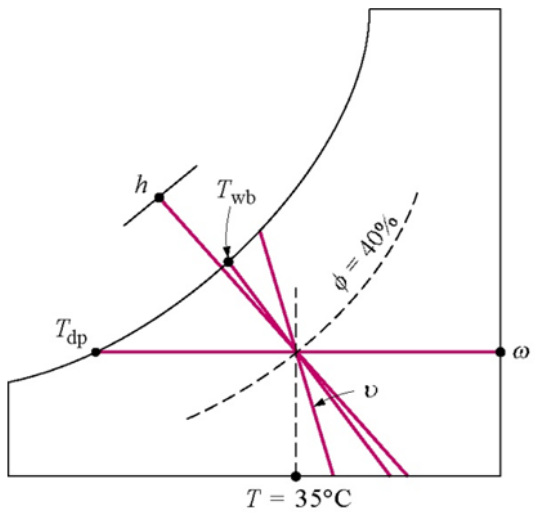
The T_{AST} is impractical. Another measure of relative humidity is the **Wet Bulb Temperature T_{WB}**. At atmospheric pressure and for air-water vapor mixtures, $T_{WB} \approx T_{AST}$. T_{WB} determination uses two thermometers: one is kept dry and the other bulb is surrounded by a wet wick. The greater the difference between the measured temperatures, the lower the relative humidity. An improved device for measuring T_{WB} is the **sling psychrometer**. T_{WB} can be used in place of T_2 in the formulas for ω_1 above derived from T_{AST}.

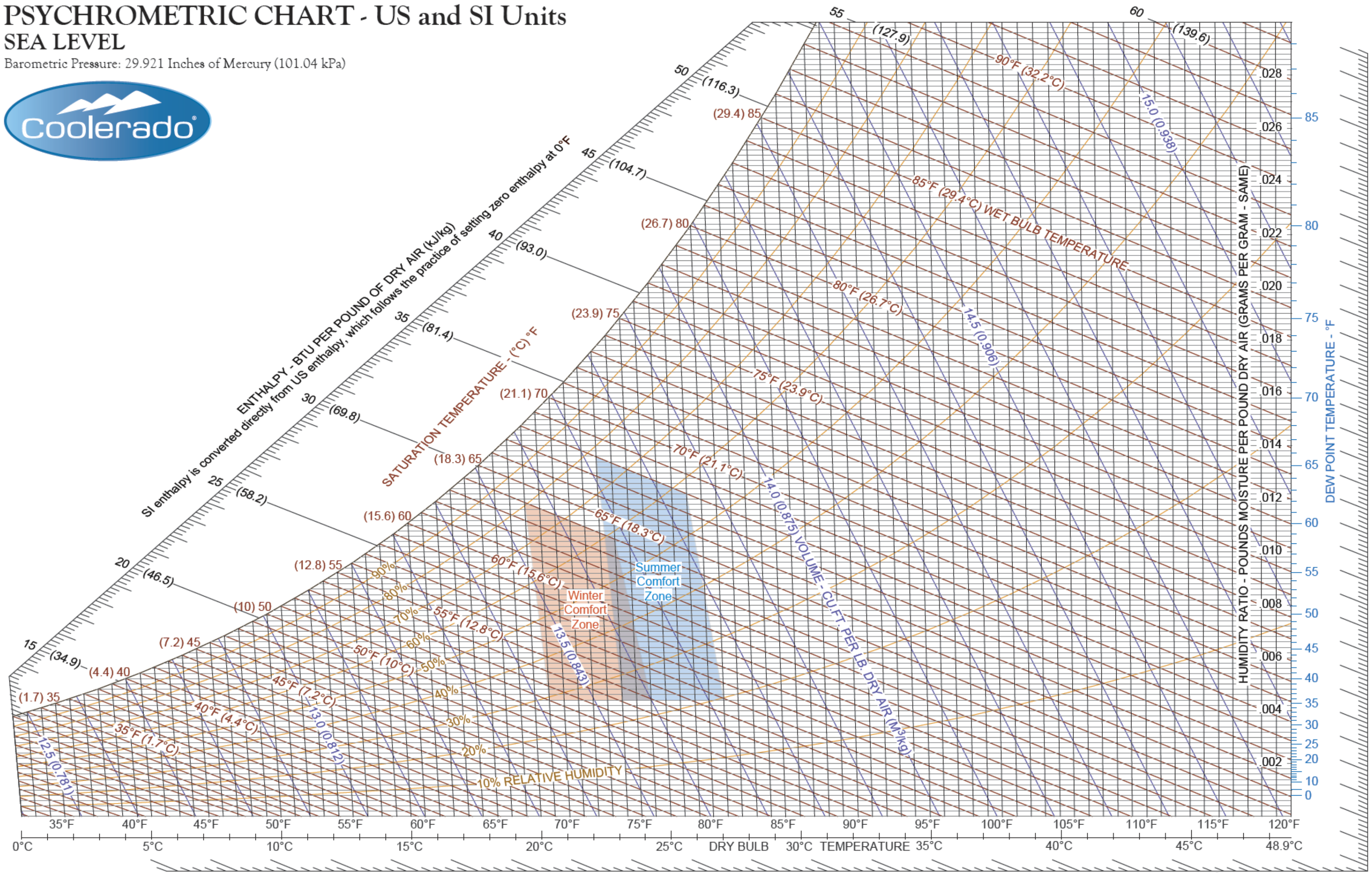
Electronic devices are replacing all of these older methods for determining relative humidity, though they have accuracy problems of their own.

