Introduction

Thermodynamics can be defined as the science of energy. And energy can be defined as the ability to cause changes.

The *first law* of thermodynamics says that the total quantity of energy in the universe remains constant. This is the principle of the conservation of energy. The *second law* of thermodynamics states that the quality of this energy is degraded irreversibly. This is the principle of the degradation of energy. In other words, energy has quality as well as quantity.

A substance consists of a large number of particles called molecules. The properties of the substance depend on the behavior of these particles. For example, the pressure of a gas in a container is the result of momentum transfer between the molecules and the walls of the container. The *classical* or *macroscopic* approach in thermodynamics does not require knowledge of the behavior of molecules. The *statistical* thermodynamics, on the other hand, involves the average behavior of groups of individual particles.

Dimensions and Units

Any physical quantity can be characterized by *dimensions*. The magnitudes assigned to the dimensions are called *units*.

We use SI or metric unit in this course. The SI is based on a decimal relationship between the various units. There are seven fundamental (primary) dimensions in the SI system:

Table 1-1: Primary dimensions in SI system.

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

Other dimensions, secondary dimensions, can be derived from the primary dimensions, such as velocity (m/s).

Table 1-2: Standard prefixes in SI units.

MULTIPLE	10^{12}	10^{9}	10^{6}	10^{3}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}
PREFIX	tetra, T	giga, G	mega, M	kilo, k	centi, c	mili, m	micro, μ	nano, n	pico, p

In engineering, all equations must be dimensionally homogenous, i.e., every term in an equation must have the same unit. This can serve as a valuable tool to spot errors.

Example 1-1: Unit Conversion

The heat dissipation rate density of an electronic device is reported as 10.72 $\mathrm{mW/mm^2}$ by the manufacturer. Convert this to $\mathrm{W/m^2}$.

$$10.72\frac{mW}{mm^2}\times\left(\frac{1000mm}{1m}\right)^2\times\frac{1W}{1000mW}=10720\frac{W}{m^2}$$

Closed and Open Systems

A system is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the surroundings.

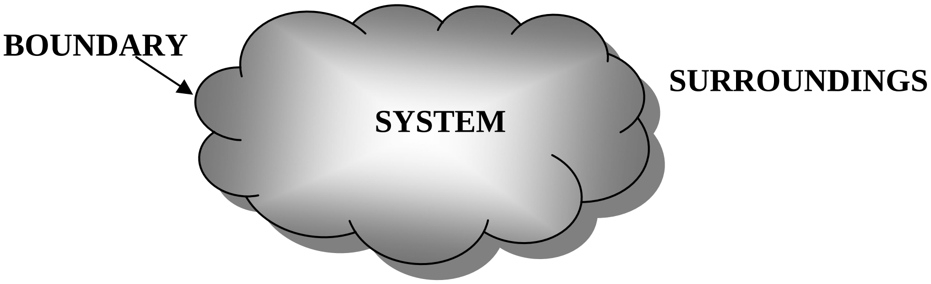


Fig. 1-1: System, surroundings, and boundary.

Boundary: the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

Closed system or control mass: consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

Open system or control volume: is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

Important note: some thermodynamics relations that are applicable to closed and open systems are different. Thus, it is extremely important to recognize the type of system we have before start analyzing it.

Isolated system: A closed system that does not communicate with the surroundings by any means.

Rigid system: A closed system that communicates with the surroundings by heat only.

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.

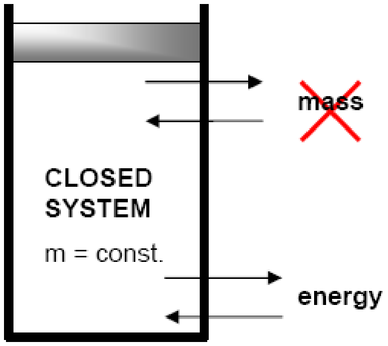


Fig. 1-2: Closed system, mass cannot cross the boundaries, but energy can.

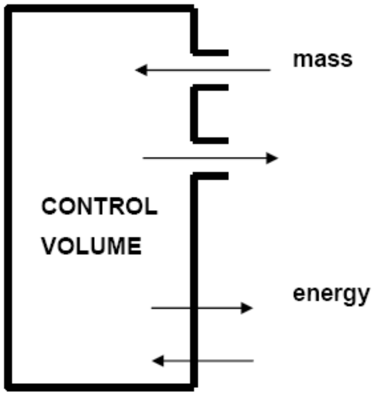


Fig. 1-3: Control volume, both mass and energy can cross the boundaries.

Properties of a System

Any characteristic of a system is called a *property*. In classical thermodynamics, the substance is assumed to be a *continuum*, homogenous matter with no microscopic holes. This assumption holds as long as the volumes, and length scales are large with respect to the intermolecular spacing.

<u>Intensive properties</u>: are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.

<u>Extensive properties</u>: values that are dependant on size of the system such as mass, volume, and total energy U. They are additive.

- Generally, uppercase letters are used to denote extensive properties (except mass m), and lower case letters are used for intensive properties (except pressure P, temperature T).
- Extensive properties per unit mass are called specific properties, e.g. specific volume (v=V/m).

State and Equilibrium

At a given *state*, all the properties of a system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

Thermodynamics deals with equilibrium. In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings.

Thermal equilibrium: when the temperature is the same throughout the entire system.

Mechanical equilibrium: when there is no change in pressure at any point of the system. However, the pressure may vary within the system due to gravitational effects.

Phase equilibrium: in a two phase system, when the mass of each phase reaches an equilibrium level.

Chemical equilibrium: when the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

Processes and Cycles

Any change a system undergoes from one equilibrium state to another is called a *process,* and the series of states through which a system passes during a process is called a *path*.

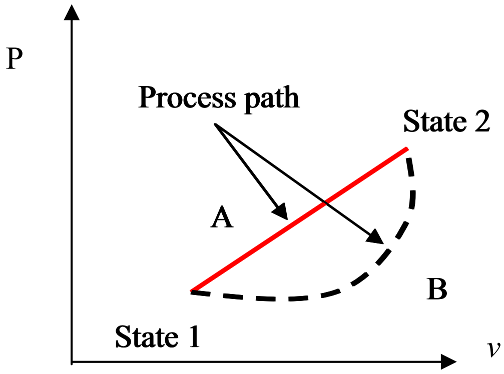


Fig. 1-4: To specify a process, initial and final states and path must be specified.

Quasi-equilibrium process: can be viewed as a sufficiently slow process that allows the system to adjust itself internally and remains infinitesimally close to an equilibrium state at all times. Quasi-equilibrium process is an idealized process and is not a true representation of the actual process. We model actual processes with quasi-equilibrium ones. Moreover, they serve as standards to which actual processes can be compared.

Process diagrams are used to visualize processes. Note that the process path indicates a series of equilibrium states, and we are not able to specify the states for a non-quasi-equilibrium process.

Prefix *iso-* is used to designate a process for which a particular property is constant.

Isothermal: is a process during which the temperature remains constant

Isobaric: is a process during which the pressure remains constant

Isometric: is a process during which the specific volume remains constant.

A system is said to have undergone a *cycle* if it returns to its initial state at the end of the process.

Pure Substance

A substance that has a fixed chemical composition throughout is called a *pure substance* such as water, air, and nitrogen.

A pure substance may exist in different phases. There are three principal phases *solid*, *liquid*, and *gas*.

A phase: is defined as having a distinct molecular arrangement that is homogenous throughout and separated from others (if any) by easily identifiable boundary surfaces.

Phase-Change Processes of Pure Substances

Consider a process where a pure substance starts as a solid and is heated up at constant pressure until it all becomes gas. Depending on the prevailing pressure, the matter will pass through various phase transformations. At P_0:

1. Solid, 2. Mixed phase of liquid and solid, 3. Sub-cooled or compressed liquid (means it is not about to vaporize), 4. Wet vapor or saturated liquid-vapor mixture, the temperature will stop rising until the liquid is completely vaporized, 5. Superheated vapor (a vapor that is not about to condense).

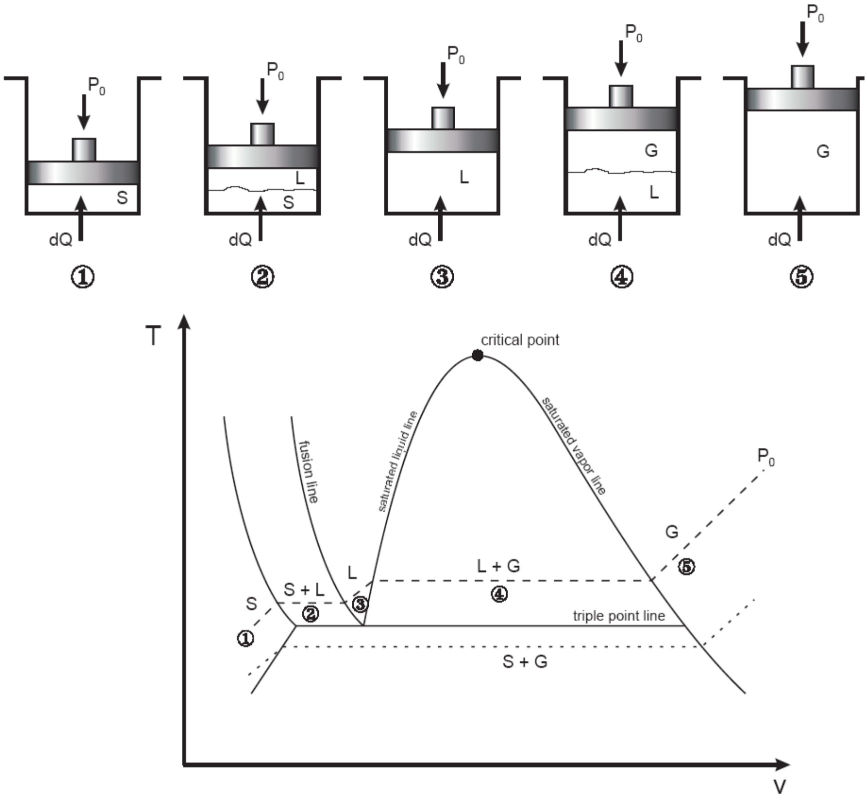


Fig. 1-5: T-v diagram for the heating process of a pure substance.

- At a given pressure, the temperature at which a pure substance starts boiling is called the *saturation temperature*, T_{sat}.
- Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the *saturation pressure*, P_{sat}.
- During a phase-change process, pressure and temperature are dependent properties, $T_{sat} = f\,(P_{sat})$.
- Quality is the ratio of the mass of the vapor to the total mass, $x = m_v / m_{total}$

Example 1-2: Saturated liquid-vapor mixture

A closed, rigid container of volume 0.5 m^3 is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated water vapor at P_1= 1 bar with a quality of 0.5. After heating, the pressure in the container is P_2=1.5 bar. Indicate the initial and final states on a T-v diagram, and determine:

a) the temperature, in °C, at each state.

b) the mass of vapor present at each state, in kg.

c) if heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

Solution:

Assumptions:

1. Water in the container is a closed system.
2. States 1, 2, and 3 are equilibrium states.
3. The volume of container remains constant.

