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CHAPTER I

Introduction and Basic Concepts

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I.1. Definition

The most common definition of Thermodynamics is “The science of energy”.
Thermodynamics stems from the Greek words:

“Therm”	for heat
“dynamis”	for power

Thermodynamics deals, therefore, with the conversion of heat to power or the inverse. Like all sciences, the basis of thermodynamics is experimental observation. These observations have been formalized into laws: ***zeroth law***; ***first law***; ***second law*** and ***third law*** of thermodynamics. The engineer’s objective in studying thermodynamics is most often the analysis or design of a large scale system [from an air-conditioner, gas turbines, propulsion systems to a nuclear power plant]

I.2. Dimensions and units

We will usually use the system MLT of primary dimensions to solve our problems.

M	**M**ass
L	**L**ength
T	**T**ime

From this primary system, secondary dimensions can be derived.

<u>Example:</u>

Velocity	m/s	LT^{-1}
Acceleration	m/s^2	LT^{-2}
Force	N	MLT^{-2}

We will also use the SI system of units [SI for Système International]. Why? Because the relationship between the various units in the SI system is simple and logical and based on a decimal relationship.

SI system	Imperial system
1 km = 1000 m	1 mile = 5280 ft
1 m = 1000 mm	1 ft = 12 in

Table.1.1. Comparison between the SI units systems and the Imperial units system.

The SI system is based on seven fundamental quantities:

Dimension	**Units**
Length	meter (m)
Mass	kilogram (kg)
Time	second (s)
Temperature	kelvin (K)
Electric current	ampere (A)
Amount of light	candela (cd)
Amount of matter	mole (mol)

Table.1.2. Fundamental dimensions and their units in the SI system.

I.3. Rule for notations

Here are the two principal unit rules:

1. Do not use the degree symbol $^{(o)}$ with the absolute temperature (K).
2. All unit names are to be written without capitalization even if they were derived from proper names (newton (not Newton); pascal (not Pascal); ampere (not Ampere); kelvin (not Kelvin); …)

However, if the abbreviation of the unit derived from a proper name is used, the first letter of the abbreviation must be capitalized.

10 **n**ewton (not 10 **N**ewton)	but	10 **N** (not 10 **n**)
5 **a**mpere (not 5 **A**mpere)	but	5 **A** (not 5 **a**)
101 **p**ascal (not 101 **P**ascal)	but	101 **P**a (not 101 **p**a)
300 **k**elvin (not 300 **K**elvin)	but	300 **K** (not 300 **k**)

I.4. Unit prefixes

10^{12}	tera	(T)	10^{-1}	deci	(d)
10^{9}	giga	(G)	10^{-2}	centi	(c)
10^{6}	mega	(M)	10^{-3}	milli	(m)
10^{3}	kilo	(k)	10^{-6}	micro	(μ)
10^{2}	hecto	(h)	10^{-9}	nano	(n)
10^{1}	deka	(da)	10^{-12}	pico	(p)

I.5. (-1) law of thermodynamics: dimensional homogeneity

"Never add apples and oranges principle"

When solving a physical problem, all the equations must be dimensionally homogeneous, i.e, all the terms in the equation have to have the same units.
So, if at a certain step of the solution, you are adding two quantities with different units: this means that there is an error somewhere.

Example

Heat input: Q_{in} = 200 kJ
Heat ouput: Q_{out} = 100 kJ/kg

The work generated is:
$W = Q_{in} - Q_{out} = 200\ \mathbf{kJ} - 100\ \mathbf{kJ/kg}$

Our equation is not homogeneous, and to solve the problem we have to multiply Q_{out} by the mass (in kg) to get kJ, and then we will be able to do the summation and to compute the work (W). [Note that we can also divide Q_{in} by the mass in (kg)].

I.6. Systems and Control volumes

I.6.1. System

It is defined as a quantity of matter or region in space chosen for the study.

The region outside the system is called: **the surroundings**

The surface (real or imaginary) that separates the system from its surroundings is the **boundary**. A boundary of a system can be fixed or movable.

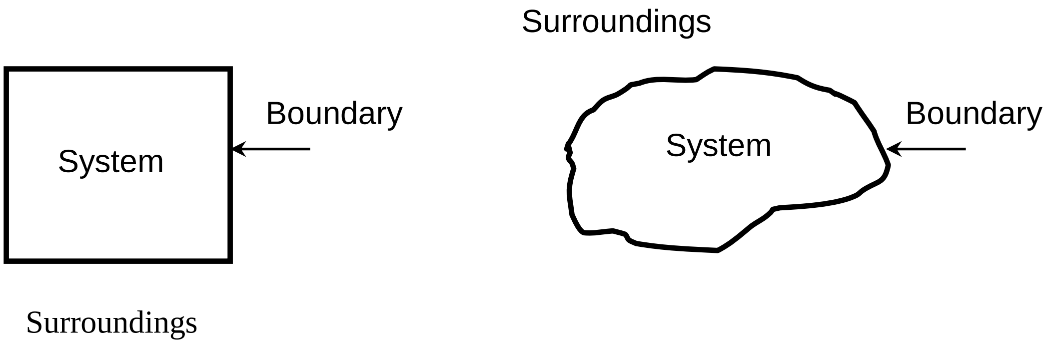


Figure.1.1. A system, its boundary and its surroundings.

I.6.2. Closed and open systems

I.6.2.1. Closed system (control mass)

In a closed system, the amount of mass is fixed. Therefore, ***no mass can cross the boundary of the system***.
However, energy in the form of heat or work can cross the boundary of the system.

In the particular case where no energy crosses the boundary of the system, the system is considered as **isolated**.

No mass crossing the boundary ⇒ closed system

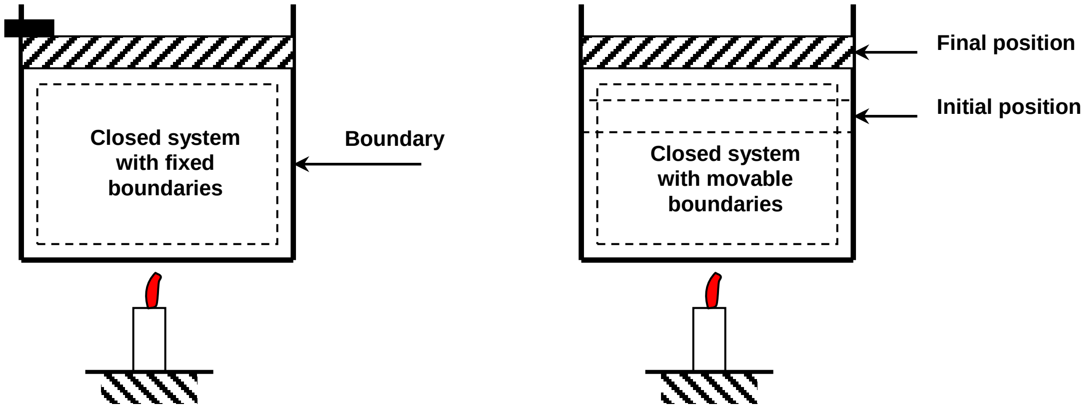


Figure.1.2. Closed system with fixed or movable boundaries.

I.6.2.2. Open system (control volume)

It is a specific region in space that usually encloses a device that involves mass flow such as a compressor, turbine or nozzle.
Both mass and energy can cross the boundary of a control volume.
There is no general rule for the selection of the control volume. However, a good selection of the control volume makes the analysis of the problem easier.

I.6.2.2.1. Control surface

The boundaries of a control volume are called: **control surface**. They can be real (physical boundary) or imaginary (no physical boundary).

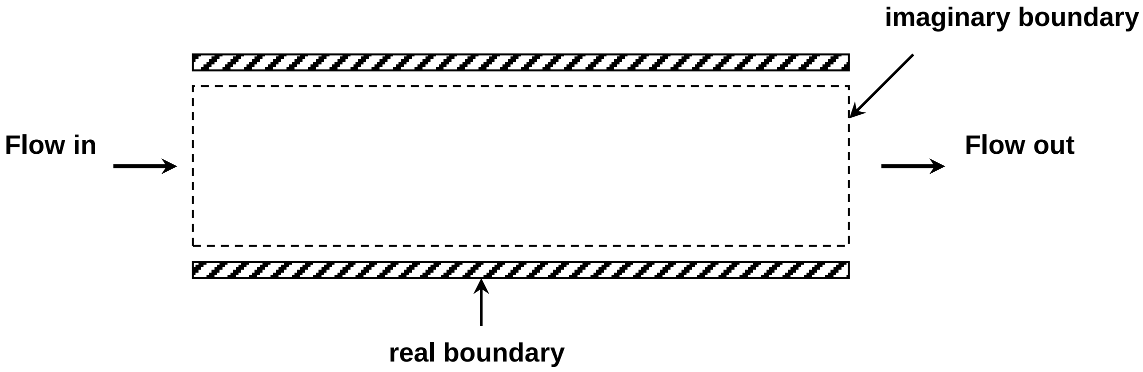


Figure.1.3. Control surface with real or imaginary boundaries.

Remark:
A control volume can be fixed in size and shape or it may involve a moving boundary. However, most control volumes have fixed boundaries.

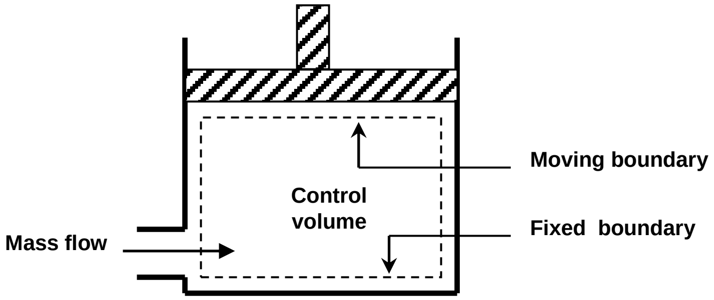


Figure.1.4. Control volume with a fixed and a moving boundary.

I.7. Properties of a system

Any characteristic of a system is called a property. Examples of properties are: temperature of the system (T), pressure of the system (P), volume of the system (V), mass of the system (m) and some other properties such as viscosity, thermal conductivity, electric resistivity and even the velocity of the system and its elevation.

The properties of a system are divided into two distinct families:

I.7.1. Intensive properties

They are the properties that are independent from the mass of the system.

Intensive ⇒ **In**dependent

Examples: temperature; pressure, density, …

I.7.2. Extensive properties

They are the properties that are dependent on the size –or extent- of the system.

Examples: total mass, total volume, …

To determine if a property is intensive or extensive use an imaginary partition of the system.
→ divide the system into two equal parts with an imaginary partition.

If a property is still the same for both parts, it is an intensive property.

If a property is equal to half the initial state, it is an extensive property.

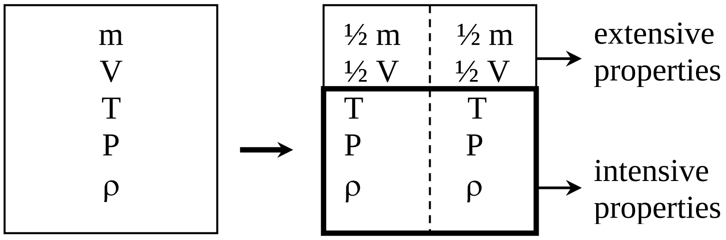


Figure.1.5. Difference between intensive and extensive properties.

I.7.3. Designation of the properties: "a not so general rule!"

Usually, uppercase letters are used for extensive properties (with mass (m) as an exception) and lower case letters for intensive properties (temperature (T) and pressure (P) are major exceptions).

I.7.4. Specific properties

A specific property is the result of the division of an extensive property by mass.

<u>Example</u>

Volume (V)	Specific volume ($v = \frac{volume}{mass}$)
Extensive property	**Intensive property**

I.7.5. Continuum

The matter is composed of atoms that are widely spaced in gas phase. However, as it might be complex to analyze a system in which the properties vary from one point to the other, we make the realistic assumption, at our scale, that the properties are the same everywhere (we do not consider the "void" between the atoms). The matter is considered, therefore, as continuous and homogeneous, that is**, continuum**.

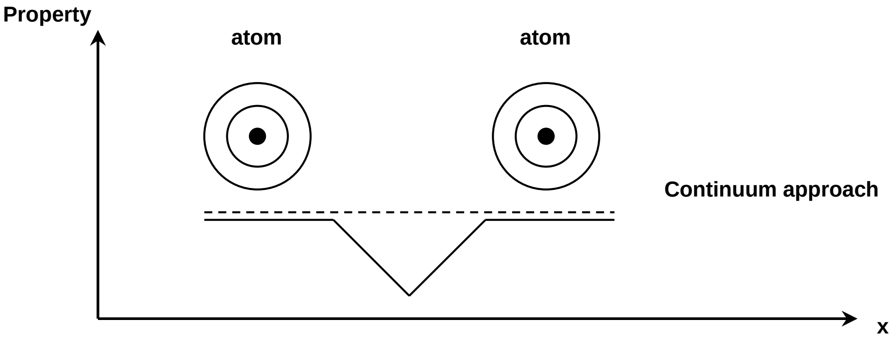
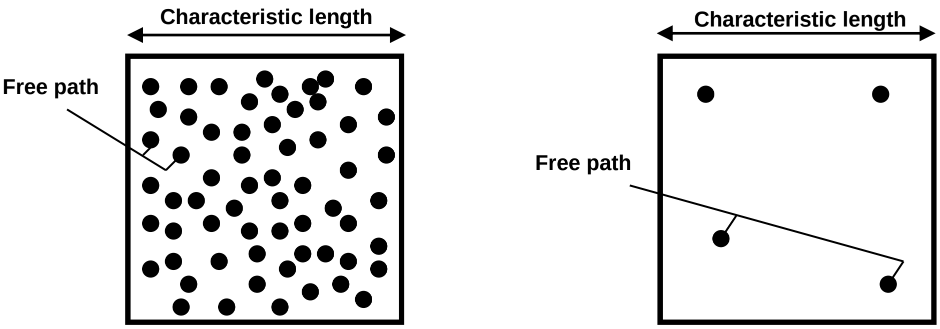


Figure.1.6. Schematic representation of the continuum approach.

I.7.5.1. Validity and limitations of the continuum approach

Considering matter as a continuum is valid as long as the characteristic length of the system (such as its diameter, it length) is much larger than the mean free path of the molecules.
The mean free path is the distance that a molecule has to cover before it collides with another molecule.



Free path << system characteristic length
Continuum approach is applicable

Free path ≈ system characteristic length
Continuum approach is not applicable

Figure.1.7. Limitations of the continuum approach.

High free paths are encountered in very high vacuums or very high elevations. In this case, rarified gas flow theory should be used.

Example:

Free path of O_2 at 1 atm is 6.3 10^{-8} m, which represents 200 times its diameter.

In this course, substances will always be modeled as a continuum

Additional information

The **Knudsen number** (**Kn**) is a dimensionless number defined as the ratio of the molecular mean free path length to a representative physical length scale. This length scale could be, for example, the radius of a body in a fluid. The number is named after Danish physicist Martin Knudsen (1871–1949).

The Knudsen number is defined as:

$$Kn = \frac{free\ \ path}{charateristic\ length}$$

The Knudsen number is useful for determining whether statistical mechanics or the continuum mechanics formulation of fluid dynamics should be used: If the Knudsen number is near or greater than one, the mean free path of a molecule is comparable to a length scale of the problem, and the continuum assumption of fluid mechanics is no longer a good approximation. In this case statistical methods must be used.

I.8. Density and specific gravity

I.8.1. Density

It is defined as the mass per unit volume:

$$\rho = \frac{m}{V} \quad \left[\frac{kg}{m^3}\right]$$

[Intensive property]

The inverse of density is called specific volume:

$$v = \frac{1}{\rho} = \frac{V}{m} \quad \left[\frac{m^3}{kg}\right]$$

I.8.1.1. Variation of density with pressure and temperature

	Gas	**Liquid or solid**
↑ P	ρ ↑	ρ ≈ constant [incompressible substance]
↑ T	ρ ↓	

I.8.2. Specific gravity

Specific gravity represents the density of a substance relative to the density of a well-known, reference, substance (at a specific temperature). For liquids, we use water at 4^oC and ρ_{H2O}=1000 kg/m^3.

$$Specific\ gravity[SG] = \frac{\rho}{\rho_{H_2O}}$$

This is a very intersting property since it will allow us to immediately determine if our liquid floats on water (SG<1).

Substance	**SG**
Water	1.0
Blood	1.05
Seawater	1.025
Gasoline	0.7
Wood	0.3-0.9
Ice	0.92
Bones	1.7-2.0

Table.1.3. Specific gravity for several substances.

Note: when dealing with a gas, its density is compared to the density of air.

Linguistic note (Fr *vs.* En):
masse volumique = density
densité = specific gravity

I.8.3. Specific weight

It is defined as the weight of a unit volume of a substance:

$$\gamma_s = \rho\ g \quad \left[\frac{N}{m^3}\right]$$

g is the gravitational acceleration.

I.9. State and equilibrium

I.9.1. State

Imagine a system not undergoing any change. At this point, all the properties of the system can be determined (T, P, v, …). We are, therefore, able to completely describe the conditions or the **state** of the system.

For each state corresponds fixed values of the properties of the system.
If any property is changed, the state also changes.

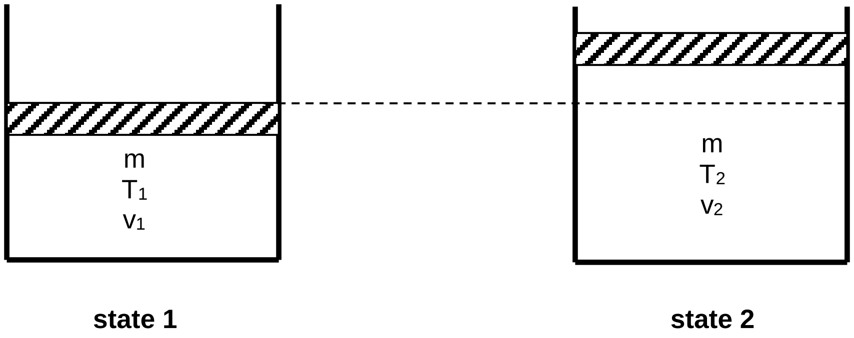


Figure.1.8. A system at two different states.

I.9.2. Equilibrium

Thermodynamics deals with equilibrium states. A system in equilibrium experiences no changes when it is isolated from its surroundings.

I.8.2.1. Thermal equilibrium

A system is in thermal equilibrium if the temperature is the same in the entire system.

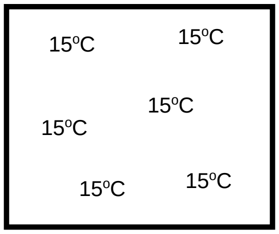


Figure.1.9. Thermal equilibrium.

I.9.2.2. Mechanical equilibrium

A system is in mechanical equilibrium if there is no change in pressure at any point of the system with time. This does not mean (such as for thermal equilibrium) that the pressure must be the same everywhere.

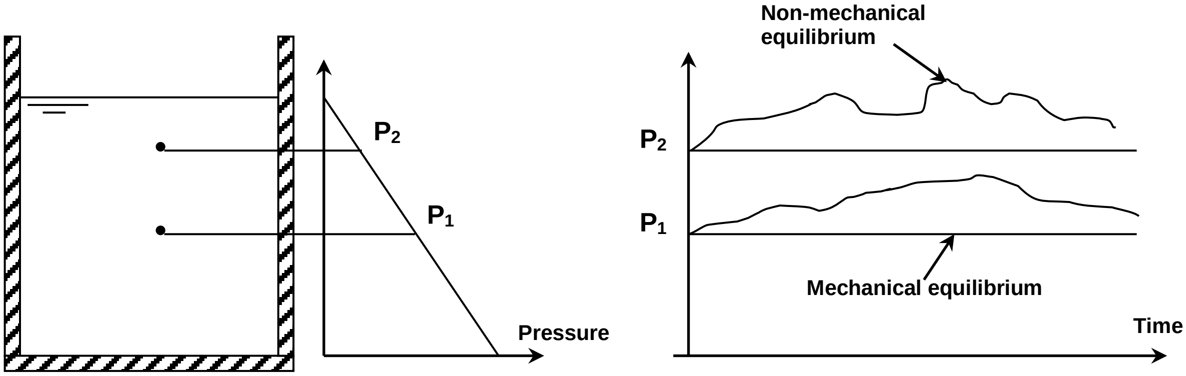


Figure.1.10. Schematic representation of mechanical equilibrium.

I.9.2.3. Phase equilibrium

When a system involves two phases (or more), the phase equilibrium is reached when the mass of each phase reaches an equilibrium level and stays there.

I.9.2.4. Chemical equilibrium

A system is in chemical equilibrium if its chemical composition remains the same with time: no chemical reactions are involved.

I.9.2.5. Thermodynamics equilibrium

THERMODYNAMICS EQUILIBRIUM

↓

Thermal equilibrium
+ Mechanical equilibrium
+ Phase equilibrium
+ Chemical equilibrium

I.10. The state postulate

To determine the state of a system, it is necessary to know its properties, but what is the minimal sufficient number of properties that have to be known? This number of properties required to determine the state of a system (knowing everything about the system) is given by the state postulate:

Very important →

The state of a system is completely specified by

TWO INDEPENDENT INTENSIVE

This postulate is valid for compressible systems [systems in the absence of electrical, magnetic, gravitational, motion, and surface tension], which will be the case in mostly all our problems.
In the specific case where one of these effects has to be taken into account, an additional property (specific to this effect, example: the elevation, if the gravitational effect is significant) has to be added in order to determine the state of the system.

I.10.1. Selecting the appropriate intensive variables

As stated by the state postulate, the two intensive variables have to be independent, that is, one property can be varied while the other one is held constant.

Example

Temperature (T) and specific volume (v) are independent variables, and they can be used to determine the state of our system.

I.10.2. The ambiguity of the couple (T,P)

It is important to pay attention to the two intensive properties which are temperature and pressure.
Why specifically T and P?

Because, they are the easiest intensive properties to measure.

Why do we have to pay attention to T and P?

Because T and P are independent only for a single phase state, but T=f(P) during a phase change. Hence, the temperature is a function of the pressure, and as a consequence T and P are not independent and are not sufficient to fix the state of a system.

Example

at	P=0.1 MPa	water boils at 100°C
	P=1.0 MPa	water boils at 179.88°C
	P=10 MPa	water boils at 311°C

We are enable to change one property and maintain the other constant, so T and P are not independent.

Single phase	**Phase change**
(T,P) are sufficient	(T,P) are insufficient ⇒ (T, other intensive property) or (P, other intensive property)

I.11. Processes and Cycles

Imagine we have a system at a state (1) and we want to bring it to another state (state (2)). This change from the equilibrium state (1) to the equilibrium state (2) is called a **process**, and the series of states from state (1) to state (2) are called the **path** of the process.

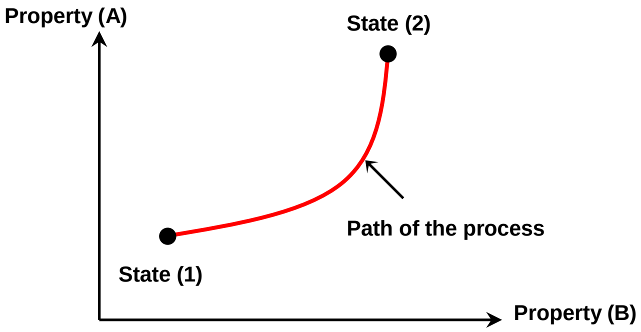


Figure.1.11. The process between state (1) to state (2) and its path.

To completely define a process we need to specify, therefore:

The initial point	The end point	How to go from the initial to the end points?
State (1)	State (2)	Path

We also have to specify the interactions between the system and the surroundings (heat addition, heat rejection, work …).

I.11.1. Quasi-static or quasi-equilibrium process

The quasi-equilibrium process is a specific process in which the system remains infinitesimally close to the equilibrium state at all times.

To do so, the process must be sufficiently slow to allow the system to adjust itself internally. As a consequence, no property at a certain point changes faster than any other point in the system.

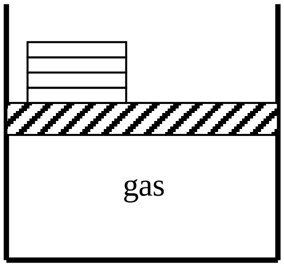


Figure.1.12. Quasi-static process:
The compression of the gas is performed by putting small weights one after the other.

<u>Example</u>

We will always replace combustion processes (like in internal combustion engines) [non-quasi-static process] by a slow heat addition [quasi-static process].

A quasi-static process is an idealized process, but it is a very convenient model because:

1- It is very easy to analyze [at each instant, the system is in equilibrium]
2- A work-producing device delivers the most work when it operates on quasi-static processes. The work computed under such conditions will serve as a reference that will be compared to the actual work.