Use of the Psychrometric Chart in Air-Conditioning Applications

This complex chart is widely used in the HVAC industry. Each chart is for a fixed (constant) total P, specific to a particular locale elevation or at least to an elevation—for elevations for which there is no chart, one must resort to the tables and developed relationships. Some of the properties found in it are shown in these next simplified diagrams, and 2 representative sea-level commercial Psychrometric Charts follow (from Coolerado and Carrier, resp.):







Psychrometric Chart for Sea Level[371]. Chart is in mostly USCS English units, some SI units also shown, T scales are in °F and °C.

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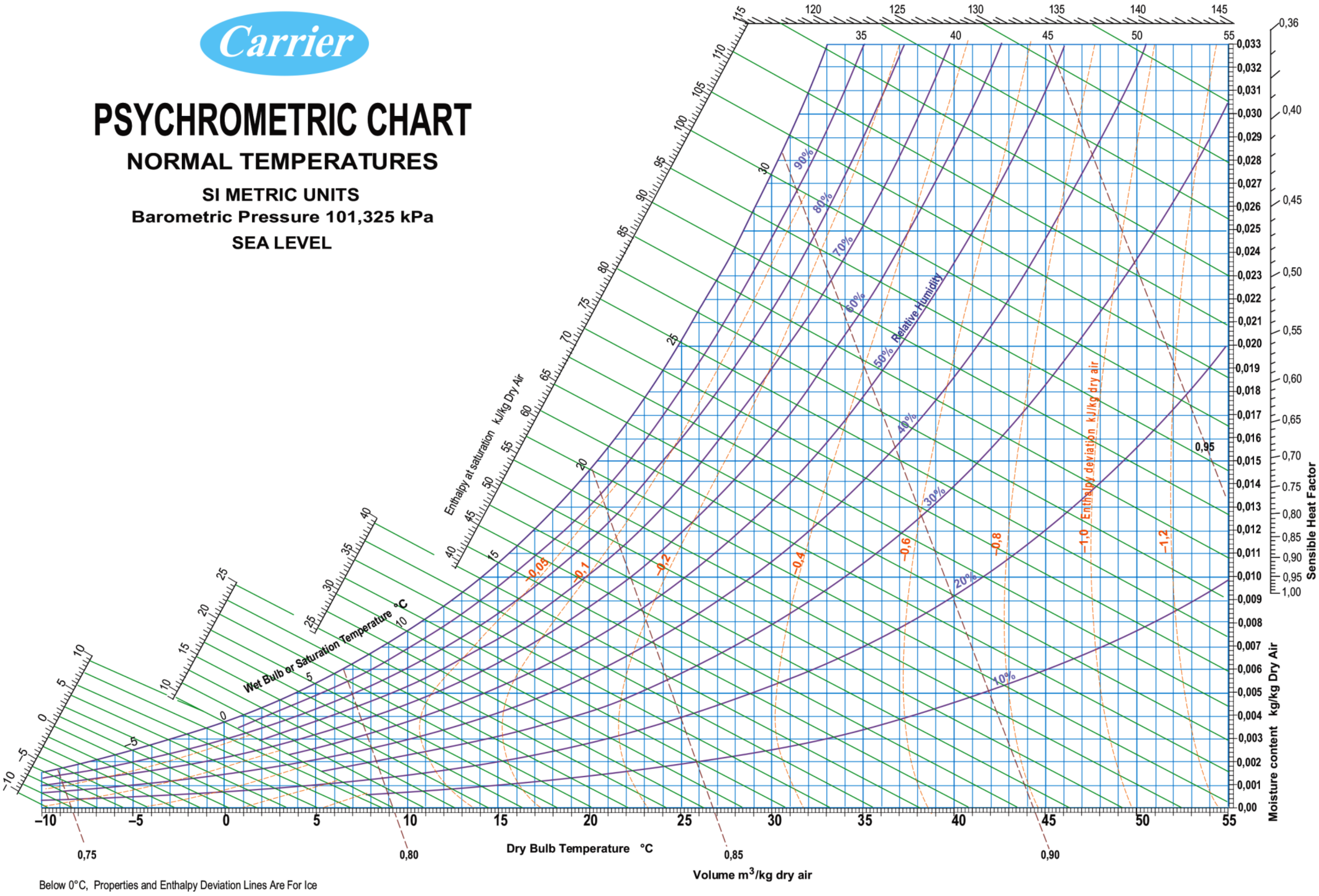
[371] http://www.coolerado.com/pdfs/Psychrmtrcs/0000Psych11x17US_SI.pdf