Two independent properties are required to fix state 1 and 2. At the initial state, the pressure and quality are known. Thus state 1 is known, as shown in Fig. 1-6. The specific volume at state 1 is found using the given quality:

$$v_1 = v_{f1} + x_1\left(v_{g1} - v_{f1}\right)$$

$$\text{From Table A - 5 at P} = 1\text{ bar} = 100\text{ kPa}$$

$$v_1 = 0.001043 + 0.5\ (1.694 - 0.001043) = 0.8475 \quad m^3/kg$$

At state 2, the pressure is known. Volume and mass remain constant during the heating process within the container, so v_2=v_1. For P_2= 0.15 MPa, Table A-5 gives v_{f2}= 0.001053 and v_{g2}=1.1593 m^3/kg. Since

$$v_{f2} < v_2 < v_{g2}$$

State 2 must be in the two-phase region as well. Since state 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given. Table A-5:

$$T_1 = 99.63\ °C \text{ and } T_2 = 111.4\ °C$$

To find the mass of water vapor present, we first find the total mass, m.

$$m = \frac{V}{v} = \frac{0.5m^3}{0.8475m^3/kg} = 0.59kg$$

$$m_{g1} = x_1 m = 0.5(0.59kg) = 0.295kg$$

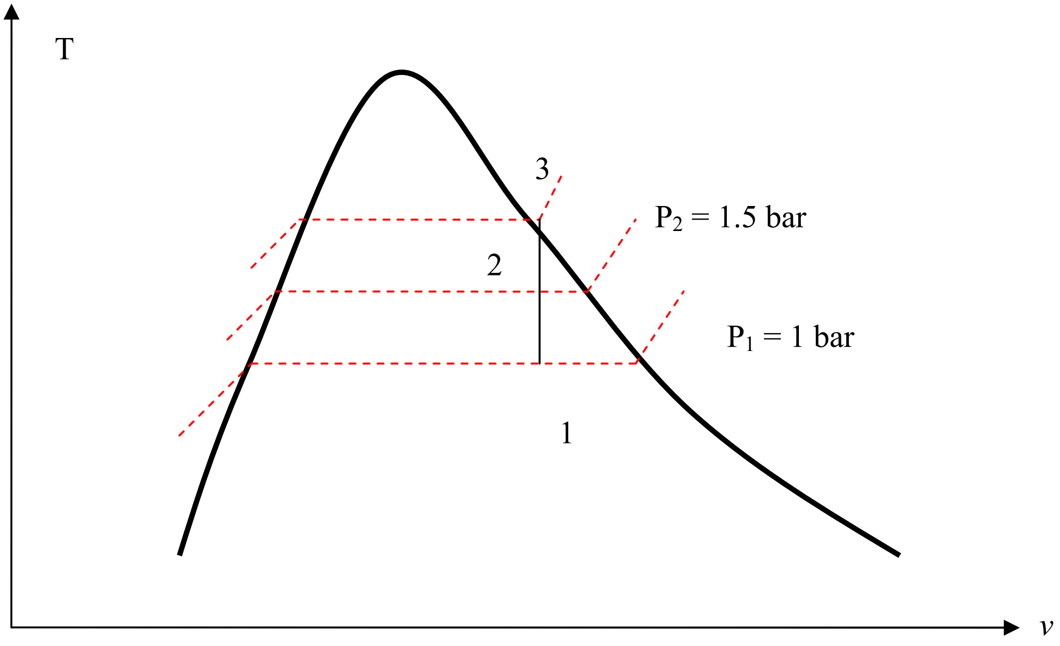


Fig. 1-6: T-v diagram for example 1-2.

The mass of vapor at state 2 is found similarly using quality x_2. From Table A-5, for P_2 = 1.5 bar, we have:

$$x_2 = \frac{v - v_{f2}}{v_{g2} - v_{f2}}$$

$$x_2 = \frac{0.8475 - 0.001053}{1.159 - 0.001053} = 0.731$$

$$m_{g2} = 0.731\,(0.59kg) = 0.431 \quad kg$$

If heating continued, state 3 would be on the saturated vapor line, as shown in on the *T-v* diagram above. Thus, the pressure would be the corresponding saturation pressure. Interpolating in Table A-5 at $v_g = 0.8475$ m^3/kg, we get $P_3 = 2.11$ bar.

The Ideal-Gas Equation of State

Any equation that relates the pressure, temperature, and specific volume of a substance is called an *equation of state*.

The simplest and best known equation of state for substances in the gas phase is the *ideal-gas* equation of state.

Gas and *vapor* are often used as synonymous words. The vapor phase of a substance is called a *gas* when it is above the critical temperature. *Vapor* usually implies a gas that is not far from a state of condensation.

It is experimentally observed that at a low pressure the volume of a gas is proportional to its temperature:

$$Pv = RT$$

Where R is the gas constant. The above equation is called the ideal-gas equation of state (ideal gas relation). Since R is a constant for a gas, one can write:

$$R = \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

where 1 and 2 denote two states of an ideal gas. The constant R is different for each gas; see Table A-2 in Cengel book.

R_u = 8.314 kJ / (kmol. K) is the universal gas constant, $R = R_u /M$.

The Molar mass, M: is defined as the mass of one mole of a substance (in gmole or kgmol). The mass of a system is equal to the product of its molar mass M and the mole number N:

$$m = MN \qquad (kg)$$

See Table A-1 (Cengel book) for R and M for several substances.

An ideal gas is an *imaginary* substance that obeys the relation $Pv = RT$. It is experimentally observed that the ideal gas closely approximate the P-v-T behavior of real gases at low densities.

- In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, and CO_2 can be treated as ideal gases with negligible error.
- Water vapor and refrigerant vapor in refrigerators should not be treated as ideal gases.
- Water vapor at pressures below 10 kPa can be treated as an ideal gas, regardless of temperature.

Compressibility Factor

The assumption of ideal gas relation implies that:

- the gas particles take up negligible volume
- the intermolecular potential energy between particles is small
- particles act independent of one another.

However, real gases deviate from ideal gas behavior. This deviation at given temperature and pressure can be accurately accounted for by introduction of a correction factor called the *compressibility factor* Z.

$$Z = \frac{Pv}{RT} \qquad or \qquad Pv = ZRT$$

or $Z = v_{actual} / v_{ideal}$. Obviously, $Z=1$ for ideal gases.

Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

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

Here P_R and T_R are called the *reduced pressure* and *temperature*, respectively.

By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases.

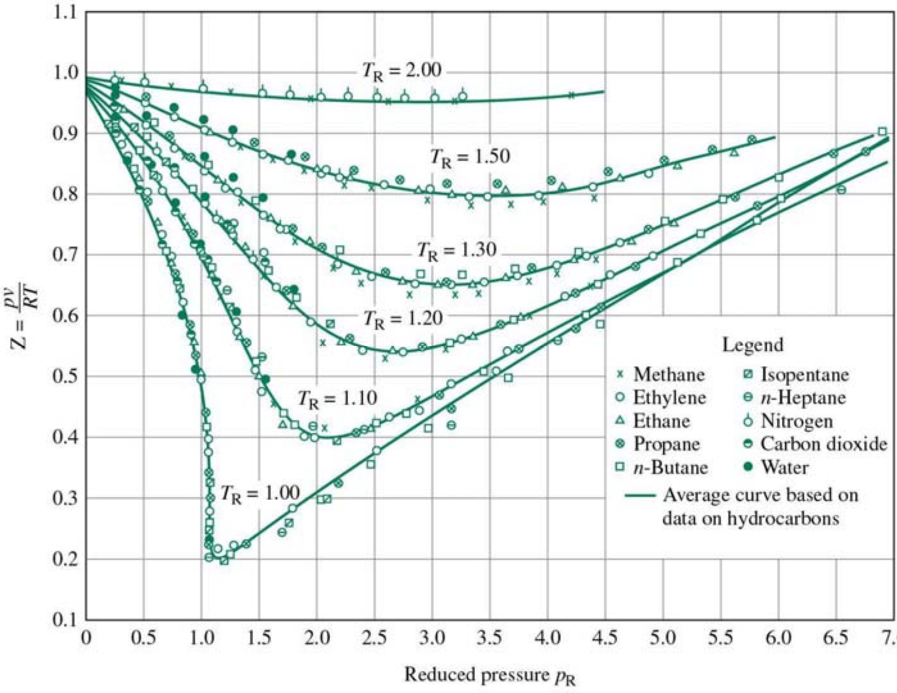


Fig. 1-7: Z factor, general compressibility chart.

The First Law of Thermodynamics: Closed Systems

The first law of thermodynamics can be simply stated as follows: during an interaction between a system and its surroundings, the amount of energy gained by the system must be exactly equal to the amount of energy lost by the surroundings.

A closed system can exchange energy with its surroundings through *heat* and *work* transfer. In other words, work and heat are the forms that energy can be transferred across the system boundary.

Heat Transfer

Heat is defined as the form of energy that is transferred between two systems by virtue of a *temperature difference*.

Note: there **cannot** be any heat transfer between two systems that are at the **same temperature**.

Heat is a directional (or vector) quantity; thus, it has magnitude, direction and point of action.

Notation:

– Q (kJ) amount of heat transfer

– $Q°$ (kW) rate of heat transfer (power)

– q (kJ/kg) - heat transfer per unit mass

– $q°$ (kW/kg) - power per unit mass

Sign convention: Heat transfer *to a system is positive*, and heat transfer *from a system is negative*. It means any heat transfer that increases the energy of a system is positive, and heat transfer that decreases the energy of a system is negative.

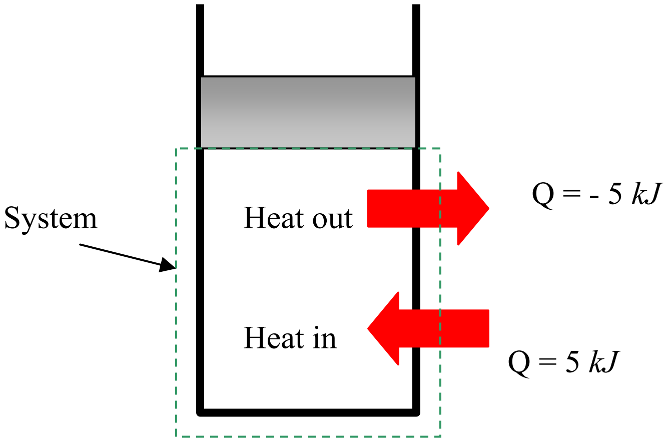


Fig. 1-8: Sign convention: positive if to the system, negative if from the system.

Heat can be transferred in three different modes *conduction, convection*, and *radiation*. All modes of heat transfer require the existence of a temperature difference.

Work

Work is the energy interaction between a system and its surroundings. More specifically, work is the energy transfer associated with *force acting through a distance*.

Notation:

– W (kJ) amount of work transfer

– W° (*kW*) power

– w (*kJ/kg*) - work per unit mass

– w° (*kW/kg*) - power per unit mass

<u>Sign convention</u>: work *done by* a system is *positive*, and the *work done on* a system is *negative*.

