JIWAJI UNIVERSITY GWALIOR

SELF LEARNING MATERIAL

FOR

B.SC. 1 YEAR PHYSICS

PAPER 102: Thermodynamics and Statistical Physics

PAPER CODE: 102

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The First Law Of Thermodynamics

The laws of thermodynamics are deceptively simple to state, but they are far-reaching in their consequences. The first law asserts that if heat is recognized as a form of energy, then the total energy of a system plus its surroundings is conserved; in other words, the total energy of the universe remains constant.

The first law is put into action by considering the flow of energy across the boundary separating a system from its surroundings. Consider the classic example of a gas enclosed in a cylinder with a movable piston. The walls of the cylinder act as the boundary separating the gas inside from the world outside, and the movable piston provides a mechanism for the gas to do work by expanding against the force holding the piston (assumed frictionless) in place. If the gas does work W as it expands, and/or absorbs heat Q from its surroundings through the walls of the cylinder, then this corresponds to a net flow of energy $W - Q$ across the boundary to the surroundings. In order to conserve the total energy U, there must be a counterbalancing change

$$\Delta U = Q - W \quad (1)$$

in the internal energy of the gas. The first law provides a kind of strict energy accounting system in which the change in the energy account (ΔU) equals the difference between deposits (Q) and withdrawals (W).

There is an important distinction between the quantity ΔU and the related energy quantities Q and W. Since the internal energy U is characterized entirely by the quantities (or parameters) that uniquely determine the state of the system at equilibrium, it is said to be a state function such that any change in energy is determined entirely by the initial (i) and final (f) states of the system: $\Delta U = U_f - U_i$. However, Q and W are not state functions. Just as in the example of a bursting balloon, the gas inside may do no work at all in reaching its final expanded state, or it could do maximum work by expanding inside a cylinder with a movable piston to reach the same final state. All that is required is that the change in energy (ΔU) remain the same. By analogy, the same change in one's bank account could be achieved by many different combinations of deposits and withdrawals. Thus, Q and W are not state functions, because their values depend on the particular process (or path) connecting the same initial and final states. Just as it is more meaningful to speak of the balance in one's bank account than its deposit or withdrawal content, it is only meaningful to speak of the internal energy of a system and not its heat or work content.

From a formal mathematical point of view, the incremental change dU in the internal energy is an exact differential (*see* differential equation), while the corresponding incremental changes $d'Q$ and $d'W$ in heat and work are not, because the definite integrals of these quantities are path-dependent. These concepts can be used to great advantage in a precise mathematical formulation of thermodynamics (*see below* Thermodynamic properties and relations).

HEAT ENGINES:-

The classic example of a heat engine is a steam engine, although all modern engines follow the same principles. Steam engines operate in a cyclic fashion, with the piston moving up and down once for each cycle. Hot high-pressure steam is admitted to the cylinder in the first half of each cycle, and then it is allowed to escape again in the second half. The overall effect is to take heat Q_1 generated by burning a fuel to make steam, convert part of it to do work, and exhaust the remaining heat Q_2 to the environment at a lower temperature. The net heat energy absorbed is then $Q = Q_1 - Q_2$. Since the engine returns to its initial state, its internal energy U does not change ($\Delta U = 0$). Thus, by the first law of thermodynamics, the work done for each complete cycle must be $W = Q_1 - Q_2$. In other words, the work done for each complete cycle is just the difference between the heat Q_1 absorbed by the engine at a high temperature and the heat Q_2 exhausted at a lower temperature. The power of thermodynamics is that this conclusion is completely independent of the detailed working mechanism of the engine. It relies only on the overall conservation of energy, with heat regarded as a form of energy.

In order to save money on fuel and avoid contaminating the environment with waste heat, engines are designed to maximize the conversion of absorbed heat Q_1 into useful work and to minimize the waste heat Q_2. The Carnot efficiency (η) of an engine is defined as the ratio W/Q_1—i.e., the fraction of Q_1 that is converted into work.

Since $W = Q_1 - Q_2$, the efficiency also can be expressed in the form

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (2)$$

If there were no waste heat at all, then $Q_2 = 0$ and $\eta = 1$, corresponding to 100 percent efficiency. While reducing friction in an engine decreases waste heat, it can never be eliminated; therefore, there is a limit on how small Q_2 can be and thus on how large the efficiency can be. This limitation is a fundamental law of nature—in fact, the second law of thermodynamics .

Isothermal and adiabatic processes

Because heat engines may go through a complex sequence of steps, a simplified model is often used to illustrate the principles of thermodynamics. In particular, consider a gas that expands and contracts within a cylinder with a movable piston under a prescribed set of conditions. There are two particularly important sets of conditions. One condition, known as an isothermal expansion, involves keeping the gas at a constant temperature. As the gas does work against the restraining force of the piston, it must absorb heat in order to conserve energy. Otherwise, it would cool as it expands (or conversely heat as it is compressed). This is an example of a process in which the heat absorbed is converted entirely into work with 100 percent efficiency. The process does not violate fundamental limitations on efficiency, however, because a single expansion by itself is not a cyclic process.

The second condition, known as an adiabatic expansion (from the Greek *adiabatos*, meaning "impassable"), is one in which the cylinder is assumed to be perfectly insulated so that no heat can flow into or out of the cylinder. In this case the gas cools as it expands, because, by the first law, the work done against the restraining force on the piston can only come from the internal energy of the gas. Thus, the change in the internal energy of the gas must be $\Delta U = -W$, as manifested by a decrease in its temperature. The gas cools, even though there is no heat flow, because it is doing work at the expense of its own internal energy. The exact amount of cooling can be calculated from the heat capacity of the gas.

Many natural phenomena are effectively adiabatic because there is insufficient time for significant heat flow to occur. For example, when warm air rises in the atmosphere, it expands and cools as the pressure drops with altitude, but air is a good thermal insulator, and so there is no significant heat flow from the surrounding air. In this case the surrounding air plays the roles of both the insulated cylinder walls and the movable piston. The warm air does work against the pressure provided by the surrounding air as it expands, and so its temperature must drop. A more-detailed analysis of this adiabatic expansion explains most of the decrease of temperature with altitude, accounting for the familiar fact that it is colder at the top of a mountain than at its base.

Efficiency

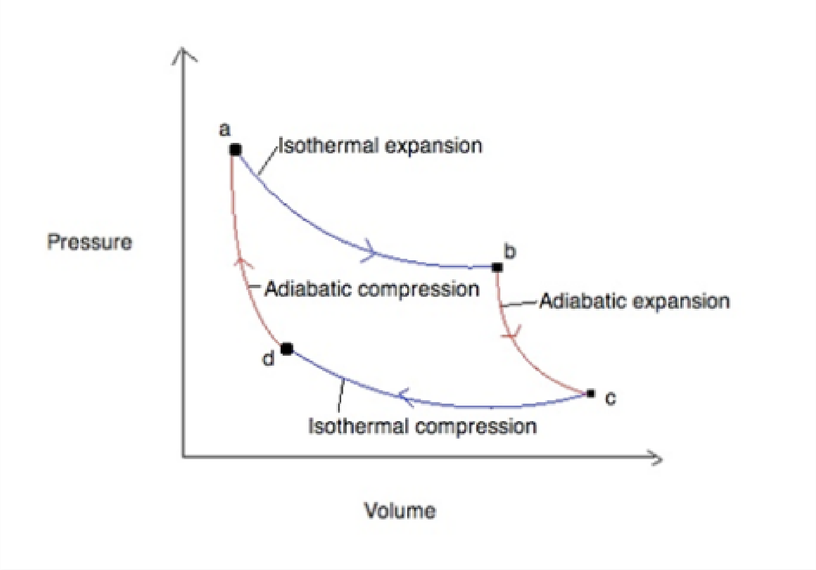
A word can have multiple and ambiguous meanings in everyday language but they have precise meanings in science. **Efficiency**in physics (and often for chemistry) is a comparison of the energy output to the energy input in a given system. It is defined as the percentage ratio of the output energy to the input energy, given by the equation:

This equation is commonly used in order to represent energy in the form of heat or power.

"Efficiency" is often confused with "effectiveness", and the two should be recognized as distinct from one another when analyzing energy systems. Energy efficiency measures how much a system is getting out of the fuel or flow it is using. If the energy system is effective, it is making use of this energy towards the right goal. For example, a car is a very effective form of transportation, since it is able to move people across long distances and to specific places. However, a car may not transport people very efficiently because of how it uses fuel.

Carnot Engine - Thermodynamic Engine

Carnot engine is a theoretical thermodynamic cycle proposed by Leonard Carnot. It gives the estimate of the maximum possible efficiency that a heat engine during the conversion process of heat into work and conversely, working between two reservoirs, can possess. In this section, we will learn about Carnot cycle in detail.



For an ideal gas operating inside a Carnot cycle, following are the steps involved:

Step 1: Isothermal expansion: The gas is taken from P_1, V_1, T_1 to P_2, V_2, T_2. Heat Q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero and the heat absorbed by the gas is equal to the work done by the gas on the environment, which is given as:

$$W_{1\to 2} = Q1 = \mu \times R \times T_1 \times ln\frac{v_2}{v_1}$$

Step 2: Adiabatic expansion: The gas expands adiabatically from P_2, V_2, T_1 to P_3, V_3, T_2. Here work done by the gas is given by

$$W_{2\to 3} = \frac{\mu R}{\gamma - 1}(T_1 - T_2)$$

Step 3: Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by

$$W_{3\to 4} = \mu R T_2 ln\frac{v_3}{v_4}$$

Step 4: Adiabatic compression: The gas is compressed adiabatically from the state (P_4, V_4, T_2) to (P_1, V_1, T_1).

Here, the work done on the gas by the environment is given by:

$$W_{4\to 1} = \frac{\mu R}{\gamma - 1}(T_1 - T_2)$$

Step 3: Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by

$$W_{3\to 4} = \mu R T_2 ln \frac{v_3}{v_4}$$

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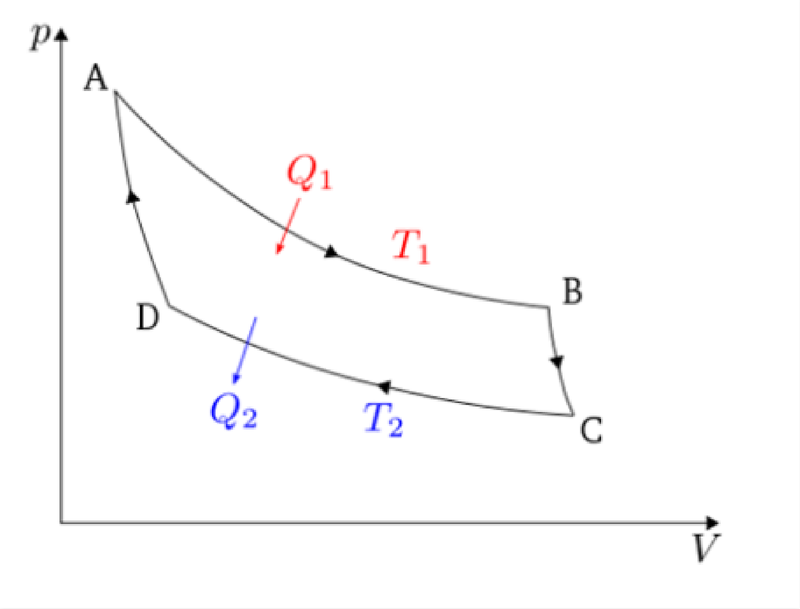
Here, the work done on the gas by the environment is given by:

$$W_{4\to 1} = \frac{\mu R}{\gamma - 1}(T_1 - T_2)$$



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Hence, the total work done by the gas on the environment in one complete cycle is given by:

$$W = W_{1\rightarrow2} + W_{2\rightarrow3} + W_{3\rightarrow4} + W_{4\rightarrow1}$$
$$W = \mu\, RT_1\, ln\frac{v_2}{v_1} - \mu\, RT_2\, ln\frac{v_3}{v_4}$$

$$Net\ efficiency = \frac{Net\ workdone\ by\ the\ gas}{Heat\ absorbed\ by\ the\ gas}$$

$$Net\ efficiency = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}\frac{ln\frac{v_3}{v_4}}{ln\frac{v_2}{v_1}}$$

Since the step 2–>3 is an adiabatic process, we can write $T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$

Or,

$$\frac{v_2}{v_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}$$

Similarly, for the process 4–>1, we can write

$$\frac{v_1}{v_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}$$

This implies,

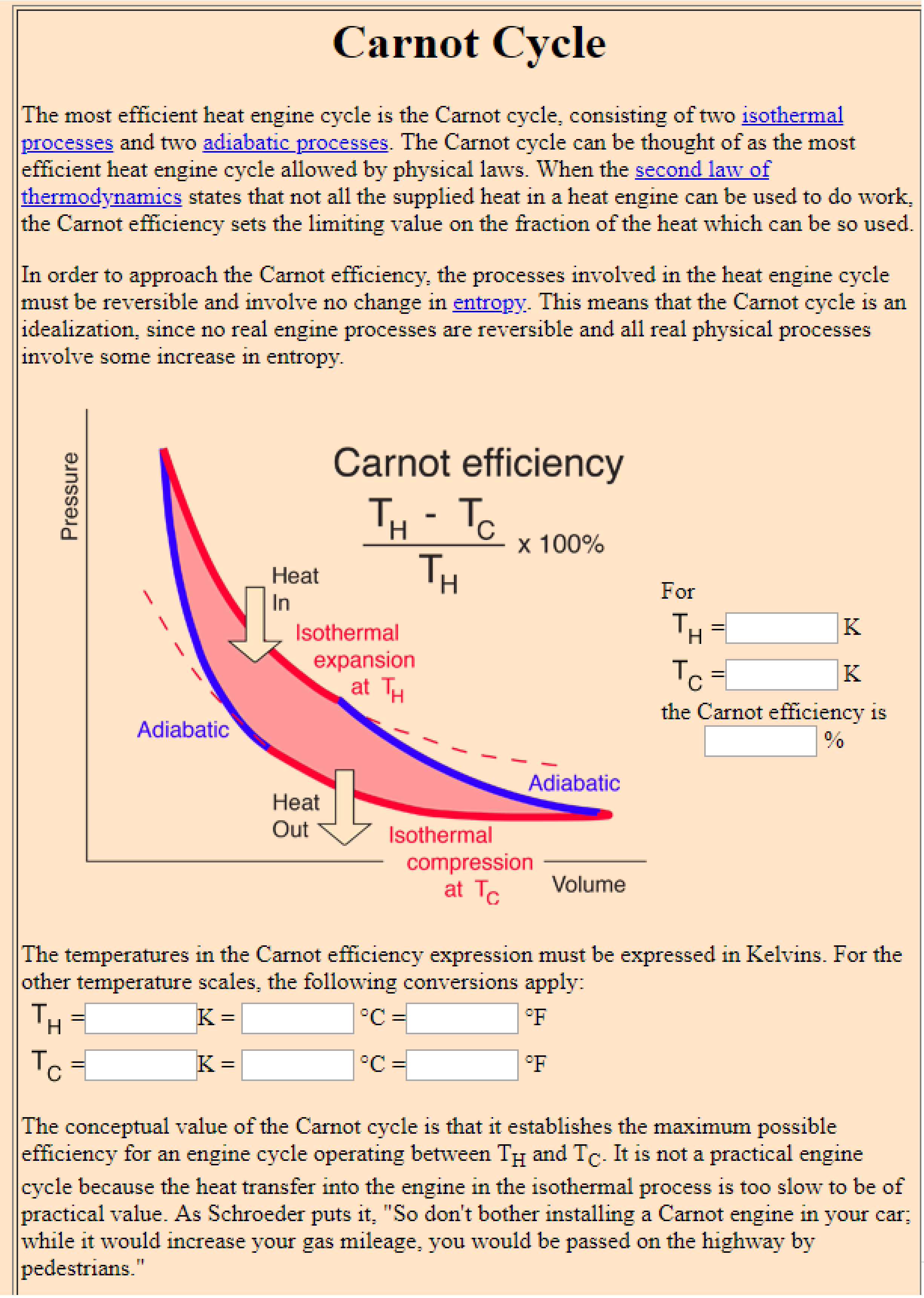
$$\frac{v_2}{v_3} = \frac{v_1}{v_2}$$

So, the expression for net efficiency of carnot engine reduces to:

$$Net\ efficiency = 1 - \frac{T_2}{T_1}$$

Carnot Theorem – As per the this theorem, any system working between two given temperatures T_1(hot reservoir) and T_2 (cold reservoir), can never have an efficiency more than the Carnot engine working between the same reservoirs respectively. Also, the efficiency of this type of engine is independent of the nature of the working substance and is only dependent on the temperature of the hot and cold reservoirs.

Stay tuned with BYJU'S to learn more about the carnot engine, thermodynamics and much more with video lectures and interactive sessions.



Carnot Cycle

The most efficient heat engine cycle is the Carnot cycle, consisting of two isothermal processes and two adiabatic processes. The Carnot cycle can be thought of as the most efficient heat engine cycle allowed by physical laws. When the second law of thermodynamics states that not all the supplied heat in a heat engine can be used to do work, the Carnot efficiency sets the limiting value on the fraction of the heat which can be so used.

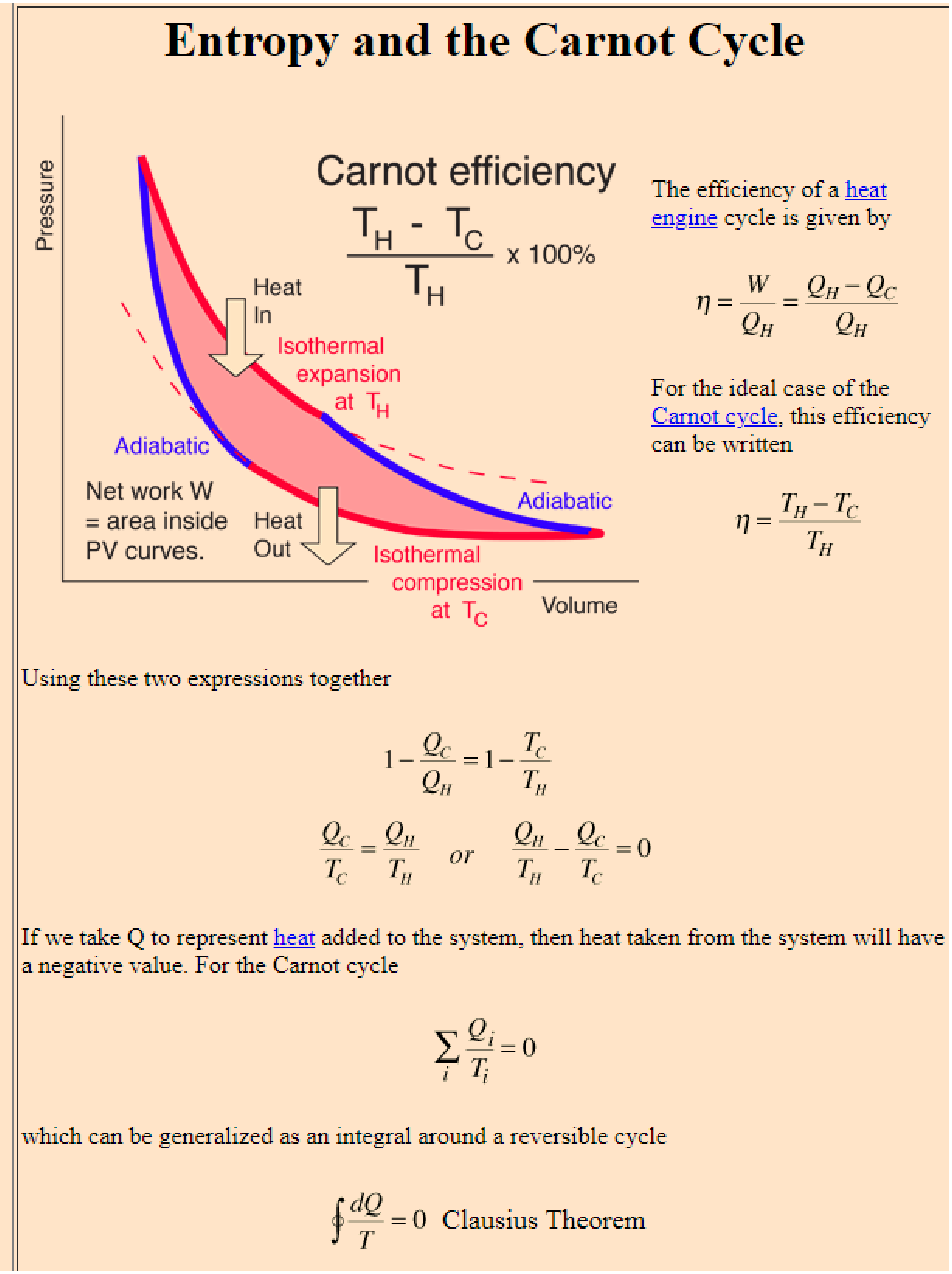
In order to approach the Carnot efficiency, the processes involved in the heat engine cycle must be reversible and involve no change in entropy. This means that the Carnot cycle is an idealization, since no real engine processes are reversible and all real physical processes involve some increase in entropy.

For
T_H = K
T_C = K
the Carnot efficiency is
%

The temperatures in the Carnot efficiency expression must be expressed in Kelvins. For the other temperature scales, the following conversions apply:

T_H = K = °C = °F
T_C = K = °C = °F

The conceptual value of the Carnot cycle is that it establishes the maximum possible efficiency for an engine cycle operating between T_H and T_C. It is not a practical engine cycle because the heat transfer into the engine in the isothermal process is too slow to be of practical value. As Schroeder puts it, "So don't bother installing a Carnot engine in your car; while it would increase your gas mileage, you would be passed on the highway by pedestrians."



Entropy and the Carnot Cycle

The efficiency of a heat engine cycle is given by

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

For the ideal case of the Carnot cycle, this efficiency can be written

$$\eta = \frac{T_H - T_C}{T_H}$$

Using these two expressions together

$$1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H} \quad or \quad \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

If we take Q to represent heat added to the system, then heat taken from the system will have a negative value. For the Carnot cycle

$$\sum_i \frac{Q_i}{T_i} = 0$$

which can be generalized as an integral around a reversible cycle

$$\oint \frac{dQ}{T} = 0 \quad \text{Clausius Theorem}$$

For any part of the heat engine cycle, this can be used to define a change in entropy S for the system

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

or in differential form at any point in the cycle

$$dS = \frac{dQ}{T}$$

For any irreversible process, the efficiency is less than that of the Carnot cycle. This can be associated with less heat flow to the system and/or more heat flow out of the system. The inevitable result is

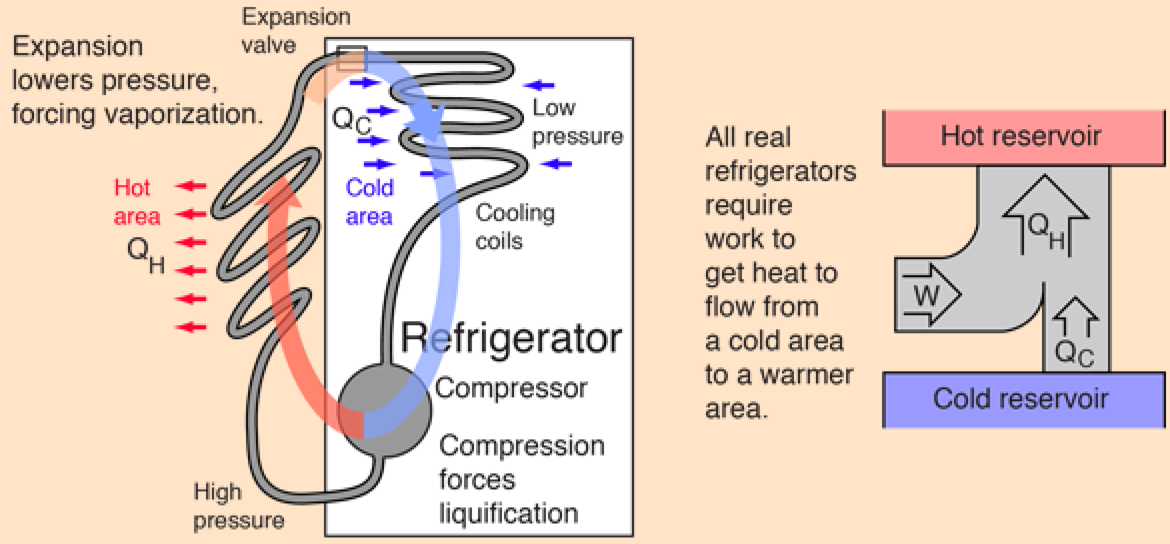
$$\oint \frac{dQ}{T} \leq 0 \quad \text{Clausius Inequality}$$

Any real engine cycle will result in more entropy given to the environment than was taken from it, leading to an overall net increase in entropy.