Psychrometric Chart for Sea Level[372]. Chart is in SI units.

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[372] http://www.alder.co.za/psy_02.pdf Contrast enhanced by MCM

Properties Shown on the Psychrometric chart[373]

A current **state point** of the system is defined by any two independent intensive properties, such as (ω, T_{DB}).

Dry bulb temperature T_{DB}: These lines are nearly vertical straight lines (as in the Coolerado chart)—on the right they are more vertical, on the left they become more tilted toward the left—but in some charts (like the Carrier chart), they are truly vertical. They arise from the T_{DB} axis at the bottom (the abscissa or horizontal axis), as shown by T_{DB} labels along the bottom. Each T_{DB} represents a constant temperature T_{DB}, and a T_{DB} line passing through a state point represents the true temperature of that state. If the T_{DB} lines are slanted, the grid does not usually include any precisely vertical lines except along the right axis scales.

Specific Humidity ratio ω (Absolute humidity, **humidity ratio, Moisture Content, W)**: These are the horizontal lines on the chart. Specific Humidity is expressed as mass of water vapor per mass of dry air. The range is from 0 for dry air up to about 0.03, as shown in labels along the right hand ω-axis, the ordinate or vertical axis of the chart.

Saturation Line for φ = 100% and Saturation Temperatures. This curved line forms the left margin of the main body of the graph. It represents the locus of state points for which the water vapor saturation is 100% and thus the relative humidity φ = 100%. The T values along this curve are defined by the intersection of a T_{DB} vertical or near-vertical line with the curve. The value of the saturation T may be read from the label on the horizontal T_{DB} axis or from the corresponding labels of T along the saturation line. Along this line, $T_{DB} = T_{WB} = T_{DP}$.

Relative humidity φ (RH): These hyperbolic-like curving lines follow similar contours as the Saturation Line for φ = 100%, though gradually changing, and are shown in intervals of 10%. The saturation curve is at φ = 100%, while dry air is at φ = 0%. The lines of constant φ are shown in the Coolerado graph above in gold-yellow color and are labeled 10% to 90% toward the left of the graph.

Wet bulb temperature T_{WB}: These lines are oblique lines tilting upward to the left. They are straight but are not exactly parallel to each other. These intersect the saturation line at the T_{WB} point. They are shown in the graph above in dark brownish color and are labeled in increments of 5 °F toward the upper left of the graph near the line of 70% Relative humidity. They differ slightly in tilt from the lines of constant enthalpy h_{const}. They appear to be omitted from the Carrier chart.

Specific enthalpy h: These lines express the total enthalpy of both the dry air and water vapor per kilogram of dry air (kJ/kg dry air). They are oblique lines also tilting upward to the left that are parallel to each other. In the Carrier diagram, they appear as green lines. They do not appear within the grid in the Coolerado diagram above, but their endpoints can be found along the Enthalpy at saturation scale at far left and along the vertical scale at far right. These are not exactly parallel to wet bulb temperature T_{WB} lines, but similar in obliquity angle. Specific enthalpy is used in calculating energy needed for cooling and heating goals.

Dew point temperature T_{DP}: From a state point, follow the horizontal line of constant Specific Humidity ratio ω to the intercept with the Saturation Line (φ = 100%). The dew point temperature is equal to the fully saturated dry bulb T_{DB} or wet bulb temperature T_{WB}, which coincide along the saturation line. For the Coolerado diagram, the scale of T_{DB} values is shown in light blue along the right margin. They are omitted on the Carrier diagram.

Specific volume v (volume per mass of dry air): These are a family of equally spaced straight lines that are nearly parallel and tilt steeply upward and to the left. On the Coolerado diagram, they appear as darker blue lines labeled within and toward the midregion of the diagram. There is no scale on the periphery for these values. On the Carrier diagram, they appear as dashed brown lines.

