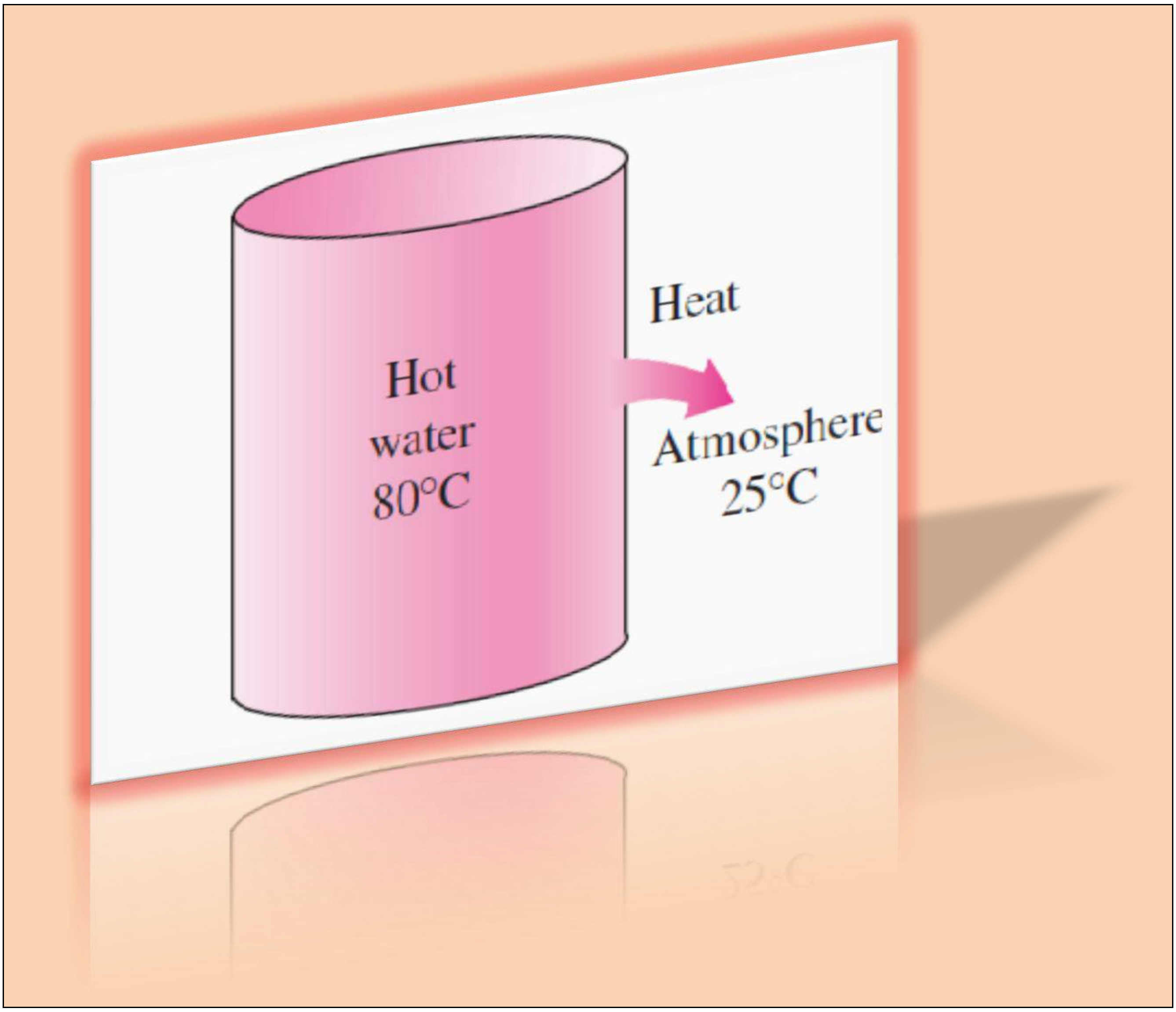
Chemical Engineering Department
Kumasi Polytechnic

Lecture Notes

CHEMICAL ENGINEERING THERMODYNAMICS



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Chapter 1 FUNDAMENTAL CONCEPTS AND DEFINITIONS

Nature of thermodynamics

Thermodynamics emerged as a science in the 18th century when Savery and Newcomen attempted to build a steam engine. The engine developed by Newcomen was very inefficient but it opened the way for the development of thermodynamics. The term 'thermodynamics' was coined by Kelvin in 1849 and the first thermodynamics book was written by Rankine.

Classical thermodynamics embodies a macroscopic approach to the study of thermodynamics and it does not require knowledge of the behaviour of the individual particles of a system; it is concerned only with **continua**. It provides a direct and easy way to obtain the solution of engineering problems without being overly cumbersome. In contrast, **Statistical** thermodynamics involves the collective study of the behaviour of individual particles; it is very elaborate and will not be used in this text.

Thermodynamics is the science which deals with energy as a property of matter and its transformation into heat and work; it deals with the conversion of energy from one form to another. It also deals with various properties of substances and the changes in these properties due to energy transformations. Energy can be viewed as the capacity to do work or as the ability to cause changes.

Thermodynamics finds its origin in experience and experiment, from which are formulated a few postulates that form the foundation of the subject. The **first law** of thermodynamics, for example, is simply an expression of the conservation principle. The **second law** asserts that processes occur in a certain direction but not in the reverse direction; for example, a cup of hot water left in the open eventually cools, but a cup of cold coffee left in the open never gets hot by **itself.**

Application of thermodynamics

It is used to describe the performance of propulsion systems, power generation systems, and refrigerators, and to describe fluid flow, combustion, and many other phenomena.

Dimensions and units

An important component to the solution of any engineering thermodynamic problem requires the proper use of units. Any physical quantity can be characterized by dimensions. The magnitudes assigned to the dimensions are called units. Primary dimensions include mass, length, time, and temperature. Secondary or derived dimensions are expressed in terms of the primary dimensions.
Two systems of units are still used extensively: the English system (a.k.a United States Customary System) and the metric SI system.

Some SI and English units

Unit	**Metric system**	**English system**
Mass	Kilogram, *kg*	Pound-mass, *Ibf*
Length	Meter , *m*	Foot, *ft*
Time	Second, *s*	Second, *s*
Mole or gram mole	Mol or gmol	Pound-mol, *Ib-mol*

Force[1]	Newton, *N*	Pound-force, *Ibf*
Energy	Joule, *J*	British thermal unit, *Btu*

Note:
(1 Ibm = 0.45359 kg; 1 ft = 0.3048 m; ***;*** *1 N = 1 kg. m/s*^{2}*; 1 Ibf = 32.174 Ibm.ft/s*^{2}*; I Btu = 1.055 kJ)*

Prefixes for SI units

Multiple	Prefix	Symbol	Multiple	Prefix	symbol
10^{-9}	Nano	*N*	10^{3}	kilo	*K*
10^{-6}	Micro	μ	10^{6}	mega	*M*
10^{-3}	*Milli*	*M*	10^{9}	*giga*	*G*
10^{-2}	centi	C			

Force

From Newton's second law, force is expressed as the product of mass *m* and acceleration *a*:

$$F = ma$$

The Newton is defined as the force which when applied to a mass of 1 kg produces an acceleration of 1 m/s^2; thus the Newton is a derived unit representing 1 kg m s^{-2}. In the English Eng. System of units, the pound force is defined as that force which accelerates 1 pound mass 32.174 feet per second per second. Newton's law must therefore include a proportionality constant if it is to be reconciled with this definition. Hence, we can write

$$F = \frac{1}{g_c} ma$$

wherefrom

$$1\,(\mathrm{Ib_f}) = \frac{1}{\mathrm{g_c}} \times 1(Ibm) \times 32.174(ft)(s)^{-2}$$

and $$\mathrm{g_c} = 32.1740(Ibm)(ft)(Ib_f)(s)^{-2}$$

The pound force is equivalent to 4.4482216 N.
Note: Weight properly refers to the force of gravity on a body, and is therefore correctly expressed in Newton or in pounds force.

Temperature

Temperature is commonly measured with liquid-in-glass thermometers, wherein the liquid expands when heated. The SI unit is Kelvin, K. Celcius temperatures, which is equal in size to the Kelvin, are defined in relation to Kelvin temperatures by

$$T\,(^0C) = T\,(K) - 273.15.$$

Engineers in US still use two other scales: the Rankine scale and the Fahrenheit scale. The Rankine scale is directly related to the Kelvin scale by

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[1] Force is taken to be a primary unit in the English system. Also note that, the acceleration due to gravity, g, is 9.807 m/s^2 or 32.174 ft/s^2 at sea level and 45^0 latitude.

$$T\,(R) = 1.8\,T\,K$$

The Fahrenheit scale is related to the Rankine scale by an equation analogous to the relation between the Celcius and Kenvin scales:

$$T\,(^0F) = T\,(K) - 459.67$$

The relation between the Fahrenheit and Celcius scales is given by

$$T\,(^0F) = 1.8\,T\,(^0C) + 32$$

Zeroth law of thermodynamics

It states that whenever two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with one another.

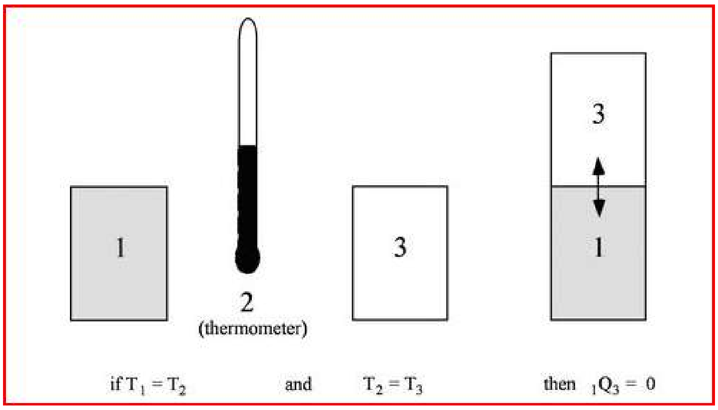


Figure 1.2: Schematic representation of the Zeroth law

From the Zeroth law, if we want to know if two bodies are at the same temperature, it is not necessary to bring them into contact and see if the observable properties change with time. It is necessary only to see if they are individually in thermal equilibrium with a third body, which we call **thermometer.** A thermometer has at least one property which is very sensitive to temperature. This property is called a **thermometric property.**

Volume

It is a quantity representing the product of 3 lengths. The volume of a substance, like its mass, depends on the amount of material considered. Specific volume is defined as volume per unit mass. Density is the reciprocal of specific volume.

Pressure

The pressure exerted by a fluid on a surface is defined as the normal force exerted by the fluid per unit area of the surface. The SI unit of pressure is Newton per square meter, called the Pascal; in English system, the most common unit is the *pound force per square inch (psi).*

Pressure is also expressed as the equivalent height of a column of fluid, since a vertical column of a given fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height. This is the basis for the use of manometers for pressure measurement.

For a mass of fluid in a column, which is being acted upon by the force of gravity, we can write the mass as

$$m = A\,h\,\rho$$

where A is the cross-sectional area of the column, h is the height, and ρ is the fluid density. Thus

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{Ah\rho g}{A} = h\rho g$$

The *torr* is the pressure equivalent of 1 mm of Hg at 0 ^{0}C in a standard gravitational field, and is equal to 133.322 Pa. Another unit of pressure is the standard atmosphere (*atm*), the approximate average pressure exerted by the earth's atmosphere at sea level, defined as 101,325 Pa, 101.325 kPa, or 0.101325 MPa. The bar, an SI unit defined as 10^5 Pa, is equal to 0.986923 atm.

1 MPa = 10^6 N/m^2 = 10^3 kPa = 10 bar

The pressure used in **all** calculations of state is the **absolute pressure**. However, pressures are often measured relative to **atmospheric pressure,** called **gauge** or **vacuum** pressures. In the English system the absolute pressure and gage pressures are distinguished by their units, psia (pounds force per square inch absolute) and psig (pounds force per square inch gage), respectively; but, the SI system makes no distinction between absolute and gage pressures.

Absolute pressures must be used in thermodynamic calculations.

These pressures are related by

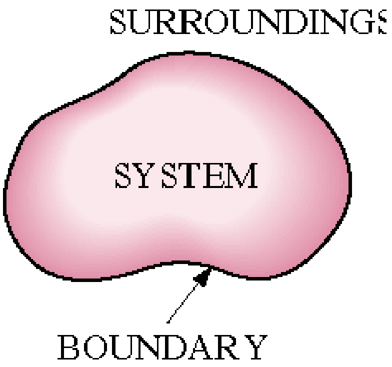
$$P_{gage} = P_{abs} - P_{atm}$$
$$P_{vac} = P_{atm} - P_{abs}$$

Chapter 2 BASIC TERMINOLOGIES AND CONCEPTS

System and Surrounding

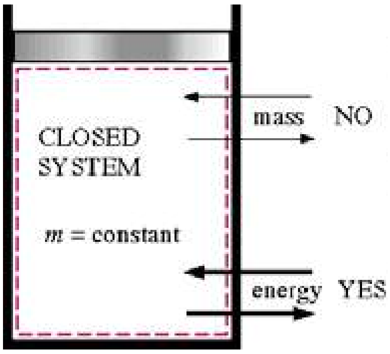
A *system* is taken to be any object, any quantity of matter, or any region, selected for study and set apart (mentally) from everything else, which is called the *surroundings*. The surroundings represent the region outside the system. The imaginary envelope which encloses the system and separates it from its surroundings is called the *boundary* of the system.

The boundary may be stationary or in motion, real or imaginary, heat conducting or insulated, permeable or impermeable.



Classification of systems

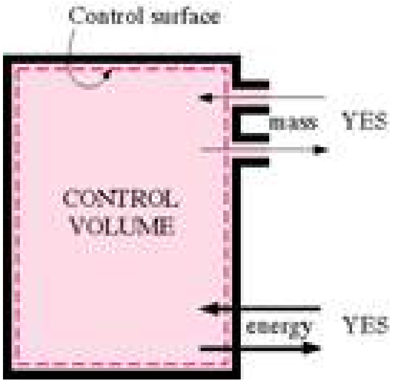
A **closed system** consists of a fixed amount of mass and no mass may cross the system boundary. The closed system boundary may move. Examples of closed systems are sealed tanks and piston cylinder devices. However, energy in the form of heat and work may cross the boundaries of a closed system.



An open system (control volume) is one that exchanges both energy and matter with its surroundings. It is bounded by a control surface. Examples of open systems are pumps, compressors, turbines, valves, and heat exchangers.

An isolated system does not interact with the surroundings in any manner since the boundary does not permit the exchange of heat or energy with its surroundings. It is a general system of fixed mass where no heat or work may cross the boundaries.

Since some of the thermodynamic relations that are applicable to closed and open systems are different, it is extremely important to identify the type of system before analyzing it.



Thermodynamic properties

A property is a **characteristic** of a system and it is used to specify the condition or state of a system. E.g. pressure, temperature, mass, volume. Usually the value of a property is directly measurable.

Extensive properties such depend on the size of the system and hence the mass of the system. Examples include mass, volume, and total energy.

Intensive properties are independent of the size of the system. They include pressure and temperature. A specific property (denoted by lower case letters) refers to an extensive property per unit mass. *eg.* $v = V/m$.

It is important to note that properties describe states only when the system is in equilibrium.

Thermodynamic state

The word **state** refers to the condition of a system as described by its properties. A system's state is often specified by providing a few of its properties; all other properties may be determined from the known ones.

Thermodynamic Process

Any change from one state to another is called a process. If the state of a system changes, then it is undergoing a process. The succession of states through which the system passes defines the **path** of the process.

Isothermal, isobaric and **isochoric** (isometric) processes occur at constant temperature, pressure and volume respectively. In a **steady state** process, none of the properties changes with time.

Thermodynamic cycle

A system has completed a thermodynamic cycle when the system undergoes a series of processes and then returns to its original state, so that the properties of the system at the end of the cycle are the same as at its beginning. In other words, if, at the end of the process, the properties have returned to their original values, the system has undergone a **cyclic** process or a **cycle**; the net change of any property **x** is equal to zero: $\oint dx = \Delta x = 0$

State function and path function

Thermodynamic quantities can be grouped into 2: state functions and path functions. The change in value of a state function depends only on its initial and final states and not on the path taken. Thus, properties are state functions. In contrast, the change in the value of a path function depends on the path of the process. Work and heat form the two major process functions in thermodynamics.

State Postulate

The state of a system is described by its properties. In practice not all properties must be known before the state is specified. Once a sufficient number of properties are known, the state is specified and all other properties are determined. The number of properties required to determine the state of a simple, homogeneous system is given by the state postulate:

The thermodynamic state of a simple compressible system is completely specified by two independent, intensive properties.

Thermodynamic equilibrium

Thermodynamics deals with equilibrium states. A system is said to be in equilibrium with its surroundings if there is no change when it is isolated from its surroundings; in other words there must be:

- mechanical equilibrium, ie. Forces are balanced or there is no change in pressure
- thermal equilibrium, ie. No temperature differences
- chemical equilibrium, ie. There is no change in composition and no transfer of matter or no occurrence of chemical reaction; and
- phase equilibrium, ie. If the system involves two phases and the mass of each phase is in equilibrium.

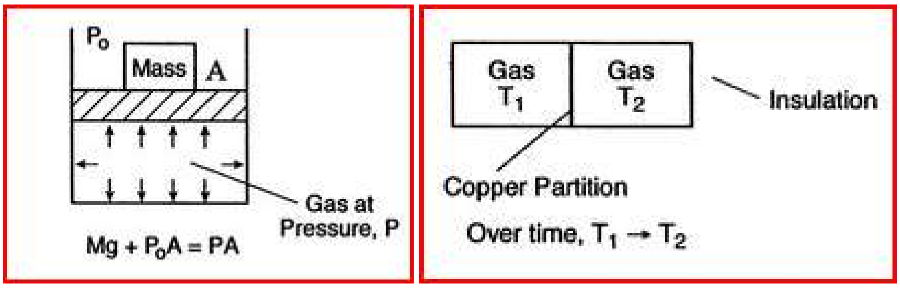


Figure 1.3: a. Mechanical equilibrium; b. Thermal equilibrium

The quasi-static (or quasi[2]-equilibrium) process

During a quasi-equilibrium or quasi-static process the system remains practically in equilibrium at all times. Even though many actual processes closely approximate the quasi-static process, it (quasi-static) is not a true representation of an actual process; it is an idealized process. A quasi-static process is easy to analyse and work-producing devices deliver the most work when they operate on this process.

Reversible and irreversible processes

A reversible process is one in which the system and its surroundings can be exactly restored to their respective initial states after a process had taken place. An irreversible process is one that is not reversible and it is represented in a property diagram by a broken line.

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[2] The term ‘quasi’ means ‘as if’

Equations of state

Two properties are needed to define the state of any pure substance in equilibrium or undergoing a steady or quasi-steady process. Any relation among pressure, temperature, and specific volume of a substance is called an *equation of state. The ideal gas equation is the simplest equation of state given by:*

$$P\bar{v} = RT$$

where $\bar{v}$ *= molar volume of gas and R is the universal gas constant = 8.314 kJ/kmol.K*

The gas constant (R_g) for ideal gases is related to the universal gas constant valid for all substances through the molar mass (or molecular weight).

$$R_g = \frac{R}{M}; \qquad \mathrm{M = molar\ mass\ of\ the\ gas}$$

Real gases exhibit ideal-gas behaviour at low pressures and high temperatures. The deviation from ideal gas behaviour can be accounted for by using the compressibility factor *Z*, defined as

$$Z = \frac{Pv}{RT} \quad \text{or} \quad Z = \frac{v_{actual}}{v_{ideal}}$$

For an ideal gas *Z* = 1, and the deviation of *Z* from unity measures the deviation of the actual *P-V-T* relation from the ideal gas equation of state.

Combined Gas Law – A Useful Ideal Gas Relation

By writing the ideal gas equation twice for a fixed mass and simplifying, the properties of an ideal gas at two different states are related by

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Ideal gas mixtures

The ideal gas law, under proper assumptions, can be used for a mixture of gases by taking **p** as the total pressure of the mixture, **V** as the volume occupied by the mixture, **n** as the total moles of all components of the mixture, and **T** as the temperature of the mixture. It is also possible to calculate the pressure or volume for the individual components by using the following laws:

1. Dalton’s law

It is the pressure exerted by a single component in a gaseous mixture if it existed by itself in the same volume as occupied by the mixture and at the same temperature of the mixture:

$$p_i V_t = n_i R T_t$$

where p_i is the partial pressure of component i

Dividing the above equation by the ideal gas relation for the mixture, we have

$$\frac{p_i V_t}{p_t V_t} = \frac{n_i R T_t}{n_t R T_t}$$

$$p_i = p_t \frac{n_i}{n_t} = p_i y_i$$

where y_i is the mole fraction of component i.

It is obvious that

$$p_1 + p_2 + \ldots + p_n = p_t$$

2. Amagat's law

Amagat's law of additive volumes states that the volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure. In other words, the partial volume of Amagat is the volume that would be occupied by a single component of the mixture if the component were at the same temperature and total pressure as the mixture:

$$p_t V_i = n_i R T_t$$

$$V_i = V_t \left(\frac{n_i}{n_t} \right) = V_t y_i$$

$$\textit{Thus,}\quad V_1 + V_2 + \ldots + V_n = V_t$$

Real gas relationships

At room temperature and pressure many gases can be assumed to behave ideally; but for some gases under normal conditions, and for most gases under high pressure, values of the gas properties obtained using the ideal gas law would deviate substantially from empirical results. Real gases do not obey the ideal gas law and there are essentially four methods of predicting real gas properties:

- equation of state
- compressibility charts
- estimated properties
- actual experimental data

Equations of state

These equations relate the p-V-T properties of a pure substance or mixtures by theoretical or empirical equations. The van der Waal equation of state is simple and semi-empirical[3] and generally gives good results:

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

where n = number of moles
a , b = constants, different for each gas
V = volume

The term $\frac{n^2a}{V^2}$ is symbolic of the attractive forces that exist between gas molecules whiles ***b*** represents the effect of molecular volume. The constants ***a*** and ***b*** are determined by fitting the van der Waals equation to experimental p-V-T data.

The equation can be explicitly solve for p as

$$p=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$$

Solving for V, we obtain

$$V^3-\left(nb+\frac{nRT}{p}\right)V^2+\frac{n^2a}{p}V-\frac{n^3ab}{p}=0 \quad \text{whic is cubic in V or n}$$

Other equations of state include Beattie-Bridgeman and Benedict-Webb-Rubin.

Energy

Energy is a fundamental concept in thermodynamics and one of the most important aspects of engineering analysis. It is the capacity to do work. The total energy *E* of a system is the sum of all forms of energy that exist within the system such as thermal, mechanical, kinetic, potential, electric, magnetic, chemical, and nuclear.