Refrigerator

If you place your hand behind an operating refrigerator, you will notice that this area is warmer than the room temperature. Or you may notice that the refrigerator blows warm air on your feet as you stand in front of it. Yet the interior of the freezing compartment is very cold! The refrigerator is taking energy from the freezing compartment, making it colder, and exhausting that heat to the room, making it warmer.

A refrigerator is a heat engine in which work is done on a refrigerant substance in order to collect energy from a cold region and exhaust it in a higher temperature region, thereby further cooling the cold region.



All real refrigerators require work to get heat to flow from a cold area to a warmer area.

Refrigerators have made use of fluorinated hydrocarbons with trade names like Freon-12, Freon-22, etc. which can be forced to evaporate and then condense by successively lowering and raising the pressure. They can therefore "pump" energy from a cold region to a hotter region by extracting the heat of vaporization from the cold region and dumping it in the hotter region outside the refrigerator. The statements about refrigerators apply to air conditioners and heat pumps, which embody the same principles.

Although this process works very well and has been in place for decades, the bad news about it is that fluorinated hydrocarbons released into the atmosphere are potent agents for the destruction of the ozone in the upper atmosphere. Therefore tighter and tighter restrictions are being placed on their use.

Steam engines

Imagine living off nothing but coal and water and still having enough energy to run at over 100 mph! That's exactly what a steam locomotive can do. Although these giant mechanical dinosaurs are now extinct from most of the world's railroads, steam technology lives on in people's hearts and locomotives like this still run as tourist attractions on many heritage railways.

Steam locomotives were powered by **steam engines**, and deserve to be remembered because they swept the world through the Industrial Revolution of the 18th and 19th centuries. Steam engines rank with cars, airplanes, telephones, radio, and television among the greatest inventions of all time. They are marvels of machinery and excellent examples of engineering, but under all that smoke and steam, how exactly do they work?

What powers a steam engine?

It takes energy to do absolutely anything you can think of—to ride on a skateboard, to fly on an airplane, to walk to the shops, or to drive a car down the street. Most of the energy we use for transportation today comes from oil, but that wasn't always the case. Until the early 20th century, **coal** was the world's favorite fuel and it powered everything from trains and ships to the ill-fated steam planes invented by American scientist Samuel P. Langley, an early rival of the Wright brothers. What was so special about coal? There's lots of it inside Earth, so it was relatively inexpensive and widely available.

Coal is an **organic** chemical, which means it's based on the element carbon. Coal forms over millions of years when the remains of dead plants get buried under rocks, squeezed by pressure, and cooked by Earth's internal heat. That's why it's called a **fossil fuel**. Lumps of coal are really lumps of energy. The carbon inside them is locked to atoms of hydrogen and oxygen by joints called chemical bonds. When we burn coal on a fire, the bonds break apart and the energy is released in the form of heat.

Coal contains about *half* as much energy per kilogram as cleaner fossil fuels such as gasoline, diesel, and kerosene—and that's one reason why steam engines have to burn so much of it.

What is a steam engine?

A steam engine is a machine that burns coal to release the heat energy it contains—so it's an example of what we call a heat engine. It's a bit like a giant kettle sitting on top of a coal fire. The heat from the fire boils the water in the kettle and turns it into steam. But instead of blowing off uselessly into the air, like the steam from a kettle, the steam is captured and used to power a machine. Let's find out how!

How a steam engine works

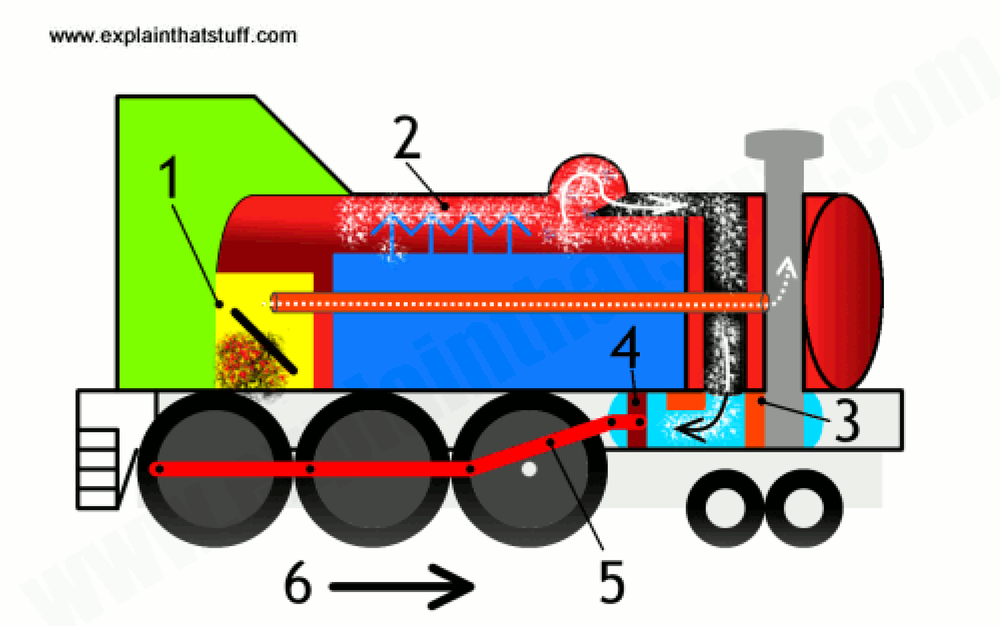
Crudely speaking, there are four different parts in a steam engine:

1. A fire where the coal burns.
2. A boiler full of water that the fire heats up to make steam.
3. A cylinder and piston, rather like a bicycle pump but much bigger. Steam from the boiler is piped into the cylinder, causing the piston to move first one way then the other. This in and out movement (which is also known as "reciprocating") is used to drive...
4. A machine attached to the piston. That could be anything from a water pump to a factory machine... or even a giant steam locomotive running up and down a railroad.

That's a very simplified description, of course. In reality, there are hundreds or perhaps even thousands of parts in even the smallest locomotive.

Step-by-step

It's easiest to see how everything works in our little animation of a steam locomotive, below. Inside the locomotive cab, you load coal into the **firebox** (1), which is quite literally a metal box containing a roaring coal fire. The fire heats up the boiler—the "giant kettle" inside the locomotive.



The **boiler** (2) in a steam locomotive doesn't look much like a kettle you'd use to make a cup of tea, but it works the same way, producing steam under high pressure. The boiler is a big tank of water with dozens of thin metal tubes running through it (for simplicity, we show only one here, colored orange). The tubes run from the firebox to the chimney, carrying the heat and the smoke of the fire with them (shown as white dots inside the tube). This arrangement of boiler tubes, as they are called, means the engine's fire can heat the water in the boiler tank much faster, so it produces steam more quickly and efficiently. The water that makes the steam either comes from tanks mounted on the side of the locomotive or from a separate wagon called a tender, pulled behind the locomotive. (The tender also carries the locomotive's supply of coal.) You can see a photo of a tender showing its water tank further down this page.

The steam generated in the boiler flows down into a **cylinder** (3) just ahead of the wheels, pushing a tight-fitting plunger, the **piston** (4), back and forth. A little mechanical gate in the cylinder, known as an inlet valve (shown in orange) lets the steam in. The piston is connected to one or more of the locomotive's wheels through a kind of arm-elbow-shoulder joint called a crank and connecting rod (5).

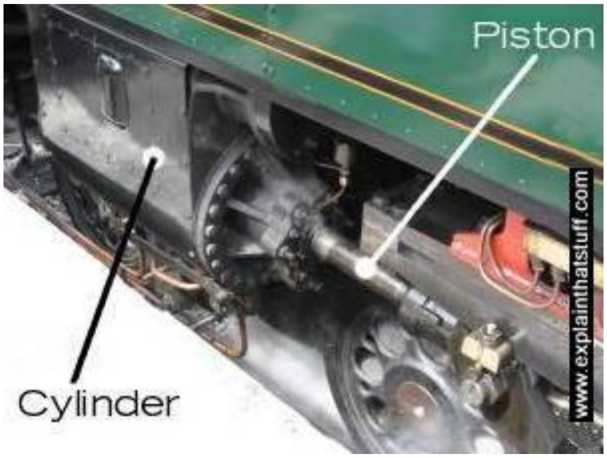
As the piston pushes, the crank and connecting rod turn the locomotive's **wheels** and power the train along (6). When the piston has reached the end of the cylinder, it can push no further. The train's momentum (tendency to keep moving) carries the crank onwards, pushing the piston back into the cylinder the way it came. The steam inlet valve closes. An outlet valve opens and the piston pushes the steam back through the cylinder and out up the locomotive's chimney (7). The intermittent chuff-chuff noise that a steam engine makes, and its intermittent puffs of smoke, happen when the piston moves back and forth in the cylinder.

There's a cylinder on each side of the locomotive and the two cylinders fire slightly out of step with one another to ensure there's always some power pushing the engine along.

Types of steam engine

Our diagram up above shows a very simple, one-cylinder steam engine powering a steam locomotive down a track. This is called a **rotary** steam engine, because the piston's job is to make a wheel *rotate*. The earliest steam engines worked in an entirely different way. Instead of turning a wheel, the piston pushed a beam up and down in a simple back-and-forth or **reciprocating** motion. Reciprocating steam engines were used to pump water out of flooded coal mines in the early 18th century.

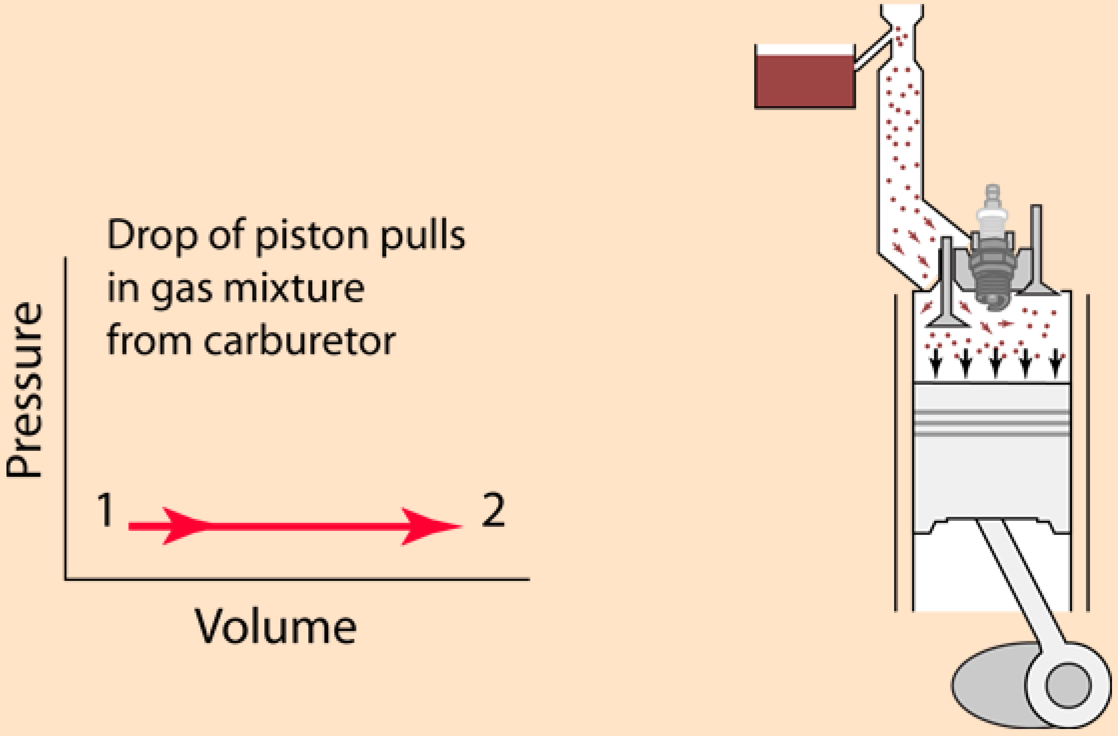
Our diagram shows steam pushing the piston one way and the momentum of the locomotive driving it the other way. This is called a **single-acting** steam engine and it's quite an inefficient design because the piston is being powered only half the time. A much better (though slightly more complex) design uses extra steam pipes and valves to make steam push the piston first one way and then the other. This is called a **double-acting** (or **counterflow**) steam engine. It's more powerful because steam is driving the piston all the time. If you look closely at the wheels of a typical steam engine, you'll see that everything is more complex than we've seen in the simple animation up above: there's much more machinery than just a single crank and connecting rod. In fact, there's an intricate collection of shiny levers, sliding back and forth with meticulous precision. This is called the **valve gear**. Its job is to open and close the cylinder valves at just the right moments to let steam in from either end, both to make the engine work as efficiently and powerfully as possible and to allow it to drive in reverse. There are quite a few different types of valve gear; one of the most common designs is called the Walschaerts, named for its Belgian inventor Egide Walschaerts (1820–1901). The tank engine 80104 shown in the second photo on this page has a Walschaerts-type valve gear, and so does Eddystone, the locomotive pictured below.

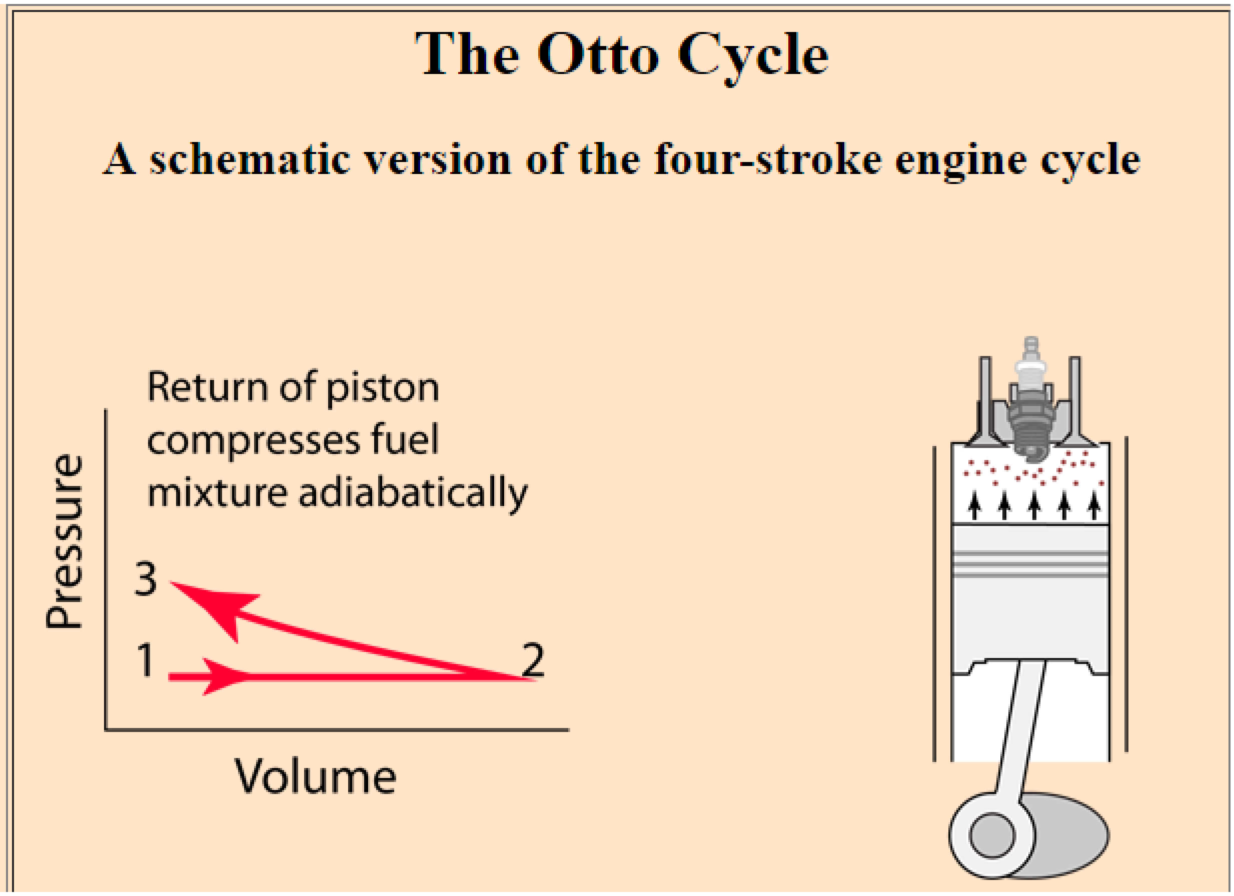


The first steam engines were very large and inefficient, which means it took huge amounts of coal to get them to do anything. Later engines produced steam at much higher pressure: the steam was produced in a smaller, much stronger boiler so it squeezed out with more force and blew the piston harder. The extra force of **high-pressure** steam engines allowed engineers to make them lighter and more compact, and it was this that paved the way for steam locomotives, steam ships, and steam cars.

The Otto Cycle

A schematic version of the four-stroke engine cycle

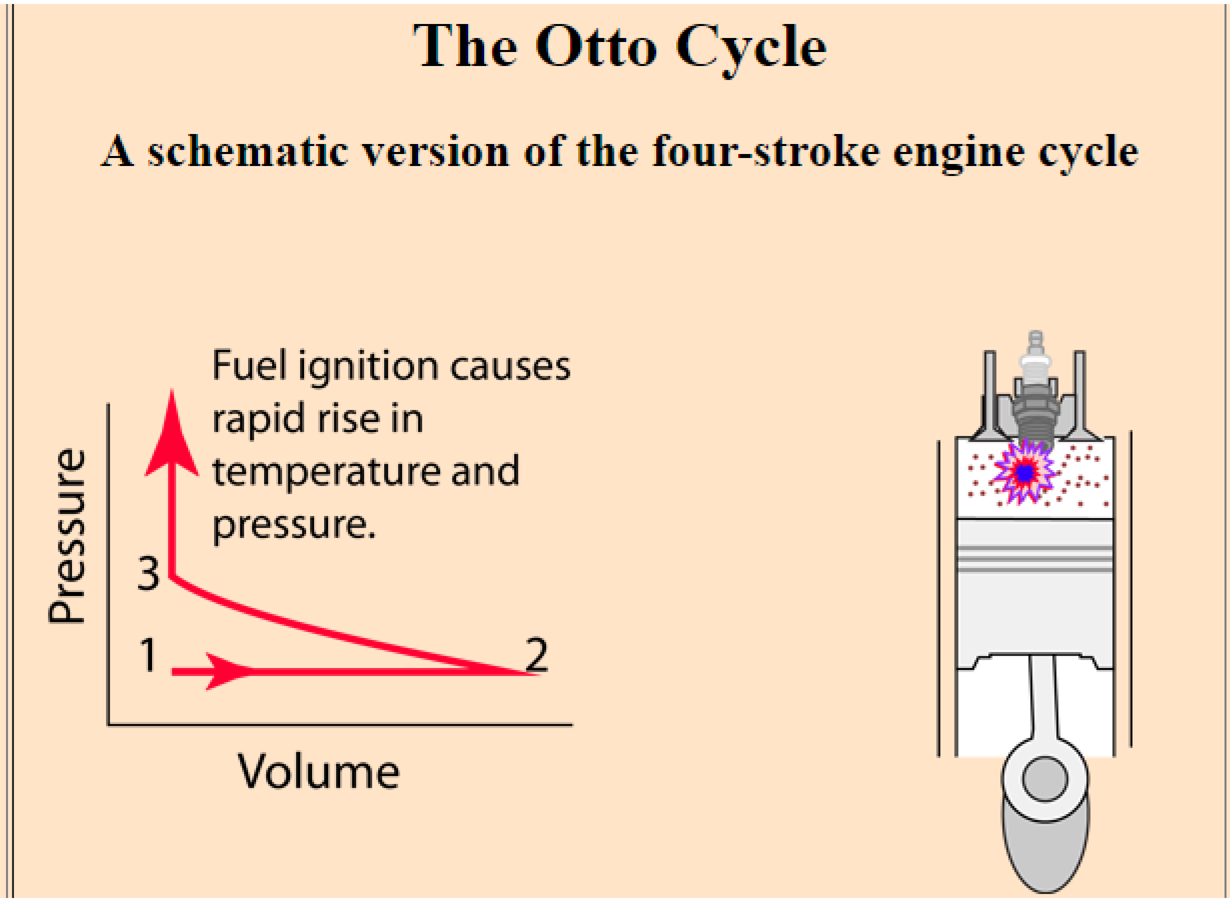




The Otto Cycle

A schematic version of the four-stroke engine cycle

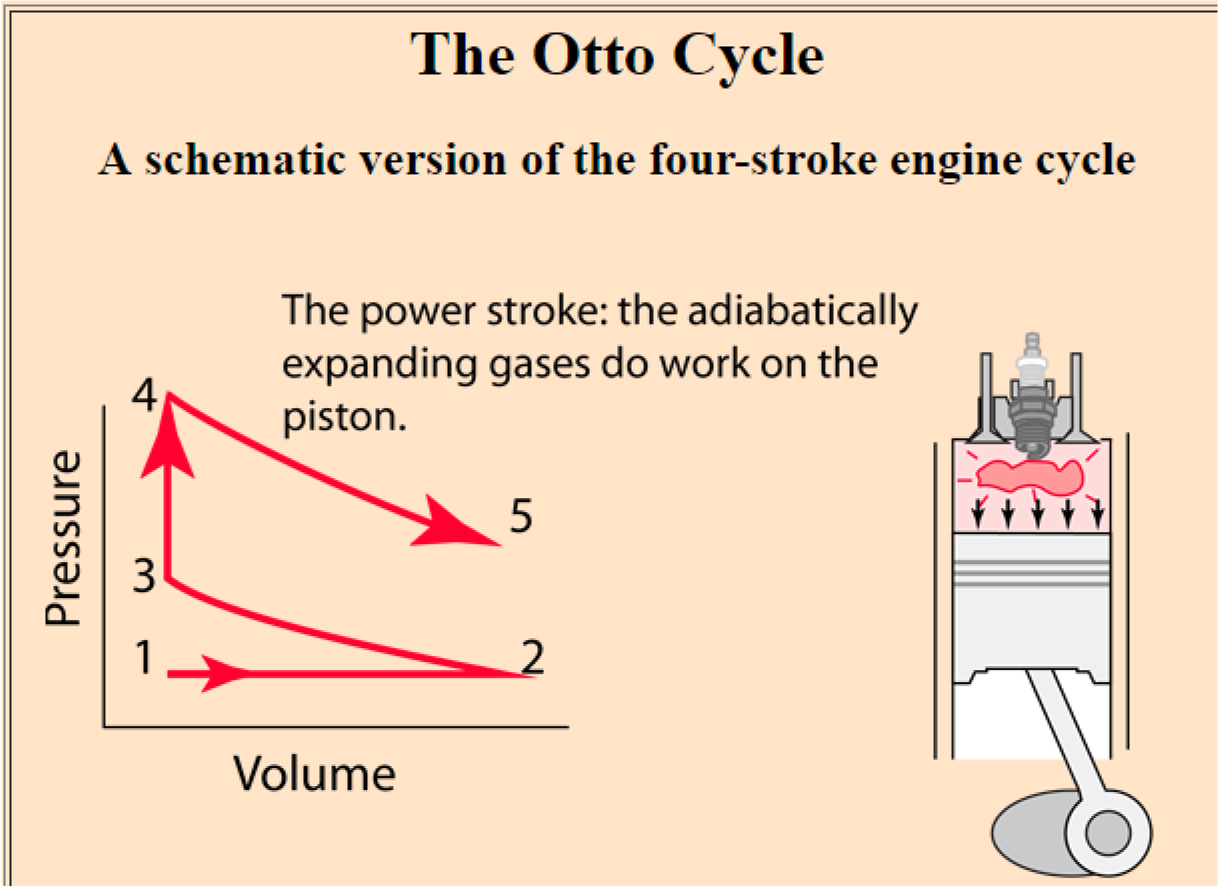
Return of piston compresses fuel mixture adiabatically



The Otto Cycle

A schematic version of the four-stroke engine cycle

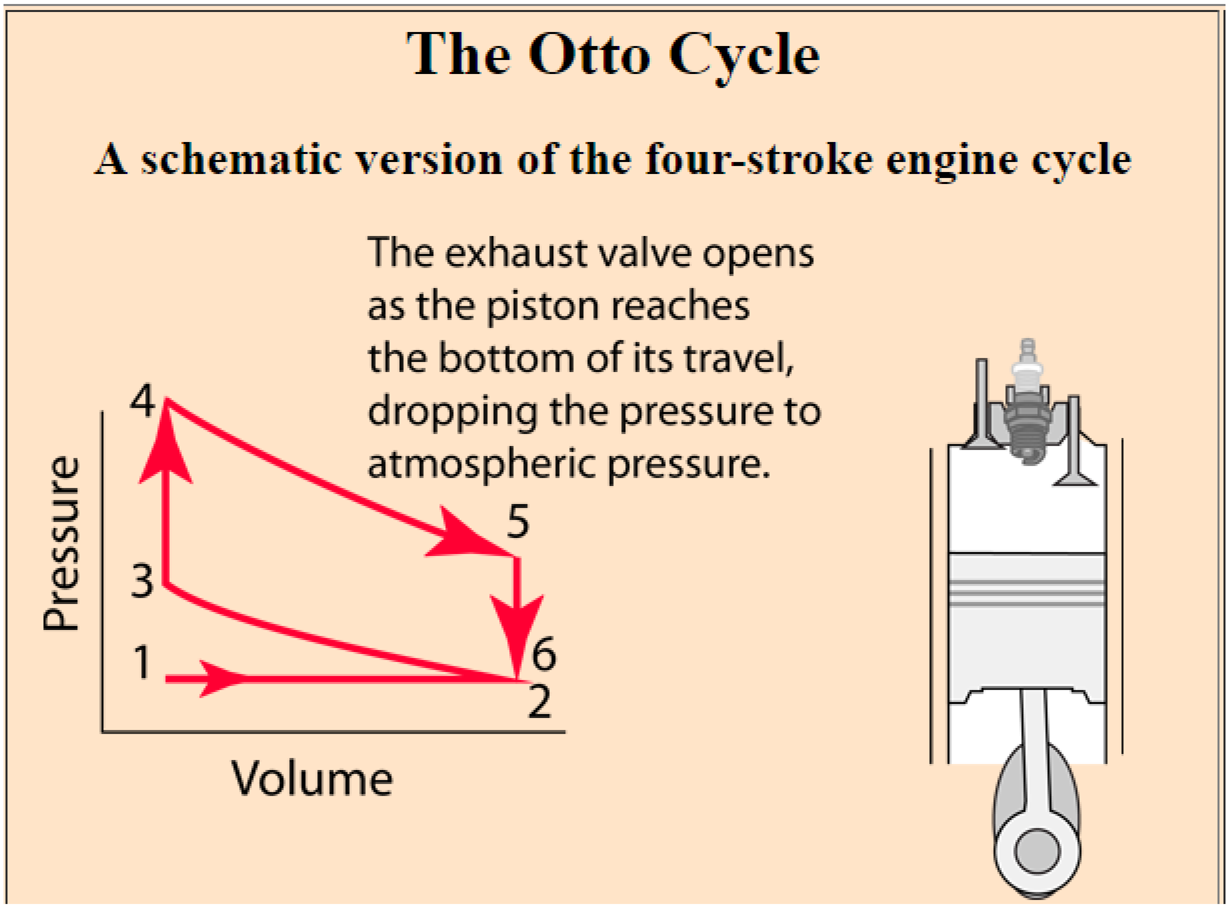
Fuel ignition causes rapid rise in temperature and pressure.



