Chapter 1

Thermodynamics in Everyday Life

In This Chapter

- Seeing thermodynamics in the world around you
- Changing energy from one form to another
- Getting energy to do work and move heat for you
- Figuring out relationships, reactions, and mixtures (nothing personal)
- Inspiring you to save the world from an energy shortage

Thermodynamics is as old as the universe itself, and the universe is simply the largest known thermodynamic system. When the universe ends in a whimper and the total energy of the universe dissipates to nothingness, so will thermodynamics end.

Broadly speaking, thermodynamics is all about energy: how it gets used and how it changes from one form to another. In many cases, thermodynamics involves using heat to provide work, as in the case of your automobile engine, or doing work to move heat, as in your refrigerator. With thermodynamics, you can find out how efficient things are at using energy for useful purposes, such as moving an airplane, generating electricity, or even riding a bicycle.

The word *thermodynamics* has a Greek heritage. The first part, *thermo,* conveys the idea that heat is somehow involved, and the second part, *dynamics,* makes you think of things that move. Keep these two ideas in mind as you look at your world in terms of the basic laws of thermodynamics. This book is written to help you understand that thermodynamics is about turning heat into power, a concept that really isn't so complicated after all.

Grasping Thermodynamics

Many thermodynamic systems are at work in the natural world. That sun you see in the sky is the ultimate energy source for the earth, warming the air, the ground, and the oceans. Huge masses of air move over the earth's surface. Giant currents of water swirl in the oceans. This movement and swirling happens because of the transformation of heat into work.

Energy takes many different forms — it can't be created or destroyed, but it can change form. This statement is one of the fundamental laws of thermodynamics. Consider how energy changes form in storm clouds:

- Storm clouds have motion within them.
- Motion between moisture droplets in clouds rubbing against each other creates friction.
- Friction causes a buildup of static charge.
- When the charge becomes high enough, the clouds produce lightning.
- This electrical surge of energy can then start a fire on the ground, and before you know it, you have a combustion problem on your hands.

Not only does energy change form, but *matter* (that is, a material or substance) also changes form in many thermodynamic systems. Storm clouds are formed by water evaporating into the air. As the water vapor reaches the colder parts of the atmosphere, it condenses to form clouds. Eventually, the amount of moisture the clouds contain becomes great enough to collect into droplets and form liquid water again, so it rains.

One thing people have observed about energy is that it flows in a preferred direction. This observation is another fundamental law of thermodynamics. Heat flows from a hot object to a cold object. Wind blows from a region of high pressure to a region of low pressure. Some forms of energy are developed by forces of nature. Air bubbles move upwards in water against gravity because buoyancy forces them to rise. Water droplets fall in the atmosphere because the force of gravity pulls them toward the ground.

Another brilliant observation about energy is that if you have absolutely no energy at all, you have no temperature. The concept of absolute zero temperature is a fundamental law of thermodynamics.

I cover the changing forms of energy and matter and the fundamental laws that govern how these changes work in Part I.

Examining Energy's Changing Forms

Many clever people have observed the fundamental laws of thermodynamics in natural systems and applied them to create some wonderful ways of doing work by harnessing energy. Heat is used to generate steam or heat up air that moves a piston in a cylinder or spins a turbine. This movement is used to turn a shaft that can operate a lawn mower; move a car, a truck, a locomotive, or a ship; turn an electric generator; or propel an airplane.

Other clever people have used thermodynamic principles to use work to move heat from one place to another. Refrigerators and heat pumps remove heat from one location to produce a desirable cooling or heating effect. The work required for this cooling shows up on your electric bill every month.

In Part II, I show you how the fundamental laws of thermodynamics can tell you how much heat you need to provide to produce work that can be used to move a car, fly an airplane, or turn an electric generator. You can also use the laws of thermodynamics to find out how efficient something is at using energy.

Energy is the basis of every thermodynamic process. When you use energy to do something, it changes form along the way. When you start your car, the battery causes the starter to turn. The battery is a big, heavy box of chemical energy. The battery's job is to change chemical energy into electrical energy. An electric motor rotates (a form of kinetic energy) the engine, and the spark plugs fire. These sparks ignite fuel via a combustion process wherein the chemical energy from gasoline is turned into a form of thermal energy called internal energy. In the few seconds it takes to start your car, energy changes from chemical to electrical to kinetic to thermal or internal energy.