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[3] Constants in the equation are determined empirically even though the equation was theoretically derived

In engineering thermodynamics, the change in the total energy of a system comprises three macroscopic contributions:

- change in kinetic energy
- change in gravitational potential energy
- internal energy

Internal energy *U* represents the sum of all the microscopic forms of energy of a system; it is the sum of all the energies of the particles of the system. **Kinetic energy *KE*** is the energy that a system possesses as a result of its motion relative to some reference frame. It is expressed as

$KE = mv^2/2$ or $ke = v^2/2$.

Finally, **Potential energy *PE*** represents the energy possessed by a system as a result of its elevation in a gravitational field; it is expressed as

$PE = mgz$ or $pe = gz$;

where z = elevation of the system's centre of gravity with respect to a reference plane.

The total energy of a system is therefore expressed as:

$$E = U + KE + PE = U + m\frac{v^2}{2} + mgz \qquad (KJ); \quad or$$

$$e = u + ke + pe = u + \frac{v^2}{2} + gz \qquad (KJ/kg)$$

where $e = E/m$ is the specific stored energy, and $u = U/m$ is the specific internal energy.

The change in stored energy of a system is given by

$$\Delta E = \Delta U + \Delta KE + \Delta PE \qquad (kJ)$$

Energy is exchanged between such a system and its surroundings in two forms: heat and work.

Heat

Energy transfer across a system boundary due solely to the temperature difference between a system and its surroundings is called heat. In other words, it is energy crossing the system boundary under the influence of temperature difference or gradient.

- Heat transfer can alter system states;
- Bodies don't contain' heat; heat is identified as it comes across system boundaries;
- The amount of heat needed to go from one state to another is path dependent;

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

The convention with respect to sign makes numerical values of Q positive when heat is added to the system and negative when heat leaves the system. Until about 1930, the units of heat were based on the temperature changes of a unit of water; the *calorie* is defined as that quantity of heat needed to raise the temperature of 1 gram of water by 1 ^{0}C. Likewise, the British thermal unit (*Btu*) is defined as the quantity of heat which when transferred to 1 pound-mass of water raised its temperature 1 ^{0}F.

Note: 1 ft-Ibf =1.3558179 J; 1 calorie = 4.184 J; 1 Btu = 1055.04 J

Work

Work is energy in transit between a system and its surroundings, but resulting from the displacement of an external force acting on the system. Like heat, a quantity of work W represents an amount of energy, and is not a property of the system. The sign convention, analogous to that for heat, makes numerical values of W positive when work is done on the system by the surroundings and negative when work is done on the surroundings by the system.

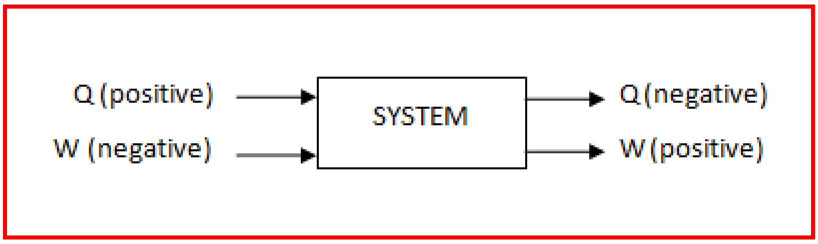

Figure 1.4: Sign convention

There are many forms of work depending on the nature of the system and type of forces prevailing; they may include electrical, magnetic, chemical and mechanical work. Since we are dealing with electrically-neutral, non-magnetic, and chemically-stable fluids, we shall consider only mechanical work, including expansion and compression.

Consider a simple compressible substance, for example, a gas (the system), exerting a force on the surroundings via a piston, which moves through some distance; the work done on the surround is

$$dW = F \times dl = \frac{F}{A} \times (A \times dl) = p \times dV$$

$$Thus\ \ \mathrm{W} = \int_{V_1}^{V_2} p \times dV$$

Example: Work on two simple paths

Consider Figure 1.5 which shows a system undergoing quasi-static processes for which we can calculate work interactions as:

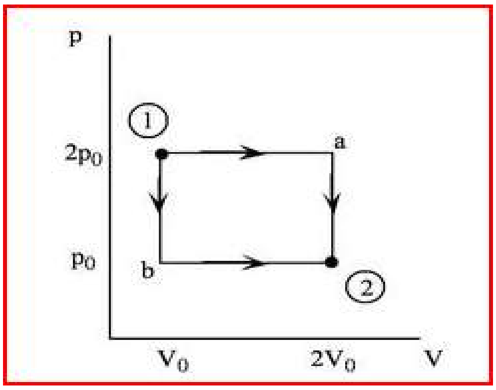

Figure 1.5: Work on two simple paths

Along path a: $W = 2p_0 (2V_0 - V_0) = 2p_0\, v_0$

Along path b: $W = p_0 (2V_0 - V_0) = p_0\, v_0$

Expansion work of an ideal gas

Consider the quasi-static, isothermal expansion of an ideal gas as shown below. To find the work we must know the path – the path is isothermal.

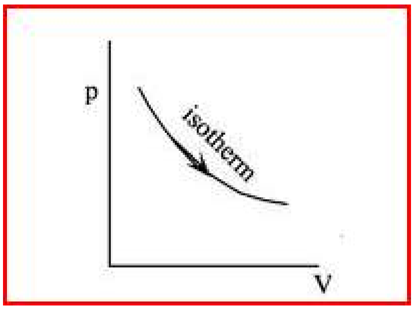

Figure 1.6.: Reversible isothermal expansion of an ideal gas

From the ideal gas equation of state:

$$pV = nRT$$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ In\left(\frac{V_2}{V_1}\right) = nRT \ In\left(\frac{p_1}{p_2}\right)$$

In terms of specific volume, $W = mRT \ In\left(\frac{v_2}{v_1}\right)$

Chapter 3 FIRST LAW OF THERMODYNAMICS AND OTHER BASIC CONCEPTS

Like the Zeroth Law, which defined a useful property, ``temperature," the First Law defines a useful property called ``energy." The system energy (E) can be considered as a sum of internal energy, kinetic energy, and potential energy. The first law of thermodynamics is an expression of the conservation of energy principle. Energy can cross the boundaries of a closed system in the form of heat or work. ***The* total *energy of any system and its surroundings is conserved***[4]**.** In other words, the change in energy of a system is equal to the difference between the heat added to the system and the work done by the system:

$$\Delta \boldsymbol{E} = \boldsymbol{Q} - \boldsymbol{W} \ \ ; \mathbf{J}$$

Where

E = *total energy of the system*

$$= U + KE + PE$$

Q = *heat input to the system*

W = *work done by the system*

The equation can also by written on a per unit mass basis

$$\Delta e = q - w \ ; J/kg$$

In many situations the potential energy and kinetic energy are constant or negligible and we can write

$\Delta E = \Delta U \ \ or \ \Delta e = \Delta u$; and

$$\Delta U = Q - W \quad or \quad \Delta u = q - w$$

Note*:*

Q and W are not state functions, but U, which arises from molecular motion, depends only on the state of the system – it does not depend on how the system got to that state. Thus

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[4] Note: A corollary of the first law states that *a perpetual machine of the first kind is impossible*. A perpetual machine of the first kind is a machine which produces continuous supply of work without absorbing energy from the surroundings.

ΔU is path independent even though Q and W are path dependent – this is mathematically emphasized by writing the first law in differential form,

$dU = \delta Q \; - \delta W$

where δ is used to denote that these are not exact differentials and thus are path dependent.

For quasi-static processes we can write the first law as,

$dU = \delta Q - pdV$

Simple applications of the first law

The form of the first law depicted diagrammatically below is usually called the *control mass* because it is suited to dealing with systems of a fixed mass. We heat a gas and the gas expands against a weight causing work to be done.

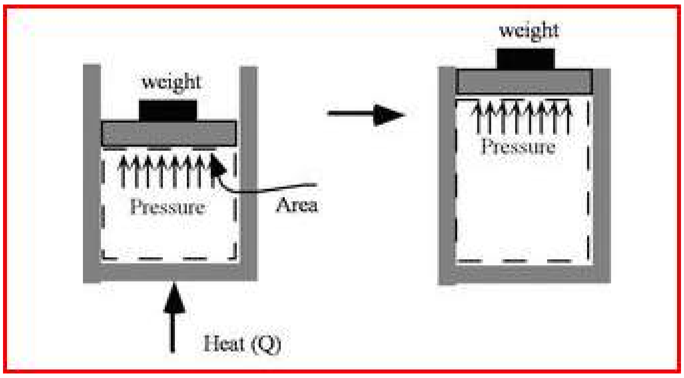


Figure 2.1: Change in energy of a system relates heat added to the work done

Corollaries of the First Law

Adiabatic process

No heat is exchanged between the system and the surroundings since the system is perfectly insulated.

$Q = 0$

Work done under adiabatic process is a state function. The first law reduces to

$W = - \Delta U = - (U_2 - U_1)$

Reversible adiabatic process for an ideal gas

From the first law, we obtain

$du = -pdv$; since q = 0, du = $c_v dt$, and W = pdv

Also from the definition of enthalpy, we obtain

$h = u + pv$

$dh = du + pdv + vdp = vdp$

Now we can write

$\gamma c_v dT = -\gamma pdv$

$c_p dT = vdp$

Combining the above two equations we obtain

$-\gamma pdv = vdp$ or $-\gamma\, dv/v = dp/p$

Integrating the above equation from states 1 and 2, we have

$$-\gamma In\left(\frac{v_2}{v_1}\right) = In\left(\frac{p_2}{p_1}\right) \quad \text{or} \quad \left(\frac{p_2}{p_1}\right)\left(\frac{v_2}{v_1}\right)^{\gamma} = 1$$

Therefore, for an ideal gas undergoing a reversible, adiabatic process, the relation between pressue and volume is thus

$pv^{\gamma} = const.$

Note: It may also be shown that

$$\left(\frac{p_2}{p_1}\right) = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}} \quad \text{and} \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

Cyclic process

$$U_2 - U_1 = 0 \text{ or } \Delta U = 0$$
$$Q = W$$

Enthalpy

The enthalpy is defined as:

H = U + PV

In terms of specific units, the enthalpy per unit mass is

$h = u + Pv = u + P/\rho$

It is a function of the state of the system. H has units of Joules and h has units of Joules per kilogram. The enthalpy is a very significant parameter in flow systems. Levenspiel, 1996, gives the following explanation of the enthalpy:

When you evaluate the energy of an object of volume *V*, you have to remember that the object had to push the surroundings out of the way to make room for itself. With pressure, p, on the object, the work required to make a place for itself is *pV*. This is so with any object or system, and this work may not be negligible. (The force of one atmosphere pressure on one square meter is equivalent to the force of a mass of about *10 tons*.) Thus the total energy of a body is its internal energy plus the extra energy it is credited with by having a volume V at pressure p. We call this total energy the enthalpy, *H*.

Constant pressure process

Consider a system with a piston working inside a cylinder in Figure 2.2 the cylinder has unit mass of working substance. The boundary of the system is a frictionless piston and a cylinder. The volume of the boundary increases, but its pressure remains constant. In general, for any inert gas, pressure falls with expansion of cylinder contents, but constant pressure can only be maintained by the addition of heat.

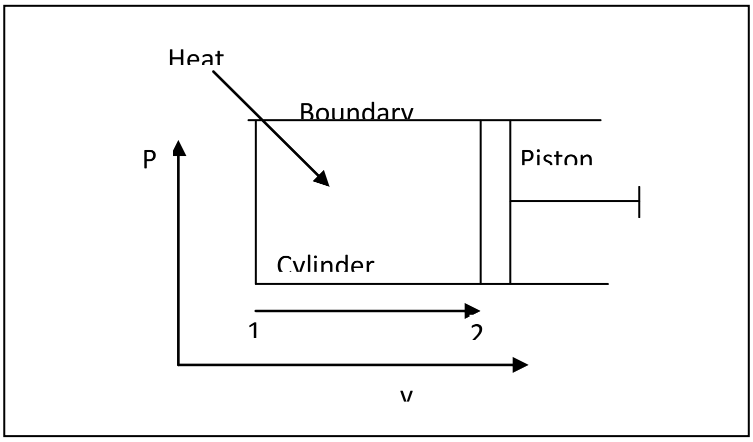


Figure 2.2: A constant pressure process

From the first law

$$Q = \Delta U + W = (U_2 - U_1) + W = (U_2 - U_1) + p(V_2 - V_1) \quad since\ p_1 = p_2 = p$$

Regrouping terms

$$Q = (U_2 + pV_2) - (U_1 + p\,V_1) = H_2 - H_1$$

Polytropic Process

It is a process defined by the law:

$pv^n = const.$; where n is known as the polytropic index

The first law in terms of enthalpy

$H = U + PV$

Differentiating (using the chain rule) the above equation we have

$$dH = dU + pdV + VdP$$

Substituting the dU from the first law, we obtain

$dH = \delta Q - \delta W + pdV + VdP$, (valid for any process)

$dH = \delta Q + VdP$, (valid for any quasi-static process)

Specific heats: the relation between heat and temperature change

$Q = C \Delta T$

The specific heat is usually determined at constant pressure C_p and at constant volume C_p.

1. The Specific Heat at Constant Volume

Let

$u = u(T, v)$

using the chain rule, we can show how u changes with respect to T and v:

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$= \left(\frac{\partial u}{\partial T}\right)_v dT \quad ; \qquad \text{for a constant volume process } (dv \; = \; 0)$$

Now from the first law: $du = \delta q;$ since $W \; = \; pdV \; = \; 0$

Thus, $\delta q = \left(\frac{\partial u}{\partial T}\right)_v dT$

and rearranging $\left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial q}{\partial T}\right)_v$

Therefore, $c_v = \left(\frac{\partial u}{\partial T}\right)_v$

2. Specific heat capacity at constant pressure

Writing h = h(T, p), we can show that $c_p = \left(\frac{\partial h}{\partial T}\right)_p$

Specific heats of an ideal gas

An important feature of an ideal gas is that its internal energy depends only on its temperature. Hence, we can write

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$= \left(\frac{\partial u}{\partial T}\right)_v dT$$

$$= \mathrm{c}_v(T)dT$$

$$Also,\; dh = \left(\frac{\partial h}{\partial T}\right)_p dT$$

$$= \mathrm{c}_p(T)dT$$

Heat capacities are often treated as constants, in that case, our equations become

$du = c_v dT$ or $\Delta \mathrm{u} = \mathrm{c}_v(T_2 - T_1)$
$dh = c_p dT$ or $\Delta \mathrm{h} = \mathrm{c}_p(T_2 - T_1)$

Relationship between the specific heats and the gas constant of an ideal gas

From the first law for a reversible process, we can write

$$\delta q = du + pdv$$

$$\delta q = dh - vdp$$

Equating the above equations

$$du + pdv = dh - vdp$$

$$c_v dT + pdv = c_p dT - vdp$$

$$(c_p - c_c)dT = d(pv)$$

$$c_p - c_v = \frac{d(pv)}{dT} = R$$

Ratio of specific heats, $\gamma = \frac{c_p}{c_v}$

Quick facts about specific heats

1. The specific heat ratio is a function of temperature only and is greater than zero.

2. For monatomic gases, such as He, Ne, Ar, and most metallic vapours at a wide range of temperatures: $c_v = (3/2)R$; *and* $c_p = (3/2)R + R = (5/2)R$

3. For permanent diatomic gases, namely H_2 , O_2 , N_2 , Air, NO, and CO at ordinary temperatures: $c_v = (5/2)R$ *and* $c_p = (5/2)R + R = (7/2)R$

4. The specific heats of polyatomic gases such as CO_2 and NH_3 depend heavily on temperature.

In general, for substances other than ideal gases, u and h depend on pressure as well as on temperature, and the above relations will not all apply. Note that the specific heats are thermodynamic properties and can be used even if the processes are not constant pressure or constant volume.

Chapter 4 CONTROL VOLUME FORM OF THE CONSERVATION EQUATIONS

The conservation of mass and the conservation of energy principles for open systems (control volumes) apply to systems having mass crossing the system boundary or control surface. In addition to the heat transfer and work crossing the system boundaries, mass carries energy with it as it crosses the system boundaries. Thus, the mass and energy content of the open system may change when mass enters or leaves the control volume.

Engineers are usually interested in the rates of heat and work into and out of a system. For this reason, the control volume form of the system laws is of great importance.

Thermodynamic processes involving control volumes can be considered in two groups: steady-flow processes and unsteady-flow processes. Steady implies **no change with time**. The opposite of steady **is unsteady** or **transient**. The term **uniform** implies **no change with location** over a specified region.

Conservation of mass

For the control volume shown, the rate of change of mass inside the volume is given by the difference between the mass flow rate in and the mass flow rate out. This is expressed as

$$\begin{bmatrix} \text{Rate of change of mass} \\ \text{in control volume} \end{bmatrix} = \begin{bmatrix} \text{Rate of mass flowing} \\ \text{into control volume} \end{bmatrix} - \begin{bmatrix} \text{Rate of mass flowing} \\ \text{out of control volume} \end{bmatrix}$$

For a single flow coming in and a single flow coming out this is given by

$$\frac{dm_{cv}}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

If the mass inside the CV changes with time it is because some material is added or taken out. For a steady flow we have

$$\frac{dm_{cv}}{dt} = 0 \quad \text{or} \quad \dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

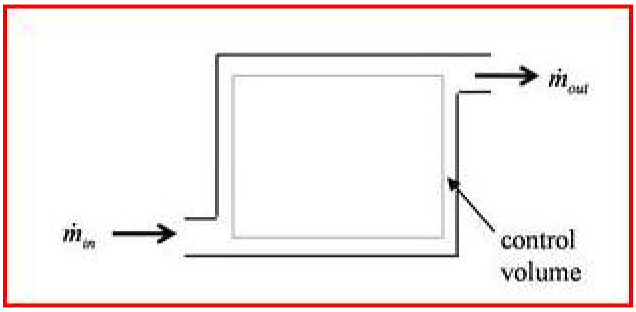


Figure 2.3: Control volume depicting mass flows

Conservation of energy

The first law for a flow system or a control volume (with only one inlet and one outlet) can be written as

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \dot{m}_i e_i - m_o e_o$$

where $\frac{dE}{dt}$ is the rate of change of energy within the CV

$\dot{Q}$ is the rate of heat transfer between the CV and its surroundings

$\dot{W}$ is the rate of work done by the system

e is the total energy of the flowing fluid and is given by

m is the mass flow rate

$$e = u + \frac{c^2}{2} + gz + pv = h + \frac{c^2}{2} + gz$$

Rate of change of energy in CV = Rate of heat added to CV – Rate of work done + Rate of energy flow into CV – Rate of energy leaving control volume

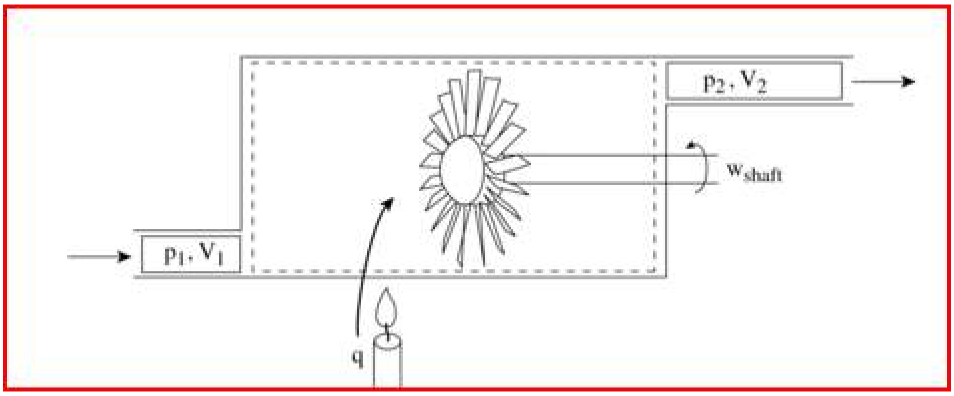


Figure 2.4: Control volume with mass flow, heat transfer and shaft work

In the special case of a steady-state flow,

$$\frac{d}{dt} = 0 \quad \text{and} \quad \mathrm{m}_i = m_e = m$$

Our steady flow energy equation is thus given by

$$\dot{\mathrm{Q}} - \dot{W} = \dot{m}\left[\left(h_o + \frac{c_o}{2} + gz_o\right) - \left(h_i + \frac{c_i}{2} + gz_i\right)\right]$$

Note:

For flow in some machines including turbines and compressors, the terms gz and $c^2/2$ *may* be neglected and our steady-state equation reduces to

$$\dot{\mathrm{Q}} - \dot{W} = \dot{m}\left(h_o - h_i\right) \quad \text{or} \quad \dot{q} - \dot{w} = \left(h_o - h_i\right)$$

Note: $\dot{\mathrm{m}} = \rho \mathrm{c}_{av} \mathrm{A}$

A = cross-sectional area, c_{av} = average velocity

The first law applied to engineering cycles

This chapter describes the fundamentals of how various heat engines work. A **heat engine** is a device that uses heat to produce work, or uses work to move around heat. Refrigerators, internal combustion (automobile) engines, and jet engines are all types of heat engines. We will model these heat engines as thermodynamic cycles and apply the First Law of Thermodynamics to estimate thermal efficiency and work output as a function of pressures and temperatures at various points in the cycle. This is called ideal cycle analysis. The estimates we obtain from the analysis represent the best achievable performance that may be obtained from a heat engine. In reality, the performance of these systems will be somewhat less than the estimates obtained from ideal cycle analysis.

Isothermal expansion of an ideal gas

One example of a process in which heat is converted to work is the isothermal (constant temperature) expansion of an ideal gas, as sketched in Figure 2.5. The system is the gas inside the chamber. As the gas expands, the piston does work on some external device. For an ideal gas, the internal energy is a function of temperature only, so that if the temperature is constant for some process the internal energy change is zero. To keep the temperature constant during the expansion, heat must be supplied. Because $\Delta U = 0$, the first law takes the form $Q = W$. This is a process that has **100 %** conversion of heat into work

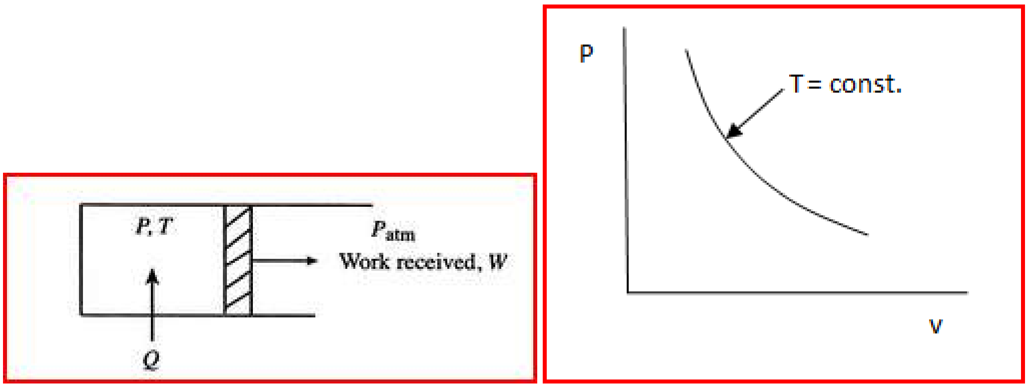


Figure 2.5: Isothermal expansion of an ideal gas

$$W = \int_1^2 PdV$$

$$= \text{nRT} \int_1^2 \frac{dV}{V} \qquad \text{since } P = nRT/V$$

$$= nRT\ \text{In}\left(\frac{V_2}{V_1}\right) = \text{nRT In}\left(\frac{P_1}{P_2}\right)$$

The lowest pressure to which we can expand and still receive work from the system is atmospheric pressure. Below this, we would have to do work on the system to pull the piston out further. There is thus a bound on the amount of work that can be obtained in the isothermal expansion; we cannot continue indefinitely. For a power or propulsion system, however, we would like a source of continuous power, in other words a device that would give power or propulsion as long as fuel was added to it. To do this, we need a series of processes where the system does not progress through a one-way transition from an initial state to a different final state, but rather cycles back to the initial state. What is looked for is in fact a thermodynamic cycle for the system.