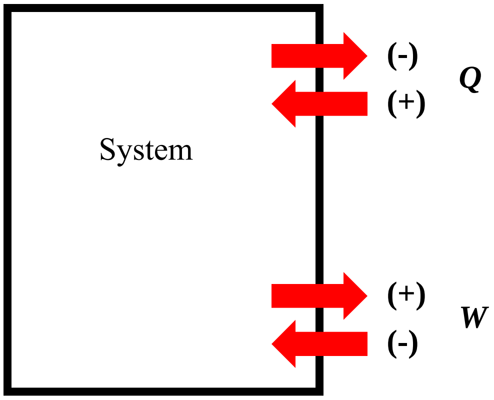


Fig. 1-9: Sign convention for heat and work.

Similarities between work and heat transfer:

- Both are recognized at the boundaries of the system as they cross them (boundary phenomena).
- Systems posses energy, but not heat or work (transfer phenomena).
- Both are associated with a process, not a state. Heat or work has no meaning at a state.
- Both are path functions, their magnitudes depend on the path followed during a process as well as the end states.

<u>Path functions</u>: have **inexact differentials** designated by symbol δ. Properties, on the other hand, are <u>point functions</u> which depend on the state only (not on how a system reaches that state), and they have **exact differentials**.

$$\int_1^2 dV = V_2 - V_1 = \Delta V \qquad \text{(Point function)}$$

$$\int_1^2 \delta W = W_{12} \qquad \text{(Path function, not } \Delta W \text{ nor } W_2 - W_1\text{)}$$

Electrical Work

The work that is done on a system by *electrons*. When N coulombs of electrons move through a potential difference V, the electrical work done is:

$W_e = VN \quad (kJ)$

Which can be explained in the rate form as

$\dot{W}_e = VI \qquad (kW)$

Example 1-3: Electrical work

A well-insulated electrical oven is being heated through its heating element. Determine whether it is work or heat interaction. Consider two systems: a) the entire oven (including the heater), and b) only the air in the oven (without the heater) see Fig 1-9.

Solution:

The energy content of the oven is increased during this process.

- **a)** The energy transfer to the oven is not caused by a temperature difference between the oven and air. Instead, it is caused by electrical energy crossing the system boundary and thus: **this is a work transfer process**.
- **b)** This time, the system boundary includes the outer surface of the heater and will not cut through it. Therefore, no electrons will be crossing the system boundary. Instead, the energy transfer is a result of a temperature difference between the electrical heater and air, thus: **this is a heat transfer process.**

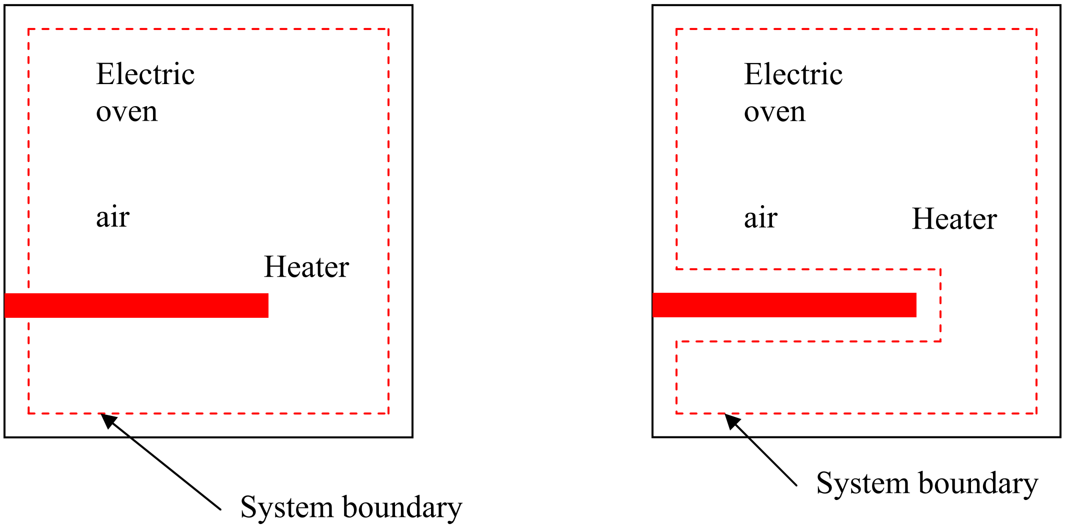


Fig. 1-10: Schematic for example 1-3.

Mechanical work

There are several ways of doing work, each in some way related to a force acting through a distance.

$$W = F.s \qquad (kJ)$$

If the force is not constant, we need to integrate:

$$W = \int_1^2 F.ds \qquad (kJ)$$

There are two requirements for a work interaction:

- there must be a force acting on the boundary
- the boundary must move

Therefore, the displacement of the boundary without any force to oppose or drive this motion (such as expansion of a gas into evacuated space) is not a work interaction, W=0.

Also, if there are no displacements of the boundary, even if an acting force exists, there will be no work transfer W = 0 (such as increasing gas pressure in a rigid tank).

Moving Boundary Work

The expansion and compression work is often called moving boundary work, or simply *boundary work*.

We analyze the moving boundary work for a quasi-equilibrium process. Consider the gas enclosed in a piston-cylinder at initial P and V. If the piston is allowed to move distance ds in a quasi-equilibrium manner, the differential work is:

$$\delta W_b = F.ds = PAds = PdV$$

The quasi-equilibrium expansion process is shown in Fig. 1-10. On this diagram, the differential area *dA* under the process curve in P-V diagram is equal to *PdV*, which is the differential work.

Note: a gas can follow several different paths from state 1 to 2, and each path will have a different area underneath it (work is path dependent).

The net work or cycle work is shown in Fig. 1-10. In a cycle, the net change for any properties (point functions or exact differentials) is zero. However, the net work and heat transfer depend on the cycle path.

$$\Delta U = \Delta P = \Delta T = \Delta(\text{any property}) = 0$$

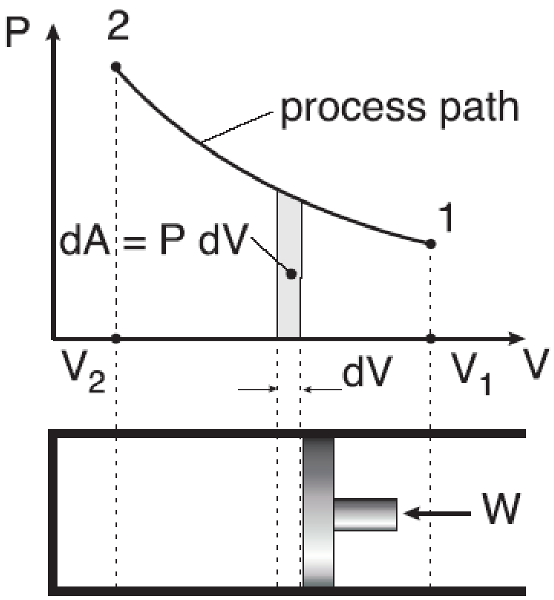


Fig. 1-11: the area under P-V diagram represents the boundary work.

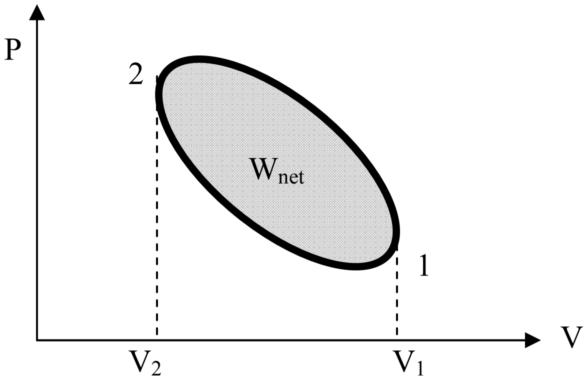


Fig. 1-12: network done during a cycle.

Polytropic Process

During expansion and compression processes of real gases, pressure and volume are often related by $PV^n=C$, where n and C are constants. The moving work for a polytropic process can be found:

$$W_{polytopic} = \int_1^2 PdV = \int_1^2 CV^{-n}dV = \frac{P_2V_2 - P_1V_1}{1-n}$$

Since $P_1V_1^n = P_2V_2^n = C$. For an ideal gas ($PV= mRT$) it becomes:

$$W_{polytropic} = \frac{mR(T_2 - T_1)}{1-n}, \quad n \neq 1 \quad (kJ)$$

The special case n =1 is the *isothermal* expansion $P_1V_1 = P_2V_2 = mRT_0 = C$, which can be found from:

$$W_{b,isothermal} = \int_1^2 PdV = \int_1^2 \frac{C}{V}dV = P_1V_1 \ln\left(\frac{V_2}{V_1}\right), \quad n = 1 \qquad (kJ)$$

Since for an ideal gas, $PV=mRT_0$ at constant temperature T_0, or $P=C/V$.

Spring work

For linear elastic springs, the displacement x is proportional to the force applied:

$$F = k_s x$$

where k_s is the spring constant and has the unit *kN/m*. The displacement x is measured from the undisturbed position of the spring. The spring work is:

$$W_{spring} = \frac{1}{2}k_s\left(x_2^2 - x_1^2\right) \qquad (kJ)$$

Note: the work done on a spring equals the energy stored in the spring.

Non-mechanical forms of work

Non-mechanical forms of work can be treated in a similar manner to mechanical work. Specify a *generalized force F* acting in the direction of a *generalized displacement x*, the work transfer associated with the displacement *dx* is:

$$\delta W = F.dx$$

First Law of Thermodynamics

First law, or the *conservation of energy principle*, states that energy can be neither created nor destroyed; it can only *change forms*.

The first law cannot be proved mathematically, it is based on *experimental* observations, i.e., there are no process in the nature that violates the first law.

The first law for a closed system or a fixed mass may be expressed as:

net energy transfer to (or from) the system as heat and work	=	net increase (or decrease) in the total energy of the system

$$Q - W = \Delta E \quad (kJ)$$

where

Q = net heat transfer ($=\Sigma Q_{in} - \Sigma Q_{out}$)

W= net work done in all forms ($=\Sigma W_{in} - \Sigma W_{out}$)

ΔE= net change in total energy ($= E_2 - E_1$)

The change in total energy of a system during a process can be expressed as the sum of the changes in its internal, kinetic, and potential energies:

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

$$\Delta U = m\left(u_2 - u_1\right)$$

$$\Delta KE = \frac{1}{2} m \left(V_2^2 - V_1^2\right)$$

$$\Delta PE = mg\left(z_2 - z_1\right)$$

Note: for stationary systems $\Delta PE=\Delta KE=0$, the first law reduces to

$$Q - W = \Delta U$$

The first law can be written on a unit-mass basis:

$$q - w = \Delta e \qquad (kJ/kg)$$

or in *differential form*:

$$\delta Q - \delta W = dU (kJ)$$

$$\delta q - \delta W = du \qquad (kJ/kg)$$

or in the rate form:

$$Q° - W° = dE / dt \qquad (kW)$$

For a cyclic process, the initial and final states are identical, thus ΔE=0. The first law becomes:

$$Q - W = 0 \qquad (kJ)$$

Note: from the *first law* point of view, there is no difference between *heat transfer* and *work*, they are both *energy interactions*. But from the *second law* point of view, heat and work are *very different*.