I.11.1.1. Process diagrams

It is very convenient to visualize a process from state (1) to state (2) through a certain path using a process diagram.
The most common process diagrams are (T, v); (P, v) and (T, s) [s for entropy]

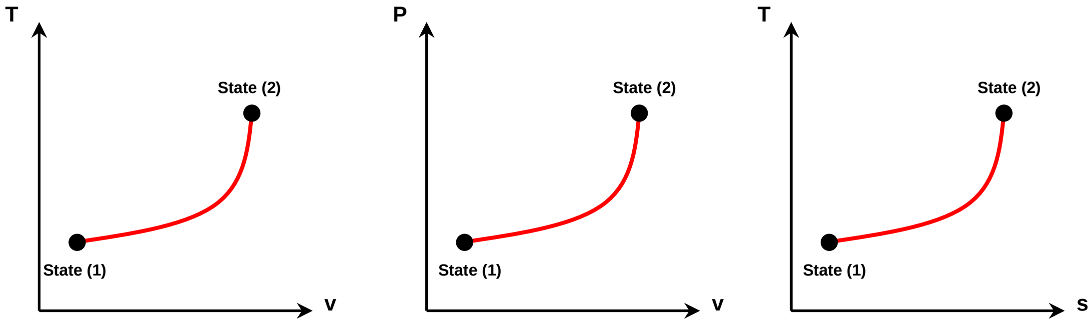
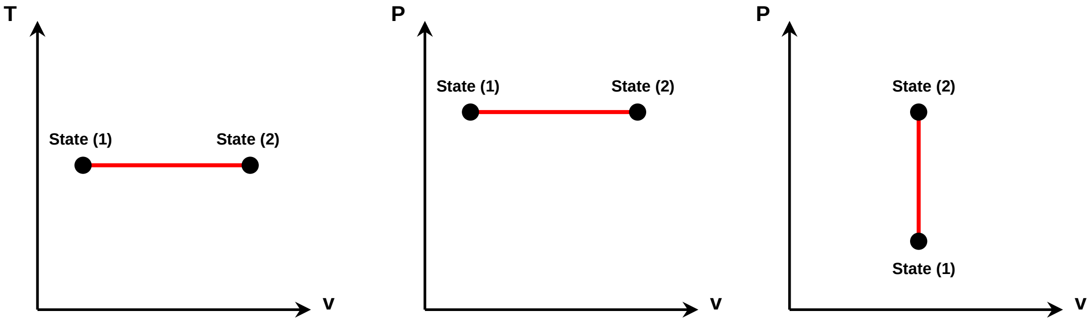


Figure.1.13. (T,v); (P,v); (T, s) process diagrams.

I.11.1.2. Prefixes

The prefix (iso) represents a process in which a particular property remains constant.

Isothermal process	the temperature remains constant during the process
Isobaric process	the pressure remains constant during the process
Isochoric process	the specific volume remains constant during the process



Isothermal process **Isobaric process** **Isochoric process**

Figure.1.14. Isothermal, isobaric and isochoric processes.

I.11.2. Cycle

The process is said to have a cycle, if it returns to its initial state at the end of the process.

Initial state = final state

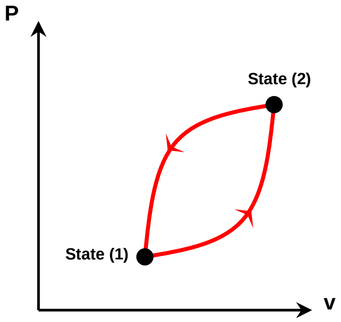


Figure.1.15. a cycle.

I.11.3. Steady flow process

A steady flow process is a process where the properties do not change with time. The opposite of a steady flow process is an unsteady flow process or transient flow process.
It is important to know the difference between a steady flow and a uniform flow:

A uniform flow is a flow where a specific property does not change with location over a specific region.

Using the concept of control volume, a steady flow process is defined as a process during which a fluid flows through a control volume steadily. That is, the fluid properties can change from one location to an other within the control volume <u>but</u> at a specific point the properties must remain the same during the process.

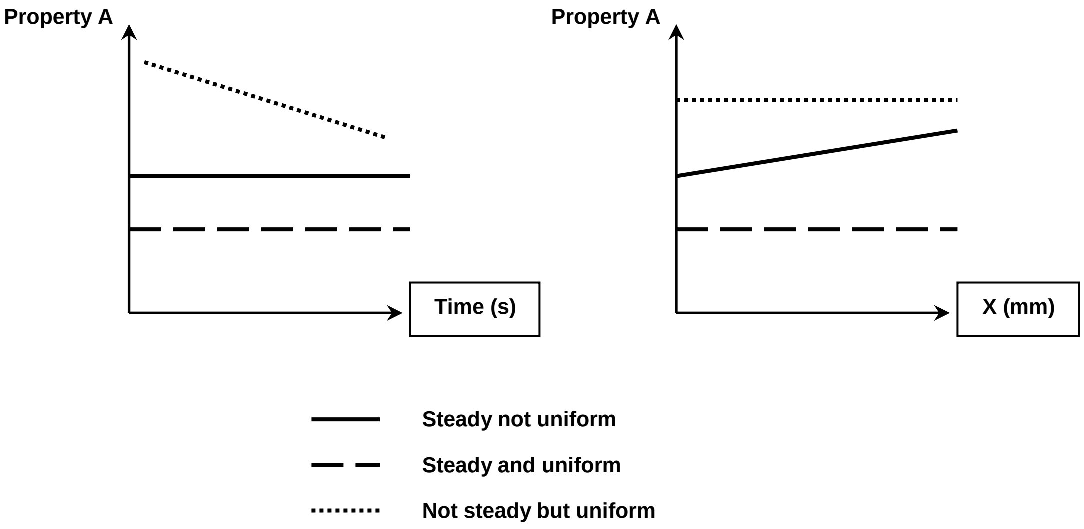


Figure.1.16. Difference between steady and uniform flow processes.

Devices working in continuous operation can be considered as steady flow devices (example: turbines, pumps, boilers …).

Some cyclic devices such as reciprocating engines can still be considered as steady flow devices, if we use the time-averaged values for the properties.

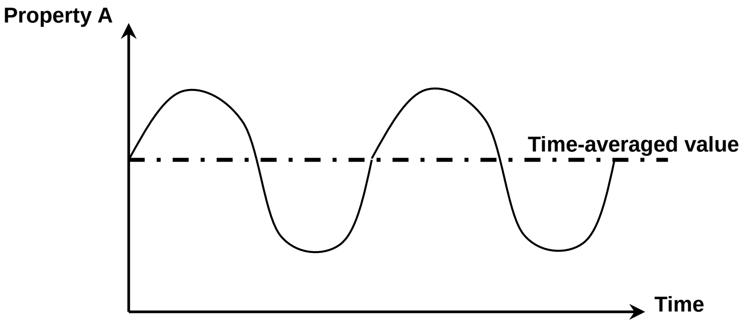


Figure.1.17. Time-averaged value for a cyclic property.

I.12. Temperature and zeroth law of thermodynamics

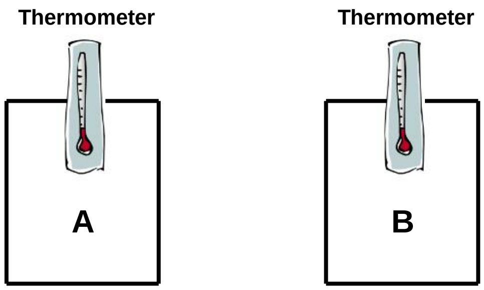
Although we are very familiar with the concept of temperature, it is very difficult to define exactly what temperature is. We usually refer to it by considering its effect: this is cold, this is hot, this is warm …
However, we cannot assign numerical values to the temperature based on our sensations alone: In winter, a piece of metal will feel much colder than a piece of wood even if both are at the same temperature.

The only way that we have to estimate the temperature is to consider the variation of properties of a material with temperature. As an example, the mercury in glass thermometer is based on the expansion of mercury with temperature.
Then, when you want to measure the temperature of your cup of tea, you will put the thermometer within the cup. What is happening? The thermometer is first at much lower temperature than the tea. Then, heat is transferred from tea (body at high temperature) to the thermometer (body at law temperature) until both bodies attain the same temperature. At this point, heat transfer stops and the cup of tea and the thermometer are said to be in thermal equilibrium. Thermal equilibrium means the equality in temperature.

ZEROTH LAW OF THERMODYNAMICS

“If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other”

The zeroth law of thermodynamics may seem obvious, but this simple law cannot be concluded from other laws of thermodynamics, and it is the basis of temperature measurement. This law is called zeroth law, because it was formulated after the first and the second laws of thermodynamics and it should have preceded them. It was formulated by R.H. Fowler in 1931.



If
The thermometer and A are in thermal equilibrium
and
The thermometer and B are in thermal equilibrium
Therefore
A and B are in thermal equilibrium [$T_A = T_B$]

Figure.1.18. Zeroth law of thermodynamics.

I.12.1. Temperature scales

The definition of a temperature scale is an important step, since it allows us to use the same reference for our calculations.
The most common temperature scales used are:

1- Celsius scale
The references are: 0°C represents the ice point (freezing point at 1 atm)
100°C represents the steam point (boiling point at 1 atm)

Anders Celsius (11/27/1701 – 4/25/1744) was a Swedish astronomer. Celsius was born in Uppsala in Sweden. He was professor of astronomy at Uppsala University from 1730 to 1744.

Celsius founded the Uppsala Astronomical Observatory in 1741, and in 1742 he proposed the Celsius temperature scale in a paper to the Royal Swedish Academy of Sciences. His thermometer had 0 for the boiling point of water and 100 for the freezing point.

In 1744 he died of tuberculosis in Uppsala, and his scale was later reversed to its present form.

2- Fahrenheit scale
The references are: 0°C = 32°F
100°C = 212°F

Daniel Gabriel Fahrenheit (*Gabriel Daniel Fahrenheit*) (24 May 1686 in Danzig (Gdańsk) – 16 September 1736 in The Hague, Netherlands) was a German physicist and engineer who worked most of his life in the Netherlands. The °F Fahrenheit scale of temperature is named after him. This was used long before the Celsius scale.

Fahrenheit developed precise thermometers. He filled his first thermometers with alcohol before using mercury, which gave better results.

The coldest temperature attainable under laboratory conditions at that time, using a mixture of water, salt and ice, was defined by him as 0°F (approx. -17,8°C). The body temperature of a healthy horse was defined about 100°F (~37,8°C).

These scales are very useful, but they are problematic since they depend on the property of a substance (the boiling and the freezing point may change with pressure).

Therefore, it is very interesting to look for a temperature scale that is not substance dependent. This scale designed as thermodynamic temperature scale was introduced by Lord Kelvin and is called the Kelvin scale, the temperature in the Kelvin scale is designed by K (remember not °K). The degree symbol was officially dropped from Kelvin in 1967.
The lowest temperature on the Kelvin scale is absolute zero or 0 K.

In English units, the thermodynamic scale is the Rankine scale, the temperature is designed by R.

Relationship between thermodynamic scales	
Fahrenheit	$T(^oF) = 1.8 \times T(^oC) + 32$
Kelvin scale	$T(K) = T(^oC) + 273.15$
Rankine scale	$T(R) = T(^oF) + 459.67$ $T(R) = 1.8 \times T(K)$

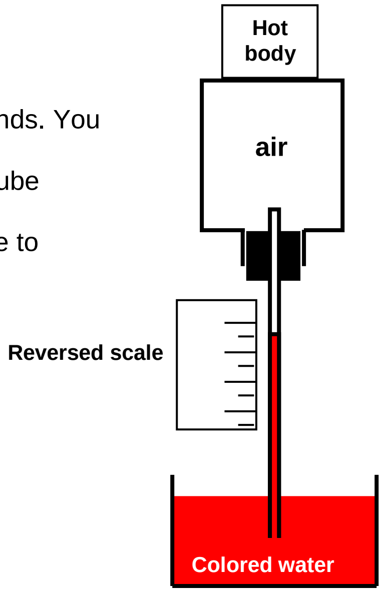
PROBLEM

A physical process is able to freeze a body to -470°F. Compute the temperature in rankine and in kelvin.

Additional information

How to build an air-thermometer

When you put the hot body on the upper reversed bottle, air expends. You Will notice some air bubbles escaping from the bottom.
Then, if you remove the hot body, colored water will rise into the tube to compensate for air.
By reading the elevation on a pre-calibrated scale, you will be able to determine the temperature of the body.



I.13. Pressure

Pressure is defined as a normal force exerted by a fluid per unit area. The term pressure is only used for liquids and gases, for solids we use the term normal stress.

$$P = \frac{F}{A} = \frac{ML}{L^2T^2} = \frac{M}{LT^2} = \frac{N}{m^2}$$

and

$$1 \ \frac{N}{m^2} = 1 \ Pa \text{ [pascal]}$$

As the pascal is a too small unit to represent practically engineering problems, we often use the kPa or MPa.

1 kPa = 1000 Pa
1 MPa = 1000 kPa = 10^6 Pa

Other pressure units are usually used in practice, especially:

1 bar = 10^5 Pa = 0.1 MPa = 100 kPa

and, the standard atmosphere:

1 atm = 101 325 Pa = 101.325 kPa = 1.01325 bar

I.13.1. Absolute, gage and vacuum pressures

Absolute pressure (P_{abs})	is the pressure relative to the absolute vacuum (absolute zero pressure).
Gage pressure (P_{gage})	is the difference between the measured pressure (absolute pressure) and the local atmospheric pressure. $P_{gage} = P_{abs} - P_{atm}$
Vacuum pressure (P_{vac})	is a pressure below atmospheric pressure. $P_{vac} = P_{atm} – P_{abs}$

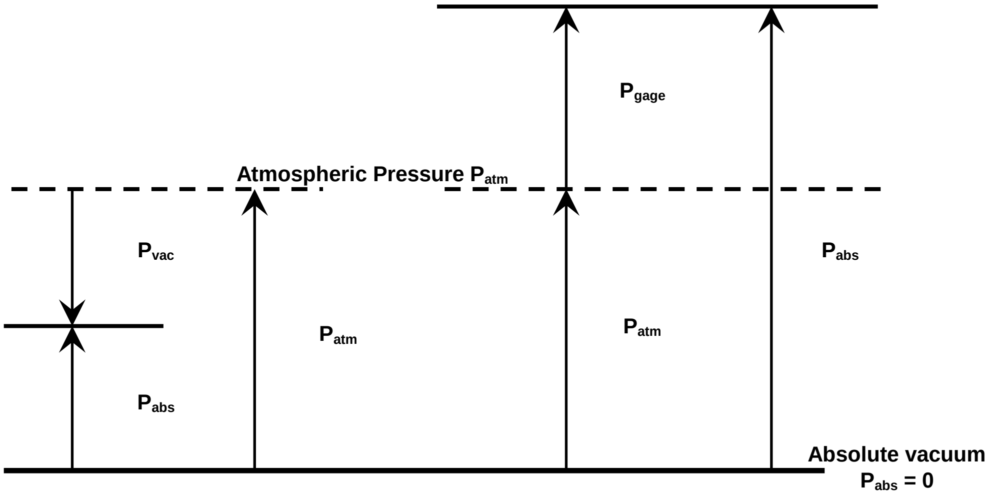


Figure.1.19. absolute, atmospheric and gauge pressures.

In thermodynamics, in order to have the same reference everywhere, we will always use absolute pressure and it will be denoted P

I.13.2. Variation of pressure with depth

Although pressure does not change in the horizontal direction, it does in the vertical direction in a gravity field.

The deeper you go, the higher amount of fluid is above you, and higher is the pressure.

To find the expression of pressure variation with depth, let us consider a rectangular fluid element of height Δz, length Δx in equilibrium.

If we apply, Newton's second law to this element, we will get:

$$\sum \vec{F} = m\ \vec{a} = 0$$

$P_2\ \Delta x\ \Delta y - P_1\ \Delta x\ \Delta y - \rho\ g\ \Delta x\ \Delta z\ \Delta y = 0$

Thus

$\Delta P = P_2 - P_1 = \rho\ g\ \Delta z = \gamma_s\ \Delta z$

γ_s is the specific weight of the fluid.

Hence, **pressure increases linearly with depth.**

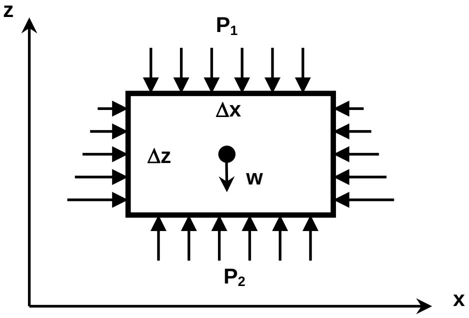
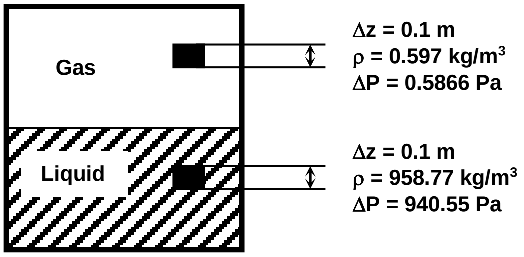


Figure.1.20. A rectangular fluid element for the determination of the pressure distribution

Note 1: for a given fluid, the vertical distance Δz is sometimes used as a measure of pressure, and it is called the pressure head.

Note 2: For gases the effect of variation in high is damped by the small density of the gas.



The increase in pressure in the liquid (in this case water) is 1603 times the increase in pressure in the vapor for the same Δz.

If we consider now the special case where one point is at the free surface (atmospheric pressure), therefore the pressure at a depth (h) from the free surface becomes:

$P = P_{atm} + \rho g h$ or $P_{gage} = \rho g h$

The above relations have been developed for a constant density. Now, imagine there is a significant variation of density with elevation (due to compressive effects).
The variation of pressure with elevation can be obtained by:

$$\frac{dP}{dz} = -\rho g$$

(-) sign because when z increases; P decreases.

Therefore

$$P = P_2 - P_1 = -\int_1^2 \rho g \, dz$$

In this case, the variation in density with elevation must be known to integrate and to compute ΔP.

I.13.3. Stevin principle

The pressure in a fluid at rest is independent of the shape or cross section of the container. It changes with depth, but remains constant in the horizontal direction.
As a consequence, the pressure is the same at all points on a horizontal plane in a given fluid whatever is the shape of the container [Figure.1.21] . This principle is due to the Dutch mathematician Simon Stevin [1548-1620].

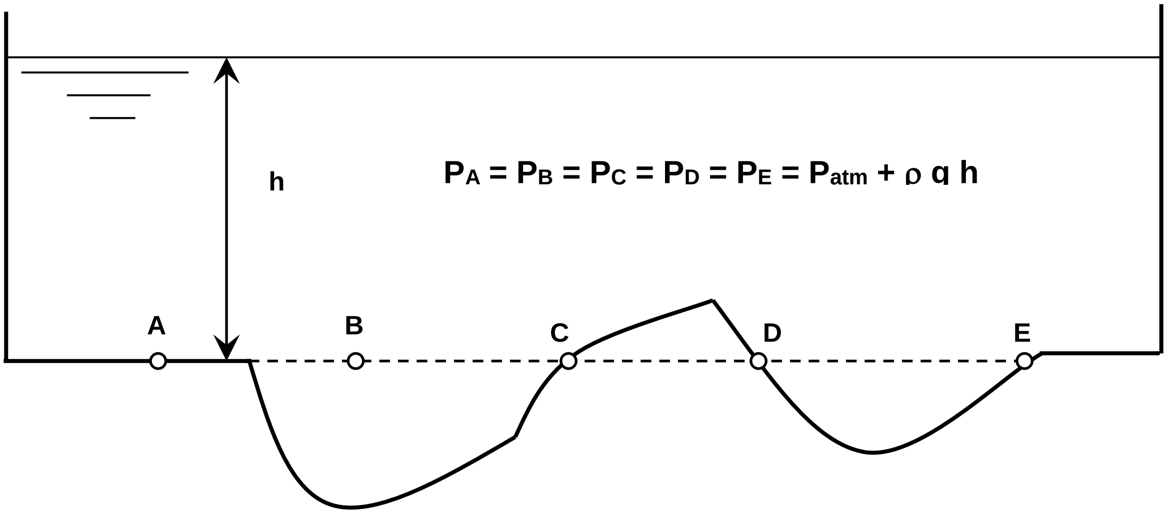


Figure.1.21. Stevin principle: the pressure is the same at all points on a horizontal plan [Considering the same fluid above all points].

If we consider know the case in the figure below:

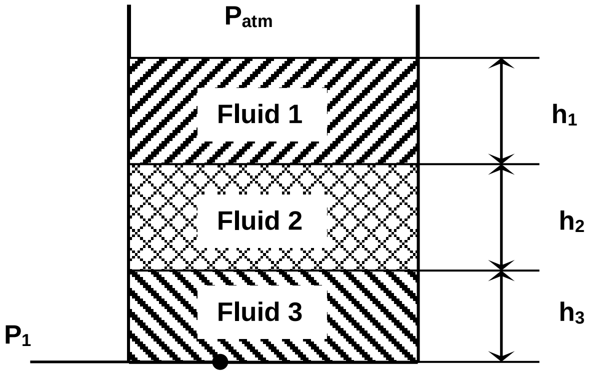


Figure.1.22. a tacked fluid layers.

$P_{atm} + \rho_1 g h_1 + \rho_2 g h_2 + \rho_3 g h_3 = P_1$

We can verify that in the particular case where: $\rho_1 = \rho_2 = \rho_3$

$P_{atm} + \rho g (h_1 + h_2 + h_3) = P_1$

$P_{atm} + \rho g h = P_1$

I.13.4. The manometer

When we look at the equation:

$$\Delta P = \rho \ g \ \Delta z$$

It can be rearranged in such a way that:

$$\Delta z = \frac{\Delta P}{\rho\ g}$$

As a consequence, elevation change can be used to measure the pressure. The device based on this principle is called a manometer.

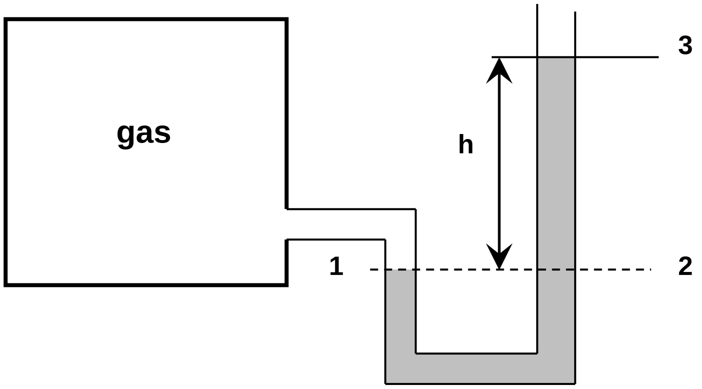


Figure.1.23. The principle of a manometer.

On the above figure, we have:

$P_2 = P_1$ [no horizontal change in pressure]
$P_2 - P_3 = \rho\ g\ h$ but;
$P_3 = 1$ atm therefore;
$P_2 = P_{atm} + \rho\ g\ h$

To determine the pressure using a manometer it is important to know:

1- the pressure change across a fluid column of height h is $\Delta P = \rho\ g\ h$
2- pressure increases downward in a given fluid and decreases upward (i.e, $P_{bottom} > P_{top}$)
3- two points at the same elevation in a continuous fluid at rest are the at the same pressure.

Manometers are also very useful to compute the pressure drop due to the presence of a device (inducing an hydraulic resistance) in the flow.

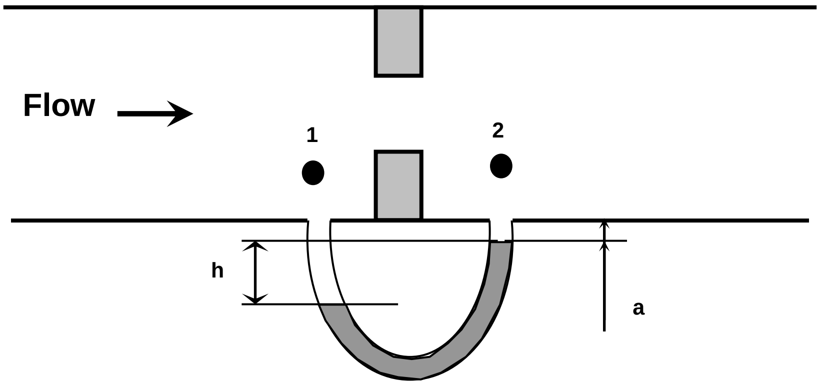


Figure.1.24. Measurement of the pressure drop caused by a device using a manometer.

The two legs of the manometer are connected to the wall of the device.
If the working fluid has a density ρ_1 and the density of the manometer fluid is ρ_2 and the differential fluid height is h, therefore:

$P_1 + \rho_1 g (a + h) - \rho_2 g h - \rho_1 g a = P_2$;

Therfore
$P_1 – P_2 = (\rho_2 - \rho_1) g h$

Note 1: the parameter (a) has no effect on the computation of the pressure.

Note 2: if the fluid considered is a gas ($\rho_2 >> \rho_1$)

The relation becomes:

$P_1 – P_2 \approx \rho_2 g h$

I.13.5. The barometer and atmospheric pressure

The atmospheric pressure is measured using a barometer. The first device invented to measure the atmospheric pressure was designed by Evangelista Torricelli [1608-1647].

Evangelista Torricelli (October 15, 1608 – October 25, 1647) was an Italian physicist and mathematician, best known for his invention of the barometer.
Torricelli's chief invention was the barometer, which arose from solving an important practical problem. Pumpmakers of the Grand Duke of Tuscany attempted to raise water to a height of 12 meters of more, but found that 10 meters was the limit to which it would rise in the suction pump. Torricelli thought to employ mercury, fourteen times as heavy as water. In 1643 he created a tube c. 1 meters long, sealed at the top end, filled it with mercury, and set it vertically into a basin of mercury. The column of mercury fell to about 70cm, leaving a Torricellian vacuum above. As we now know, the column's height fluctuated with changing atmospheric pressure; this was the first barometer. This discovery has perpetuated his fame, and the torr, a unit of pressure, was named in his honor.