Kinetic energy

A car battery provides electricity to operate your starter. As the motor turns, the electrical energy is converted into a form of mechanical energy called *kinetic energy.* Kinetic energy involves moving a mass so that it has velocity. The mass doesn't have to be very large to have kinetic energy — even electrons have kinetic energy — but the mass has to be moving. Before you start the car, nothing in the engine is moving so it has no kinetic energy. After the engine is started, it has kinetic energy because of its moving pistons and rotating shafts. If the car is parked while the engine is running, the car as a "system" has no kinetic energy until the engine makes the car move.

Potential energy

If you drive your car up a hill and park it there, you change the kinetic energy of the car into another form of energy called *potential energy.* Potential energy is only available with gravity. You must have a mass located at an elevation above some ground state. Potential energy gets its name from its potential to be converted into kinetic energy. You see this conversion process when you park on a hill and forget to apply the parking brake. Potential energy changes back into kinetic energy as your car rolls down the hill.

Internal energy

When you apply the brakes to stop your car, you make energy change form again. You know the car has kinetic energy because it's moving. Stopping the car changes all this kinetic energy into heat. Brake pads squeeze onto steel disks or steel drums, creating friction. Friction generates heat — sometimes a lot of heat. When materials heat up, another form of energy called *internal energy* increases. Have you ever smelled a burning odor while driving down long hills? That odor indicates that someone used their brakes to slow down, and the brakes overheated. Do your brakes a favor: Shift into a lower gear and allow the engine to do the braking for you. When the engine is used as a brake, the kinetic energy of the moving car compresses the air in the cylinders, and the energy changes into internal energy because the air heats up from compression. All that internal energy just goes out the tailpipe.

Watching Energy and Work in Action

Until the invention of the steam engine, man had to slug it out against nature with nature. Horses pulled coaches, mules pulled plows, sails moved ships, windmills ground grain, and water wheels pressed apples into cider that fermented and made man feel happy for all his labors. The steam engine was able to replace these natural work sources and move coaches, plows, and ships, among many other things. For the first time, fire was harnessed to provide something more than just heat — it was used to do work. This use of heat to accomplish work is what Part III is all about. Over time, many different kinds of work machines were developed, theories were made, and experiments were done until a rational system of analyzing heat and work was developed into the field of thermodynamics.

Engines: Letting energy do work

A *heat engine* is a machine that can take some source of heat — burning gasoline, coal, natural gas, or even the sun — and make it do work, usually in the form of turning a shaft. With a rotating shaft, you can make things move — think of elevators or race cars. Every heat engine uses four basic processes that interact with the surroundings to accomplish the engine's job. These processes are heat input, heat rejection, work input, and work output.

Take your automobile engine as an example of a heat engine. Here are the four basic processes that go on under the hood:

1. **Work input**

   Air is compressed in the cylinders. This compression requires work from the engine itself. Initially, this work comes from the starter. As you can imagine, this process takes a lot of work, which is why they don't have those crank handles on the front of cars any more.

2. **Heat input**

   Fuel is burned in the cylinder, where the heat is added to the engine. The heated air in the cylinder naturally wants to increase in pressure and expand. The pressure and expansion move the piston down the cylinder.

3. **Work output**

   As the expanding gas in the cylinder pushes the piston, work is output by the engine. Some of this work compresses the air in adjacent cylinders.

4. **Heat rejection**

   The last process removes heat with the exhaust from the engine.

Refrigeration: Letting work move heat

When Willis Carrier made air conditioners a popular home appliance, he did more than make people comfortable and give electric utilities a reason for growth and expansion. He brought thermodynamics into the home. Thermodynamics has been there all along, and you never realized it. Refrigerators, freezers, air conditioners, and heat pumps are all the same in thermodynamics. Only three basic processes involve energy interacting with the surroundings in what is known as the *refrigeration cycle:*

1. **Heat input**

   Heat is absorbed from the cold space to keep it cold.

2. **Work input**

   Work is added to the system to pump the heat absorbed from the cold space out to the hot space.

3. **Heat rejection**

   Heat is rejected to the hot space.

Actually, a fourth process takes place in most refrigeration cycles, but it doesn't involve a change in energy. Instead of having a work-output process in the cycle like heat engines do, refrigerators simply utilize a pressure-reducing device in the system. Energy doesn't change form in such a device.

Getting into Real Gases, Gas Mixtures, and Combustion Reactions

Using energy to generate electric power, cool your house, fly a jet, or race cars around the Indianapolis Motor Speedway is the glamorous side of thermodynamics. But behind the movie stars are a supporting cast and crew of *thermodynamic relationships* (this is jargon for "mathematical equations") for real gases, gas mixtures, and combustion reactions that make it all happen.