Example 1-4: Fist law (closed system)

Air is contained in a vertical piston-cylinder assembly fitted with an electrical resistor. The atmospheric pressure is 100 *kPa* and piston has a mass of 50 *kg* and a face area of 0.1 m^2. Electric current passes through the resistor, and the volume of air slowly increases by 0.045 m^3. The mass of the air is 0.3 kg and its specific energy increases by 42.2 kJ/kg. Assume the assembly (including the piston) is insulated and neglect the friction between the cylinder and piston, g = 9.8 m/s^2. Determine the heat transfer from the resistor to air for a system consisting a) the air alone, b) the air and the piston.

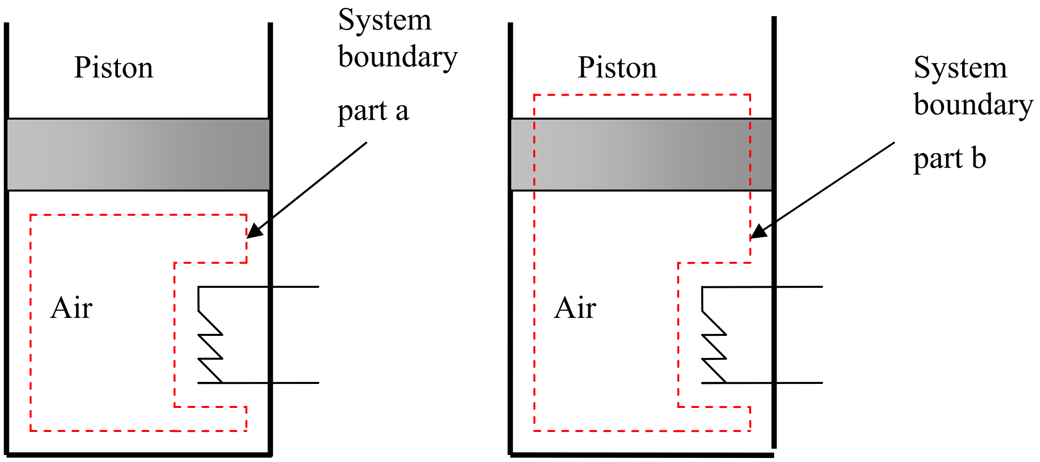


Fig. 1-13: Schematic for problem 1-4.

Assumptions:

- Two closed systems are under consideration, as shown in schematic.
- The only heat transfer is from the resistor to the air. ΔKE = ΔPE= 0 (for air)
- The internal energy is of the piston is not affected by the heat transfer.

a) Taking the air as the system,

$$(\Delta KE + \Delta PE + \Delta U)_{air} = Q - W$$

$$Q = W + \Delta U_{air}$$

For this system work is done at the bottom of the piston. The work done by the system is (at constant pressure):

$$W = \int_{V1}^{V2} PdV = P(V_2 - V_1)$$

The pressure acting on the air can be found from:

$$PA_{piston} = m_{piston}\, g + P_{atm}\, A_{piston}$$

$$P = \frac{m_{piston}\, g}{A_{piston}} + P_{atm}$$

$$P = \frac{(50kg)(9.81m/s^2)}{(0.1m^2)}\left(\frac{1Pa}{1N/m^2}\right)\left(\frac{1kPa}{1000Pa}\right) + 100kPa = 104.91\ kPa$$

Thus, the work is

$$W = (104.91\text{ kPa})(0.045\text{m}^3) = 4.721\text{ kJ}$$

With $\Delta U_{air} = m_{air}\, \Delta u_{air}$, the heat transfer is:

$$Q = W + m_{air}\, \Delta u_{air} = 4.721\text{ kJ} + (0.3\text{ kg})(42.2\text{ kJ/kg}) = 17.38\text{ kJ}$$

b) System consists of the air and the piston. The first law becomes:

$$(\Delta KE + \Delta PE + \Delta U)_{air} + (\Delta KE + \Delta PE + \Delta U)_{piston} = Q - W$$

where $(\Delta KE = \Delta PE)_{air} = 0$ and $(\Delta KE = \Delta U)_{piston} = 0$. Thus, it simplifies to:

$$(\Delta U)_{air} + (\Delta PE)_{piston} = Q - W$$

For this system, work is done at the top of the piston and pressure is the atmospheric pressure. The work becomes

$$W = P_{atm}\,\Delta V = (100\text{ kPa})(0.045\text{m}^3) = 4.5\text{ kJ}$$

The elevation change required to evaluate the potential energy change of the piston can be found from the volume change:

$$\Delta z = \Delta V / A_{piston} = 0.045\text{ m}^3/\,0.1\text{ m}^2 = 0.45\text{ m}$$

$$(\Delta PE)_{piston} = m_{piston}\,g\,\Delta z = (50\text{ kg})(9.81\text{ m/s}^2)(0.45\text{ m}) = 220.73\text{ J} = 0.221\text{ kJ}$$

$$Q = W + (\Delta PE)_{piston} + m_{air}\,\Delta u_{air}$$

$$Q = 4.5\text{ kJ} + 0.221\text{ kJ} + (0.3\text{ kg})(42.2\text{ kJ/kg}) = 17.38\text{ kJ}$$

Note that the heat transfer is identical in both systems.

Specific Heats

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree. There are two kinds of specific heats:

- specific heat at constant volume, C_v (the energy required when the volume is maintained constant)
- specific heat at constant pressure, C_p (the energy required when the pressure is maintained constant)

The specific heat at constant pressure C_p is **always higher than** C_v because at constant pressure the system is allowed to expand and energy for this expansion must also be supplied to the system.

Let's consider a stationary closed system undergoing a constant-volume process ($w_b = 0$). Applying the first law in the differential form:

$$\delta q - \delta w = du$$

at constant volume (no work) and by using the definition of C_v, one can write:

$$C_v dT = du$$

or

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

Similarly, an expression for the specific heat at constant pressure C_p can be found. From the first law, for a constant pressure process ($w_b + \Delta u = \Delta h$). It yields:

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p$$

- Specific heats (both C_v and C_p) are properties and therefore independent of the type of processes.
- C_v is related to the changes in internal energy u, and C_p to the changes in enthalpy, h.

It would be more appropriate to define: C_v is the change in specific internal energy per unit change in temperature at constant volume. C_p is the change in specific enthalpy per unit change in temperature at constant pressure.

Specific Heats for Ideal Gases

It has been shown mathematically and experimentally that the internal energy is a function of temperature only. For ideal gases:

$$u = u(T)$$

Using the definition of enthalpy ($h = u + Pv$) and the ideal gas equation of state ($Pv = RT$), we have:

$$h = u + RT$$

Since R is a constant and u is a function of T only:

$$h = h(T)$$

Therefore, at a given temperature, u, h, C_v and C_p of an ideal gas will have fixed values regardless of the specific volume or pressure. For an ideal gas, we have:

$$du = C_v(T)\,dT$$
$$dh = C_p(T)\,dT$$

The changes in internal energy or enthalpy for an ideal gas during a process are determined by integrating:

$$\Delta u = u_2 - u_1 = \int_1^2 C_v(T)\,dT \qquad (kJ/kg)$$

$$\Delta h = h_2 - h_1 = \int_1^2 C_p(T)\,dT \qquad (kJ/kg)$$

As low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only. The specific heats of real gases at low pressures are *called ideal-gas specific heats* (or *zero-pressure specific heats)* and are often denoted by C_{p0} and C_{v0}. To carry out the above integrations, we need to know $C_v(T)$ and $C_p(T)$. These are available from a variety of sources:

- Table A-2a: for various materials at a fixed temperature of T = 300 K
- Table A-2b: various gases over a range of temperatures $250 \leq T \leq 1000$ K
- Table A-2c: various common gases in the form of a third order polynomial

For an ideal gas, we can write:

$$RT = h(T) - u(T)$$

$$R = \frac{dh}{dT} - \frac{du}{dT}$$

$$R = C_p - C_v$$

The ratio of specific heats is called the *specific heat ratio* $k = C_p/C_v$:

- varies with temperature, but this variation is very mild.
- for monatomic gases, its value is essentially constant at 1.67.
- Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

Specific Heats for Solids and Liquids

A substance whose specific volume (or density) is constant is called *incompressible substance*. The specific volumes of solids and liquids (which can be assumed as incompressible substances) essentially remain constant during a process.

The constant volume assumption means that the volume work (boundary work) is negligible compared with other forms of energy. As a result, it can be shown that the constant-volume and constant-pressure specific heats are identical for incompressible substances:

$$C_p = C_v = C$$

Specific heats of incompressible substances are only a function of temperature,

$$\mathrm{C} = \mathrm{C(T)}$$

The change of internal energy between state 1 and 2 can be obtained by integration:

$$\Delta u = u_2 - u_1 = \int_1^2 C(T)\,dT \qquad (kJ/kg)$$

For small temperature intervals, a C at averaged temperature can be used and treated as a constant, yielding:

$$\Delta u \approx C_{ave}(T_2 - T_1)$$

The enthalpy change of incompressible substance can be determined from the definition of enthalpy $(h = u + Pv)$

$$h_2 - h_1 = (u_2 - u_1) + v(P_2 - P_1)$$

$$\Delta h = \Delta u + v\Delta P \quad (kJ/kg)$$

The term $v\Delta P$ is often small and can be neglected, so $\Delta h = \Delta u$.

The first Law: Control Volumes

We extend the conservation of energy to systems that involve mass flow across their boundaries, *control volumes*. Any arbitrary region in space can be selected as *control* *volume*. There are no concrete rules for the selection of control volumes. The boundary of control volume is called a *control surface*.

Conservation of Mass

Like energy, mass is a conserved property, and it cannot be created or destroyed. Mass and energy can be converted to each other according to Einstein's formula: $E = mc^2$, where c is the speed of light. However, except for nuclear reactions, the conservation of mass principle holds for all processes.

For a control volume undergoing a process, the conservation of mass can be stated as:

$$\begin{array}{ccccc}\text{total mass} & - & \text{total mass} & = & \text{net change in}\\ \text{entering CV} & & \text{leaving CV} & & \text{mass within CV}\end{array}$$

$$\sum m_i - \sum m_e = \Delta m_{CV}$$

The conservation of mass can also be expressed in the rate form:

$$\sum m^\bullet{}_i - \sum m^\bullet{}_e = dm_{CV} / dt$$

The amount of mass flowing through a cross section per unit time is called the mass flow rate and is denoted by m°. The mass flow rate through a differential area dA is:

$$dm^\circ = \rho V_n \, dA$$

where V_n is the velocity component normal to dA. Thus, the mass flow rate for the entire cross-section is obtained by:

$$m^\bullet = \int_A \rho V_n dA \qquad \text{(kg/s)}$$

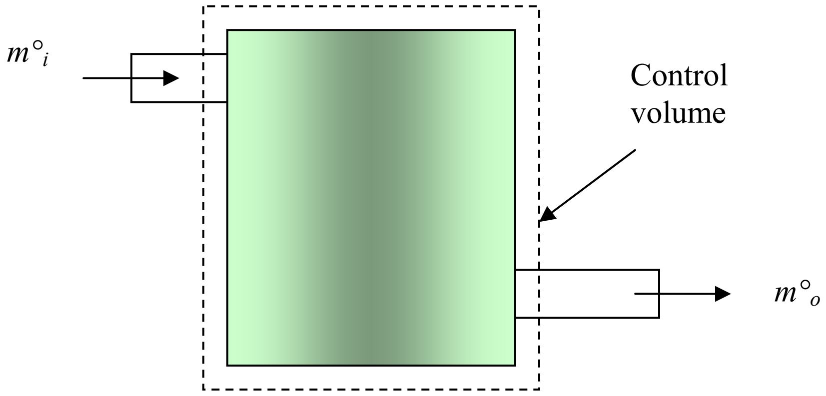


Fig. 1-14: Conservation of mass principle for a CV.

