



# Lecture 7. Thermodynamics

# Thermodynamics

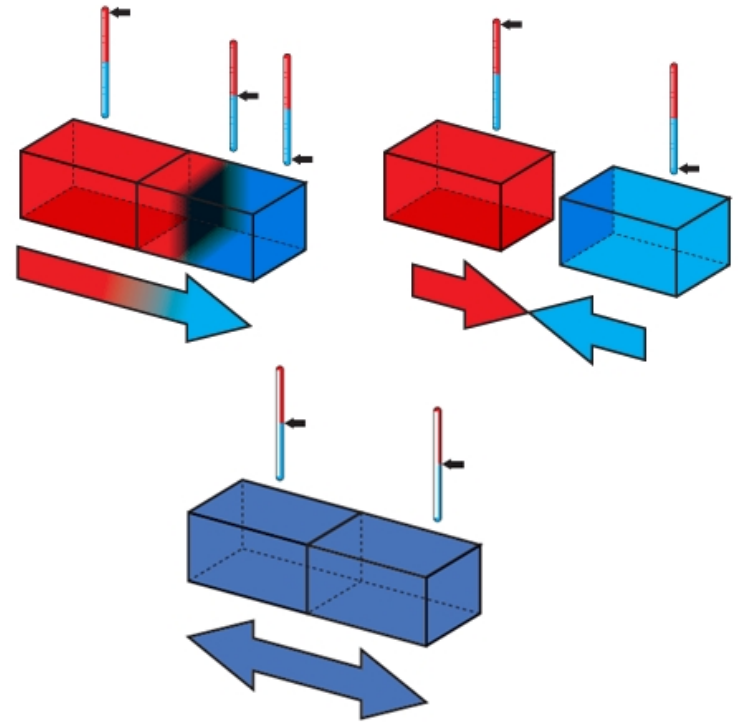
## 0th Law of Thermodynamics Summary

### *Thermal Equilibrium*

A system with many microscopic components (for example, a gas, a liquid, a solid with many molecules) that is isolated from all forms of energy exchange and left alone for a “long time” moves toward a state of *thermal equilibrium*.

A system in thermal equilibrium is characterized by a set of macroscopic quantities that depend on the system in question and characterize its “state” (such as pressure, volume, density) that do not change in time.

Two systems are said to be in (mutual) thermal equilibrium if, when they are placed in “thermal contact” (basically, contact that permits the exchange of energy between them), their state variables do not change.



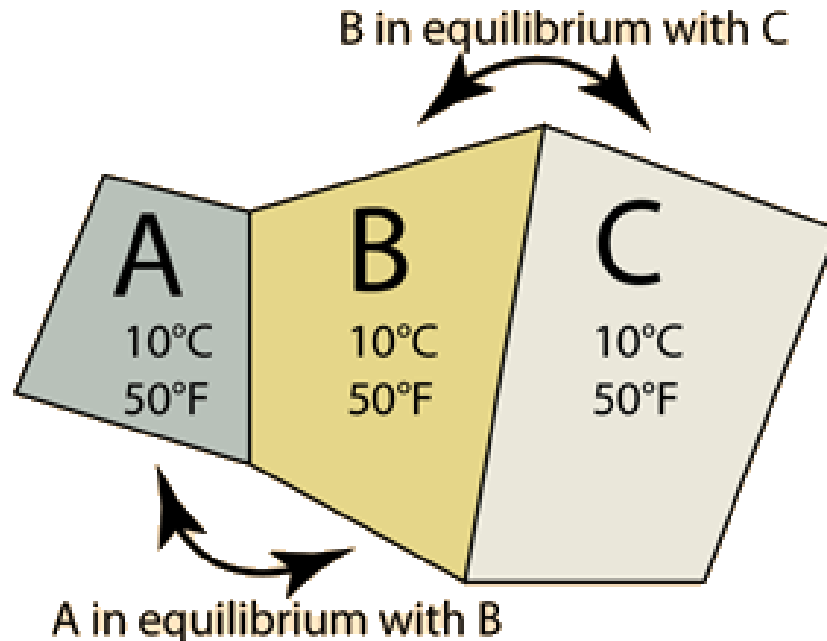


# Lecture 7. Thermodynamics

## 0th Law of Thermodynamics Summary

### *Zeroth Law of Thermodynamics*

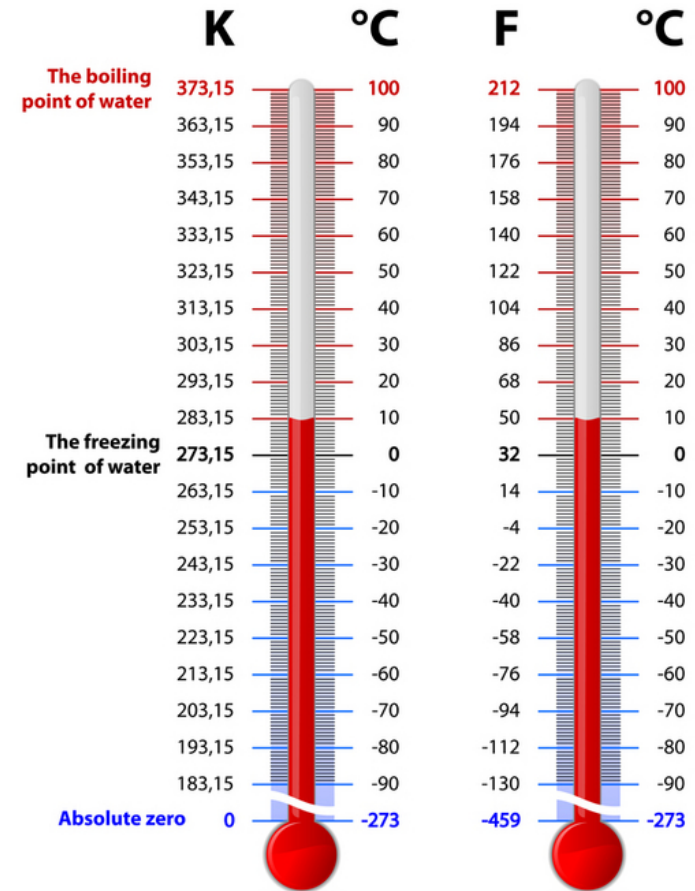
If system A is in thermal equilibrium with system C, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system B.