The Otto Cycle

A schematic version of the four-stroke engine cycle

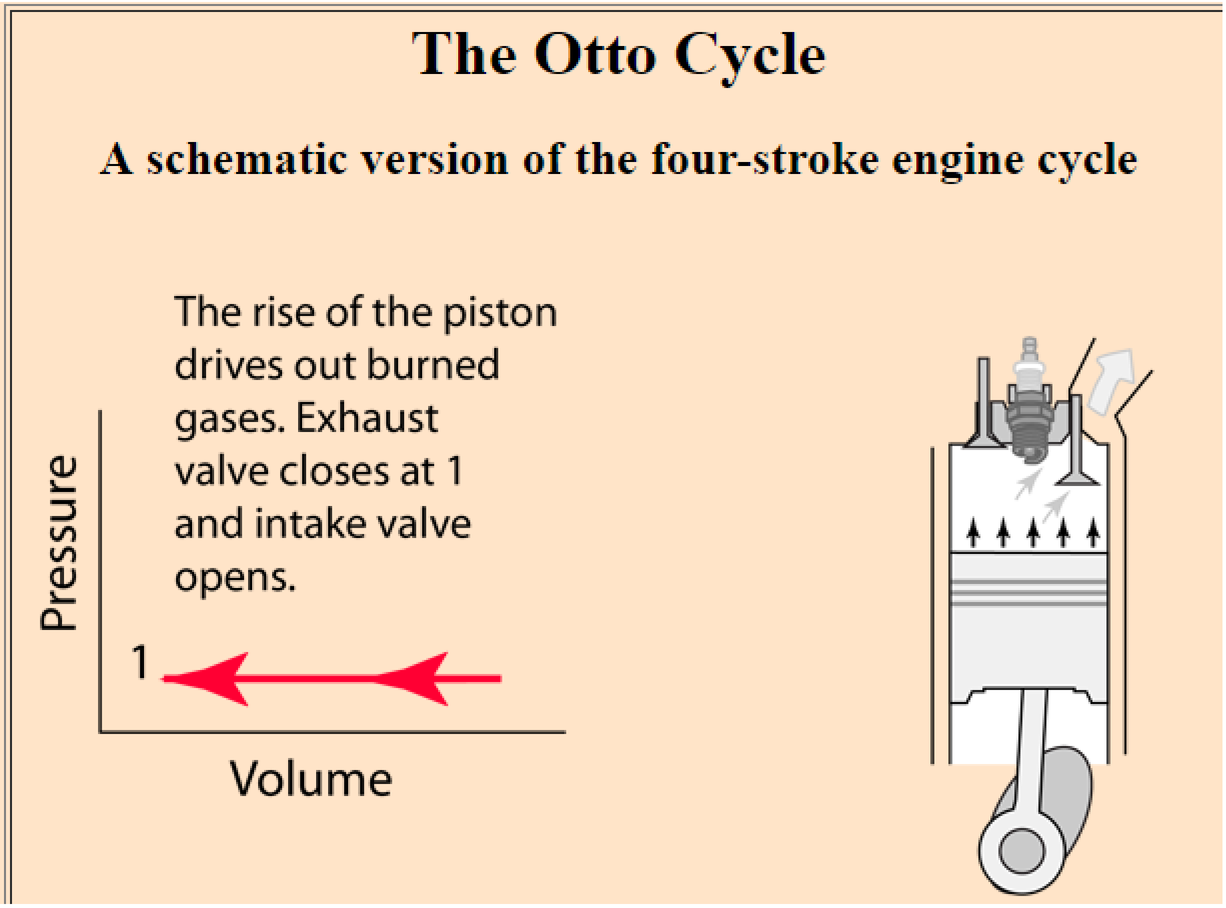
The power stroke: the adiabatically expanding gases do work on the piston.



The Otto Cycle

A schematic version of the four-stroke engine cycle

The exhaust valve opens as the piston reaches the bottom of its travel, dropping the pressure to atmospheric pressure.

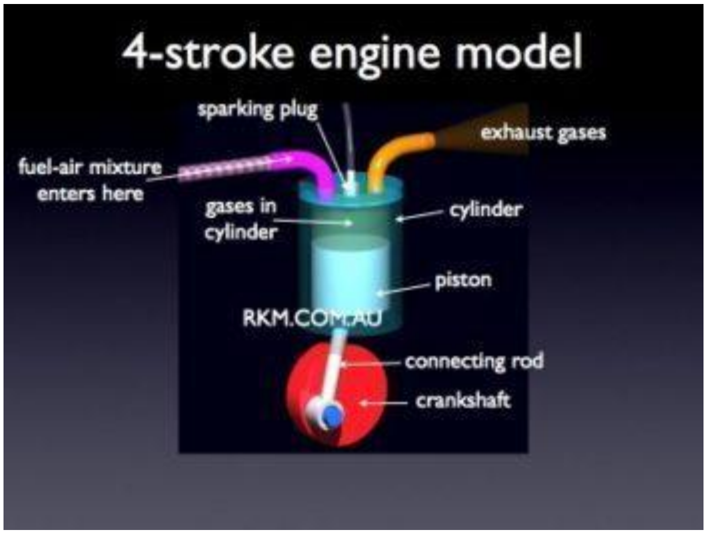


The Otto Cycle

A schematic version of the four-stroke engine cycle

The rise of the piston drives out burned gases. Exhaust valve closes at 1 and intake valve opens.

Petrol Engine Principle and Working Cycle



An engine is a power generating machine, which converts potential energy of the fuel into heat energy and then into motion. It produces power and also runs on its own power. The engine's power is generated by burning the fuel in a self-regulated and controlled 'Combustion' process. The combustion process involves many sub-processes; which burn the fuel efficiently to effect the smooth running of the engine

Petrol Engine

A petrol engine (known as a gasoline engine in American English) is an internal combustion engine with spark-ignition, designed to run on petrol (gasoline) and similar volatile fuels. The first practical petrol engine was built in 1876 in Germany by Nikolaus August Otto. In most petrol engines, the fuel and air are usually pre-mixed before compression (although some modern petrol engines now use cylinder-direct petrol injection). The pre-mixing was formerly done in a carburetor, but now it is done by electronically controlled fuel injection, except in small engines where the cost/complication of electronics does not justify the added engine efficiency.

How an Engine Works?

The Heat Energy is converted into Kinetic Energy in the form of 'Reciprocating Motion'. The expansion of heated gases and their forces act on the engine pistons, pushing them downwards; resulting in reciprocating motion of pistons. The reciprocating motion of the piston enables the crank-shaft to rotate and finally gets converted into the 'Rotary motion' and passed on to wheels.

Operation / Working Principle:

The conventional internal combustion engine operates on two basic principals –

1. Otto Cycle &
2. Diesel Cycle

What is 'Otto Cycle'?

Otto Cycle is also known as Four-Stroke Spark-Ignition Cycle. It was named after German engineer Nikolaus Otto, who invented, developed and patented first Four-Stroke petrol engine. The Four-Stroke petrol engine works on the following cycle –

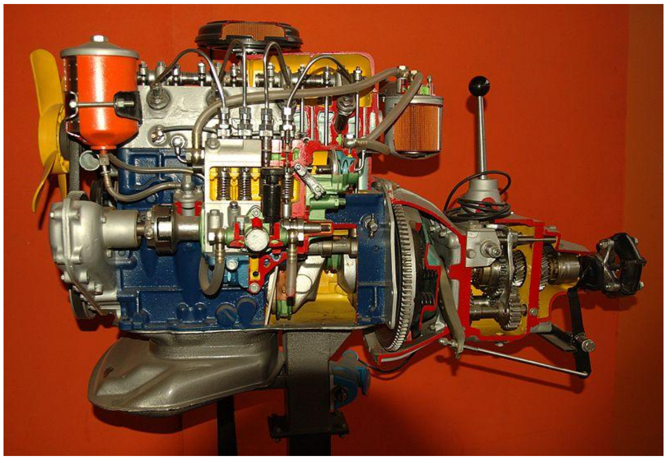
1. Suction Stroke– with pistons moving downwards and opening of the inlet valve creates suction of the air-fuel mixture.
2. Compression Stroke– With closing of Inlet valve, the area above the piston gets closed. The piston moves up resulting in compression of the air-fuel mixture in a confined space.
3. Power Stroke – These forces again push the pistons downwards resulting in their reciprocating motion.
4. Exhaust Stroke– On their way up, the pistons push the exhaust gases above them thru' the exhaust valve which opens during the exhaust stroke.

Combustion Process – At this stage a spark is fired by the spark-plug resulting in instantaneous burning of petrol resulting in an explosion. This causes heat to release resulting in generation of expanding forces known as power.

Cooling

Petrol engines may be air-cooled, with fins (to increase the surface area on the cylinders and cylinder head); or liquid-cooled, by a water jacket and radiator. The coolant was formerly water, but is now usually a mixture of water and either ethylene glycol or propylene glycol.

Diesel Cycle



Diesel engine cutaway [6].

The diesel engine is an example of an internal combustion engine, which converts chemical energy into mechanical energy by moving pistons up and down in enclosed spaces, called cylinders. Energy is released in a series of small explosions when the fuel reacts, or combusts with oxygen from the air.

A diesel engine can be designed to operate using either a two-stroke or four-stroke cycle. A full cycle in a four-stroke diesel engine consists of two complete rotations of the crankshaft. The four-strokes that make up the cycle are the intake, compression, power, and exhaust.

In the four four-stroke process, the intake stroke starts at top dead center (TDC) and as the piston moves down to bottom dead center (BDC), fresh air is drawn into the cylinder. The air is then compressed as the piston moves back up to TDC. The fuel is injected near the end of the compression stroke where it ignites due to the high temperature and pressure. The mechanical work is generated when the piston is forced down due to the expansion of the gases that the combustion produces. The last stroke is the exhaust stroke, when the piston travels from BDC to TDC, during which the products of combustion are expelled from the cylinder. After the exhaust stroke, the cycle starts all over again with the intake stroke. Four-stroke engines are found in most automobiles, trucks, and farm equipment.

A two-stroke engine, on the other hand, completes a full cycle in one rotation of the crankshaft. The engine is constructed so that the intake and exhaust is done within the same rotation. There is no need for an intake valve because the cylinder is designed with an opening nearing BDC through which fresh air is drawn in. The intake starts at BDC where the opening in the cylinder is with the exhaust valve open. This allows a flow of air through the cylinder. The engine then compresses the air as the piston moves to TDC. The fuel is injected the same way it is in a four-stroke engine, and the piston travels back down in the power stroke. Close to the bottom of the cylinder, the exhaust valve opens to begin the release of the combustion gases.

Theoretically, the two-stroke engine can produce twice as much power as a four-stroke engine because there is a power stroke for every turn of the crankshaft instead of every other turn. In practice, the limited amount of time that is allowed for the intake and exhaust makes the two-stroke cycle less efficient and not very clean burning. Two-stroke engines are commonly used to power chainsaws, jet skis, and dirt bikes, for example. Because a two-stroke cycle can produce more power than a four-stroke cycle when it is operated properly, two-stroke engines are also used in large applications such as locomotives and big cargo ships. Laws controlling emission levels are not as strict for these vehicles, which allows for the use of a two-stroke system.

Small engines may have only one piston cylinder assembly but large engines will have more piston cylinder pairs. When multiple pistons are connected to the crankshaft, they are staggered so that the power stroke of one piston cylinder pair helps drive the rest of the piston cylinders to complete whichever stroke they are in. This generates a continuous power supply because not all of the piston cylinder sets are producing power at the same time.

How Stuff Works → Crankshaft

The crankshaft converts the linear motion of the pistons into rotational motion that is transmitted to the load, whether it be a generator or to power a vehicle.

The crankshaft is a rod that has offset sections called throws, which are attached to the pistons. The placement of these throws depends on the setup of the engine (inline or V), and they are arranged so that when the pistons travel upward and downward, the crankshaft is turned.
Because diesel engines are usually used for heavy duty equipment the crankshafts must be strong enough to handle the load without bending or twisting. They are usually made out of a one-piece casting of heat-treated alloy steel or, sometimes, cast iron, depending on the application, which allows for good mechanical strength. Crankshafts for very heavy duty usage have a hardened bearing surface to provide extra strength.

Turbochargers and Aftercoolers

Turbocharger cutaway.

To increase an engine's efficiency, turbochargers and aftercoolers are installed on the generators. The turbocharger draws in exhaust air, which still contains energy and the energy is extracted when it is sent through a small turbine. The turbine subsequently powers a small compressor placed before the air intake.

The compressor increases the pressure of the intake air going through the cylinders. Unfortunately, compressing the air also heats it slightly, so it must then be sent through an aftercooler. The aftercooler lowers the temperature of the air, making it more dense, resulting in pre-compressed and denser air. Because the exhaust waste is used, less work is needed during the compression stroke for the air to reach a critical temperature.

For diesel vehicles, the term intercooler is usually used in place of aftercooler, which had been used before more recent developments in combustion engine design. The meaning of intercooler has changed to specify a cooling stage in between two heating stages, while aftercoolers are the final cooling stage before the engine.

Transportation

Transportation

Most of the major manufacturers that produce personal vehicles with diesel engines are based in Europe. Diesel cars are more popular in Europe where 54.9% of registered cars are powered by diesel engines [88]. Comparatively, only about 3% of cars in the U.S. are diesels [89]. Because gasoline is much less expensive in this country most vehicles produced in the U.S. run on gasoline engines, even though diesel engines are up to 40% more efficient than gasoline engines [89].

Semi trucks

Semis are the vehicles that most people associate with diesel engines. Because 18 wheeler trucks have to haul extremely heavy loads (up to 80,000 lb maximum weight [90]), they need the extra torque that is produced by a diesel engine. As of 2012, 68.5% of all freight shipped in U.S. are transported using diesel trucks [91]. Most 18 wheelers have engines that are between 400-600 horsepower, which is about three times greater than the horsepower for the typical family vehicle (150-200 hp). Semi trucks also generally produce over 1200 lb-ft of torque with some of the most powerful semi truck engines producing over 2000 lb-ft of torque [90].

Power Generation

The combination of a diesel engine and an electrical generator is referred to as a diesel generating set or diesel genset. The engine produces mechanical energy that is transformed into electrical energy by the generator. The engine and the generator work together to produce an electrical current. Depending on the size of the components, a diesel generator can produce anywhere from 8 kW for a home application to 2000 kW for an industrial complex [56].

Caterpillar diesel engine [129].

Diesel generators are used in many applications, including backup or standby power sources in remote locations where access to a power grid is not possible. Diesel generators are commonly used on construction and mining sites to power lights and other electrical tools. Sites such as schools, hospitals, and military bases usually have diesel gensets in case of the electricity outages.

Diesel vs. Gasoline

Diesel engines have a much higher compression ratio, lean burn operation, and direct injection, and are therefore more energy efficient and have more torque than a spark-ignition gasoline engine of the same displacement. In addition, diesel fuel contains about 11% more energy by volume than gasoline, increasing the diesel's fuel efficiency ratio [92].

In a gasoline engine the air and fuel are mixed before entering the cylinder. It is much more difficult to compress an air/fuel mixture than it is to compress air alone. In a diesel engine, the compression problem is solved, which greatly increases the mileage and efficiency of a diesel car. Over the diesel's operating range, the average thermodynamic efficiency is in the mid-40% range, which is about 15% better than a gas engine [93].

A diesel engine is less complicated than a gasoline engine because it does not need an ignition system, but diesel engines can be noisy and may require more maintenance than gasoline engines.

Diesel engines can tow or carry heavier loads for longer distances because they produce more torque, so most large trucks, pickups, and vehicles that transport large amounts of cargo or have a high towing capacity have diesel engines.

Selecting correct engine

A buyer should assess many different design characteristics before purchasing a diesel engine, depending on what is needed for a particular job. One of the first things to evaluate is the amount of energy or torque the engine can generate; matching the size to the work needs is critical. The size and weight of the engine will affect vehicle performance. If the engine is going to be used as a backup or standby unit, the potential noise level should be assessed. Fuel efficiency of the unit is also important, as well as the cost depending on the application.

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UNIT-2

Entropy and the second law

The second law of thermodynamics is one of the most fundamental laws of nature, having profound implications. In essence, it says this:

The second law - The level of disorder in the universe is steadily increasing. Systems tend to move from ordered behavior to more random behavior.

One implication of the second law is that heat flows spontaneously from a hotter region to a cooler region, but will not flow spontaneously the other way. This applies to anything that flows: it will naturally flow downhill rather than uphill.

If you watched a film forwards and backwards, you would almost certainly be able to tell which way was which because of the way things happen. A pendulum will gradually lose energy and come to a stop, but it doesn't pick up energy spontaneously; an ice cube melts to form a puddle, but a puddle never spontaneously transforms itself into an ice cube; a glass falling off a table might shatter when it hits the ground, but the pieces will never spontaneously jump back together to form the glass again. Many processes are irreversible, and any irreversible process increases the level of disorder. One of the most important implications of the second law is that it indicates which way time goes - time naturally flows in a way that increases disorder.

The second law also predicts the end of the universe: it implies that the universe will end in a "heat death" in which everything is at the same temperature. This is the ultimate level of disorder; if everything is at the same temperature, no work can be done, and all the energy will end up as the random motion of atoms and molecules.

Entropy

A measure of the level of disorder of a system is entropy, represented by S. Although it's difficult to measure the total entropy of a system, it's generally fairly easy to measure changes in entropy. For a thermodynamic system involved in a heat transfer of size Q at a temperature T , a change in entropy can be measured by:

$$\Delta S = Q / T$$

The second law of thermodynamics can be stated in terms of entropy. If a reversible process occurs, there is no net change in entropy. In an irreversible process, entropy always increases, so the change in entropy is positive. The total entropy of the universe is continually increasing.

There is a strong connection between probability and entropy. This applies to thermodynamic systems like a gas in a box as well as to tossing coins. If you have four pennies, for example, the likelihood that all four will land heads up is relatively small. It is six times more likely that you'll get two heads and two tails. The two heads - two tails state is the most likely, shows the most disorder, and has the highest entropy. Four heads is less likely, has the most order, and the lowest entropy. If you tossed more coins, it would be even less likely that they'd all land heads up, and even more likely that you'd end up with close to the same number of heads as tails.

With a gas in a box, the probability that all the gas molecules are in one corner of the box at the same time is very small (for a typical box full of 10^{20} molecules or more, incredibly small): this is therefore a low entropy state. It is much more likely that the molecules are randomly distributed around the box, and are moving in random directions; this high disorder state is a considerably higher entropy state. The second law doesn't rule out all the molecules ending up in one corner, but it means it's far more likely that the molecules will be randomly distributed, and to move towards a random distribution from an orderly distribution, as opposed to the other way around.

Increase in Entropy Principle $\boxed{\Delta S \ge 0}$

1. Non-flow Processes

We previously found from considerations of the **Clausius Inequality** that the following cyclic integral is always less than or equal to zero, where the equality occurred for a reversible cycle.