In Part IV, you discover the difference between a real gas and an ideal gas. There you see that real gases behave a bit differently than ideal gases. You also figure out the thermodynamic properties of a mixture of gases, such as water vapor and air for heating, air conditioning, and ventilating purposes. Lastly, you calculate how much energy you can get out of fuel in a combustion reaction to power your jet, your race car, or your lawn mower.

If you want to sell jet engines to an aircraft manufacturer, you have to show that your engine burns fuel efficiently. To build a jet engine, you need to know how much energy a combustion reaction adds to an engine and how much the air in the engine heats up as a result of the combustion. To figure out the latter, you use thermodynamic relationships of real gases to calculate properties such as temperature, pressure, and energy.

Discovering Old Names and New Ways of Saving Energy

As you learn about thermodynamics, you'll run across a number of names. Some of the names may be familiar; others may be new to you. For example, when you get your electric bill, it tells you how many watt-hours of electricity you used last month. If you reheat yesterday's leftover pizza, you set your oven to 350 degrees Fahrenheit. (Or, if you live outside the U.S., you set your oven to some temperature in degrees Celsius.) That big rig that's riding your bumper on the highway burns diesel fuel.

How did these terms — watt, Fahrenheit, Celsius, and Diesel — become part of our language? In Part V, you discover that these words (and six more) are actually the last names of characters bent on figuring out what energy is and how to harness it for the benefit of mankind (and maybe to line their pockets with some folding money).

Pioneers in thermodynamics didn't just work in the good old days; there are modern-day pioneers as well. The world's demand for energy steadily increases while energy resources dwindle. Part V shows you ten ways innovative thinkers have improved energy consumption for automobiles, air conditioners, refrigerators, and electric power plants. Making a better future for all has motivated many people to think of better ways to use energy.

Even Albert Einstein got a patent for making a better air-conditioning system (see Chapter 18). Maybe you'll be inspired to create your own innovation and make a name for yourself in thermodynamics.

Thermodynamics

Calorimetry: The Experimental Measurement of Heat

Outline

- Background
- Exothermic vs Endothermic Reactions
- Heat Capacity
- Specific Heat
- Specific Heat of Selected Substances and Mixtures
- Relevance

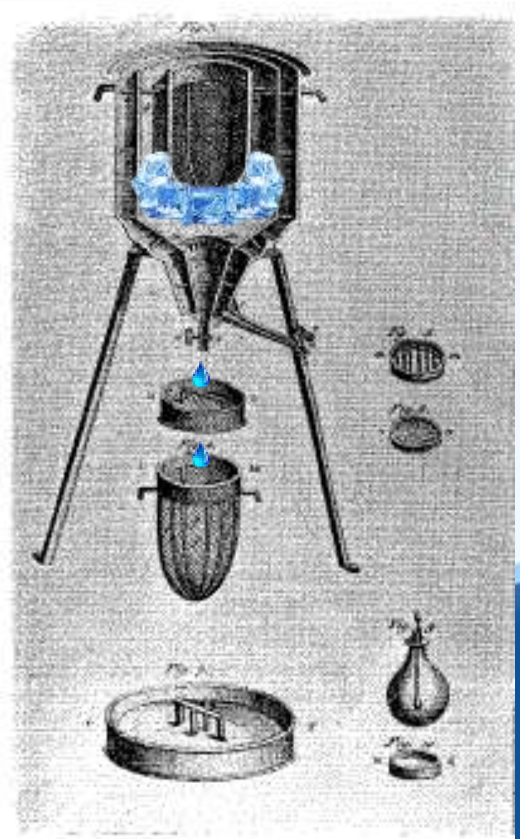
Background

Thermodynamics: Study of interactions among work, energy, and heat

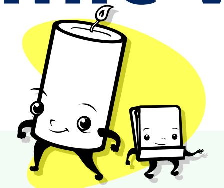
Calorimetry: Experimental measurement of heat

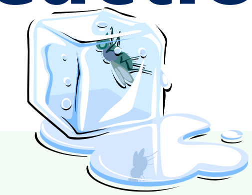
How did they first measure heat?

- Antoine Lavoisier (1782)
- World's first ice-calorimeter
- Published in his book "Elements of Chemistry"



Exothermic vs. Endothermic Reactions





EXOTHERMIC

Reaction that gives off heat to its surroundings

- A candle flame 
- Burning sugar
- Rusting iron
- Making ice cubes
- Forming bonds

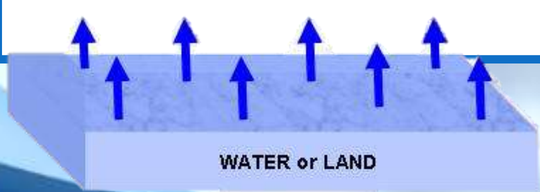
ENDOTHERMIC

Reaction that absorbs heat from its surroundings

- Forming cation from atom in gas phase
- Producing sugar by photosynthesis
- Cooking an egg 
- Melting ice cubes
- Breaking bonds

Pop Quiz!