Condensation Region: The region above and to the left of the saturation line is a two-phase region that represents a mixture of saturated moist air and liquid water, in thermal equilibrium. State points that fall in this region are accompanied by condensation until water vapor content falls to the saturated level. Enthalpy scales are drawn in this region in both diagrams.

Comfort Zones: The Coolerado diagram show a winter comfort zone (salmon shading, centered at about 71 °F and 50% RH) and summer comfort zone (blue shading, centered at about 77 °F and 45% RH)

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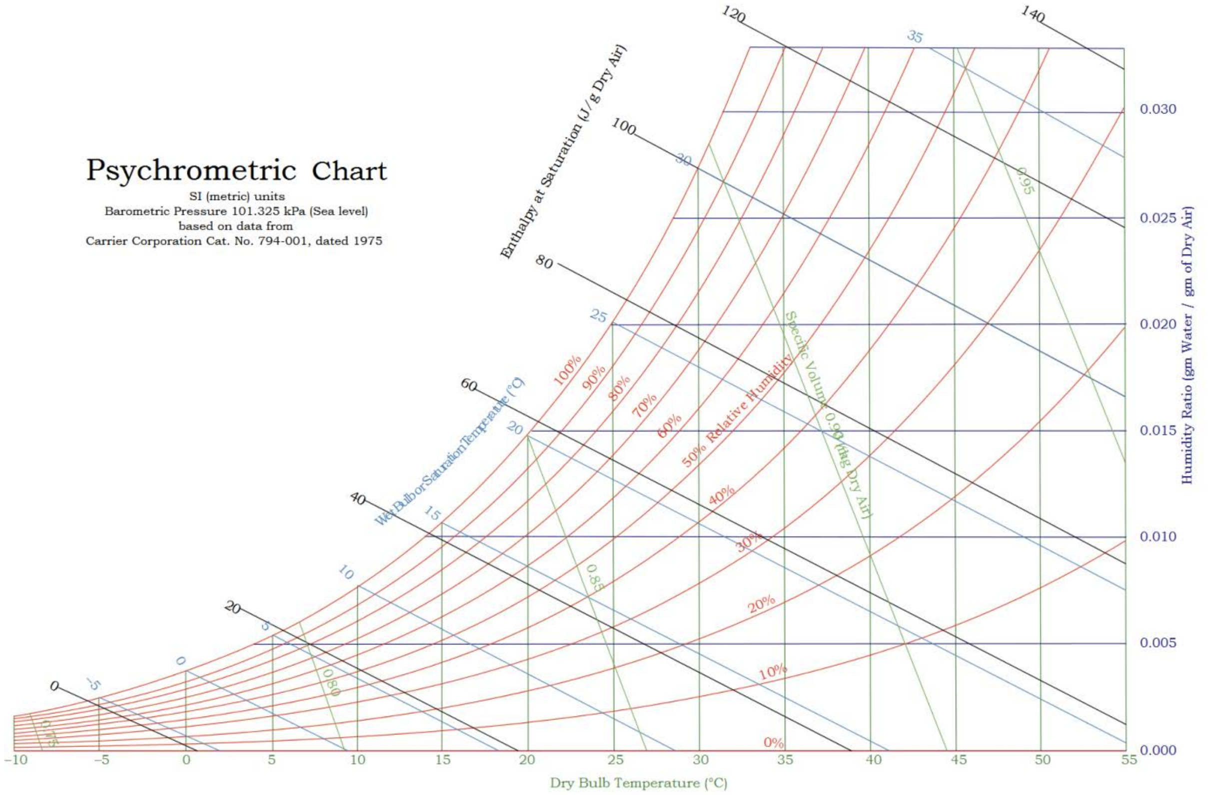
[373] https://en.wikipedia.org/wiki/Psychrometrics#Psychrometric_charts modified by MCM



Simplified Psychrometric Chart for Sea Level location[374]
Showing Dry Bulb T_{DB}, Wet Bulb T_{WB} (blue lines), (Dew Point T_{DP} not shown), Relative Humidity φ (red curves), Absolute Humidity ω, Specific Enthalpy h (black lines), & Specific volume v (green lines)

Air-Conditioning Goals and the Psychrometric Chart

The following types of actions can be visualized and approximated on the psychrometric diagram:

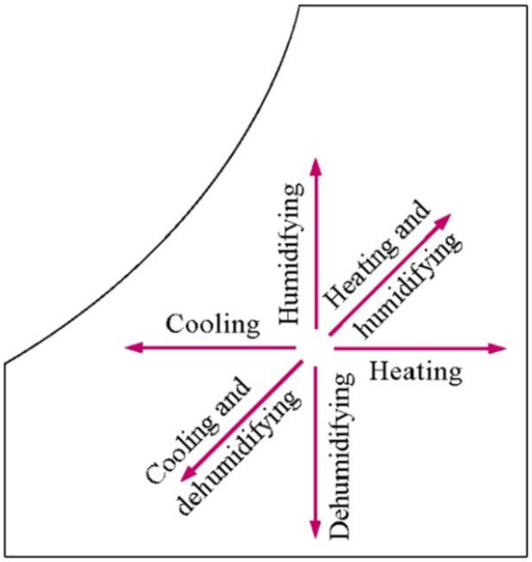
Simple Heating: Move horizontally to the right along a line of constant Specific Humidity ratio ω, increasing T_{DB} but decreasing Relative Humidity φ.

Problems involving starting (1) and ending (2) states for simple cooling or heating applications assume a constant mass balance of dry air flow and can be solved by an energy balance equation involving enthalpies per unit mass of dry air, such as[375]

$$\dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a \qquad \text{(kg/s)}$$

$$\dot{Q} = \dot{m}_a (h_2 - h_1) \qquad \text{or} \qquad \text{(W)}$$

$$q = h_2 - h_1 \qquad \text{(kJ/kg dry air)}$$



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[374] https://en.wikipedia.org/wiki/Psychrometrics per Carrier Corp.

[375] *TAEA7* p. 744

Simple Cooling: Move horizontally to the left along a line of constant Specific Humidity ratio ω, decreasing T_{DB} but increasing Relative Humidity φ.

Simple Humidification: Move vertically upward approximately along a line of constant T_{DB}, increasing Specific Humidity ratio ω and Relative Humidity φ.

Simple Dehumidification: Move vertically downward approximately along a line of constant T_{DB}, decreasing Specific Humidity ratio ω and Relative Humidity φ.

Heating with Humidification: This is commonly desirable in the winter. Move horizontally to the right increasing T_{DB} while also increasing Specific Humidity ratio ω and keeping Relative Humidity φ in a comfortable zone (perhaps by injecting steam).

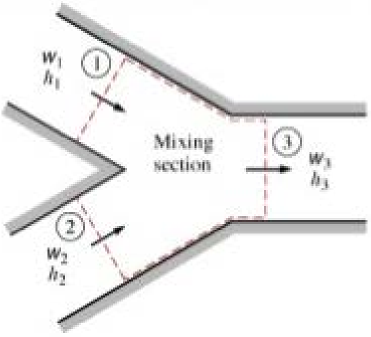
Problems involving Humidification or Dehumidification as well as heating or cooling must consider the water mass balance as well as the above relationships (most details omitted):

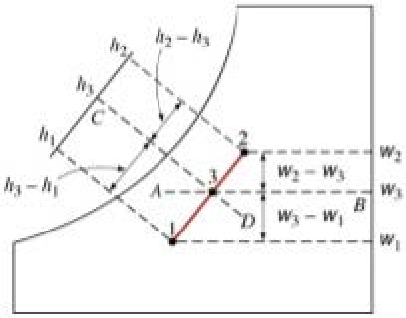
$\dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$	(kg/s)	dry air mass balance before humidification
$\dot{m}_{a1}\omega_1 = \dot{m}_{a2}\omega_2$	(kg/s)	water balance before humidification
$\dot{Q}_{in} + \dot{m}_a h_1 = \dot{m}_a h_2$ or	(W)	energy balance w heating, before humidification
$\dot{m}_{a2}\omega_2 + \dot{m}_{water} = \dot{m}_{a3}\omega_3$	(kg/s)	water balance in humidification stage, etc.

Cooling with Dehumidification: This is commonly desirable in the summer. Move horizontally to the left decreasing T_{DB} while decreasing Specific Humidity ratio ω and decreasing Relative Humidity φ. This will involve inducing condensation of some water vapor by cooling below the T_{DP}, possibly then reheating to bring the air back to a comfortable T_{DB} and Relative Humidity φ.

