## Thermodynamics



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## Thermodynamic Systems, States, and Processes



A thermodynamic system is described by an equation of state, such as the ideal gas law. The "location" of the state can be plotted on a p–V diagram, as at left.

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### Thermodynamic Systems, States, and Processes



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A process changes the state of a system. A process may be: reversible (3-4) or irreversible (1-2); if it proceeds through a sequence of equilibrium states it is reversible.

The first law is a statement of conservation of energy in thermodynamic processes:

$$Q = \Delta U + W$$

Here,  $Q_{is}$  the heat transferred,  $\Delta U_{is}$  the change in internal energy, and  $W_{is}$  the work.



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It is important to get the signs of Q,  $\Delta U$ , and W correct. The diagram below illustrates the sign conventions.







It can be shown that the work done in expanding a gas is given by:

 $W = p\Delta V$ 

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Generalizing, we see that: The work done by a system is equal to the area under the process curve on a p–V diagram.

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(b)



The heat transferred and the work done both depend on the path taken from state 1 to state 2; the change in internal energy depends only on the end points.



An isothermal process is one in which the temperature does not change.

The first law of thermodynamics gives:

Q = W

The work done is:

$$W_{\rm isothermal} = nRT \ln\left(\frac{V_2}{V_1}\right)$$



An isobaric process is one in which the pressure does not change.

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The first law of thermodynamics gives:

$$Q = \Delta U + W = \Delta U + p\Delta V$$

The work done is:

$$W_{\text{isobaric}} = p(V_2 - V_1) = p\Delta V$$



An isometric process is one in which the volume is constant. In this case, no work is done, so

 $Q = \Delta U$ 



An adiabatic process is one where there is no heat transfer.

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In this case,

$$\Delta U = -W$$

And

$$W_{\text{adiabatic}} = \frac{p_1 V_1 - p_2 V_2}{\gamma - 1}$$

where

 $\gamma = c_{\rm p}/c_{\rm v}$ 

TABLE 12.1		Important Thermodynamic Processes		
Process	Cha	aracteristic	Result	The First Law of Thermodynamics
Isothermal	T =	= constant	$\Delta U = 0$	Q = W
Isobaric	<i>p</i> =	= constant	$W = p\Delta V$	$Q = \Delta U + p \Delta V$
Isometric	<i>V</i> =	= constant	W = 0	$Q = \Delta U$
Adiabatic	Q =	= 0		$\Delta U = -W$

As a final summary for these thermodynamic processes, their characteristics and consequences are listed in Table 12.1.

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The second law of thermodynamics:

1. In a thermal cycle, heat energy cannot be completely transformed into mechanical work.

2. It is impossible to construct an operational perpetualmotion machine.

3. It's impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body

Another statement of the second law of thermodynamics: All naturally occurring processes move toward a state of greater disorder or disarray.

It is a lot easier to break things than it is to put them back together again!

What is entropy? We cannot measure it directly, only changes in it.

#### Entropy:

- -Is a measure of disorder
- -Is increasing in the universe
- -Is a measure of a system's ability to do useful work

#### Determines the direction of time

$$\Delta S = \frac{Q}{T}$$

*(change in entropy at constant temperature)* 

The entropy of an isolated system never decreases. The universe is the ultimate isolated system; therefore, the total energy of the universe increases during every natural process.

There are processes during which the entropy does not change; however, during any process the entropy of the universe can only increase or remain constant.

### $\Delta S \ge 0$

A heat engine converts heat energy into work. According to the second law of thermodynamics, however, it cannot convert \*all\* of the heat energy supplied to it into work. Basic heat engine: hot reservoir, cold reservoir, and a machine to convert heat energy into work.

This is a simplified diagram of a heat engine, along with its thermal cycle.



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An important quantity characterizing a heat engine is the net work it does when going through an entire cycle.



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Thermal efficiency of a heat engine:

$$\varepsilon = \frac{\text{net work out}}{\text{heat in}} = \frac{W_{\text{net}}}{Q_{\text{in}}}$$

For an ideal gas heat engine,

$$\varepsilon = \frac{W_{\text{net}}}{Q_{\text{h}}} = \frac{Q_{\text{h}} - Q_{\text{c}}}{Q_{\text{h}}} = 1 - \frac{Q_{\text{c}}}{Q_{\text{h}}}$$

Yet another restatement of the second law of thermodynamics: No cyclic heat engine can convert its heat input completely to work.

A thermal pump is the opposite of a heat engine: it transfers heat energy from a cold reservoir to a hot one.

As this will not happen spontaneously, work must be done on the pump as well.

Examples of thermal pumps: refrigerator, air conditioner

An air conditioner removes heat from the house and exhausts it outside, where it is hotter.



(a)

(b)

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A refrigerator does the same thing, except the warm air is exhausted into the kitchen.

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The purpose of a refrigerator or air conditioner is to keep a cool place cool; we describe such a device by its coefficient of performance (COP).

$$\text{COP}_{\text{ref}} = \frac{Q_{\text{c}}}{W_{\text{in}}} = \frac{Q_{\text{c}}}{Q_{\text{h}} - Q_{\text{c}}}$$

Typical COPs are in the range of 3–5; this is the ratio of the heat removed to the work done to remove it.

Heat pumps can also be used to warm cool places, such as a house in winter. The fundamental operation is the same—heat is taken from a cool place and sent to a warm one—but now the point is to keep the house warm, not to keep the outside cold. There is a different COP that describes how well a heat engine is doing this:

$$\text{COP}_{\text{hp}} = \frac{Q_{\text{h}}}{W_{\text{in}}} = \frac{Q_{\text{h}}}{Q_{\text{h}} - Q_{\text{c}}}$$

## The Carnot Cycle and Ideal Heat Engines

The Carnot cycle consists of two isotherms and two adiabats.



## The Carnot Cycle and Ideal Heat Engines

An ideal Carnot engine—with perfect isotherms and adiabats—has the maximum efficiency a heat engine can have.

$$\varepsilon_{\rm C} = 1 - \frac{T_{\rm c}}{T_{\rm h}}$$

This leads to the third law of thermodynamics: It is impossible to reach absolute zero in a finite number of thermal processes.

# Summary

First law of thermodynamics is conservation of energy:

$$Q = \Delta U + W$$

Thermodynamic processes: isothermal, isobaric, isometric, adiabatic

Work done:

$$W_{\text{isothermal}} = nRT \ln\left(\frac{V_2}{V_1}\right)$$
$$W_{\text{isobaric}} = p(V_2 - V_1) = p\Delta V$$
$$W_{\text{adiabatic}} = \frac{p_1 V_1 - p_2 V_2}{\gamma - 1}$$

## Summary

Second law of thermodynamics specifies the direction a spontaneous interaction can take. Entropy is a measure of disorder:

$$\Delta S = \frac{Q}{T}$$

During any kind of process, the entropy of the universe can only stay the same or increase.

## Summary

A heat engine converts heat energy into work. Efficiency:

$$\varepsilon = \frac{W_{\text{net}}}{Q_{\text{h}}} = \frac{Q_{\text{h}} - Q_{\text{c}}}{Q_{\text{h}}} = 1 - \frac{Q_{\text{c}}}{Q_{\text{h}}}$$

A thermal pump extracts heat from a cold reservoir and transfers it to a hot one. A Carnot engine has the highest efficiency possible:

$$\varepsilon_{\rm C} = 1 - \frac{T_{\rm c}}{T_{\rm h}}$$