Is evaporation of water H_2O (l) → H_2O(g) an endothermic or exothermic reaction?



Heat Capacity

Objects differ in their abilities to transform heat transfer into temperature change

- Heat Capacity (denoted by letter "C")
  - Measurement of the amount of heat required to change a substance's temperature by a certain amount

$$C = \frac{q}{\Delta T}$$

C= Heat Capacity (J/K)
q= quantity of heat transferred
ΔT= temperature change

An object has a heat capacity of 57.5 J/K. If its temperature changes from 150.4°C to 121.8°C, how much heat is transferred?

-1,640 J

1640 joules of heat are released by the object

Specific Heat

Heat capacity per unit mass

- Specific Heat (denoted by letter "C_p")
  - Measurement of the amount of heat required to change a substance's temperature by a certain amount

$$C_p = \frac{C}{m} = \frac{q}{m\Delta T}$$

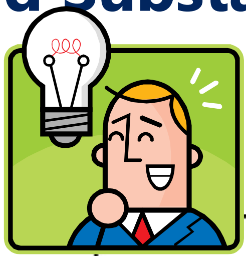
C= Heat Capacity (J/ g K)
q= quantity of heat transferred
m= mass
ΔT= temperature change

Calculate the heat absorbed by 50.0 g of Cu(s) as it changes its temperature from 300 K to 500K.

3,850J
3850 joules of heat are absorbed by Cu(s)

Specific Heats of Selected Substances and Mixtures

Substance	Cp (J/g K)
Ag(s)	0.235
Al (s)	0.897
Au(s)	0.129
Ca(s)	0.647
$CaCO_3$ (s)	0.920
Cu(s)	0.385
Fe(s)	0.449
H_2O (s)	2.06
H_2O (l)	4.19
H_2O (g)	2.02

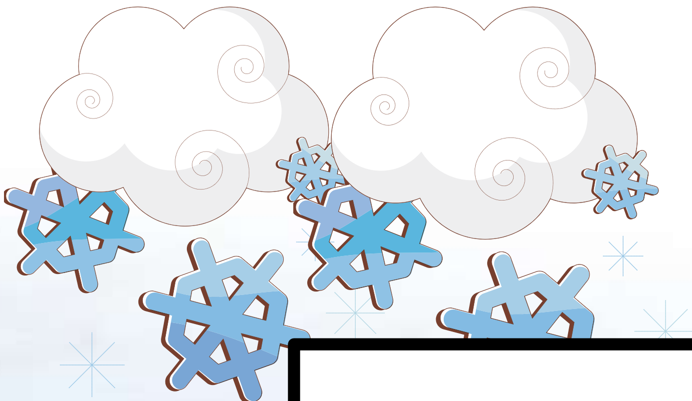


Did you notice anything peculiar?

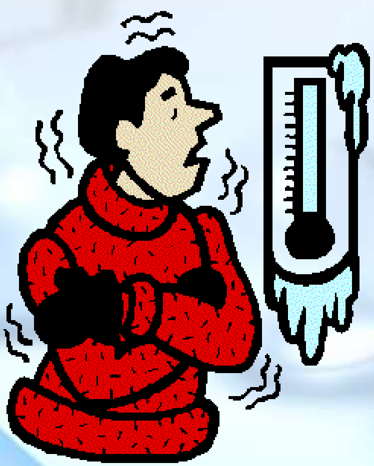
Cp(Ag) < Cp (H2O)
Cp (metal) < Cp (nonmetal)

Small specific heat= substance translate heat transfer to relatively large temperature change

Relevance



How do these work?



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*.

The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not.