## 0th Law of Thermodynamics Summary

### *Temperature Scales*

- **Fahrenheit:** This is one of the oldest scales, and is based on the coldest temperature that could be achieved with a mix of ice and alcohol. In it the freezing point of water is at  $32^{\circ}\text{F}$ , the boiling point of water is at  $212^{\circ}\text{F}$ .
- **Celsius or Centigrade:** This is a very sane system, where the freezing point of water is at  $0^{\circ}\text{C}$  and the boiling point is at  $100^{\circ}\text{C}$ . The degree size is thus  $9/5$  as big as the Fahrenheit degree.
- **Kelvin or Absolute:**  $0^{\circ}\text{K}$  is the lowest possible temperature, where the internal energy of a system is at its absolute minimum. The degree size is the same as that of the Centigrade or Celsius scale. This makes the freezing point of water at atmospheric pressure  $273.16^{\circ}\text{K}$ , the boiling point at  $373.16^{\circ}\text{K}$ .





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## The First Law of Thermodynamics

### *Internal Energy*

Internal energy is all the mechanical energy in all the components of a system. For example, in a monoatomic gas it might be the sum of the kinetic energies of all the gas atoms. In a solid it might be the sum of the kinetic and potential energies of all the particles that make up the solid.

### *Heat*

Heat is a bit more complicated. It is internal energy as well, but it is internal energy that is *transferred* into or out of a given system. Furthermore, it is in some fundamental sense “disorganized” internal energy – energy with no particular organization, random energy. Heat flows into or out of a system in response to a temperature difference, always flowing from hotter temperature regions (cooling them) to cooler ones (warming them).

Common units of heat include the ever-popular Joule and the *calorie* (the heat required to raise the temperature of 1 gram of water at 14.5°C to 15.5°C. Note that 1 cal = 4.186 J.



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## The First Law of Thermodynamics

### *Heat Capacity*

If one adds heat to an object, its temperature usually increases (exceptions include at a state boundary, for example when a liquid boils). In many cases the temperature change is linear in the amount of heat added. We define the heat capacity  $C$  of an object from the relation:.

$$\Delta Q = C\Delta T$$

where  $Q$  is the heat that flows into a system to increase its temperature by  $T$ .

Many substances have a known heat capacity per unit mass. This permits us to also write:

$$\Delta Q = mC\Delta T$$

where  $C$  is the specific heat of a substance. The specific heat of liquid water is approximately:

$$C_{\text{water}} = 1 \frac{\text{calorie}}{\text{kg} \cdot ^\circ\text{C}}$$



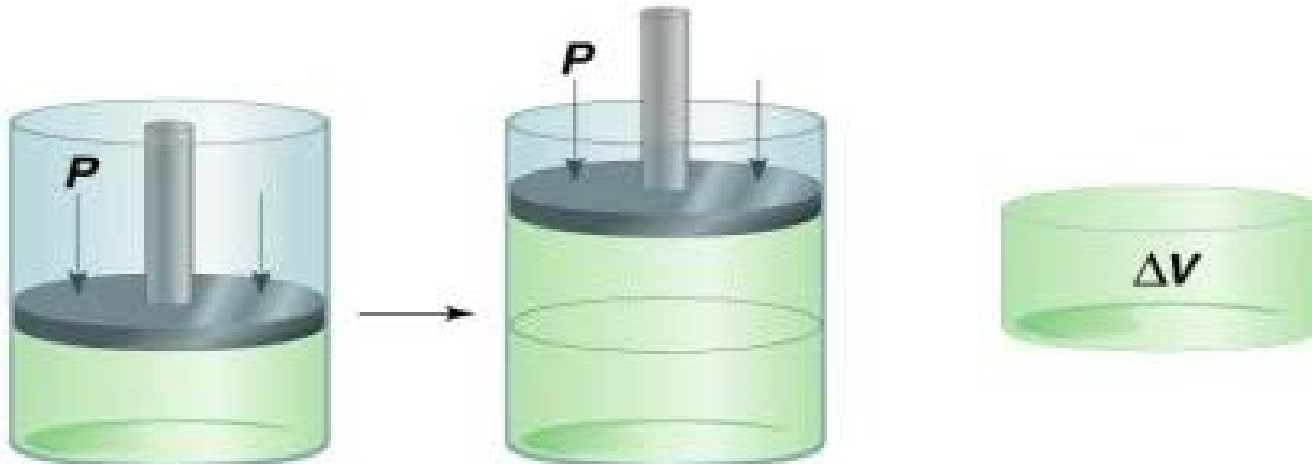
# Lecture 7. Thermodynamics

## The First Law of Thermodynamics

### *Work Done by a Gas*

$$W = \int_{V_i}^{V_f} P dV$$

This is the area under the  $P(V)$  curve, suggesting that we draw lots of state diagrams on a  $P$  and  $V$  coordinate system. Both heat transfer and work depend on the path a gas takes  $P(V)$  moving from one pressure and volume to another.





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## The First Law of Thermodynamics

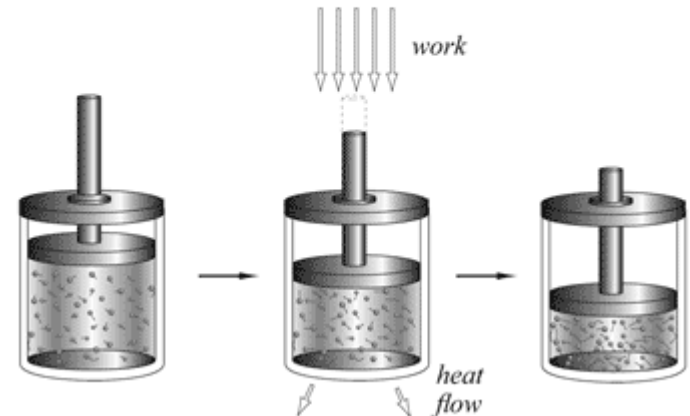
### *The First Law of Thermodynamics*

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

In words, this is that the change in total mechanical energy of a system is equal to heat put into the system plus the work done *on* the system (which is minus the work done *by* the system, hence the minus above).

This is just, at long last, the fully *generalized* law of conservation of energy. All the cases where mechanical energy was not conserved in previous chapters because of nonconservative forces, the missing energy appeared as *heat*, energy that naturally flows from hotter systems to cooler ones.

$$\begin{aligned}\Delta U &= Q - W \\ &= Q - P^* \Delta V\end{aligned}$$







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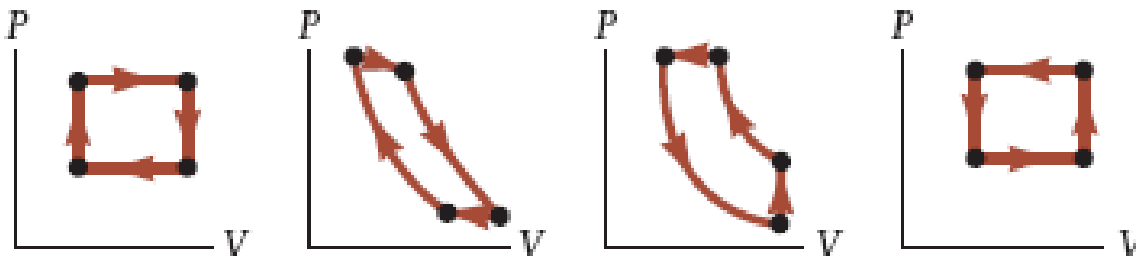
## The First Law of Thermodynamics

### *Cyclic Processes*

Most of what we study in these final sections will lead us to an understanding of simple heat engines based on gas expanding in a cylinder and doing work against a piston. In order to build a true engine, the engine has to go around in a repetitive *cycle*. This cycle typically is represented by a closed loop on a state e.g.  $P(V)$  curve. A direct consequence of the 1st law is that the ***net work done by the system per cycle is the area inside the loop of the  $P(V)$  diagram.*** Since the internal energy is the same at the beginning and the end of the cycle, it also tells us that:

$$\Delta Q_{\text{cycle}} = W_{\text{cycle}}$$

the heat that flows into the system per cycle must exactly equal the work done by the system per cycle.