Applications

Tank Filling

Using what we have just learned we can attack the tank filling problem. In this problem the shaft work is zero, and the heat transfer, kinetic energy changes, and potential energy changes are neglected. In addition there is no exit mass flow.

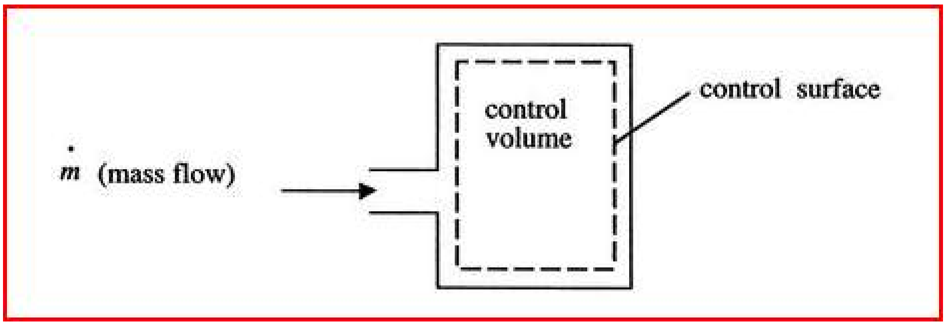


Figure 2.6: Control volume approach to the tank filling problem

The control volume form of the first law is therefore

$$\frac{dU}{dt} = m_i h_i$$

And the equation of mass is

$$\frac{dm}{dt} = m_i$$

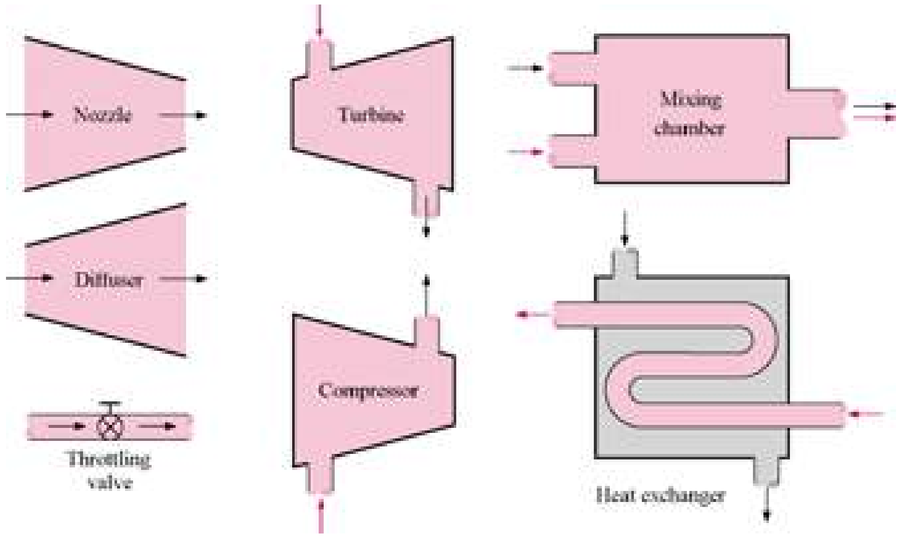
Combining we have

$$\frac{dU}{dt} = \frac{dm}{dt} h_i$$

Integrating from initial time to final time and noting that h_i is constant and that U = mu gives the result

$$u_{final} = h_i$$

Some steady-flow engineering devices



Nozzles and diffusers

These devices are found in rockets, jet-engines, space-crafts, and even garden hoses. They are ducts of varying cross-sectional area. A nozzle increases the velocity of a fluid whiles decreasing its pressure. In contrast, a diffuser increases the pressure of a fluid by slowing it down, i.e. decreasing its velocity. The cross-sectional area of a nozzle decreases in the flow direction for subsonic flows and increases for supersonic flows. The reverse is true for diffusers.

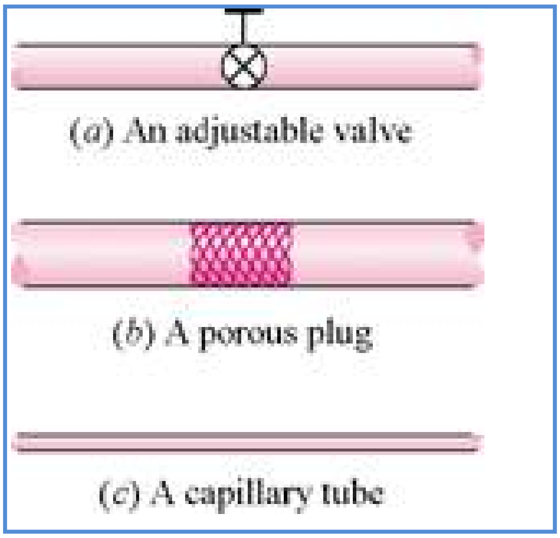
Application of the steady-flow energy equation to nozzles and diffusers reduces to:

$$\frac{c_2^2 - c_1^2}{2} = h_1 - h_2; \quad \text{by assuming } \dot{q} = \dot{w} = 0 \text{ and by neglecting potential energy}$$

Turbines, compressors, fans and pumps

A turbine is a *rotary* engine that extracts energy from a fluid flow. There are many types of turbines, but in general *gas* and steam *turbines* are of much interest in thermodynamics. Steam turbines are used for the generation of electricity in thermal power plants, such as plants using coal or fuel oil or nuclear power. They were once used to directly drive mechanical devices such as ship's propellers. Gas turbines are sometimes referred to as turbine engines. Such engines usually feature an inlet, fan, compressor, combustor and nozzle in addition to one or more turbines. Other types include *water and wind turbines.*

Compressors, fans, and pumps on the other hand are devices which require mechanical power to increase the pressure of fluid. Compressors and fans are essentially the same devices. However, compressors operate over larger pressure ratios than fans. The ratio of outlet to inlet pressure is much lower in fans (slightly above 1) than in compressors (up to about 10). Compressors handle gases while pumps are used for liquids.



Applying the steady-flow energy equation to these devices, we again assume adiabatic flow and assume KE and PE to be negligible; hence we obtain

$$w = \dot{m}(h_1 - h_2)$$

For turbines, w > 0 which means $h_1 > h_2$; and
for compressors, fans and pumps, w < 0, meaning $h_1 < h_2$

Boilers and condensers

A boiler is a heating device which converts liquids into vapours. Steam boilers are classified as **water tube** if water flow in the boiler tubes or **fire tube** if combustion gases flow in the boiler tubes.

The condenser, however, is a device which cools vapours and condenses them into liquid. They are used in thermal power plants, refrigeration systems, and the process industry. Applying the steady flow energy equation to boilers and condensers, we neglect the change in PE and KE while noting that no work is done; thus we have

$$\dot{Q} = \dot{m}(h_2 - h_1)$$

For condensers, $\dot{Q} < 0$ and for boilers $\dot{Q} > 0$

Throttling Devices

The flow of a fluid is throttled if there is a restriction in the passage. For example, fluid of a pipe line is throttled if the valve is partially closed. The pressure of the fluid is reduced by throttling which is due to friction in the flow. There is neither work nor heat transfer and no energy crosses the boundary. It is irreversible and adiabatic. Thus

$$h_1 = h_2$$

Throttling phenomenon is used to investigate the dryness fraction of wet vapour, which becomes drier due to throttling. In refrigerators, liquid refrigerant is throttled either by passing through a narrow constriction of an expansion valve or a long capillary tube. Throttling is used for cooling and drying of vapours.

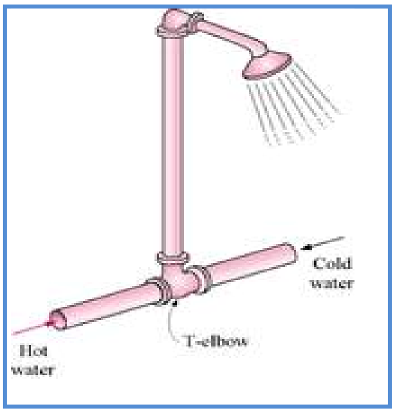
When throttling an ideal gas, the temperature does not change. Why?

Mixing Chambers

The mixing of two fluids occurs frequently in engineering applications. The section where the mixing process takes place is called a mixing chamber. The ordinary shower is an example of a mixing chamber.

Heat exchangers

Heat exchangers are normally well-insulated devices that allow energy exchange between hot and cold fluids without mixing the fluids. The pumps, fans, and blowers causing the fluids to flow across the control surface are normally located outside the control surface.



Pipe and duct flow

The flow of fluids through pipes and ducts is often a steady-state, steady flow process. We normally neglect the kinetic and potential energies; however, depending on the flow situation, the work and heat transfer may or may not be zero.

Procedure for Solving Thermodynamic Problems

Thermodynamics problems are relatively easy to solve if a methodical solution procedure is applied. The steps below give a good insight into problem solving approach in thermodynamics:

- Sketch the system and show energy interactions across the boundaries.
- Determine the property relation. Is the working substance an ideal gas or a real substance? Begin to set up and fill in a property table.
- Determine the process and sketch the process diagram. Continue to fill in the property table.
- Apply conservation of mass and conservation of energy principles.
- Bring in other information from the problem statement, called physical constraints, such as the volume doubles or the pressure is halved during the process.
- Develop enough equations for the unknowns and solve.

Chapter 5 HEAT EFFECTS

Standard heat of reaction

Chemical reactions are accompanied either by transfer of heat or by temperature changes during the course of the reaction and in some cases by both. For example, in a combustion reaction, the reactants possess greater energy than the products on account of their structure and this energy must either be transferred to the surroundings as heat or produce products at an elevated temperature. The amount of heat required for a specific chemical reaction depends on the temperatures of both the reactants and the products.

Consider the reaction $aA + bB \rightarrow lL + mM$; The standard heat of reaction is the enthalpy change when *a* moles of *A* and *b* moles of *B* in their *standard states at temperature T* react to form l moles of L and m moles of M in their *standard states also at temperature T.* A *standard state* is a particular state of a species at temperature T and at specified conditions of pressure, composition, and physical state.

The standard states usually used are:

- Gases: the pure substance in the ideal gas state at 1 bar
- Liquids and solids: the actual pure liquid or solid at 1 bar

All conditions for a standard state are fixed except temperature, which is always the temperature of the system. Standard state properties are therefore functions of temperature only.

When a heat of reaction is given for a particular reaction, it applies to the stoichiometric coefficients as well. If each stoichiometric coefficient is doubled, the heat of reaction is doubled. For example, the ammonia synthesis reaction may be written

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \qquad \Delta H^0_{298} = -46{,}110\ J$$

or

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H^0_{298} = -92{,}220\ J$$

The symbol ΔH^0_{298} indicates that the heat of reaction is the standard value for a temperature of 298.15 K

Standard heat of formation

When a compound is formed from its elements (e.g., methane, CH4, from C and H_2), heat transfer occurs. When heat is given off, the reaction is called **exothermic**. When heat is required, the reaction is called **endothermic**.

Tabulation of data for the standard heats of reaction for all of the vast number of possible reactions is impractical; fortunately, the standard heat of any reaction can be calculated if the *standard heats of formation* of the compounds taking part in the reaction are known.

A formation reaction is one that forms a single compound from its constituent elements. It is based on 1 *mole of the compound formed.* For example, the reaction

$C+\frac{1}{2}O_2+2H_2 \rightarrow CH_3OH$ is the formation reaction for methanol. The reaction

$H_2O+SO_3 \rightarrow H_2SO_4$ is not a formation reaction, since sulphuric acid is formed from other compounds and not from the elements

Heat of reaction at any temperature can be calculated from heat-capacity data if the value for one temperature is known.

Standard heat of combustion

One kind of reaction that readily lends itself to experiment is the combustion reaction, and many standard heats of formation come from standard heats of combustion, measured calorimeterically. A combustion reaction is one between an element or compound and oxygen only; the products are carbon dioxide and water, but the state of the water may be either vapour or liquid. Data are always based on 1 mol of the substance burned.

A reaction such as the formation of n-butane:

$$4C(s)+5H_2(g) \rightarrow C_4H_{10}$$

cannot be carried out in practice.

However, this equation results from combinations of the ff combustion equations :

$$4C(s)+4O_2(g) \rightarrow 4CO_2(g) \qquad \Delta H^0_{298}=4(-393{,}509)$$

$$5H_2(g)+2\frac{1}{2}O_2(g) \rightarrow 5H_2O(l) \qquad \Delta H^0_{298}=5(-285{,}830)$$

$$4CO_2(g)+5H_2O(l) \rightarrow C_4H_{10}(g)+6\frac{1}{2}O_2(g) \qquad \Delta H^0_{298}=2{,}877{,}396$$

$$4C(s)+5H_2(g) \rightarrow C_4H_{10}(g) \qquad \Delta H^0_{298}=-125{,}790\ J$$

This is the value of the standard heat of formtion on n - butane.

Fuels are usually composed of some compound or mixture containing carbon, C, and hydrogen, H_2. Examples of hydrocarbon fuels are CH_4 Methane, C_8H_{18} Octane, and Coal Mixture of C, H_2, S, O_2, N_2 and non-combustibles.

A complete combustion process is one where all carbon is burned to carbon dioxide (CO_2) and all hydrogen is converted into water (H_2O). The complete combustion process is also called the stoichiometric combustion, and all coefficients are called the stoichiometric coefficients.

In most combustion processes, oxygen is supplied in the form of air rather than pure oxygen. Air is assumed to be 21 percent oxygen and 79 percent nitrogen on a volume basis. For ideal gas mixtures, percent by volume is equal to percent by moles. Thus, for each mole of oxygen in air, there exists 79/21 = 3.76 moles of nitrogen.

Therefore, complete or theoretical combustion of octane with air can be written as

$$C_8 H_{12} + 12.5 (O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 9 H_2 O + 47 N_2$$

Air-Fuel Ratio

Since the total moles of a mixture are equal to the sum of moles of each component, there are 12.5 (1 + 3.76) = 59.5 moles of air required for each mole of fuel for the complete combustion process. Often complete combustion of the fuel will not occur unless there is an excess of air present greater than just the theoretical air required for complete combustion.

To determine the amount of excess air supplied for a combustion process, let us define the air-fuel ratio *AF* as

$$AF = \frac{kmol\ air}{kmol\ fuel}$$

Thus, for the above example, the theoretical air-fuel ratio is

$$AF = \frac{12.5(1+3.76)}{1} = 59.5\frac{kmol\ air}{kmol\ fuel}$$

On a mass basis, the theoretical air-fuel ratio is

$$AF = 59.5\frac{kmol\ air}{kmol\ fuel}\frac{28.97\frac{kg\ air}{kmol\ air}}{[8(12)+18(1)]\frac{kg\ fuel}{kmol\ fuel}}$$

$$= 15.12\frac{kg\ air}{kg\ fuel}$$

Percent Theoretical and Percent Excess Air

In practical cases, more than the theoretical amount of air is supplied to ensure complete combustion and to reduce or eliminate carbon monoxide (CO) from the products of combustion. The amount of excess air is usually expressed as percent theoretical air and percent excess air.

$$\text{Percent theoritical air} = \frac{AF_{actual}}{AF_{th}} 100\%$$

$$\text{Percent excess air} = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$

Chapter 6 THE SECOND LAW OF THERMODYNAMICS

Reversible and Irreversible Processes

Processes can be classed as reversible or irreversible. The concept of reversible process is an important one which directly relates to our ability to recognize, evaluate, and reduce irreversibilities in practical engineering processes.

The second law of thermodynamics states that processes occur in a certain direction, not in just any direction. Physical processes in nature can proceed toward equilibrium spontaneously:

- Water flows down a waterfall.
- Gases expand from a high pressure to a low pressure.
- Heat flows from a high temperature to a low temperature.

Once it has taken place, a spontaneous process can be reversed, but it will not reverse itself spontaneously. Some external energy must be expended to reverse the process. Spontaneous processes can proceed only in a particular direction. The first law of thermodynamics gives no information about direction; it states only that when one form of energy is converted into another, identical quantities of energy are involved regardless of the feasibility of the process.

Note that the first law of thermodynamics is not violated if heat flows from a low temperature to a high temperature without the expenditure of work. The first law gives no information about direction; it states only that when one form of energy is converted into another, identical quantities of energy are involved regardless of the feasibility of the process.

Energy in the form of heat cannot be completely converted into work; but, work can be completely converted into heat. Clearly, heat and work are not completely interchangeable forms of energy. Furthermore, when energy is transferred from one form to another, there is often a degradation of the supplied energy into a less “useful” form (lost energy).

A process will not occur unless it satisfies both the first and the second laws of thermodynamics.

Important Terminologies

Heat (thermal) reservoir

A heat reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of heat can be transferred without any change in its temperature. A high temperature heat reservoir from which heat is transferred is sometimes called a **heat source**. A low temperature heat reservoir to which heat is transferred is sometimes called a **heat sink**.

Work reservoir

A work reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of work can be transferred adiabatically without any change in its pressure.

Perpetual-Motion Machines

Any device that violates the first or second law of thermodynamics is called a perpetual-motion machine. If the device violates the first law, it is a perpetual-motion machine of the first kind; and if it violates the second law, it is a perpetual-motion machine of the second kind.

Second law of thermodynamics for an isolated system

Consider an isolated system. The second law says that any process that would reduce the entropy of the isolated system is impossible. Suppose a process takes place within the isolated system in what we shall call the forward direction. If the change in state of the system is such that the entropy increases for the forward process, then for the backward process (that is, for the reverse change in state) the entropy would decrease. The backward process is therefore impossible, and we therefore say that the forward process is irreversible.

The key idea of a reversible process is that it does not produce any entropy

If a process occurs, however, in which the entropy is unchanged by the forward process, then it would also be unchanged by the reverse process. Such a process could go in either direction without contradicting the second law. Processes of this latter type are called reversible.

Entropy is produced in irreversible processes. All real processes (with the possible exception of superconducting current flows) are in some measure irreversible, though many processes can be analyzed quite adequately by assuming that they are reversible. Some processes that are clearly irreversible include: mixing of two gases, spontaneous combustion, friction, and the transfer of energy as heat from a body at high temperature to a body at low temperature.

Recognition of the irreversibilities in a real process is especially important in engineering. Irreversibility, or departure from the ideal condition of reversibility, reflects an increase in the amount of disorganized energy at the expense of organized energy. The organized energy (such as that of a raised weight) is easily put to practical use; disorganized energy (such as the random motions of the molecules in a gas) requires ``straightening out" before it can be used effectively. Further, since we are always somewhat uncertain about the microscopic state, this straightening can never be perfect. Consequently the engineer is constantly striving to reduce irreversibilities in systems, in order to obtain better performance.

Examples of Reversible and Irreversible Processes

Processes that are usually idealized as reversible include:

- Frictionless movement
- Restrained compression or expansion
- Energy transfer as heat due to infinitesimal temperature nonuniformity
- Electric current flow through a zero resistance
- Restrained chemical reaction
- Mixing of two samples of the same substance at the same state.

Processes that are irreversible include:

- Movement with friction
- Unrestrained expansion
- Energy transfer as heat due to large temperature non uniformities
- Electric current flow through a non zero resistance
- Spontaneous chemical reaction
- Mixing of matter of different composition or state.

Concepts and Statements of the Second Law

There are several ways in which the second law of thermodynamics can be stated. Listed below are three that are often encountered. Although the three may not appear to have much connection with each other, they are equivalent.

1. No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work. [Kelvin-Planck statement of the second law]

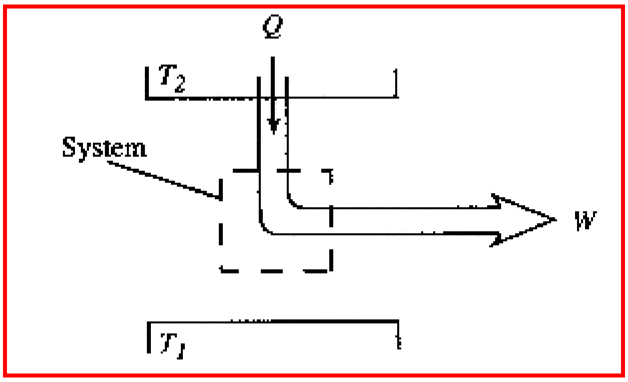


Figure 4.1: Impossible (Kelvin- Planck)

2. No process is possible whose sole result is the transfer of heat from a cooler to a hotter body. [Clausius statement of the second law]

Note: The second law thus tells us that we cannot get work from a single reservoir **only**.

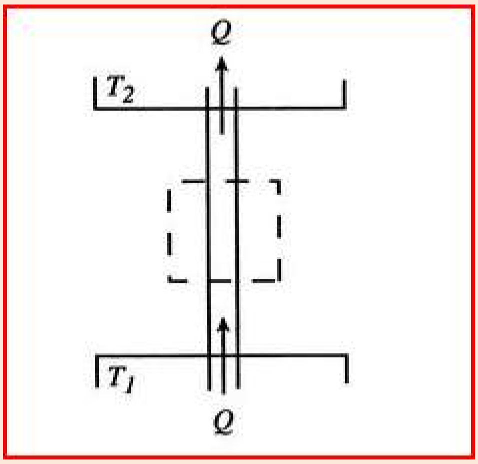


Figure 4.2: For $T_1 < T_2$, this is impossible (Classius)

3. There exists for every system in equilibrium a property called entropy, *S*, which is a thermodynamic property of a system. For a reversible process, changes in this property are given by

$$dS = dQ_{rev}T$$

The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility.

$$\Delta S_{total} \geq 0$$

*F*or an isolated system, changes in the system have no effect on the surroundings.
In this case, only the system must be considered, and the first and second laws become

$$\Delta E_{system} = 0$$
$$\Delta S_{system} \geq 0$$

For an isolated system the total energy (E = U + KE + PE + ...) is constant.
The entropy can only increase or, in the limit of a reversible process, remain constant.