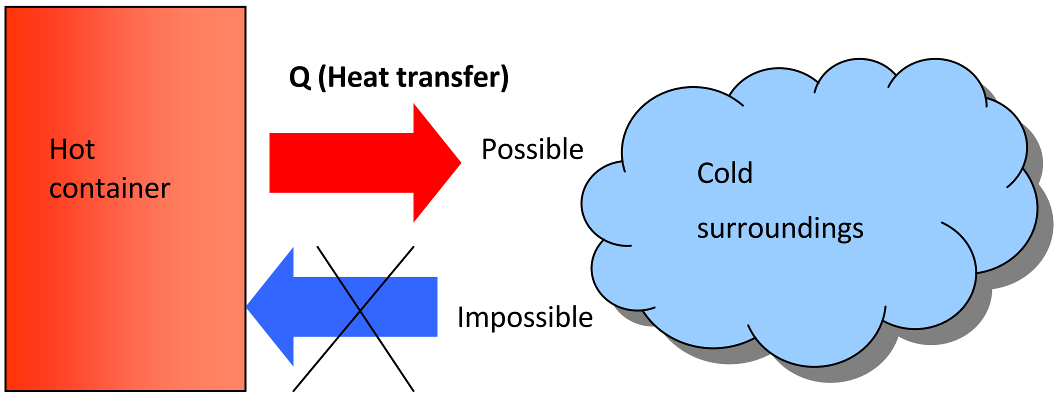


Fig. 1: Heat transfer from a hot container to the cold surroundings is possible; however, the reveres process (although satisfying the first law) is impossible.

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

The second law also asserts that energy has a quality. Preserving the quality of energy is a major concern of engineers. In the above example, the energy stored in a hot container (higher temperature) has higher quality (ability to work) in comparison with the energy contained (at lower temperature) in the surroundings.

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 two-phase system can be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

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.

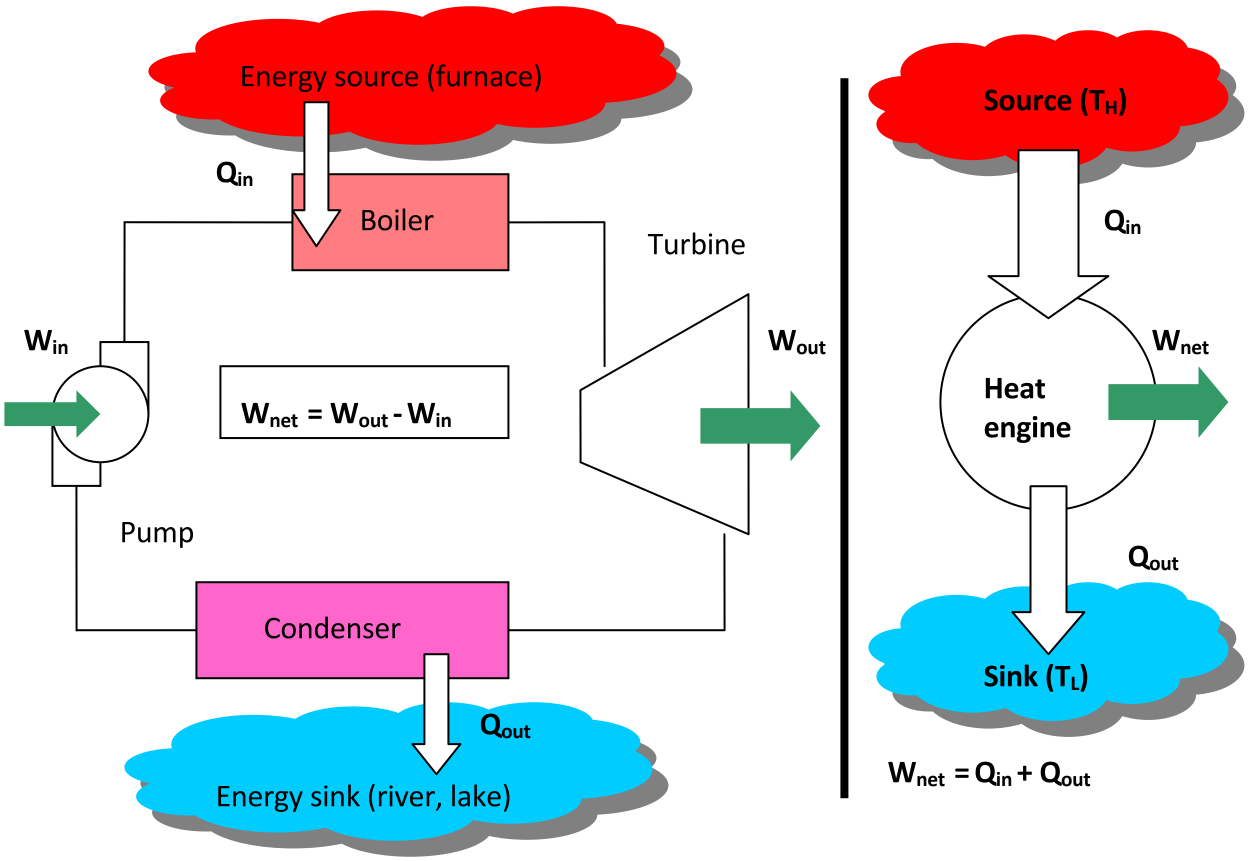


Fig. 2: Steam power plant is a heat engine.