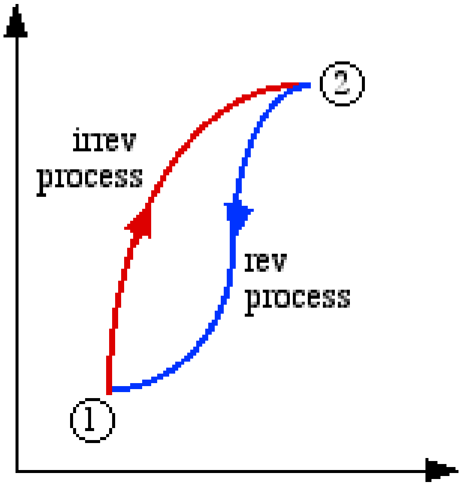
$$\boxed{\text{The Clausius Inequality:} \quad \oint \frac{\delta Q}{T} \le 0}$$

This lead to the definition of the property Entropy (S). Consider now an irreversible cycle in which process (1) –> (2) follows an irreversible path, and process (2) –> (1) a reversible path, as shown:

$$\oint \frac{\delta Q}{T} = \int_{1\ \text{irrev}}^{2} \frac{\delta Q}{T} + \int_{2\ \text{rev}}^{1} \frac{\delta Q}{T} < 0$$

$$\int_{1\ \text{irrev}}^{2} \frac{\delta Q}{T} + \int_{2}^{1} dS = \int_{1\ \text{irrev}}^{2} \frac{\delta Q}{T} + (S_1 - S_2) < 0$$

$$\Delta S = (S_2 - S_1) > \int_{1}^{2} \frac{\delta Q}{T}$$

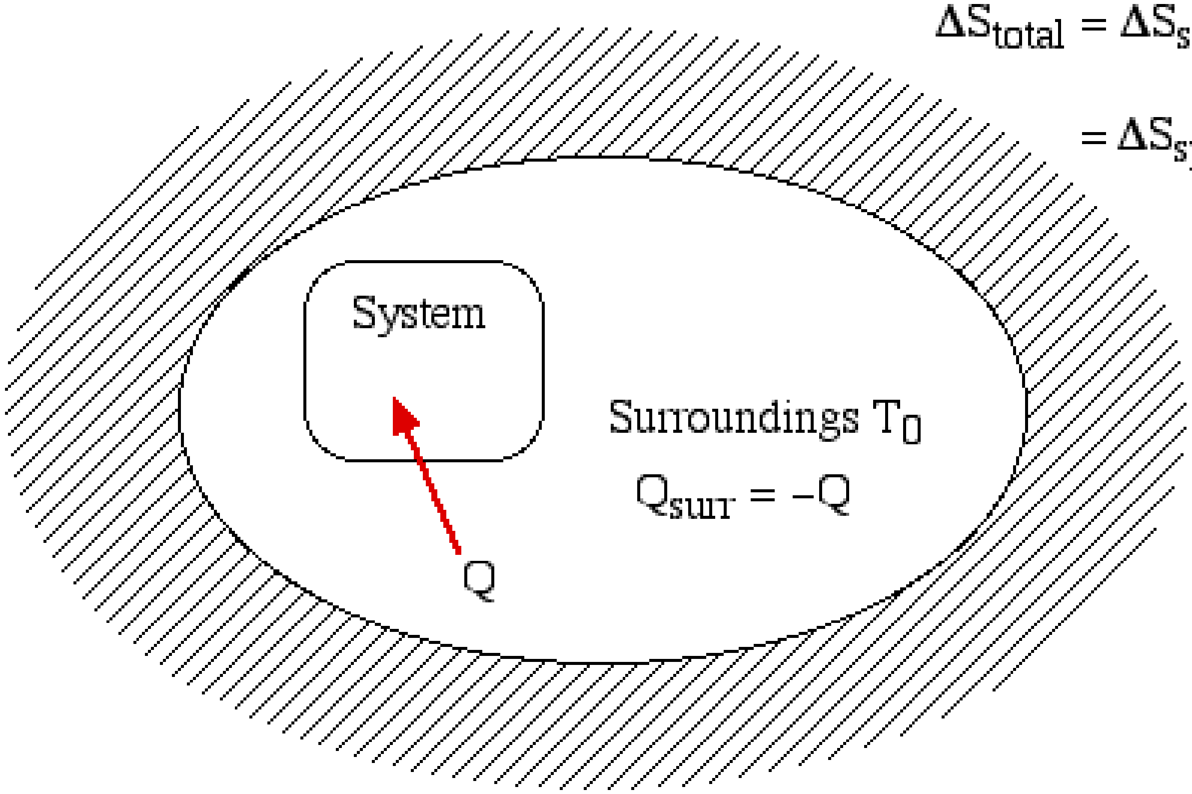


For adiabatic processes $(\delta Q = 0) \Rightarrow \boxed{\Delta S \geq 0}$

Thus the entropy change of an adiabatic process is always greater than or equal to zero, where the equality applies to reversible processes. However not all processes are adiabatic. Nevertheless we can always enclose a system in a surrounding environment which is adiabatic, thus considering the total entropy change of both the system and surroundings we obtain:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{su}}$$

$$= \Delta S_{\text{system}} + \frac{Q_{\text{sur}}}{T_0}$$



Entropy generated S_{gen}:

$$\boxed{S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{system}} + \frac{Q_{\text{surr}}}{T_0} \geq 0} \quad (Q_{\text{surr}} = -Q)$$

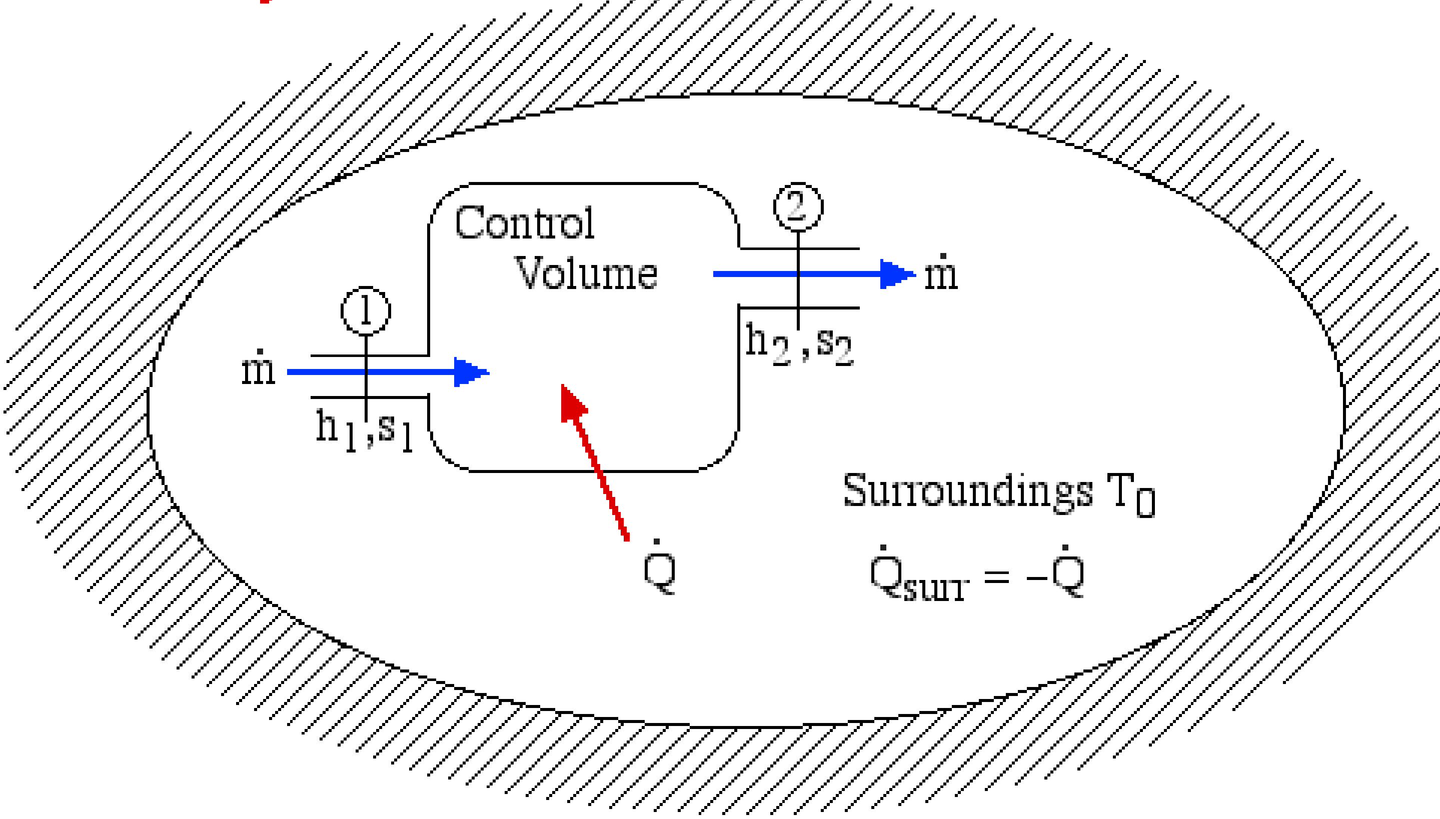
Dividing by m: $\boxed{s_{\text{gen}} = \Delta s_{\text{system}} + \frac{q_{\text{surr}}}{T_0} \geq 0}$

Thus the Increase in Entropy Principle states that for any process the total change in entropy of a system together with its enclosing adiabatic surroundings is always greater than or equal to zero. This total change of entropy is denoted the Entropy Generated during the process (S_{gen} [kJ/K] or s_{gen} [kJ/kg.K]).

2. Flow Processes (Steady Flow)

We now consider the entropy generated during a steady flow process through a single-input/single-output Control Volume (CV) enclosed in an adiabatic surroundings as shown:

$$\Delta\dot{S}_{total} = \overset{\text{steady flow}}{\cancel{\Delta\dot{S}_{ControlVol}}} + \Delta\dot{S}_{surr} = \Delta\dot{S}_{surr} \geq 0$$



Notice that for a steady flow system there can be no change of any of its property values with time, thus the rate of increase of entropy can only be associated with the surroundings. Notice also that at station (2) we are also dumping entropy from the control volume into the surroundings, and at station (1) we are sucking entropy out of the surroundings, leading to:

Rate of Entropy Generated $\dot{S}_{gen}$:

$$\boxed{\dot{S}_{gen} = \Delta\dot{S}_{total} = \Delta\dot{S}_{surr} = \dot{m}(s_2 - s_1) + \frac{\dot{Q}_{surr}}{T_0} \geq 0} \qquad (\dot{Q}_{surr} = -\dot{Q})$$

Dividing by $\dot{m}$: $\boxed{s_{gen} = \Delta s_{CV} + \frac{q_{surr}}{T_0} \geq 0}$

Surprisingly the form of the specific entropy generated function s_{gen} for a control volume is identical to that for a system.

For multiple-input, multiple-output control volumes under steady flow conditions, the entropy generated function is extended to:

$$\boxed{\dot{S}_{gen} = \sum_e \dot{m}_e s_e - \sum_i \dot{m}_i s_i + \frac{\dot{Q}_{surr}}{T_0} \geq 0 \qquad (\dot{Q}_{surr} = -\dot{Q})}$$

where the summations (Σ) are taken over all the exit ports (e) and inlet ports (i).

Change of entropy in irreversible processes

the change of entropy only in reversible-processes. Let us turn now to the problem associated with the change of entropy in irreversible processes and, in particular, in irreversible processes proceeding in an isolated system, which are of the greatest interest. *Isolated* is the name given to a system with a rigid boundary with ideal heat insulation. The ideal heat insulation prevents any heat exchange between the system and the surroundings ($dQ_{sys} = 0$), and the rigid boundary protects the system against any exchange of expansion work with the surroundings. Sine $dQ_{sys} = 0$ and $p\, dV_{sys} = 0$, it is clear from Eq. (2.37a) that $dU_{sys} = 0$, i.e. $U_{sys} =$ const. The analysis of the processes proceeding in an isolated system is of interest mostly because in the limit any non-isolated system and its surroundings can be treated as an integral isolated system.

Inasmuch as for an isolated system $dQ_{sys} = 0$, any process proceeding in such a system is an adiabatic process for the system as a whole.

Consider an isolated system comprising two bodies at different temperatures T_1 and T_2 with $T_1 > T_2$. Heat transfer will take place between these bodies of the system; heat will flow from the body at the higher temperature T_1 to the body at the lower temperature T_2. If an amount of heat dQ flows from the first body to the second, consequently, in accordance with Eq. (3.115), the entropy of the first body will be reduced by

$$dS_1 = -\frac{dQ}{T_1},$$

(3.130)

and the entropy of the second body will increase by

$$dS_2 = \frac{dQ}{T_2}.$$

(3.131)

It is clear that the total change in the entropy of the entire system is

$$dS_{sys} = dQ\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

(3.132)

Since

$$T_2 < T_1,.$$

we have

$$dS_{sys} > 0,$$

(3.133)

i.e. an irreversible process results in an increase in the entropy of an isolated system.

If the process of heat transfer between the component parts of the system was reversible (it will be recalled that the condition for the reversibility of a process is an infinitesimal temperature difference $T_1 - T_2 = dT$), the entropy of the first body would diminish by

$$dS_1 = -\frac{dQ}{T_1},$$

and the entropy of the second body would increase by

$$dS_2 = \frac{dQ}{T_1 - dT},$$

so that for the system as a whole the change in entropy would he negligibly small:

$$dS_{sys} = dQ\left(\frac{1}{T_1 - dT} - \frac{1}{T_1}\right) \cong dQ\frac{dT}{T_1^2} \cong 0.$$

(3.134)

Another method of reversible heat transfer from a body at a higher temperature to a body at a lower temperature involves, as already mentioned, the Carnot cycle. To realize any irreversible cycle, a system consisting of three elements out of equilibrium - a high-temperature heat source, a low-temperature heat sink, and a working medium - must be available. If during one cycle heat Q_1 is removed from the high-temperature heat source (at temperature T_1) and heat Q_2 is added to the low-temperature heat sink (at temperature T_2), the entropy of the high-temperature heat source will diminish by

$$\Delta S_{\text{ht.}} = -\frac{Q_1}{T_1},$$

(3.135)

and the entropy of the low-temperature sink will increase by

$$\Delta S_{\text{lt.}} = \frac{Q_2}{T_2}.$$

(3.136)

As regards the entropy of the working medium, since upon completion of the cycle the working medium returns into its initial state, its entropy does not change:

$$\Delta S_{\text{wm.}} = 0.$$

(3.137)

Hence, after a system undergoes a cycle the change in the entropy of the system considered is equal to

$$dS_{sys} = \Delta S_{\text{ht.}} + \Delta S_{\text{wm.}} + \Delta S_{\text{lt.}} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}.$$

(3.138)

Equation (3.138) is true for any reversible and irreversible cycles operated between two heat sources (a source and a sink).

As was shown above, for a reversible Carnot cycle,

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0.$$

Hence, if a reversible Carnot cycle is realized in a system (or any other cycle is accomplished between a heat source and a heat sink), the entropy of the system does not change:

$$dS_{sys} = 0.$$

(3.139)

The same conclusion can be drawn for reversible cycles realized between any number of heat sources.

But if a system undergoes an arbitrary irreversible cycle, the entropy of the system will change without fail. The thermal efficiency of any irreversible cycle, $\eta_{\text{T}}^{\text{irr.}}$, has. been shown above to be less than the thermal efficiency of a reversible Carnot cycle, $\eta_T^{\text{r.C.c.}}$, realized between the same heat sources.

Bearing in mind that for a reversible Carnot cycle

$$\eta_T^{\text{r.C.c.}} = \frac{T_1 - T_2}{T_1}$$

and, in accordance with the general definition for irreversible cycle:

$$\eta_T^{\text{ir.c.}} = \frac{Q_1 - Q_2}{Q_1},$$

the inequality

$$\eta_T^{\text{ir.c.}} < \eta_T^{\text{r.C.c.}}$$

can be presented in the following form:

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1},$$

(3.140)

whence it follows that for an irreversible cycle

$$\frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

(3.141)

(here the temperatures refer not to the working medium but to the heat sources). Hence, if an irreversible process is accomplished between two heat sources, the entropy of the system increases:

$$dS_{sys} > 0.$$

(3.142)

The same conclusion is true for irreversible cycles realized between any other number of heat sources.

The increase in the system's entropy is associated with the fact that the entropy of the working medium does not change during the cycle, and the drop in the entropy of the high-temperature sources is less than the increase in the entropy of the low-temperature sources. Thus, an irreversible cycle results in an increase in the entropy of an isolated system.

This conclusion can be proved in the most general form in the following manner. The inequality (3.141), which is true for an irreversible Carnot cycle, as well as for any irreversible cycle, can be presented in the following form:

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$$

or, which is the same,

$$\sum \frac{Q}{T} < 0.$$

(3.143)

Considering the irreversible cycle as a totality of an infinite number, *n*, of irreversible elementary Carnot cycles and taking into account that

$$\lim_{n\to\infty} \sum_{i=1}^{n} \frac{\Delta Q}{T} = \oint \frac{dQ}{T},$$

we obtain [see Eq. (3.143)]:

$$\oint \frac{dQ}{T} < 0.$$

(3.144)

Thus, for an arbitrary irreversible cycle the Clausius integral is always negative.

It should be stressed that this integral pertains to the work done by the system (high-temperature source - working medium - low-temperature heat sink) as a whole. As regards the working medium, its entropy does not change, inasmuch as upon completion of the cycle the working medium returns into its initial state, as was already mentioned above. In other words, for the working medium Eq. (3.116),

$$\oint dS = 0,$$

or, which is the same, the equation

$$\oint \frac{dQ}{T} = 0.$$

is always true.

A question may arise whether there is any contradiction here. Indeed, on one hand, the Clausius integral was shown to be always negative in an irreversible cycle [Eq. (3.144)]; on the other hand, according to Eq. (3.114) this integral is equal to zero. But there is no contradiction here. In Eq. (3.114) the integral refers to the working medium, and the quantity *T*, present in this equation, is the temperature of the working medium. As regards the Clausius integral present in Eq. (3.144), it pertains, as was already mentioned above, to the system as a whole and, as it is clear from the meaning of the conclusion [see Eq. (3.144)], the temperature present in this equation is the temperature of the heat source, which is not equal to the temperature of the working body in the event of an irreversible process.

Consider now an arbitrary irreversible cycle comprising two processes, an irreversible process *1-2* and a reversible process *2-1* (Fig. 3-18).

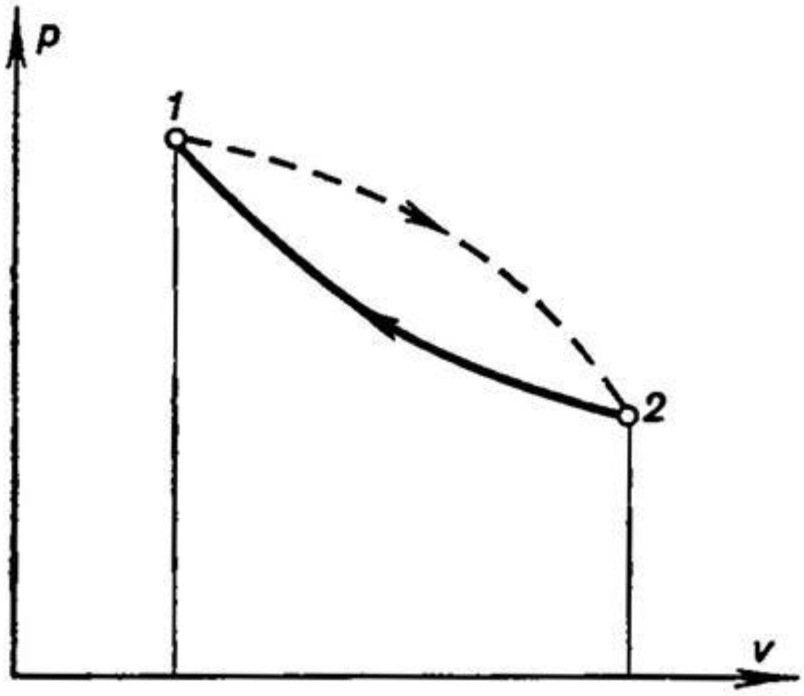


Fig. 3.18

For the cycle considered, the Clausius integral can obviously be presented as the sum of two line integrals:

$$\oint \frac{dQ}{T} = \int_{(1-2)} \left(\frac{dQ}{T}\right)_{\text{ir}} + \int_{(2-1)} \left(\frac{dQ}{T}\right)_{\text{r}},$$

(3.145)

whence with account taken of Eq. (3.144) it follows that

$$\int_{(1-2)}\left(\frac{dQ}{T}\right)_{ir} + \int_{(2-1)}\left(\frac{dQ}{T}\right)_{r} < 0.$$

(3.146)

For the reversible process *2-1,* in accordance with Eqs. (3.115) and (3.117)

$$\int_{(2-1)}\left(\frac{dQ}{T}\right)_{r} = \int_{2}^{1}\frac{dQ}{T} = S_1 - S_2.$$

Substituting this expression in the inequality (3.146), we obtain for any irreversible process:

$$S_1 - S_2 > \int_{(1-2)}\left(\frac{dQ}{T}\right)_{ir},$$

(3.147)

whence, in the differential form

$$dS > \frac{dQ}{T};$$

(3.148)

it should be stressed once more that this relationship holds for any irreversible process proceeding in a system. Consequently, if a reversible process develops in an isolated system (for which, by definition, $dQ_{sys} = 0$), then according to Eq. (3.133),

$$dS_{sys} > 0.$$

The entropy of an isolated system increases as a result of irreversible processes developing in the system.

From the relationship (3.115)

$$dS = \frac{dQ}{T}$$

it follows that **if a reversible process takes place in an isolated system ($dQ_{sys} = 0$), the entropy of the system remains constant:**

$$dS_{sys} = 0.$$

No matter what processes proceed in an isolated system, entropy cannot decrease:

$$dS_{sys} \geq 0.$$

(3.149)

[In Eq. (3.149) the equality sign pertains to reversible and the inequality sign to irreversible processes.]

Hence, an important conclusion is drawn (already mentioned above, in Sec. 3.2) that after coming into a state of equilibrium an isolated system remains in this state, i.e. the system is incapable of a spontaneous change of state. Indeed, any spontaneous process is irreversible and, consequently, proceeds with an increase in entropy. The entropy of an isolated system, however, has a maximum value in the state of equilibrium. Consequently, spontaneous processes are impossible in an isolated equilibrium system.

Thus, spontaneous processes continue in an isolated system until the system's entropy reaches its maximum value. Upon reaching the state of equilibrium, for which the entropy is the maximum possible, the spontaneous processes in the system terminate, and the system stays in a state of equilibrium.

Equations (3.115) and (3.148) can be combined in the following form:

$$dS_{sys} \geq \frac{dQ}{T}.$$

(3.150)

Relation (3.150), which is true both for reversible (the sign of equality) and irreversible (the sign of inequality) processes in any system, is the mathematical expression for the second law of thermodynamics. The inequality (3.149) is a particular case of the general inequality (3.150) written for an isolated system ($dQ_{sys} = 0$).

Temperature Entropy (T-s) Diagram

A T-s diagram is the type of diagram most frequently used to analyze energy transfer system cycles. This is because the work done by or on the system and the heat added to or removed from the system can be visualized on the T-s diagram. By the definition of entropy, the heat transferred to or from a system equals the area under the T-s curve of the process. Figure 13 is the T-s diagram for pure water. A T-s diagram can be constructed for any pure substance. It exhibits the same features as P-u diagrams.

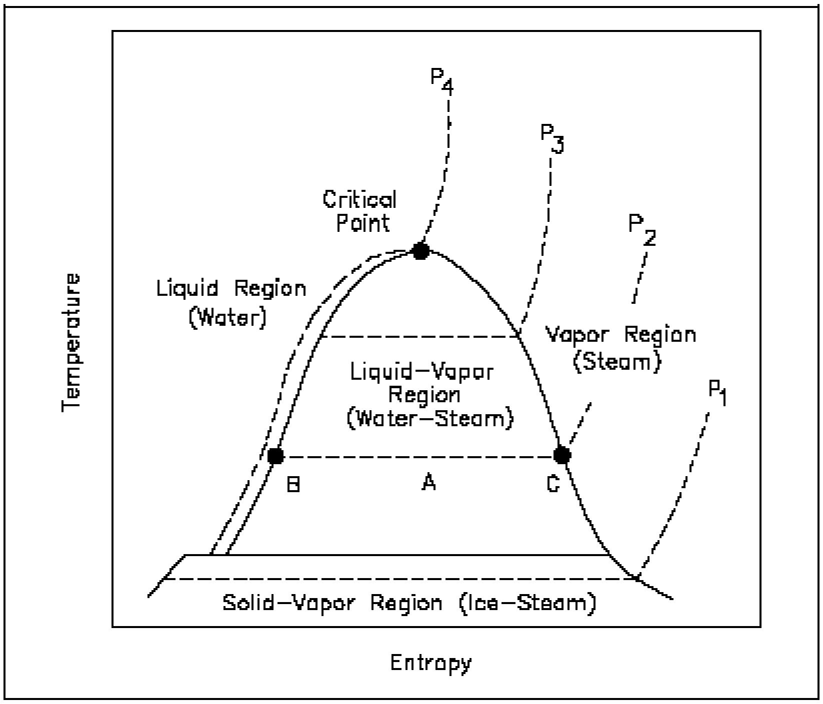
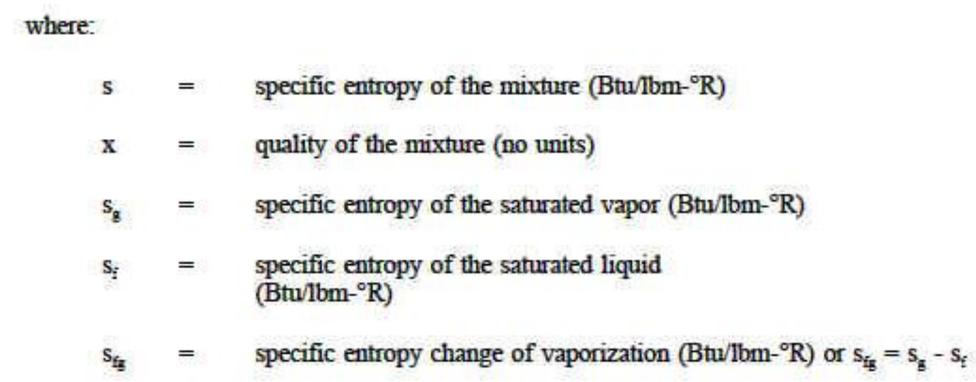


Figure 13 T-s Diagram for Water

In the liquid-vapor region in Figure 13, water and steam exist together. For example, at point A, water with an entropy (s_f) given by point B, exists together with steam with an entropy (s_g) given by point C. The quality of the mixture at any point in the liquid-vapor region can be found using the following relationship.

$$s = xs_g + (1 - x)s_f$$

$$x = \frac{s - s_f}{s_{fg}}$$



where:

s = specific entropy of the mixture (Btu/lbm-°R)

x = quality of the mixture (no units)

s_g = specific entropy of the saturated vapor (Btu/lbm-°R)

s_f = specific entropy of the saturated liquid (Btu/lbm-°R)

s_{fg} = specific entropy change of vaporization (Btu/lbm-°R) or $s_{fg} = s_g - s_f$

Physical significance of Entropy

The entropy of a substance is real physical quantity and is a definite function of the state of the body like pressure, temperature, volume of internal energy.