The limit, $S_{total} = const$ or $\Delta S_{total} = 0$, represents the best that can be done.

Some attributes of entropy are summarized below:

- Entropy is a function of the state of the system and can be found if any two properties of the system are known, e.g. $s = s(p,T)$ or $s = s(T,v)$ or $s = s(p,v)$.
- S is an extensive variable. The entropy per unit mass, or specific entropy, is s.
- The unit of entropy is Joules per degree Kelvin (J/K). The unit for specific entropy is J/K-kg.
- For a system, $dS = dQ_{rev}/T$, where the numerator is the heat given to the system and the denominator is the temperature of the system at the location where the heat is received.
- $dS = 0$ for pure work transfer.

Combined First and Second law expressions for a reversible process

From the first law, $dU = dQ - dW$

For reversible processes, $dW = PdV$

$dQ = TdS$

*S*ubstitution leads to other forms of the first law true for reversible processes only:

$dU = TdS - PdV$ Always true since it is a relation between properties

In terms of specific quantities,

$du = Tds - Pdv$

The combined first and second laws are often more useful when written in terms of enthalpy: $h = u + pv$

$$\begin{aligned} dh &= du + Pdv + vdP \\ &= Tds - Pdv + Pdv + vdP, \quad \text{using the first law} \\ &= Tds + vdP \end{aligned}$$

Entropy changes in an ideal gas

In this section, we examine the entropy relations for ideal gas behaviour. From the combined law

$$Tds = du + Pdv$$

$$= c_v dT + Pdv \quad \text{or} \quad ds = c_v \frac{dT}{T} + \frac{P}{T} dv$$

Using the equation of state for an ideal gas, we can write the entropy change as

$$\text{ds} = c_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating from state "1" and "2",

$$\Delta \text{s} = s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

Taking c_v as constant,

$$\Delta \text{s} = s_2 - s_1 = c_v In \left(\frac{T_2}{T_1} \right) + RIn \left(\frac{v_2}{v_1} \right)$$

Calculation of entropy change in some basic processes

Heat transfer from, or to, a heat reservoir

A heat reservoir is a constant temperature heat source or sink. Because the temperature is uniform, there is no heat transfer across a finite temperature difference and the heat exchange is reversible. From the definition of entropy ($dS = dQ_{rev}/T$),

$$\Delta S = {}^{Q}\!/_{T}$$

where Q is the heat into the reservoir (defined here as positive if heat flows into the reservoir.)

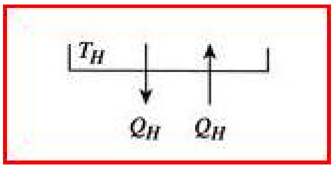


Figure 4.3: Heat transfer from/to a heat reservoir

Heat transfer between two heat reservoirs

The entropy change of the two reservoirs is the sum of the entropy change of each. If the high temperature reservoir is at T_H and the low temperature reservoir is at T_L, the total entropy change is

$$\Delta S = \left(\frac{-Q}{T_H}\right) + \left(\frac{Q}{T_L}\right) = \frac{Q}{T_H T_L}\left(T_H - T_L\right)$$

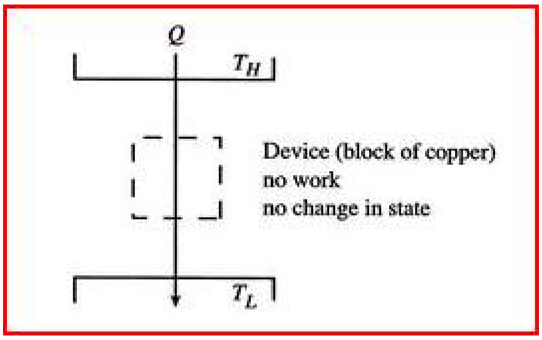


Figure 4.4: heat transfer between two reservoirs

The second law says that the entropy change must be equal to or greater than zero. This corresponds to the statement that heat must flow from the higher temperature source to the lower temperature source. This is one of the statements of the second law

Representation of thermodynamic coordinates in T-s coordinates

It is often useful to plot the thermodynamic state transitions and the cycles in terms of temperature (or enthalpy) and entropy, T, S, rather than, P, V. The maximum temperature is often the constraint on the process and the enthalpy changes show the work done or heat received directly, so that plotting in terms of these variables provides insight into the process.

Summary (Entropy)

- Entropy is a thermodynamic property that measures the degree of randomization or disorder at the microscopic level. The natural state of affairs is for entropy to be produced by all processes.
- A macroscopic feature which is associated with entropy production is a loss of ability to do useful work. Energy is degraded to a less useful form, and it is sometimes said that there is a decrease in the availability of energy.
- Entropy is an extensive thermodynamic property. In other words, the entropy of a complex system is the sum of the entropies of its parts.
- The notion that entropy can be produced, but never destroyed, is the second law of thermodynamics.

Entropy Generation

Irreversibilities such as friction, mixing, chemical reactions, heat transfer through a finite temperature difference, unrestrained expansion, non-quasiequilibrium expansion, or compression always cause the entropy of a system to increase, and entropy generation is a measure of the entropy created by such effects during a process.

For a reversible process, the entropy generation is zero and the entropy change of a system is equal to the entropy transfer. The entropy transfer by heat is zero for an adiabatic system and the entropy transfer by mass is zero for a closed system.

Exergy (Useful work)

The useful work potential of a system at the specified state is called *exergy*. Exergy is a property and is associated with the state of the system and the environment. A system that is in equilibrium with its surroundings has zero exergy and is said to be at the *dead state*. The exergy of the thermal energy of thermal reservoirs is equivalent to the work output of a Carnot heat engine operating between the reservoir and the environment.

Reversible work is defined as the maximum amount of useful work that can be produced. The difference between the reversible work and the useful work is due to the irreversibilities present during the process. Exergy destroyed represents the lost work potential and is also called the *wasted work* or *lost work.*

Chapter 7 PURE SUBSTANCES & STEAM TABLES

Homogeneous Substance

A substance that has uniform thermodynamic properties throughout is said to be homogeneous.

Pure Substance

A pure substance has a fixed chemical composition and may exist in more than one phase. Examples of pure substances include:

- Water (solid, liquid, and vapour phases);
- Mixture of liquid water and water vapour;
- Carbon dioxide, CO_2;
- Oxygen, O_2; and
- Mixtures of gases, such as air, as long as there is no change of phase.

State Postulate

The state postulate for a simple, pure substance states that the equilibrium state can be determined by specifying any two independent intensive properties.

Real substances that readily change phase from solid to liquid to gas such as water, refrigerant-134a, and ammonia cannot be analysed as ideal gases in general. The pressure, volume, temperature relation, or equation of state for these substances is generally very complicated, and the thermodynamic properties are given in table or chart form.

Properties of Pure substances

A pure substance exists in different phases depending on its energy level. The term ***phase*** refers to a quantity of matter that is **homogeneous** throughout. Common examples of systems that contain more than one phase are a liquid and its vapour and a glass of ice water. A system which has three phases is a container with ice, water, and water vapour. In the liquid phase, a substance which is not about to vapourize is called a ***compressed*** or ***subcooled*** liquid. In the gas phase, a substance which is not about to condense is called ***superheated***[5] vapour.

During a phase-change process, the temperature and pressure of a pure substance are dependent properties. At a given pressure, a substance boils at a fixed temperature called the ***saturation*** temperature. Likewise, at a give temperature, the pressure at which a substance starts boiling is called the ***saturation pressure***. During a phase-change process, both the liquid and the vapour phases exist in equilibrium, and under this condition the liquid is called ***saturated liquid***[6] and the vapour ***saturated vapour***[7]**.**

In a saturated liquid-vapour mixture, the mass fraction of the vapour phase is called the quality and is defined as:

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

Where $m_{total} = (1-x)m_f + xm_g$

The quality may have values between 0 (saturated liquid) and 1 (saturated vapour). In the saturated mixture region, the average value of any intensive property y is determined from

$$y = y_g x + y_f(1-x); \quad \text{subsripts } g \text{ and } f \text{ stand for vapour and liquid respectively}$$

$$= y_f + y_{fg}x; \quad \text{since } \mathrm{y}_{fg} = (y_g - y_f)x$$

For example, specific volume, specific enthalpy, specific entropy, and specific internal energy are expressed as:

$$v = (1-x)v_f + xv_g = v_f + x(v_g - v_f) \approx xv_g \quad \text{since } \mathrm{v_g} >> v_f$$

$$h = (1-x)h_f + xh_g = h_f + x(h_g - h_f) = h_f + xh_{fg}$$

$$s = (1-x)s_f + xs_g = \mathrm{s_f} + xs_{fg}$$

$$u = (1-x)u_f + xu_g \text{ , respectively.}$$

Note: In the absence of compressed liquid data, a general approximation is to treat a compressed liquid as a saturated liquid at the given temperature:

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

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[5] Note that *degrees of superheat* is the temperature difference between the actual temperature of the superheated steam and the saturation temperature for the same pressure.

[6] A liquid about to condense (Dew point)

[7] A gas about to condense its first drop of liquid (Bubble point)

PVT behaviour of Pure Substances

PVT relationships are important for such purposes as the metering of fluids and the sizing of vessels and pipelines. Homogeneous fluids are usually divided into liquids and gases. The two phases become indistinguishable at the *critical point.* Measurements of the vapour pressure of a pure solid at temperatures up to its *triple point* and measurements of the vapour pressure of the pure liquid at temperatures above the triple point lead to a P-T curve such as lines 1 -2 and 2 – C in Figure 5.1 Line 2 – 3 gives the solid/liquid equilibrium relationship. Line 1 – 2, the sublimation[8] curve, separates the solid and gas regions; line 2 – 3, the fusion curve, separates the solid and liquid regions; line 2 – C, the vapourization curve, separates and liquid and gas regions. The 3 curves meet at the triple point, where all 3 phases coexist in equilibrium.

The vapourization curve *2 – C* terminates at C, the critical point, with coordinates P_c and T_c, the highest temperatue and pressure at which a pure chemical substance can exist in vapour/liquid equilibrium.

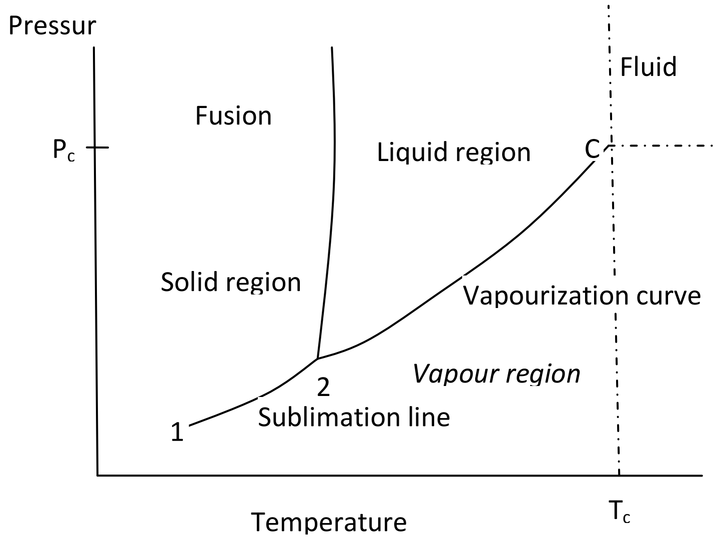

Figure 5.1: P-T diagram of a pure substance

Behaviour of Two-Phase Systems

We are interested in finding the relations between phases and the relations that describe the change of phase (from solid to liquid, or from liquid to vapour) of a **pure** substance, including the work done

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[8] When a solid passes directly into the vapour phase without first melting to become liquid, it is said to sublime. Iodine crystals do this at room temperature; water sublimes only below 0 ^{0}C, as when frost disappears in winter when the thermometer reads - 6^{0}C.

and the heat transfer. To start we consider a system consisting of a liquid and its vapour in equilibrium, which are enclosed in a container under a moveable piston, as shown below. The system is maintained at constant temperature through contact with a heat reservoir at temperature ***T***, so there can be heat transfer to or from the system.

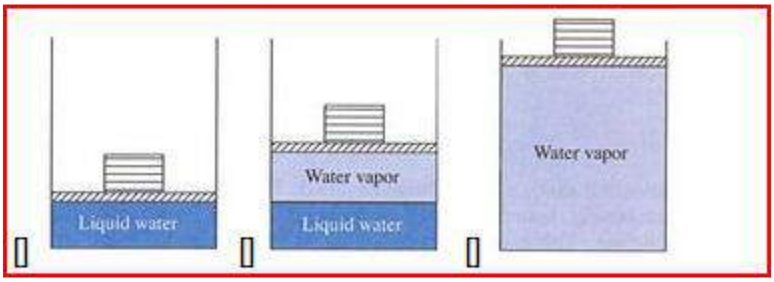

Figure 5.2: Two-phase system in contact with constant temperature heat reservoir

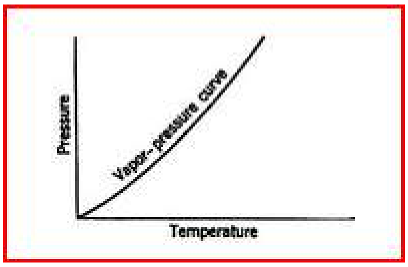

Figure 5.3: P – T relationship for a liquid - vapour system

For a pure substance, as shown in Figure 5.3, there is a one-to-one correspondence between the temperature at which vaporization occurs and the pressure. These values are called the saturation pressure and saturation temperature.

This means there is an additional constraint for a liquid-vapour mixture, in addition to the equation of state. The consequence is that we only need to specify one variable to determine the state of the system. For example, if we specify ***T*** then ***P*** is set. In summary, for two phases in equilibrium, ***P = P (T)***. If both phases are present, any quasi-static process at constant ***T*** is also at constant ***P***.

Pressure-volume behaviour of a liquid-vapour system at constant temperature.

For a single-phase ideal gas we know that the curve would be ***Pv = constant***. For the two-phase system the curve looks quite different, as indicated in Figure 5.4.

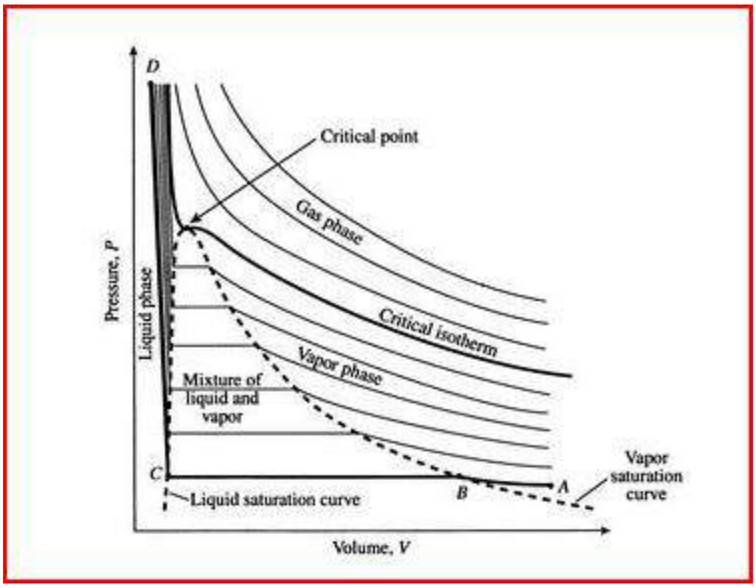

Figure 5.4: P – v diagram for two-phase system showing isotherms

Several features of the figure should be noted. First, there is a region in which liquid and vapor can coexist, bounded by the liquid saturation curve on the left and the vapor saturation curve on the right. This is roughly dome-shaped and is thus often referred to as the ``vapor dome." Outside of this regime, the equilibrium state will be a single phase. The regions of the diagram in which the system will be in the liquid and vapour phases respectively are indicated. Second is the steepness of the isotherms in the liquid phase, due to the small compressibility of most liquids. Third, the behaviour of isotherms at temperatures below the ***critical point*** in the region to the right of the vapour dome approach those of an ideal gas as the pressure decreases, and the ideal gas relation is a good approximation in this region.

The behaviour shown is found for all the isotherms that go through the vapour dome. At a high enough temperature, specifically at a temperature corresponding to the pressure at the peak of the vapour dome, there is no transition from liquid to vapour and the fluid goes continuously from a liquid-like behaviour to a gas-type behaviour. This behaviour is unfamiliar, mainly because the temperatures and pressures are not ones that we typically experience; for water the critical temperature is 374 ^{0}C and the associated critical pressure is 220 atm.

There is a distinct nomenclature used for systems with more than one phase. In the zone where both liquid and vapour exist, there are two bounding situations. When the last trace of vapour condenses, the state becomes ***saturated liquid***. When the last trace of liquid evaporates the state becomes ***saturated vapour*** (or ***dry vapour***). If we put heat into a saturated vapour it is referred to as ***superheated vapour***. For example, water at 1 atm and 120 ^{0}C (at 1 atm, the vaporization temperature of water is 100 ^{0}C) is a superheated vapour.

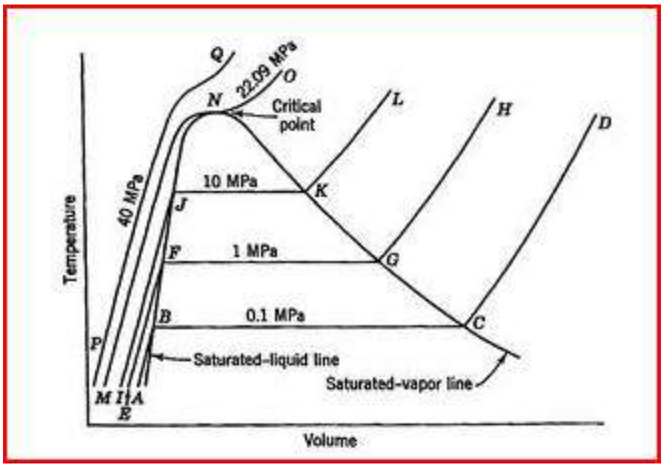

*Figure 5.5: Constant pressure curves in **T-v** coordinates showing vapour dome*

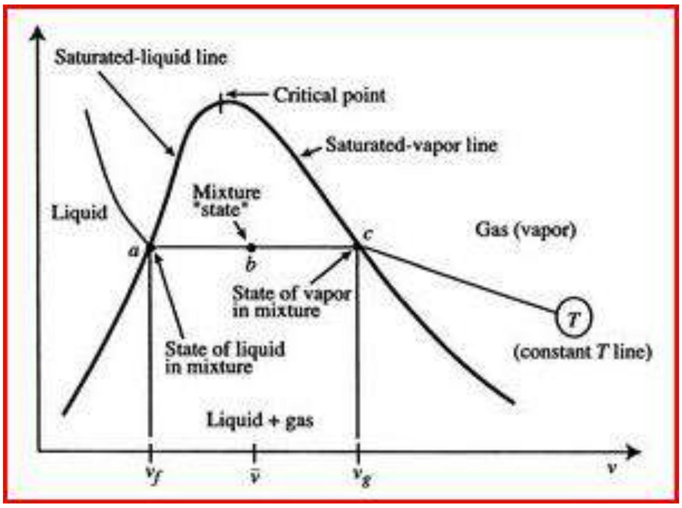

Figure 5.6: Specific volumes at constant temperature and states within the vapor dome in a liquid-vapour system

Let v_f = specific volumeof liquid phase

v_g = specific volume of gas phase

v = average specific volume of two phase system

then $v = v_g x + v_g(1-x)$

where x = quality of a liquid-vapour system

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

Chapter 8 BASICS OF ENERGY CONVERSION CYCLES

Heat engine

A heat engine is a thermodynamic system operating in a thermodynamic cycle to which net heat is transferred and from which net work is delivered. In other words, a heat engine acts by transferring energy from a warm region to a cool region of space and, in the process, converting some of that energy to mechanical work. The system, or working fluid, undergoes a series of processes that constitute the heat engine cycle.

Thermal efficiency, η_{th}

The thermal efficiency is the index of performance of a work-producing device or a heat engine and is defined as the ratio of the net work output to the heat input.

$$\eta_{th} = \frac{Desired\ result}{\mathrm{Re}\,quired\ input} = \frac{W_{net,out}}{Q_{in}} \qquad \text{; Where}$$

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

$$Q_{in} = Q_{out}$$

For a heat engine the desired result is the net work done and the input is the energy (heat) supplied to make the cycle operate. The thermal efficiency is always less than 1 or less than 100 %.

Applying the First Law to the cycle heat engine

$$Q_{net,in} - W_{net,out} = \Delta U; \qquad \Delta \mathrm{U} = 0 \text{ for a cycle}$$

$$= 0$$

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

$$= Q_{\mathrm{in}} - Q_{out}$$

The cycle efficiency may be written as

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

Generalized representation of thermodynamic cycles

All heat engines can be represented generally as a transfer of heat from a high temperature reservoir to a device, which does work on the surroundings, followed by a rejection of heat from that device to a low temperature reservoir.

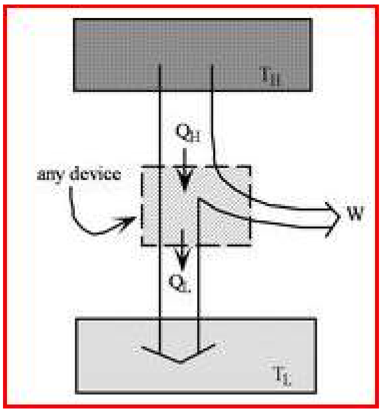

Figure 6.1: Generalized heat engine

Heat engines are cyclic devices[9]. The working fluid of a heat engine returns to its initial state at the end of each cycle. Work is done by the working fluid during one part of the cycle and on the working fluid during another part. The difference between these two is the net work delivered by the heat engine. The cycle efficiency can be maximized by using processes that require the least amount of work and deliver the most; i.e. by using reversible processes.

Reversible cycles cannot be achieved in practice and therefore serve as starting points in the development of actual cycles. The Carnot cycle is best known reversible cycle; it was proposed by Frenchman Sadi Carnot in 1824.

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[9] They also include refrigerators and heat pumps

Note: The thermal efficiency applied to above heat engine gives

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

The Carnot cycle

A *Carnot heat engine* is a hypothetical engine that operates on the reversible Carnot cycle. The Carnot cycle is the most efficient cycle possible for converting a given amount of thermal energy into work. A Carnot cycle has four processes. The system can be regarded as a chamber enclosed by a piston and filled with an ideal gas (working fluid).

There are *two adiabatic reversible paths* and *two isothermal reversible paths*.