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## The First Law of Thermodynamics

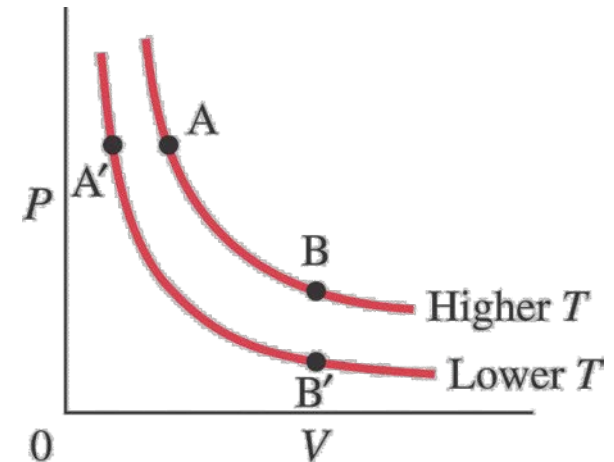
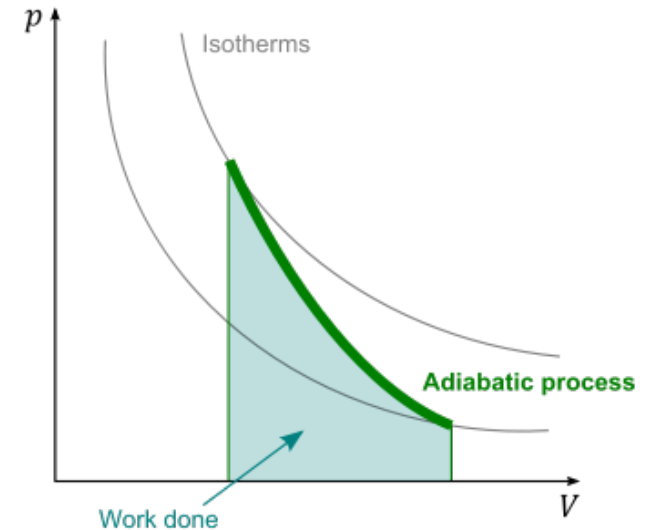
**Adiabatic Processes** are processes ( $PV$  curves) such that no heat enters or leaves an (insulated) system.

The adiabatic condition:

$$PV^\gamma = \text{const}$$

**Isothermal Processes** are processes where the temperature  $T$  of the system remains constant.

$$PV = \text{const}$$



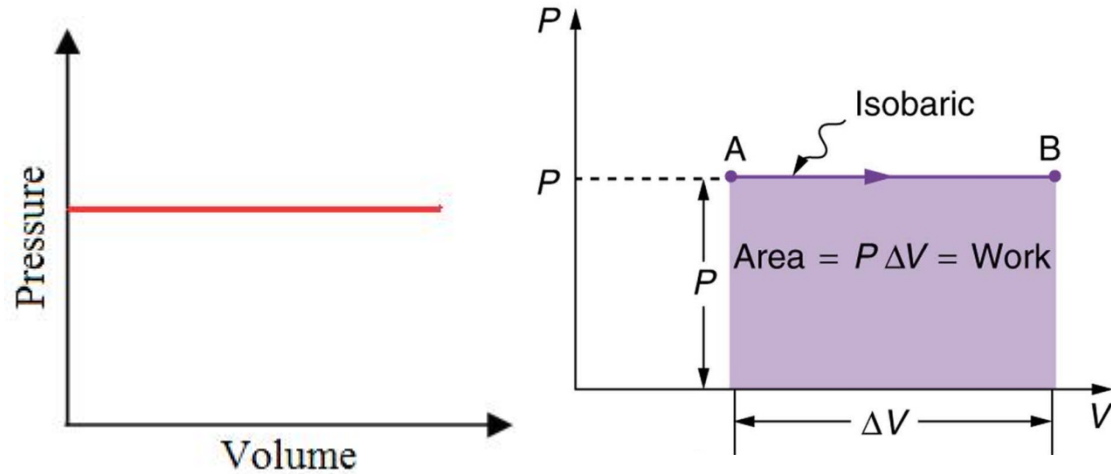


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## The First Law of Thermodynamics

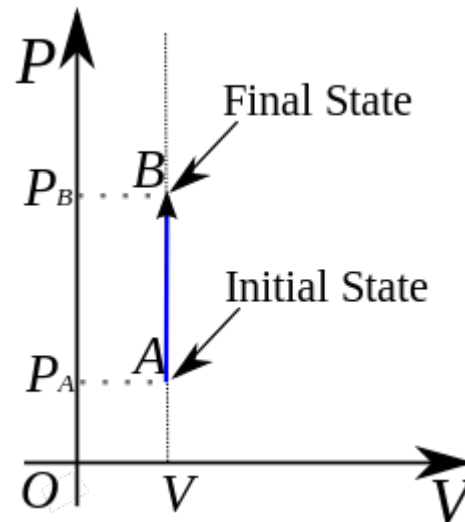
**Isobaric Processes** are processes that occur at constant pressure.

$$V \sim T$$



**Isovolumetric Processes** are processes that occur at constant volume

$$P \sim T$$





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## The First Law of Thermodynamics