It is difficult to form a tangible conception of this quantity because it can not be felt like temperature or pressure. We can, however, readily infer it from the following aspects:

1. Entropy and unavailable energy

The second law of thermodynamics tells us that whole amount of internal energy of any substance is not convertible into useful work. A portion of this energy which is used for doing useful work is called **available energy**. The remaining part of the energy which cannot be converted into useful work is called **unavailable energy**. Entropy is a measure of this unavailable energy. In fact, the entropy may be regarded as the unavailable energy per unit temperature.

I.e.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

or, $Unavailable\ \ energy\ \ = Entropy \times Temperature$

The concept of entropy is of great -value and it provides the information regarding structural changes accompanying a given process.

2. Entropy and disorder

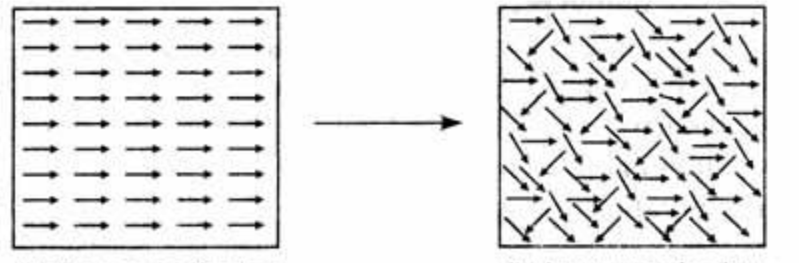
Entropy is a measure of the disorder or randomness in the system. When a gas expands into vacuum, water flows out of a reservoir, spontaneous chain reaction takes place, an increase in the disorder occurs and therefore entropy increases.

Similarly, when a substance is heated or cooled there is also a change in entropy. *Thus increase in entropy implies a transition from on ordered to a less ordered state of affair.*

3. Entropy and probability

Why is disorder favoured? This can be answered by considering an example, when a single coin is flipped, there is an equal chance that head or tail will show up. When two coins are flipped, there is a chance of two heads or two tails showing up but there are double chance of occurrence of one head and one tail. This shows that disorder is more frequent than order.

Changes in order are expressed quantitatively in terms of entropy change, ΔS. How are entropy and order in the system related? Since a disordered state is more probable for systems than of order(see figure), the entropy and thermodynamic probabilities are closely related.



(a) More organised or ordered (less probable)

(b) Less organised or disordered (more probable)

Order and probability

Order and probality

Features of entropy:

(1) It is an extensive properly and a state function

(2) It's value depends upon mass of substance present in the system

(3) $\Delta S = S_{final} - S_{initial}$

(4) At equilibrium $\Delta S = zero$

(5) For a cyclic process $\Delta S = 0$

(6) For natural process $\Delta S > 0$ i.e Increasing.

(7) For a adiabatic process ΔS zero

Entropy Changes in an Ideal Gas

Many aerospace applications involve flow of gases (e.g., air) and we thus examine the entropy relations for ideal gas behavior. The starting point is form (a) of the combined first and second law,

$$du = Tds - Pdv.$$

For an ideal gas, $du = c_v dT$. Thus

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

Using the equation of state for an ideal gas ($Pv = RT$), we can write the entropy change as an expression with only exact differentials:

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}. \qquad (5..2)$$

We can think of Equation (5.2) as relating the fractional change in temperature to the fractional change of volume, with scale factors c_v and R ; if the volume increases without a proportionate decrease in temperature (as in the case of an adiabatic free expansion), then s increases. Integrating Equation (5.2) between two states ``1" and ``2":

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

For a perfect gas with constant specific heats

$$\Delta s = s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right).$$

In non-dimensional form (using $R/c_v = (\gamma - 1)$)

$$\frac{\Delta s}{c_v} = \ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1)\ln\left(\frac{v_2}{v_1}\right), \quad \text{Entropy change of a perfect} \qquad (5..3)$$

Equation 5.3 is in terms of specific quantities. For N moles of gas,

$$\frac{\Delta S}{C_v} = N\left[\ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1)\ln\left(\frac{V_2}{V_1}\right)\right].$$

This expression gives entropy change in terms of temperature and volume. We can develop an alternative form in terms of pressure and volume, which allows us to examine an assumption we have used. The ideal gas equation of state can be written as

$$\ln P + \ln v = \ln R + \ln T.$$

Taking differentials of both sides yields

$$\frac{dP}{P}+\frac{dv}{v}=\frac{dT}{T}.$$

Using the above equation in Eq. (5.2), and making use of the relations $c_p = c_v + R$; $c_p/c_v = \gamma$, we find

$$ds = c_v\left[\frac{dP}{P}+\frac{dv}{v}\right]+R\frac{dv}{v},$$

or

$$\frac{ds}{c_v}=\frac{dP}{P}+\gamma\frac{dv}{v}.$$

Integrating between two states 1 and 2

$$\frac{\Delta s}{c_v}=\ln\left(\frac{P_2}{P_1}\right)+\gamma\ln\left(\frac{v_2}{v_1}\right)=ln\left[\frac{P_2}{P_1}\left(\frac{v_2}{v_1}\right)^{\gamma}\right]. \qquad (5..4)$$

Using both sides of (5.4) as exponents we obtain

$$\frac{P_2 v_2^{\gamma}}{P_1 v_1^{\gamma}}=[Pv^{\gamma}]_1^2=e^{\Delta s/c_v}. \qquad (5..5)$$

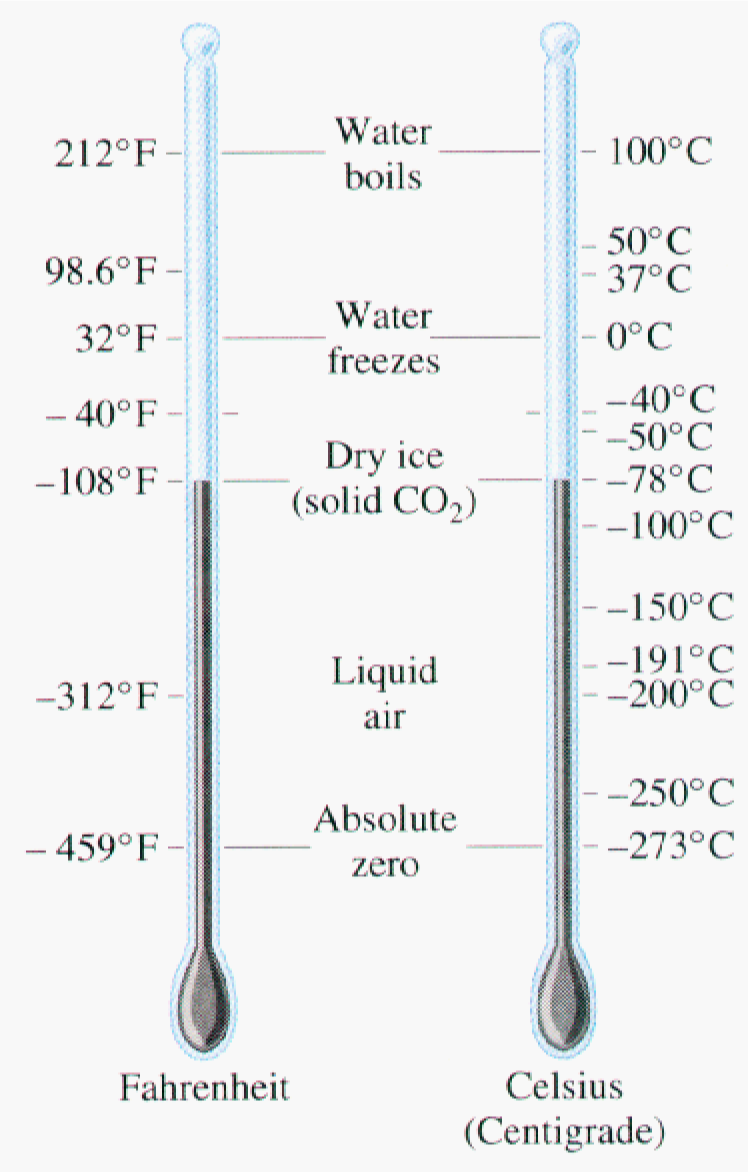
Equation (5.5) describes a general process. For the specific situation in which $\Delta s = 0$, i.e., the entropy is constant, we recover the expression $Pv^{\gamma} = \text{constant}$. It was stated that this expression applied to a reversible, adiabatic process. We now see, through use of the second law, a deeper meaning to the expression, and to the concept of a reversible adiabatic process, in that both are characteristics of a constant entropy, or **isentropic**, process.

Temperature Scale

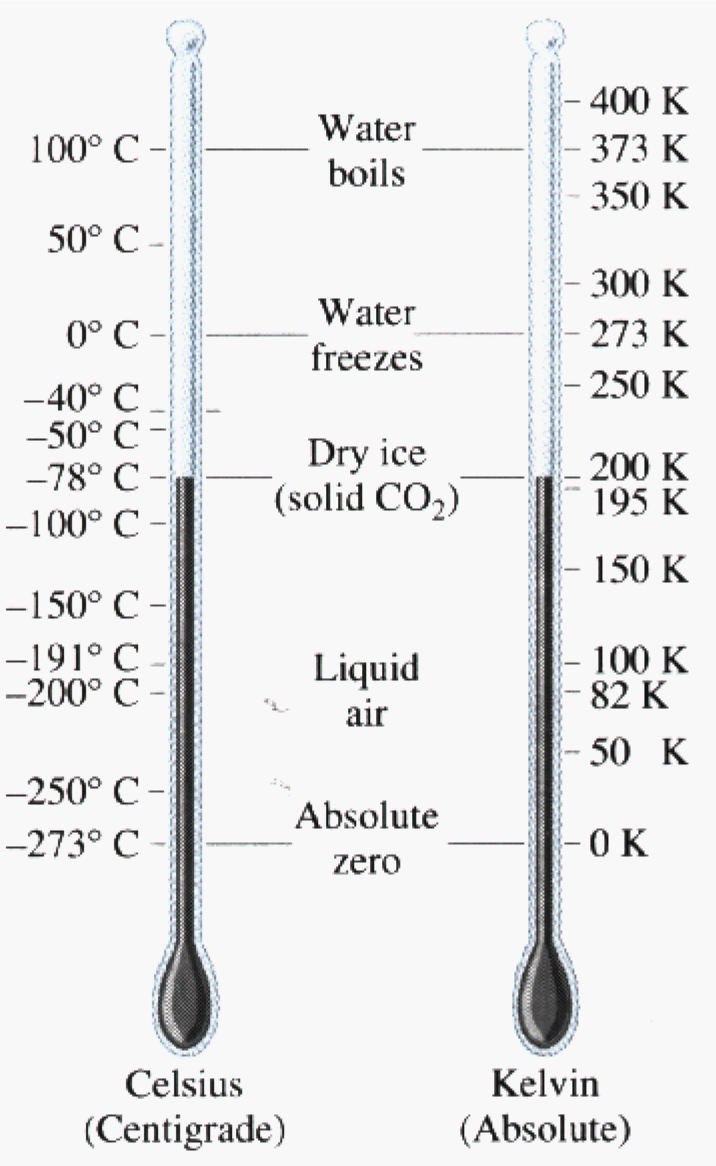
There are three temperature scales in use today, Fahrenheit, Celsius and Kelvin.

Fahrenheit temperature scale is a scale based on 32 for the freezing point of water and 212 for the boiling point of water, the interval between the two being divided into 180 parts. The 18th-century German physicist Daniel Gabriel Fahrenheit originally took as the zero of his scale the temperature of an equal ice-salt mixture and selected the values of 30 and 90 for the freezing point of water and normal body temperature, respectively; these later were revised to 32 and 96, but the final scale required an adjustment to 98.6 for the latter value.

Until the 1970s the Fahrenheit temperature scale was in general common use in English-speaking countries; the Celsius, or centigrade, scale was employed in most other countries and for scientific purposes worldwide. Since that time, however, most English-speaking countries have officially adopted the Celsius scale. The conversion formula for a temperature that is expressed on the Celsius (C) scale to its Fahrenheit (F) representation is: $F = 9/5C + 32$.



Celsius temperature scale also called centigrade temperature scale, is the scale based on 0 for the freezing point of water and 100 for the boiling point of water. Invented in 1742 by the Swedish astronomer Anders Celsius, it is sometimes called the centigrade scale because of the 100-degree interval between the defined points. The following formula can be used to convert a temperature from its representation on the Fahrenheit (F) scale to the Celsius (C) value: C = 5/9(F - 32). The Celsius scale is in general use wherever metric units have become accepted, and it is used in scientific work everywhere.



Kelvin temperature scale is the base unit of thermodynamic temperature measurement in the International System (SI) of measurement. It is defined as 1/ 273.16 of the triple point (equilibrium among the solid, liquid, and gaseous phases) of pure water. The kelvin (symbol K without the degree sign []) is also the fundamental unit of the Kelvin scale, an absolute temperature scale named for the British physicist William Thomson, Baron Kelvin. Such a scale has as its zero point absolute zero, the theoretical temperature at which the molecules of a substance have the lowest energy. Many physical laws and formulas can be expressed more simply when an absolute temperature scale is used; accordingly, the Kelvin scale has been adopted as the international standard for scientific temperature measurement. The Kelvin scale is related to the Celsius scale. The difference between the freezing and boiling points of water is 100 degrees in each, so that the kelvin has the same magnitude as the degree Celsius.

Absolute Scale

Temperatures exist which are much colder than the freezing point of ice, 0°C on the Celsuis scale. Experiments suggest that there is a limit to how cold things can get. At a temperature of -273°C all the heat energy has been removed from any substance. We call this lowest possible temperature absolute zero. A new temperature scale is now used which has the zero of its scale at this absolute zero of temperature. This scale is called the absolute scale or kelvin scale, after Lord Kelvin who devised it. One division on the kelvin temperature scale is called a kelvin and is exactly equal to one division or degree on the Celsius scale. It follows that there are 100 kelvins between the ice point and steam point of water.

Absolute Scale of Temperature

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Absolute scale of temperature was proposed by Lord Kelvin, and therefore is also called the Kelvin scale of temperature. The absolute scale or the thermodynamical scale of temperature has its zero, called the absolute zero, below which it is not possible to cool a body by any physical means. As there does not exist any body cooler than one whose temperature is absolute zero, no transfer of energy can take place from this body to any other body. This is the genuine sense of the meaning of the absolute zero of temperature. As the thermal energy does not characterize the direction of the flow of heat or thermal energy when bodies are brought into thermal contact with each other., it does not measure the temperature of bodies. On the other hand, the difference in temperature of two bodies indicates only the direction of the net flow of heat between the bodies. Temperature does not therefore measure the thermal energy of the body.

Therefore, a body at the thermodynamic or absolute zero of temperature can possess a large thermal energy, for example, if it has large number of constituent particles. A body at the absolute zero of temperature is however so constituted that its thermal energy cannot be transferred to another body, but can only receive thermal energy from another body at a higher temperature. The thermal energy possessed by a body at the absolute zero of temperature is then called the zero point energy. In the laboratory, it has been possible to reach temperature within a few millionths of a degree of the absolute zero of temperature.

Absolute Scale Grading

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Grading is a difficult aspect of teaching for many instructors. Making judgments about others is often uncomfortable, especially since, teachers want to be helpful and motivate students to do their best. There are different philosophies about grading, and these result in different methods of evaluating students. There are two basic frameworks to consider. One uses a relative scale and the other an absolute scale. Grading that uses a relative scale is sometimes referred to as norm referenced: grades are assigned on the basis of how a student's performance compares with others' in the class. Those preferring this approach base their arguments on the value of knowing a student's standing compared with others and the reality of competition in life.

Grading that uses an absolute scale is sometimes referred to as task-referenced grading: grades are assigned by comparing each student's performance to a defined set objectives to be learned or tasks to be done. With an absolute scale, all students in a class could receive grades of A if they all meet the absolute standards. The argument for using this approach is that it is of value to know what each student has learned, and each student's grade should be independent of that of other students.

Absolute Scale Map

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With a map the scale is nominally constant. Although with a large scale map this nominal scale may apply fundamentally to the whole of the content, there will always be exceptions, as small features or abstractions have to be represented by legible symbols. For medium and small scale topographic maps the requirements of legibility and relative importance will introduce sufficient exaggeration to ensure that important small features will be retained, regardless of nominal map scale. In this sense they remain part of the 'foreground' in pictorial terms. So in both cases scale and generalization are used in combination, although to different ends. By manipulating selection and symbolization, the map ensures that what is regarded as most important is included and if necessary emphasized regarded as most important is included and if necessary emphasized regardless of absolute size, and so given detailed treatment, within absolute scale limitations.

Third Law of Thermodynamics

The Third Law of Thermodynamics is concerned with the limiting behavior of systems as the temperature approaches absolute zero. Most thermodynamics calculations use only entropy *differences*, so the zero point of the entropy scale is often not important. However, we discuss the Third Law for purposes of completeness because it describes the condition of zero entropy.

The Third Law states, “The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).” According to Purdue University, “The crystal must be perfect, or else there will be some inherent disorder. It also must be at 0 K; otherwise there will be thermal motion within the crystal, which leads to disorder.”

Siabal Mitra, a professor of physics at Missouri State University, provides another implication of this law. “One version of the Third Law states that it would require an infinite number of steps to reach absolute zero, which means you will never get there. If you could get to absolute zero, it would violate the Second Law, because if you had a heat sink at absolute zero, then you could build a machine that was 100 percent efficient.”

In theory it would be possible to grow a perfect crystal in which all of the lattice spaces are occupied by identical atoms. However, it is generally believed that it is impossible to achieve a temperature of absolute zero (although scientists have come quite close). Therefore, all matter contains at least some entropy owing to the presence of some heat energy.

Implications of the Third Law

Because a temperature of absolute zero is physically unattainable, the Third Law may be restated to apply to the real world as: the entropy of a perfect crystal approaches zero as its temperature approaches absolute zero. We can extrapolate from experimental data that the entropy of a perfect crystal reaches zero at absolute zero, but we can never demonstrate this empirically.

According to David McKee, a professor of physics at Missouri Southern State University, "There's a field of ultra-low-temperature research, and every time you turn around there's a new record low. These days, nanokelvin (nK = 10^{-9}K) temperatures are reasonably easy to achieve, and everyone's now working on picokelvins (pK =, 10^{-12} K)." As of this writing, the record-low temperature was achieved 1999 by the YKI-group of the Low Temperature Laboratory at Aalto University in Finland. They cooled a piece of rhodium metal to 100 pK, or 100 trillionths of a degree Celsius above absolute zero besting the previous record of 280 pK set by them in 1993.

While a temperature of absolute zero does not exist in nature, and we cannot achieve it in the laboratory, the concept of absolute zero is critical for calculations involving temperature and entropy. Many measurements imply a relationship to some starting point. When we state a distance, we have to ask, distance from what? When we state a time, we have to ask, time since when? Defining the zero value on the temperature scale gives meaning to positive values on that scale. When a temperature is stated as 100 K, it means that the temperature is 100 K above absolute zero, which is twice as far above absolute zero as 50 K and half as far as 200 K.

On first reading, the Third Law seems rather simple and obvious. However, it serves and the final period at the end of a long and consequential story that fully describes the nature of heat and thermal energy.

What is "Negative Temperature"?

Not all systems have the property that the entropy increases monotonically with energy. In some cases, as energy is added to the system, the number of available microstates, or configurations, actually decreases for some range of energies. For example, imagine an ideal "spin-system", a set of N atoms with spin 1/2 on a one-dimensional wire. The atoms are not free to move from their positions on the wire. The only degree of freedom allowed to them is spin-flip: the spin of a given atom can point up or down. The total energy of the system, in a magnetic field of strength B, pointing down, is (N+ - N-)*uB, where u is the magnetic moment of each atom and N+ and N- are the number of atoms with spin up and down respectively. Notice that with this definition, E is zero when half of the spins are up and half are down. It is negative when the majority are down and positive when the majority are up.

The lowest possible energy state, all the spins pointing down, gives the system a total energy of -NuB, and temperature of absolute zero. There is only one configuration of the system at this energy, i.e., all the spins must point down. The entropy is the log of the number of microstates, so in this case is log(1) = 0. If we now add a quantum of energy, size uB, to the system, one spin is allowed to flip up. There are N possibilities, so the entropy is log(N). If we add another quantum of energy, there are a total of N(N-1)/2 allowable configurations with two spins up. The entropy is increasing quickly, and the temperature is rising as well.

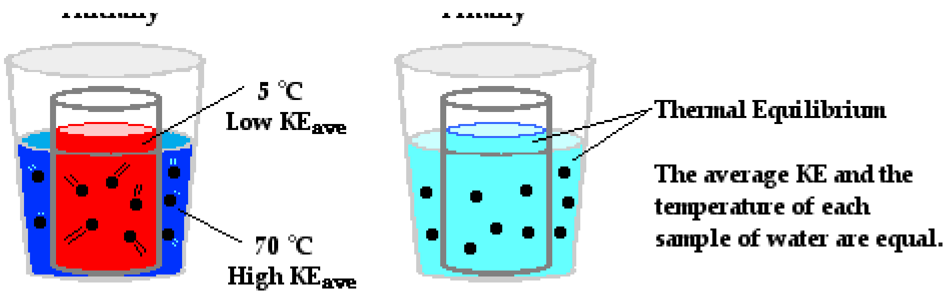
However, for this system, the entropy does not go on increasing forever. There is a maximum energy, +NuB, with all spins up. At this maximal energy, there is again only one microstate, and the entropy is again zero. If we remove one quantum of energy from the system, we allow one spin down. At this energy there are N available microstates. The entropy goes on increasing as the energy is lowered. In fact the maximal entropy occurs for total energy zero, i.e., half of the spins up, half down.

So we have created a system where, as we add more and more energy, temperature starts off positive, approaches positive infinity as maximum entropy is approached, with half of all spins up. After that, the temperature becomes negative infinite, coming down in magnitude toward zero, but always negative, as the energy increases toward maximum. When the system has negative temperature, it is *hotter* than when it is has positive temperature. If you take two copies of the system, one with positive and one with negative temperature, and put them in thermal contact, heat will flow from the negative-temperature system into the positive-temperature system.

the heat death of the universe

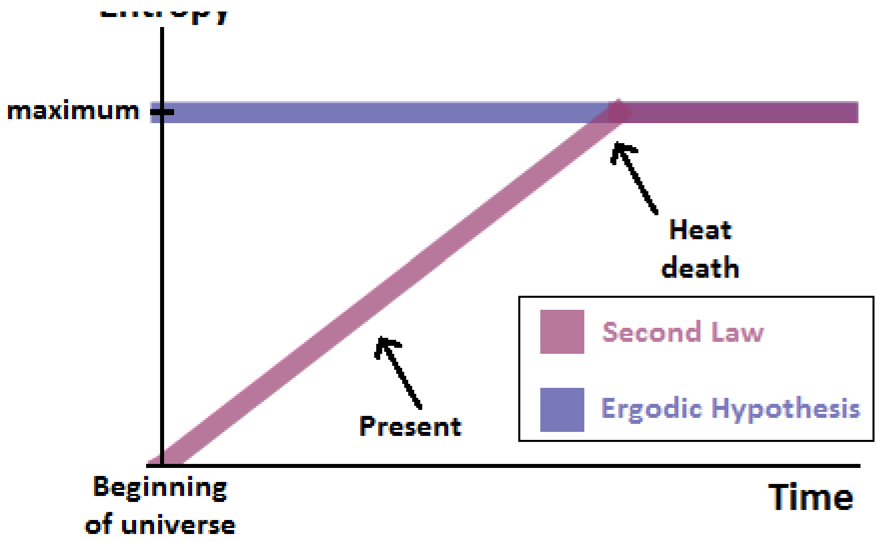
The heat death is one of the many proposed fates of the universe. The idea of a heat death primarily involves the idea of increasing entropy, eventually leading to a stage where no thermodynamic energy transfer would be possible, because of the uniform temperatures and energy distributions everywhere in the universe(thermodynamic equilibrium).