The four processes are shown below:

- Process 1-2 Reversible isothermal heat addition at high temperature, $T_H > T_L$, to the working fluid in a piston cylinder device that performs boundary work;
- Process 2-3 Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to $T_{L;}$
- Process 3-4 The system is brought in contact with a heat reservoir at $T_L < T_H$ and a reversible isothermal heat exchange takes place while work of compression is done on the System; and
- Process 4-1 A reversible adiabatic compression process increases the working fluid temperature from T_L to T_H

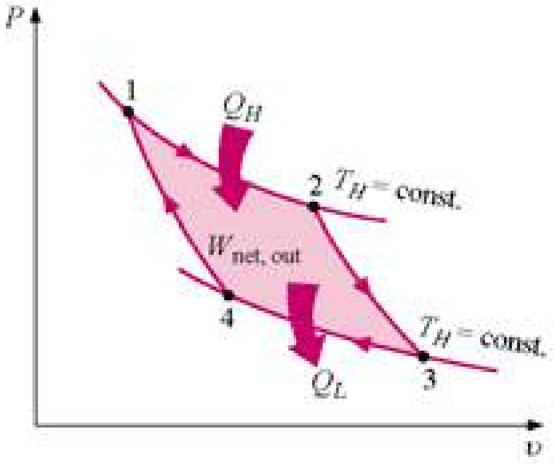


Figure 6.3: The Carnot cycle

Simplified analysis of the Carnot cycle

The heat, Q, for the whole cycle is

$$Q = Q_H + Q_L$$

And the work for the entire cycle is

$$W = W_{1,2} + W_{2,3} + W_{3,4} + W_{4,1}$$

Since it is a cyclic process, the change in U is zero and from the First Law,

$$\Delta U = Q - W = 0$$

$$or\ Q = W$$

The efficiency of the Carnot cycle (Carnot efficiency) is given by

$$\eta_{th} = \frac{W}{Q_H} = 1 - \frac{T_L}{T_H}$$

This is the maximum possible efficiency of a heat engine operating between two heat reservoirs at temperatures T_H and T_L. Note that the temperatures are absolute temperatures.

The Carnot 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 constant-temperature heat reservoirs are the same.

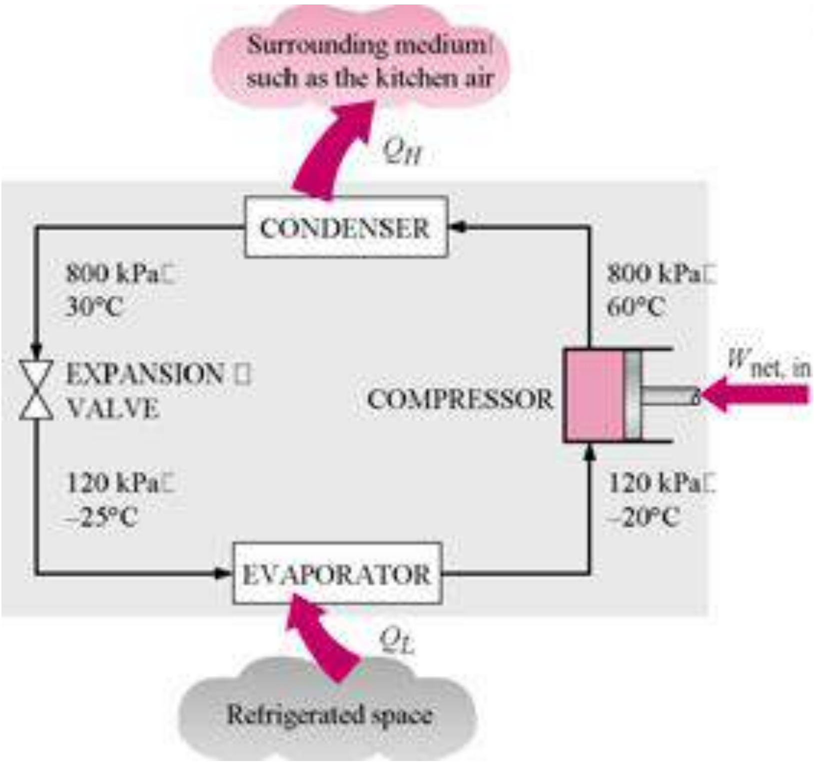
Refrigerators and heat pumps

Refrigerators are special devices used to transfer heat from a low-temperature medium to a high-temperature medium. Refrigerators are cyclic devices just like heat engines. The working fluid in the refrigeration cycle is called a refrigerant.

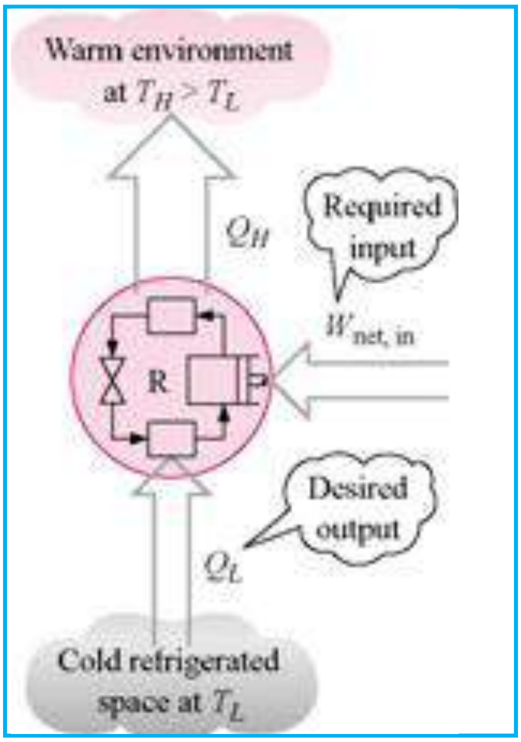
The efficiency of a refrigerator is expressed in terms of the coefficient of performance (COP). A refrigerator removes heat from the cold space and therefore requires a work input. Air conditioners are refrigerators whose refrigerated space is a room or building instead of the food compartment.

A heat pump is a thermodynamic system operating in a thermodynamic cycle that removes heat from a low-temperature environment (such as cold outside air in a wintry weather) and rejects heat to a high-temperature body (such as a high-temperature medium like a house). To accomplish this energy transfer, the heat pump receives external energy in the form of work or heat from the surroundings.

The figure below shows a refrigerator operating in a thermodynamic cycle:



Coefficient of Performance, COP



The performance of a refrigerator or heat pump is expressed in terms of the coefficient of performance, COP, the ratio of desired result to input. This measure of performance may be larger than 1; the larger the COP, the more efficient the refrigerator or heat pump.

$$COP = \frac{Desired\ result}{\mathrm{Re}quired\ input}$$

The primary function of the heat pump is the transfer of heat to the high-temperature system. The coefficient of performance for a heat pump is

$$COP_{HP} = \frac{\text{Heating effect}}{\text{Work input}} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L}$$

For a refrigerator or an air conditioner the desired result is the heat supplied at the low temperature and the input is the net work into the device to make the cycle operate.

$$COP_R = \frac{\text{Cooling effect}}{\text{Work input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L}$$

It can be shown that under the same working conditions the COP_{HP} and COP_R are related by

$COP_{HP} = COP_R + 1$

Chapter 9 GAS POWER CYCLES

Gas Power Cycles involve the study of heat engines in which the working fluid remains in the gaseous state throughout the cycle. In the ideal cycle internal irrevessiblities and complexities (the actual intake of air and fuel, the actual combustion process, and the exhaust of products of combustion among others) are removed.

Often the Carnot efficiency is compared to the efficiencies of other cycles as a means to improving the efficiency of other cycles. From the Carnot efficiency it is observed that thermal efficiency increases with an increase in the average temperature at which heat is supplied to the system or with a decrease in the average temperature at which heat is rejected from the system.

$$\eta_{th,Carnot} = \frac{1 - T_L}{T_H}$$

Air-Standard Assumptions

In analyzing gas power cycles, it is assumed that the working fluid is air, and the air undergoes a thermodynamic cycle even though the working fluid in the actual power system does not undergo a cycle.

To simplify the analysis, the following assumptions are used to approximate the cycles:

- The air continuously circulates in a closed loop and always behaves as an ideal gas.
- All the processes that make up the cycle are internally reversible.
- The combustion process is replaced by a heat-addition process from an external source.
- A heat rejection process that restores the working fluid to its initial state replaces the exhaust process.
- The cold-air-standard assumptions apply when the working fluid is air and has constant specific heat evaluated at room temperature (25 ^{o}C).

Otto Cycle: The Ideal Cycle for Spark-Ignition Engines

The Internal combustion engine (Otto cycle)

The Otto cycle is a set of processes used by spark ignition internal combustion engines (2-stroke or 4-stroke cycles). These engines a) ingest a mixture of fuel and air, b) compress it, c) cause it to react, thus effectively adding heat through converting chemical energy into thermal energy, d) expand the combustion products, and then e) eject the combustion products and replace them with a new charge of fuel and air.

The processes are summarized below:

Processes

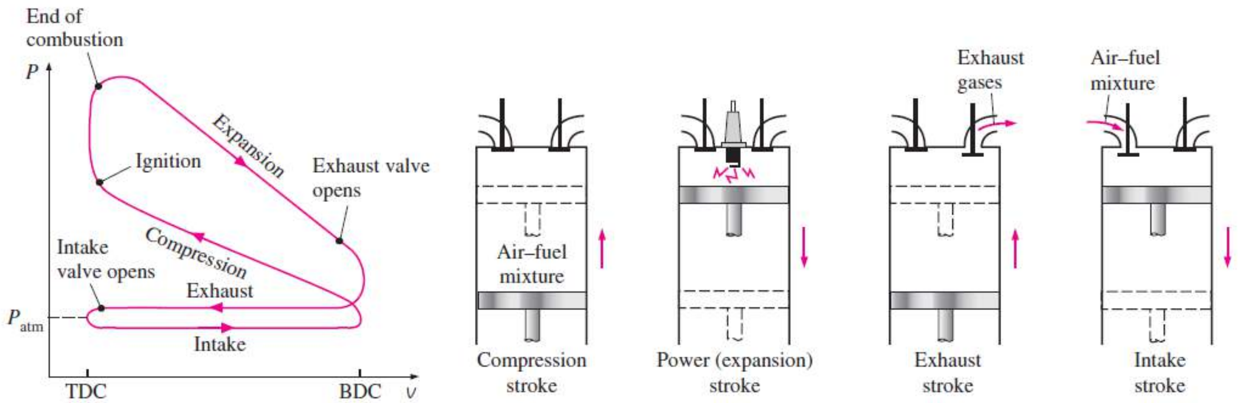
Intake stroke

Compression stroke

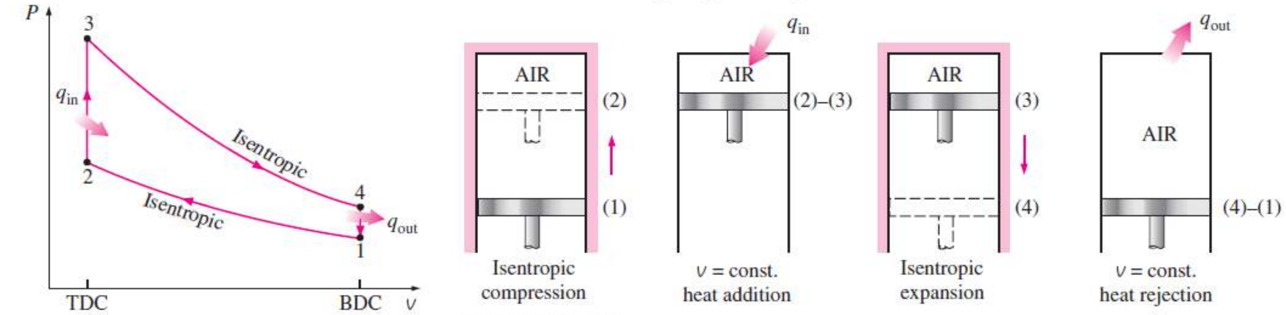
Power (expansion) stroke

Exhaust stroke

Often the ignition and combustion process begins before the completion of the compression stroke.



(a) Actual four-stroke spark-ignition engine



(b) Ideal Otto cycle

Top dead center (TDC) – position of the piston when it forms the smallest volume in the cylinder

Bottom dead center (BDC) –position of the piston when it forms the largest volume in the cylinder.

Actual and ideal cycles in spark-ignition engines and their *P-v* diagrams

The air-standard Otto cycle is the ideal cycle that approximates the spark ignition combustion engine:

Process Description

1-2	Isentropic compression
2-3	Constant volume heat addition
3-4	Isentropic expansion
4-1	Constant volume heat rejection

The net efficiency of the Otto cycle is given by

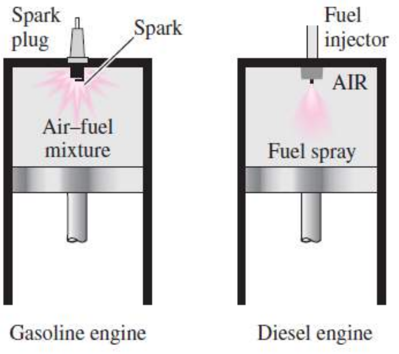
$$\eta_{th,Otto} = \frac{1-Q_{out}}{Q_{in}} = 1-\frac{T_1}{T_2} = 1-\frac{1}{r^{k-1}}$$

where

$$r = V_1 / V_2$$

$$k = c_p / c_v$$

Air-Standard Diesel Cycle



In diesel engines, the spark plug is replaced by a fuel injector, and only air is compressed during the compression process.

The Diesel cycle is a compression ignition (rather than spark ignition) engine. Fuel is sprayed into the cylinder at high pressure when the compression is complete, and there is ignition without a spark

The air-standard Diesel cycle is the ideal cycle that approximates the Diesel combustion engine

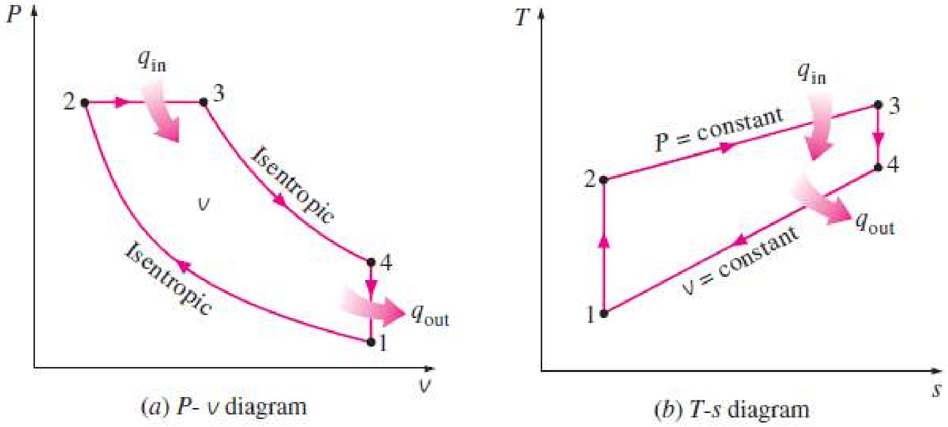
Process Description

1-2 Isentropic compression

2-3 Constant pressure heat addition

3-4 Isentropic expansion

4-1 Constant volume heat rejection



T-s and P-v diagrams for the ideal Diesel cycle.

The thermal efficiency of the Diesel cycle

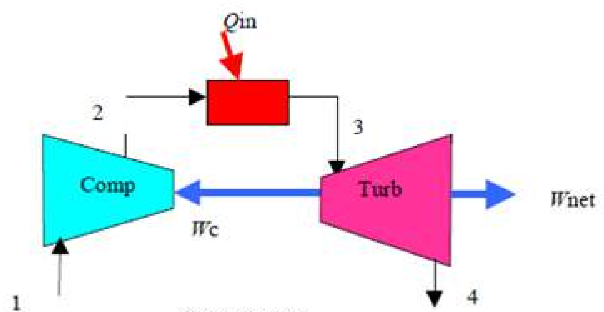
$$\eta_{th,Diesel} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{1}{r^{k-1}} \frac{r_c^k - 1}{k(r_c - 1)}$$

where

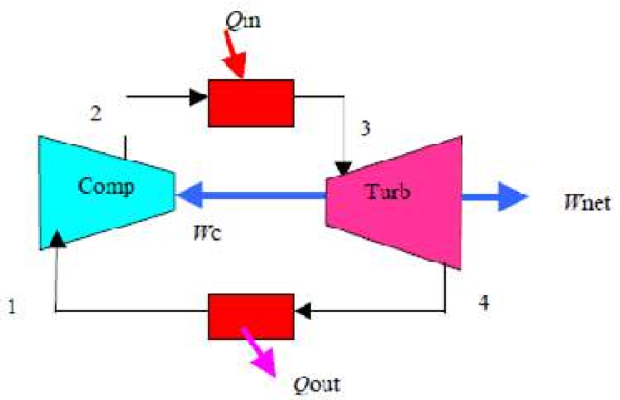
$$r_c = \frac{T_3}{T_2} = \frac{V_3}{V_2}$$

Brayton Cycle

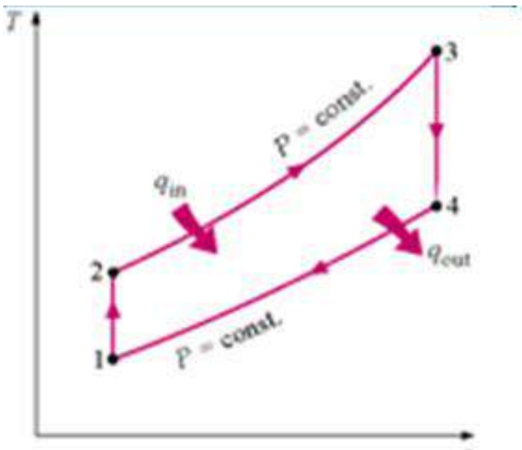
The Brayton cycle is the air-standard ideal cycle approximation for the gas turbine engine. This cycle differs from the Otto and Diesel cycles in that the processes making the cycle occur in open systems or control volumes. Therefore, an open system, steady-flow analysis is used to determine the heat transfer and work for the cycle.



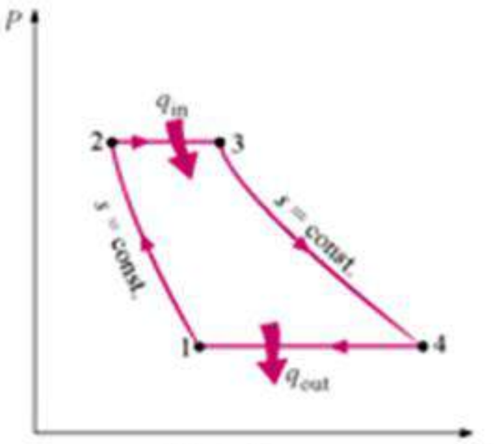
Brayton cycle



Closed Brayton cycle



(a) T-s diagram



(b) P-v diagram

The working fluid is assumed to be air and the specific heats are also assumed to be constant.

Process Description

1-2 Isentropic compression (in a compressor)
2-3 Constant pressure heat addition
3-4 Isentropic expansion (in a turbine)
4-1 Constant pressure heat rejection

The thermal efficiency is expressed as

$$\eta_{th,Brayton} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r_p^{(k-1)/k}}$$

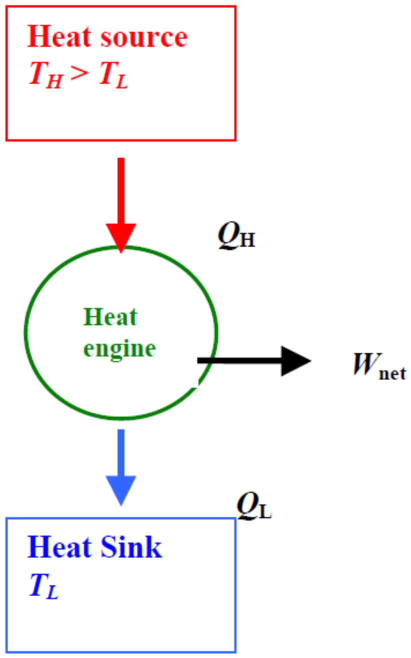
where

$$pressure\ ration, r_p = p_2 / p_1$$

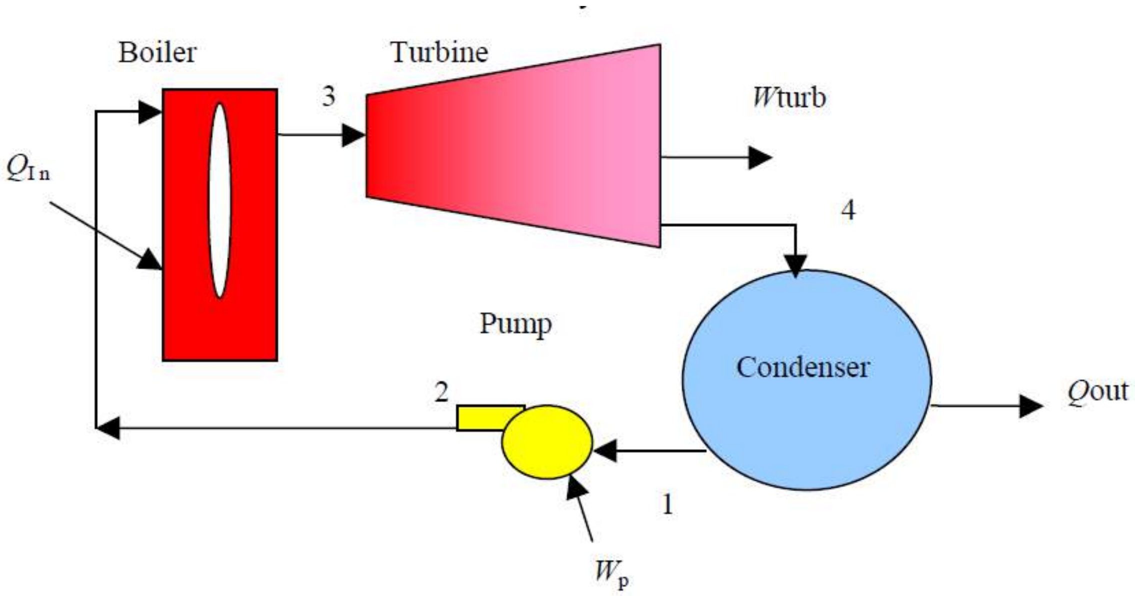
Chapter 10 VAPOUR POWER CYCLES

The working fluid in these cycles undergoes phase changes. The best example of this cycle is the steam power cycle where water (steam) is the working fluid.