Assuming one-dimensional flow, a uniform (averaged or bulk) velocity can be defined:

$$m^\circ = \rho \, V A \qquad \text{(kg/s)}$$

where V (m/s) is the fluid velocity normal to the cross sectional area. The volume of the fluid flowing through a cross-section per unit time is called the volumetric flow, V°:

$$V^{\bullet} = \int_A V_n dA = VA \qquad (\mathrm{m^3/s})$$

The mass and volume flow rate are related by: $m^{\circ} = \rho V^{\circ} = V^{\circ}/ v$.

Conservation of Energy

For control volumes, an additional mechanism can change the energy of a system: mass flow in and out of the control volume. Therefore, the conservation of energy for a control volume undergoing a process can be expressed as

total energy crossing boundary as heat and work + total energy of mass entering CV − total energy of mass leaving CV = net change in energy of CV

$$Q - W + \sum E_{in,mass} + \sum E_{out,mass} = \Delta E_{CV}$$

This equation is applicable to *any* control volume undergoing *any* process. This equation can also be expressed in rate form:

$$Q^{\bullet} - W^{\bullet} + \sum dE_{in,mass} / dt + \sum dE_{out,mass} / dt = dE_{CV} / dt$$

Work flow: is the energy that required to push fluid into or out of a control volume. Consider an imaginary piston (that push the fluid to CV) where the fluid pressure is P and the cross sectional area is A. The force acting on the piston is F = PA. The work done in pushing the fluid is:

$$W_{flow} = F.s = PA.s = PV \qquad (kJ)$$

or in a unit mass basis,

$$w_{flow} = W_{flow} / m = Pv \qquad (kJ/kg)$$

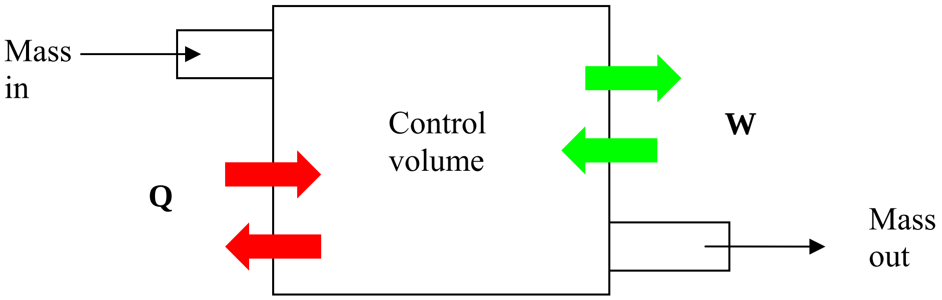


Fig. 1-15: Energy content of CV can be changed by mass flow in/out and heat and work interactions.

Note that the flow work is expressed in terms of properties. The flow work can also be written as a rate equation.

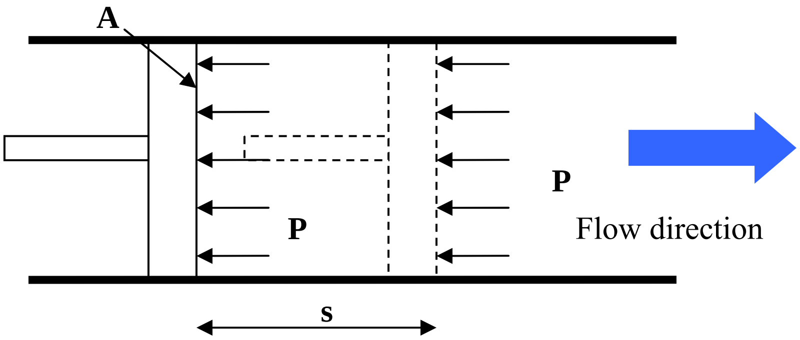


Fig. 1-16: schematic for flow work.

The fluid entering or leaving a control volume possesses an additional form of energy (flow energy Pv). Therefore, the total energy of a flowing fluid on a unit-mass basis (denoted by θ) becomes:

$$\theta = Pv + e = Pv + (u + ke + pe) \qquad \text{(kJ/kg)}$$

Recall that enthalpy is defined as: $h = u + Pv$. Therefore, the above equation becomes:

$$\theta = h + ke + pe = h + V^2 / 2 + gz \qquad \text{(kJ/kg)}$$

The property θ is called **methalpy**. By using enthalpy instead of internal energy, the energy associated with *flow work into/out of control volume is automatically taken care of*.

This is the main reason that enthalpy is defined!

Steady-State Flow Process

A process during which a fluid flows through a control volume steadily is called *steady-state process*. A large number of devices such as turbines, compressors, and nozzles operates under the same conditions for a long time and can be modeled (or classified) as steady-flow devices.

The term *steady* implies no change with time. The term *uniform* implies no change with location over a specified region.

A **steady flow** is characterized by the following:

1- No properties within the CV change with time. Thus, volume, mass, and energy of CV remain constant. Total mass entering the CV must be equal to total mass leaving CV.

2- No properties change at the boundary of the CV with time. It means that the mass flow rate and the properties of the fluid at an opening must remain constant during a steady flow.

3- The heat and mass interactions between the CV and its surroundings do not change with time.

Using the above observation, the conservation of energy principle for a general steady-flow system with multiple inlets and exits can be written as:

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

$$\dot{Q}-\dot{W}=\sum \dot{m}_e\theta_e-\sum \dot{m}_i\theta_i$$

Example 1-5: Heat exchanger (the 1st law for CV)

Engine oil is to be cooled by water in a condenser. The engine oil enters the condenser with a mass flow rate of 6 kg/min at 1 MPa and 70°C and leaves at 35°C. The cooling water enters at 300 kPa and 15°C and leaves at 25°C. Neglecting any pressure drops; determine a) the mass flow rate of the cooling water required, and b) the heat transfer rate from the engine oil to water.

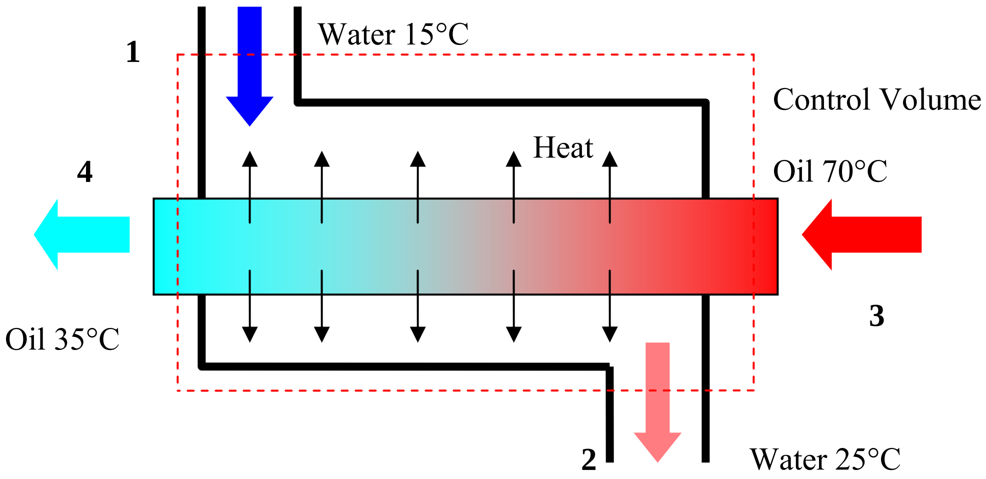


Fig. 1-17: Schematic for example 1-5.

Assumptions:

1- Insulated heat exchanger (no heat loss to the surroundings)
2- ΔKE = ΔPE = 0
3- No friction losses.

We choose the entire heat exchanger as our control volume, thus work transfer and heat transfer to the surroundings will be zero. From mass balance:

$$\dot{m}_1=\dot{m}_2=\dot{m}_W \qquad \text{and} \qquad \dot{m}_3=\dot{m}_4=\dot{m}_{Oil}$$

The conservation of energy equation is:

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

$$\sum \dot{m}_i h_i=\sum \dot{m}_e h_e$$

$$\dot{m}_W h_1+\dot{m}_{Oil} h_3=\dot{m}_W h_2+\dot{m}_{Oil} h_4$$

$$\dot{m}_W=\frac{h_3-h_4}{h_2-h_1}\dot{m}_{Oil}$$

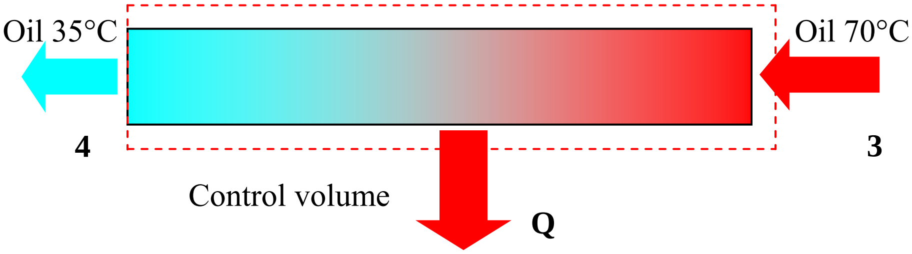
Assuming constant specific heat for both the oil and water at their average temperatures,

$$\dot{m}_W = \dot{m}_{oil} \frac{C_{P,Oil}(T_3 - T_4)}{C_{P,Water}(T_2 - T_1)} = \frac{\left(2.016 \frac{kJ}{kg.C}\right)(70-35)}{\left(4.18 \frac{kJ}{kg.C}\right)(25-15)}(6\ kg/\min) = 10.1\ kg/\min$$

b) To determine the heat transfer from the oil to water, choose the following CV. The energy equation becomes:

$$\dot{Q}_{Oil} - \dot{W} = \dot{m}_{Oil}(\Delta h) = \dot{m}_{Oil} C_{P,Oil}(T_4 - T_3)$$

$$\dot{Q}_{Oil} = (6\ kg/\min)\left(\frac{1\min}{60s}\right)\left(2.016 \frac{kJ}{kg.C}\right)(35-70) = -7.056\ kJ/s\,(kW)$$



Note that the negative sign indicates the heat transfer is from the CV to the surroundings.

The Second Law of Thermodynamics

The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has *quality* as well as *quantity*.

A process can occur when and only when it satisfies both the first and the second laws of thermodynamics.

The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.

Thermal Energy Reservoirs

Thermal energy reservoirs are hypothetical bodies with a *relatively* large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat *without undergoing any change in temperature*. Lakes, rivers, atmosphere, oceans are example of thermal reservoirs.