This 'heat death of the universe' is analogues to a bucket of lukewarm water which emerges from the combination of two ordered states - hot water and cold water. When these two systems come in contact, the cold water is heated, which in turn lowers the energy of the hot water as well, subsequently cooling it. These interactions continue until the temperature of the water molecules become uniform throughout i.e. the vibrations of the water molecules become spatially uniform(discounting the uncertainties arising from quantum mechanics). At this stage, the system is no longer capable of performing any mechanical or thermal work and therefore, no energy transfer can take place in the system.



Just like thermal equilibrium is achieved at a local level, the universe might too have to suffer from a heat death

Coming back to the context of the universe, the heat death arises as a result of maximum entropy. Because of accelerated expansion of the universe due to what is dubbed as 'dark energy', galaxies would get further and further apart. This would eventually lead to stage where astronomy would become nearly impossible because of the immense distances separating our galaxy from the others(as they would cross the line of sight of our observable universe). Gradually, all stars would run out of fuel, and collapse into white dwarfs, neutron stars or black holes, depending upon their respective masses(The distinctions arising from the Chandrasekhar Limit). Even worse news would be that new celestial bodies wouldn't be able form either because of the lack of concentrated gaseous nebulae and very few interstellar dust clouds. Only these star remnants would remain, which too would become part of super-massive black holes sooner or later. Eventually these black holes would evaporate too(through the slow and gradual process of Hawking radiation). Now, after the exhaustion of all the 'useful' forms of energy, the only things which would remain would be some stable species of leptons(neutrinos and electrons) and electromagnetic radiation(light).



Nothing ever, would be able to interact in the future as well, because any reaction or interaction would result in the violation of the Second Law of Thermodynamics. The universe would become a dark, lonely and lifeless place.

Now, now. There might still be hope, our only hope. An event called a Poincare Recurrence(arising from the theorem of the same name), might just jolt the universe back to a state of lower entropy without breaking any laws. This event is just one configuration out of the infinite configurations out there, and can only happen in a universe which lasts forever. Its just like, if hot water and cold water spontaneously get separated into different halves in a bucket of lukewarm water. The odds of that happening are mind-bogglingly low, but as long as there is infinite time available, it can happen. The universe might be reset to a stage of lower entropy and the flow of energy might again become possible.

The Maxwell Relations

The equations that relate the partial derivatives of properties P, v, T, and s of a simple compressible system to each other are called the Maxwell relations. They are obtained from the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

Two of the Gibbs relations were derived in earlier lecture and were expressed as

$$du = Tds - Pdv \dots\dots A - 1$$

$$dh = Tds + v\,dP \dots\dots A - 2$$

The other two Gibbs relations are based on two new combination properties—the Helmholtz function a and the Gibbs function g, defined as

$$a = u - Ts$$

$$g = h - Ts$$

The Helmholtz and Gibbs functions are properties because each is defined in terms of properties. From inspection of these two equations we find that, the units of a and g are the same as those of u and h. These two new properties are introduced solely because they contribute to the present discussion, and no physical significance need be attached to them at this point.

Forming the differential da we get

$$da = du - d(Ts) = du - Tds - sdT$$

Substituting the value of $du - Tds = -Pdv$ from Gibbs equation, we get

$$da = -Pdv - s\,dT$$

Similarly, forming the differential dg

$$dg = dh - d(Ts) = dh - Tds - s\,dT$$

Substituting the value of $dh - Tds = v\,dp$ from Gibbs equation, we get

$$dg = \; v\,dp - s\,dT$$

Property Relations from Exact Differentials

$$du = Tds - Pdv$$

$$dh = Tds + v\,dP$$

$$da = -Pdv - s\,dT$$

$$dg = \; v\,dp - s\,dT$$

The four differential equations introduced in the previous section, provide the basis for several important property relations. Since only properties are involved, each is an exact differential exhibiting the general form $dz = Mdx = Ndy$.

Underlying these exact differentials are, respectively, functions of the form $u(s,\ v)$,

$h(s,\ p), a(y, T)$, and $g(T, p\ )$.

Let us consider these functions in the order given.

The differential of the function $u(s,\ v)$, is

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

By comparing with Gibbs first equation we conclude that,

$$du = Tds - Pdv$$

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

$$-P = \left(\frac{\partial u}{\partial v}\right)_s$$

The differential of the function $h(s,\ P)$, is

$$dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$$

By comparing with Gibbs second equation we conclude that,

$$dh = Tds + v\,dP$$

$$T = \left(\frac{\partial h}{\partial s}\right)_P$$

$$v = \left(\frac{\partial h}{\partial P}\right)_s$$

Similarly, the coefficients $-p$ and $-s$ of this equation

$$da = -Pdv - s\,dT$$

are partial derivatives of $a(v, T\ )$, therefore

$$-p = \left(\frac{\partial a}{\partial v}\right)_T$$

$$-s = \left(\frac{\partial a}{\partial T}\right)_v$$

And the coefficients v and $-s$ of this equation

$$dg = v\,dp - s\,dT$$

are partial derivatives of g $(T,\ p)$, therefore

$$v = \left(\frac{\partial g}{\partial P}\right)_T$$

$$-s = \left(\frac{\partial g}{\partial T}\right)_P$$

As each of the four differentials introduced here is exact, the second mixed partial derivatives are equal. Thus, comparing these two equations

$$du = Tds - Pdv \ldots\ldots\ldots A-1$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \ldots\ldots B-1$$

We find that, T plays the role of M in B-1 and $-p$ plays the role of N in B-1, so

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

$$dh = Tds + v\,dP \ldots\ldots A-2$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \ldots\ldots B-1$$

In equation A- 2, T and v play the roles of M and N in equation B-1, respectively. Thus

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

$$da = -Pdv - s\,dT$$

$$dg = v\,dp - s\,dT$$

Similarly, from these two equations follows that

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

and

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

These four equations are known as the Maxwell relations.

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

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

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

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

They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P, v, and T. Note that the Maxwell relations given here are limited to simple compressible systems. However, other similar relations can be written just as easily for non-simple systems such as those involving electrical, magnetic, and other effects.

UNIT-3

Microstates and Macrostates

Classical thermodynamics describes macroscopic systems in terms of a few variables (functions of state): temperature, pressure, volume... But such a system is really made of atoms, so a much richer description must be possible in principle: we could specify the quantum state of all the atoms--the microstate. Of course as the atoms interact this state changes very rapidly-perhaps 10^{35} times a second. But the observed macrostate doesn't change. Many different microstates all correspond to the same macrostate.

This suggests we can calculate the macroscopic behaviour of the system by averaging over the corresponding microstates. We can derive thermodynamics from the quantum behaviour of atoms and molecules.

Of course only a few systems are really fully calculable: those in which the interactions between atoms are particularly simple--or absent. We will be able to tackle the ideal paramagnet and the ideal gas, including the latter at densities so high that the quantum nature of the system becomes important. The van der Waals gas and a paramagnet with nearest neighbour interactions can be worked out, as can crystalline solids with simple defects. Going beyond that is tough. But the proof-of-principle that these give is compelling.

The crucial link from microscopic to macroscopic properties is as follows. If the value of some quantity X in the ith microstate is X_i, and the probability that the system is in that microstate is p_i, then the value of X in the macrostate is the **ensemble average** (more details here.)

$$\langle X\rangle = \sum_i p_i X_i$$

We start by considering an isolated system (constant energy, volume and particle number). The fundamental principle that allows the averaging over microstate to be done is the **postulate of equal *a priori* probabilities** or, in plain English, the assumption that all allowed microstates are equally likely. (Allowed or accessible means having the same volume, particle number and and total energy as the macrostate.) We use Ω for the number of such microstates, so the probability of the system being in any one microstate is

$$p_i = \frac{1}{\Omega} \qquad \text{and} \qquad \sum_i p_i = \Omega\frac{1}{\Omega} = 1$$

the First Law of Thermodynamics:-

We will now start to consider other external parameters which can affect different systems. We will see a few of these as we move through the course, but the most important one is perhaps the most obvious – the volume V of a system. This didn't play a role in the two-state example because the particles were fixed. But as soon as objects are free to move about, it becomes crucial to understand how far they can roam.

We'll still use the same notation for the number of states and entropy of the system, but now these quantities will be functions of both the energy and the volume,

$$S(E,V) = k_B \log \Omega(E,V)$$

The temperature is again given by $1/T = \partial S/\partial E$, where the partial derivative implicitly means that we keep V fixed when we differentiate. But now there is a new, natural quantity that we can consider — the differentiation with respect to V. This also gives a quantity that you're all familiar with — *pressure*, p. Well, almost. The definition is

$$p = T\frac{\partial S}{\partial V} \tag{1.15}$$

To see that this is a sensible definition, we can replay the arguments of Section 1.2.2. Imagine two systems in contact through a moveable partition as shown in the figure above, so that the total volume remains fixed, but system 1 can expand at the expense of system 2 shrinking. The same equilibrium arguments that previously lead to (1.8) now tell us that the volumes of the systems don't change as long as $\partial S/\partial V$ is the same for both systems. Or, in other words, as long as the pressures are equal.

Despite appearances, the definition of pressure actually has little to do with entropy. Roughly speaking, the S in the derivative cancels the factor of S sitting in T. To make

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[1] The data is taken from Chirico and Westrum Jr., J. Chem. Thermodynamics 12 (1980), 311, and shows the spin contribution to the heat capacity of $Tb(OH)_3$

this mathematically precise, consider a system with entropy $S(E, V)$ that undergoes a small change in energy and volume. The change in entropy is

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV$$

Rearranging, and using our definitions (1.7) and (1.15), we can write

$$dE = TdS - pdV \tag{1.16}$$

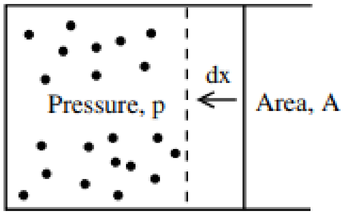

Figure 7: Work Done

The left-hand side is the change in energy of the system. It is easy to interpret the second term on the right-hand side: it is the work done on the system. To see this, consider the diagram on the right. Recall that pressure is force per area. The change of volume in the set-up depicted is dV = Area × dx. So the work done on the system is Force × $dx = (pA)dx = pdV$. To make sure that we've got the minus signs right, remember that if $dV < 0$, we're exerting a force to squeeze the system, increasing its energy. In contrast, if $dV > 0$, the system itself is doing the work and hence losing energy.

Alternatively, you may prefer to run this argument in reverse: if you're happy to equate squeezing the system by dV with doing work, then the discussion above is sufficient to tell you that pressure as defined in (1.15) has the interpretation of force per area.

What is the interpretation of the first term on the right-hand side of (1.16)? It must be some form of energy transferred to the system. It turns out that the correct interpretation of TdS is the amount of *heat* the system absorbs from the surroundings. Much of Section 4 will be concerned with understanding why this is right way to think about TdS and we postpone a full discussion until then.

Equation (1.16) expresses the conservation of energy for a system at finite temperature. It is known as the *First Law of Thermodynamics*. (You may have noticed that we're not doing these laws in order! This too will be rectified in Section 4).

As a final comment, we can now give a slightly more refined definition of the heat capacity (1.9). In fact, there are several different heat capacities which depend on which other variables are kept fixed. Throughout most of these lectures, we will be interested in the heat capacity at fixed volume, denoted C_V,

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V \tag{1.17}$$

Using the first law of thermodynamics (1.16), we see that something special happens when we keep volume constant: the work done term drops out and we have

$$C_V = T \left.\frac{\partial S}{\partial T}\right|_V \tag{1.18}$$

This form emphasises that, as its name suggests, the heat capacity measures the ability of the system to absorb *heat* TdS as opposed to any other form of energy. (Although, admittedly, we still haven't really defined what heat is. As mentioned above, this will have to wait until Section 4).

The equivalence of (1.17) and (1.18) only followed because we kept volume fixed. What is the heat capacity if we keep some other quantity, say pressure, fixed? In this case, the correct definition of heat capacity is the expression analogous to (1.18). So, for example, the heat capacity at constant pressure C_p is defined by

$$C_p = T \left.\frac{\partial S}{\partial T}\right|_p$$

For the next few Sections, we'll only deal with C_V. But we'll return briefly to the relationship between C_V and C_p in Section 4.4.

The Canonical Ensemble:-

The microcanonical ensemble describes systems that have a fixed energy E. From this, we deduce the equilibrium temperature T. However, very often this is not the best way to think about a system. For example, a glass of water sitting on a table has a well defined average energy. But the energy is constantly fluctuating as it interacts with the environment. For such systems, it is often more appropriate to think of them as sitting at fixed temperature T, from which we then deduce the average energy.

To model this, we will consider a system — let's call it S — in contact with a second system which is a large *heat reservoir* – let's call it R. This reservoir is taken to be at some equilibrium temperature T. The term "reservoir" means that the energy of S is negligible compared with that of R. In particular, S can happily absorb or donate energy from or to the reservoir without changing the ambient temperature T.

How are the energy levels of S populated in such a situation? We label the states of S as $|n\rangle$, each of which has energy E_n. The number of microstates of the combined systems S and R is given by the sum over all states of S,

$$\Omega(E_{\text{total}}) = \sum_n \Omega_R(E_{\text{total}} - E_n) \equiv \sum_n \exp\left(\frac{S_R(E_{\text{total}} - E_n)}{k_B}\right)$$

I stress again that the sum above is over all the states of S, rather than over the energy levels of S. (If we'd written the latter, we would have to include a factor of $\Omega_S(E_n)$ in the sum to take into account the degeneracy of states with energy E_n). The fact that

R is a reservoir means that $E_n \ll E_{\text{total}}$. This allows us to Taylor expand the entropy, keeping just the first two terms,

$$\Omega(E_{\text{total}}) \approx \sum_n \exp\left(\frac{S_R(E_{\text{total}})}{k_B} - \frac{\partial S_R}{\partial E_{\text{total}}}\frac{E_n}{k_B}\right)$$

But we know that $\partial S_R/\partial E_{\text{total}} = 1/T$, so we have

$$\Omega(E_{\text{total}}) = e^{S_R(E_{\text{total}})/k_B}\sum_n e^{-E_n/k_BT}$$

We now apply the fundamental assumption of statistical mechanics — that all accessible energy states are equally likely — to the combined system + reservoir. This means that each of the $\Omega(E_{\text{total}})$ states above is equally likely. The number of these states for which the system sits in $|n\rangle$ is $e^{S_R/k_B}e^{-E_n/k_BT}$. So the probabilty that the system sits in state $|n\rangle$ is just the ratio of this number of states to the total number of states,

$$p(n) = \frac{e^{-E_n/k_BT}}{\sum_m e^{-E_m/k_BT}} \qquad (1.19)$$

This is the *Boltzmann distribution*, also known as the *canonical ensemble*. Notice that the details of the reservoir have dropped out. We don't need to know $S_R(E)$ for the reservoir; all that remains of its influence is the temperature T.

The exponential suppression in the Boltzmann distribution means that it is very unlikely that any of the states with $E_n \gg k_BT$ are populated. However, all states with energy $E_n \leq k_BT$ have a decent chance of being occupied. Note that as $T \to 0$, the Boltzmann distribution forces the system into its ground state (i.e. the state with lowest energy); all higher energy states have vanishing probability at zero temperature.

A Density Matrix for the Canonical Ensemble

In statistical mechanics, the inherent probabilities of the quantum world are joined with probabilities that arise from our ignorance of the underlying state. The correct way to describe this is in term of a density matrix, $\hat{\rho}$. The canonical ensemble is really a choice of density matrix,

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z} \tag{1.24}$$

If we make a measurement described by an operator $\hat{\mathcal{O}}$, then the probability that we find ourselves in the eigenstate $|\phi\rangle$ is given by

$$p(\phi) = \langle \phi | \hat{\rho} | \phi \rangle$$

For energy eigenstates, this coincides with our earlier result (1.22). We won't use the language of density matrices in this course, but it is an elegant and conceptually clear framework to describe more formal results.

Energy and Fluctuations

Let's see what information is contained in the partition function. We'll start by thinking about the energy. In the microcanonical ensemble, the energy was fixed. In the canonical ensemble, that is no longer true. However, we can happily compute the average energy,

$$\langle E\rangle = \sum_n p(n)E_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z}$$

But this can be very nicely expressed in terms of the partition function by

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\log Z \tag{1.25}$$

We can also look at the spread of energies about the mean — in other words, about fluctuations in the probability distribution. As usual, this spread is captured by the variance,

$$\Delta E^2 = \langle (E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2$$

This too can be written neatly in terms of the partition function,

$$\Delta E^2 = \frac{\partial^2}{\partial\beta^2}\log Z = -\frac{\partial\langle E\rangle}{\partial\beta} \tag{1.26}$$

There is another expression for the fluctuations that provides some insight. Recall our definition of the heat capacity (1.9) in the microcanonical ensemble. In the canonical ensemble, where the energy is not fixed, the corresponding definition is

$$C_V = \left.\frac{\partial\langle E\rangle}{\partial T}\right|_V$$

Then, since $\beta = 1/k_BT$, the spread of energies in (1.26) can be expressed in terms of the heat capacity as

$$\Delta E^2 = k_BT^2C_V \tag{1.27}$$

There are two important points hiding inside this small equation. The first is that the equation relates two rather different quantities. On the left-hand side, ΔE describes the probabilistic fluctuations in the energy of the system. On the right-hand side, the heat capacity C_V describes the ability of the system to absorb energy. If C_V is large, the system can take in a lot of energy without raising its temperature too much. The equation (1.27) tells us that the fluctuations of the systems are related to the ability of the system to dissipate, or absorb, energy. This is the first example of a more general result known as the *fluctuation-dissipation theorem*.

The other point to take away from (1.27) is the size of the fluctuations as the number of particles N in the system increases. Typically $E \sim N$ and $C_V \sim N$. Which means that the relative size of the fluctuations scales as

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \tag{1.28}$$

The limit $N \to \infty$ in known as the *thermodynamic limit*. The energy becomes peaked closer and closer to the mean value $\langle E \rangle$ and can be treated as essentially fixed. But this was our starting point for the microcanonical ensemble. In the thermodynamic limit, the microcanonical and canonical ensembles coincide.

All the examples that we will discuss in the course will have a *very* large number of particles, N, and we can consider ourselves safely in the thermodynamic limit. For that reason, even in the canonical ensemble, we will often write E for the average energy rather than $\langle E \rangle$.

Free Energy

We've left the most important quantity in the canonical ensemble to last. It is called the *free energy*,

$$F = \langle E \rangle - TS \tag{1.32}$$

There are actually a number of quantities all vying for the name "free energy", but the quantity F is the one that physicists usually work with. When necessary to clarify, it is sometimes referred to as the Helmholtz free energy. The word "free" here doesn't mean "without cost". Energy is never free in that sense. Rather, it should be interpreted as the "available" energy.

Heuristically, the free energy captures the competition between energy and entropy that occurs in a system at constant temperature. Immersed in a heat bath, energy is not necessarily at a premium. Indeed, we saw in the two-state example that the ground state plays little role in the physics at non-zero temperature. Instead, the role of entropy becomes more important: the existence of many high energy states can beat a few low-energy ones.

The fact that the free energy is the appropriate quantity to look at for systems at fixed temperature is also captured by its mathematical properties. Recall, that we started in the microcanonical ensemble by defining entropy $S = S(E, V)$. If we invert this expression, then we can equally well think of energy as a function of entropy and volume: $E = E(S, V)$. This is reflected in the first law of thermodynamics (1.16) which reads $dE = TdS - pdV$. However, if we look at small variations in F, we get

$$dF = d\langle E\rangle - d(TS) = -SdT - pdV \tag{1.33}$$

This form of the variation is telling us that we should think of the free energy as a function of temperature and volume: $F = F(T, V)$. Mathematically, F is a Legendre transform of E.

Given the free energy, the variation (1.33) tells us how to get back the entropy,

$$S = -\left.\frac{\partial F}{\partial T}\right|_V \tag{1.34}$$

Similarly, the pressure is given by

$$p = -\left.\frac{\partial F}{\partial V}\right|_T \tag{1.35}$$

The free energy is the most important quantity at fixed temperature. It is also the quantity that is most directly related to the partition function Z:

$$F = -k_B T \log Z \tag{1.36}$$

This relationship follows from (1.25) and (1.31). Using the identity $\partial/\partial\beta = -k_B T^2 \partial/\partial T$, these expressions allow us to write the free energy as

$$\begin{aligned} F = E - TS &= k_B T^2 \frac{\partial}{\partial T} \log Z - k_B T \frac{\partial}{\partial T}(T \log Z) \\ &= -k_B T \log Z \end{aligned}$$

as promised.

Grand Canonical Ensemble

When we made the transition from microcanonical to canonical ensemble, we were no longer so rigid in our insistence that the system has a fixed energy. Rather it could freely exchange energy with the surrounding reservoir, which was kept at a fixed temperature. We could now imagine the same scenario with any other conserved quantity. For example, if particles are free to move between the system and the reservoir, then N is no longer fixed. In such a situation, we will require that the reservoir sits at fixed chemical potential μ as well as fixed temperature T.

The probability distribution that we need to use in this case is called the *grand canonical ensemble*. The probability of finding the system in a state $|n\rangle$ depends on both the energy E_n and the particle number N_n. (Notice that because N is conserved, the quantum mechanical operator necessarily commutes with the Hamiltonian so there is no difficulty in assigning both energy and particle number to each state). We introduce the *grand canonical partition function*

$$\mathcal{Z}(T, \mu, V) = \sum_n e^{-\beta(E_n - \mu N_n)} \tag{1.39}$$

Re-running the argument that we used for the canonical ensemble, we find the probability that the system is in state $|n\rangle$ to be

$$p(n) = \frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}}$$

In the canonical ensemble, all the information that we need is contained within the partition function Z. In the grand canonical ensemble it is contained within $\mathcal{Z}$. The entropy (1.30) is once again given by

$$S = k_B \frac{\partial}{\partial T}(T \log \mathcal{Z}) \tag{1.40}$$

while differentiating with respect to β gives us

$$\langle E \rangle - \mu \langle N \rangle = -\frac{\partial}{\partial \beta} \log \mathcal{Z} \tag{1.41}$$

The average particle number $\langle N \rangle$ in the system can then be separately extracted by

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \mathcal{Z} \tag{1.42}$$

and its fluctuations,

$$\Delta N^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \log \mathcal{Z} = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \tag{1.43}$$

Just as the average energy is determined by the temperature in the canonical ensemble, here the average particle number is determined by the chemical potential. The grand canonical ensemble will simplify several calculations later, especially when we come to discuss Bose and Fermi gases in Section 3.

The relative size of these fluctuations scales in the same way as the energy fluctuations, $\Delta N / \langle N \rangle \sim 1/\sqrt{\langle N \rangle}$, and in the thermodynamic limit $N \to \infty$ results from all three ensembles coincide. For this reason, we will drop the averaging brackets $\langle \cdot \rangle$ from our notation and simply refer to the average particle number as N.

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UNIT-4

Definition of Thermodynamic Phases and Phase Transitions

There are various thermodynamic variables one can use to describe matter in thermal equilibrium, some of the common ones being: mass or number density ρ, energy density e, temperature T, pressure P, and chemical potential μ (assuming for simplicity that the material is composed of one pure substance, not a mixture such as brass). By definition the states of a "simple" system can be parameterized by two such (independent) variables, in which case the others can be regarded as functions of these. We will assume we are modelling a simple material. Then a particularly good choice for independent variables is T and μ. It is a fundamental fact of thermodynamics that the pressure P is a convex function of these variables, and, in particular, this convexity embodies certain mechanical and thermal stability properties of the system. Moreover, all thermodynamic properties of the material can be obtained from P as a function of T and μ by differentiation.[1] We give the following definitions.

Definitions: A thermodynamic phase of a simple material is an open, connected region in the space of thermodynamic states parametrized by the variables T and μ, the pressure P being analytic in T and μ. Specifically, P is analytic in T and μ at (T_0, μ_0) if it has a convergent power series expansion in a ball about (T_0, μ_0) that gives its values. Phase transitions occur on crossing a phase boundary. See Figure 1.