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

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

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

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%.

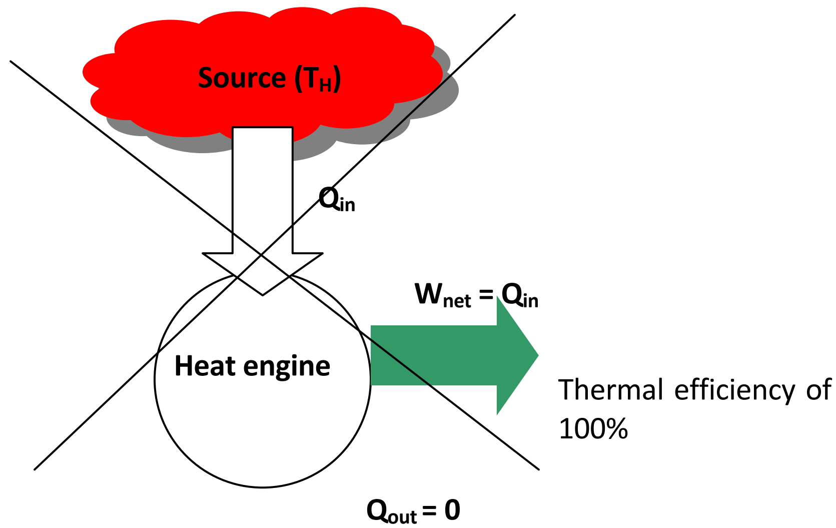


Fig.3: A heat engine that violates the Kelvin-Planck statement of the second law cannot be built.

Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. 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.

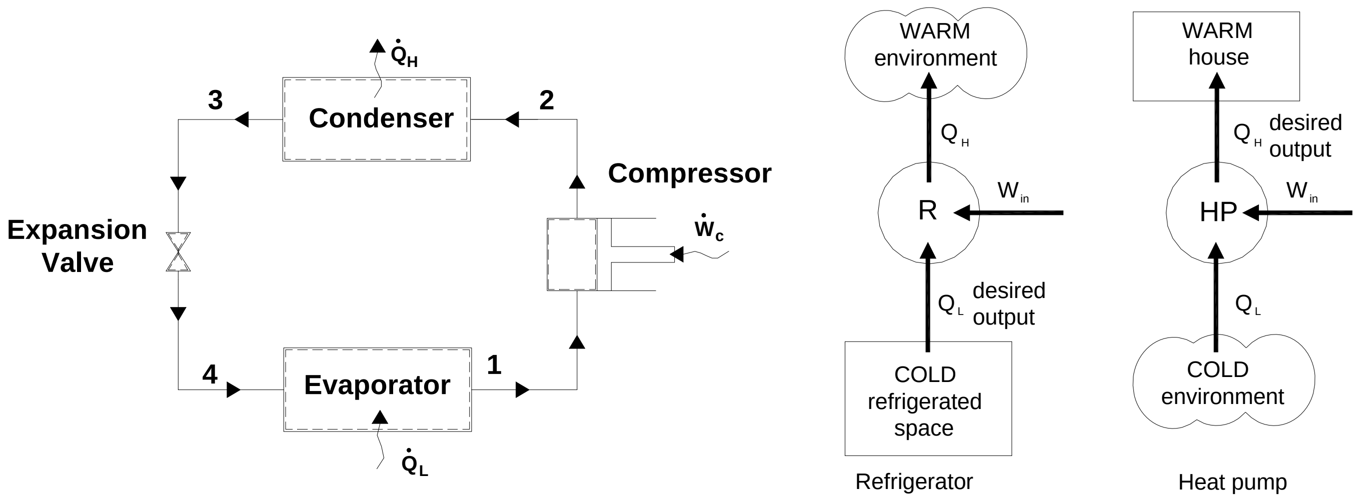


Fig. 4: Objectives of refrigerator and heat pump.

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

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

It can be seen that

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

Air conditioners are basically refrigerators whose refrigerated space is a room or a building.

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.

Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.

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.