Consider the following device below, the force balance for the dashed element within the tube gives:

$P_B \Delta s – P_A \Delta s = \rho \Delta s h g$

But P_B is equal to the atmospheric pressure and we can easily consider that $P_A << P_B$, therefore:

P_B = atmospheric pressure = $\rho g h$

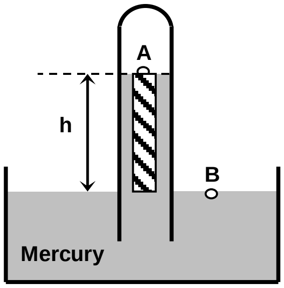


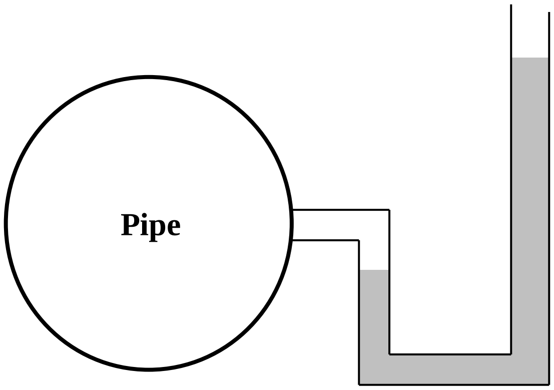
Figure.1.25. Schematic representation of the device used by Torricelli to measure the atmospheric pressure.

Usually, the atmospheric pressure is determined using a specific unit: standard atmosphere. It is defined as the pressure produced by a column of mercury of 760 mm height at 0°C and for g=9.807 m s^{-2}.

The standard atmospheric pressure is 760 mmHg at 0°C. The unit mmHg (millimeter of mercury) is also called [Torr] in honor to Torricelli.

PROBLEMS

1- The manometer is used to measure the pressure in a water pipe. Determine the water pressure if the manometer reading is 0.6 m. Mercury is 13.6 times heavier that water.



2- Calculate the force due to the pressure acting on the 1-m-diameter horizontal hatch of a submarine submerged 600 m below the surface.

Additional information

1- your popcorn is ready when its temperature reaches 180°C and its pressure 8 atm.

2- Since atmospheric pressure represents physically the weight of the air above a certain location, atmospheric pressure will obviously change with elevation.

Physical Properties of Standard Atmosphere in SI Units

Altitude (meters)	**Temperature (degrees K)**	**Pressure (Pa)**	**Density (kg/m^3)**	**Viscosity ($N\text{-}s/m^2$)**
-5,000	320.7	1.778E+5	1.931	1.942E-5
-4,000	314.2	1.596E+5	1.770	1.912E-5
-3,000	307.7	1.430E+5	1.619	1.882E-5
-2,000	301.2	1.278E+5	1.478	1.852E-5
-1,000	294.7	1.139E+5	1.347	1.821E-5
0	288.2	1.013E+5	1.225	1.789E-5
1,000	281.7	8.988E+4	1.112	1.758E-5
2,000	275.2	7.950E+4	1.007	1.726E-5
3,000	268.7	7.012E+4	9.093E-1	1.694E-5
4,000	262.2	6.166E+4	8.194E-1	1.661E-5
5,000	255.7	5.405E+4	7.364E-1	1.628E-5
6,000	249.2	4.722E+4	6.601E-1	1.595E-5
7,000	242.7	4.111E+4	5.900E-1	1.561E-5
8,000	236.2	3.565E+4	5.258E-1	1.527E-5
9,000	229.7	3.080E+4	4.671E-1	1.493E-5
10,000	223.3	2.650E+4	4.135E-1	1.458E-5
15,000	216.7	1.211E+4	1.948E-1	1.422E-5
20,000	216.7	5.529E+3	8.891E-2	1.422E-5
30,000	226.5	1.197E+3	1.841E-2	1.475E-5
40,000	250.4	2.871E+2	3.996E-3	1.601E-5
50,000	270.7	7.978E+1	1.027E-3	1.704E-5
60,000	255.8	2.246E+1	3.059E-4	1.629E-5
70,000	219.7	5.520	8.754E-5	1.438E-5
80,000	180.7	1.037	1.999E-5	1.216E-5
90,000	180.7	1.644E-1	3.170E-6	1.216E-5

CHAPTER II

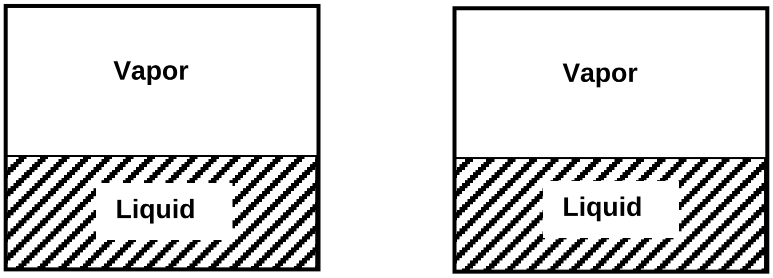
Properties of Pure Substances

CHAPTER II

Properties of Pure Substances

II.1. What is a pure substance?

A pure substance is defined as a substance that has a fixed chemical composition (example: water; CO_2; nitrogen; …).
A mixture of several gases can be considered as a pure substance, if it has a uniform chemical composition.



Water
(pure substance)

Air
(not a pure substance because the composition of liquid air is different from the composition of air vapor)

Figure.2.1. Liquid vapor mixture and the definition of a pure substance.

If we add ice to a mixture of liquid water and water vapor, as ice is also considered as pure substance, the mixture will be considered, therefore, as a pure substance.

As noticed above, a substance can exist under several forms: solid; liquid or gas. Furthermore, each phase may not be unique. Example: there are two possible arrangements for solid carbon: graphite or diamond.

The difference between the phases is highly related to intermolecular bonds:

- Strong intermolecular bonds → solid
- Intermediate intermolecular bonds → liquid
- Weak intermolecular bonds → gas

II.2. Phase-change processes of pure substances

In several applications two phases coexist in the same device (example: in refrigerators; the refrigerant turns from liquid to vapor in the freezer).

In this part, we will focus our attention on the coexistence of liquid and vapor phases. Why? Because remember that in thermodynamics, “dynamis” means “power”, and almost all power plants use the conversion of a liquid to a gas to generate power.

Imagine you put some water at room temperature (20°C=293.15 K) and normal atmospheric pressure (1 atm) in a piston-cylinder device.

The water is in liquid phase, and it is called **compressed liquid** or **subcooled liquid** (liquid is not ready to vaporize yet) (Fig.II.3. Point 1)

Now, if we add some heat to the water, its temperature will increase; let us say until 50°C (325.15 K). Due to the increase in temperature, the specific volume v (volume/mass) will increase (the same mass of water will occupy more volume). As a consequence, the piston will move slightly upward (as a result, the pressure will remain constant)

Now, if we continue adding some heat to the water, the temperature will increase until 100°C (373.15 K). At this point, any extra addition of heat will vaporize some water. This specific point where water starts to vaporize is called **saturated liquid** (Fig.II.3. Point 2).

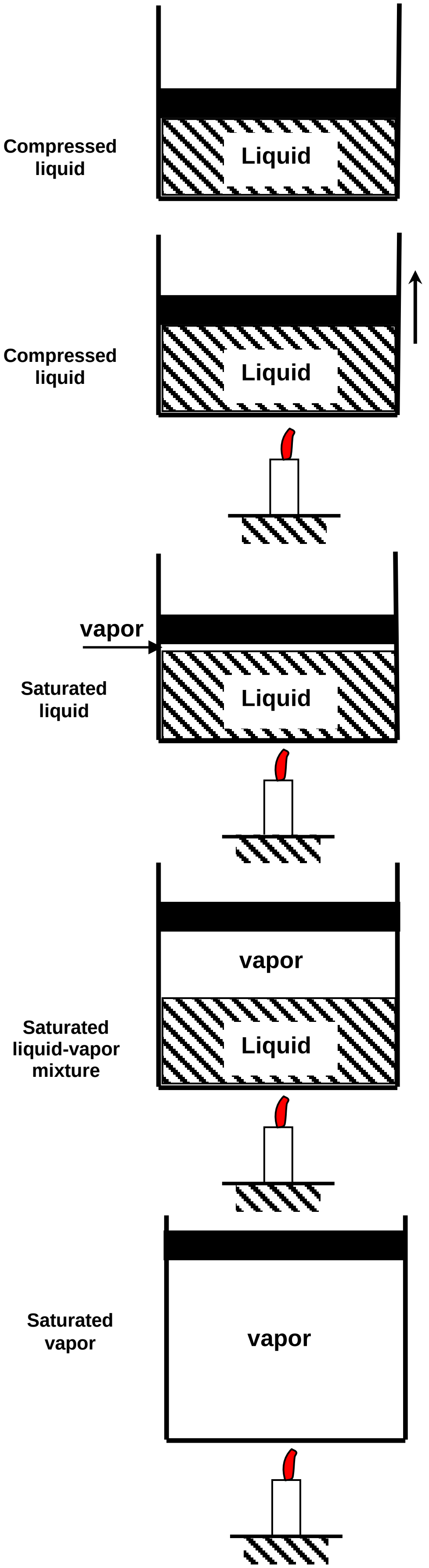
If we continue to add some heat to the water, more and more vapor will be created, while the temperature and the pressure remain constant (T=100°C=373.15 K and P=1 atm), the only property that changes is the specific volume. These conditions will remain the same until the last drop of liquid is vaporized. At this point, the entire cylinder is filled with vapor at 100°C (373.15 K). This state is called **saturated vapor** (Fig.II.3. Point 4).

The state between saturated liquid (only liquid) and saturated vapor (only vapor) where two phases exist is called **saturated liquid-vapor mixture** (Fig.II.3. Point 3).

After the saturated vapor phase, any addition of heat will increase the temperature of the vapor, this state is called **superheated vapor** (Fig.II.3. Point 5).

The difference between saturated vapor and superheated vapor is that for saturated vapor, if we extract a relatively small amount of heat from the vapor, it will start to condense. Whereas, for superheated vapor, the state will remain only vapor.

Figure.2.2. Different states for a pure substance.



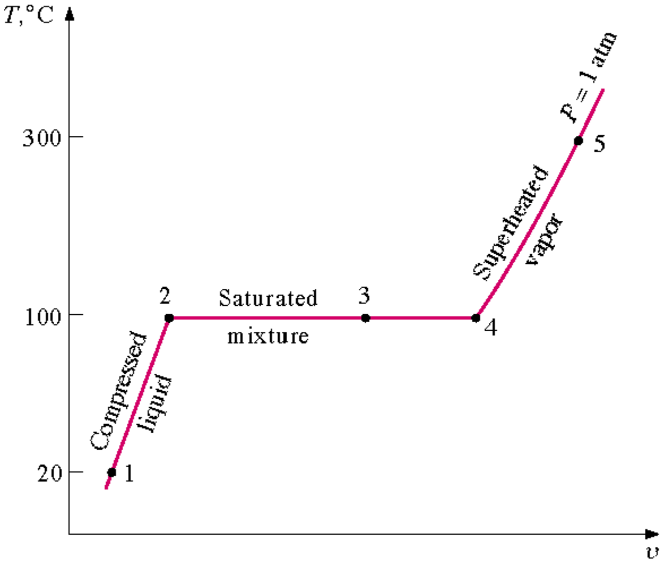


Figure.2.3. Phase change for a pure substance.

II.3. Saturation temperature and saturation pressure

Remember that during a phase change, pressure and temperature are not independent intensive properties. As a consequence, the temperature at which water starts boiling depends on the pressure.
At a given pressure, the temperature at which a pure substance changes phase is called the **saturation temperature (T_{sat})**.
Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the **saturation pressure (P_{sat})**.

II.4. Latent heat

The energy absorbed during vaporization is called latent heat of vaporization and it is equivalent to the energy released during condensation.

Example: at 1 atm, the latent heat of vaporization of water is 2257.1 kJ/kg.

Note: the latent energy is a function of the temperature and the pressure at which the phase change occurs.

II.5. Relation between the saturation temperature and the saturation pressure

In all pure substances, the relation between the temperature of saturation and the pressure of saturation can be plotted under the following form:

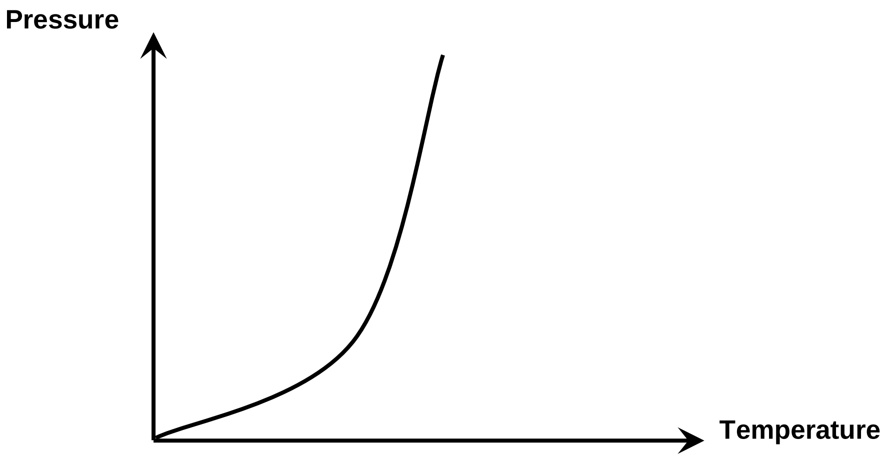


Figure.2.4. Saturated pressure and saturated temperature relation for a pure substance.

One of the consequences of the dependence of the saturation temperature upon the saturation pressure is that we are able to control the boiling temperature of a pure substance by changing its pressure.

II.5.1. Effect of elevation

As the atmospheric pressure changes with elevation, the saturation temperature also changes. As a consequence, water boils at a lower temperature with elevation. A simple law states that for each 1000 m of elevation, the saturation temperature decreases by 3°C. Therefore, it takes longer to cook at higher altitudes than at sea level.

II.6. Property diagrams for phase-change processes

II.6.1. T-v Diagram

If we increase the pressure of water in the piston-cylinder device, the process from compressed liquid to superheated vapor will follow a path that looks like the process for P=1 atm, the only difference is that the width of the mixture region will be shorter.

Then, at a certain pressure, the mixture region will be represented only by one point. This point is called the **critical point**. It is defined as the point at which the saturated liquid and saturated vapor states are identical.
At the critical point, the properties of a substance are called critical properties (critical temperature (T_{cr}), critical pressure (P_{cr}) and critical specific volume (v_{cr})).

Example

Water $P_{cr} = 22.09$ MPa
$T_{cr} = 374.148$°C = 647.298 K
$v_{cr} = 0.003155\ m^3/kg$

Air $P_{cr} = 3.77$ MPa
$T_{cr} = 132.5$°C = 405.65 K
$v_{cr} = 0.0883\ m^3/kg$

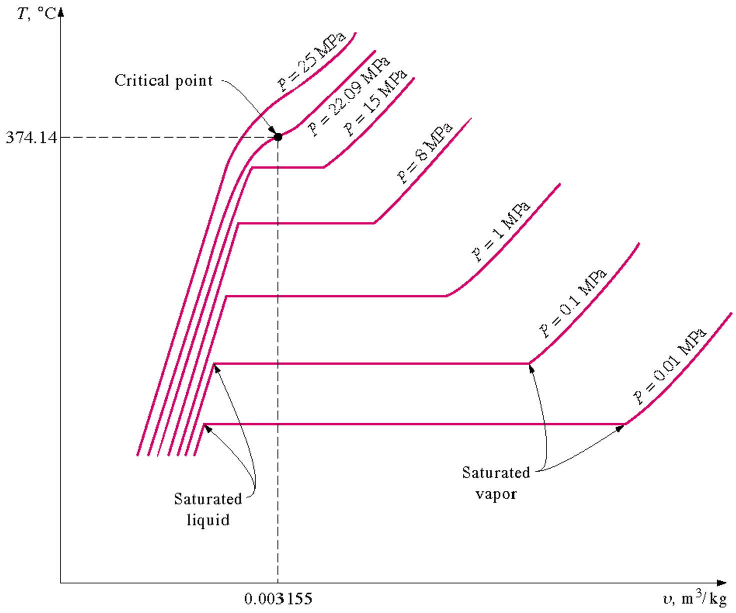


Figure.2.5. T-v diagram.

Above the critical point, there is only one phase that will resemble to a vapor, but we are enable to say when the change has occurred.

II.6.1.1 Saturated liquid and saturated vapor lines

If we connect all the points representing saturated liquid we will obtain the **saturated liquid line**. If we connect all the points representing saturated vapor we will obtain the **saturated vapor line**.

The intersection of the two lines is the critical point.

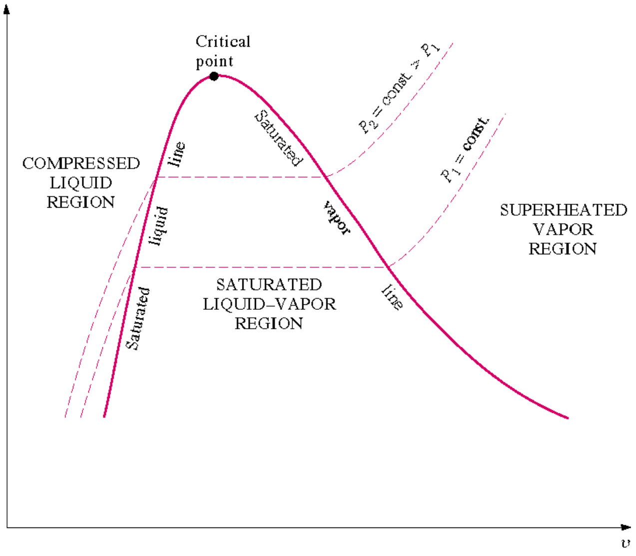


Figure.2.6. T-v diagram and saturation lines.

II.6.2. P-v Diagram

Let us now consider the pressure-cylinder device but with some weights above the piston. If we remove the weights one by one to decrease the pressure, and we allow a heat transfer to obtain an isothermal process, we will obtain one of the curves of the P-v diagram.

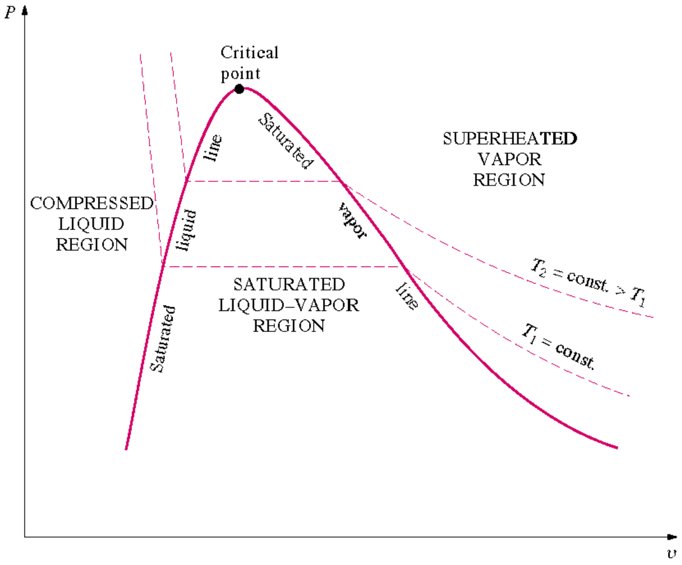


Figure.2.7. P-v diagram.

The P-v diagram can be extended to include the solid phase, the solid-liquid and the solid-vapor saturation regions.
Some substances, as water, expand when they freeze, and the rest (the majority) contracts during freezing process, we have then two configurations for the P-v diagram with solid phase.

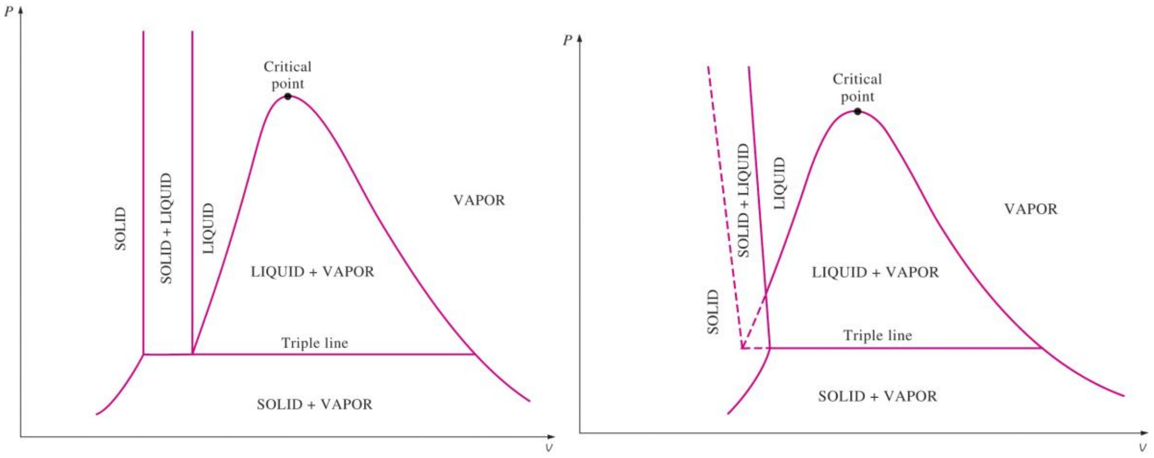


Figure.2.8. P-v diagram for a substance that contracts during freezing (left) and for a substance that expends during freezing (right).

II.6.2.1. Triple point

Until now, we have defined the equilibrium between two phases. However, under certain conditions, water can exist at the same time as ice (solid), liquid and vapor. Such conditions define the so-called **triple point**.
On a P-T diagram, these conditions are represented by a point.

<u>Example</u>

Water T = 0.01°C = 273.16 K and P = 0.6113 kPa

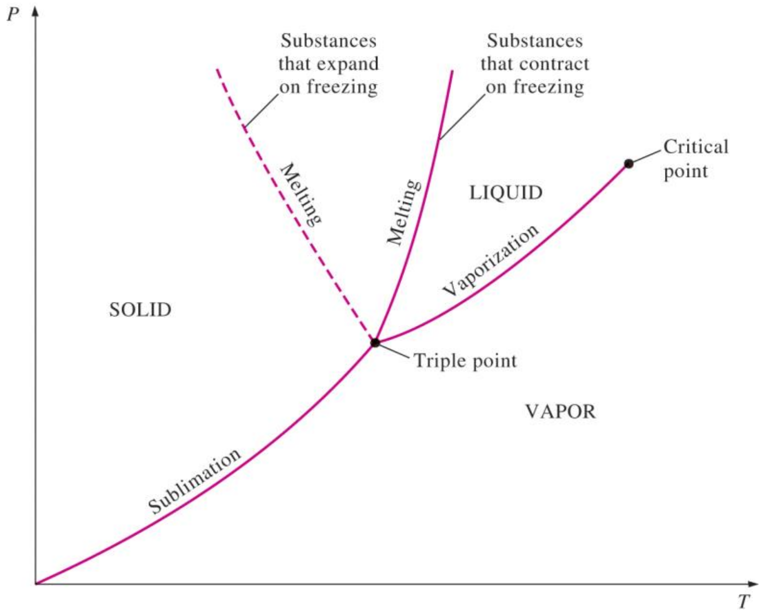


Figure.2.9. P-T diagram and the triple point.

II.6.3. P-T Diagram

The P-T diagram is often called the phase diagram since all three phases are separated by three lines.

Solid → vapor	sublimation
Solid → liquid	melting
Liquid → vapor	vaporization

II.6.4. P-T-v Diagram

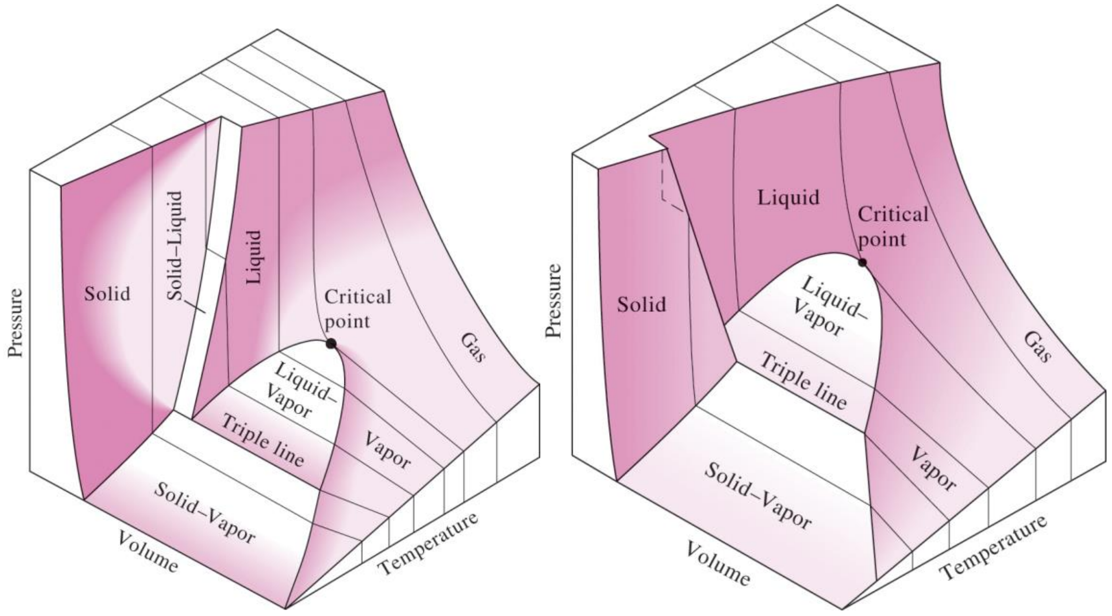


Figure.2.10. P-T-v diagram for a substance that contracts during freezing (left) and for a substance that expends during freezing (right).