The graph of $P = P(T, \mu)$ is not only convex but (for all reasonable physical systems) also has no (flat) facets. We use this in our definition of phase; without this property there would typically be open regions of states representing the coexistence of distinct phases. Figure 2 below illustrates how the choice of independent variables can lead to the appearance of domains representing two or more coexisting phases. Note in particular the isothermal (i.e., constant T) "tie lines" connecting the distinct phases that can coexist at the range of overall intermediate densities spanned at a fixed temperature.

The figures also illustrate an intrinsic difference between vapor and liquid "phases", which can be analytically connected, and between these regions of the fluid phase and the solid phase, which cannot be so connected. Note that in these figures failure of the analyticity of the function P occurs on curves in the (T, μ) and (T, ρ) planes. In the modern literature[2] an important distinction is made between "field" variables and "density" variables, which helps to explain various consequences of the choice of independent and dependent variables.

The foregoing constitutes a "thermodynamic" description of phases and phase transitions. There is a deeper description, that of *statistical mechanics*, deeper in that it allows natural ("molecular") models from which one can in principle compute the pressure as a function of T and μ. Statistical mechanics can be based on either quantum or classical mechanics; we will use the latter here for convenience.

In the statistical mechanical description the thermodynamic states are realized or represented as probability measures on a certain space K, the measures still parameterized by thermodynamic variables as above (two variables for our simple system, say, specifically temperature T and chemical potential μ). The space K is, in a common model of a simple material, the space of all possible positions x and momenta p of infinitely many point particles. We will use the notation $\mathbf{x} = \{x_1, x_2, \ldots\}$ and $\mathbf{p} = \{p_1, p_2, \ldots\}$ to denote the sets of the position and momentum variables for all the particles.

It is valuable, in particular, to consider a finite system of N particles contained in a reasonably shaped domain, say Ω, of volume V. In this case the probability densities, on the disjoint union $\cup_N S_N$ of the $(\mathbf{x}, \mathbf{p})$ spaces $S_N = \Omega^N \times \mathbb{R}^{3N}$ for N particles, are proportional to the weights

$$f_N(T, \mu; \mathbf{x}, \mathbf{p}) = e^{-\beta E_N(\mathbf{x}, \mathbf{p}) + \beta\mu N}, \tag{1}$$

while the overall normalization constant (or "partition function") is

$$\Xi_V(T, \mu) = 1 + \sum_{N=1}^{\infty} \int d\mathbf{x} d\mathbf{p} f_N(T, \mu; \mathbf{x}, \mathbf{p}), \tag{2}$$

where $\beta = 1/k_B T$, k_B being Boltzmann's renowned constant.

The structure of the energy E_N is determined only when one settles on the type of "interactions" the constituent particles can undergo; that not only depends on the material being modelled but also on what environment (external forces, etc.) one may want to impose on the system. In the simplest case the particles are assumed to interact only among themselves, through some translation invariant "interaction potential" $\varphi(x_i - x_j)$ which decays to zero sufficiently rapidly as the separation $|x_i - x_j| \to \infty$. The "kinetic energy" of the j^{th} particle is, classically, $p_j^2/2m$, m being the mass of the particle. The total energy is then

$$E_N = \sum_j \frac{p_j^2}{2m} + \frac{1}{2} \sum_{i,j:i \neq j} \varphi(x_i - x_j). \tag{3}$$

And the so-called "grand canonical" pressure of the finite-volume system is given by

$$P_V(T, \mu) = \frac{k_B T \ln[\Xi_V(T, \mu)]}{V}. \tag{4}$$

(Note that the convexity of $P_V(T, \mu)$ is ensured by this formulation.) However, it is not hard to see for reasonable interaction potentials φ that the pressure P_V as a function of T and μ is everywhere analytic. Consequently, in order to model a sharp phase transition it is necessary to consider the thermodynamic limit[3]

$$P(T, \mu) = \lim_{V \to \infty} P_V(T, \mu). \tag{5}$$

Then $P(T, \mu)$ may be identified as the thermodynamic pressure to which our definitions of a phase and a phase transition applies.

Footnotes

1. For this reason the function $P(T, \mu)$ is referred to as a "thermodynamic potential". Alternative potentials (for describing the same physical system) follow by Legendre transforms.
2. R.B. Griffiths and J.C. Wheeler, Phys. Rev. A **2** (1970) 1047-1064.
3. The proof of the existence of the thermodynamic limit requires conditions on the interaction potential $\varphi(x)$ for $|x| \to 0$ and $|x| \to \infty$ and on the sequence of domains Ω_k as $V_k \to \infty$ with $k \to \infty$. See M.E. Fisher, Arch. Ratl. Mech. Anal. **17** (1964) 377-410.

Figures

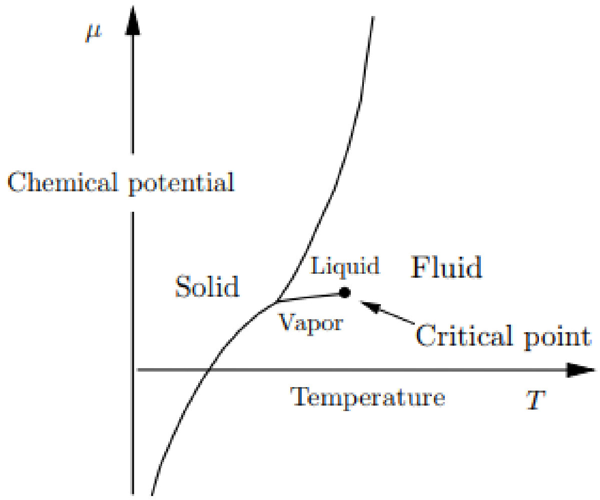


Fig 1. A simple phase diagram in the (μ, T) plane.

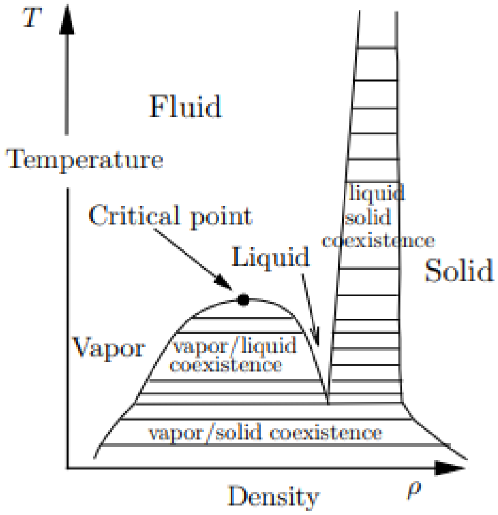


Fig 2. A simple (T, ρ) diagram illustrating coexisting phases.

Maxwell-Boltzmann statistics

Let us consider an ensemble of "hypothetical" identical particles which can be individually identified. Since it does not obey the principle of quantum indistinguishability, it is often referred to as classical particles.

The thermodynamic partition function for distinguishable particles should be modified from Eq. (2.9) since all particles are "different" or have "unique labels" in an ensemble of distinguishable particles,

$$\begin{aligned} Z &= \sum_{\{n_1, n_2, \cdots\}} \left(\frac{N!}{n_1! n_2! \cdots} \right) e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)} \\ &= \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \cdots \right)^N \quad , \qquad (2.23) \\ \log Z &= N \log \left(\sum_r e^{-\beta\varepsilon_r} \right) \quad . \qquad (2.24) \end{aligned}$$

Using Eq. (2.23) in Eq. (2.17), we obtain the mean particle number in a specific state,

$$\begin{aligned} \langle n_s \rangle &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_s} \log Z \\ &= N \times \frac{e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}} \quad . \qquad (2.25) \end{aligned}$$

This is a Maxwell-Boltzmann distribution. The variance of the particle number is calculated using Eq. (2.19),

$$\begin{aligned}\langle \Delta n_s^2 \rangle &= -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\langle n_s \rangle \\ &= \langle n_s \rangle \left(1 - \frac{\langle n_s \rangle}{N}\right) \\ &\simeq \langle n_s \rangle \quad . \end{aligned} \tag{2.26}$$

The above result suggests that the probability of finding n_s particles in a specific state in the Maxwell-Boltzmann distribution obeys a Poisson distribution.

Bose-Einstein statistics

If an ensemble of identical bosonic particles is at thermal equilibrium, it is enough to specify how many particles are in each state $\{n_1, n_2, \cdots\}$. Therefore, the mean particle number in a microscopic state s is

$$\begin{aligned}\langle n_s \rangle &= \frac{\displaystyle\sum_{\{n_1,n_2,\cdots\}} n_s e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)}}{\displaystyle\sum_{\{n_1,n_2,\cdots\}} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)}} \\ &= \frac{\displaystyle\sum_{n_s} n_s e^{-\beta\varepsilon_s n_s} \cdot \sum^{(s)} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)}}{\displaystyle\sum_{n_s} e^{-\beta\varepsilon_s n_s} \cdot \sum^{(s)} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)}} \quad . \end{aligned} \tag{2.27}$$

Here $\sum^{(s)}$ stands for the summation over $\{n_1, n_2, \cdots\}$ except for the particular microscopic state s.

If the particular microscopic state s does not have a particle, i.e. $n_s = 0$, N particles must be distributed over the states other than s,

$$\begin{aligned}Z_s(N) &= \sum^{(s)} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)} \\ \sum_r^{(s)} n_r &= N \quad . \end{aligned} \tag{2.28}$$

If the particular state s has one particle, i.e. $n_s = 1$, the remaining $N-1$ particles must be distributed over the states other than s,

$$\begin{aligned} Z_s(N-1) &= \sum^{(s)} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \cdots)} \\ \sum_r^{(s)} n_r &= N-1 \quad . \end{aligned} \tag{2.29}$$

Using these notations, Eq. (2.27) can be rewritten as

$$\langle n_s \rangle = \frac{0 \times Z_s(N) + e^{-\beta\varepsilon_s} Z_s(N-1) + 2e^{-2\beta\varepsilon_s} Z_s(N-2) + \cdots}{Z_s(N) + e^{-\beta\varepsilon_s} Z_s(N-1) + e^{-2\beta\varepsilon_s} Z_s(N-2) + \cdots} \quad . \tag{2.30}$$

In order to proceed the evaluation of Eq. (2.30), we introduce a new parameter α by

$$\begin{aligned} \log Z_s(N - \Delta N) &\simeq \log Z_s(N) + \left[\frac{\partial}{\partial N} \log Z_s(N)\right](-\Delta N) \\ &= \log Z_s(N) - \alpha_s \Delta N \quad , \end{aligned} \tag{2.31}$$

where

$$\alpha_s = \frac{\partial}{\partial N} \log Z_s(N) \simeq \frac{\partial}{\partial N} \log Z(N) = \alpha \quad . \tag{2.32}$$

Eq.(2.32) holds by the following reason. Since $Z_s(N)$ is a summation over very many states, variation of its logarithm with respect to the total number of particles should be insensitive as to which particular state s is omitted. Using Eq. (2.32) in Eq. (2.31), we obtain

$$Z_s(N - \Delta N) = Z_s(N) e^{-\alpha \Delta N} \quad , \tag{2.33}$$

$$\begin{aligned} \langle n_s \rangle &= \frac{Z_s(N)\left[0 + e^{-\beta\varepsilon_s - \alpha} + 2e^{-2\beta\varepsilon_s - 2\alpha} + \cdots\right]}{Z_s(N)\left[1 + e^{-\beta\varepsilon_s - \alpha} + e^{-2\beta\varepsilon_s - 2\alpha} + \cdots\right]} \\ &= \frac{\sum_{n_s} n_s e^{-n_s(\beta\varepsilon_s + \alpha)}}{\sum_{n_s} e^{-n_s(\beta\varepsilon_s + \alpha)}} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_s} \log\left(\sum_{n_s} e^{-n_s(\beta\varepsilon_s + \alpha)}\right) \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_s} \log\left[\frac{1}{1 - e^{-(\beta\varepsilon_s + \alpha)}}\right] \\ &= \frac{1}{e^{\beta\varepsilon_s + \alpha} - 1} \quad . \end{aligned} \tag{2.34}$$

The parameter α is determined by the total number of particles,

$$N=\sum_r\langle n_r\rangle=\sum_r\frac{1}{e^{\beta\varepsilon_r+\alpha}-1}\quad . \tag{2.35}$$

Rewriting α in terms of $\mu=-\frac{\alpha}{\beta}=-k_BT\alpha$, Eq. (2.34) is reduced to

$$\langle n_s\rangle=\frac{1}{e^{\beta(\varepsilon_s-\mu)}-1}\quad . \tag{2.36}$$

This is a Bose-Einstein distribution and μ is called a chemical potential. Note that the chemical potential μ must be always smaller than the minimum energy $\varepsilon_{s,\mathrm{min}}$ of the system to conserve the particle number.

The variance in the particle number is

$$\begin{aligned}\langle\Delta n_s^2\rangle &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\langle n_s\rangle\\ &= \frac{1}{\beta}\cdot\frac{e^{\beta(\varepsilon_s-\mu)}}{\left[e^{\beta(\varepsilon_s-\mu)}-1\right]^2}\cdot\beta\left(1-\frac{\partial\mu}{\partial\varepsilon_s}\right)\\ &= \langle n_s\rangle(1+\langle n_s\rangle)\left(1-\frac{\partial\mu}{\partial\varepsilon_s}\right)\quad .\end{aligned} \tag{2.37}$$

Unless a temperature is so low that only a very few states are occupied, a small change of ε_s leaves μ unchanged and we have $\frac{\partial\mu}{\partial\varepsilon_s}=0$. In this case, we have the two limiting cases:

$$\langle\Delta n_s^2\rangle=\begin{cases}\langle n_s\rangle^2 & : \ \varepsilon_s-\mu\ll k_BT \quad (\mathrm{quantumdegenerategas})\\ \langle n_s\rangle & : \ \varepsilon_s-\mu\gg k_BT \quad (\mathrm{non-degenerategas})\end{cases}\quad . \tag{2.38}$$

If a temperature is very low, most of the particles are at the lowest energy ground state or nearly degenerate low-energy state, which satisfy $\varepsilon_s-\mu\ll k_BT$. Such a situation is called Bose-Einstein condensation.

Fermi-Dirac statistics

Due to the Pauli exclusion principle, each state has the occupation number, either 0 or 1, for an ensemble of identical Fermionic particles. Thus, the mean particle number is

$$\begin{aligned}\langle n_s\rangle &= \frac{\sum_{n_s} n_s e^{-\beta\varepsilon_s n_s}\cdot\sum^{(s)} e^{-\beta(\varepsilon_1 n_1+\varepsilon_2 n_2+\cdots)}}{\sum_{n_s} e^{-\beta\varepsilon_s n_s}\cdot\sum^{(s)} e^{-\beta(\varepsilon_1 n_1+\varepsilon_2 n_2+\cdots)}}\\ &= \frac{0\times Z_s(N)+e^{-\beta\varepsilon_s}Z_s(N-1)}{Z_s(N)+e^{-\beta\varepsilon_s}Z_s(N-1)}\end{aligned}$$

$$\begin{aligned} &= \frac{1}{e^{\beta\varepsilon_s+\alpha}+1} \\ &= \frac{1}{e^{\beta(\varepsilon_s-\mu)}+1} \quad , \end{aligned} \tag{2.41}$$

where $Z_s(N-1) = Z_s(N)e^{-\alpha}$ and $\mu = -\frac{\alpha}{\beta}$ are used. Note that there is no constraint for a chemical potential μ with respect to ε_s in this case. The chemical potential can be much smaller or much larger than the minimum energy $\varepsilon_{s,\min}$. The variance in the particle number is

$$\begin{aligned} \langle \Delta n_s^2 \rangle &= -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\langle n_s \rangle \\ &= \langle n_s \rangle \Big(1 - \langle n_s \rangle\Big)\left(1 - \frac{\partial \mu}{\partial \varepsilon_s}\right) \\ &\simeq \langle n_s \rangle \Big(1 - \langle n_s \rangle\Big) \quad . \end{aligned} \tag{2.42}$$

The maximum variance is $\langle \Delta n_s^2 \rangle = \frac{1}{4}$ at $\varepsilon_s = \mu$ (at Fermi energy) and the variance disappears at $\varepsilon_s \ll \mu$ due to constant and full occupation of $n_s = 1$. If a temperature is very low, most of the particles are under this full occupation and there are very few particles near the chemical potential and subject to a finite variance $\langle \Delta n_s^2 \rangle$. Such a gas is called Fermi degeneracy.

It is interesting to note that the quantum statistics play an important role in the particle distribution when a temperature is very low and only a few states are occupied. When a temperature is very high and the particles are distributed over very many states the Bose-Einstein distribution and the Fermi-Dirac distribution become indistinguishable from the (classical) Maxwell-Boltzmann distribution because the mean particle number per state is much smaller than one at such a high temperature limit. However, for photon statistics, the mean particle number can be much greater than one whenever $\varepsilon_s \ll k_B T$ and so the photon statistics can never be reduced to the (classical) Maxwell-Boltzmann statistics no matter how high a temperature is.

Photon statistics

There is another type of bosonic particles, which are photons and phonons. Those particles are quantized electromagnetic fields and lattice vibrations. Such elementary excitations do not have any constraint on the total number of particles when a temperature is varied. Thus we cannot determine a chemical potential μ through the relation Eq. (2.35). We set the chemical potential μ to be zero for this case.

The mean particle number is

$$\begin{aligned} \langle n_s \rangle &= \frac{\sum\limits_{n_s} n_s e^{-\beta\varepsilon_s n_s}}{\sum\limits_{n_s} e^{-\beta\varepsilon_s n_s}} \\ &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\log\left(\sum_{n_s} e^{-\beta\varepsilon_s n_s}\right) \\ &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\log\left[\frac{1}{1-e^{-\beta\varepsilon_s}}\right] \\ &= \frac{1}{e^{\beta\varepsilon_s}-1} \quad . \end{aligned} \tag{2.39}$$

Here $\varepsilon_s = \hbar\omega_s$ is an energy of photon or phonon, which is uniquely determined by the oscillation frequency ω_s. This is called a Planck distribution. The variance in the particle number is

$$\begin{aligned} \langle \Delta n_s^2 \rangle &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\langle n_s \rangle \\ &= \langle n_s \rangle \big(1 + \langle n_s \rangle\big) \\ &= \begin{cases} \langle n_s \rangle^2 & : \ \varepsilon_s \ll k_B T \\ \langle n_s \rangle & : \ \varepsilon_s \gg k_B T \end{cases} \quad . \end{aligned} \tag{2.40}$$

UNIT-5

Contributions of physicists

Satyendra Nath Bose Biography

Physicist, Scientist (1894–1974)

Synopsis

Physicist Satyendra Nath Bose, born on January 1, 1894, in Calcutta, India, discovered what became known as bosons and went on to work with Albert Einstein to define one of two basic classes of subatomic particles. Much of the credit for discovering the boson, or "God particle," was given to British physicist Peter Higgs, much to the chagrin of the Indian government and people.

Early Life

Physicist Satyendra Nath Bose was born in Calcutta (now Kolkata), West Bengal, India, on January 1, 1894, the eldest and only male of seven children. Bose was a brainiac early on. He passed the entrance exam to the Hindu School, one of India's oldest schools, with flying colors and stood fifth in the order of merit. From there, Bose attended

Presidency College, where he took an intermediate science course and studied with renowned scientists Jagadish Chandra Bose and Prafulla Chandra Ray.

Research and Teaching Career

While studying at the University of Calcutta, Bose also served as a lecturer in the physics department. In 1919, he and Saha prepared the first English-language book based on German and French translations of Albert Einstein's original special and general relativity papers.

Meghnad Saha: Physicist and nationalist

Meghnad Saha (1893–1956) was an Indian physicist who did much of his work in the last decades of British colonial rule. In the 1920s he made important contributions to the theory of thermal ionization and its application to stellar spectra. He would continue to be a leader in modern physics in colonial and postcolonial India and to earn international renown. His story is particularly noteworthy for at least two reasons. First, he was born in an obscure village in Bengal, to a lower-caste family with no educational background; he had to work hard to transcend the stereotypes associated with his social status. Second, he saw his work as facilitating the process of decolonization, a goal that was finally achieved with the Indian Independence Act of 1947.

Norwegian astrophysicist Svein Rosseland, in the introduction to his well-known *Theoretical Astrophysics: Atomic Theory and the Analysis of Stellar Atmospheres and Envelopes*(Clarendon Press, 1936), remarked on the importance of Saha's contributions:

> Although Bohr must thus be considered the pioneer in the field [of atomic theory], it was the Indian physicist Megh Nad Saha who (1920) first attempted to develop a consistent theory of the spectral sequence of the stars from the point of view of atomic theory… . The impetus given to astrophysics by Saha's work can scarcely be overestimated, as nearly all later progress in this field has been influenced by it and much of the subsequent work has the character of refinements of Saha's ideas.

EARLY LIFE

Saha was born in 1893 in Seoratali, in the Dacca (now Dhaka) district of what is now Bangladesh. He was the fifth of eight children born to Jagannath Saha, a poor shopkeeper, and his wife, Bhubaneshwari Devi. His elder brother failed in high school, so his father decided that Meghnad and his brother should work at selling groceries. However, Meghnad's mother and uncle intervened and allowed him to continue his high school education. In 1905 he went to the city of Dacca where, in preparation for college, he attended the Government Collegiate School with a full scholarship. It was an eventful year in the history of India: George Nathaniel Curzon partitioned Bengal into Muslim-majority East Bengal (which included the Dacca district) and Hindu-majority West Bengal. That event sparked off a nationalist movement manifested by protests all over Bengal. When the British lieutenant governor of Eastern Bengal and Assam, Joseph Bampfylde Fuller, visited Dacca, the citizens there organized a boycott. All students who participated in the protests—Saha among them—were expelled. As a consequence, he lost his scholarship; his brothers helped him survive.

In 1911 Saha graduated from Dacca College (shown in figure 1) with the equivalent of a US high school degree. He ranked first in physics and mathematics but third in the whole intermediate science examination. He then joined Presidency College at the University of Calcutta, where he worked toward a bachelor's of science degree in mixed mathematics, which he received in 1913. While at Calcutta, Saha boarded at the Eden Hindu Hostel (see figure 2), which was college housing. There he experienced painful discrimination because he belonged to the *shudra*, the lowest tier of the Indian caste system. The system was particularly problematic in the early 20th century in India; unfortunately, prejudice persists in parts of the country even today. When Saha was at the Eden Hindu Hostel, some students objected to eating in the same dining hall with him because of his caste status. Some Brahmins (the highest, priestly caste) also prevented him from making an offering to the goddess of learning, Mother Saraswati.

James Clerk Maxwell, (born June 13, 1831, Edinburgh, Scotland—died November 5, 1879, Cambridge, Cambridgeshire, England), Scottish physicist best known for his formulation of electromagnetic theory. He is regarded by most modern physicists as the scientist of the 19th century who had the greatest influence on 20th-century physics, and he is ranked with Sir Isaac Newton and Albert Einsteinfor the fundamental nature of his contributions. In 1931, on the 100th anniversary of Maxwell's birth, Einstein described the change in the conception of reality in physics that resulted from Maxwell's work as "the most profound and the most fruitful that physics has experienced since the time of Newton."

The concept of electromagnetic radiation originated with Maxwell, and his field equations, based on Michael Faraday's observations of the electric and magnetic lines of force, paved the way for Einstein's special theory of relativity, which established the equivalence of mass and energy. Maxwell's ideas also ushered in the other major innovation of 20th-century physics, the quantum theory. His description of electromagnetic radiation led to the development (according to classical theory) of the ultimately unsatisfactory law of heat radiation, which prompted Max Planck's formulation of the quantum hypothesis—i.e., the theory that radiant-heat energy is emitted only in finite amounts, or quanta. The interaction between electromagnetic radiation and matter, integral to Planck's hypothesis, in turn has played a central role in the development of the theory of the structure of atoms and molecules.

Rudolf Clausius

Rudolf Clausius, in full **Rudolf Julius Emanuel Clausius**, (born January 2, 1822, Köslin, Prussia[Poland]—died August 24, 1888, Bonn, Germany), German mathematical physicist who formulated the second law of thermodynamics and is credited with making thermodynamics a science.