Work done by an Ideal Gas:

$$PV = NkT$$

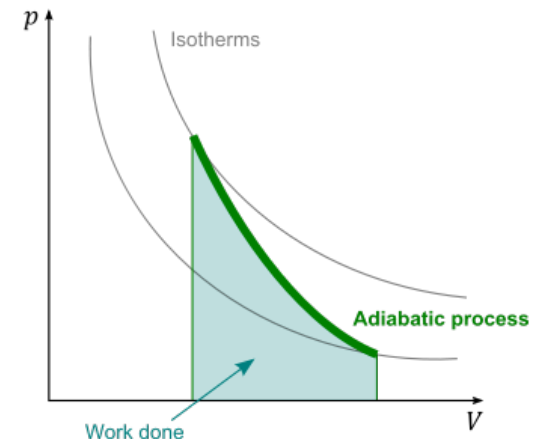
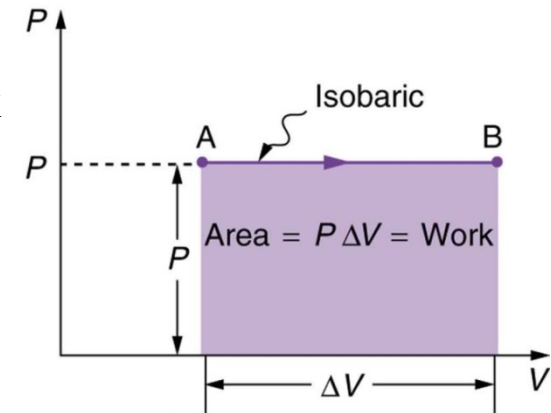
where  $N$  is the number of gas atoms or molecules. Isothermal work at (fixed) temperature  $T_0$  is thus:

$$W = \int_{V_1}^{V_2} \frac{NkT_0}{V} dV = NkT \ln \left( \frac{V_2}{V_1} \right)$$

Isobaric work is trivial.  $P = P_0$  is a constant, so

$$W = \int_{V_1}^{V_2} P_0 dV = P_0(V_2 - V_1)$$

Adiabatic work is a bit tricky and depends on some of the internal properties of the gas (for example, whether it is mono- or diatomic).



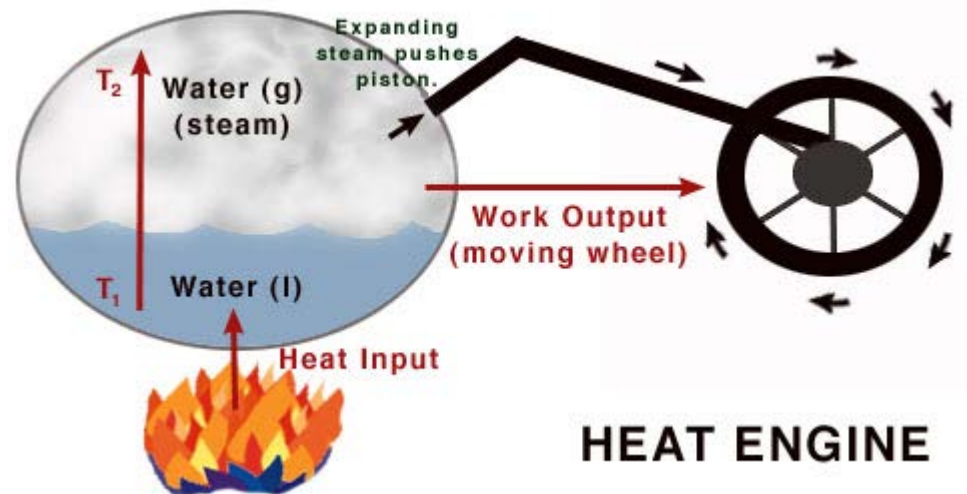
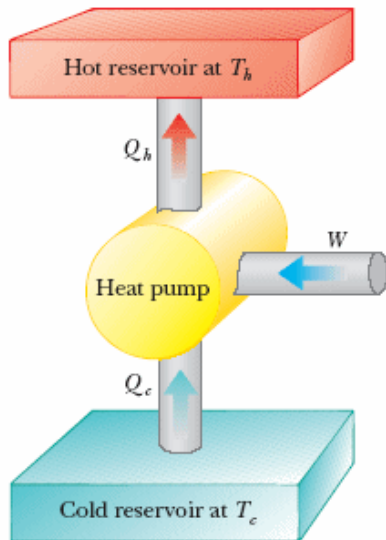
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## Second Law of Thermodynamics

A **heat engine** is a cyclic device that takes heat  $Q_H$  in from a *hot reservoir*, converts *some* of it to work  $W$ , and rejects the rest of it  $Q_C$  to a *cold reservoir* so that at the end of a cycle it is in the same state (and has the same internal energy) with which it began. The net work done per cycle is the area inside the  $PV$  curve.

The *efficiency* of a heat engine is defined to be:

$$\epsilon = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$





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## Kelvin-Planck statement of the Second Law of Thermodynamics

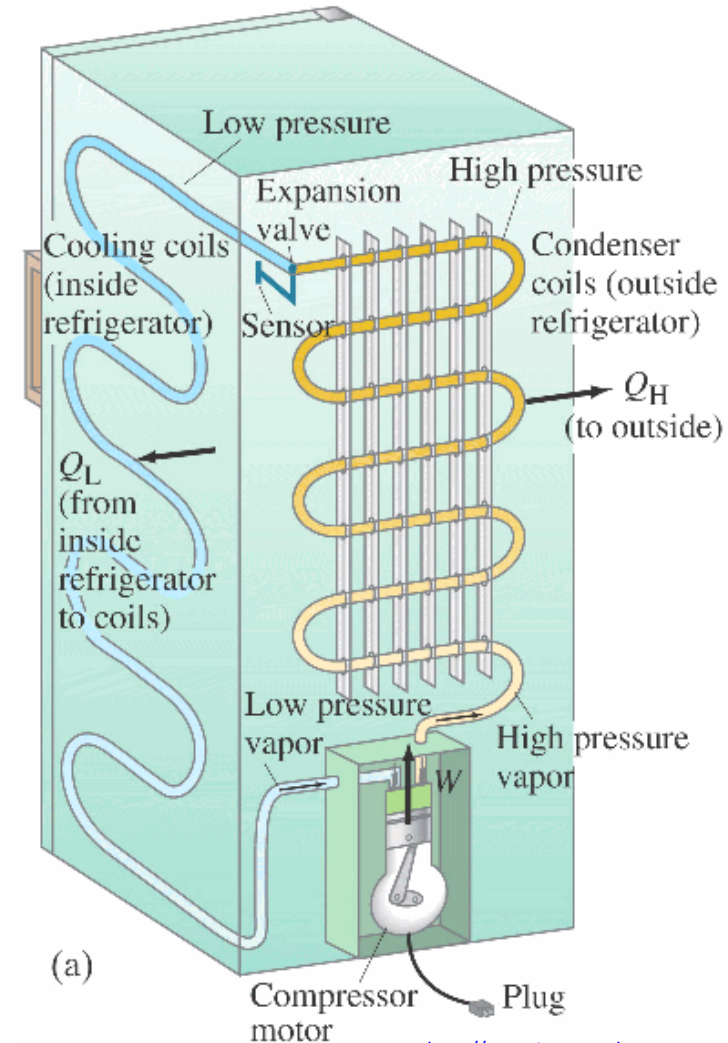
*It is impossible to construct a cyclic heat engine that produces no other effect but the absorption of energy from a hot reservoir and the production of an equal amount of work.*

## Refrigerators (and Heat Pumps)

A *refrigerator* is basically a cyclic heat engine run backwards. In a cycle it takes heat  $Q_C$  in from a cold reservoir, does work  $W$  on it, and rejects a heat  $Q_H$  to a hot reservoir. Its net effect is thus to make the cold reservoir colder (refrigeration) by removing heat from inside it to the warmer warm reservoir (warming it still further, e.g. as a heat pump).