II.7. Property Tables

In addition to temperature, pressure, and volume data, Tables A-4 through A-8 contain the data for the specific internal energy *u* the specific enthalpy *h* and the specific entropy *s*. The enthalpy is a convenient grouping of the internal energy, pressure, and volume (more details will be given when the 1st law will be introduced) and is given by

$$H = U + PV$$

The enthalpy per unit mass is

$$h = u + Pv$$

We will find that the enthalpy *h* is quite useful in calculating the energy of mass streams flowing into and out of control volumes. The enthalpy is also useful in the energy balance during a constant pressure process for a substance contained in a closed piston-cylinder device. The enthalpy has units of energy per unit mass, kJ/kg. The entropy *s* is a property defined by the AMAZING!!! second law of thermodynamics and is related to the heat transfer to a system divided by the system temperature; thus, the entropy has a unit of energy divided by temperature. The concept of entropy is explained in Chapters 6 and 7.

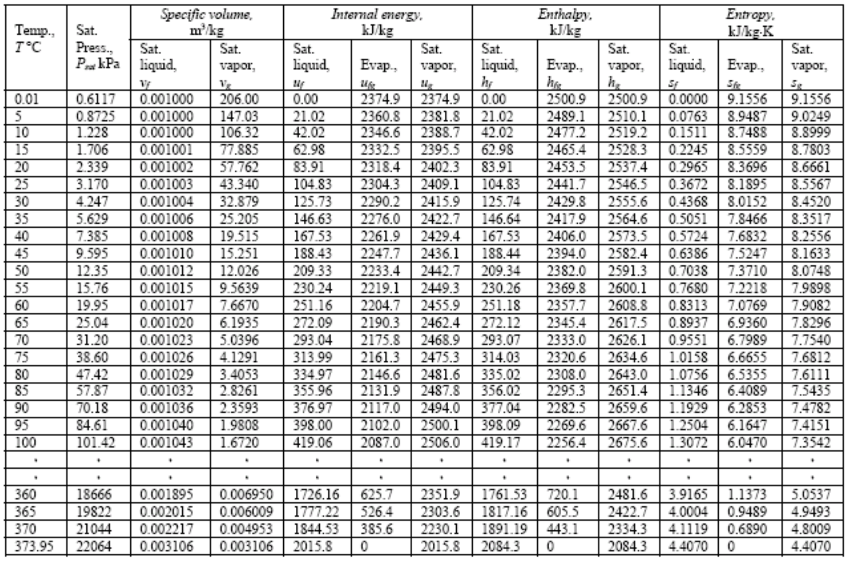
II.7.1. Saturated Water Tables

Since temperature and pressure are dependent properties during a phase change, two tables are given for the saturation region. Table A-4 has temperature as the independent property; Table A-5 has pressure as the independent property. These two tables contain the same information and often only one table is given.

For the complete Table A-4, the last entry is the critical point at 373.95 °C.

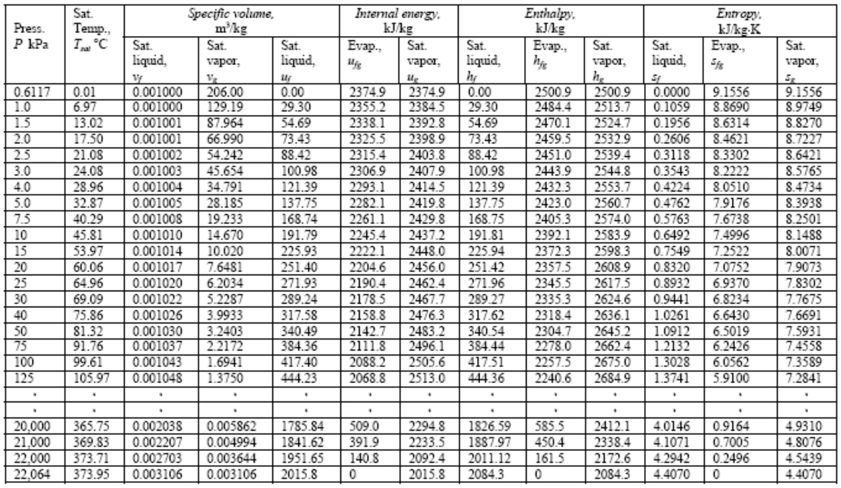
TABLE A-4

Saturated water-Temperature table



Temp., T °C	Sat. Press., P_{sat} kPa	*Specific volume,* m³/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg·K		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.02	2360.8	2381.8	21.02	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.228	0.001000	106.32	42.02	2346.6	2388.7	42.02	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.706	0.001001	77.885	62.98	2332.5	2395.5	62.98	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.339	0.001002	57.762	83.91	2318.4	2402.3	83.91	2453.5	2537.4	0.2965	8.3696	8.6661
25	3.170	0.001003	43.340	104.83	2304.3	2409.1	104.83	2441.7	2546.5	0.3672	8.1895	8.5567
30	4.247	0.001004	32.879	125.73	2290.2	2415.9	125.74	2429.8	2555.6	0.4368	8.0152	8.4520
35	5.629	0.001006	25.205	146.63	2276.0	2422.7	146.64	2417.9	2564.6	0.5051	7.8466	8.3517
40	7.385	0.001008	19.515	167.53	2261.9	2429.4	167.53	2406.0	2573.5	0.5724	7.6832	8.2556
45	9.595	0.001010	15.251	188.43	2247.7	2436.1	188.44	2394.0	2582.4	0.6386	7.5247	8.1633
50	12.35	0.001012	12.026	209.33	2233.4	2442.7	209.34	2382.0	2591.3	0.7038	7.3710	8.0748
55	15.76	0.001015	9.5639	230.24	2219.1	2449.3	230.26	2369.8	2600.1	0.7680	7.2218	7.9898
60	19.95	0.001017	7.6670	251.16	2204.7	2455.9	251.18	2357.7	2608.8	0.8313	7.0769	7.9082
65	25.04	0.001020	6.1935	272.09	2190.3	2462.4	272.12	2345.4	2617.5	0.8937	6.9360	7.8296
70	31.20	0.001023	5.0396	293.04	2175.8	2468.9	293.07	2333.0	2626.1	0.9551	6.7989	7.7540
75	38.60	0.001026	4.1291	313.99	2161.3	2475.3	314.03	2320.6	2634.6	1.0158	6.6655	7.6812
80	47.42	0.001029	3.4053	334.97	2146.6	2481.6	335.02	2308.0	2643.0	1.0756	6.5355	7.6111
85	57.87	0.001032	2.8261	355.96	2131.9	2487.8	356.02	2295.3	2651.4	1.1346	6.4089	7.5435
90	70.18	0.001036	2.3593	376.97	2117.0	2494.0	377.04	2282.5	2659.6	1.1929	6.2853	7.4782
95	84.61	0.001040	1.9808	398.00	2102.0	2500.1	398.09	2269.6	2667.6	1.2504	6.1647	7.4151
100	101.42	0.001043	1.6720	419.06	2087.0	2506.0	419.17	2256.4	2675.6	1.3072	6.0470	7.3542
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
360	18666	0.001895	0.006950	1726.16	625.7	2351.9	1761.53	720.1	2481.6	3.9165	1.1373	5.0537
365	19822	0.002015	0.006009	1777.22	526.4	2303.6	1817.16	605.5	2422.7	4.0004	0.9489	4.9493
370	21044	0.002217	0.004953	1844.53	385.6	2230.1	1891.19	443.1	2334.3	4.1119	0.6890	4.8009
373.95	22064	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

TABLE A-5
Saturated water-Pressure table



Press. P kPa	Sat. Temp., T_{sat} °C	*Specific volume,* m³/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg·K		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.6117	0.01	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
1.0	6.97	0.001000	129.19	29.30	2355.2	2384.5	29.30	2484.4	2513.7	0.1059	8.8690	8.9749
1.5	13.02	0.001001	87.964	54.69	2338.1	2392.8	54.69	2470.1	2524.7	0.1956	8.6314	8.8270
2.0	17.50	0.001001	66.990	73.43	2325.5	2398.9	73.43	2459.5	2532.9	0.2606	8.4621	8.7227
2.5	21.08	0.001002	54.242	88.42	2315.4	2403.8	88.42	2451.0	2539.4	0.3118	8.3302	8.6421
3.0	24.08	0.001003	45.654	100.98	2306.9	2407.9	100.98	2443.9	2544.8	0.3543	8.2222	8.5765
4.0	28.96	0.001004	34.791	121.39	2293.1	2414.5	121.39	2432.3	2553.7	0.4224	8.0510	8.4734
5.0	32.87	0.001005	28.185	137.75	2282.1	2419.8	137.75	2423.0	2560.7	0.4762	7.9176	8.3938
7.5	40.29	0.001008	19.233	168.74	2261.1	2429.8	168.75	2405.3	2574.0	0.5763	7.6738	8.2501
10	45.81	0.001010	14.670	191.79	2245.4	2437.2	191.81	2392.1	2583.9	0.6492	7.4996	8.1488
15	53.97	0.001014	10.020	225.93	2222.1	2448.0	225.94	2372.3	2598.3	0.7549	7.2522	8.0071
20	60.06	0.001017	7.6481	251.40	2204.6	2456.0	251.42	2357.5	2608.9	0.8320	7.0752	7.9073
25	64.96	0.001020	6.2034	271.93	2190.4	2462.4	271.96	2345.5	2617.5	0.8932	6.9370	7.8302
30	69.09	0.001022	5.2287	289.24	2178.5	2467.7	289.27	2335.3	2624.6	0.9441	6.8234	7.7675
40	75.86	0.001026	3.9933	317.58	2158.8	2476.3	317.62	2318.4	2636.1	1.0261	6.6430	7.6691
50	81.32	0.001030	3.2403	340.49	2142.7	2483.2	340.54	2304.7	2645.2	1.0912	6.5019	7.5931
75	91.76	0.001037	2.2172	384.36	2111.8	2496.1	384.44	2278.0	2662.4	1.2132	6.2426	7.4558
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.51	2257.5	2675.0	1.3028	6.0562	7.3589
125	105.97	0.001048	1.3750	444.23	2068.8	2513.0	444.36	2240.6	2684.9	1.3741	5.9100	7.2841
·	·	·	·	·	·	·	·	·	·	·	·	·
·	·	·	·	·	·	·	·	·	·	·	·	·
20,000	365.75	0.002038	0.005862	1785.84	509.0	2294.8	1826.59	585.5	2412.1	4.0146	0.9164	4.9310
21,000	369.83	0.002207	0.004994	1841.62	391.9	2233.5	1887.97	450.4	2338.4	4.1071	0.7005	4.8076
22,000	373.71	0.002703	0.003644	1951.65	140.8	2092.4	2011.12	161.5	2172.6	4.2942	0.2496	4.5439
22,064	373.95	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

For the complete Table A-5, the last entry is the critical point at 22.064 MPa.

Saturation pressure is the pressure at which the liquid and vapor phases are in equilibrium at a given temperature.

Saturation temperature is the temperature at which the liquid and vapor phases are in equilibrium at a given pressure.

The subscript **fg** used in Tables A-4 and A-5 refers to the difference between the saturated vapor value and the saturated liquid value. That is,

$$u_{fg} = u_g - u_f$$
$$h_{fg} = h_g - h_f$$
$$s_{fg} = s_g - s_f$$

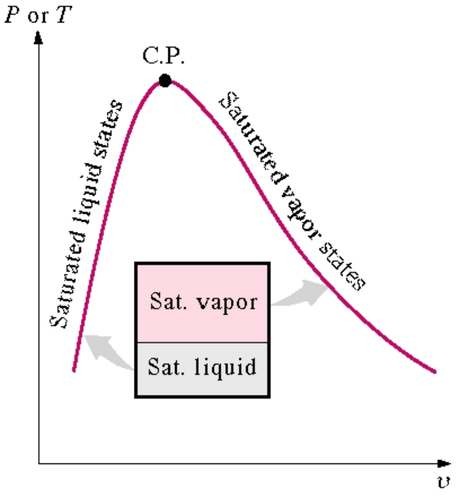
The quantity $\boldsymbol{h_{fg}}$ is called the enthalpy of vaporization (or latent heat of vaporization). It represents the amount of energy needed to vaporize a unit of mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increases, and becomes zero at the critical point.

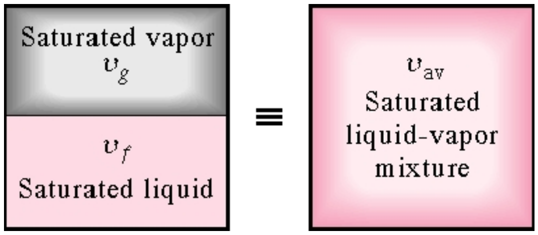
II.7.2. Quality and Saturated Liquid-Vapor Mixture

Now, let's review the constant pressure heat addition process for water shown in Figure 2-3 (page 26). Since state 3 is a mixture of saturated liquid and saturated vapor, how do we locate it on the T-v diagram? To establish the location of state 3, a new parameter called the quality *x* is defined as:

$$x = \frac{mass\ of\ \ saturated\ \ vapor}{total\ \ mass} = \frac{m_g}{m_f + m_g}$$

The quality is zero for the saturated liquid and one for the saturated vapor $(0 \le x \le 1)$. The average specific volume at any state 3 is given in terms of the quality as follows: Consider a mixture of saturated liquid and saturated vapor. The liquid has a mass m_f and occupies a volume V_f. The vapor has a mass m_g and occupies a volume V_g.





We note

$$V = V_f + V_g$$

$$m = m_f + m_g$$

$$V = mv, \quad V_f = m_f v_f, \quad V_g = m_g v_g$$

$$mv = m_f v_f + m_g v_g$$

$$v = \frac{m_f v_f}{m} + \frac{m_g v_g}{m}$$

Using the definition of the quality x

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g}$$

Then

$$\frac{m_f}{m} = \frac{m - m_g}{m} = 1 - x$$

Note, quantity 1- *x* is often given the name: moisture. The specific volume of the saturated mixture becomes

$$v = (1 - x)\ v_f + x\ v_g$$

The form that we use most often is

$$v = v_f + x\ (v_g - v_f)$$

It is noted that the value of any extensive property per unit of mass in the saturation region is calculated from an equation having a form similar to that of the above equation. Let's *Y* be any extensive property and let's *y* be the corresponding intensive property, *Y/m*, then

$$y = \frac{y}{m} = y_f + x(y_g - y_f)$$
$$y = y_f + x\ y_{fg}$$
$$where\ y_{fg} = y_g - y_f$$

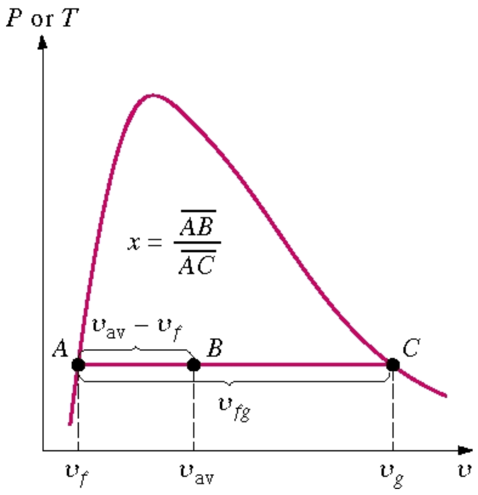
The term y_{fg} is the difference between the saturated vapor and the saturated liquid values of the property *y*; *y* may be replaced by any of the variables *v, u, h*, or *s*.

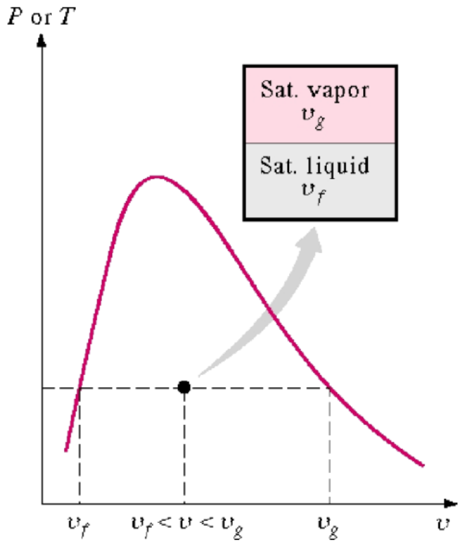
We often use the above equation to determine the quality *x* of a saturated liquid-vapor state.

The following application is called the Lever Rule:

$$x = \frac{y - y_f}{y_{fg}}$$

The Lever Rule is illustrated in the following figures.





II.7.3. Superheated Water Table

A substance is said to be superheated if the given temperature is greater than the saturation temperature at given pressure.

State 5 in Figure 2-3 (page 26) is a superheated state.

In the superheated water Table A-6, T and P are the independent properties. The value of temperature at the right of the pressure is the saturation temperature for the pressure. The first entry in the table is the saturated vapor state at the corresponding pressure.

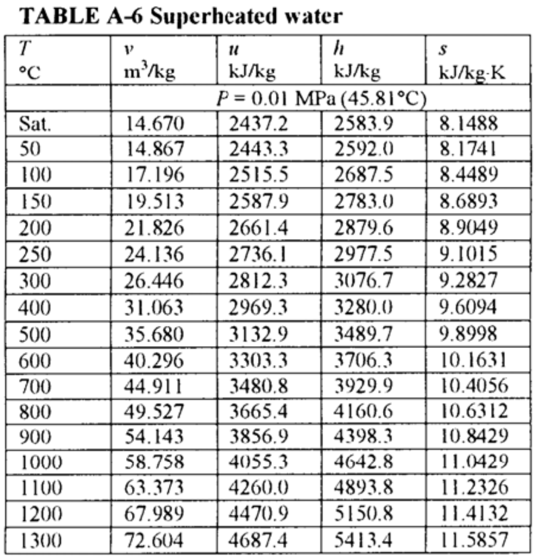
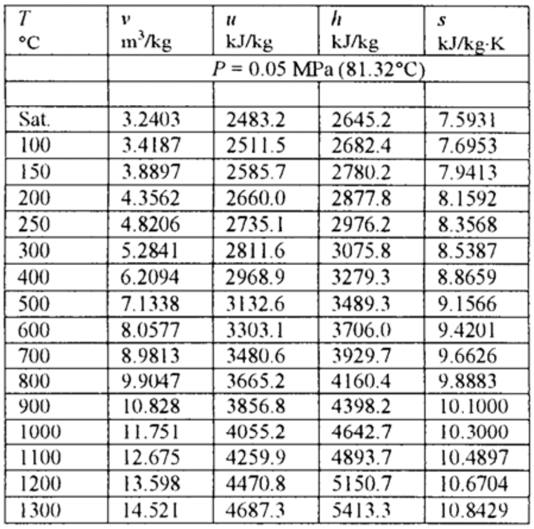


TABLE A-6 Superheated water

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.01 MPa (45.81°C)			
Sat.	14.670	2437.2	2583.9	8.1488
50	14.867	2443.3	2592.0	8.1741
100	17.196	2515.5	2687.5	8.4489
150	19.513	2587.9	2783.0	8.6893
200	21.826	2661.4	2879.6	8.9049
250	24.136	2736.1	2977.5	9.1015
300	26.446	2812.3	3076.7	9.2827
400	31.063	2969.3	3280.0	9.6094
500	35.680	3132.9	3489.7	9.8998
600	40.296	3303.3	3706.3	10.1631
700	44.911	3480.8	3929.9	10.4056
800	49.527	3665.4	4160.6	10.6312
900	54.143	3856.9	4398.3	10.8429
1000	58.758	4055.3	4642.8	11.0429
1100	63.373	4260.0	4893.8	11.2326
1200	67.989	4470.9	5150.8	11.4132
1300	72.604	4687.4	5413.4	11.5857



T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.05 MPa (81.32°C)			
Sat.	3.2403	2483.2	2645.2	7.5931
100	3.4187	2511.5	2682.4	7.6953
150	3.8897	2585.7	2780.2	7.9413
200	4.3562	2660.0	2877.8	8.1592
250	4.8206	2735.1	2976.2	8.3568
300	5.2841	2811.6	3075.8	8.5387
400	6.2094	2968.9	3279.3	8.8659
500	7.1338	3132.6	3489.3	9.1566
600	8.0577	3303.1	3706.0	9.4201
700	8.9813	3480.6	3929.7	9.6626
800	9.9047	3665.2	4160.4	9.8883
900	10.828	3856.8	4398.2	10.1000
1000	11.751	4055.2	4642.7	10.3000
1100	12.675	4259.9	4893.7	10.4897
1200	13.598	4470.8	5150.7	10.6704
1300	14.521	4687.3	5413.3	10.8429

II.7.4. Compressed Liquid Water Table

A substance is said to be a compressed liquid when the pressure is greater than the saturation pressure for a given temperature.

It is now noted that state 1 in Figure 2-3 (page 26) is called a compressed liquid state because the saturation pressure for the temperature T_1 is less than P_1.

Data for water compressed liquid states are found in the compressed liquid tables, Table A-7. Table A-7 is arranged like Table A-6, except the saturation states are the saturated liquid states. Note that the data in Table A-7 begins at 5 MPa or 50 times atmospheric pressure.

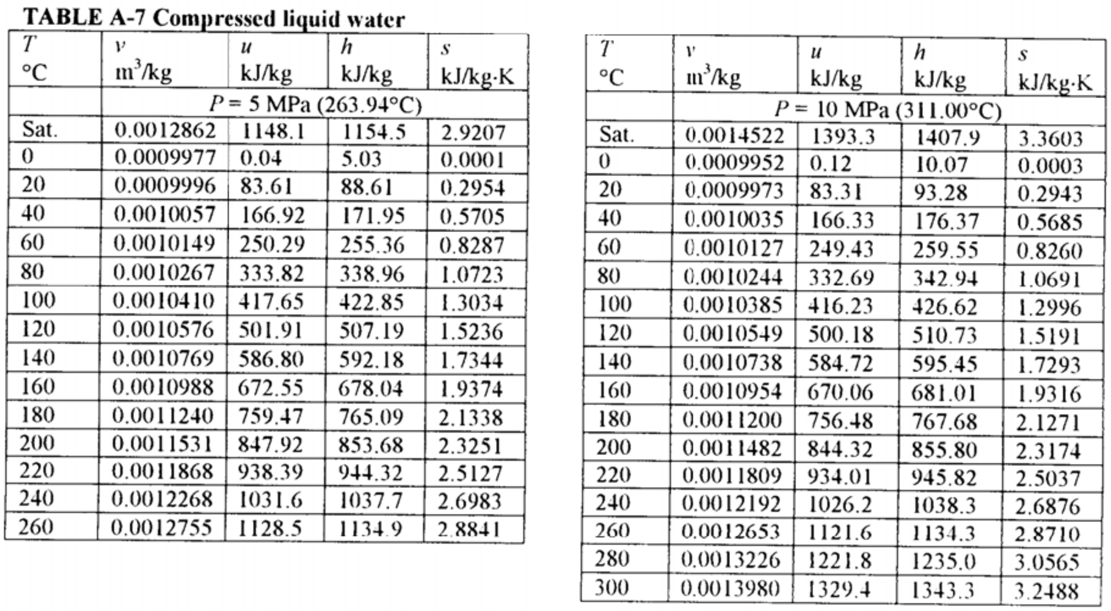


TABLE A-7 Compressed liquid water

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 5 MPa (263.94°C)			
Sat.	0.0012862	1148.1	1154.5	2.9207
0	0.0009977	0.04	5.03	0.0001
20	0.0009996	83.61	88.61	0.2954
40	0.0010057	166.92	171.95	0.5705
60	0.0010149	250.29	255.36	0.8287
80	0.0010267	333.82	338.96	1.0723
100	0.0010410	417.65	422.85	1.3034
120	0.0010576	501.91	507.19	1.5236
140	0.0010769	586.80	592.18	1.7344
160	0.0010988	672.55	678.04	1.9374
180	0.0011240	759.47	765.09	2.1338
200	0.0011531	847.92	853.68	2.3251
220	0.0011868	938.39	944.32	2.5127
240	0.0012268	1031.6	1037.7	2.6983
260	0.0012755	1128.5	1134.9	2.8841

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 10 MPa (311.00°C)			
Sat.	0.0014522	1393.3	1407.9	3.3603
0	0.0009952	0.12	10.07	0.0003
20	0.0009973	83.31	93.28	0.2943
40	0.0010035	166.33	176.37	0.5685
60	0.0010127	249.43	259.55	0.8260
80	0.0010244	332.69	342.94	1.0691
100	0.0010385	416.23	426.62	1.2996
120	0.0010549	500.18	510.73	1.5191
140	0.0010738	584.72	595.45	1.7293
160	0.0010954	670.06	681.01	1.9316
180	0.0011200	756.48	767.68	2.1271
200	0.0011482	844.32	855.80	2.3174
220	0.0011809	934.01	945.82	2.5037
240	0.0012192	1026.2	1038.3	2.6876
260	0.0012653	1121.6	1134.3	2.8710
280	0.0013226	1221.8	1235.0	3.0565
300	0.0013980	1329.4	1343.3	3.2488

At pressures below 5 MPa for water, the data are approximately equal to the saturated liquid data at the same **TEMPERATURE**. We approximate intensive parameter *y*, that is *v, u, h*, and *s* data as

$$y \cong y_{f\,@T}$$

The enthalpy is more sensitive to variations in pressure; therefore, at high pressures the enthalpy can be approximated by

$$h \cong h_{f\,@T} + v_f\left(P - P_{sat}\right)$$

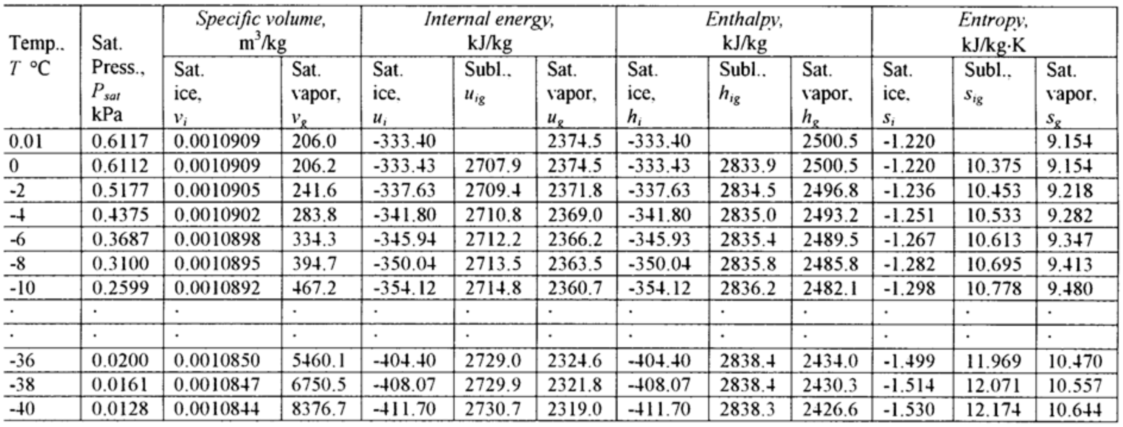
For our work, the compressed liquid enthalpy may be approximated by

$$h \cong h_{f\,@T}$$

II.7.5. Saturated Ice-Water Vapor Table

When the temperature of a substance is below the triple point temperature, the saturated solid and liquid phases exist in equilibrium. Here, we define the quality as the ratio of the mass in vapor phase to the total mass (solid and vapor in the saturated solid-vapor mixture). The process of changing directly from the solid phase to the vapor phase is called sublimation. Data for saturated ice and water vapor are given in Table A-8. In Table A-8, the term **Subl.** refers to the difference between the saturated vapor value and the saturated solid value.