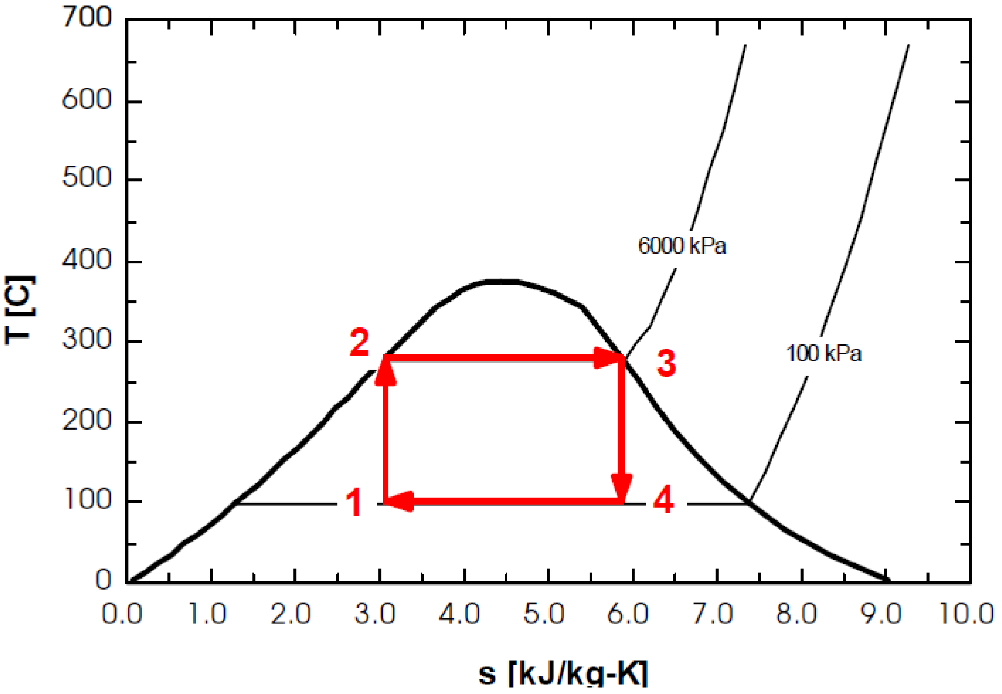
Carnot vapour cycle



The heat engine may be composed of the following components



The working fluid, steam (water), undergoes a thermodynamic cycle from 1-2-3-4-1. The cycle is shown below on a *T*-*s* diagram.



Carnot vapour cycle using steam

The thermal efficiency of this cycle is given as

$$\eta_{th,Carnot} = \frac{W_{net}}{Q_{in}} = \frac{1 - T_L}{T_H}$$

Note the effect of T_H and T_L on the efficiency:

- The larger the T_H the larger the efficiency
- The smaller the T_L the larger the efficiency

To increase the thermal efficiency in any power cycle, the maximum temperature at which heat is added must be increased.

The Carnot cycle is practically not used because of the following reasons:

- Pumping process 1-2 requires the pumping of a mixture of saturated liquid and saturated vapor at state 1 and the delivery of a saturated liquid at state 2.
- To superheat the steam to take advantage of a higher temperature, elaborate controls are required to keep T_H constant while the steam expands and does work.

The Carnot cycle also has a low work ratio. To resolve the complications associated with the Carnot cycle, the Rankine cycle was devised.

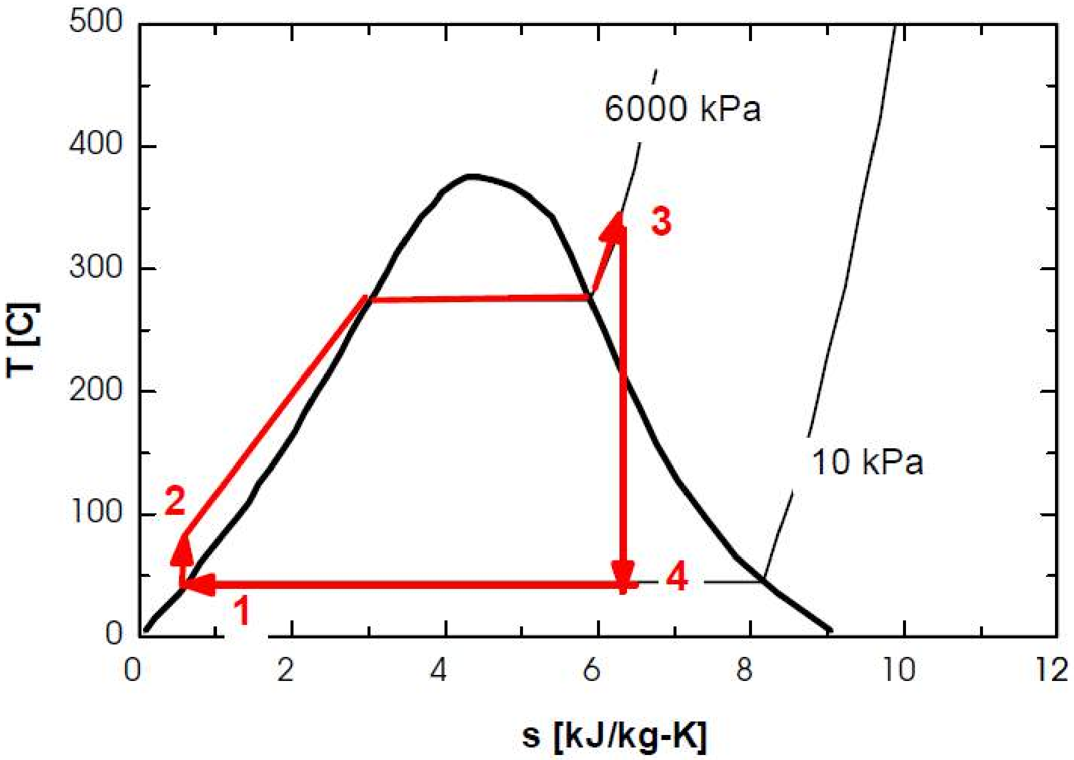
Rankine Cycle

The simple Rankine cycle has the same component layout as the Carnot cycle shown above. The simple Rankine cycle continues the condensation process 4-1 until the saturated liquid line is reached.

The Ideal Rankine Cycle Processes are shown below:

Process	Description
1-2	Isentropic compression in pump
2-3	Constant pressure heat addition in boiler
3-4	Isentropic expansion in turbine
4-1	Constant pressure heat rejection in condenser

The *T-s* diagram for the Rankine cycle is given below.



The Rankine cycle is less efficient than the Carnot cycle for given maximum and minimum temperatures, even though, it is more effective as a practical power production device.

Pump

The pump work is obtained from the conservation of mass and energy for steady-flow but neglecting potential and kinetic energy changes and assuming the pump is adiabatic and reversible.

$$W_{pump} = \dot{m}(h_2 - h_1) = v_1(p_2 - p_1)$$

Boiler

To find the heat supplied in the boiler, we apply the steady-flow conservation of mass and energy to the boiler. If we neglect the potential and kinetic energies, and note that no work is done on the steam in the boiler, then

$$Q_{in} = \dot{m}(h_3 - h_2)$$

Turbine

The turbine work is obtained from the application of the conservation of mass and energy for steady flow. We assume the process is adiabatic and reversible and neglect changes in kinetic and potential energies.

$$\dot{W}_{turb} = \dot{m}(h_3 - h_4)$$

The thermal efficiency is given as $\eta = \frac{W_{net}}{Q_{in}}$

There are several ways of improving the simple Rankine cycle efficiency:

Superheat the vapour

Average temperature is higher during heat addition.

Moisture is reduced at turbine exit (moisture percentage should not go below 88 percent)

Increase boiler pressure (for fixed maximum temperature)

Availability of steam is higher at higher pressures

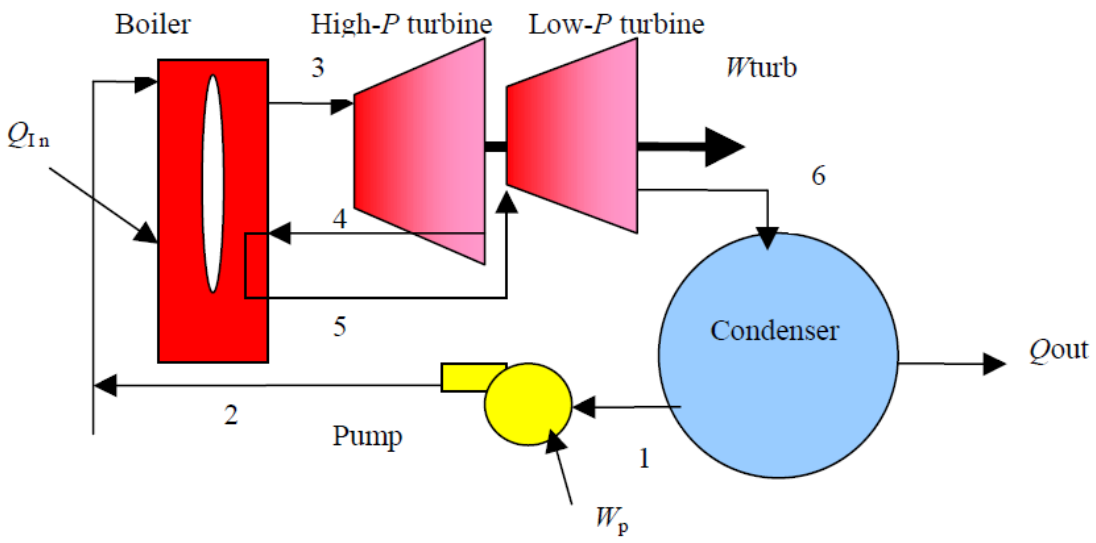
Moisture is increased at turbine exit

Lower condenser pressure

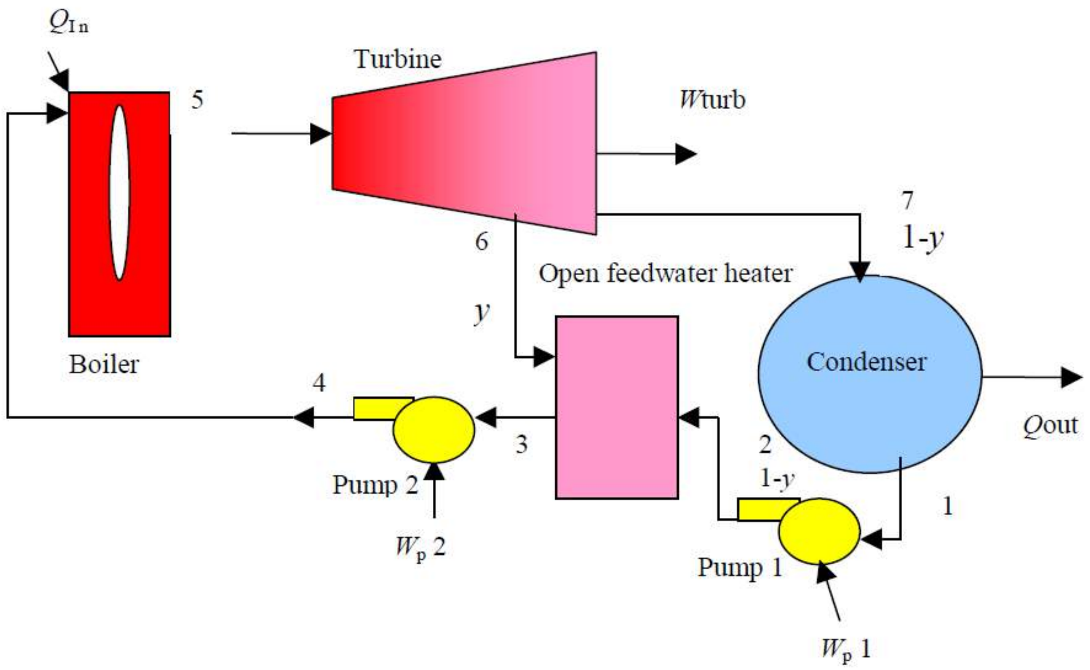
Less energy is lost to surroundings

Moisture is increased at turbine exit

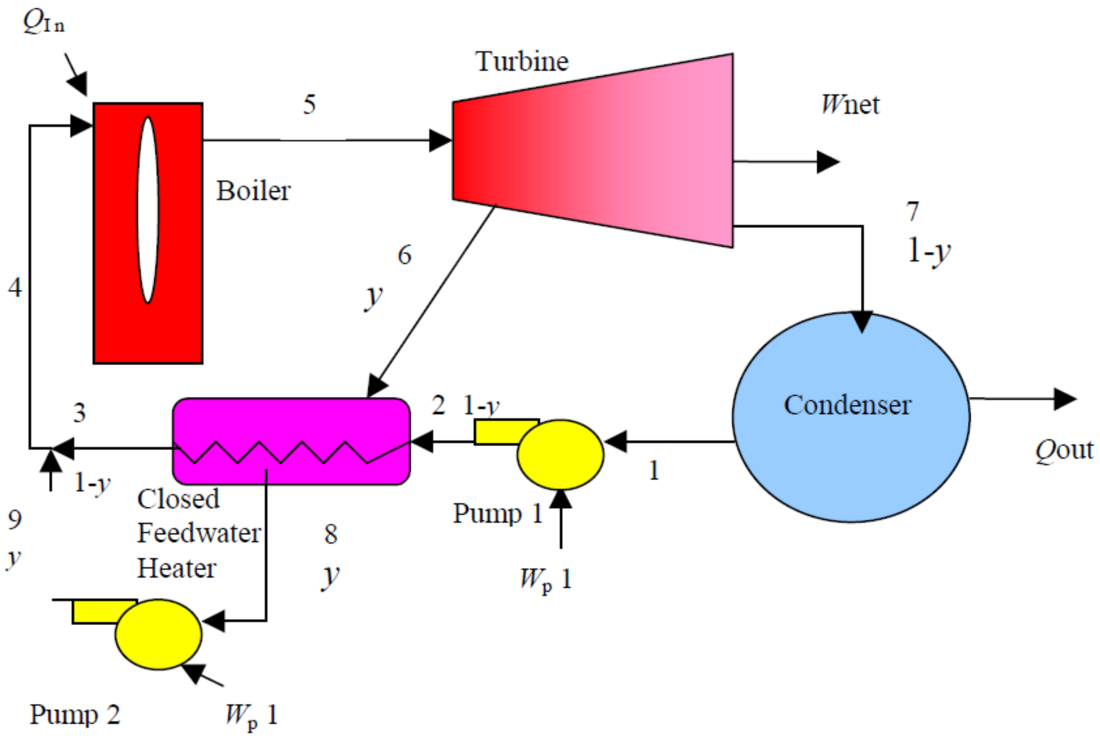
Complex Rankine Cycles



Rankine Cycle with Reheat



Rankine Steam Power Cycle with an Open Feedwater Heater



Rankine Steam Power Cycle with a Closed Feedwater Heater

Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a pure crystalline substance at absolute zero temperature is zero. This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is called absolute entropy.

Chapter 11 THERMODYNAMIC PROPERTY RELATIONS

Consider a function that depends on two (or more) variables, such as $z = z(x, y)$. This time the value of z depends on both x and y. It can be shown from first principles that the fundamental relation for the total differential of a dependent variable, z, in terms of its partial derivatives with respect to the independent variables, x and y, is given as:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

The above equation can be rewritten as:

$dz = M\,dx + N\,dy$; *where*

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

Taking the partial derivative of M with respect to y and of N with respect to x yields

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x\, \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y\, \partial x}$$

Since the order of differentiation is immaterial for properties, the above relations are identical:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This relation forms the basis for the development of the Maxwell relations.

The function $z = z(x, y)$ can also be expressed as $x = x(y, z)$ if y and z are taken to be the independent variables.

Then the total differential of *x* becomes

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Eliminating *dx*, we obtain

$$dz = \left[\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy + \left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial x}\right)_y dz$$

$$\left[\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy = \left[1 - \left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial x}\right)_y\right] dz$$

For this equation to be valid at all times, the terms in the brackets must equal zero, regardless of the values of *y* and *z*. Setting the terms in each bracket equal to zero gives

$$\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y}$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial y}\right)_x \rightarrow \left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$$

The first relation is called the reciprocity relation, and it shows that the inverse of a partial derivative is equal to its reciprocal. The second relation is called the cyclic relation, and it is frequently used in thermodynamics.

Maxwell's relations

Maxwell's relations are a set of equations in thermodynamics which are derivable from the definitions of the thermodynamic potentials. The Maxwell relations relate the partial derivatives of properties *P*, *v*, *T*, and *s* of a simple compressible system to one other. Maxwell relations are usually obtained from the Gibbs equations:

$$du = T\,ds - P\,dv$$

$$dh = T\,ds + v\,dP$$

$$da = -s\,dT - P\,dv$$

$$dg = -s\,dT + v\,dP$$

A careful examination of the four Gibbs relations reveals that they are of the form

$$dz = M\,dx + N\,dy$$

Applying the above relation to the Gibbs relations, we obtain the Maxwell relations

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P, v, and T.

Chapter 12 INTRODUCTORY TOPICS IN PHASE EQUILIBRIA

Phase equilibria is one of the foundations of the chemical engineering field.

The Phase Rule

The state of a pure homogeneous fluid is fixed whenever two intensive thermodynamic properties are set at definite values. On the contrary, when two phases are in equilibrium, the state of the system is fixed when only a single such property is specified. For example, a mixture of steam and liquid water in equilibrium at 1 atm can exist only at 100 ^{0}C. It is impossible to change the temperature without also changing the pressure if vapour and liquid are to continue staying in equilibrium.

The number of independent variables that must be arbitrarily fixed to establish the intensive state of any system, i.e., *the degrees of freedom F* of the system, is given by the well-known ***phase rule*** propounded by Gibbs.

$F = 2 – \text{л} + N$[10]

Where л *= number of phases, and N = number of chemical species*

It tells us that the specification of a certain number of intensive properties of a system also fixes the values of all other intensive properties. A phase is a homogeneous region of matter; a gas or a mixture of gases, a liquid or a liquid solution, and a solid crystal are examples of phases. A phase can be discontinuous; examples of discontinuous phases are a gas dispersed as bubbles in a liquid, and a liquid dispersed as droplets in another liquid with which it is immiscible. An abrupt change in properties always occurs at the boundary between phases. Various phases can coexist, but they must be in equilibrium for the phase rule to apply. An example of a system at equilibrium which is made up of 3 phases is a boiling saturated solution of a salt in water with excess salt crystals present. The 3 phases are crystalline salt, the saturated aqueous solution, and the vapour generated by boiling.

The phase rule variables are *intensive* properties, which are independent of the extent of the system and of the individual phases. Thus, the phase rule gives the same information for a large system as for a small one and for different relative amounts of the phases present.

The minimum number of degrees of freedom for any system is zero. When F = 0, the system is invariant, which means

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[10] Applicable to nonreacting systems only

$$Л = 2 + N$$

This value of л is the maximum number of phases which can coexist at equilibrium for a system containing N chemical species. When N = 1, this number is 3, characteristic of a triple point. For example, the triple point of water, where liquid, vapour, and the common form of ice exist together in equilibrium, occurs at 0.01 ^{0}C and 0.0061 bar. Any change from these conditions causes at least one phase to disappear.

Vapour pressure and liquids

The vapor pressure of a liquid is defined as the pressure at which the liquid boils at a given temperature. Vaporization and condensation at constant temperature and pressure are equilibrium processes, and the equilibrium pressure is called the vapour pressure. At a given temperature there is only one pressure at which the liquid and vapour phases of a pure substance may exist. At any given temperature, water exerts its vapour pressure (at equilibrium), and as the temperature goes up, the vapour pressure goes up.

Any substance has an infinite number of boiling points, but by custom the 'normal' boiling point is the temperature at which boiling takes place under 1 atm. Unless another pressure is specified, 1 atm is assumed. A piston exerting a force of 101.3 kPa could just as well take the place of the atmosphere.

Change of vapour pressure with temperature

A plot of the vapour pressure (p^*) of a compound against temperature does not yield a straight line but a curve. Several correlations have been purposed to transform this curve to a linear form ($y = mx + c$); a plot of $In\ (p^*)$ vs. (1/T), for moderate temperature intervals, is reasonably linear:

$$In(p^*) = m\left(\frac{1}{T}\right) + b$$

This equation is derived from the Clausius - Clapeyron equation

Empirical correlations of vapour pressure are frequently given in the form of the Antoine equation:

$$In(p^*) = A - \left(\frac{B}{T + C}\right)$$

where A, B, C = constants different for each substance
T = temperature, K

Liquid properties

Data for liquid densities of pure compounds as a function of temperature and pressure are common. As to liquid mixtures, it is more difficult to predict the p-V-T properties than real gas mixtures. For compounds with like molecular structures, such as hydrocarbons of similar molecular weight, called *ideal liquids*, the density of a liquid mixture can be approximated by assuming that the specific volumes are additive:

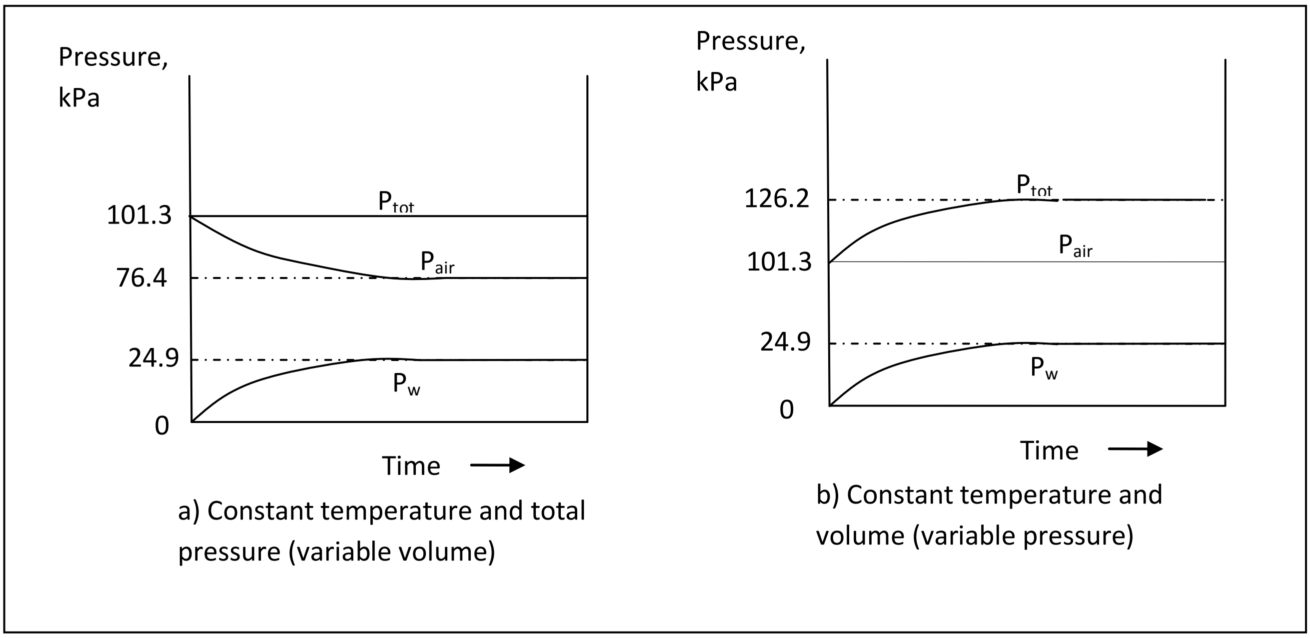
$$\hat{V}_{avg} = \hat{V}_1 + \hat{V}_2 + ... + \hat{V}_n = \sum_{i=1}^{n} \hat{V}_i$$

where *n* is the number of components in the mixture. For nonideal liquids or solids dissolved in liquids, experimental data or estimation techniques must be used, as the specific volumes are not additive.

