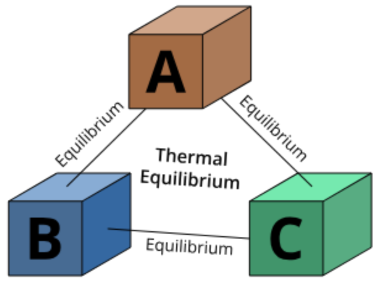
Fundamentals of Thermodynamics
Lecture 4. The First Law of Thermodynamics

4.1 The Four Laws of Thermodynamics

A. Zeroth Law

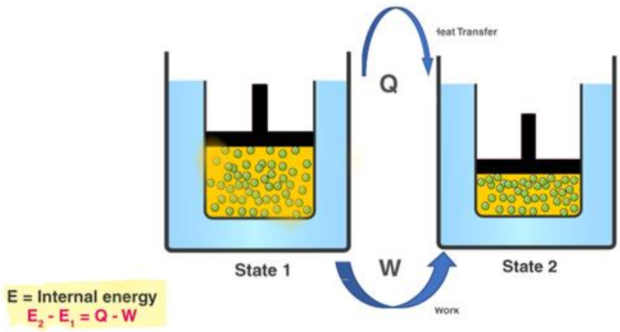
The *Zeroth Law* of Thermodynamics states that if two systems are each separately in equilibrium with a third system, then the first two systems are also in equilibrium with each other.



Zeroth law of Thermodynamics

B. First Law

The First law of Thermodynamics is nothing more than a statement that energy is conserved.



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C. Second Law

- ❖ The second law of thermodynamics states that there exists a valuable physical quantity, called entropy, that increases during a natural and spontaneous process. Its change is zero for a reversible process. The second law is also known as the law of increased entropy.
- ❖ The second law quantifies energy and asserts that a process has a specific direction While the first law does not predict the direction of the process nor guarantee that the process will occur. Thus, the second law was developed to ascertain if a process will happen or not, which is only possible if it satisfies both the first and second laws.

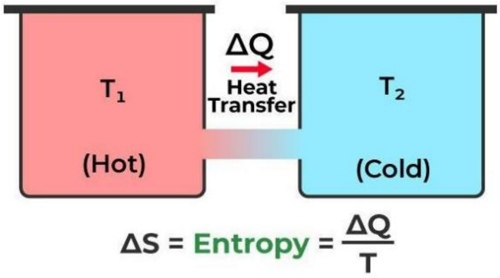
❖ Several eminent scientists have contributed to the second law. These include French physicist Sadi Carnot, German physicist Rudolf Clausius, and Scottish-Irish physicist Lord Kelvin.

❖ The second law of thermodynamics has several possible equivalent statements. Two of them are:

(1) The entropy of an isolated system can never decrease.

(2) It is impossible for an engine operating in a cyclic process to convert energy into work with 100 % efficiency.

The above two statements are indeed equivalent.

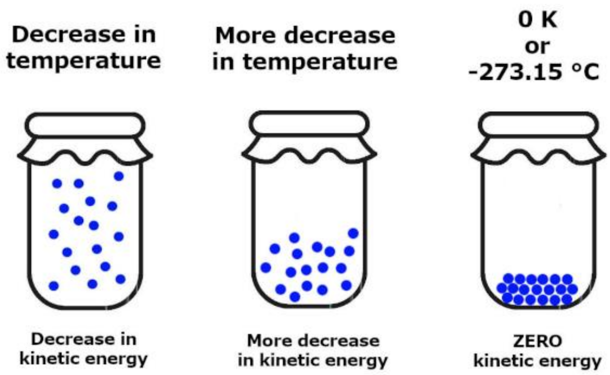


D. Third Law

❖ The third law of thermodynamics is the least robust of the laws of thermodynamics. There are several different statements of the third law, among them are:

(1) The entropy change of a substance goes to zero as temperature approaches absolute zero.

(2) The entropy of a pure substance is zero at absolute zero.



A consequence of the first, second, and third laws is that it is impossible to reduce the temperature of a substance to absolute zero (0 K) in a finite number of steps.

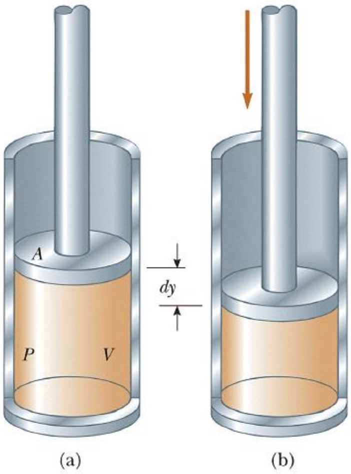
❖ In other words, it would take an infinite number of steps to reach absolute zero, so therefore, it is unattainable.

❖ The unattainability of absolute zero is sometimes regarded as being another alternate statement of the Third Law of Thermodynamics, however, it is actually a consequence of the First, Second, and Third Laws.