Adiabatic Mixing of Two Air Streams

Consider two streams of air in states 1 and 2 which are mixed adiabatically at the same pressure (in air-conditioning situations, air pressure is typically considered approximately equal to atmospheric pressure). The resulting state 3 of the final mixture on the psychrometric chart lies along the straight line connecting the two states 1 and 2. When there is higher flow rate in state 1 than state 2, the final state 3 point will be closer to state 1 on this line than to state 2.[376]





The final state (h_3 ω_3) can be determined and located on the psychrometric chart using the values of mass flow rates of dry air (which must be calculated), the incoming specific humidities ω_1 and ω_2, and incoming enthalpies h_1 and h_2:

$\dot{m}_{a3} = \dot{m}_{a1} + \dot{m}_{a2}$	by mass conservation, where $\dot{m}_{a1}(\text{kg/min}) = \frac{\dot{V}_1}{v_1}$ etc. and $\dot{V}$ is in m^3/min
$\frac{\dot{m}_{a1}}{\dot{m}_{a2}} = \frac{\omega_2 - \omega_3}{\omega_3 - \omega_1} = \frac{h_2 - h_3}{h_3 - h_1}$	(formulas derived from mass of water vapor, and energy balance)

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[376] Image from http://www.slideshare.net/manimaranabcd/ps1-43982236 , adapted by MCM

where $\dot{m}_{a1}$ is the dry air mass flow rate (kg/min) for state 1
ω_n is the specific humidity for state n
h_n is the enthalpy per unit mass of dry air for state n

The values of ω_n and h_n determine the final state 3 point on the chart. Specifically,

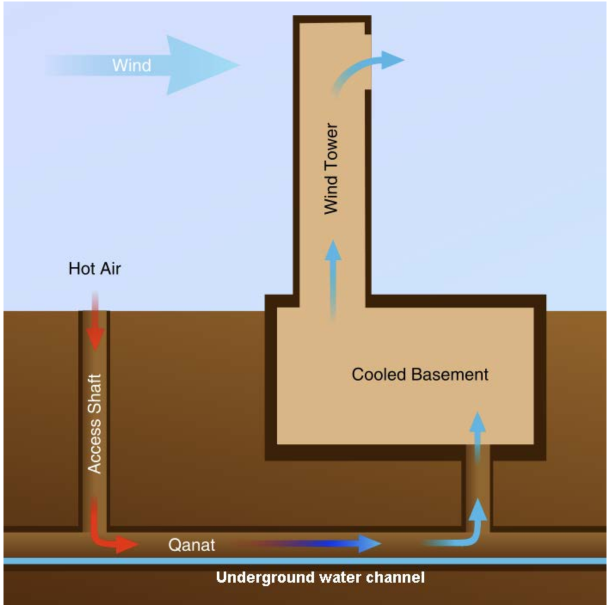
$$\omega_3 = \frac{\dot{m}_{a1}\omega_1 + \dot{m}_{a2}\omega_2}{\dot{m}_{a1} + \dot{m}_{a2}} \quad \text{and} \qquad (\text{kg } H_2O/\text{kg dry air})$$

$$h_3 = \frac{h_1(\omega_2 - \omega_3) + h_2(\omega_3 - \omega_1)}{\omega_2 - \omega_1} \qquad (\text{kJ / kg dry air})$$

The final volume flow rate (m^3/min) is given by $\dot{V}_3 = \dot{m}_{a3} v_3$, where v_3 is the specific volume of state 3.

Resulting state points that appear to lie outside the diagram can occur when very cold air is mixed adiabatically with warmer moister air—in such cases, condensation will occur to bring the state back to the saturation line.[377]

Evaporative Cooling



Throughout history, there have been many forms of evaporative cooling. The Egyptians used porous clay jars holding water, the Persians used qanats or underground water channels combined with wind towers (image to right),[378] animals use sweating, and power plants use wet cooling towers. A once-commonly used device is the evaporative cooler.

Evaporative Coolers ("swamp coolers") cool warm dry incoming external air by passing it over a wet surface, causing evaporation of the water. "Evaporative cooling is the addition of water vapor into air, which causes a lowering of the temperature of the air. The energy needed to evaporate the water is taken from the air in the form of sensible heat, [lowering] the temperature of the air, and [is] converted into latent heat, the energy present in the water vapor component of the air, whilst the air remains at a constant enthalpy value. This conversion of sensible heat to latent heat [enthalpy of vaporization h_{fg}] is known as an adiabatic process because it occurs at a constant enthalpy value. Evaporative cooling therefore causes a drop in the temperature of air proportional to the sensible heat drop and an increase in humidity proportional to the latent heat gain. Evaporative cooling can be visualized using a psychrometric chart by finding the initial air condition and moving along a line of constant enthalpy toward a state of higher humidity [see Psychrometric Charts above and example below]. Most designs take advantage of the fact that water has one of the highest known enthalpy of vaporization (latent heat of vaporization) of any common substance. Because of this, evaporative coolers use only a fraction of the energy of vapor-compression or absorption air-conditioning systems. Unfortunately, except in very dry climates, the single-stage (direct) cooler [diagram shown below] can increase relative humidity φ (RH) to a level that makes occupants uncomfortable. Indirect and Two-stage evaporative coolers keep the φ (RH) lower [by preventing introduction of water into the cooled air]."[379]