Vapour and a Noncondensable Gas at Equilibrium

A mixture containing a vapour behaves somewhat differently than does a pure component by itself. An example is water vapour in air. When any pure gas comes in contact with a liquid, the gas will acquire vapour from the liquid. If contact is maintained for a considerable length of time, vaporization continues until equilibrium is established, at which time the partial pressure of the vapour in the gas will equal the vapour the vapour pressure of the liquid at the system's temperature. At equilibrium the gas is said to be saturated or the gas mixture is at its dew point. Dew point for the mixture of pure vapour and noncondensable gas means the temperature at which the vapour just starts to condense when cooled at constant pressure.

Suppose you inject liquid water at 65 ^{0}C into a cylinder of air at the same temperature, and keep the system at a constant temperature of 65. ^{0}C. The pressure at the top of the cylinder is maintained at 1 atm. It is observed that the volume of the air and water vapour increases until the air is saturated with vapour, after which stage the volume remains constant. Moreover, the partial pressure of the water vapour increases with time until it reaches its vapour pressure of 24.0 kPa.



a) Constant temperature and total pressure (variable volume)

b) Constant temperature and volume (variable pressure)

Figure 8.1: change of partial and total pressures on vaporisation of water and air at constant temperature

Next, suppose an experiment is undertaken by maintaining a constant volume whiles allowing the total pressure to vary in the cylinder. Will the pressure go up or down with respect to time?

Assuming that the ideal gas laws apply to both air and water vapour, as they do with excellent precision, we can say that the following relations hold at saturation:

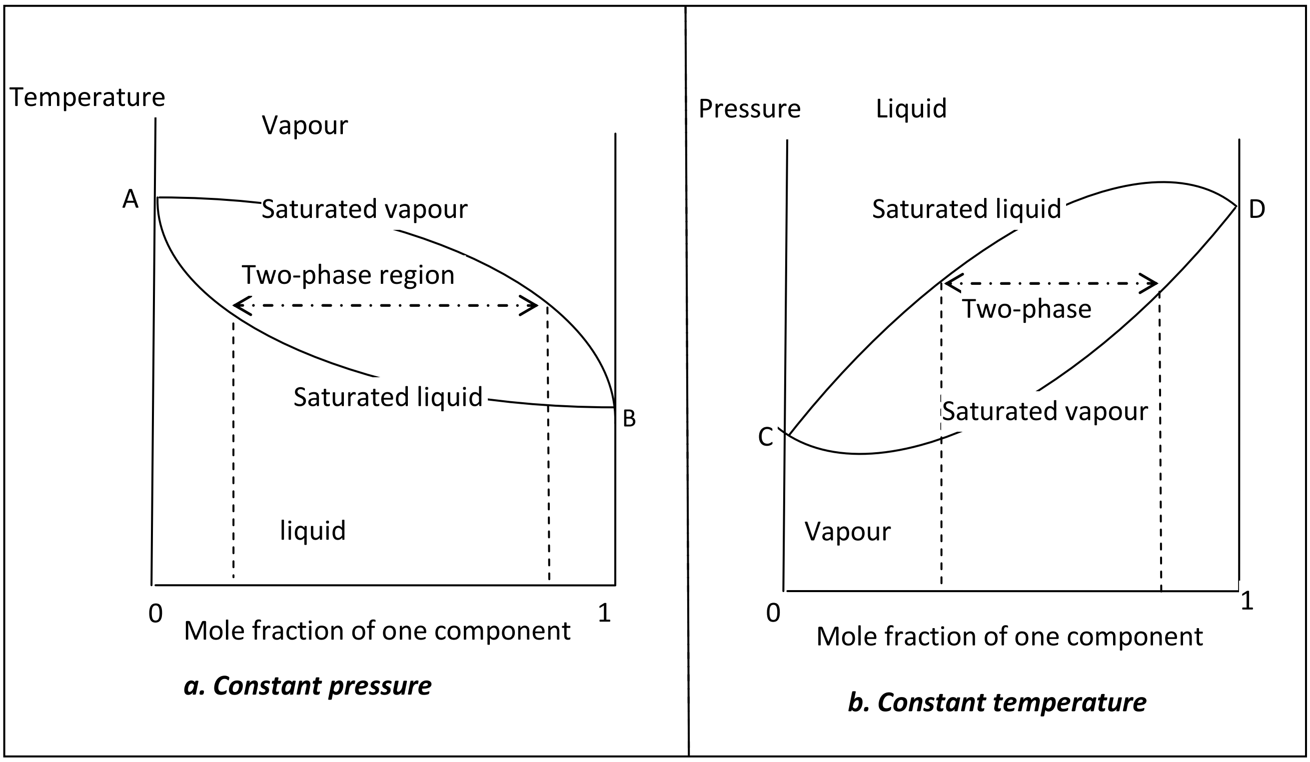
$$\frac{p_{air}V}{p_w V} = \frac{n_{air}RT}{n_w RT}$$

or

$$\frac{p_{air}}{p_w} = \frac{n_{air}}{n_w} = \frac{p_{air}}{p_{tot} - p_w} \qquad \text{in a volume V at temperature T}$$

Vapour –liquid equilibria for multicomponent systems

In a two-phase vapour-liquid mixture at equilibrium, if all the components can vaporize and condense, a component in one phase is in equilibrium with the same component in the other phase. The equilibrium relationship depends on temperature, pressure, and the composition of the mixture. Two cases are shown in the diagram below: one at constant temperature and the other at constant pressure.



a. Constant pressure

b. Constant temperature

Figure 8.2: Vapour-liquid equilibria for a binary mixture. The dashed lines show the equilibrium positions.

At A and B, and C and D, the respective pure components exert their respective vapour pressures at the equilibrium temperature. In between the pairs of points, as the overall composition of the mixture changes, two phases exist, each having a different composition for the same component as indicated by the dashed lines.

Raoult's law

This law is used mainly for a component whose mole fraction approaches unity or for solutions of components quite similar in chemical nature, such as straight-chain hydrocarbons. The saw is given as

$$p_i = p_i^* x_i$$

where subscript i denote component,
p_i is the partial pressure of component i in the gas phase
y_i is the gas - phase mole fraction
x_i is the liquid - phase mole fraction

When $x_i \equiv 1$, $p_i = p_i^*$; an equilibrium constant K_i *is* defined from the above equation by assuming that Dalton's law apply to the gas phase ($p_i = p_t y_i$):

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{p_i}$$

This equation gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures. For nonideal mixtures, the equation can be adapted if K_i is made a function of temperature, pressure, and composition so that relations for K_i can be fit by experimental data, and used directly.

Henry's law

This law is used mainly for a component whose mole fraction approaches zero, such as dilute gas dissolved in a liquid:

$$p_i = H_i x_i$$

where H_i is the Henry's law constant.

When $x_i \equiv 0$, $p_i \equiv 0$

Values of H_i can be found in Perry & Green, and other handbooks.

Enthalpy Changes for Phase Transitions

The name given to enthalpy changes for phase transitions is *latent heat changes*[11]. Ice at 0 ^{0}C can absorb 334 J/g of energy without undergoing a temperature rise or a pressure change; similarly,

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[11] Latent means *hidden* in the sense that the substance, eg. Water, can absorb a large amount of heat without any noticeable increase in temperature.

liquid water at 1 atm can absorb 2256.1 J/g before the temperature and water will change. The various enthalpy changes are termed:

Enthalpy change	Phase change
Heat of fusion	Solid to liquid
Heat of vaporization	Liquid to vapour
Heat of condensation	Vapour to liquid
Heat of sublimation	Solid to vapour

The diagram below shows, by the vertical lines at constant temperature, the enthalpies for the phase changes for water at 1 atm.

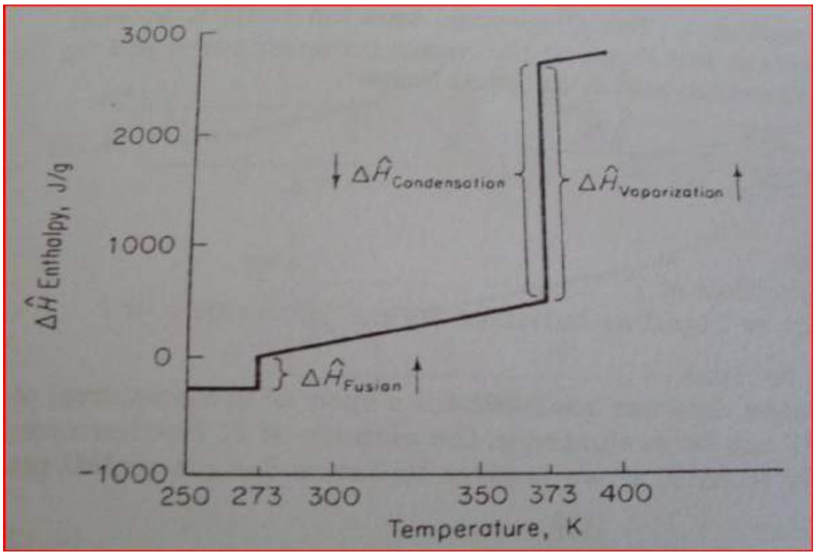


Figure 8.3: enthalpy change for water at 1 atm showing the phase transitions

Note that the enthalpy changes for vaporization given in the steam tables are for water under its vapour pressure at the indicated temperature. In the absence of experimental values, the following approximate methods can be used:

Heat of fusion

The heat of fusion for many elements and compounds can be roughly determined by

$$\frac{\Delta H_f}{T_f} = constant = \begin{cases} 2-3 & \text{for elements} \\ 5-7 & \text{for inorganic compounds} \\ 9-11 & \text{for organic compounds} \end{cases}$$

$$where \quad \Delta H_f = molar \text{ heat of reaction, cal/g mol}$$
$$\mathrm{T_f} = melting \text{ point,K}$$

Heat of vaporization

It is important to estimate ΔH_v accurately since is usually very large. Three methods are given of which two will be discussed.

Clausius – Clapeyron equation

The Clapeyron equation, given below, is itself an exact thermodynamic relationship between the slope of the vapour pressure curve and the molar heat of vaporization:

$$\frac{dp^*}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

$where \; p^* = vapour \text{ pressure}$

$\text{T} = \text{absolute temperature}$

$\Delta H_v = \text{molar heat of vaporization at T}$

$\text{V}_\text{i} = \text{molar volume of gas or liquid is indicated by the subscript g or l}$

Note that any set of units may be used.

For a nonideal gas, V_i may be neglected and we obtain

$$\frac{dp^*}{dT} = \frac{\Delta H_v}{z(RT^2/p^*)}$$

which can then be solved for ΔH_v

Derivation of Clausius - Clapeyron equation

From the equation

$$\frac{dp^*}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

we make the following assumptions :

- $\text{V}_\text{l} << \text{V}_\text{g}$
- The ideal gas law is applicable for to the vapour :

$$\text{V}_\text{g} = RT/p^*$$

Thus

$$\frac{dp^*}{p^*} = \frac{\Delta H_v dT}{RT^2}$$

$$\Rightarrow \frac{d\,\text{In p}^*}{d\left(1/T\right)} = 2.303\frac{d\,\text{log p}^*}{d\left(1/T\right)} = -\frac{\Delta H_v}{R}$$

Assuming ΔH_v is consant over the temperature range of interest, we obtain

$$\log\, p^* = -\frac{\Delta H_v}{2.303RT} + B$$

This is the *Clausius-Clapeyron* equation. Usually, a plot of *In* p^* versus 1/T does not yield a straight line and the equation is modified; one version is the Antoine equation.
Another version comes directly from integration of the above second equation

$$\log\frac{p_1^*}{p_2^*} = \frac{\Delta H_v}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Either the above equation or the Antoine equation can be used graphically or analytically to obtain ΔH_v for a short temperature interval.

Reference substance plots

A number of graphical techniques are also available. They are used to estimate ΔH_v of a liquid at any temperature by comparing the ΔH_v for the unknown liquid with that of a known liquid such as water.

Duhring plot

The temperature of the wanted compound A is plotted against the temperature of the known (reference) liquid at equal vapour pressure. For example, if the temperature of A and the reference substance B are determined at 760, 500, and 300 mm Hg pressure, then a plot of the temperatures of A versus the temperatures of B will be approximately a straight line over a wide temperature range, having a slope of

$$\frac{\Delta H_{v,A}}{\Delta H_{v,B}}\left(\frac{T_B}{T_A}\right)^2$$

A second method is the Othmer plot which will not be discussed in this text. Finally, several empirical correlations are also available for estimating ΔH_v of liquids. The interested student can consult Perry & Green for detailed information.

Chapter 13 CHEMICAL REACTION EQUILIBRIA – BASIC CONCEPTS

Consider the following gas-phase chemical reaction:

$$H_2 + I_2 \leftrightarrow 2\ HI$$

As the reaction progresses, the concentrations of iodine and hydrogen decrease as they are consumed while the concentration of hydrogen iodide increases as it is formed. Eventually, however, the concentrations of all three species reach constant values. This behaviour is as a result of the back reaction in which hydrogen iodide reacts to form iodine and hydrogen. Initially there is no hydrogen iodide, so the back reaction cannot occur. As hydrogen iodide accumulates, the back reaction becomes significant.

Eventually the rate at which iodine is being consumed by the forward reaction is perfectly balanced by the rate at which it is being produced by the back reaction. The same is true for hydrogen and hydrogen iodide. When the rates of forward and reverse reactions are perfectly balanced in this way, the reaction is said to be at equilibrium.

The equilibrium criterion for reacting systems is based on the second law of thermodynamics with respect to the increase in entropy principle. For adiabatic systems, chemical equilibrium is established when the entropy of the reacting system reaches a maximum. However, most reacting systems encountered in practice are not adiabatic; therefore, an equilibrium criterion must be developed which can be applied to any reacting system.

Criterion for chemical equilibrium

Consider a reaction chamber containing CO, O_2, and CO_2 at a specified temperature and pressure.

There are three possibilities of possible occurrence:

a. A chemical reaction between CO and O_2 to form more CO_2;

b. A dissociation reaction of CO_2 into CO and O_2; and

c. No reaction or system is in chemical equilibrium

Even though we may know the temperature, pressure, and composition of the system, we may not be able to predict whether the system is in equilibrium.

Assuming there is equilibrium at the specified temperature and pressure, the chemical composition will not change unless the temperature or pressure of the mixture is changed. We therefore consider reacting systems at fixed temperature and pressure when developing a general criterion for chemical equilibrium.

From the second law of thermodynamics, the increase in entropy principle for any system can be expressed as

$$dS_{sys} \geq \frac{\delta Q}{T}$$

For an adiabatic system

$$dS_{sys} \geq 0$$

Thus, a chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy; when the entropy reaches a maximum, the reaction stops.

For reacting systems with heat transfer, the increase in entropy principle becomes impractical to use. Consider the first and second law relations for a reacting (or nonreacting) simple compressible system of fixed mass with only quasi-equilibrium work:

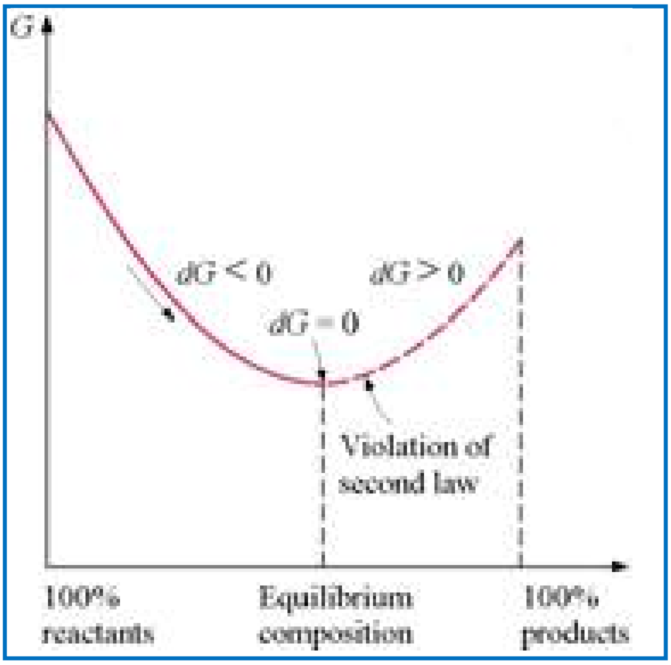
$$\left.\begin{aligned} dQ - Pdv &= dU \\ dS_{sys} &\geq \frac{\delta Q}{T} \end{aligned}\right\} dU + PdV - TdS \leq 0$$

Writing the differential of the Gibbs function (*G* = *H* - *TS*) at constant temperature and pressure

$$\begin{aligned} (dG)_{T,P} &= dH - TdS - SdT \\ &= (dU + pdV + VdP) - TdS - SdT \\ &= dU + PdV - TdS \end{aligned}$$

It can be seen that

$$(dG)_{T,P} \leq 0$$



Hence, an equilibrium reaction at a specified temperature and pressure will proceed in a direction of a decreasing Gibbs function. The reaction will stop and chemical equilibrium will be established when the Gibbs function attains a minimum value; therefore the criterion for chemical equilibrium can be expressed as

$$(dG)_{T,P} = 0$$

A chemical reaction at a specified temperature and pressure cannot proceed in the direction of the increasing Gibbs function since this will contradict the second law of thermodynamics. To obtain a relation for chemical equilibrium in terms of the properties of the individual components, we consider a mixture of 4 chemical components A, B, C, and D that exist in equilibrium at a specified T and P. Let the number of moles of the respective components be n_A, n_B, n_C, *and* n_D. Consider a reaction which differential amounts of reactants A and B are converted into C and D (products) at constant T and P:

$$dn_A A + dn_B B \rightarrow dn_C C + dn_D D$$

Applying the equilibrium criteria, we have

$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (g_i dn_i)_{T,P} = 0$$
$$or$$
$$g_c dn_c + g_D dn_D + g_A dn_A + g_B dn_B = 0$$

where g = molar Gibbs function (or chemical potentials) at the specified T and P and
dn = differential changes in the numbe of moles of the components

Determination of a relation between the *dn's*

Writing the stoichiometric reaction, we have

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C + \nu_D D$$
where the ν's are the stoichiometric coefficients

The changes in the number of moles of the components are proportional to the stoichiometric coefficients; that is,

$$dn_A = -\varepsilon \nu_A \qquad dn_C = \varepsilon \nu_C$$
$$dn_B = -\varepsilon \nu_B \qquad dn_D = \varepsilon \nu_D$$

$where \;\; \varepsilon$ is a proportionality constant and represents the extent of reaction

Substituting the above system of equations into $g_c dn_c + g_D dn_D + g_A dn_A + g_B dn_B = 0$, we obtain

$$\nu_c g_C + \nu_D g_D - \nu_A g_A - \nu_B g_B = 0$$

The above equation is the *criterion for chemical equilibrium* and is valid for any chemical reaction.

Equilibrium constant for ideal gas mixtures

For a mixture of ideal gases that exists in equilibrium at a specified temperature and pressure, the equilibrium constant K_p is given as

$$K_p = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

$$= e^{-\Delta G^*(T)/(RT)}$$

$where \;\; \Delta G^*$ is the standard-state Gibbs function change

Therefore, the equilibrium constant of an ideal gas mixture at a specified temperature can be determined from knowledge of the standard-state Gibbs function change at the same temperature.

Finally, the equilibrium constant for an ideal gas mixture can also be obtained via the relation

$$K_p = \frac{n_C^{\nu_C} n_D^{\nu_D}}{n_A^{\nu_A} n_B^{\nu_B}} \left(\frac{P}{n_{total}} \right)^{\Delta \nu}$$

$$where \;\; \Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$$

Clearly the equilibrium constant is a function of the mole numbers, temperature, and pressure at equilibrium as well as the stoichiometric coefficients in the assumed equilibrium reaction. n_{total} is the total moles of all components present in the equilibrium reaction, including any inert gases.

Note:

- The K_p of a reaction depends on temperature only since it depends on $\Delta G^*(T)$, which depends on temperature only;
- The K_p of the reverse reaction is $1/K_p$;
- The larger the K_p, the more complete the reaction;
- The mixture pressure affects the equilibrium composition but not K_p;
- The presence of inert gases affects the equilibrium composition but not K_p[12];
- When the stoichiometric coefficients are doubled, the value of K_p is squared; and
- Equilibrium calculations provide information on the equilibrium composition of a reaction, not on the reaction rate.

From values of $ln\ K_P(T)$ for several equilibrium reactions, the following observations are made by considering the typical equilibrium reaction:

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C + \nu_D D$$

$$If$$

$$In`K_p(T) < 0; \quad then \quad K_P(T) < 1$$

$$In`K_p(T) > 0; \quad then \quad K_P(T) > 1$$

When $ln\ K_P(T) < -7$, ($KP(T) << 1$), the components are so stable that the reaction will not occur (left to right).

When $ln\ K_P(T) > 7$, ($KP(T) >> 1$), the components are so active that the reaction will proceed to completion (left to right).

Variation of K_p with temperature

The van't Hoff equation is an expression of the variation of K_p with temperature in terms of the enthalpy of reaction, and is given by:

$$\frac{d(InK_p)}{dT} = \frac{h_R(T)}{RT^2}$$

$$where\ \ \mathrm{h_R}(T) = enthalpy\ \text{of reaction at temperature T}$$

We need to know how $h_R(T)$ varies with T in order to integrate the above equation. For small temperature intervals, h_R can be treated as a constant and the equation becomes

---

[12] Note that $\Delta G^*(T)$ of inert gases is zero.

$$In \frac{K_{p_2}}{K_{p_2}} \cong \frac{h_R}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This equation provides a means of calculating the h_R of a reaction from knowledge of K_p, which is easier to determine. Second, it shows that exothermic reaction ($h_R < 0$) such as combustion processes will be less complete at higher temperatures since K_p decreases with temperature for such reactions.

Example

Consider the disassociation of H_2

$$H_2 \longrightarrow xH_2 + yH$$

The equilibrium reaction is assumed to be

$$H_2 \Leftrightarrow 2H$$

For $T < 2400$ K, $ln\ K_P(T) < -8.276$, and the reaction does not occur. $x \approx 1$ and $y \approx 0$;

For $T > 6000$ K, $ln\ K_P(T) > 5.590$, and the reaction occurs so rapidly that the products will be mostly H with traces of H_2. $x \approx 0$ and $y \approx 2$.