Clausius was appointed professor of physics at the Artillery and Engineering School at Berlin in 1850, the same year in which he presented a paper stating the second law of thermodynamics in the well-known form: "Heat cannot of itself pass from a colder to a hotter body." He applied his results to an exhaustive development of the theory of the steam engine, stressing the concept of entropy(dissipation of available energy). He became professor of physics at Zürich Polytechnikum in 1855, and, two years later, contributed to the theory of electrolysis (the breaking down of a compound by electricity) by suggesting that molecules are made up of continually interchanging atoms and that electric force does not cause but simply directs the interchange. This view later was used as the basis of the theory of electrolytic dissociation (breakdown of molecules into charged atoms or ions).

He became professor of physics at the University of Würzburg in 1867 and at the University of Bonn in 1869. In molecular physics, Clausius restated the French physicist Sadi Carnot's principle concerning efficiency of heat engines and thus provided a much sounder basis for the theory of heat.

Ludwig Boltzmann

Ludwig Boltzmann, in full **Ludwig Eduard Boltzmann**, (born February 20, 1844, Vienna, Austria—died September 5, 1906, Duino, Italy), physicist whose greatest achievement was in the development of statistical mechanics, which explains and predicts how the properties of atoms (such as mass, charge, and structure) determine the visible properties of matter (such as viscosity, thermal conductivity, and diffusion).

After receiving his doctorate from the University of Vienna in 1866, Boltzmann held professorships in mathematics and physics at Vienna, Graz, Munich, and Leipzig.

In the 1870s Boltzmann published a series of papers in which he showed that the second law of thermodynamics, which concerns energy exchange, could be explained by applying the laws of mechanics and the theory of probability to the motions of the atoms. In so doing, he made clear that the second law is essentially statistical and that a system approaches a state of thermodynamic equilibrium (uniform energy distribution throughout) because equilibrium is overwhelmingly the most probable state of a material system. During these investigations Boltzmann worked out the general law for the distribution of energy among the various parts of a system at a specific temperature and derived the theorem of equipartition of energy (Maxwell-Boltzmann distribution law). This law states that the average amount of energy involved in each different direction of motion of an atom is the same. He derived an equation for the change of the distribution of energy among atoms due to atomic collisions and laid the foundations of statistical mechanics.

Boltzmann was also one of the first continental scientists to recognize the importance of the electromagnetic theory proposed by James Clerk Maxwell of England. Though his work on statistical mechanics was strongly attacked and long-misunderstood, his conclusions were finally supported by the discoveries in atomic physics that began shortly before 1900 and by recognition that fluctuation phenomena, such as Brownian motion (random movement of microscopic particles suspended in a fluid), could be explained only by statistical mechanics.

James Prescott Joule

Early Life and Education:

Born in Salford, Lancashire on December 24, 1818, James Prescott Joule's father, Benjamin Joule was a rich brewer, and his mother was Alice Prescott. James was mostly home schooled due to being delicate in health. He studied arithmetic and geometry under John Dalton at the Manchester Literary and Philosophical Society. He was later taught by famous scientist and lecturer, John Davies.

At the age of fifteen he started working in the brewery in addition to his studies. James enjoyed experimenting with electricity and a servant girl became unconscious as he inadvertently gave her electric shocks.

Contributions and Achievements:

Joule managed the family brewery from 1837 to 1856 and he carried out experiments in laboratories in his house and in the brewery.

His first experiments concerned electric motors with a view to replacing the steam engines in the brewery with electric ones. This led him to discovering "Joules Law" in 1840.

He established a relationship between the flow of current through a resistance and the heat generated. Joule's law states that the amount of heat per second that develops in a wire carrying a current is proportional to the electrical resistance of the wire and the square of the current.

$P = I^2R$ where P = Power, I = Current and R = Resistance

Joule then carried out experiments using a paddlewheel and calorimeter and in 1843 Joule announced his determination of the amount of work required to produce a unit of heat (the mechanical equivalent of heat).

The results his experiments were fully described in his famous 1845 paper "On the Mechanical Equivalent of Heat" and they established that heat and mechanical work are both forms of energy. His efforts became the cornerstone of the theory of conversation of energy (the First Law of Thermodynamics).

He collaborated with Lord Kelvin on the formulation of the absolute scale of temperature. In 1852 they discovered the Joule-Thomson effect, showing that that when gas is expanded, without production of work, its temperature falls. This concept was later used in refrigeration.

Joule also carried out extensive research on magnetostriction; a property of ferromagnetic materials that makes them modify their shapes when exposed to a magnetic field. He was the first scientist to identify this property in 1842 during an experiment with a sample of nickel.

He is also credited with the first-ever calculation the velocity of a gas molecule.

The derived unit of energy or work, the Joule, (J) is named after him.

Joule was elected to the Royal Society of London in 1850 and he received the Royal Medal in 1852 for his paper “on the mechanical equivalent of heat”.

In 1870 he was awarded the prestigious Copley Medal of the Royal Society “for his experimental researches on the dynamical theory of heat”. He also served as the president of the British Association for the Advancement of Science.

Personal, Later Life and Death:

In 1847, Joule married Amelia Grimes and they had two sons and a daughter. Amelia and his second son both died in 1854.

James Prescott Joule died on October 11, 1889 in Sale, Greater Manchester, England after a long illness. He was 70 years old.

Wilhelm Wien

Wilhelm Wien, in full **Wilhelm Carl Werner Otto Fritz Franz Wien**, (born January 13, 1864, Gaffken, Prussia [now Parusnoye, Russia]—died August 30, 1928, Munich, Germany), German physicist who received the Nobel Prize for Physics in 1911 for his displacement law concerning the radiation emitted by the perfectly efficient blackbody (a surface that absorbs all radiant energy falling on it).

Wien obtained his doctorate at the University of Berlin in 1886 and soon began to work on the problem of radiation. Although the radiation emitted from a blackbody is distributed over a wide range of wavelengths, there is an intermediate wavelength at which the radiation reaches a maximum. In 1893 Wien stated in his law that this maximum wavelength is inversely proportional to the absolute temperature of the body. Because the accuracy of Wien’s law declined for longer wavelengths, Max Planck was led to further investigations culminating in his quantum theory of radiation.

Wien was appointed professor of physics at the University of Giessen in 1899 and at the University of Munich in 1920. He also made contributions in the study of cathode rays (electron beams), X rays, and canal rays (positively charged atomic beams). His autobiography was published under the title *Aus dem Leben und Wirken eines Physikers* (1930; “From the Life and Work of a Physicist”).

Albert Einstein

Albert Einstein**, (born March 14, 1879, Ulm, Württemberg, Germany—died April 18, 1955, Princeton, New Jersey, U.S.), German-born physicist who developed the special and general theories of relativity and won the Nobel Prize for Physics in 1921 for his explanation of the photoelectric effect. Einstein is generally considered the most influential physicist of the 20th century.**

Childhood And Education

Einstein's parents were secular, middle-class Jews. His father, Hermann Einstein, was originally a featherbed salesman and later ran an electrochemical factory with moderate success. His mother, the former Pauline Koch, ran the family household. He had one sister, Maria (who went by the name Maja), born two years after Albert.

Max Planck

Max Planck, in full **Max Karl Ernst Ludwig Planck**, (born April 23, 1858, Kiel, Schleswig [Germany]—died October 4, 1947, Göttingen, Germany), German theoretical physicist who originated quantum theory, which won him the Nobel Prize for Physics in 1918.

Planck made many contributions to theoretical physics, but his fame rests primarily on his role as originator of the quantum theory. This theory revolutionized our understanding of atomic and subatomic processes, just as Albert Einstein's theory of relativityrevolutionized our understanding of space and time. Together they constitute the fundamental theories of 20th-century physics. Both have forced humankind to revise some of the most-cherished philosophical beliefs, and both have led to industrial and military applications that affect every aspect of modern life.

Early Life

Max Karl Ernst Ludwig Planck was the sixth child of a distinguished jurist and professor of law at the University of Kiel. The long family tradition of devotion to church and state, excellence in scholarship, incorruptibility, conservatism, idealism, reliability, and generosity became deeply ingrained in Planck's own life and work. When Planck was nine years old, his father received an appointment at the University of Munich, and Planck entered the city's renowned Maximilian Gymnasium, where a teacher, Hermann Müller, stimulated his interest in physics and mathematics. But

Planck excelled in all subjects, and after graduation at age 17 he faced a difficult career decision. He ultimately chose physics over classical philology or music because he had dispassionately reached the conclusion that it was in physics that his greatest originality lay. Music, nonetheless, remained an integral part of his life. He possessed the gift of absolute pitch and was an excellent pianist who daily found serenity and delight at the keyboard, enjoying especially the works of Schubert and Brahms. He also loved the outdoors, taking long walks each day and hiking and climbing in the mountains on vacations, even in advanced old age.

Planck entered the University of Munich in the fall of 1874 but found little encouragement there from physics professor Philipp von Jolly. During a year spent at the University of Berlin (1877–78), he was unimpressed by the lectures of Hermann von Helmholtz and Gustav Robert Kirchhoff, despite their eminence as research scientists. His intellectual capacities were, however, brought to a focus as the result of his independent study, especially of Rudolf Clausius's writings on thermodynamics. Returning to Munich, he received his doctoral degree in July 1879 (the year of Einstein's birth) at the unusually young age of 21. The following year he completed his *Habilitationsschrift* (qualifying dissertation) at Munich and became a *Privatdozent* (lecturer). In 1885, with the help of his father's professional connections, he was appointed *ausserordentlicher Professor* (associate professor) at the University of Kiel. In 1889, after the death of Kirchhoff, Planck received an appointment to the University of Berlin, where he came to venerate Helmholtz as a mentor and colleague. In 1892 he was promoted to *ordentlicher Professor* (full professor). He had only nine doctoral students altogether, but his Berlin lectures on all branches of theoretical physics went through many editions and exerted great influence. He remained in Berlin for the rest of his active life.

Planck recalled that his "original decision to devote myself to science was a direct result of the discovery…that the laws of human reasoning coincide with the laws governing the sequences of the impressions we receive from the world about us; that, therefore, pure reasoning can enable man to gain an insight into the mechanism of the [world]…." He deliberately decided, in other words, to become a theoretical physicist at a time when theoretical physics was not yet recognized as a discipline in its own right. But he went further: he concluded that the existence of physical laws presupposes that the "outside world is something independent from man, something absolute, and the quest for the laws which apply to this absolute appeared…as the most sublime scientific pursuit in life."

The first instance of an absolute in nature that impressed Planck deeply, even as a *Gymnasium* student, was the law of the conservation of energy, the first law of thermodynamics. Later, during his university years, he became equally convinced that the entropy law, the second law of thermodynamics, was also an absolute law of nature. The second law became the subject of his doctoral dissertation at Munich, and it lay at the core of the researches that led him to discover the quantum of action, now known as Planck's constant *h*, in 1900.

Werner Heisenberg

Physicist

,

Germany

Werner Heisenberg (1901-1976) was a German theoretical physicist and 1932 Nobel Prize winner.

Heisenberg was a main contributor to the German atomic program during World War II, in direct competition with the Manhattan Project. In 1941, he visited Niels Bohr in Copenhagen to discuss nuclear research. Nazi architect Albert Speer consulted Heisenberg about the possibility of turning the knowledge into a nuclear weapon. Heisenberg told Speer that a bomb could not be built before 1945, and would require significant monetary and manpower resources. By the end of 1942, it was apparent the German nuclear energy program would not end the war effort in the near term. Instead, German scientists focused their efforts on more pressing matters which would have an immediate impact on the war.
In 1943, the Manhattan Project established the Alsos Mission to investigate German progress in developing a nuclear weapon. The United States took numerous German nuclear scientists into custody throughout 1944 and 1945. Heisenberg and a number of other prominent German physicists were interned at Farm Hall in England immediately following the war.

SCIENTIFIC CONTRIBUTIONS

Heisenberg is best known for his uncertainty principle and theory of quantum mechanics, which he published at the age of twenty-three in 1925. He was awarded the Nobel Prize for Physics in 1932 for his subsequent research and application of this principle.

Enrico Fermi:

Enrico Fermi

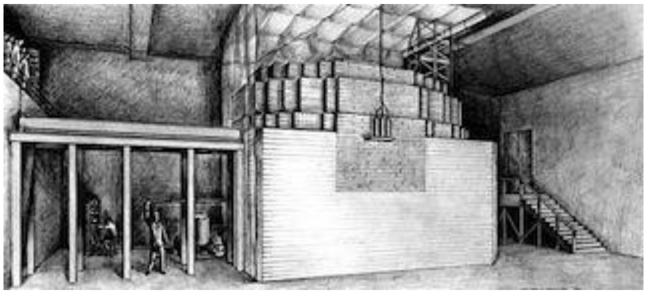
About 40 miles southwest of the city of Chicago, you'll find numerous places to visit. There's the charming town of Geneva, the nationally recognized city of Naperville, and a 6,800-acre particle physics laboratory, the second largest in the world, where the smallest building blocks of matter, energy, space and time are studied.

This facility is called 'Fermilab', named after Enrico Fermi, a pioneer in nuclear fission and the creation of the atomic bomb.

Let's learn a little more about his life and the impact he had in the field of Nuclear Physics.

Inventions

Does your electricity come from nuclear power? If so, you have Enrico Fermi to thank for that. In 1942, he and a team of scientists constructed the **first nuclear reactor**, famously called the **Chicago Pile-1** to produce the first self-sustaining and controlled reaction. Currently, his reactors are used in nuclear power plants around the world, providing energy to millions.



Artist sketch of the first nuclear reactor - the Chicago Pile-1

Fermi's subsequent inventions were all changes in and improvements to reactors and how they operate. Some of these are listed below:

- The materials that make up reactors need to be tested to determine if they can withstand nuclear reaction. Fermi therefore invented a way of **testing the nuclear properties of materials** that are used in nuclear reactors.
- If you wanted to build a nuclear reactor, you'd probably want to know how to use it. Not to worry because in 1957, Fermi received a posthumous patent for his invention of the **method of operating a reactor**.
- Because of the dangers of radiation during nuclear reactors, Fermi devised a shield, called the **Neutronic Reactor Shield**to protect those working around reactors.

PAUL DIRAC

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(1902 - 1984)


Paul Dirac

Paul Dirac was a British theoretical physicist who made fundamental contributions to the development of quantum mechanics, quantum field theory and quantum electrodynamics, and is particularly known for his attempts to unify the theories of quantum mechanics and relativity theory. His Dirac Equation, which was formulated in 1928 and describes the behavior of fermions like the electron, predicted the existence of antimatter such as the positron. He shared the 1933 Nobel Prize in Physics for 1933 with Erwin Schrödinger "for the discovery of new productive forms of atomic theory" and is regarded by some as one of the greatest physicists of all time.

Paul Adrien Maurice Dirac was born on 8 August 1902 in Bristol, England. He was brought up in an unusually strict and authoritarian household by his Swiss immigrant father, and was educated at the Merchant Venturers' Technical College (where his father was a French teacher), an institution attached to the University of Bristol which emphasized scientific subjects and modern languages.

Dirac went on to study at the University of Bristol, completing his degree in electrical engineering in 1921, and then earning a BA in applied mathematics in 1923. He obtained a grant to conduct research at St John's College, Cambridge, where he would remain for most of his career, pursuing his interests in general relativity and in the nascent field of quantum theory, initially under the supervision of Ralph Fowler.

He began working on quantum mechanics almost as soon as it was introduced by Werner Heisenberg in 1925, and he earned a PhD in 1926 for his canonical quantization of classical mechanics based on Heisenberg's recently proposed matrix formulation of quantum mechanics. His independent mathematical equivalent to Heisenberg's matrix formulation consisted of a non-commutative algebra for calculating atomic properties.

Building on Wolfgang Pauli's work on non-relativistic spin systems, he proposed the “Dirac equation” in 1928 as a relativistic equation of motion for the wave function of the electron. This work also led him to his prediction of the existence of the positron (the antiparticle of the electron, identical to it in every aspect but its charge, the existence of which was later observed and confirmed by Carl Anderson in 1932) and matter-antimatter annihilation, as well as contributing to the explanation of the origin of quantum spin as a relativistic phenomenon. He was also responsible for developing “bra-ket” notation (or Dirac notation), the standard notation for describing quantum states in the theory of quantum mechanics, composed of angle brackets (chevrons) and vertical bars.

Dirac traveled extensively, especially in his younger years, and studied at various foreign universities, including

Copenhagen, Göttingen, Leyden, Wisconsin, Michigan and Princeton, as well as visiting the Soviet Union several times. In 1929, after having spent five months in America, he continued around the world, visiting Japan (together with Heisenberg), and then returning across Siberia.

His 1930 book “Principles of Quantum Mechanics” is considered a landmark in the history of science, and it quickly became one of the standard textbooks on the subject (and is still used today). In the book, Dirac incorporates Heisenberg’s previous work on matrix mechanics and Erwin Schrödinger’s work on wave mechanics into a single mathematical formalism. He earned his share in the 1933 Nobel Prize in Physics largely as a result of the book.

He became Lucasian Professor of Mathematics at Cambridge in 1932, a post he held for the next 37 years. In the early 1930s, Dirac introduced the idea of vacuum polarization and developed the field of quantum electrodynamics (he was the first to use that term). In 1933, he showed that the existence of a single magnetic monopole in the universe would suffice to explain the observed quantization of electrical charge (although to date no convincing evidence has yet been found for the existence of physical magnetic monopoles). In 1937, he proposed a speculative cosmological model based on the so-called “large numbers hypothesis” which, although it has not gained acceptance in mainstream physics, has been highly influential among proponents of other non-standard cosmologies.

Dirac married Margit “Manci” Wigner (sister of the Hungarian-American physicist and mathematician, Eugene Wigner) in 1937. He adopted Margit's two children, Judith and Gabriel, and the couple went on to have two more children together, Mary and Florence. He was known as a very precise and ordered man but shy, modest and taciturn, and it has been argued that his autism was crucial to his success as a theoretical physicist. His important contributions to physics were largely motivated by principles of mathematical beauty and he once said, "God used beautiful mathematics in creating the world". However, he is quoted as saying, “I do not recognize any religious myth, at least because they contradict one another”, and he strongly criticized the political manipulation of religion.

Dirac shared the 1933 Nobel Prize in Physics with Erwin Schrödinger “for the discovery of new productive forms of atomic theory”. He was also awarded the Royal Medal (in 1939), the Copley Medal and the Max Planck Medal (both in 1952) among other honours, and was elected a Fellow of the Royal Society in 1930, and of the American Physical Society in 1948, and was made a member of the British Order of Merit in 1973.

During World War II, he worked on uranium separation and nuclear weapons, but his work moved increasingly out of the mainstream in later life. In the 1960s, he developed a theory of “constrained quantization”, identifying the general quantum rules for arbitrary classical systems, and his quantum field analysis of the vibrations of a membrane in the early 1960s has proved extremely useful to modern practitioners of superstring theory and its closely related successor, M-theory.

After teaching as Lucasian Professor of Mathematics at Cambridge from 1932 to 1968, he moved to Florida to be near his daughter Mary, spending his final teaching years at the University of Miami in Coral Gables and Florida State University in Tallahassee. Dirac died on 20 October 1984 in Tallahassee, Florida, where he is buried.

Max Born

Max Born, (born Dec. 11, 1882, Breslau, Ger. [now Wrocław, Pol.]—died Jan. 5, 1970, Göttingen, W.Ger.), German physicist who shared the Nobel Prize for Physics in 1954 with Walther Bothe for his probabilistic interpretation of quantum mechanics.
Born came from an upper-middle-class, assimilated, Jewish family. At first he was considered too frail to attend public school, so he was tutored at home before being allowed to attend the König Wilhelm Gymnasium in Breslau. Thereafter he continued his studies in physics and mathematics at universities in Breslau, Heidelberg, Zürich, and Göttingen. At the University of Göttingen he wrote his dissertation (1906), on the stability of elastic wires and tapes, under the direction of the mathematician Felix Klein, for which he was awarded a doctorate in 1907.

After brief service in the army and a stay at the University of Cambridge, where he worked with physicists Joseph Larmor and J.J. Thomson, Born returned to Breslau for the academic year 1908–09 and began an extensive study of Albert Einstein’s theory of special relativity. On the strength of his papers in this field, Born was invited back to Göttingen as an assistant to the mathematical physicist Hermann Minkowski. In 1912 Born met Hedwig Ehrenberg, whom he married a year later. Three children, two girls and a boy, were born from the union. It was a troubled relationship, and Born and his wife often lived apart.

In 1915 Born accepted a professorship to assist physicist Max Planck at the University of Berlin, but World War I intervened and he was drafted into the German army. Nonetheless, while an officer in the army, he found time to publish his first book, *Dynamik der Kristallgitter* (1915; *Dynamics of Crystal Lattices*).

In 1919 Born was appointed to a full professorship at the University of Frankfurt am Main, and in 1921 he accepted the position of professor of theoretical physics at the University of Göttingen. James Franck had been appointed professor of experimental physics at Göttingen the previous year. The two of them made the University of Göttingen one of the most important centres for the study of atomic and molecular phenomena. A measure of Born's influence can be gauged by the students and assistants who came to work with him—among them, Wolfgang Pauli, Werner Heisenberg, Pascual Jordan, Enrico Fermi, Fritz London, P.A.M. Dirac, Victor Weisskopf, J. Robert Oppenheimer, Walter Heitler, and Maria Goeppert-Mayer.

The Göttingen years were Born's most creative and seminal. In 1912 Born and Hungarian engineer Theodore von Karman formulated the dynamics of a crystal lattice, which incorporated the symmetry properties of the lattice, allowed the imposition of quantum rules, and permitted thermal properties of the crystal to be calculated. This work was elaborated when Born was in Göttingen, and it formed the basis of the modern theory of lattice dynamics.

In 1925 Heisenberg gave Born a copy of the manuscript of his first paper on quantum mechanics, and Born immediately recognized that the mathematical entities with which Heisenberg had represented the observable physical quantities of a particle—such as its position, momentum, and energy—were matrices. Joined by Heisenberg and Jordan, Born formulated all the essential aspects of quantum mechanics in its matrix version. A short time later, Erwin Schrödinger formulated a version of quantum mechanics based on his wave equation. It was soon proved that the two formulations were mathematically equivalent. What remained unclear was the meaning of the wave function that appeared in Schrödinger's equation. In 1926 Born submitted two papers in which he formulated the quantum mechanical description of collision processes and found that in the case of the scattering of a particle by a potential, the wave function at a particular spatiotemporal location should be interpreted as the probability amplitude of finding the particle at that specific space-time point. In 1954 he was awarded the Nobel Prize for this work.

Born remained at Göttingen until April 1933, when all Jews were dismissed from their academic posts in Germany. Born and his family went to England, where he accepted a temporary lectureship at Cambridge. In 1936 he was appointed Tait Professor of Natural Philosophy at the University of Edinburgh. He became a British citizen in 1939 and remained at Edinburgh until his retirement in 1953. The next year, he and his wife moved to Bad Pyrmont, a small spa town near Göttingen.

John Bardeen

John Bardeen, (born May 23, 1908, Madison, Wis., U.S.—died Jan. 30, 1991, Boston, Mass.), American physicist who was cowinner of the Nobel Prize for Physics in both 1956 and 1972. He shared the 1956 prize with William B. Shockley and Walter H. Brattain for their joint invention of the transistor. With Leon N. Cooper and John R. Schrieffer he was awarded the 1972 prize for development of the theory of superconductivity.

Bardeen earned bachelor's and master's degrees in electrical engineering from the University of Wisconsin (Madison) and obtained his doctorate in 1936 in mathematical physics from Princeton University. A staff member of the University of Minnesota, Minneapolis, from 1938 to 1941, he served as principal physicist at the U.S. Naval Ordnance Laboratory in Washington, D.C., during World War II.

After the war Bardeen joined (1945) the Bell Telephone Laboratories in Murray Hill, N.J., where he, Brattain, and Shockley conducted research on the electron-conducting properties of semiconductors. On Dec. 23, 1947, they unveiled the transistor, which ushered in the electronic revolution. The transistor replaced the larger and bulkier vacuum tube and provided the technology for miniaturizing the electronic switches and other components needed in the construction of computers.

In the early 1950s Bardeen resumed research he had begun in the 1930s on superconductivity, and his Nobel Prize-winning investigations provided a theoretical explanation of the disappearance of electrical resistance in materials at temperatures close to absolute zero. The BCS theory of superconductivity (from the initials of Bardeen, Cooper, and Schrieffer) was first advanced in 1957 and became the basis for all later theoretical work in superconductivity. Bardeen was also the author of a theory explaining certain properties of semiconductors. He served as a professor of electrical engineering and physics at the University of Illinois, Urbana-Champaign, from 1951 to 1975.