A reservoir that supplies energy in the form of heat is called a *source* and one that absorbs energy in the form of heat is called a *sink*.

Heat Engines

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1- They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)

2- They convert part of this heat to work

3- They reject the remaining waste heat to a low-temperature sink

4- They operate in a cycle.

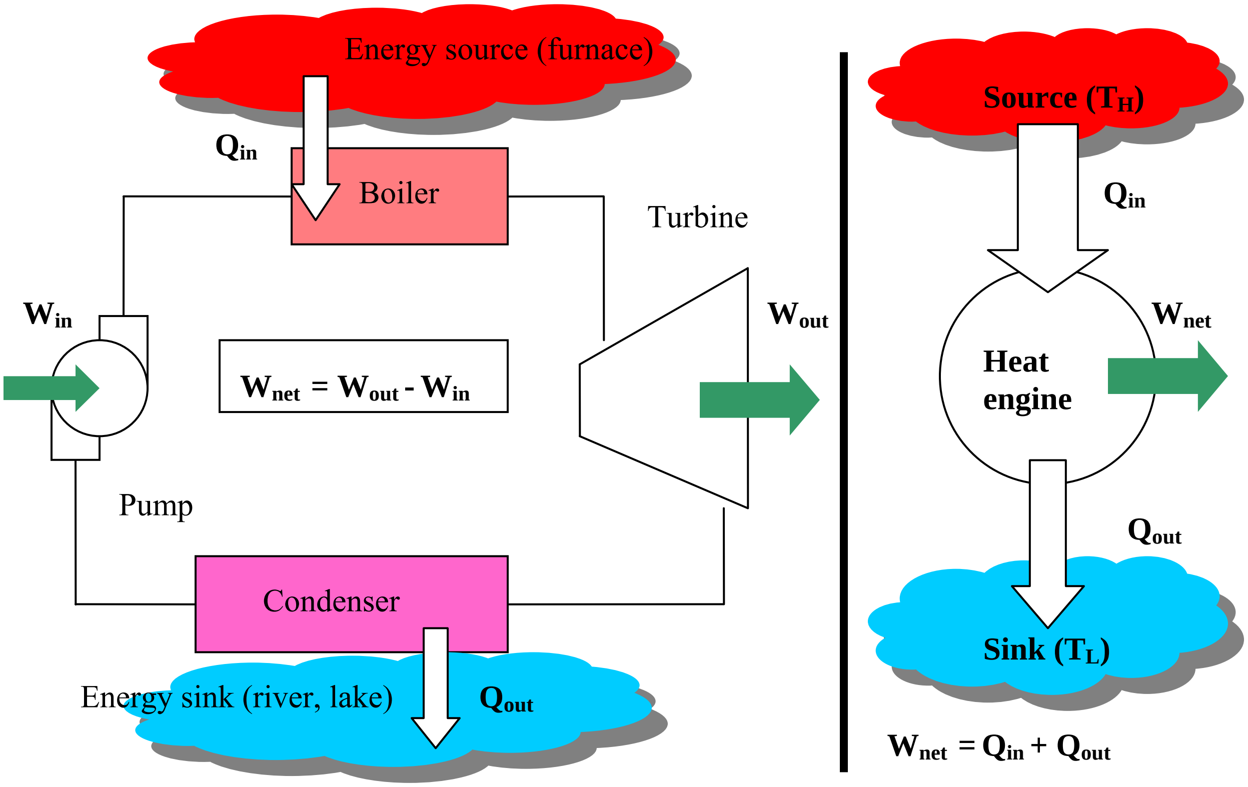


Fig. 1-18: Steam power plant is a heat engine.

Thermal efficiency: is the fraction of the heat input that is converted to the net work output (efficiency = benefit / cost).

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

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}} < 1$$

The thermal efficiencies of work-producing devices are low. Ordinary spark-ignition automobile engines have a thermal efficiency of about 20%, diesel engines about 30%, and power plants in the order of 40%.

Is it possible to save the rejected heat Q_{out} in a power cycle? The answer is NO, because without the cooling in condenser the cycle cannot be completed. Every heat engine *must* waste some energy by transferring it to a *low-temperature* reservoir in order to complete the cycle, *even in idealized cycle*.

The Second Law: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%.

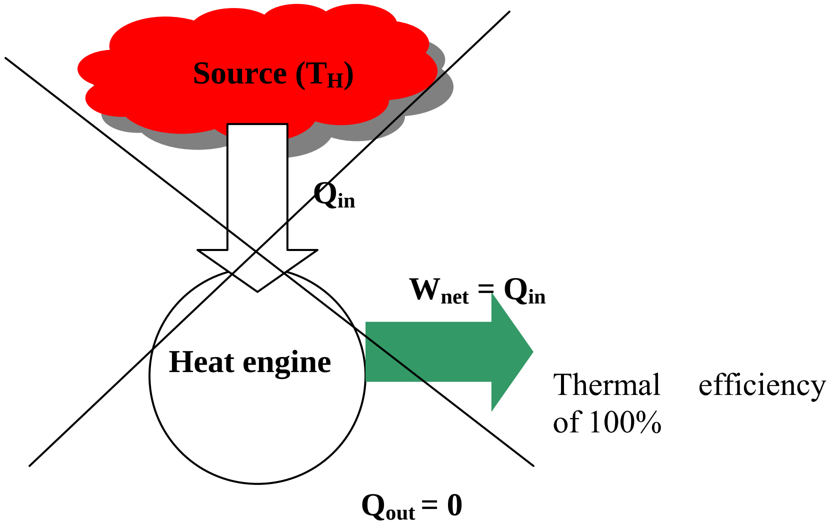


Fig.1-19: A heat engine that violates the Kelvin-Planck statement of the second law cannot be built.

Refrigerators and Heat Pumps

The transfer of heat from a low-temperature region to a high-temperature one requires special devices called *refrigerators*. Refrigerators are cyclic devices, and the working fluids used in the cycles are called *refrigerant*.

Heat pumps transfer heat from a low-temperature medium to a high-temperature one. Refrigerators and heat pumps are essentially the same devices; they differ in their objectives only. Refrigerator is to maintain the refrigerated space at a low temperature. On the other hand, a heat pump absorbs heat from a low-temperature source and supplies the heat to a warmer medium.

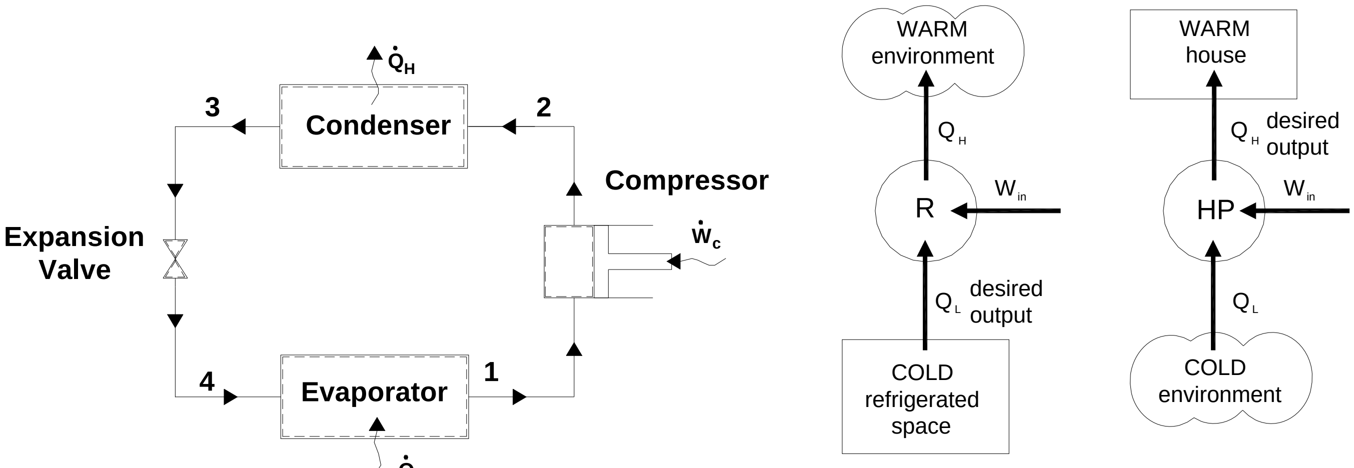
Coefficient of Performance (COP)

The performance of refrigerators and heat pumps is expressed in terms of the coefficient of performance (COP) which is defined as

$$COP_R = \frac{Benefit}{Cost} = \frac{q_L}{w_c} \qquad COP_{HP} = \frac{Benefit}{Cost} = \frac{q_H}{w_c}$$

It can be seen that

$$COP_{HP} = COP_R + 1$$



Refrigerator

Heat pump

Fig.1-20: Objectives of refrigerator and heat pump.

The Energy Efficiency Rating (**EER**): is the amount of heat removed from the cooled space in BTU's for 1 Wh (watt-hour)

$$EER = 3.412\ COP_R$$

Most air conditioners have an EER between 8 to 12 (COP of 2.3 to 3.5).

The Second Law of Thermodynamics: Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source.

The two statements of the second law are equivalent. In other words, any device violates the Kelvin-Planck statement also violates the Clausius statement and vice versa.

Any device that violates the first law of thermodynamics (by creating energy) is called a *perpetual-motion machine of the first kind* (PMM1), and the device that violates the second law is called a *perpetual-motion machine of the second kind* (PMM2).

Reversible and Irreversible Process

A *reversible* process is defined as a process that can be reversed without leaving any trace on the surroundings. It means both system and surroundings are returned to their initial states at the end of the reverse process. Processes that are not reversible are called *irreversible*.

Reversible processes do not occur and they are only idealizations of actual processes. We use reversible process concept because, a) they *are easy to analyze* (since system passes through a series of equilibrium states); b) they *serve as limits* (idealized models) to which the actual processes can be compared.

Some factors that cause a process to become *irreversible*:

- Friction
- Unrestrained expansion and compression
- mixing
- Heat transfer (finite ΔT)
- Inelastic deformation
- Chemical reactions

Internally reversible process: if no irreversibilities occur within the boundaries of the system. In these processes a system undergoes through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state.

Externally reversible process: if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

Totally reversible (reversible): both externally and internally reversible processes.

The Carnot Cycle

The best known reversible cycle is the *Carnot cycle*. Note that the reversible cycles cannot be achieved in practice because of irreversibilities associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.

Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

1-2 Reversible isothermal expansion: The gas expands slowly, doing work on the surroundings. Reversible heat transfer from the heat source at T_H to the gas which is also at T_H.

2-3 Reversible adiabatic expansion: The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from T_H to T_L.

3-4: Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature T_L as the gas is being slowly compressed. So, the surroundings is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_L.

4-1: Reversible adiabatic compression: The gas temperature is increasing from T_L to T_H as a result of compression.

Carnot cycle is the most efficient cycle operating between two specified temperature limits.