TABLE A-8
Saturated ice-water vapor



Temp., T °C	Sat. Press., P_{sat} kPa	*Specific volume,* m^3/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg·K		
		Sat. ice, v_i	Sat. vapor, v_g	Sat. ice, u_i	Subl., u_{ig}	Sat. vapor, u_g	Sat. ice, h_i	Subl., h_{ig}	Sat. vapor, h_g	Sat. ice, s_i	Subl., s_{ig}	Sat. vapor, s_g
0.01	0.6117	0.0010909	206.0	-333.40		2374.5	-333.40		2500.5	-1.220		9.154
0	0.6112	0.0010909	206.2	-333.43	2707.9	2374.5	-333.43	2833.9	2500.5	-1.220	10.375	9.154
-2	0.5177	0.0010905	241.6	-337.63	2709.4	2371.8	-337.63	2834.5	2496.8	-1.236	10.453	9.218
-4	0.4375	0.0010902	283.8	-341.80	2710.8	2369.0	-341.80	2835.0	2493.2	-1.251	10.533	9.282
-6	0.3687	0.0010898	334.3	-345.94	2712.2	2366.2	-345.93	2835.4	2489.5	-1.267	10.613	9.347
-8	0.3100	0.0010895	394.7	-350.04	2713.5	2363.5	-350.04	2835.8	2485.8	-1.282	10.695	9.413
-10	0.2599	0.0010892	467.2	-354.12	2714.8	2360.7	-354.12	2836.2	2482.1	-1.298	10.778	9.480
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
-36	0.0200	0.0010850	5460.1	-404.40	2729.0	2324.6	-404.40	2838.4	2434.0	-1.499	11.969	10.470
-38	0.0161	0.0010847	6750.5	-408.07	2729.9	2321.8	-408.07	2838.4	2430.3	-1.514	12.071	10.557
-40	0.0128	0.0010844	8376.7	-411.70	2730.7	2319.0	-411.70	2838.3	2426.6	-1.530	12.174	10.644

The specific volume, internal energy, enthalpy, and entropy for a mixture of saturated ice and saturated vapor are calculated similarly to that of saturated liquid-vapor mixtures.

$$y_{ig} = y_g - y_i$$

$$y = y_i + x \; y_{ig}$$

where the quality *x* of a saturated ice-vapor state is

$$x = \frac{m_g}{m_i + m_g}$$

II.7.6. How to Choose the Right Table

The correct table to use to find the thermodynamic properties of a real substance can always be determined by comparing the state properties known to the properties in the saturation region. Given the temperature or pressure and one other property from the group *v, u, h,* and *s,* the following procedure is used: for example if the pressure and specific volume are specified, three questions have to be asked: For the given pressure,

$$is\ \ v < v_f\ ?$$

$$is\ \ v_f < v < v_g\ ?$$

$$is\ \ v > v_g\ ?$$

The answer to one of these questions must be yes. If the answer to the first question is yes, the state is in the compressed liquid region, and the compressed liquid tables are used to find the other properties of the state. If the answer to the second question is yes, the state is in the saturation region, and either the saturation temperature table or the saturation pressure table is used to find the other properties. Then the quality is calculated and is used to calculate the other properties, *u, h,* and *s*. If the answer to the third question is yes, the state is in the superheated region and the superheated tables are used to find the other properties.

Some tables may not always give the internal energy. When internal energy is not listed, it is calculated from the definition of the enthalpy as:

$$u = h - Pv$$

II.8. Equations of State

The tables described in the previous sections provide an accurate relationship between temperature, pressure and other important thermodynamic properties. If we restrict our attention to vapor state only, then we may often find a simple algebraic relationship between temperature, pressure and specific volume; such a **relationship** is called **an equation of state**.

For gases at low pressure it has been observed that pressure, P, is directly proportional to temperature, T, (this is known as Charles' law) and inversely proportional to specific volume, v (Boyle's law).

$$P = R \cdot \frac{T}{v}$$

Here, R is known as the gas constant.

It has also been found that there is a relationship between the various gas constants and the molecular weight of the particular gas. Specifically, the product of the gas constant and the gas molecular weight yields the same constant for all gases. This product is known as the **Universal Gas Constant**.

Jacques Alexandre César Charles (November 11, 1746 - April 7, 1823) was a French inventor, scientist, mathematician, and balloonist.
Circa 1787 he discovered Charles' Law, which states that under constant pressure, an ideal gas' volume is proportional to its temperature. The volume of a gas at constant pressure increases linearly with the temperature of the gas. The formula he created was $V_1/T_1=V_2/T_2$. His discovery anticipated Joseph Louis Gay-Lussac's published law of the expansion of gases with heat (1802).
Charles was elected to the Institut Royal de France, Académie des sciences, in 1793, and subsequently became professor of physics at the Conservatoire des Arts et Métiers. He died in Paris on April 7, 1823.

Robert Boyle (January 25, 1627 – December 30, 1691) was an Irish natural philosopher, chemist, physicist, inventor, and early gentleman scientist, noted for his work in physics and chemistry. Although his research and personal philosophy clearly has its roots in the alchemical tradition, he is largely regarded today as the first modern chemist. Among his works, The Sceptical Chymist is seen as a cornerstone book in the field of chemistry.

Calculate the product in the final column

Gas	Molecular Weight kg/kmol	Gas Constant kJ/kg K	Product kJ/ kmol K
Argon	**39.948**	**0.2081**	
Ethane	**30.070**	**0.2765**	
Helium	**4.003**	**2.0769**	

Therefore, the gas constant for a specific (R) gas is equal to:

$$R = \frac{R_u}{M}$$

The Universal gas constant is considered a fundamental constant, similar to the gravitational constant.

$R_U = 8.314$ kJ/kmol K

Alternate forms of the ideal gas law:

$\mathbf{P \cdot v = R \cdot T}$
$\mathbf{P = \rho \cdot R \cdot T}$
$\mathbf{P \cdot V = m \cdot R \cdot T}$
$\mathbf{P \cdot V = N \cdot R_u \cdot T}$

Remember that: mass (m) = Number of moles (N) × Molecular Mass (M)

Following the ideal gas law, for a process from (1) to (2), we can write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

II.8.1. Compressibility Factor

It was stated previously that the ideal gas law is valid for low pressure. The question is, “what does it mean ‘low’ pressure”? One way to approach this question is through the compressibility factor, defined as follows:

$$Z = \frac{P \cdot v}{R \cdot T}$$

For an ideal gas, Z = 1. As the compressibility factor deviates from 1, the gas may be considered to be increasingly non-ideal.

In attempting to make a general characterization of many gases, it has be proven useful to try to put the phase diagrams for many gases together. In order to “normalize” the graphs, we introduce a normalized pressure and temperature:

$$P_R = \frac{P}{P_{critical}} \qquad T_R = \frac{T}{T_{critical}}$$

The critical temperature and pressure of several gases are tabulated. The ratio of the vapor pressure to the critical pressure for the same gas and the temperature to the critical temperature for the same gas is termed the reduced pressure and reduced temperature, respectively.

The figure below represents the compressibility factor, Z, as a function of the reduced pressure, P_R, for various reduced temperatures, T_R.

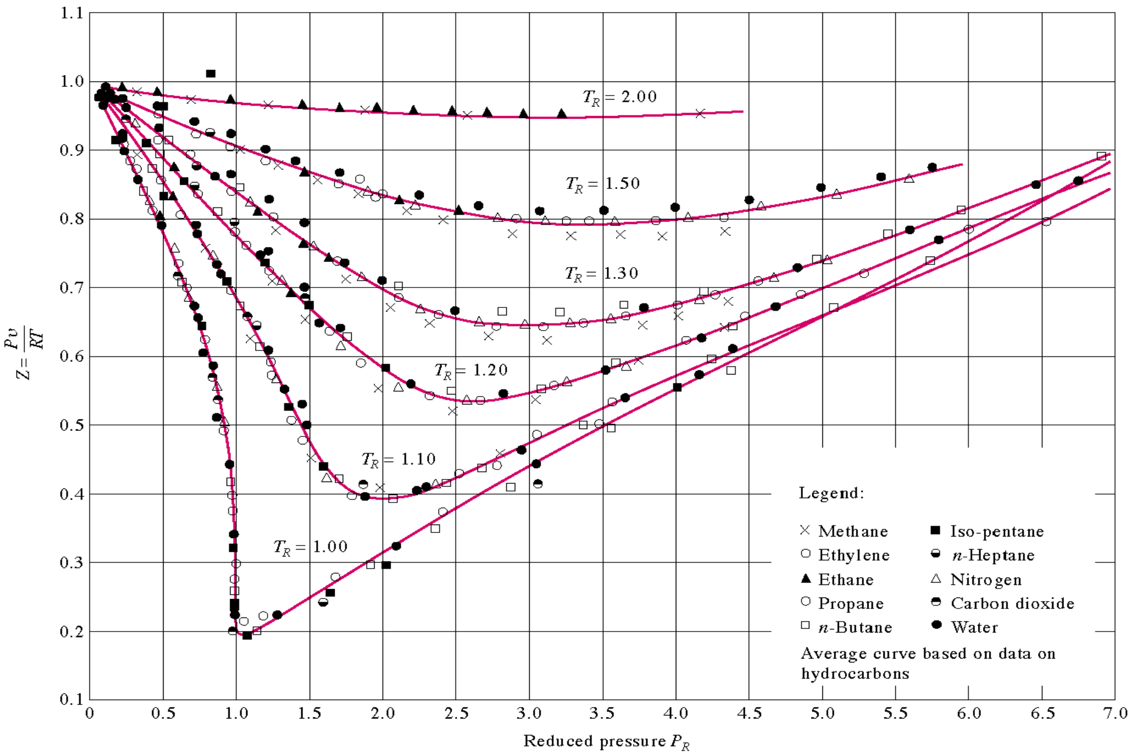


Figure.2.13. Compressibility factor as a function of reduced pressure and reduced temperature.

The worst correlation for the ideal gas law is near the critical point, i.e. $P_R = 1$ and $T_R = 1$.
These charts show then the conditions for which Z = 1 and the gas behaves then as an ideal gas:

Important

1- **$P_R < 10$ and $T_R > 2$**
2- **$P_R << 1$**

Note 1: When P_R is small, we must make sure that the state is not in the **compressed liquid region** for the given temperature. A compressed liquid is certainly not an ideal gas.

Note 2: The fact that gases behave as ideal gases when the reduced temperature is greater than 2, $T_R > 2$, is the most commonly encountered. Consider the boiling point of several gases, taken from Tables A-1 and A-1E, shown below:

Substance	**Critical Temperature**
Argon	151K
Helium	5.3K
Hydrogen	33.3K
Nitrogen	126.2K
Oxygen	154.8K

We think of each of these substances as gases because the maximum temperature at which they are liquids is very low, far below temperatures normally encountered in nature. For that reason, it is common in nature that the $T_R > 2$ for these substances and they can be treated as ideal gases

The Tables for fluid properties provided in the appendix of the any thermodynamics textbook will always provide the most accurate means of determining fluid properties. However, for fluids for which tables are not available it may prove sufficiently accurate to use the ideal gas law as corrected by the compressibility factor. It is the general applicability of the compressibility factor to all gases at all temperatures and pressures that makes the concept such a powerful tool.

II.8.2. Other Equations of State

A simple, accurate equation of state has long been desired in engineering practice. The wide spread use of computer programs in engineering has increased the need for such an equation. Obviously, virtually any algebraic equation, either implicit or explicit, would be easier to program and solve than trying to work with something so cumbersome as the vapor tables. When the program must deal with a variety of fluids, the impetus is increased even more.

II.8.2.1. Van der Waals equation

Van der Waals examined the ideal gas equation and concluded that it failed near the critical point because it failed to fully account for the attraction forces between molecules and molecular volume. Molecular repulsive forces in gases are generally quite small. Since these forces drop rapidly as the molecules move apart, it is only at very high pressure, when molecules are unusually close together, that such forces are significant. Similarly, gaseous molecules are often widely spaced and do not physically occupy a large fraction of the space in which they exist. At very high pressures, these molecules are forced together and their volume may become significant. Van der Waals proposed the model:

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

where the constant **a** accounts for the repulsion between molecules and increases the forces between them. The constant **b** accounts for the volume physically occupied by molecules and decreases the effective open volume. Numerical values of a & b can be calculated as follows:

$$a = \frac{27 \cdot R^2 \cdot T_{critical}^2}{64 \cdot P_{critical}} \qquad b = \frac{R \cdot T_{critical}}{8 \cdot P_{critical}}$$

Johannes Diderik Van der Waals (November 23, 1837 – March 8, 1923) was a Dutch scientist famous "for his work on the equation of state for gases and liquids", for which he won the Nobel Prize in physics in 1910. Van der Waals was the first to realize the necessity of taking into account the volumes of molecules and the intermolecular forces (now generally called "Van der Waals forces") in establishing the relationship between the pressure, volume and temperature of gases and liquids

II.8.2.2. Beattie-Bridgeman equation

The Beattie Bridgemen Equation of State represents another attempt, patterned after the approach used by Van der Waals, to improve the accuracy of the ideal gas law by accounting for repulsion forces and the volume of the gaseous molecules. While the algebraic is slightly different, the major difference is that the constants, corresponding to a & b, are obtained experimentally for the particular gas. While accuracy is improved the model can only be applied to gases for which data is available.

$$P = \frac{R_U T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)\left(\bar{v} + B\right) - \frac{A}{\bar{v}^2}$$

Where

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \text{ and } B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

The constants are given in specific tables for various substances.

II.8.2.3. Benedict-Webb-Rubin equation

This represents a more recent attempt to improve on the Van der Waals equation by introducing a more complicated model with additional experimental constants. Again, it is successful in improving accuracy but continues to be limited by available data.

II.8.2.4. Virial equation

This represents an alternate means of improving the Van der Waals equation of state, this time using an infinite series to represent the dependence of temperature and specific volume on pressure.

$$P = \frac{RT}{v} + \frac{B(T)}{v^2} + \frac{C(T)}{v^3} + \ldots$$

II.9. Specific heat for ideal gases

Specific Heat is the energy required to raise the temperature of a unit mass of a substance by 1 degree.

Specific heat at constant volume: This is the energy required to raise the temperature of a unit mass of a substance by 1 degree while the volume of the substance remains fixed (but the pressure is allowed to rise).

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_{v=\text{constant}}$$

Specific heat at constant pressure: This is the energy required to raise the temperature of a unit mass of a substance by 1 degree while the pressure of the substance remains fixed (but the volume is allowed to increase).

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_{P=\text{constant}}$$

Specific heat is defined in terms of thermodynamic properties. Since all of the terms used in calculating specific heat can be evaluated for any thermodynamic state, specific heat can likewise be determined for any thermodynamic state, i.e. it is also a thermodynamic property. You can find values of specific heat for several common fluids on specific tables.

Note

What is internal energy?
It is the energy associated with the translation, rotation, and vibration of molecules, electrons, protons, and neutrons, and the bounding between subatomic particles.

What is enthalpy?
It is the name given to the combination of internal energy; pressure and specific volume:
$h = u + Pv$

II.9.1. Specific heat and work generation

Fluid that is heated at constant volume will do no work on its boundary. [Work = $\int F \cdot dx$ so that if the containment sides do not move a distance dx, there can be no work.] All added energy will be used to increase the internal energy of the fluid.

Fluid which is heated at constant pressure will also have its internal energy increased but, in addition, will require energy to do work as it expands against its boundary.

II.9.2. Specific Heats of Ideal Gases

II.9.2.1. Constant Volume Specific Heat (C_v)

Experimentally it has been found that the specific heat at constant volume, C_v, for an ideal gas depends not on temperature and pressure, but only on temperature:

$$C_V = C_V(T)$$

Since the specific heat at constant volume depends only on temperature, we can replace the total derivative used in the definition by a total derivative:

$$C_V = \left(\frac{du}{dT}\right)$$

Recall that in introducing the Celsius and the Fahrenheit temperature scales, we arbitrarily chose a zero point for temperature.
Similarly, we may choose any arbitrary point to define the zero for internal energy. Because the zero state is arbitrary, is possible to define negative internal energy just as we have negative temperatures.

II.9.2.2. Constant Pressure Specific Heat (C_P)

By definition:

$$h = u + P\,v$$

In this section, we have been considering an ideal gas. Thus:

$$P\,v = R\,T$$

so that, upon substitution,

$$h = u + R\,T$$

In the previous section, we had indicated that C_v depends only upon temperature so that:

$$C_V = \left(\frac{du}{dT}\right)$$

After rearranging,

$$du = C_v\,dT$$

Since the right side of the equation depends only on T, so must the left.

$$u = u(T)$$

Then, enthalpy can also depend only on T since,

$$h = u(T) + R\,T$$

It follows that

$$C_p = \left(\frac{\partial h}{\partial T}\right)_{\text{Constant}(P)} = \left(\frac{dh}{dT}\right)_{\text{Constant}(P)}$$

Then,

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v \cdot dT$$

and

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p \cdot dT$$

Example

Determine the enthalpy change, Δh, of nitrogen, in kJ/kg, as it is heated from 600 to 1000K, using (a) the empirical data for h from the nitrogen table (Table A-18), (b) the empirical specific heat equation as a function of temperature (Table A-2c), (c) the C_P value at the average temperature (Table A-2b), and (d) the C_P value at room temperature (Table A-2a). Also determine the percentage error in each case.

Note

For non-ideal gases: internal energy and enthalpy changes are found using the empirical gas tables. Also changes in internal energy can be found using C_V for constant volume processes. Changes in enthalpy can be found using C_P, providing that the process is constant pressure.

For ideal gases: internal energy and enthalpy changes may be found using empirical gas tables. Also changes in internal energy may be found using C_V for any process since internal energy is a function of temperature alone. Also changes in enthalpy may be found using C_P for any process since enthalpy is a function of temperature alone.

II.9.3. Relationship between C_V and C_P:

We have: $h = u + P v$

For an ideal gas $Pv = RT$ so that

$h = u + R \cdot T$

Differentiating $dh = du + R \cdot dT$

Divide by dT $dh/dT = du/dT + R$

Recall definition of C_V and C_P for an ideal gas

$$C_P = C_V + R$$

We can also define specific Heat Ratio, k as

$$k \equiv \frac{C_P}{C_V}$$

CHAPTER III

Energy Transfer by Heat and Work

CHAPTER III

Energy Transfer by Heat and Work

This chapter is an important transition between the properties of pure substances and one of the most important chapters: the first law of thermodynamics.
In this chapter, we will introduce the notions of heat, work and conservation of mass.

III.1. Work

Work is basically defined as any transfer of energy (except heat) into or out of the system. In the next part, we will define several forms of work. But, first we will focus our attention on a particular kind of work called: compressive/expansive work. Why this is important? Because it is the main form of work found in gases and it is vitally important to many useful thermodynamic applications such as engines, refrigerators, free expansions, liquefactions, etc.

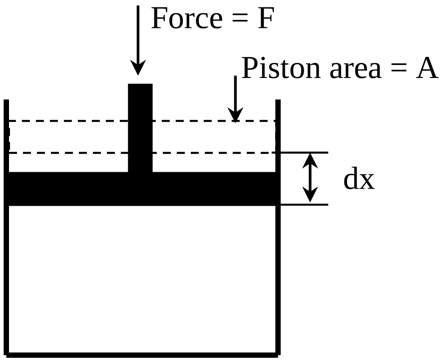
By definition, if an applied force F causes an infinitesimal displacement dx then, the work done dW is given by:

$$dW = F.dx$$

and as the force keep acting, those infinitesimal work contributions add up such that:

$$W = \sum dW = \int F.dx$$

This is the general definition of work, however, for a gas it is more convenient to write this expression under another form. Consider first the piston-cylinder arrangement:



Here we can apply a force F to the piston and cause it to be displaced by some amount *dx*. But, in thermodynamics, it is better to talk about the pressure *P* = *F*/*A* rather than the force because the pressure is size-independent. Making this shift gives a key result:

$$W = \int PA(dx) = \int PdV$$

Note that if the piston moves in, then dV is negative, so W is negative which means work is done on the system and its internal energy is increased. If the piston moves out, then dV is positive, so W is positive and the system does work on its environment and its internal energy is reduced. This is a general expression of work for a gas, it is not piston and cylinder specific. For example, in a balloon you use the same equation, but dV is just calculated slightly differently (for a spherical balloon, it will be $4\pi r^2 dr$).

As you may notice from the expression above, work is related to pressure and volume. As a consequence, work can be represented using a P-V diagram. Furthermore to compute the work, for any process, we are interested in what are the initial volume V_i and the final volume V_f since $dV = V_f - V_i$. As shown in Fig.3.3, the work done is just the area underneath the process on a PV-curve.

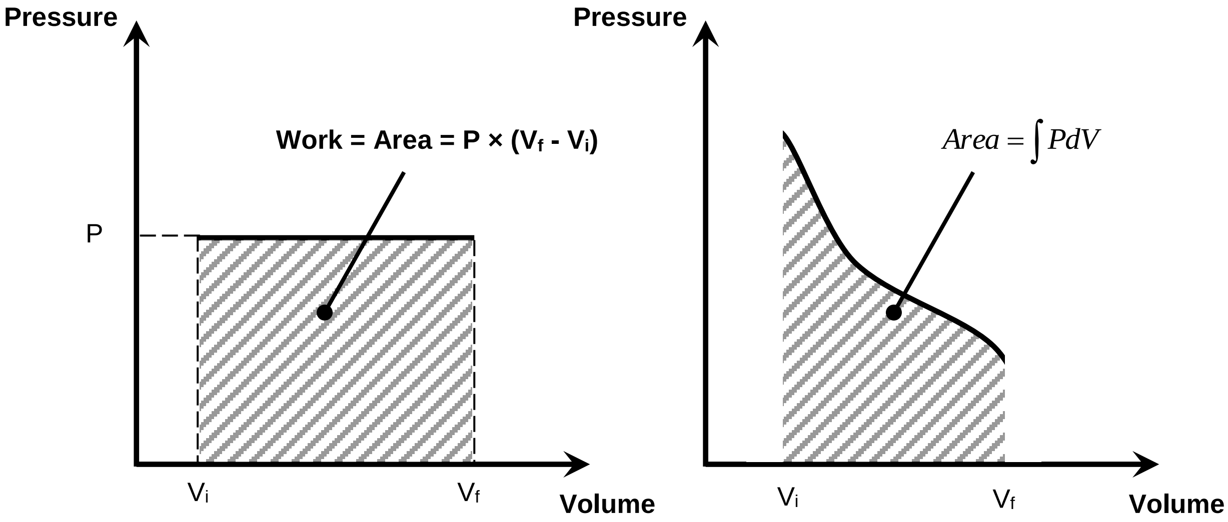


Figure.3.3. PV diagram and work definition.

An important thing to realize is that this has a significant impact on how much work is done by a particular process between a given (P_i,V_i) and (P_f,V_f). If you look at Fig.3.4, you'll see just three of many possible *PV*-processes between (P_i,V_i) and (P_f,V_f), the areas under these curves are different, which means that each has a different *W*.

This is known as a ***path dependent* process**. In contrast, a path independent process only depends on the starting and end points and not how you get from one to the other – an example is gravitational potential energy it only depends on the change in height, not the path you take in changing that height.