The *coefficient of performance* of a refrigerator is defined to be

$$\text{COP} = \frac{Q_C}{W}$$





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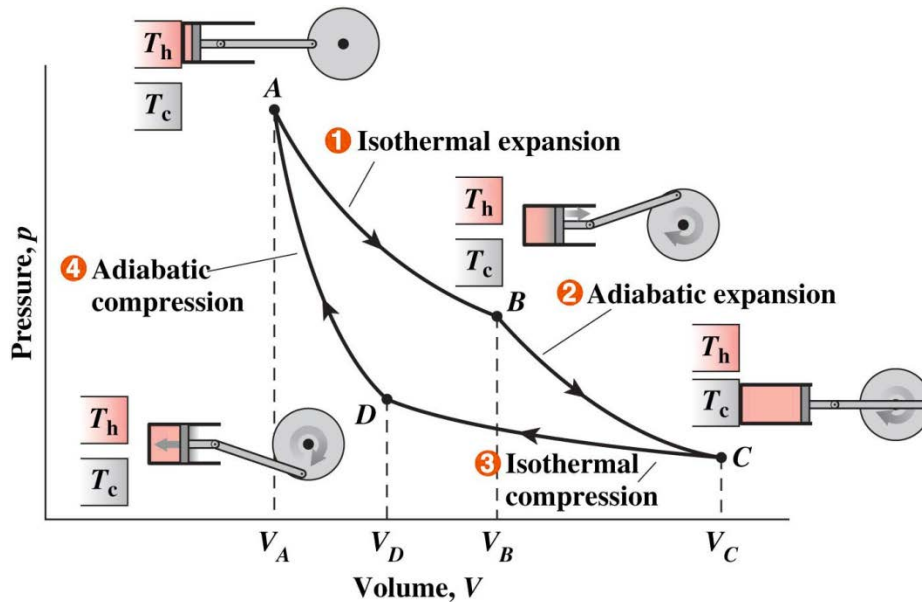
## Clausius Statement of the Second Law of Thermodynamics

*It is impossible to construct a cyclic refrigerator whose sole effect is the transfer of energy from a cold reservoir to a warm reservoir without the input of energy by work.*



## Carnot Engine

The Carnot Cycle is the archetypical reversible cycle, and a Carnot Cycle-based heat engine is one that does not dissipate any energy internally and uses only reversible steps. Carnot's Theorem states that no real heat engine operating between a hot reservoir at temperature  $T_H$  and a cold reservoir at temperature  $T_C$  can be more efficient than a Carnot engine operating between those two reservoirs.



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**A Carnot Cycle consists of four steps:**

- Isothermal expansion (in contact with the heat reservoir)
- Adiabatic expansion (after the heat reservoir is removed)
- Isothermal compression (in contact with the cold reservoir)
- Adiabatic compression (after the cold reservoir is removed)

The efficiency of a Carnot Engine is:

$$\epsilon_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$



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## Entropy

Entropy  $S$  is a measure of disorder. The change in entropy of a system can be evaluated by integrating:

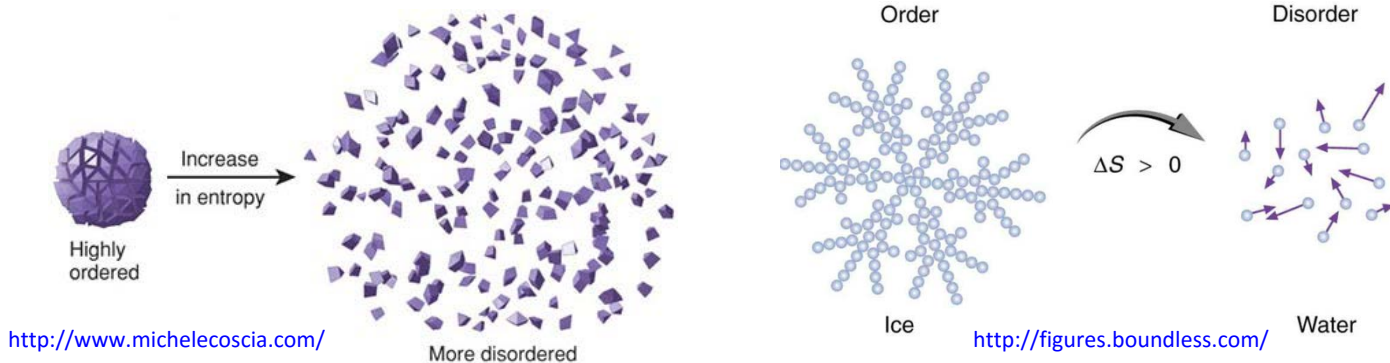
$$dS = \frac{dQ}{T}$$

between successive infinitesimally separated equilibrium states (the weasel language is necessary because temperature should be constant in equilibrium, but systems in equilibrium have constant entropy). Thus:

$$\Delta S = \int \frac{dQ}{T}$$

Entropy Statement of the Second Law of Thermodynamics:

The entropy of the Universe never decreases. It either increases (for irreversible processes) or remains the same (for reversible processes).