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

The thermal efficiency of a heat engine (reversible or irreversible) is:

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

For the Carnot cycle, it can be shown:

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H} \text{ (T in Kelvin)}$$

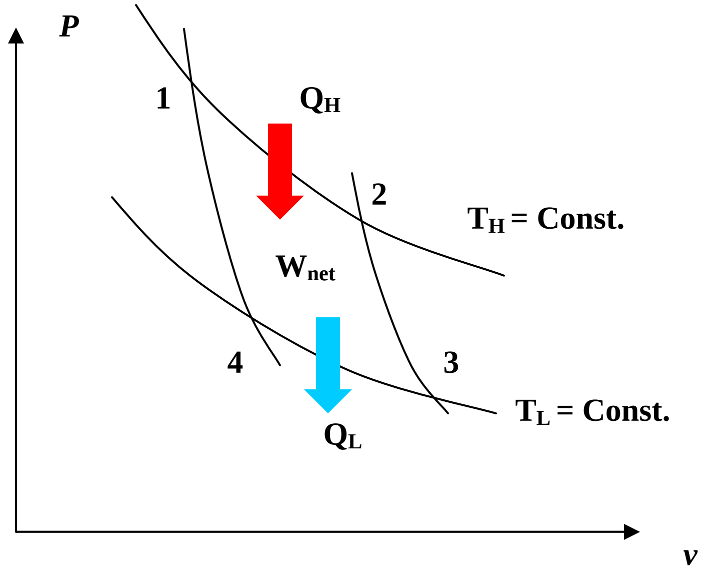


Fig. 1-21: P-v diagram for the Carnot cycle.

The efficiency of an irreversible (real) cycle is always less than the efficiency of the Carnot cycle operating between the same two reservoirs.

$$\eta_{th} = \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine!} \end{cases}$$

The thermal efficiency of actual heat engine can be maximized by supplying heat to the engine at the highest possible temperature (limited by material strength) and rejecting heat to lowest possible temperature (limited by the cooling medium temperature such as atmosphere, lake, river temperature).

The Carnot Refrigeration and Heat Pump Cycle

A refrigerator or heat pump that operates on the reverse Carnot cycle is called a *Carnot Refrigerator*, or a *Carnot heat pump*.

The Coefficient of performance of any refrigerator or heat pump (reversible or irreversible) is given by:

$$COP_R = \frac{1}{Q_H / Q_L - 1} \quad \text{and} \quad COP_{HP} = \frac{1}{1 - Q_L / Q_H}$$

COP of all reversible refrigerators or heat pumps can be determined from:

$$COP_{R,rev} = \frac{1}{T_H / T_L - 1} \quad \text{and} \quad COP_{HP,rev} = \frac{1}{1 - T_L / T_H}$$

Also, similar to heat engine, one can conclude:

$$COP_R = \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{th,rev} & \text{reversible refrigerator} \\ > COP_{th,rev} & \text{impossible refrigerator!} \end{cases}$$

Example 1-6: Refrigerator Performance

A refrigerator maintains the temperature of the freezer compartment at -5 C when the air surrounding the refrigerator is at 22 °C. The rate of heat transfer from the freezer compartment to the refrigerant (the working fluid) is 8000 kJ/h and the power input required to operate the refrigerator is 3200 kJ/h. Determine the coefficient of performance of the refrigerator and compare with the coefficient of performance of a reversible refrigeration cycle operating between reservoirs at the same temperatures.

Assumptions:

- Steady-state operation of the refrigerator.
- The freezer compartment and the surrounding air play the roles of the cold and hot reservoirs, respectively.

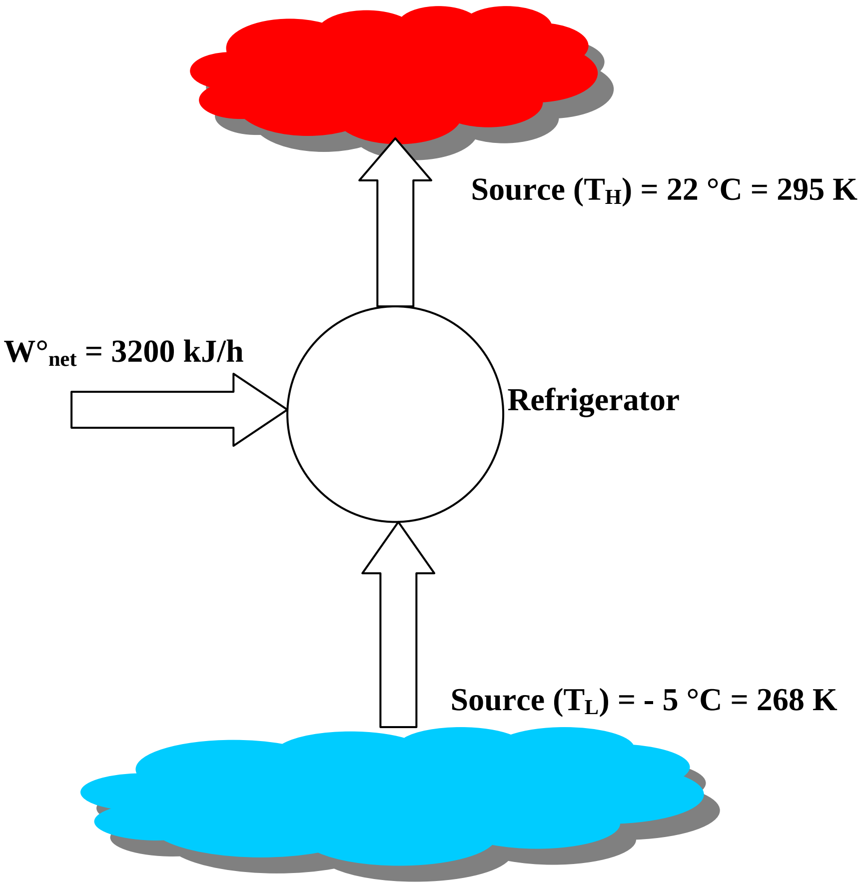
The coefficient of performance of the refrigerator is:

$$\mathrm{COP_R} = Q^{\circ}_{\mathrm{C}} / W^{\circ}_{\mathrm{cycle}}$$

$$\mathrm{COP_R} = 8000\ (\mathrm{kJ/h}) / 3200\ (\mathrm{kJ/h}) = 2.5$$

The coefficient of performance of a Carnot refrigerator working between the same two reservoirs is:

$$COP_{R,Carnot} = \frac{1}{T_H / T_C - 1} = \frac{1}{295/268 - 1} = 9.9$$



Entropy

The second law leads to the definition of a new property called *entropy*.

The first law is simply an energy balance. However, the second law leads to an inequality; an *irreversible* process is less efficient than a reversible process. Another important inequality in thermodynamics is the *Clausius* inequality:

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

That is, the cyclic integral of δQ / T is always less than or equal to zero. This is valid for all cycles, reversible or irreversible. For internally reversible cycles, it can be shown that:

$$\oint \frac{\delta Q}{T}\bigg|_{\text{int},rev} = 0$$

The Clausius inequality forms the basis for the definition of *entropy*. As can be seen in the equation above, for an internally reversible process the cyclic integral of δQ / T is zero. Clausius in 1865 realized that he discovered a new property and he called it *entropy*:

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

Entropy per unit mass is designated by s (kJ/kg.K).

The entropy change of a system during a process can be calculated:

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

Note that the cyclic integral of δQ / T will give us the entropy change *only if* the integration carried out along an internally reversible path between two states. For irreversible processes, we may imagine a reversible process between the two states (initial and final) and calculate the entropy change (since entropy is a property).

The Increase of Entropy Principle

Entropy change of a closed system during an irreversible process is greater that the integral of δQ / T evaluated for the process. In the limiting case of a reversible process, they become equal.

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

The entropy generated during a process is called *entropy generation,* and is denoted by S_{gen},

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

Note that the entropy generation S_{gen} is *always a positive quantity or zero* (reversible process). Its value depends on the process, thus it **is not a property** of a system.

The entropy change of a system or its surroundings can be negative; but entropy generation cannot.

$$S_{gen} = \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{reversible process} \\ < 0 & \text{impossible process} \end{cases}$$

1- A process must proceeds in the direction that complies with the increase of entropy principle, $S_{gen} > 0$. A process that violates this principle is impossible.

2- Entropy is a non-conserved property, and there is no such thing as the conservation of entropy. Therefore, the entropy of universe is continuously increasing.

3- The performance of engineering systems is degraded by the presence of irreversibility. The entropy generation is a measure of the magnitudes of the irreversibilities present during the process.

Entropy Balance

Entropy is a measure of molecular disorder or randomness of a system, and the second law states that entropy can be created but it cannot be destroyed.

The increase of entropy principle is expressed as

Entropy change = Entropy transfer + Entropy generation

$$\Delta S_{system} = S_{transfer} + S_{gen}$$

This is called the entropy balance.

The entropy change of a system is zero if the state of the system does not change during the process. For example *entropy change of steady flow devices* such as nozzles, compressors, turbines, pumps, and heat exchangers is *zero during steady operation*.

Mechanisms of Entropy Transfer

Entropy can be transferred to or from a system in two forms: heat transfer and mass flow. Thus, the entropy transfer for an adiabatic closed system is zero.

Heat Transfer: Heat rejection is the only way that the entropy of a fixed mass can be decreased. The ratio of the heat transfer Q/ T (absolute temperature) at a location is called entropy flow or entropy transfer

Entropy transfer with heat $$S_{heat} = \frac{Q}{T}$$

Since T (in Kelvin) is always positive, the direction of entropy transfer is the same as the direction of heat transfer.

When two systems are in contact, the entropy transfer from warmer system is equal to the entropy transfer to the colder system since the boundary has no thickness and occupies no volume.

Note that **work is entropy-free**, and no entropy is transferred with work.

Mass Flow: mass contains entropy as well as energy, both entropy and energy contents of a system are proportional to the mass. When a mass in the amount of *m* enters or leaves a system, entropy in the amount of *ms* (*s* is the specific entropy) accompanies it.

Entropy Balance for a Closed System

The entropy change of a closed system is due to the entropy transfer accompanying heat transfer and the entropy generation within the system boundaries:

Entropy change of a system = Entropy transfer with heat + Entropy generation

$$S_2 - S_1 = \sum \frac{Q_k}{T_k} + S_{gen}$$

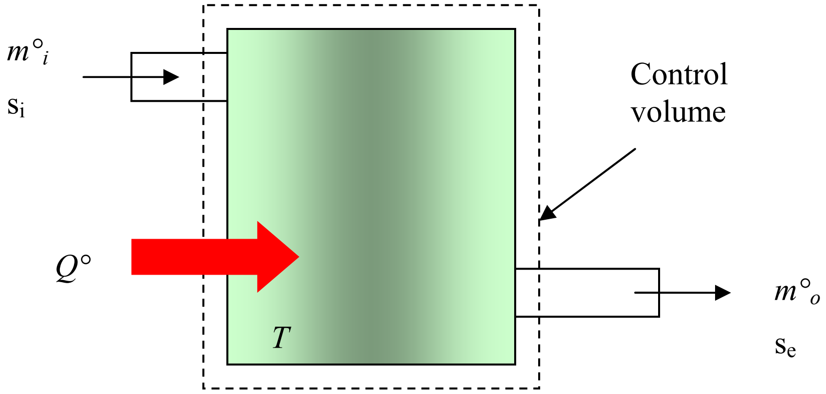
Therefore, for an adiabatic closed system, we have:

$$\Delta S_{adiabatic} = S_{gen}$$

For an internally reversible adiabatic process $\Delta S = 0$, because $S_{gen} = 0$.