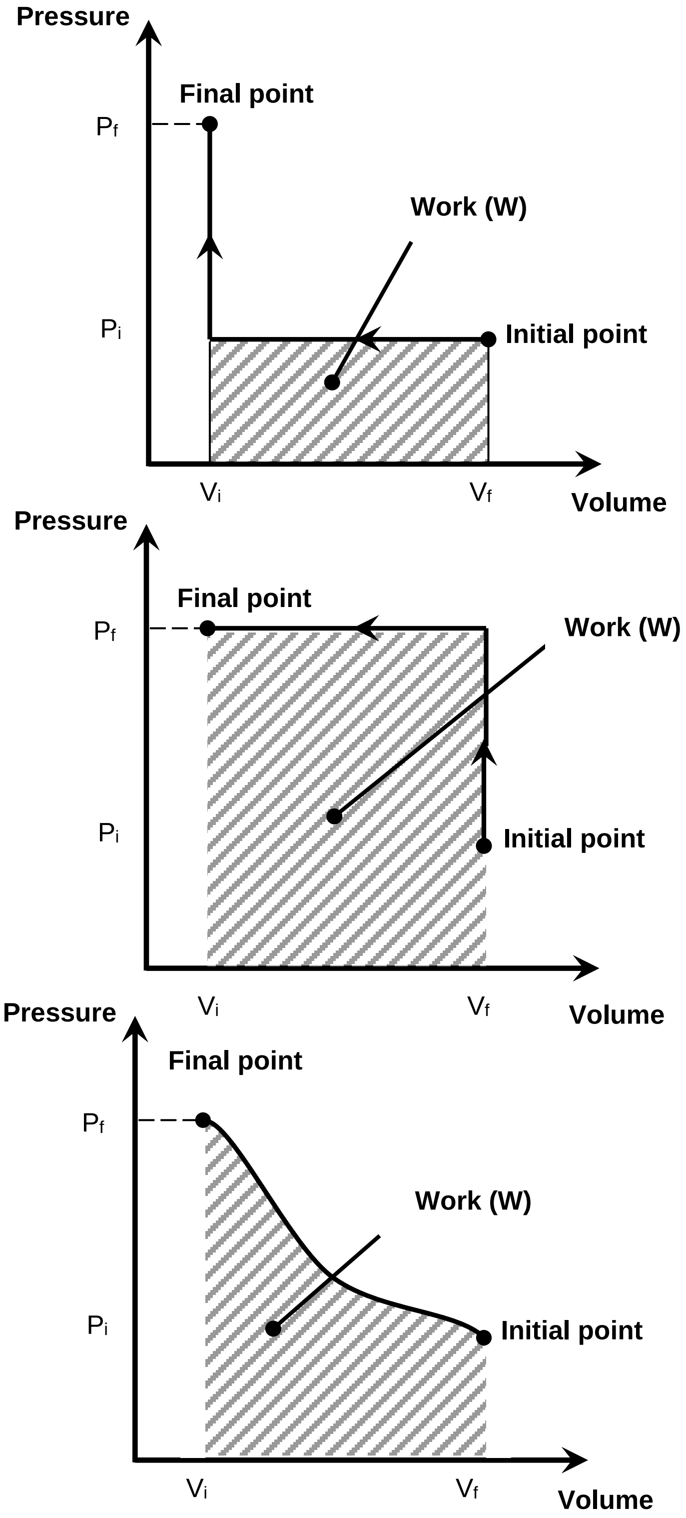


Figure.3.4. Several PV diagrams for the same initial and final conditions.

III.1.1. Some Common works

Constant Volume: In a constant volume process dV=0, and so the work W must be 0 also. There is no work in a gas unless it changes its volume.

Constant Pressure: Here P is constant, so we can take it out the integral. Hence:

$$W = P\int_{V_i}^{V_f} dV = P\left(V_f - V_i\right)$$

Isothermal Expansion: if we use the ideal gas law as P=nRTV, we obtain:

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Here, R is a constant; n and T (isothermal) are constant, therefore:

$$W = nRT\int_{V_i}^{V_f} \frac{dV}{V} = nRT\left(\ln V_f - \ln V_i\right)$$

III.1.3. Polytropic process

Example

A gas in a piston-cylinder assembly undergoes an expansion process for which the relationship between pressure and volume is given by

$$PV^n = ct$$

The initial pressure is 3 bar, the initial volume is 0.1 m^3, and the final volume is 0.2 m^3. Determine the work for the process, in kJ if:

a- n = 1.5
b- n = 1.0
c- n = 0

III.2. Several forms of work

Energy Transfer by Heat and Work

III.2.1. Electrical Work

If electrons cross the boundaries of the system a work is generated. This work can be computed as:

$$W = \int_1^2 VI \ dt$$

Where (I) is the current and V is the voltage.

III.2.2. Shaft Work

In a large majority of engineering devices, the work is transmitted by a rotating shaft. This kind of work can be computed as follow:

$$W = 2\pi \dot{N} T$$

Where, $\dot{N}$ is the number of tours per unit of time (tours/min ; tours/second, …) and T is the torque.

III.2.3. Spring Work

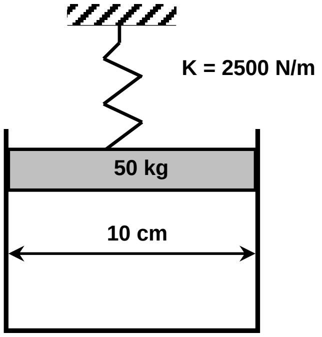
For a linear elastic spring, the work can be computed as:

$$W = \frac{1}{2} k \left(x_2^2 - x_1^2 \right)$$

Where; x_1 and x_2 are the initial and final displacements of the spring, and k is the spring constant.

Example [Schaum's page 48]

The air in a circular cylinder is heated until the spring is compressed 50 mm. Find the work done by the air on the frictionless piston. The spring is initially unstretched.



III.3. Heat

Heat can be transmitted through the boundaries of the system only during a non-thermal equilibrium state. Heat is transmitted, therefore, solely due to a temperature difference.
The net heat transferred to a system is defined as:

$$Q_{net} = \sum Q_{in} - \sum Q_{out}$$

Here, Q_{in} and Q_{out} are the magnitudes of the heat transfer values. In most thermodynamics texts, the quantity Q is meant to be the net heat transferred to the system, Q_{net}. We often think about the heat transfer per unit mass of the system, q.

$$q = \frac{Q}{m}$$

Heat transfer has the units of energy measured in joules (we will use kilojoules, kJ) or the units of energy per unit mass, kJ/kg.

Since heat transfer is energy in transition across the system boundary due to a temperature difference, there are three modes of heat transfer at the boundary that depend on the temperature difference between the boundary surface and the surroundings. These are conduction, convection, and radiation. However, when solving problems in thermodynamics involving heat transfer to a system, the heat transfer is usually given or is calculated by applying the first law, or the conservation of energy, to the system. The course regarding heart transfer specifically deals with computing heat depending on the mode of heat transfer.

An **adiabatic** process is one in which the system is perfectly insulated and the heat transfer is zero.

III.4. Summary

- Heat is defined as the spontaneous transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. There is no external force mediating this process.
- Work is basically defined as any other transfer of energy into or out of the system. The most important form of work in thermodynamics is compressive work, which is due to a change in volume against or due to an external force (or pressure) on a gas.

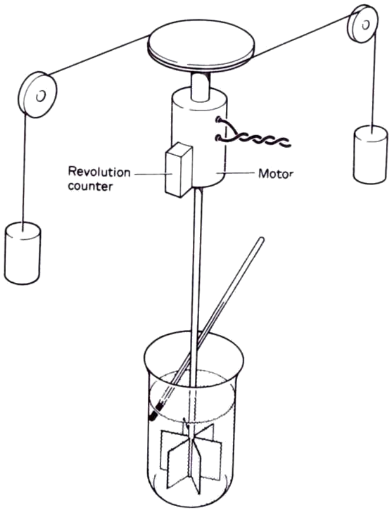
III.5. The mechanical equivalent of heat (Joule's experiment)

In the 1800s Joule spent a lot of time pondering the quantitative relationship between different forms of energy, looking to see how much is lost in converting from one form to another. As you already know, when friction is present in some mechanical systems we always end up losing some of the mechanical energy, and in 1843 Joule did a famous experiment showing that this lost in mechanical energy is converted into heat.

As shown in the figure below, Joule's apparatus consists of water in a thermally insulated vessel. Heavy blocks falling at a constant speed (mechanical energy) are connected to a paddle immersed in the liquid. Some of the mechanical energy is lost to the water as friction between the water and the paddles. This results in an increase in the temperature of the water, as measured by a thermometer immersed in the water. If we ignore the energy lost in the bearings and through the walls, then the loss in gravitational potential energy associated with the blocks equals the work done by the paddles on the water. By varying the conditions of the experiment, Joule noticed that the loss in mechanical energy $2mgh$ was proportional to the increase in water temperature ΔT, with a proportionality constant 4.18J/°C.

This was one of the key experiments leading up to the discovery of the 1st law of thermodynamics.

James Prescott Joule, (December 24, 1818 – October 11, 1889) was an English physicist, born in Sale, near Manchester. Joule studied the nature of heat, and discovered its relationship to mechanical work . This led to the theory of conservation of energy, which led to the development of the first law of thermodynamics. The SI unit of work, the joule, is named after him. He worked with Lord Kelvin to develop the absolute scale of temperature, made observations on magnetostriction, and found the relationship between the flow of current through a resistance and the heat dissipated, now called Joule's law.



CHAPTER IV

First Law of Thermodynamics

CHAPTER IV

First Law of Thermodynamics

IV.1. First Law of thermodynamics for a closed system

The first law of thermodynamics is usually written as:

$$\Delta E = Q - W$$

The variation in energy = Heat - Work

Where Q is heat; W is work and the term E includes numerous types of energy:

Internal energy	U=U(T,P)	It is the form of stored energy which can be directly influenced by a heat transfer. It is the energy stored microscopically in two forms: as the kinetic energies due to random molecular translations, vibrations and rotations, and as potential energy arising from forces between molecules.
Kinetic energy	$KE = \frac{1}{2}mV^2$	Due to the velocity of the system
Potential energy	$PE = mgz$	Due to the elevation of the system in a gravitational field.

and:

$$E = U + KE + PE + \ldots$$

You can add other terms (atomic, electromagnetic, chemical, …) to the expression of energy. However, we will usually limit ourselves to the three terms above.

Note

The relative magnitude of the three components of energy (U; KE; PE) is often quite different. The statement of a problem should give a quick clue on terms will predominate. Modest velocity changes will result in negligible changes in kinetic energy. Similarly, small changes in elevation will result in negligible changes in potential energy.

It is important to note that this is the most frequent version of the first law of thermodynamics (with minus sign). This is because when people dealt with heat engines in the 18th century, they cared about heat in and work out. You may also find a version with a (+) sign [ΔE=Q+W], this means that the convention of work in and out is not the same.

The first law can be also written under the instantaneous time rate form as:

$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

It is also interesting to note that the first law can not be derived; no algebra can be used to show how it is obtained. This is because it is a blind observation about how the world seems to work.

Example 1 [Sonntag p. 108]

A tank containing a fluid is stirred with a paddle wheel. The work input to the paddle wheel is 5090 kJ. The heat transfer from the tank is 1500 kJ. Consider the tank and the fluid inside a control surface and determine the change in internal energy of the control mass.

Example 2

A tank with a volume of 5 m^3 contains 0.05 m^3 of liquid water and 4.95 m^3 of saturated vapour at 0.1 MPa. Heat is supplied to the tank until all the volume is occupied by saturated vapour. Determine the heat supplied to the tank.

Example 3

Four kilograms of a certain gas is contained within a piston-cylinder assembly. The gas undergoes a polytropic process with n=1.5.
The initial pressure is 3 bar, the initial volume is 0.1 m^3, and the final volume is 0.2 m^3. The change in internal energy during the process is in absolute value 4.6 kJ/kg. Determine the net heat transfer for the process in kJ.

IV.2. First Law of thermodynamics for a control volume

IV.2.1. Mass rate balance

When analyzing a control volume, the first reflex should be to apply the conservation of mass. At each instant the following principle must be valid:

$$\frac{dm_{CV}}{dt} = \dot{m}_i - \dot{m}_e$$

Where the term on the left side represents the time rate of change of mass contained within the control volume at time (t); and $\dot{m}_i$ is the time rate of flow of mass IN across inlet (i) at time (t); and and $\dot{m}_e$ is the time rate of flow of mass OUT across exit (e) at time (t) (see Figure.4.1).

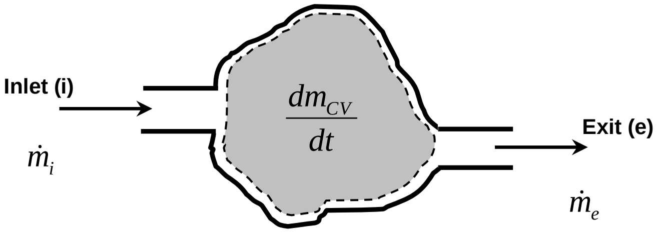


Figure.4.1. Control volume for a single inlet and a single exit.

The above formulation is valid for one inlet and one outlet. However, in general, there may be several locations on the boundary through which mass enters or exits. In this case, the general form is:

$$\frac{dm_{CV}}{dt} = \sum_i \dot{m}_i - \sum_e \dot{m}_e$$

IV.2.2. Computation of the mass flow rate

The mass flow rate can be computed under the following general form:

$$d\dot{m} = \rho\, V_n\, dA$$

Where ρ is the fluid density; V_n is the normal velocity and dA is surface element.
By integration we get:

$$\dot{m} = \int_A \rho\, V_n\, dA$$

For the special case of a one-dimensional flow, where the velocity profile is flat and normal to the surface (A) and the surface A does not change with time, we can compute the mass flow rate using the following expression:

$$\dot{m} = \rho\, V_n\, A = \frac{V_n A}{\upsilon}$$

IV.2.2.1. Computation of the mass flow rate for a steady flow

In the particular case of a steady flow, meaning that all properties are unchanging in time, the left term in the general expression of the mass rate balance vanishes. We obtain, therefore, the following expression:

$$0 = \sum_i \dot{m}_i - \sum_e \dot{m}_e$$

Or

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e$$

Example 4

A feedwater heater operating at steady state has two inlets and one exit. At inlet 1, water vapour enters at P_1=7 bar, T_1=200°C with a mass flow rate of 40 kg/s. At inlet 2, liquid water at P_2=7 bar, T_2=40°C enters through an area A_2=25 cm^2. Saturated liquid at 7 bar exits at 3 with a volumetric flow rate of 0.06 m^3/s. Determine the mass flow rates at inlet 2 and at the exit, in kg/s, and the velocity at inlet 2, in m/s.

IV.2.2.3 First Law of thermodynamics for a control volume

If we consider one inlet and one exit, the energy balance can be written under the following form:

$$\frac{dE_{CV}}{dt} = \dot{Q} - \dot{W} + \dot{m}_i\left(u_i + \frac{V_i^2}{2} + gz_i\right) - \dot{m}_e\left(u_e + \frac{V_e^2}{2} + gz_e\right)$$

Now we will try to write this energy balance under an alternative form that is more convenient for our applications. This will be done, first by writing the term $\dot{W}$ under another form where we are able to separate the work associated with the fluid pressure as mass is introduced at the inlets and removed at exits from the work due to all other effects (rotating shaft, electrical effects, …). This latest term will be denoted $\dot{W}_{CV}$.

The first term due to pressure can be written under the following form:

$$\dot{W}_{Pressure} = (PA)V$$

Where V is the velocity.

Therefore, the total work can be expressed under the following form:

$$\dot{W} = \dot{W}_{CV} + (P_e A_e)V_e - (P_i A_i)V_i$$

Here note that the work at the exit has a positive sign and the work at the inlet has a negative sign.

As we have, for a one-dimensional flow:

$$\dot{m} = \frac{AV}{\upsilon} \Leftrightarrow AV = \dot{m}\upsilon$$

Then,

$$\dot{W} = \dot{W}_{CV} + \dot{m}_e(P_e\upsilon_e) - \dot{m}_i(P_i\upsilon_i)$$

If we replace this expression in the energy balance, we can get:

$$\frac{dE_{CV}}{dt} = \dot{Q}_{CV} - \dot{W}_{CV} + \dot{m}_i\left(u_i + P_i\upsilon_i + \frac{V_i^2}{2} + gz_i\right) - \dot{m}_e\left(u_e + P_e\upsilon_e + \frac{V_e^2}{2} + gz_e\right)$$

It is interesting now to introduce the property: specific enthalpy as,

$$h = u + P\upsilon$$

We can, therefore, write the energy balance under the form:

$$\frac{dE_{CV}}{dt} = \dot{Q}_{CV} - \dot{W}_{CV} + \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gz_i\right) - \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gz_e\right)$$

Note that the introduction of enthalpy was only for convenience.

Now, for several inputs and exists, the general form for the first law of thermodynamics for a control volume is:

$$\frac{dE_{CV}}{dt} = \dot{Q}_{CV} - \dot{W}_{CV} + \sum_i \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gz_i\right) - \sum_e \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gz_e\right)$$

For a steady state, we obtain the following form:

$$\underbrace{\dot{Q}_{CV} + \sum_i \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gz_i\right)}_{Energy\ in} = \underbrace{\dot{W}_{CV} + \sum_e \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gz_e\right)}_{Energy\ out}$$

IV.3. Illustrations

IV.3.1. Nozzles and diffusers

A nozzle is a flow passage of varying cross-sectional area in which the velocity of a gas or liquid increases in the direction of flow. A diffuser is the inverse (decrease in velocity).

Example 5

Steam enters a converging-diverging nozzle operating at steady state with P_1=40 bar, T_1=400°C, and a velocity of 10 m/s. The steam flows through the nozzle with negligible heat transfer and no significant change in potential energy. At the exit, P_2=15 bar, and a velocity of 665 m/s. the mass flow rate is 2 kg/s. Determine the exit area of the nozzle, in m^2.

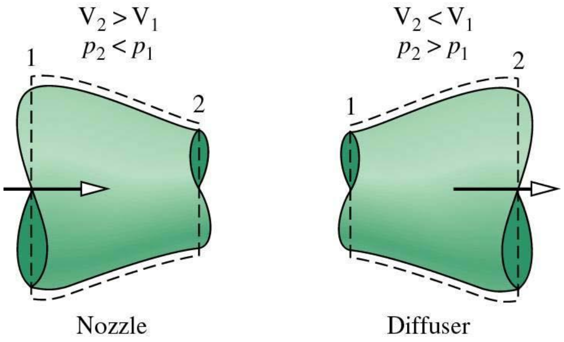


Figure.4.2. Nozzle and diffuser.

IV.3.1. Turbines

A turbine is a device in which work is developed as a result of a gas or liquid passing through a set of blades attached to a shaft free to rotate.

Example 6

Steam enters a turbine operating at steady state with a mass flow rate of 4600 kg/h. The turbine loses 63.1 kW of heat to the surroundings. At the inlet, the pressure is 60 bar, the temperature is 400°C, and the velocity is 10 m/s. At the exit, the pressure is 0.1 bar, the quality is 0.9 (90%), and the velocity is 50 m/s. Calculate the power of the turbine in kW.

Figure.4.3. Steam turbine.

V.3.2. Compressors and pumps

Compressors are devices in which work is done to increase the pressure of a GAS.
Pumps are devices in which work is done to increase the pressure of a LIQUID.

Example 7

Air enters a compressor operating at steady state pressure of 1 bar, a temperature of 290 K, and a velocity of 6 m/s through an inlet with an area of 0.1 m^2. At the exit, the pressure is 7 bar, the temperature is 450 K, and the velocity is 2 m/s. Heat transfer from the compressor to its surroundings occurs at a rate of 180 kJ/min. Employing the ideal gas model, calculate the power input to the compressor, in kW.

IV.3.3. Heat exchangers

Devices that transfer energy between fluids at different temperatures by heat transfer.

Example 8

Steam enters the condenser of a vapor power plant at 0.1 bar with a quality of 0.95 and condensate exists at 0.1 bar and 45°C. Cooling water enters the condenser in a separate stream as a liquid at 20°C and exists as a liquid at 35°C with no change in pressure. Heat transfer from the outside of the condenser can be ignored. For steady-state operation, determine:

- the ratio of the mass flow rate of the cooling water to the mass flow rate of the condensing stream.

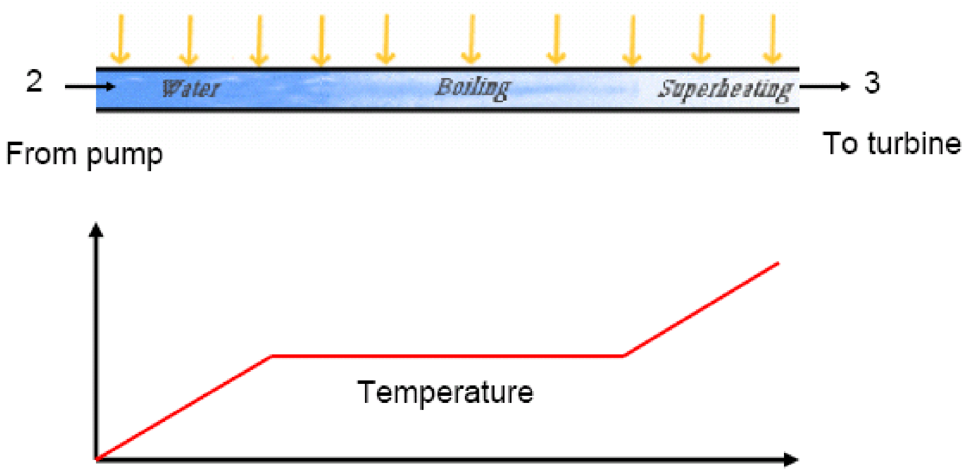


Figure.4.4. Phase change in a boiler.

IV.3.4. Cycles analysis

IV.3.4.1. Rankine Cycle

Rankine cycle is the ideal cycle for a **steam power plant**.

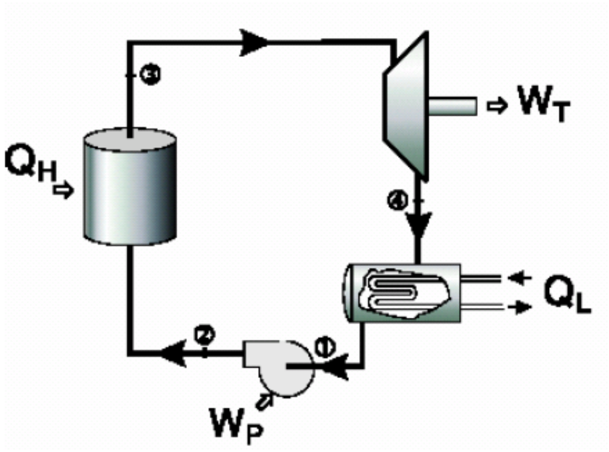


Figure.4.5. Rankine cycle.

Example 9

Consider a simple steam power plant with the following data:

Location	Pressure	Temperature or Quality
Leaving boiler	2.0 MPa	300°C
Entering the turbine	1.9 Mpa	290°C
Leaving turbine, entering condenser	15 kPa	90%
Leaving condenser, entering pump	14 kPa	45°C

Pump work = 4kJ/kg

Determine the following quantities per kilogram flowing through the unit:

- Heat transfer in line between boiler and turbine.
- Turbine work.
- Heat transfer in condenser.
- Heat transfer in boiler.

IV.3.4.2. Brayton Cycle

Brayton cycle is the ideal cycle for a **gas turbine power plant**.

Example 10

In an air-standard Brayton cycle the air enters the compressor at 0.1 Mpa and 15°C. The pressure leaving the compressor is 1.0 Mpa, and the maximum temperature in the cycle is 1100°C. If you consider that the processes through the compressor and the turbine are polytropic (with n=1.4) and the heat transfer processes are isobaric, determine:

- The pressure and the temperature at each point in the cycle.
- The compressor work, turbine work, and cycle efficiency.

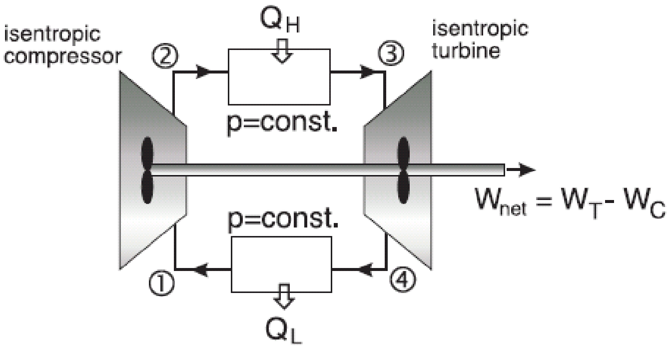


Figure.4.6. Brayton cycle.

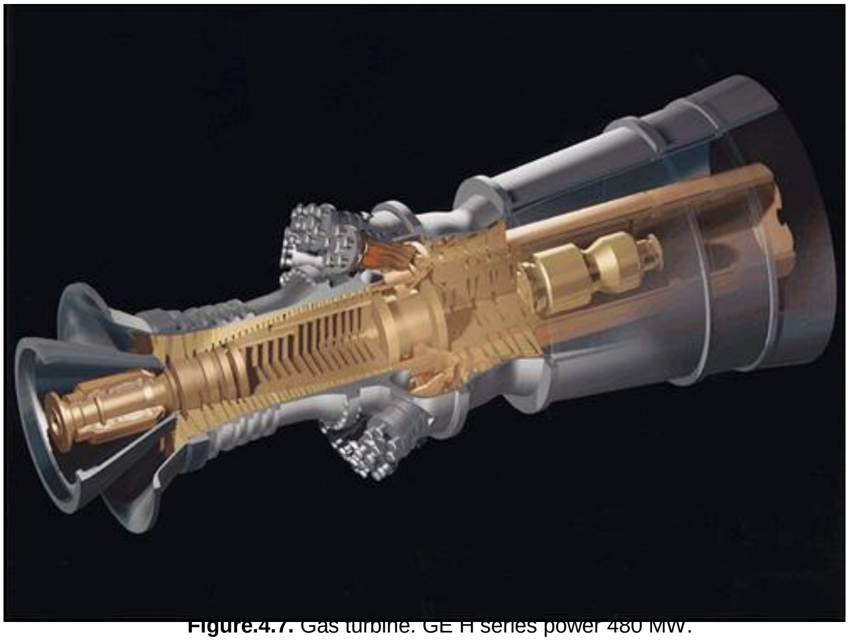


Figure.4.7. Gas turbine. GE H series power 480 MW.