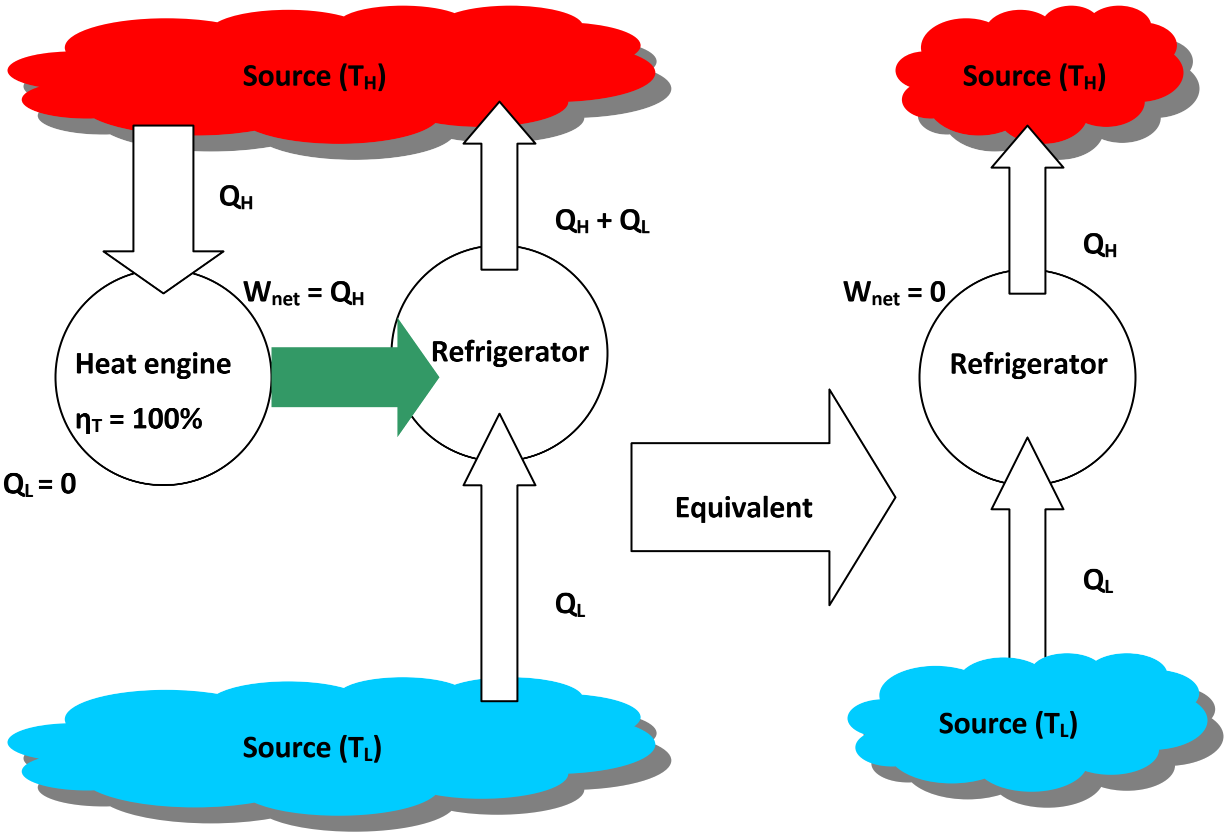


Fig. 5: The violation of the Kelvin-Planck statement leads to violation of Clausius.

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

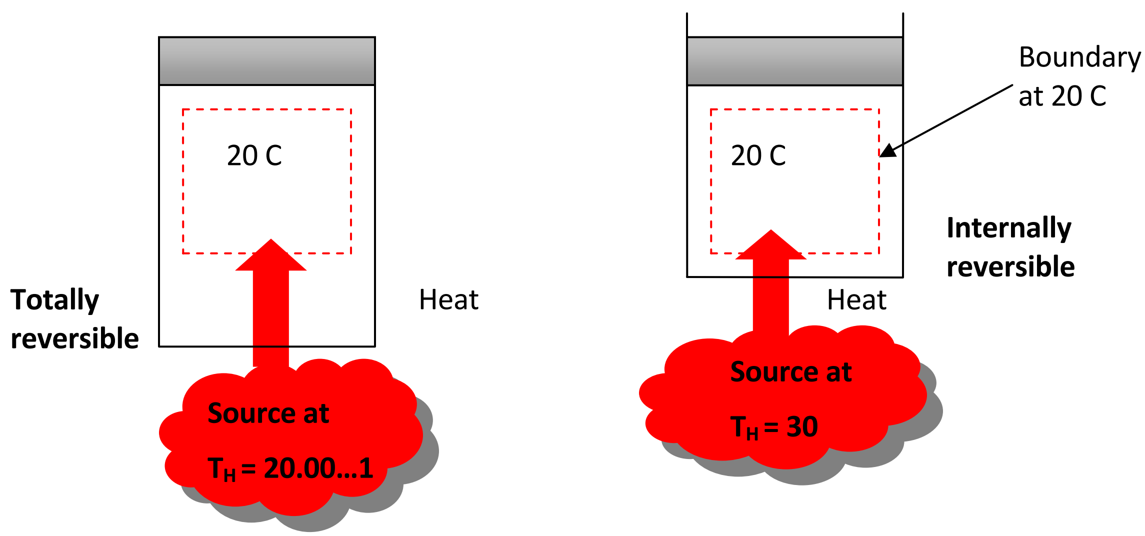
• Chemical reactions

In a reversible process things happen very slowly, without any resisting force, without any space limitation → everything happens in a highly organized way (it is not physically possible - it is an idealization).