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[377] *TAEA7* p. 750

[378] Image from author: Samuel Bailey adapted by MCM https://upload.wikimedia.org/wikipedia/commons/thumb/5/52/Qanat_wind_tower.svg/969px-Qanat_wind_tower.svg.png

[379] https://en.wikipedia.org/wiki/Evaporative_cooler excerpted quoted text and diagram to follow

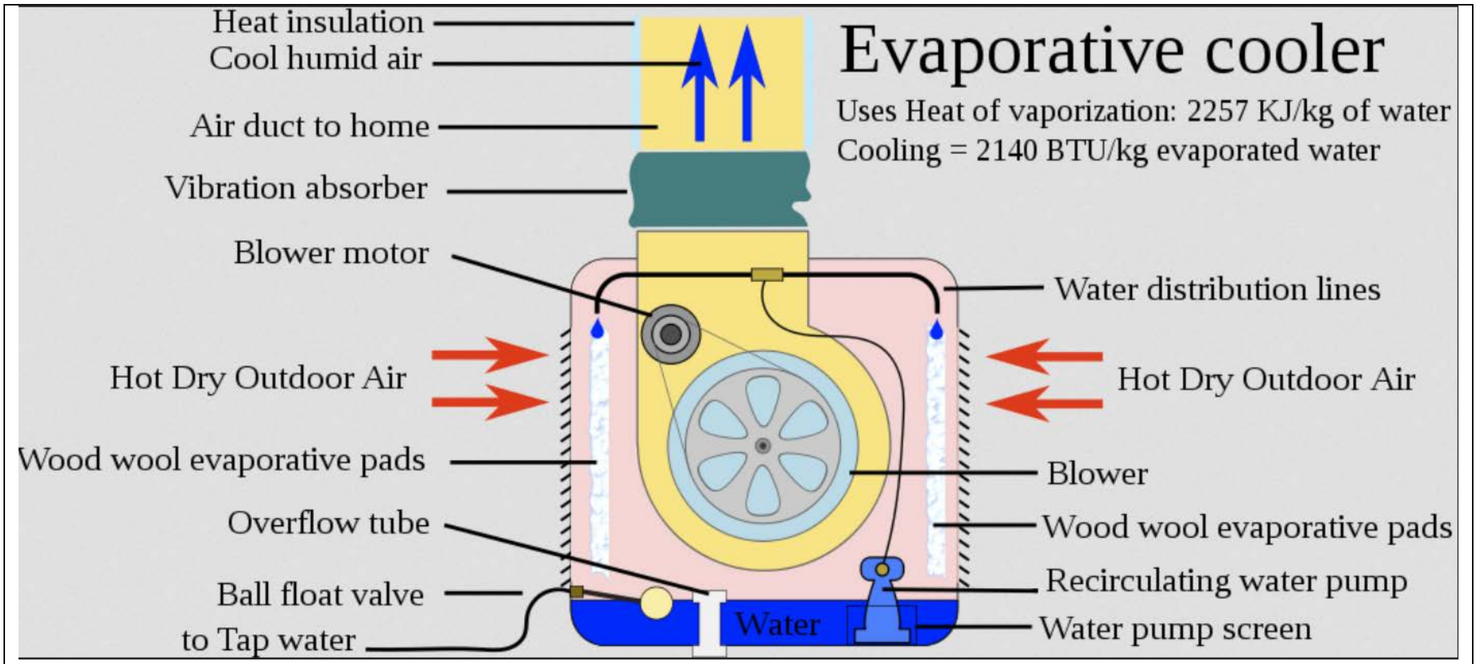

Diagram of a Single Stage Direct Evaporative Cooler
The evaporation of water converts sensible heat to latent heat of vaporization, lowering the T of the wet pads, the water on them, and the air passing through them.

The following is a psychrometric chart for summer conditions in Salt Lake City (approximate elevation of 4,327 feet). The blue cells apparently represent the statistical distribution of summer states (i.e., T_{DB} = DBT and ω = AH g/kg, etc.) The color calibration is not provided but darker color apparently signifies greater frequency of occurrence for that chart state.

Acceptable climate conditions for direct and indirect evaporative cooling are partially outlined in purple and green, respectively. With direct evaporative cooling [for example, using the swamp cooler like that depicted above], the comfort range in this city for a sedentary person can be expanded from the optimal comfort zone (parallelogram outlined in yellow) to a wider zone of comfort (extending to warmer T but with somewhat lower absolute humidities), bordered on the right and above by the purple line. Thus, if the summer conditions fall to the left and below the purple line, the addition of evaporative cooling can make the air comfortable by attaining a state lying within the comfort zone outlined in yellow.