IV.3.4.2. O^{TT}O Cycle

Definitions:

BDC: bottom dead center (maximum volume).
TDC: top dead center (clearance volume).
Bore: diameter of the piston.
Stroke: the distance the piston travels in one direction.

Mean effective pressure (MEP): the pressure that if acting on the piston during the power stroke, would produce an amount of work equal to that actually done during the entire cycle.

$$W_{cycle} = MEP\left(V_{BDC} - V_{TDC}\right)$$

$$MEP = \frac{W_{cycle}}{\left(V_{BDC} - V_{TDC}\right)}$$

Compression ratio (r):

$$r = \frac{Volume\ occupied\ by\ the\ air\ at\ BDC}{Volume\ occupied\ by\ the\ air\ at\ TDC} > 1$$

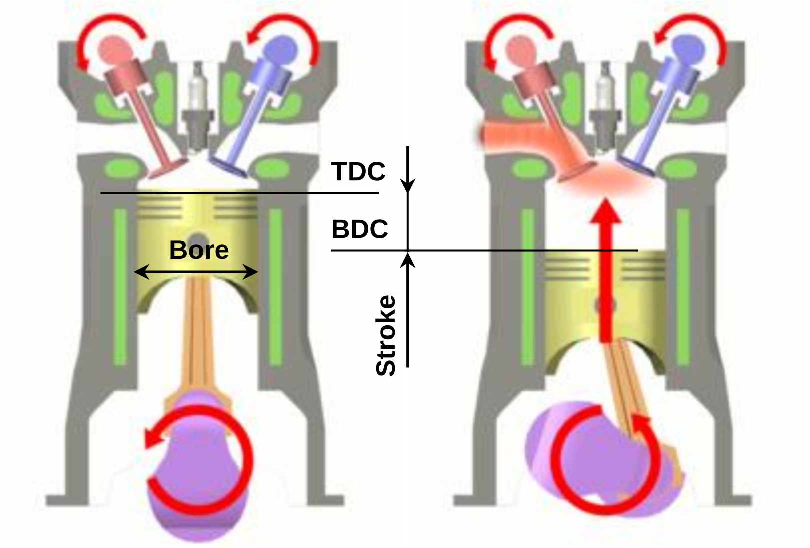


Figure.4.8. Otto cycle parameters

Nikolaus August Otto (June 14, 1832 - January 28, 1891) was the German inventor of the internal-combustion engine, the first engine to burn fuel directly in a piston chamber. Up until his invention, all engines were external-combustion engines and fuel was burned in a separate compartment. Otto's first atmospheric engine was completed in May 1867. Five years later Gottlieb Daimler and Wilhelm Maybach joined his company for a while and together they produced the idea of the four-stroke cycle or, Otto cycle engine, which was first described in 1876. The Otto Cycle engine patent was invalidated in 1886 when it was discovered that another inventor, Alphonse Beau de Rochas, had already described the four-stroke cycle principle in a privately published pamphlet. (ref. Wikipedia)

Example 11

The compression ratio (V_1/V_2) in an air-standard Otto cycle is 10. At the biginning of the compression stroke the pressure is 0.1 MPa and the temperature is 15°C. The heat transfer to the air per cycle is 1800 kJ/kg air. If you consider compression and the expansion as polytropic (with n=1.4) and the heat transfer processes are isochoric, determine:

- The pressure and the temperature at each point in the cycle.
- The thermal efficiency.

First Law of Thermodynamics: Unsteady formulation

I. Energy balance for unsteady-flow processes

In this case, the amount of mass and energy within the control volume do change with time. So, **NEVER** write $\frac{dm}{dt} = 0$ or $\frac{dE}{dt} = 0$, hence:

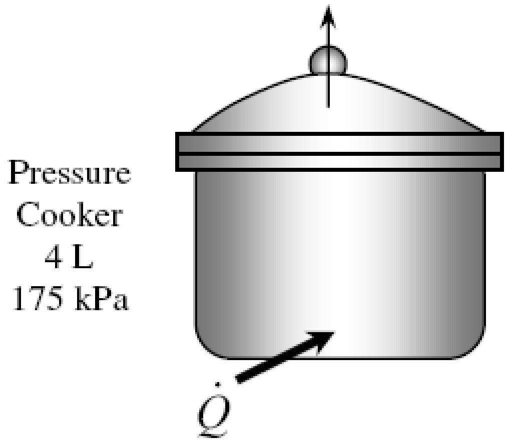
For an unsteady-flow process: $\frac{dm}{dt} \neq 0$ and $\frac{dE}{dt} \neq 0$

Under this hypothesis, and if we consider that variations in kinetic and potential energies can be neglected, the first law can be written under the following form:

$$\boxed{\left(Q_{in} + W_{in} + \sum m_i h_i\right) - \left(Q_{out} + W_{out} + \sum m_{out} h_{out}\right) = \left(m_2 u_2 - m_1 u_1\right)_{system}}$$

PROBLEM I

A pressure cooker is initially half-filled with liquid water. If the pressure cooker is not to run out of liquid water for 1 h, the highest rate of heat transfer allowed is to be determined.



PROBLEM II

A tank of 2 m^3 volume contains saturated ammonia at a temperature of 40°C. Initially the tank contains 50% liquid and 50% vapor by volume. Vapor is withdrawn from the top of the tank until the temperature is 10°C. Assuming that only vapor leaves and that the process is adiabatic, calculate the mass of ammonia that is withdrawn.

CHAPTER V

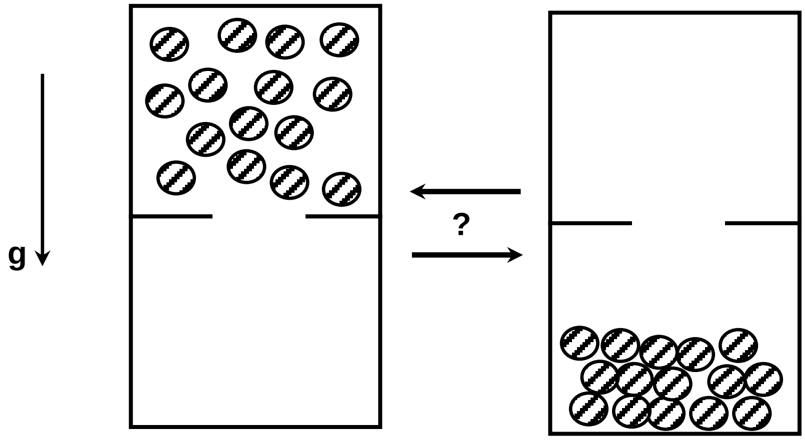
Second Law of Thermodynamics

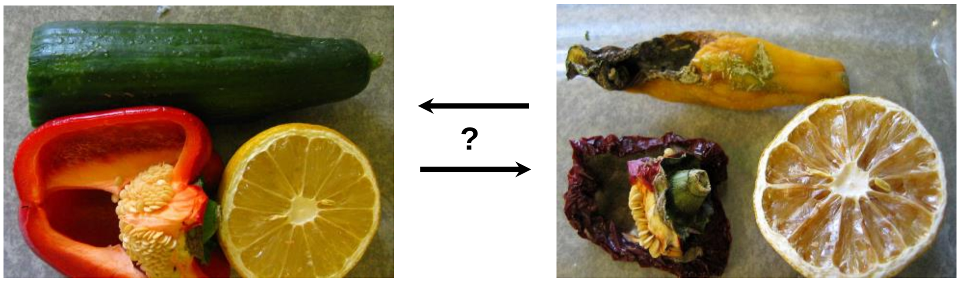
CHAPTER V

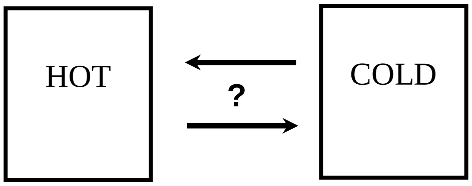
The AMAZING Second Law of Thermodynamics

The first law of thermodynamics is a representation of the conservation of energy. It is a necessary, but not a sufficient, condition for a process to occur. Indeed, no restriction is imposed by the first law on the direction of the process: this is the role of the second law.

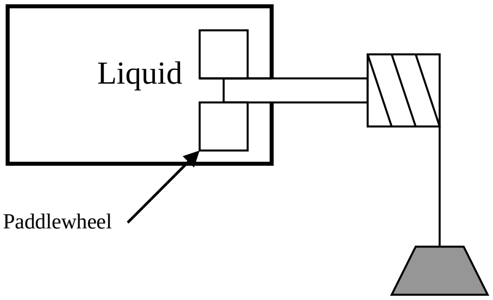
To illustrate this, let us assume the processes below, in your opinion, without any intervention from yourself, what is the most probable process (from left to right or the inverse):







Consider now the following arrangement:

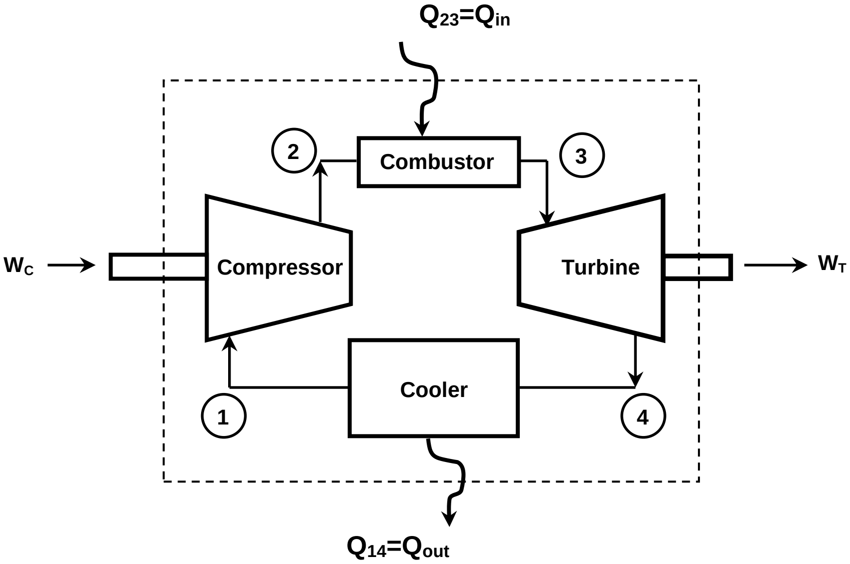


Allowing the weight to fall will turn the paddlewheel which will do work on the fluid system. Initially this may increase the kinetic energy of the fluid as it churns, but in time the circulation will stop. When this happens the temperature of the fluid will rise and the heat will be transferred to the surroundings.

From a 1st Law perspective there is no reason why one could not simply supply this same amount of heat to the fluid so that the paddlewheel would turn and the weight would be raised. However, no one has ever built a successful engine based on this principle. It simply wouldn't work. The 2nd Law provides us with a basis to determine why such a process is not feasible.

I. Heat Engines

While the 2nd Law of Thermodynamics is applicable to a wide range of topics, much of our understanding of the principle comes from the study of heat engines. We will therefore use engines as a basis for much of our study.



In this cycle, air will circulate through the heat engine to transport energy from one component to the next. This fluid is often referred to as the ***working fluid***.

W_C = Work required to compress the working fluid
W_T = Usable work produced by the engine. This work may be used to drive a truck or a car, turn a propeller, an electric generator or to perform some other useful task.

Q_{in} = Thermal energy supplied to the system. This may arise from combustion, a solar collector, a nuclear reactor or any other available heat source.
Q_{out} = Thermal energy rejected to the environment. The cooler could be a radiator similar to that used in an automobile engine.

Since operation of the engine requires a work input to turn the compressor, a portion of the output work may be utilized for this purpose, we define, therefore, the work net as:

$$|W_{net}| = |W_T| - |W_C|$$

This is a thermodynamic cycle. By definition the cycle begins and ends at the same point. In the case of an open cycle heat rejection occurs as the exhaust is emitted into the atmosphere. Hot exhaust gases are cooled to the temperature of the surroundings before entering the compressor.

From the 1st Law of Thermodynamics, we have:

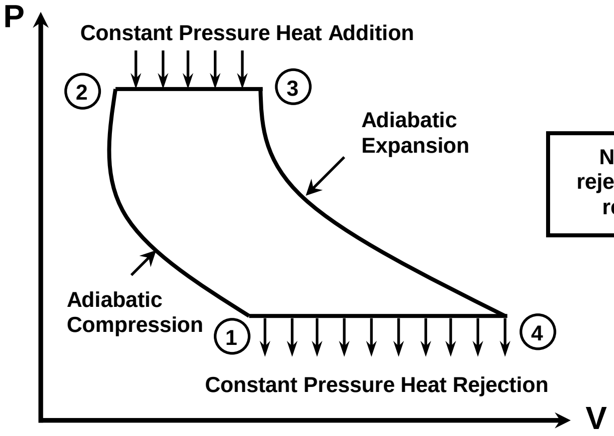
$$\Delta E_{system} = Q_{in} - W_{out}$$

For the cycle, since the starting and ending points are the same, there is no change in internal energy, so:

$$W_T - W_C = Q_{in} - Q_{out}$$

I.1. Cycle Diagram

It is very convenient to represent heat engine processes on a PV diagram:



Note that without a heat rejection, the cycle does not return to its initial state

I.2. Thermal Efficiency of a heat engine

The efficiency of a heat engine can be defined as the ratio of the useful work out (the work net) to the energy that must be input (the energy that we pay for).

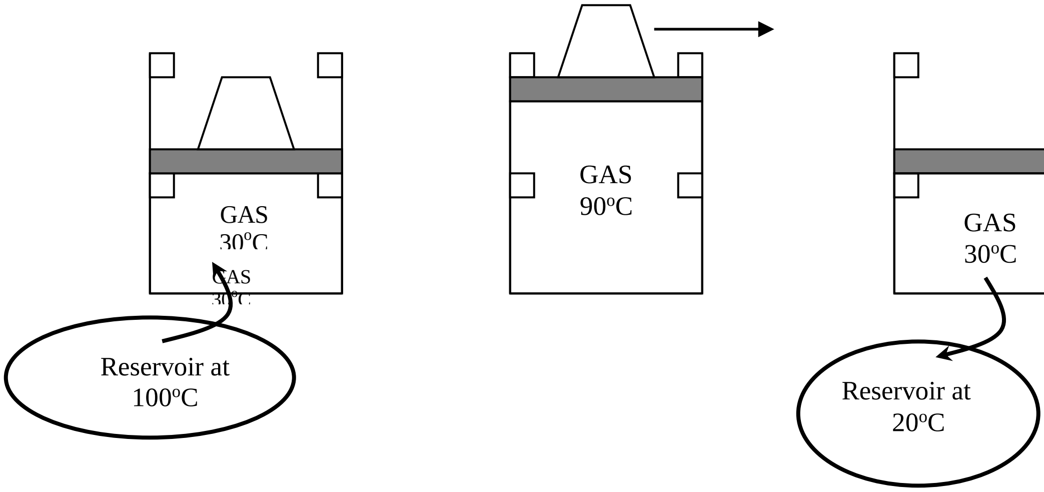
$$\eta = \frac{W_{net}}{Q_{in}}$$

Since we have that $W_{net} = Q_{in} - Q_{out}$, we may substitute into the above equation and find:

$$\boxed{\eta = \frac{\left(Q_{in} - Q_{out}\right)}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}}$$

It is probably not too surprising that we want to minimize the fraction of rejected heat in the last part of the equation in order to attain the maximum efficiency.

I.3. Second law of Thermodynamics: Kelvin-Planck statement



In the drawing above, a piston-cylinder contains a gas at 30°C. A weight is placed on the piston. Heat is then added to the gas from a reservoir at 100°C so that the gas expands. As the gas expands it does work to raise the weight and piston.

The weight now is at a higher potential energy than at state one. We slide the weight off the piston at the higher elevation. Assume that the frictional forces in sliding the weight are negligible.

Now, we wish to raise a second weight. That is, we wish the heat engine to continue to do work. The gas inside the cylinder is still heated and will not return to its initial position unless the gas is cooled.

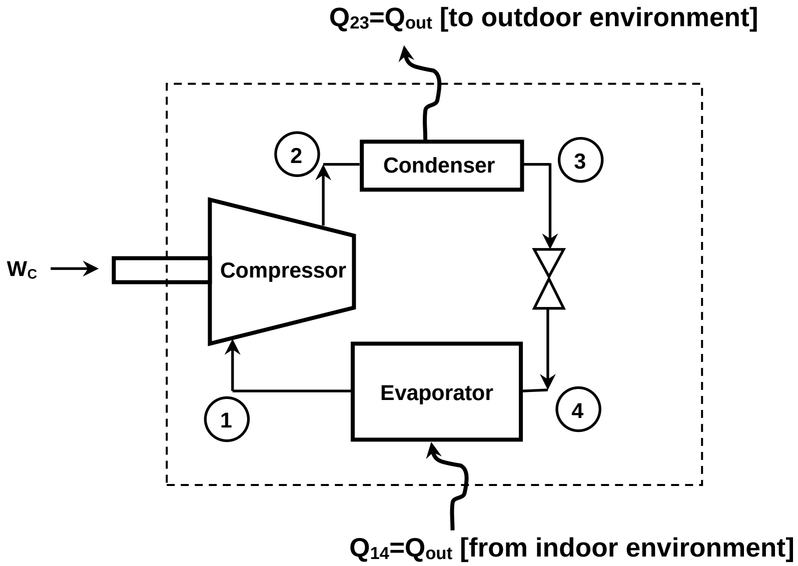
If you consider the gas turbine cycle and the piston-cylinder arrangement, in both cases we have seen that it is necessary to reject heat at the end of the work process in order to return the cycle to its initial state and repeat the process. We generalize this observation as the 2nd Law of Thermodynamics:

Second Law of Thermodynamics

"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." -- Kelvin-Planck statement of 2nd Law.

I.4. Refrigeration Cycles and Clausius statement of the second law of Thermodynamics

Up to this point we have only considered heat engines. Refrigeration cycles operate in a similar way.



The vapor refrigeration cycle involves four components, designed to produce four respective process on the working fluid.

- (Process 1-2) The compressor is designed to raise the pressure of the working fluid adiabatically. As the vapor is compressed, the temperature will rise.
- (Process 2-3) The fluid is passed through the condenser. Here no work is done on the fluid, but it is cooled to a saturated liquid. (This is the part of a residential AC unit which is located outdoors. Air is circulated around tubes containing the working fluid by a fan.)
- (Process 3-4) An expansion valve is simply a device, which does no work, nor does it transfer heat to or from the working fluid. It is simply a device to allow the pressure to drop to a lower value. A First Law analysis of this process will show that it is a constant enthalpy process. It is common for some of the liquid to flash to vapor as the fluid expands. At the same time, the temperature will drop significantly.
- (Process 4-1) The fluid is passed through the evaporator. This device consists of cold tubes often seen located inside the house in a residential unit. Here air from inside the house is blown over the cold tubes containing the working fluid. As the cold fluid gains heat, no work is done on the fluid. The working fluid is largely vaporized in this process as it returns to state 1 to begin the cycle again.

You can imagine that in a refrigeration cycle, heat will not flow from a low temperature to a high temperature without work. We see the input of work in the basic refrigeration cycle in operating the compressor. This principle is accepted as an alternate statement of the Second Law of Thermodynamics.

"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." -- Clausius statement of 2nd Law.

The two statements of the 2nd Law can be shown to be equivalent.

Practical statement of the second law of Thermodynamics

In the normal course of events, when things are not actively maintained, they deteriorate. Suns burn out, mountains crumble, cars rust, houses fall down, etc. The reverse process does not happen without intervention. You might buy an old, rusty car and restore it, but it will take work. In a like fashion, process involving an energy transfer will only occur in such a way so as to decrease the quality of energy. We can, within a finite control volume, transfer energy to the system so as to increase the quality of energy within that system. However, the work that we input required that we decrease the quality of energy from an area outside the system. When we consider the universe as a whole, the quality of energy in the universe has still deteriorated.

I.4.1. Coefficient of performance

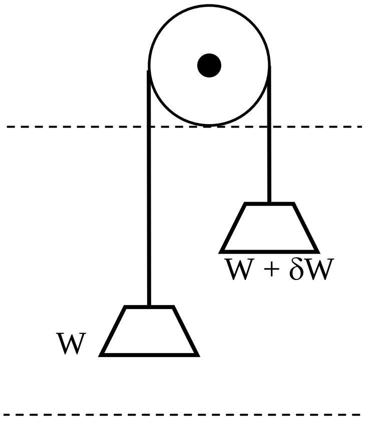
When describing heat engines, we introduced the concept of engine efficiency as the desired output divided by the energy input. Similarly, we define the coefficient of performance (COP) of a refrigerator:

$$COP = \frac{Desired\ Ouput}{Required\ Input} = \frac{Q_{14}}{W_{net}} = \frac{Q_{14}}{Q_{23} - Q_{14}}$$

The definition is basically the same as that of thermal efficiency. The primary reason for the change in terminology is that a COP: is often greater than 1. The term is used to avoid speaking of any efficiency greater than 100%.

I.5. Reversibility

Consider a system of pulleys and weights as shown:

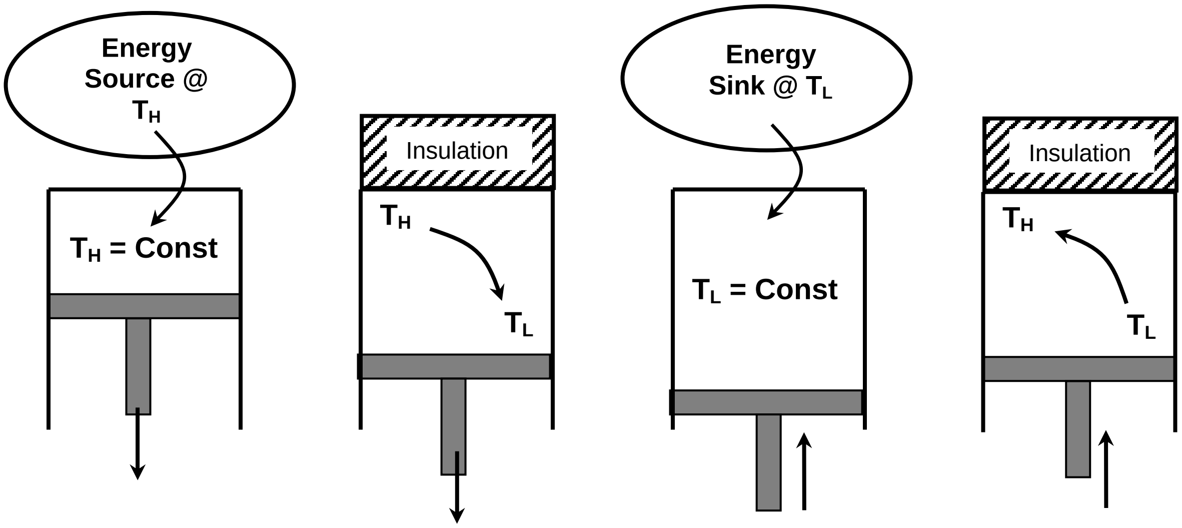


In order for the weight on the right to raise the weight on the left, it is essential that W+ δW > W. How large must δW be? Well, it must be large enough that it compensates for the effects of friction in the pulley, the friction associated with the flexing of the cable, etc. If we use very good bearings, then the required extra weight on the right may approach zero. Can it reach zero? No, this would result in static equilibrium and the weights will not move. It is essential that δW be greater than zero; it may approach, but never reaches zero, even with perfect bearings.

We see that, in order for the process of raising the left weight to occur, the loss in potential energy on the right must be greater than the gain in potential energy on the left. As an idealization only, we may assume that the weight δW may be so small that it can be treated as zero. In such a case, the weight on the right and left are equal and the direction that the pulley moves would be completely reversible. Such processes never occur in nature, but may be approached in the limit.

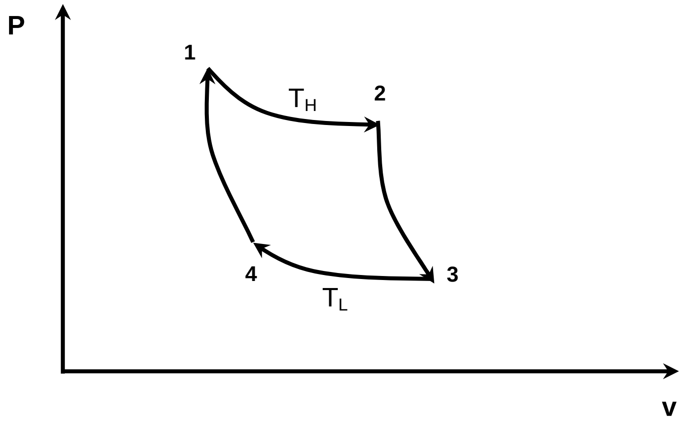
II. Carnot Cycle

The Carnot cycle was first proposed in 1824, by Sadi Carnot. The interest in the cycle is largely theoretical, as no practical Carnot cycle engine has yet been built.
Nevertheless, **it can be shown to be the most efficient cycle possible**, so that considerable attention has been given at discovering ways of making the more practical cycles look, as much as possible, like the Carnot.