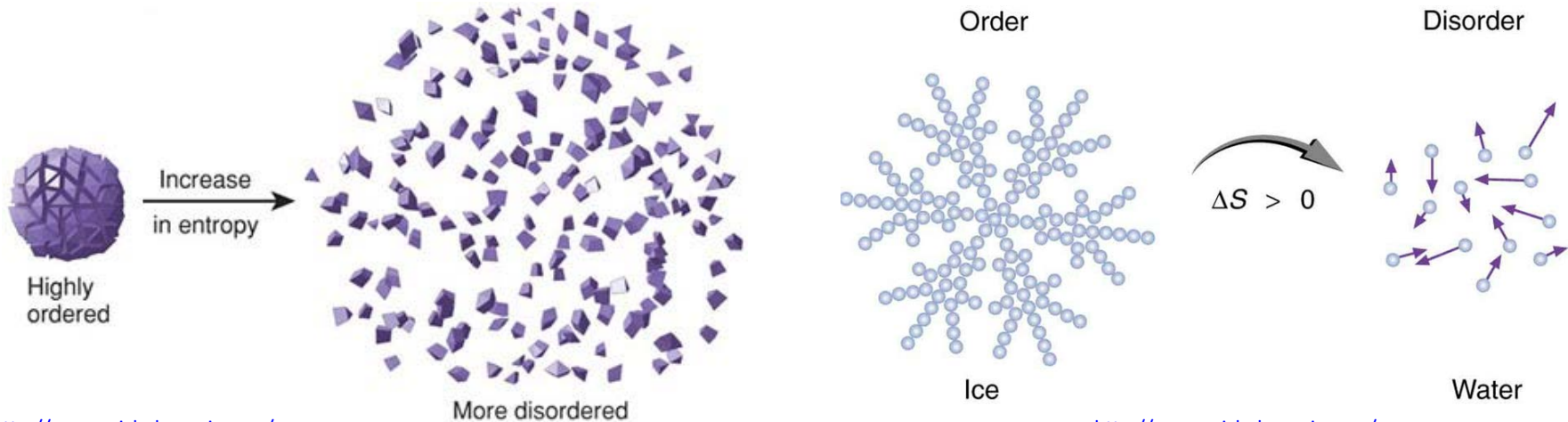




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## Entropy Statement of the Second Law of Thermodynamics

The entropy of the Universe never decreases. It either increases (for irreversible processes) or remains the same (for reversible processes).



## Phases and Phase Transitions

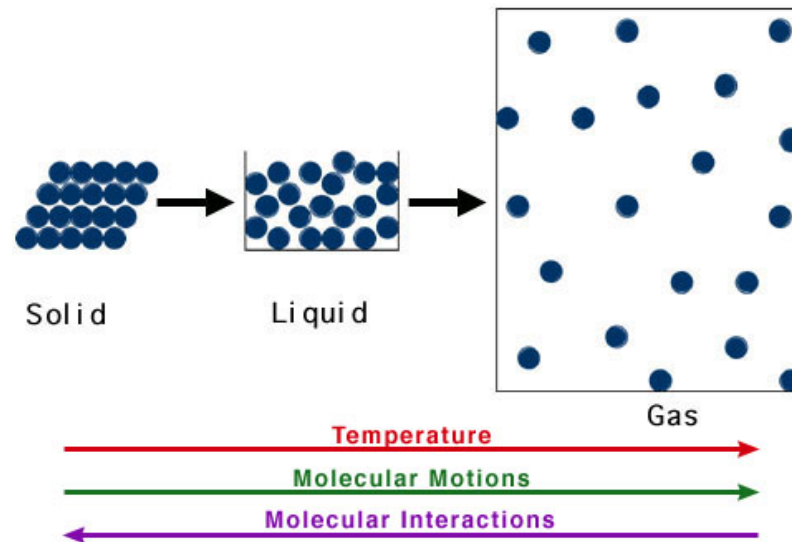
Matter can exist in three different *phases* (*physical states*):

- Solid
- Liquid
- Gas

A phase is a form of matter that is uniform throughout in chemical composition and physical properties, and that can be distinguished from other phases with which it may be in contact by these definite properties and composition.

As shown in Figure:

- a substance in the solid phase has a definite shape and rigidity;
- a substance in the liquid phase has no definite shape, but has a definite volume;
- a substance in the gas phase has no definite shape or volume, but has a shape and volume determined by the shape and size of the container.





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## Phases and Phase Transitions

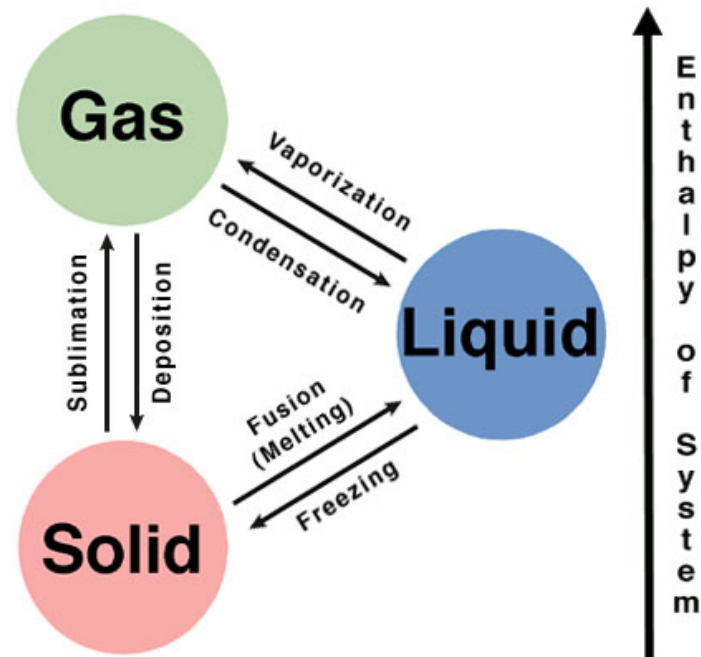
One of the major differences in the three phases is the number of intermolecular interactions they contain.

The particles in a solid interact with all of their nearest neighbors

The particles in a liquid interact with only some of the nearby particles

The particles in a gas ideally have no interaction with one another.

By breaking or forming intermolecular interactions, a substance can change from one phase to another.



For example, gas molecules condense to form liquids because of the presence of attractive intermolecular forces. The stronger the attractive forces, the greater the stability of the liquid (which leads to a higher boiling point temperature). A transition between the phases of matter is called a *phase transition*. The names of the phase transitions between solid, liquid, and gas are shown in Figure

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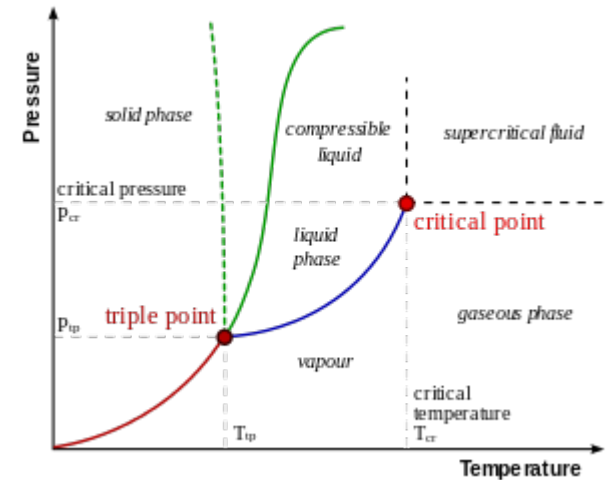
## Phases and Phase Transitions

Phase transitions involving *the breaking of intermolecular attractions* (i.e., fusion (melting), vaporization, and sublimation) require an *input* of energy to overcome the attractive forces between the particles of the substance.

Phase transitions involving *the formation of intermolecular attractions* (i.e., freezing, condensation, and deposition) *release energy* as the particles adopt a lower-energy conformation.