Phase Equilibrium

The criterion that the Gibbs be a minimum also applies to equilibrium between phases. Consider the equilibrium of saturated liquid water and saturated water vapour at 100 ^{o}C. Let g be the specific Gibbs function per unit mass, G/m.

$$G = m_f\, g_f + m_g\, g_g$$

At a fixed T, the g_f and g_g are constant, and the Gibbs function changes because mass is changing between the liquid and the vapour states. At equilibrium for constant T and P, it can be shown that

$g_f = g_g$

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PROBLEMS

1. A vacuum gage connected to a tank reads 30 kPa at a location where the atmospheric pressure is 98 kPa. What is the absolute pressure in the tank?

2. A pressure gage connected to a valve stem of a truck tire reads 240 kPa at a location where the atmospheric pressure is 100 kPa. What is the absolute pressure in the tire, in kPa and in psia?

3. Both a gage and a manometer are attached to a gas tank to measure its pressure. If the pressure gage reads 80 kPa, determine the distance between the two fluid levels of the manometer if the fluid is mercury, whose density is 13,600 kg/m^3.

4. Determine the internal energy of refrigerant-134a at a temperature of 5 ^{0}C and a quality of 60 %.

5. Determine the particular gas constant for air and hydrogen

6. An ideal gas having an initial temperature of 25 °C under goes the two processes described below. Determine the final temperature of the gas.

   Process 1-2: The volume is held constant while the pressure doubles

   Process 2-3: The pressure is held constant while the volume is reduced to one-third of the original volume.

7. Three kilograms of nitrogen gas at 27 °C and 0.15 MPa are compressed isothermally to 0.3 MPa in a piston-cylinder device. Determine the minimum work of compression, in kJ.

8. Water is placed in a piston-cylinder device at 20 °C, 0.1 MPa. Weights are placed on the piston to maintain a constant force on the water as it is heated to 400 °C. How much work does the water do on the piston?

9. Air undergoes a constant pressure cooling process in which the temperature decreases by 100 °C. What is the magnitude and direction of the work for this process?

10. A tank contains nitrogen at 27 °C. The temperature rises to 127 °C by heat transfer to the system. Find the heat transfer and the ratio of the final pressure to the initial pressure.

11. Air is expanded isothermally at 100°C from 0.4 MPa to 0.1 MPa. Find the ratio of the final to the initial volume, the heat transfer, and work.

12. A two-liter bottle of your favorite beverage has just been removed from the trunk of your car. The temperature of the beverage is 35°C, and you always drink your beverage at 10°C.

    a. How much heat energy must be removed from your two liters of beverage?

b. You are having a party and need to cool 10 of these two-liter bottles in one-half hour. What rate of heat removal, in kW, is required? Assuming that your refrigerator can accomplish this and that electricity costs 8.5 cents per kW-hr, how much will it cost to cool these 10 bottles?

13. Refrigerant-134a at 200 kPa, 40% quality, flows through a 1.1-cm inside diameter, *d*, tube with a velocity of 50 m/s. Find the mass flow rate of the refrigerant-134a.

14. Air at 100 kPa, 50 ^{o}C, flows through a pipe with a volume flow rate of 40 m^3/min. Find the mass flow rate through the pipe, in kg/s.

15. Steam at 0.4 MPa, 300 -C, enters an adiabatic nozzle with a low velocity and leaves at 10 kPa with a quality of 90 %. Find the exit velocity, in m/s.

16. High pressure air at 1300 K flows into an aircraft gas turbine and undergoes a steady-state, steady-flow, adiabatic process to the turbine exit at 660 K. Calculate the work done per unit mass of air flowing through the turbine

    When

    (a) Temperature-dependent data are used.
    (b) $C_{p,\text{ave}}$ at the average temperature is used.
    (c) C_p at 300 K is used.

17. One way to determine the quality of saturated steam is to throttle the steam to a low enough pressure that it exists as a superheated vapor. Saturated steam at 0.4 MPa is throttled to 0.1 MPa, 100oC. Determine the quality of the steam at 0.4 MPa.

18. Steam at 0.2 MPa, 300 ^{o}C, enters a mixing chamber and is mixed with cold water at 20 ^{o}C, 0.2 MPa, to produce 20 kg/s of saturated liquid water at 0.2 MPa. What are the required steam and cold water flow rates?

19. Nitrogen gas is compressed in a steady-state, steady-flow, adiabatic process from 0.1 MPa, 25 ^{o}C. During the compression process the temperature becomes 125 ^{o}C. If the mass flow rate is 0.2 kg/s, determine the work done on the nitrogen, in kW.

20. Air is heated in a heat exchanger by hot water. The water enters the heat exchanger at 45oC and experiences a 20oC drop in temperature. As the air passes through the heat exchanger, its temperature is increased by 25 ^{o}C. Determine the ratio of mass flow rate of the air to mass flow rate of the water.

21. In a simple steam power plant, steam leaves a boiler at 3 MPa, 600 ^{o}C, and enters a turbine at 2 MPa, 500oC. Determine the in-line heat transfer from the steam per kilogram mass flowing in the pipe between the boiler and the turbine.

22. Air at 100oC, 0.15 MPa, 40 m/s, flows through a converging duct with a mass flow rate of 0.2 kg/s. The air leaves the duct at 0.1 MPa, 113.6 m/s. The exit-to-inlet duct area ratio is 0.5. Find the required rate of heat transfer to the air when no work is done by the air.

23. A steam power plant produces 50 MW of net work while burning fuel to produce 150 MW of heat energy at the high temperature. Determine the cycle thermal efficiency and the heat rejected by the cycle to the surroundings.

24. A Carnot heat engine receives 500 kJ of heat per cycle from a high temperature heat reservoir at 652oC and rejects heat to a low temperature heat reservoir at 30oC. Determine

    (a) The thermal efficiency of this Carnot engine.
    (b) The amount of heat rejected to the low-temperature heat reservoir.

25. A heat pump is to be used to heat a building during the winter. The building is to be maintained at 21oC at all times. The building is estimated to be losing heat at a rate of 135,000 kJ/h when the outside temperature drops to -5 oC. Determine the minimum power required to drive the heat pump unit for this outside temperature.

26. An inventor claims to have developed a refrigerator that maintains the refrigerated space at 2oC while operating in a room where the temperature is 25 oC and has a COP of 13.5. Is there any truth to his claim?

27. An engineer claims to have invented a heat engine that develops a thermal efficiency of 80 percent when operating between two heat reservoirs at 1000 K and 300 K. Evaluate his claim.

28. Nitrogen expands isentropically in a piston cylinder device from a temperature of 500 K while its volume doubles. What is the final temperature of the nitrogen, and how much work did the nitrogen do against the piston, in kJ/kg?

29. Air, initially at 17oC, is compressed in an isentropic process through a pressure ratio of 8:1. Find the final temperature assuming constant specific heats and variable specific heats.

30. Air initially at 0.1 MPa, 27oC, is compressed reversibly to a final state.

    (a) Find the entropy change of the air when the final state is 0.5 MPa, 227^{o}C.
    (b) Find the entropy change when the final state is 0.5 MPa, 180 ^{o}C.
    (c) Find the temperature at 0.5 MPa that makes the entropy change zero.

    Show the two processes on a *T*-*s* diagram.

31. Nitrogen expands isentropically in a piston cylinder device from a temperature of 500 K while its volume doubles. What is the final temperature of the nitrogen, and how much work did the nitrogen do against the piston, in kJ/kg?

32. A Carnot engine has 1 kg of air as the working fluid. Heat is supplied to the air at 800 K and rejected by the air at 300 K. At the beginning of the heat addition process, the pressure is 0.8 MPa and during heat addition the volume triples.

    (a) Calculate the net cycle work assuming air is an ideal gas with constant specific heats.
    (b) Calculate the amount of work done in the isentropic expansion process.
    (c) Calculate the entropy change during the heat rejection process.

33. Saturated liquid water at 10 kPa leaves the condenser of a steam power plant and is pumped to the boiler pressure of 5 MPa. Calculate the work for an isentropic pumping process.

34. Air enters a compressor and is compressed adiabatically from 0.1 MPa, 27°C, to a final state of 0.5 MPa. Find the work done on the air for a compressor isentropic efficiency of 80 percent.

35. An ideal-gas mixture has the following volumetric analysis

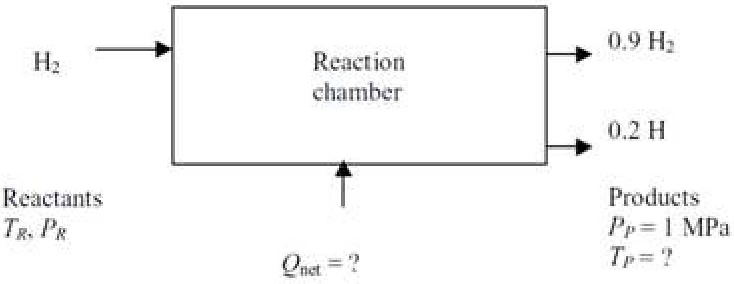
Component	% by Volume
N_2	60
CO_2	40

(a) Find the analysis on a mass basis
(b) What is the mass of 1 m^3 of this gas when $P = 1.5$ MPa and $T = 30\ ^oC$?
(c) Find the specific heats at 300 K.
Taking $c_{p,}(N_2) = 1.039$ kJ/kg. K and $c_p,(CO_2) = 0.846$ kJ/kg. K
(d) This gas is heated in a steady-flow process such that its temperature is increased by 120 °C. Find the required heat transfer. The conservation of mass and energy for steady-flow are

36. Determine the amount of N_2 that dissociates into monatomic N at 1 atm when the temperature is 3000 K and 6000 K.

    The reaction equation is
    $N_2 \rightarrow x N_2 + zN$

37. Determine the product temperature for the following when the product pressure is 1 MPa.



38. 1 kmol of CO is combusted with 0.5 kmol O_2 and 1 kmol of N_2. The products are assumed to consist of CO_2, CO, O_2, and N_2 when the product temperature is 2600 K and the product pressure is 1 atm. Write the balanced combustion equation.

39. Show that the Gibbs functions for saturated liquid water and saturated water vapour at 100 ^oC are equal.

TUTORIAL QUESTIONS – 2008/2009

Set 1

1. What is the difference between the *classical and statistical* approaches to thermodynamics?

2. A bank clerk claims that a cup of cold tea on his table warmed up to 80 ^0C by picking up energy from the surrounding air, which is at room temperature. Is there any truth to his claim?

3. Determine the mass and the weight of the air contained in a room whose dimensions are 6 m ×6 m × 6 m. Take the density of air to be 1.16 kg/m^3.

4. How many cubic meters are there in a rod of uniform cross section that is 15 in long by 0.25 in. in diameter?

5. Convert the following to the desired units:
   - a. 60 mi/hr to m/s
   - b. 25 N/m^2 to Ib_f/ft^2
   - c. 18 J to Btu
   - d. 4.5 cm/hr^2 to nm/sec^2

6. Find the Kinetic energy of a ton of water moving at 60 mi/hr expressed as
   i. (ft)(Ib_f) ii. ergs iii. Joules iv. (hp)(sec) v. Ws vi. (liter)(atm)

7. The deep body temperature of a healthy person is 37 ^0C. What is it in Kenvins?

8. The temperature of a system drops by 27 ^0F during a cooling process. Express this drop in temperature in K, R, and
^0C.

9. A vacuum gauge connected to a chamber reads 24 kPa at a location where the atmospheric pressure is 92 kPa. Determine the absolute pressure in the chamber.

10. You have 100 Ib of gas of the following composition: CH_4 – 30 %, H_2 – 10 %, and N_2 – 60 %. Determine the average molecular weight of this gas?

11. Densities may be expressed as linear functions of temperature, such as:

$\rho = \rho_0 + Bt$

Where ρ = Ib/ft^3 at temperature t
ρ_0 = Ib/ft^3 at temperature t_0
t = temperature in ^0F

If the equation is dimensionally consistent, what are the units of B?

12. Convert the following:
   - i. 120 Ib moles of NaCl to g.
   - ii. 120 Ib of NaCl to gmoles.

13. A manometer containing oil (ρ = 850 kg/m^3) is attached to a tank filled with air. If the oil-level difference between the two columns is 45 cm and the atmospheric pressure is 98 kPa, determine the absolute pressure of the air in the tank.

14. The acceleration of high-speed aircraft may be expressed in g's (in multiples of the standard acceleration of gravity). Find the net upward force, in N, that a 90 kg astronaut would experience in an aircraft whose acceleration is 6 g's.

Set II

1) A gas follows the law:

$$u = 195 + 0.72t$$

$$pv = 0.285(t + 273)$$

Find c_v and c_p.

2) A cylinder has 4 kg of oxygen (molecular weight = 32) at atmospheric pressure and room temperature of 300 K. It is heated to increase its volume two times, keeping its pressure constant. Determine

i. the heat supplied
ii. the change in internal energy

(Take R = 8.314 J/mol.K, c_p=0.921 Kj/kg.K)

(3). A natural gas from an oil well has the following composition:

Component	**Volume percent**
CH_4 (methane)	80.0
C_2H_6 (ethane)	6.0
C_3H_8 (propane)	4.0
C_4H_{10} (butane)	3.0
C_5H_{12} (pentane)	1.5
CO_2 (carbon dioxide)	3.5
N_2 (nitrogen)	2.0

i. What is the composition in percentage by weight?
ii. Find the composition in mole percent.
iii. How many cubic meters will be occupied by 100 kg of the gas at 10 ^{0}C and 0.8 atm?

3. An ideal gas undergoes the following sequence of mechanically reversible processes:

I. From an initial state of 70^{0}C and 1 bar, it is compressed adiabatically to 150^{0}C;
II. It is then cooled from 150 to 70^{0}C at constant pressure;
III. Finally, it is expanded isothermally to its original state.

a. Sketch the process on a P-V diagram;
b. Calculate W, Q, ΔU, and ΔH for each of the three processes.
c. Calculate W, Q, ΔU, and ΔH for the entire process.

(Take C_V=3R/2 and C_P= 5R/2)

4. Water flows over a cataract 100 m in height. Consider 1 kg of the water and assume that no energy is exchanged between the 1 kg and its surroundings.
a. What is the Potential Energy of the water at the top of the falls with respect to the base of the falls?
b. What is the Kinetic Energy of the water just before it strikes the bottom of the falls?
c. After the 1 kg of water enters the river below the falls, what change has occurred in its state?

5. Air at 1 bar enters a compressor at low velocity, discharges at 3 bar and enters a nozzle in which it expands to a final velocity of 600 m/s at the initial conditions of pressure and temperature. If the work of compression is 240 kJ/kg of air, how much heat must be removed during compression?

6. 0.1 m^3 air, at 27 ^{0}C and 200 kN/m^2, expands isothermally to 100 kN/m^2. Find the change in internal energy, enthalpy, and heat exchange.

7. In a cyclic process, heat transfers are +15 kJ, - 25 kJ, and + 30 kJ. Find net cycle work.

8. A lead bullet having velocity 500 m/s strikes a steel plate, falling dead after impact. Find the rise in temperature if heat energy is equally shared by the bullet and the plate. Take specific heat of lead to be 0.125 kJ/kg.K

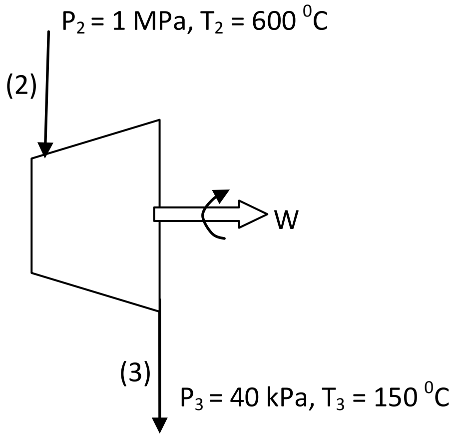
Set III

1. Predict the specific volume of CH_4 at 100 atm and 0 ^{0}F by using
   a. The ideal gas equation
   b. The van der Waals equation

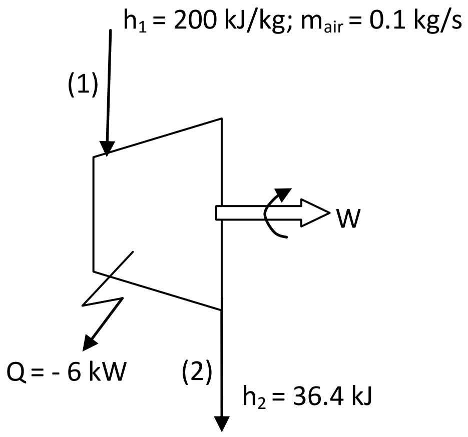
2. Air is a mixture of nitrogen, oxygen, argon, and trace amounts of other compounds. Take air to be composed of 78.03 % nitrogen, 20.99 % oxygen, and 0.98 % argon on a volume basis.
   a. Determine the composition by mass (mass fraction) of air
   b. Calculate U and S of air given the following data

Component	Molecular mass	Volume fraction
Nitrogen	28	0.7803
Oxygen	32	0.2099
Argon	39.95	0.0098

3. etermine the work output of the adiabatic steam turbine operating as shown:



4. Determine the output of the air turbine operating as shown:



5. Evaluate the Gibbs function ***g*** and the Helmholtz function ***a*** at the inlet to a turbine receiving steam at 700 ^{0}C and 2 MPa.
6. Steam at 20 bar is 0.8 dry. Find the specific volume, internal energy, enthalpy, and entropy.
7. Steam at 8 bar has enthalpy *h = 2360 kJ/kg*. Find its state, internal energy, specific volume, and entropy.

8. Find the condition of steam at 10 bar if its specific volume is 0.175 m^3/kg.
9. Steam at 150 bar is at 425 ^{0}C. Find its v, h, and s of the steam.
10. A tank contains 1 kg of saturated steam and 5 kg of saturated water at 95 ^{0}C. Find the volume of the tank, and the dryness fraction of the steam.
11. One kg of steam having a dryness fraction of 0.95 is enclosed in a constant volume bomb at 5 bar. It is cooled to 2.5 bar. Find the change in entropy and the heat transferred.
12. 0.5 kg of steam at 5 bar, dryness fraction 0.8 is heated so that its final temperature is 300 ^{0}C, pressure remaining the same. Find the work done and the heat transferred.
13. 2 kg of steam expands from a pressure of 10 bar, temperature 300 ^{0}C to 1 bar, isentropically. Find the condition of steam after expansion, and the work done.
14. What is the dryness fraction of steam? Can you name one method that can be used to determine it?
15. The standard enthalpies of formation of $C_2H_5OH(l)$, CO_2, and $H_2O(l)$ are -228, -394, and -286 kJ/mol respectively. Use the given data to determine the enthalpy of the reaction: $C_2H_5OH + 3\ O_2$ ® $2\ CO_2 + 3\ H_2O$
16. Calculate the enthalpy of the reaction:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

from the enthalpies of formation: $CH_{4,}$ -75 kJ/mol; CO_2, -394; and $H_2O(l)$, -286 kJ/mol.

Set IV

1. Evaluate the Gibbs function ***g*** and the Helmholtz function ***a*** at the inlet to a turbine receiving steam at 700 ^{0}C and 2 MPa.

2. A steam power plant supplies steam at 2 MN/m^2 and 450 ^{0}C to its turbine, which exhaust it at 10 kN/m^2. Determine the Rankine efficiency.

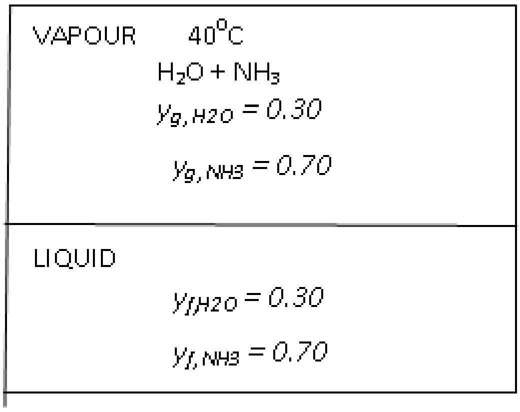
3. A steam power plant works between pressure limits of 50 bar and 0.05 bar. Steam supplied to the turbine is dry and saturated. Assuming the plant operates on the Rankine cycle, determine the following:
   I. Condition of steam from the exhaust of the turbine;
   II. Turbine work;
   III. Pump work; and
   IV. Plant efficiency

4. If the plant in Question 3 were to operate on the Carnot cycle, what will be its efficiency?

5. A steam power plant with a power output of 150 MW consumes coal at a rate of 60 tons per hour. If the Heating Value (HV) of the coal is 30000 kJ/kg, find the thermal efficiency of this plant.

6. A steel casting $(C_P = 0.5 kJ/kg.K)$ weighing 40 kg and a temperature of 450 ^{0}C is quenched in 150 kg of oil $(C_P = 2.5 kJ/kg.K)$ at 25 ^{0}C. If there are no heat losses, what is the change in entropy of
   I. The casting;
   II. The oil; and
   III. Both considered together?

7. In absorption refrigeration systems, a two-phase equilibrium mixture of liquid ammonia (NH$_3$) and water (H$_2$O) is frequently used. Consider one such mixture at 40 ^{0}C, shown below:



If the composition of the liquid phase is 70 % NH$_3$ and 30 % H$_2$O by mole numbers, determine the composition of the vapour phase of this mixture. (The saturation pressures of H$_2$O and NH$_3$ at 40^{0}C are $P_{H_2O,sat} = 7.384 kPa$ and $P_{NH_3,sat} = 1554.33 kPa$)

8. The equilibrium constant of the dissociation reaction $H_2 \rightarrow 2H$ at 3000 K and 1 atm is K_{P_1}. Express the equilibrium constant of the following reactions at 1000 K in terms of K_{P_1}:
   i. $H_2 \leftrightarrow 2H$ at 2 atm
   ii. $2H \leftrightarrow H_2$ at 1 atm

9. A liquid mixture of 50 % n-hexane and n-octane is vaporized. What is the composition of the vapour formed if the total pressure is 1 atm? Assume that the mixture behave ideally. The constants in the Antoine equation for each constituent of the mixture are:

	A	**B**	**C**
n-hexane (C$_6$)	15.8737	2697.55	- 48.784
n-octane (C$_8$)	15.9798	3127.60	- 63.633

The Antoine equation is given by

$$In(p^*) = A - \frac{B}{C + T}$$

where p^* is in mm Hg and T is in K.

Vapour pressure table for n-hexane and n-octane are given below:

Temperature, K	***Vapour pressure, mm Hg***	
	n-hexane	***n-octane***
368	1620.93	297.60
373	1846.58	351.19
393	3005.15	651.34
403	3736.98	855.95

Source: Perry & Green

10. Estimate the heat of vaporization of water at 185 ^{0}C using the Clausius-Clapeyron equation. The vapour pressure data of water are:

Pressure (MPa)	***Temperature, ^{0}C***
0.0845	95
0.2321	125
0.7005	165
0.8920	175
1.0021	180
1.3978	195

Source: Perry & Green

A definite integral of the *Clasius-Clapeyro*n equation may be written as:

$$In\frac{p_1^*}{p_2^*}=\frac{\Delta H_v}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

where T is in K

R = 8.314 J/mol.K