Entropy Balance for a Control Volume

In addition to methods discussed for closed system, the entropy can be exchanged through *mass flows* across the boundaries of the control volume.



The entropy balance in the rate form for a control volume becomes:

$$\frac{dS_{CV}}{dt} = \sum \frac{\dot{Q}_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \dot{S}_{gen,CV}$$

For a steady-state steady-flow process, it simplifies to:

$$\dot{S}_{gen,CV} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \sum \frac{\dot{Q}_k}{T_k}$$

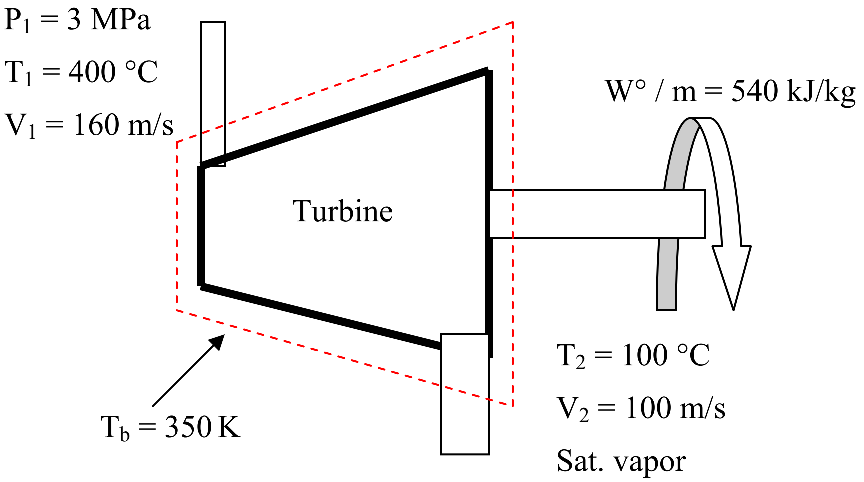
Example 1-7: Entropy balance for a CV

Steam enters a turbine with a pressure of 3 MPa, a temperature of 400 °C, and a velocity of 160 m/s. Saturated vapor at 100 °C exits with a velocity of 100 m/s. At steady-state, the turbine develops work equal to 540 kJ/kg. Heat transfer between the turbine and its surroundings occur at an average outer surface temperature of 350 K. Determine the rate at which entropy is produced within the turbine per kg of steam flowing, in kJ/kg.K. Neglect the change in potential energy between inlet and exit.

Assumptions:

1- Steady state operation in CV. $\Delta PE = 0$.

2- Turbine outer surface is at a specified average temperature.



From the mass balance, we know that $m^\circ = m^\circ_1 = m^\circ_2$

Since the process is steady-state, one can write:

$$0 = \sum \frac{Q_k^\bullet}{T_k} + m^\bullet (s_i - s_e) + S^\bullet_{gen,CV}$$

The heat transfer occurs at T_b = 350 K, the first term of the right hand side of the entropy balance reduces to Q° / T_b

$$\frac{S^\bullet_{gen,CV}}{m^\bullet} = -\frac{Q_k^\bullet}{m^\bullet T_k} + (s_2 - s_1)$$

We need to calculate the rate of heat transfer. The first law (energy balance) can be used to find the heat transfer rate. Combining the mass balance and the first law, one finds:

$$\frac{Q^\bullet_{CV}}{m^\bullet} = \frac{W^\bullet_{CV}}{m^\bullet} + (h_2 - h_1) + \left(\frac{V_2^2 - V_1^2}{2} \right)$$

From Table A-6, h_1 = 3230.9 kJ/kg, and From A-4 h_2 = 2676.1 kJ/kg. After substitution, and converting the units, one finds:

$$\frac{Q^\bullet_{CV}}{m^\bullet} = -22.6 \quad kJ/kg$$

From Table A-4, s_2 = 7.3549 kJ/kg.K and from Table A-6, s_1 = 6.9212 kJ/kg.K. Inserting values into the expression for entropy production:

$$\frac{S^\bullet_{gen,CV}}{m^\bullet} = -\frac{Q_k^\bullet}{m^\bullet T_k} + (s_2 - s_1) = 0.4983 \quad kJ/kg.K$$

Some remarks:

Work is an organized form of energy, free of disorder or randomness, thus free of entropy. Therefore, there is *no entropy associated with energy transfer as work.*

The *quantity* of energy is always preserved during an actual process, based on the *first law*, but the *quality* is bound to decrease (*the second law*).

Processes can occur only in the direction of *increasing overall entropy* or molecular disorder. Thus, the entire universe is getting more and more chaotic every day.

At *absolute zero* (0 K), molecules become completely motionless, this represents a state of ultimate molecular order (and *minimum energy*). Therefore, the entropy of a pure crystalline substance at zero temperature is zero. That is because; there is *no uncertainty* about the state of the molecules at that instant. This statement is the **third law of thermodynamics**.

Since there is a reference for entropy (absolute zero), entropy is an absolute property. The entropy measured with respect to absolute zero is called absolute entropy.

The two diagrams used most extensively in the second-law analysis are the T-s and h-s diagrams. For an internally reversible process, one can write:

$$\delta Q_{\text{int},rev} = Tds \qquad \text{(kJ)}$$

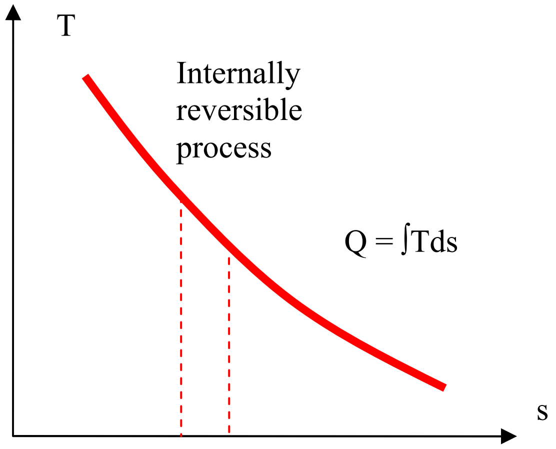


Fig. 1-22: On a T-s diagram, the area under an internally reversible process presents the heat transfer for the process.

For an internally reversible isothermal process, we have:

$$Q_{\text{int,rev}} = T_0 \, ds$$

In a T-s diagram, an isentropic process is represented by a vertical line. An isentropic process is a process in which entropy remains constant. As a result an isentropic process involves no heat transfer. Therefore:

$$\text{Isentropic process } (s_2 = s_1) = \text{Reversible} + \text{Adiabatic}$$

Evaluation of Entropy Change (Gibbs Equations)

The differential form of the conservation of energy for a closed system (fixed mass) for an internally reversible process is:

$$\delta Q_{\text{int,rev}} - \delta W_{\text{int,rev}} = dU$$

where,

$$\delta Q_{int,rev} = TdS$$

$$\delta W_{int,rev} = PdV$$

Thus,

$$TdS = dU + PdV$$

or, per unit mass

$$Tds = du + Pdv$$

This is called the *first Gibbs equation*.

From the definition of enthalpy, $h = u + Pv$, one can find:

$$h = u + Pv \rightarrow dh = du + Pdv + vdP$$

Eliminating du from the first Gibbs equation, one finds the *second Gibbs equation*:

$$Tds = dh - vdP$$

Explicit relations for differential changes in entropy can be obtained from Gibbs equations:

$$ds = \frac{du}{T} + \frac{Pdv}{T}$$

$$ds = \frac{dh}{T} - \frac{vdP}{T}$$

To calculate the entropy change, we must know the relationship between du or dh and temperature.

Entropy Change of Solids and Liquids

Solids and liquids can be assumed as incompressible substances since their volumes remains essentially constant during a process. Thus, the first Gibbs equation becomes:

$$ds = \frac{du}{T} = \frac{cdT}{T}$$

$$s_2 - s_1 = \int_1^2 C(T)\frac{dT}{T}$$

Assuming an averaged value for specific heat, one obtains:

$$s_2 - s_1 = C_{ave} \ln \frac{T_2}{T_1}$$

Note that the entropy change of an incompressible substance is only a function of temperature. Therefore, for an *isentropic process* where $s_2 = s_1$, one can find:

$$T_2 = T_1$$

Entropy Change of Ideal Gas

The entropy change of an ideal gas can be obtained, by substituting du = C_v dT and P = RT / v into Gibbs equation.

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

$$s_2 - s_1 = \int_1^2 C_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

Assuming averaged values for specific heats, one obtains:

$$s_2 - s_1 = C_{v,ave}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} \qquad \frac{kJ}{kg.K}$$

$$s_2 - s_1 = C_{p,ave}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} \qquad \frac{kJ}{kg.K}$$

For isentropic processes of ideal gases, the following relationships can be found by setting ds = 0,

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_v}\ln\frac{v_2}{v_1}$$

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{v_1}{v_2}\right)^{\frac{R}{C_v}} \quad or \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{k-1} \quad \text{isentropic process}$$

Since R = $C_p - C_v$, k = C_p / C_v, thus R / C_v = k – 1.

In a similar manner, one finds:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \quad \text{isentropic process}$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{v_1}{v_2}\right)^{k} \quad \text{isentropic process}$$

These equations can be expressed in the following compact forms:

$$Tv^{k-1} = \text{constant}$$

$$TP^{(1-k)/k} = \text{constant}$$

$$Pv^{k} = \text{constant}$$

The specific ratio *k*, varies with temperature, and in isentropic relations above an average *k* value should be used.

Reversible Steady-Flow Work

The conservation of energy equation for a steady-flow device undergoing an internally reversible process can be expressed in differential form as

$$\delta q_{rev} - \delta w_{rev} = dh + d\text{ke} + d\text{pe}$$

But

$$\left.\begin{aligned} \delta q_{rev} &= Tds \\ Tds &= dh - vdP \end{aligned}\right\} \rightarrow \delta q_{rev} = dh - vdP$$

Substituting into the relation above, after canceling dh, it yields,

$$-\delta w_{rev} = vdP + dke + dpe$$

Integrating, we find

$$w_{rev} = -\int_1^2 vdP - \Delta ke - \Delta pe \qquad (kJ/kg)$$

With negligible changes in potential and kinetic energies,

$$w_{rev} = -\int_1^2 vdP \qquad (kJ/kg)$$

From the above equation can be seen that, the larger the specific volume the larger the reversible produced or consumed work by the steady-flow device. Thus, every effort should be made to keep the specific volume of the flow as small as possible during a compression process to minimize the input work.

When the fluid is incompressible, the specific volume remains constant during the process, thus the above equation becomes:

$$\delta w_{rev} = v(P1 - P2) - \Delta ke - \Delta pe \quad (kJ/kg)$$

For a steady-state flow of a liquid through a device that involves no work interactions (such as nozzle or a pipe section), the work term is zero,

$$v(P_2 - P_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) = 0$$

This is known as *Bernoulli equation* in fluid mechanics.