Process 1-2 Process 2-3 Process 3-4 Process 4-1

(Process 1-2) A constant temperature heat addition.
(Process 2-3) An adiabatic expansion
(Process 3-4) A constant temperature heat rejection.
(Process 4-1) An adiabatic compression



II.1. Carnot Cycle Efficiency

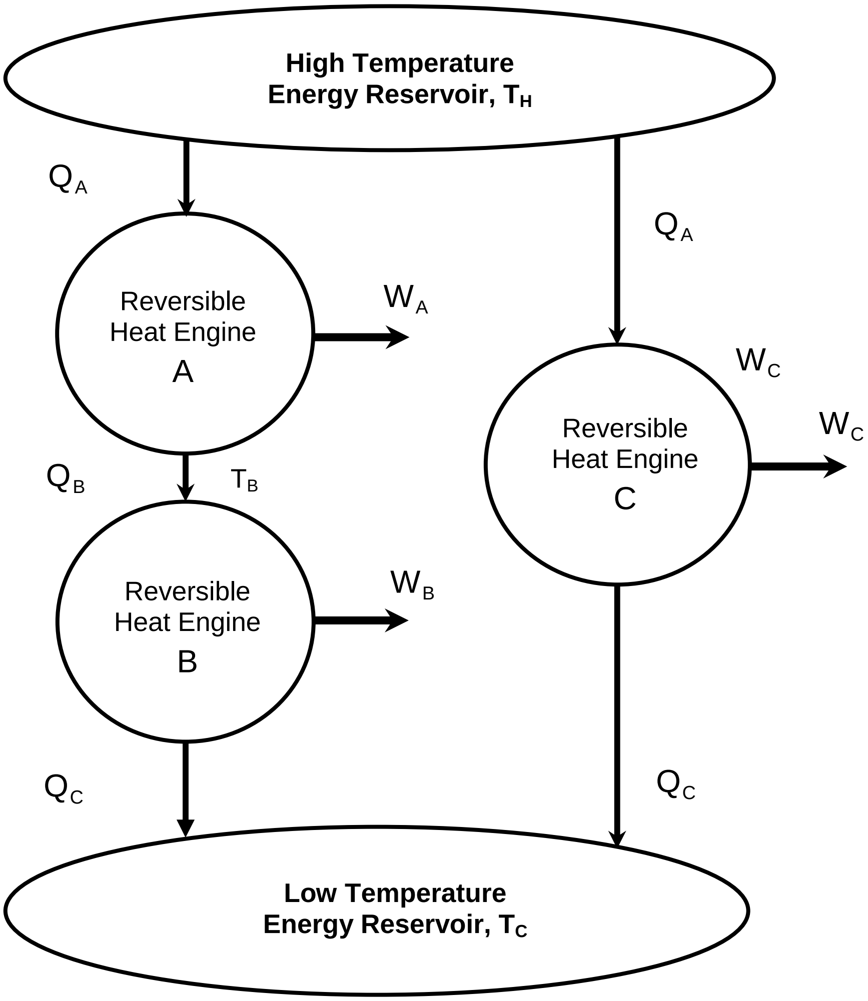
Like other heat engines, the Carnot cycle efficiency can be attained from the relationship:

$$\eta = \frac{W_{net}}{Q_{in}} = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

II.1.1. Carnot cycle principles

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.



If we consider the Carnot cycle above, since a control volume could be drawn about engines A & B together, they may be considered as a single reversible engine.
The efficiency of Engine A&B must be the same as that of Engine C since both are reversible. Also

$$\mathbf{W_A + W_B = W_C}$$

Since energy reservoirs are characterized by their temperatures, the thermal efficiency of reversible heat engines is a function of the reservoir temperatures only. That is,

$$\frac{Q_L}{Q_H} = f(T_H, T_L)$$

Applying this idea to the three engines separately,

$Q_A/Q_C = f(T_A, T_C)$, $Q_A/Q_B = f(T_A, T_B)$, $Q_B/Q_C = f(T_B, T_C)$

For the efficiency of A&B to be equal to that of C

$f(T_A, T_C) = f(T_A, T_B) \cdot f(T_B, T_C)$

A careful examination of this equation reveals that the left hand side is a function of T_A and T_C, and therefore the right hand side must also be a function of T_A and T_C only and not, T_B. This condition will be satisfied only if the function has the following form:

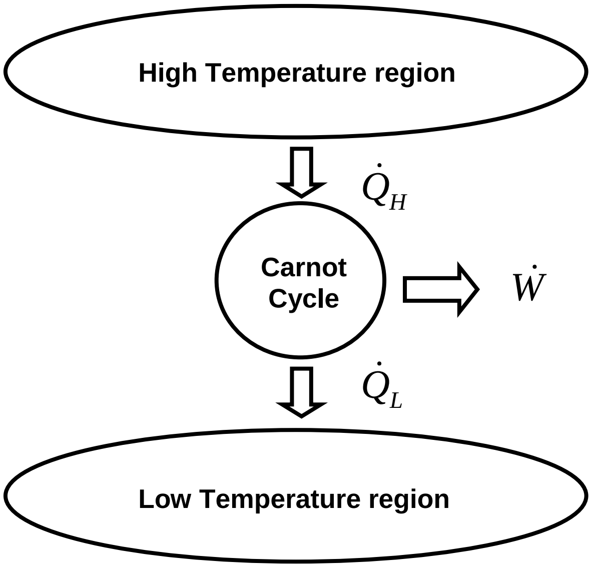
$\Phi(T_A)/\Phi(T_C) = [\Phi(T_A)/\Phi(T_B)] \cdot [\Phi(T_B)/\Phi(T_C)]$

From this relationship Kelvin proposed a **temperature scale** in which $\Phi(T) = T$, such that:

$$\boxed{\eta = 1 - \frac{T_L}{T_H}}$$

II.1.2. Applications of the Carnot Cycle

a. Carnot Cycle Engine



From the first law of thermodynamics:

$$\dot{Q}_H = \dot{Q}_L + \dot{W}$$

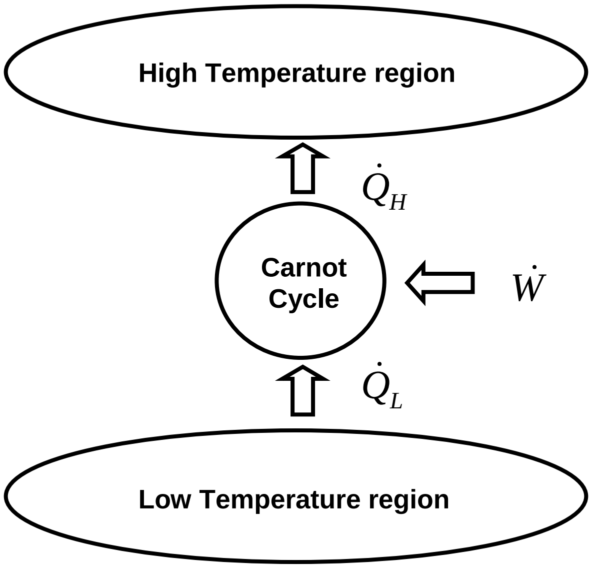
From the definition of efficiency, we find for the Carnot engine:

$$\eta = 1 - \frac{\dot{Q}_L}{\dot{Q}_H}$$

Using the thermodynamic temperature scale:

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

b. Carnot Cycle Refrigerator



From the first law of thermodynamics:

$$\dot{Q}_H = \dot{Q}_L + \dot{W}$$

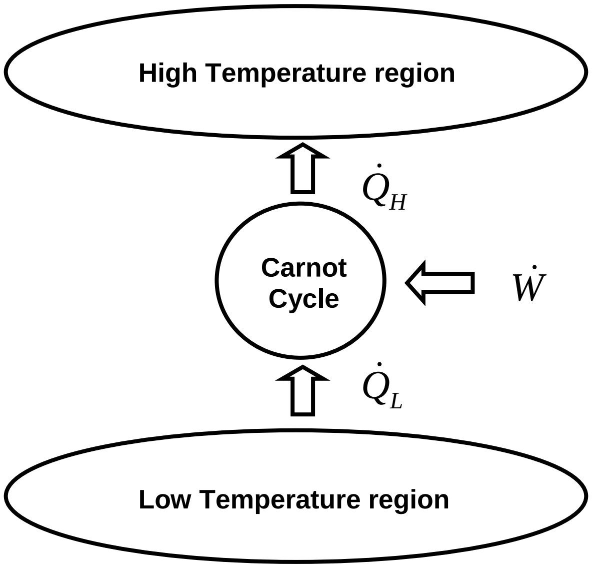
From the definition of Coefficient of Performance (COP), we find for the Carnot refrigeration cycle:

$$COP = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{1}{\frac{\dot{Q}_H}{\dot{Q}_L} - 1}$$

Using the thermodynamic temperature scale:

$$COP = \frac{1}{\frac{T_H}{T_L} - 1}$$

C. Carnot Cycle Heat Pump



From the first law of thermodynamics:

$$\dot{Q}_H = \dot{Q}_L + \dot{W}$$

From the definition of Coefficient of Performance (COP), we find for the Carnot refrigeration cycle:

$$COP = \frac{\dot{Q}_H}{\dot{W}} = \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{1}{1 - \frac{\dot{Q}_L}{\dot{Q}_H}}$$

Using the thermodynamic temperature scale:

$$COP = \frac{1}{1 - \frac{T_L}{T_H}}$$

II.2. Applications

Example 1

An inventor claims to have developed a power cycle capable of delivering a net work output of 410 kJ for an energy input by heat transfer of 1000 kJ. The system undergoing the cycle receives the heat transfer from hot gases at a temperature of 500 K and discharges energy by heat transfer to the atmosphere at 300 K. Evaluate this claim.

Example 2

When a fridge stands, in a room at 20°C, the motor has to extract 500 W of heat from the cabinet at 4°C to compensate for less than perfect insulation. How much power must be supplied to the motor if its efficiency is 80% of the maximum efficiency?

Example 3

An ideal or Carnot heat pump is used to heat a house to T_H=294 K, how much work must be done by the pump to deliver Q_H=3350 J of heat into the house when the outdoor temperature is 273 K and 252 K.

Example 4

A Carnot power cycle using air as a working fluid has a thermal efficiency of 40%. At the beginning of isothermal expansion, the pressure is 620 kPa, and the specific volume is 0.1 m^3/kg. If the heat input for the cycle is 50 kJ/kg, determine:

- The highest and the lowest temperature for the cycle.
- The work and heat for each process of the cycle.

Assume air to be an ideal gas with constant specific heats.

CHAPTER VI

Entropy

CHAPTER VI

ENTROPY

In the previous chapter, we tried to understand the 2nd law of thermodynamics from a conceptual perspective. In this chapter, we begin to consider these concepts in a more analytical manner. In the process, we will introduce a new property, **ENTROPY**, which is defined as follows:

$$\boxed{dS = \left.\frac{\delta Q}{T}\right|_{rev}}$$

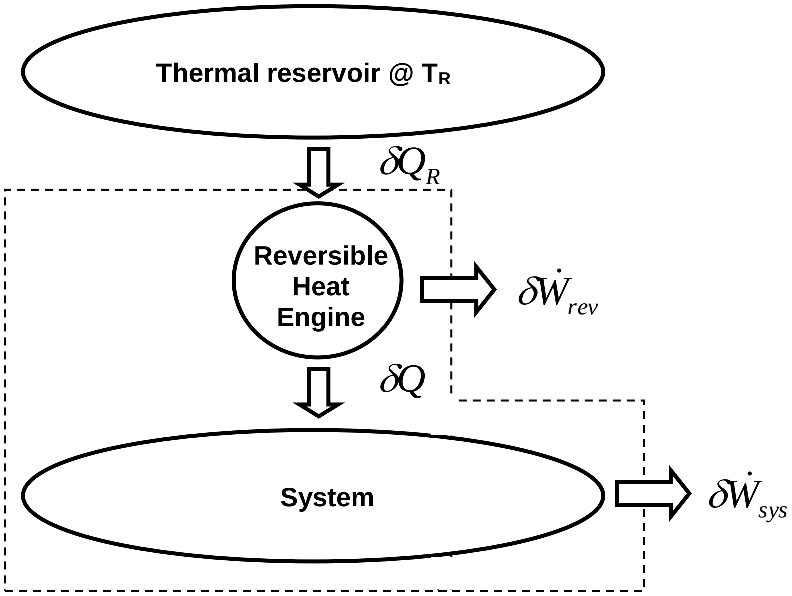
That is, a differential change in entropy corresponds to a differential quantity of heat being transferred divided by the temperature at which is it transferred in a reversible process.

I. Clausius Inequality:

Recall the Kelvin-Planck statement of the 2nd Law.

"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."

Clausius proceeded to consider a device, shown below, which violates the 2nd Law. Work is produced, but the device receives heat from a single reservoir



Let us apply the 1st Law for the control volume:

$$\Delta E_{system} = Q_{in} - W_{out}$$

The total work output is the sum of that for the system and the heat engine:

$$\delta W_T = (\delta W_{rev} + \delta W_{sys})$$

For an infinitesimal part of the engine cycle we write:

$$dE_{system} = \delta Q_R - \delta W_T$$

Since the cyclic device is a reversible heat engine, it follows from the definition of the thermodynamical temperature scale that:

$$\delta Q_R/\delta Q = T_R/T$$

Then, we can obtain:

$$dE_{system} = \delta Q \frac{T_R}{T} - \delta W_T$$

Consider the operation of the device through a complete engine cycle. For a cycle the energy of the control volume must return to its initial value so that the energy term drops out.

$$0 = T_R \oint \frac{\delta Q}{T} - W_T$$

Or

$$W_T = T_R \oint \frac{\delta Q}{T}$$

As noted previously, if the total work is positive then this device would violate the Kelvin-Planck statement of the 2nd Law. It follows that the total work must be zero or negative.

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

Now let us run the engine in reverse. If the path for the cycle is reversed, then the sign of the integral is reversed and the integral will become greater than or equal to zero. This would likewise result in a violation of the 2nd Law. The only way that the process can be reversed is if the integral gives a value of zero.

If the integral of δQ/T about a cycle is equal to zero, then the process is said to be reversible

In the special case that the cyclic integral is zero, then the quantity under the integral, δQ/T, returns to its initial value during the cycle. It behaves like a thermodynamic property. Then, the entropy (S):

$$dS = \left.\frac{\delta Q}{T}\right|_{rev}$$

II. Increase in Entropy Principle

Since δQ/T is zero for a reversible process and less than zero for an irreversible process, then

$$\oint \frac{\delta Q}{T} \le \oint \frac{\delta Q}{T}\bigg|_{rev}$$

and

$$\oint \frac{\delta Q}{T} \le dS$$

Finally, for any process between two states:

$$dS \ge \frac{\delta Q}{T}$$

or

$$S_2 - S_1 \ge \int_1^2 \frac{\delta Q}{T}$$

or

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{generated}$$

A process can only occur if the entropy generated is greater than or equal to zero

And this can be considered as a quantative statement of the second law.

Example
Air is compressed by a 8 kW compressor from P_1 to P_2. The air temperature is maintained constant at 25°C during this process as a result of heat transfer to the surrounding medium at 10°C. Determine the rate of entropy change of the air. State the assumptions made in solving this problem.

III. Gibbs equations or Tds Relationships

From the 1st Law for a closed system:

$$dE_{system} = \delta Q_{in} - \delta W_{out}$$

Neglecting kinetic and potential energy, this reduces to:

$$dU_{system} = \delta Q_{in} - \delta W_{out}$$

From the definition of entropy, S, we have:

$$\delta Q_{rev} = T \cdot dS$$

For a simple compressible substance, we can write a reversible work term as:

$$\delta W = P\,dV$$

After substitution and rearranging

$$T\,dS = dU + P\,dV$$

The alternate form of this relationship is obtained using enthalpy:

$$H = U + P\,V$$

So that after differentiation,

$$dH = dU + P\,dV + V\,dP$$

Replacing the last two terms in the above T-dS relationship:

$$T\,dS = dH - V\,dP$$

These T-dS relationships form the basis for evaluation of entropy as a thermodynamic property.

IV- Entropy for Liquids & Solids & ideal gases

IV.1. Entropy for liquids and solids

Normally, we expect volume changes to be small as liquids or solids undergo a change in thermodynamic state. Furthermore, $C_p \approx C_v \approx C$ so that:

$$T\,ds = du + P\,\cancel{dv} \approx C\,dT$$

Then,

$$ds = C\,dT/T$$

or,

$$\boxed{s_2 - s_1 = C_{avg} \ln(T_2/T_1)}$$

IV.2. Entropy for ideal gases

Using the T-ds relationships, we substitute the ideal gas law for the last terms:

$$\mathbf{T\,ds = du + P\,dv = C_v\,dT + R\,T\,dv/v}$$

and

$$\mathbf{T\,ds = dh - v\,dP = C_p\,dT - R\,T\,dP/P}$$

Divide by T and integrate:

$$\mathbf{s_2 - s_1 = C_{v,avg} \ln(T_2/T_1) + R \ln(v_2/v_1)}$$ 1st T-ds relationship

and

$$\mathbf{s_2 - s_1 = C_{p,avg} \ln(T_2/T_1) - R \ln(P_2/P_1)}$$ 2nd T-ds relationship

Note that the above expressions may be placed on a molar basis by dividing by the molecular weight of the particular gas:

$$\hat{s}_2 - \hat{s}_1 = \hat{C}_{v,avg} \ln(T_2/T_1) + (R/M) \ln(v_2/v_1)$$

and

$$\hat{s}_2 - \hat{s}_1 = \hat{C}_{p,avg} \ln(T_2/T_1) - (R/M) \ln(P_2/P_1)$$

IV.2.1. Isentropic Processes (ΔS = 0) of Ideal Gases

Isentropic refers to a process which occurs at constant entropy, s. From the definition of entropy, $dS = \int \delta Q/T \big|_{rev}$ we see that for a reversible, adiabatic process ΔS = 0.

Let us take a look at the specific heats relationships:

$$C_p = C_v + R$$
$$k = C_p/C_v$$

From the 1st T·dS relationship we developed the following relationship for an ideal gas:

$$s_2 - s_1 = C_{v,avg} \ln(T_2/T_1) + R \ln(v_2/v_1)$$

For an isentropic process Δs = 0 so that after simplifying and rearranging.

$$\ln(T_2/T_1) = (R/ C_{v,avg})\cdot\ln(v_1/v_2)$$

then, we have:

$$C_p/C_v = 1 + R/C_v$$

and

$$k - 1 = R/C_v$$

Substitute this result into our simplified T-dS relationship:

$$\ln(T_2/T_1) = (k-1) \ln(v_1/v_2)$$

Raise both sides to the e power:

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}}$$ 1st Isentropic relationship for an ideal gas

For a particular ideal gas

$$P_1v_1/T_1 = R = P_2v_2/T_2$$

so that

$$v_2/v_1 = P_2T_1/P_1T_2$$

Substitute into 1st isentropic relationship

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

2nd Isentropic relationship for an ideal gas

And, $P_2v_2/P_1v_1 = (v_1/v_2)^{k-1}$

So that

$$\boxed{\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^{k}}$$

3rd Isentropic relationship for an ideal gas

Example

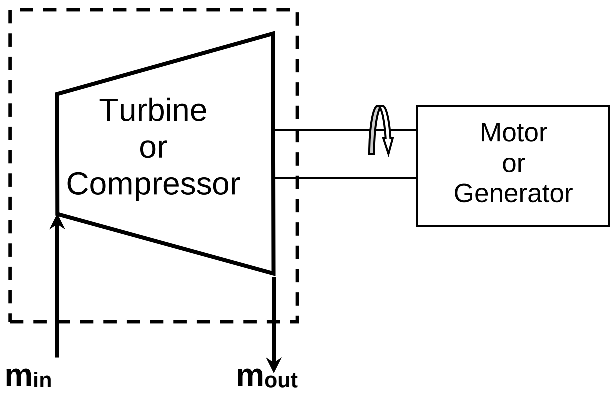
A 0.5 m^3 insulated rigid tank contains 0.9 kg of carbon dioxide at 100 kPa. Now paddle wheel work is done on the system until the pressure in the tank rises to 120 kPa. Determine the entropy change of carbon dioxide during this process in kJ/K. Assume constant specific heats.

V. Steady Flow Work

We have previously discussed work for piston-cylinder devices. In this closed system, the work obtained from the fluid can be evaluated as:

$$W = \int P \cdot dV$$

However, other devices do create work without lending themselves to this type of piston-cylinder devices (example: turbine). Consider a typical open system as represented by a turbine or a compressor.
In these cases there is no moving of the control surfaces.



Let us analyze this sytem:

We consider a control volume including the turbine or the compressor.

Conservation of Mass

$$\left.\frac{dm}{dt}\right|_{CV} = \dot{m}_{in} - \dot{m}_{out} \Rightarrow \dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

Conservation of Energy

We will assume steady state (no energy storage inside control volume) and neglect any heat transfer. We will also neglect variations in kinetic and potential energies.

$$0 = \dot{m}_{in}\ h_{in} - \dot{m}_{out}\ h_{out} + \cancel{\dot{Q}_{in}} - \dot{W}_{shaft}$$

Then:

$$\dot{W}_{shaft} = \dot{m}\ \left(h_{in} - h_{out}\right)$$

Second Law Analysis

If we do not know how much irreversibility is introduced in the system, we may be interested in finding the maximum possible work.

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{generated}$$

Since we assume an adiabatic process then $\delta Q = 0$. Further, if we assume that the process is reversible then $S_{gen} = 0$, so that

$$S_2 - S_1 = 0$$

If we then recall the 2nd T·dS relationship

$$T\, d\cancel{S} = dh - v\, dP$$

So that,

$$dh = v\, dP$$

Substitute this result back into the 1st Law result:

$$\dot{W}_{shaft} = \dot{m}\, \left(v\, \left(P_{in} - P_{out}\right)\right)$$

$$\dot{W}_{shaft} = -V\left(P_{out} - P_{in}\right)$$

$$\dot{W}_{shaft} = -V\, \Delta P$$

Please note, this is not the same as $\dot{W}_{shaft} = P\,\Delta V$ *that we obtained for a closed system.*

Example

Liquid water enters a 10 kW pump at 100 kPa pressure at a rate of 5 kg/s. Determine the highest pressure the liquid water can have at the exit of the pump. Neglect the kinetic and potential energy changes of water and take the specific volume of water to be 0.001m^3/kg.

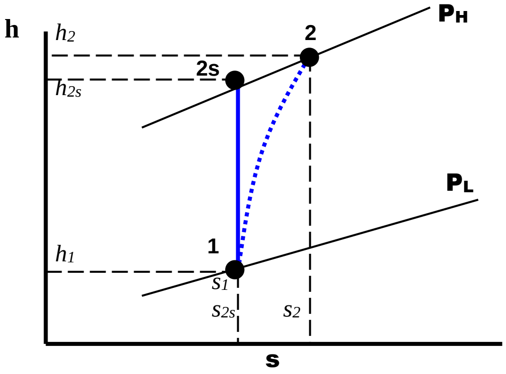
VI. Isentropic Efficiencies of Steady Flow Devices

We have been considering the performance of an ideal compressor or ideal turbine, i.e. one which operates both adiabatic ally and reversibly. However, no real equipment can operate quite so efficiently. We define the efficiency of an adiabatic compressor as:

$$\eta_{compressor} = \frac{W_{reversible+adiabatic}}{W_{real}} = \frac{\Delta h_{reversible+adiabatic}}{\Delta h_{real}}$$

Note: remember that reversible + adiabatic = isentropic ($ds = s_2 - s_1 = 0$)

Consider a typical compression process as shown on an h-s (enthalpy - entropy) diagram:

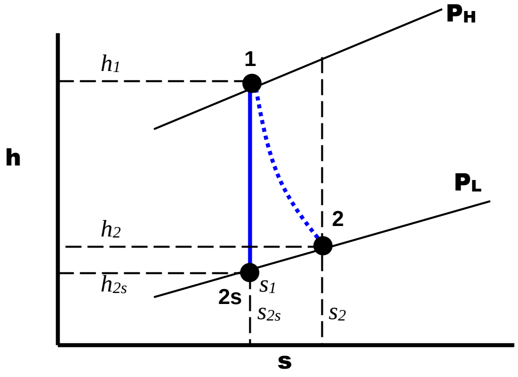


Then
$$\boxed{\eta_{compressor} = \frac{h_{2s} - h_1}{h_2 - h_1}}$$

Now, for a turbine, the definition of efficiency is a little different than for compressors in that the actual work out of a turbine is less than the reversible adiabatic work. In order to ensure that efficiencies of less than 100%, we write:

$$\eta_{Turbine} = \frac{W_{real}}{W_{reversible+adiabatic}} = \frac{\Delta h_{real}}{\Delta h_{reversible+adiabatic}}$$

Consider a typical process through a turbine as shown on an h-s diagram:



Then
$$\boxed{\eta_{Turbine} = \frac{h_2 - h_1}{h_{2s} - h_1}}$$

Example

Steam enters an adiabatic turbine at 8 MPa and 500°C with a mass flow rate of 3 kg/s and leaves at 30 kPa. The isentropic efficiency of the turbine is 0.90. Neglecting the kinetic energy change of the steam, determine (a) the temperature at the turbine exit and (b) the power output of the turbine.