The strength of the intermolecular attractions between molecules, and therefore the amount of energy required to overcome these attractive forces (as well as the amount of energy released when the attractions are formed) depends on the molecular properties of the substance.

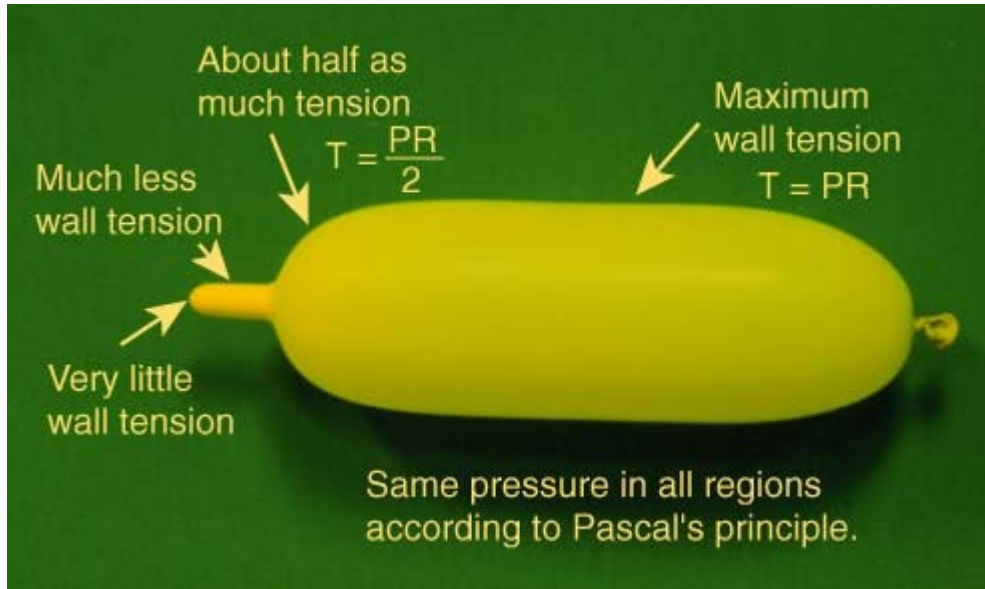
In thermodynamics, *the triple point* of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium.





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## Surface Tension and Bubbles

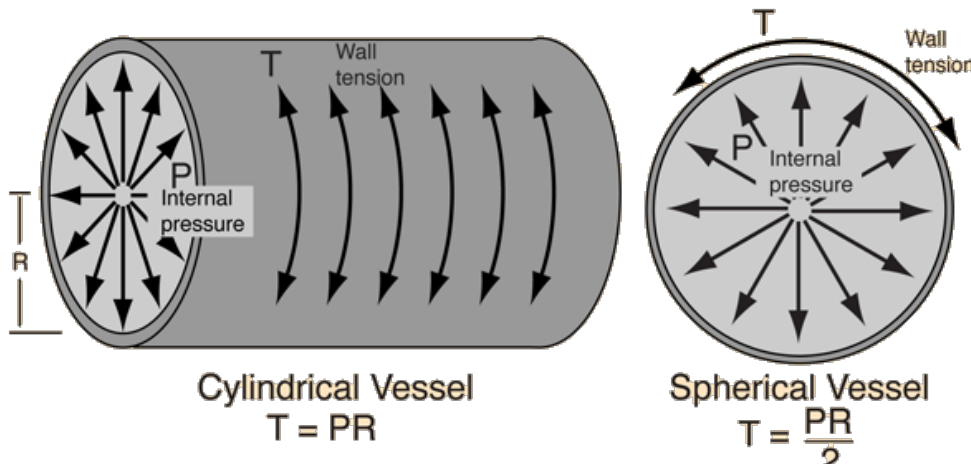


Pascal's principle requires that the pressure is everywhere the same inside the balloon at equilibrium.

But examination immediately reveals that there are great differences in wall tension on different parts of the balloon.

The variation is described by *Laplace's Law*:

*The larger the vessel radius, the larger the wall tension required to withstand a given internal fluid pressure.*

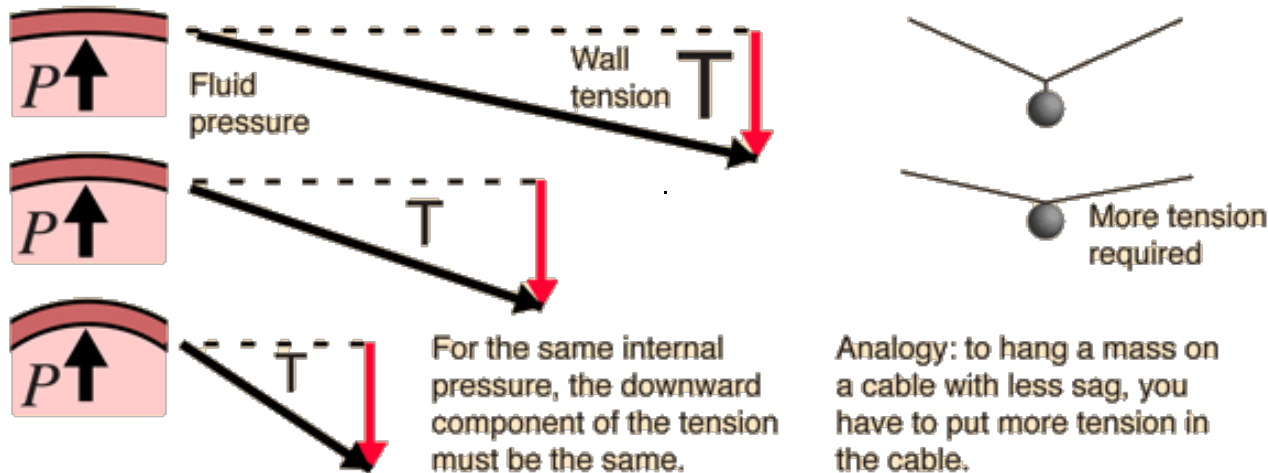


The larger the vessel radius, the larger the wall tension required to withstand a given internal fluid pressure.

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## Surface Tension and Bubbles

*Why does wall tension increase with radius?*



If the upward part of the fluid pressure remains the same, then the downward component of the wall tension must remain the same. But if the curvature is less, then the total tension must be greater in order to get that same downward component of tension.

For equilibrium of a load hanging on a cable, you can explore the effects of having a smaller angle for the supporting cable tension.





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## Surface Tension and Bubbles

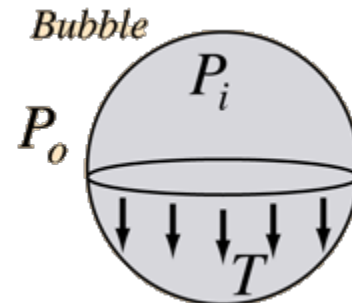
The surface tension of water provides the necessary wall tension for the formation of bubbles with water. The tendency to minimize that wall tension pulls the bubbles into spherical shapes (LaPlace's law).