❖ The coldest temperature that was reached is 3×10^{-9} K (achieved in 2009).

Thermodynamic Work

- Consider a cylinder filled with a gas and sealed with a movable piston as shown below



If the gas is compressed quasi-statically (slowly enough to allow the system to remain in thermal equilibrium at all times), the differential element of work dW done on the gas as the piston moves a distance dy is:

$$dW = \vec{F}.d\vec{r} = (-F\,\hat{j}).(-dy\,\hat{j}) = F\,dy = P\,A\,dy \qquad (1)$$

where P is the pressure of the gas and A is the area of the piston.

Note that the volume of the cylinder decreases by an amount $A\,dy$, so we can write the differential change in the volume of the cylinder $-dV = A\,dy$, and the differential element of work done on the gas as

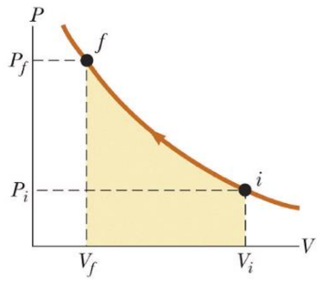
$$dW = -P\,dV \qquad (2)$$

Equation (2) is only valid if the process is quasi-static with respect to mechanical equilibrium. (Why?)

The total work done on the gas as its volume changes from V_i to V_f is

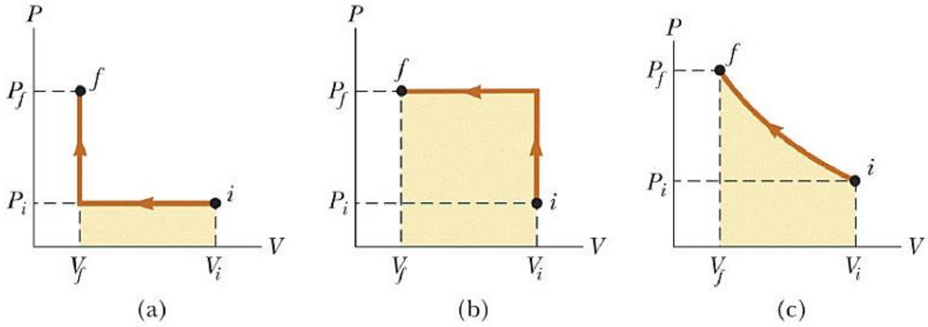
$$W = -\int_{V_i}^{V_f} P\,dV \qquad (3)$$

The work done on the gas is the negative of the area under the curve on a PV diagram



The Dependence of Thermodynamic Work on Path

The work done on a gas as it is taken from an initial state to a final state depends on the path between these states



The Formulation of the First Law of Thermodynamics

The change in internal energy of a system is equal to the heat added to the system plus the work done on the system:

$$U = Q + W \qquad (4)$$

- It is a statement of conservation of energy for thermodynamic systems.
- Q and W separately depend on the path taken.
- U (which they sometimes symbolize it as E_{int}) does not depend on the path, but only on the initial and final states, so we call U a *state variable*.
- The first law can be expressed in differential form as:

$$dU = dQ + dW \qquad (5)$$

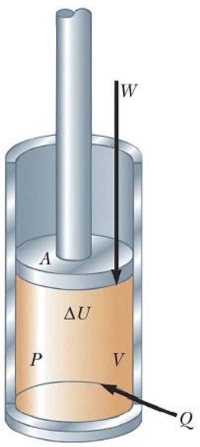
In terms of specific quantities,

$$du = dq + dw \qquad (6)$$

or

$$du = dq - pd\alpha \qquad (7)$$

where α is the specific volume (V/m, or ρ^{-1}).



The first law in this form tells us that if a gas expands then its internal energy must either decrease, or heat must be added to it in order to keep the internal energy from decreasing.

- In an adiabatic process, no heat is added or subtracted. Therefore $dq = 0$. This means that if a gas expands adiabatically its internal energy (and hence, its temperature) will decrease.

4.2 Problems

1. (a) What is the minimum amount of work done by you in blowing up a spherical party balloon to a diameter of 8 inches? Assume standard sea-level pressure.

   (b) Why is this the minimum amount of work?

2. Suppose 200 J of work are done on a system and 70 cal are extracted from the system. What is the change in internal energy of the system?

3. A piston-cylinder arrangement contains 1 kg of liquid water which is converted to steam by boiling at standard atmospheric pressure. The volume changes from an initial value of $1 \times 10^{-3} m^{-3}$ as a liquid to 1.671 m^3 as steam. (a) How much work is done on the system during the process? (b) How much energy is transferred as heat during the process? (c) What is the change in internal energy of the system during the process?

4.3 Questions

1. Why should the equation ($dW = -P\, dV$) be applied in the quasi-static process only?
2. Prove with giving sketch example that the thermodynamic work depends on the path.
3. Why do Q and W depend on path while U not?