Use of Indirect and Two-stage evaporative coolers can further widen the zone of comfort (enclosed in green) in which conditions can be made comfortable for even higher temperatures and over a wider range of absolute humidities.[380]

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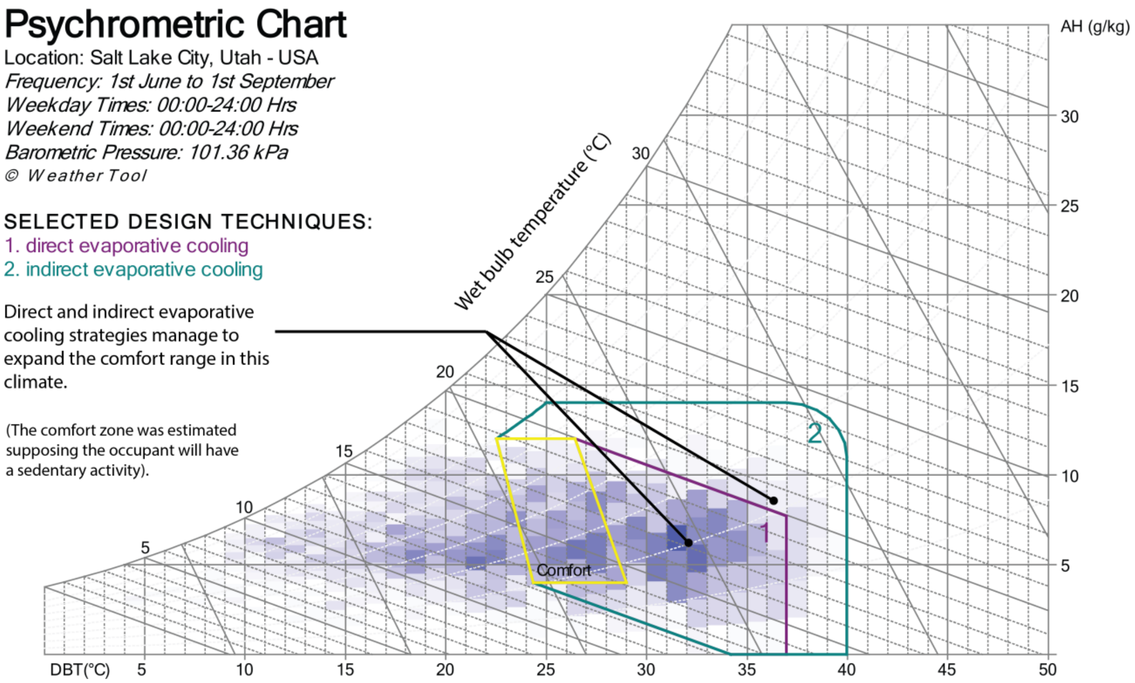
[380] https://en.wikipedia.org/wiki/Evaporative_cooler chart



Psychrometric Chart

Location: Salt Lake City, Utah - USA

Frequency: 1st June to 1st September

Weekday Times: 00:00-24:00 Hrs

Weekend Times: 00:00-24:00 Hrs

Barometric Pressure: 101.36 kPa

© Weather Tool

SELECTED DESIGN TECHNIQUES:

1. direct evaporative cooling
2. indirect evaporative cooling

Direct and indirect evaporative cooling strategies manage to expand the comfort range in this climate.

(The comfort zone was estimated supposing the occupant will have a sedentary activity).

Chemical Reactions and Phase Equilibria (16)

(from text Chapter 15 and 16. Chapters not studied and omitted here. These topics deserve future attention.)

Compressible Flow (17)

(from text Chapter 17. Chapter not studied and omitted here. This is a subject of great potential interest, and I will have to plunge in someday.)

Useful symbols and characters in writing this summary

Greek and Mathematical Characters

Greek letters: αβγδΔ∏πζεηνθκΛλμρ∑στφΦχψΩω
Mathematical & Misc. Symbols: °≈≠∂√●•· ∫ ±¶⇒∠∝∞∇* ×̂⊥□□□♦↑↓← →⇆←→ ═ ≡≡≈

V of velocity [shown in Algerian] to distinguish it from V of Volume or **V** for Voltage.

Dotted Times New Roman Unicode Characters (do not reformat):

ṁ Ṁ ṅ Ṅ V̇ ẇ Ẇ [no lower case v dot or Q dot]

Search http://www.fileformat.info/info/unicode/char/search.htm for “LETTER N WITH DOT ABOVE” etc.

Other Characters: ① ② ③ ④ ⑤