The interference colors indicate that the thickness of the soap film is on the order of a few wavelengths of visible light. Even though the soap film has less surface tension than pure water, which would pull itself into tiny droplets, it is nevertheless strong to be able to maintain the bubble with such a small thickness.

The pressure difference between the inside and outside of a bubble depends upon the surface tension and the radius of the bubble. The relationship can be obtained by visualizing the bubble as two hemispheres and noting that the internal pressure which tends to push the hemispheres apart is counteracted by the surface tension acting around the circumference of the circle.

For a bubble with two surfaces providing tension, the pressure relationship is:

$$P_i - P_o = \frac{4T}{r}$$





# Lecture 7. Thermodynamics

## Surface Tension and Bubbles

Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the cohesive forces of the surface layer. The spherical shape minimizes then necessary "wall tension" of the surface layer according to LaPlace's law.



Surface tension and adhesion determine the shape of this drop on a twig. It dropped a short time later, and took a more nearly spherical shape as it fell. Falling drops take a variety of shapes due to oscillation and the effects of air friction.

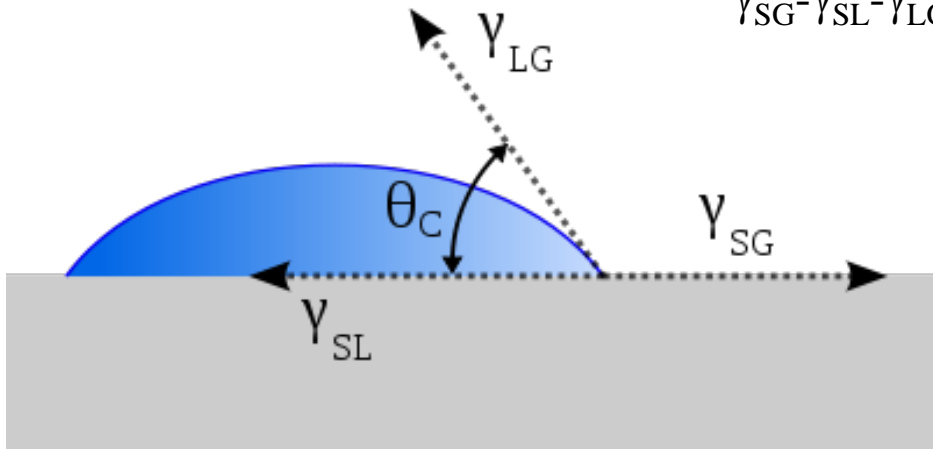


# Lecture 7. Thermodynamics

## Surface Tension and Bubbles

The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid phase (L), the solid phase (S), and the gas/vapor phase (G) (which could be a mixture of ambient atmosphere and an equilibrium concentration of the liquid vapor). The “gaseous” phase could also be another (immiscible) liquid phase. If the solid–vapor interfacial energy is denoted by  $\gamma_{SG}$ , the solid–liquid interfacial energy by  $\gamma_{SL}$ , and the liquid–vapor interfacial energy (i.e. the surface tension) by  $\gamma_{LG}$ , then the equilibrium contact angle  $\theta_C$  is determined from these quantities by Young's Equation:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_C = 0$$

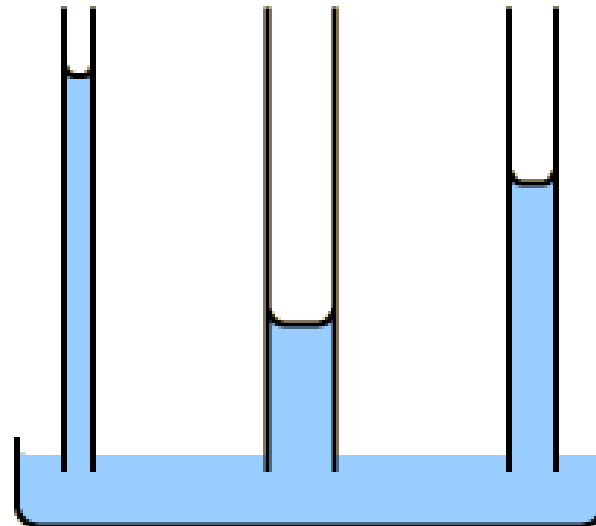
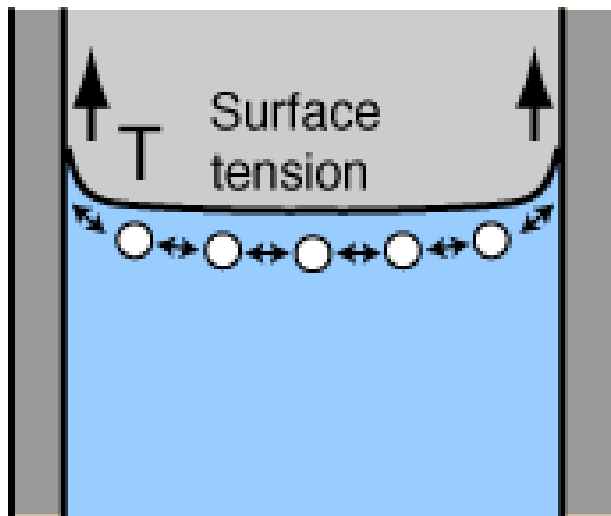




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## Capillary Action

Capillary action is the result of adhesion and surface tension. Adhesion of water to the walls of a vessel will cause an upward force on the liquid at the edges and result in a meniscus which turns upward. The surface tension acts to hold the surface intact, so instead of just the edges moving upward, the whole liquid surface is dragged upward.





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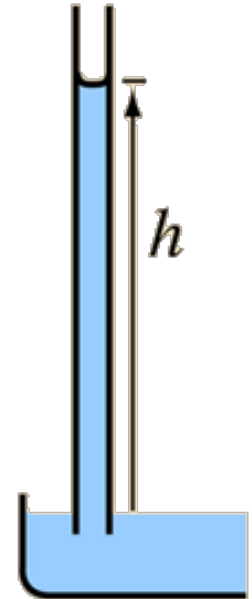
## Capillary Action

Capillary action occurs when the adhesion to the walls is stronger than the cohesive forces between the liquid molecules. The height to which capillary action will take water in a uniform circular tube is limited by surface tension.

The height  $h$  to which capillary action will lift water depends upon the weight of water which the surface tension will lift:

$$T2\pi r = \rho g(h\pi r^2)$$

The height to which the liquid can be lifted is given by  $h = \frac{2T}{\rho r g}$



Since it is weight limited, it will rise higher in a smaller tube.