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 efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work (or efficiency) can be maximized by using reversible processes. 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:

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

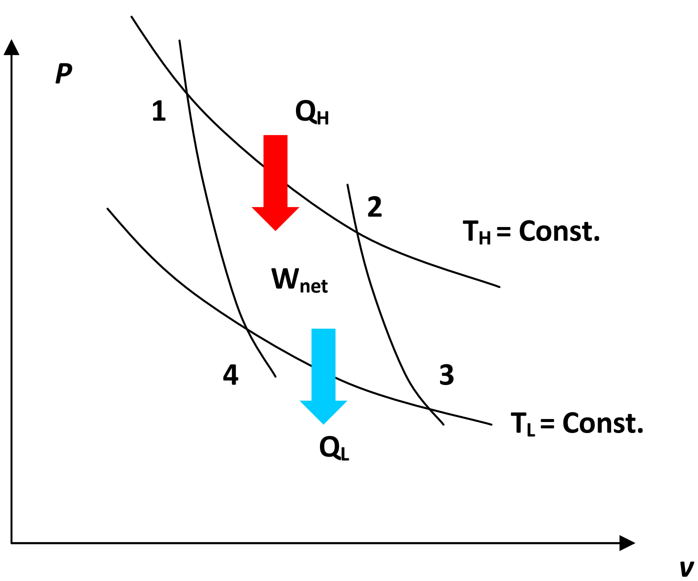


Fig. 6: P-v diagram for the Carnot cycle.

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

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

Consider a Carnot heat engine working between two thermal reservoirs T_L = 300 K and T_H. The thermal efficiency of the heat engine increases as the heat source temperature T_H is increased.

T_H K	**η_{th} %**
1000	70
900	66.6
500	40
350	14.3

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).

From the above table, it can also be seen that the energy has a quality. More of the high-temperature thermal energy can be converted to work. Therefore, the higher the temperature, the higher the quality of the energy will be.

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:

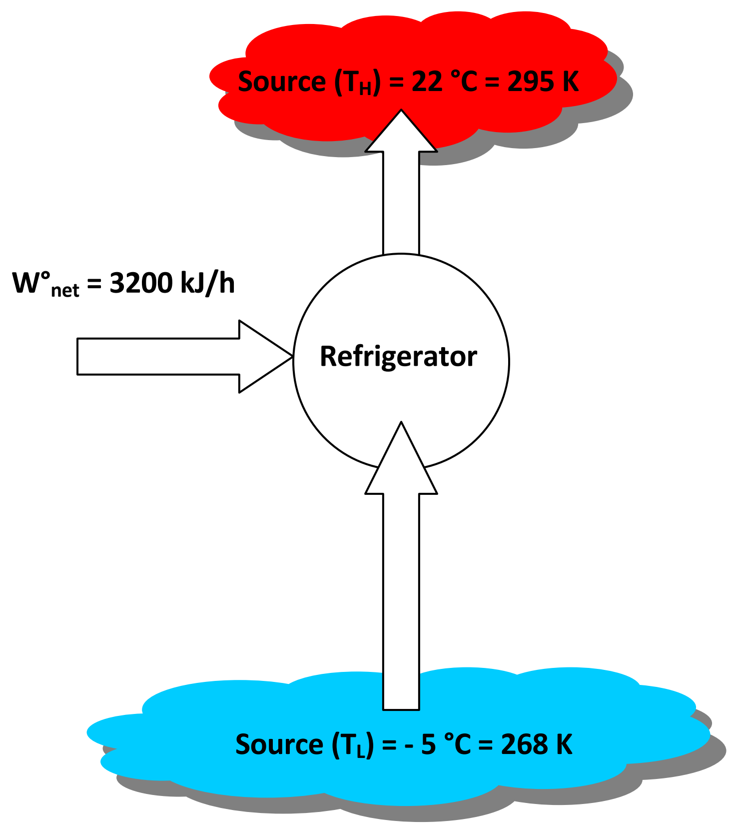
$$COP_R = \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{th,rev} & \text{reversible refrigerator} \\ > COP_{th,rev} & \text{impossible refrigerator!} \end{cases}$$

Example 1: 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:

$$COP_R = Q°_C / W°_{cycle}$$

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

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

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