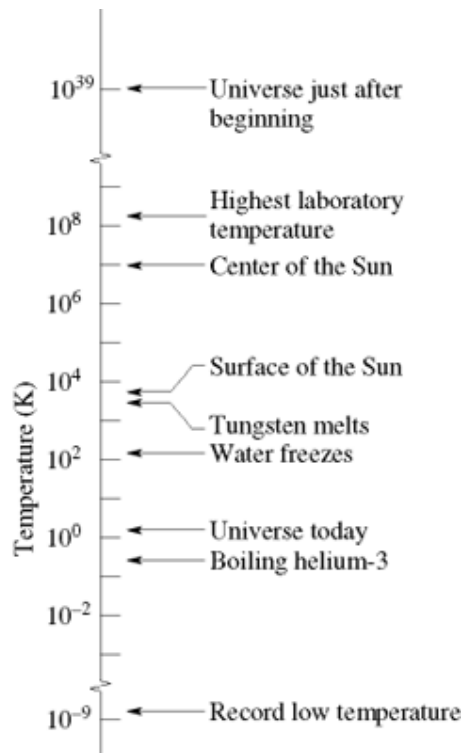


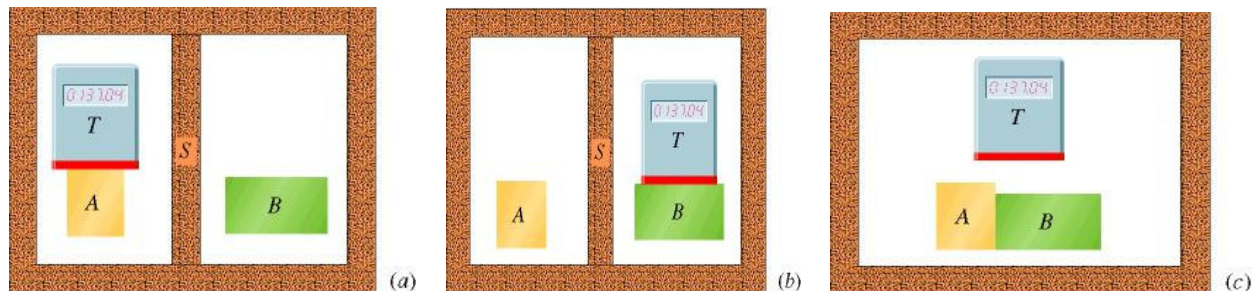
Temperature, Heat, and the First Law of Thermodynamics

Thermodynamics



Some temperatures on the Kelvin scale. Temperature $T = 0$ corresponds to $10^{-\infty}$ and cannot be plotted on this logarithmic scale.

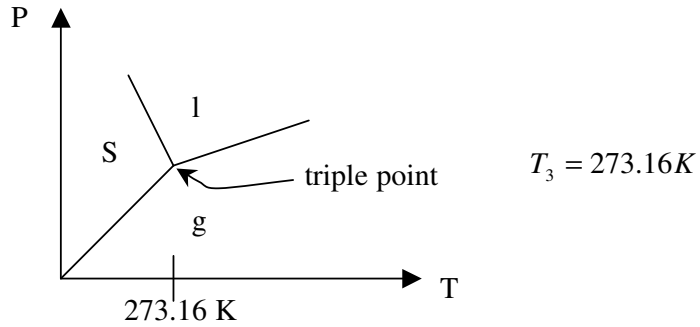
Zeroth law of thermodynamics



a) Body T (a thermoscope) and body A are in thermal equilibrium. (Body S is a thermally insulating screen.) (b) Body T and body B are also in thermal equilibrium, at the same reading of the thermoscope. (c) If (a) and (b) are true, the zeroth law of thermodynamics states that body A and body B are also in thermal equilibrium.

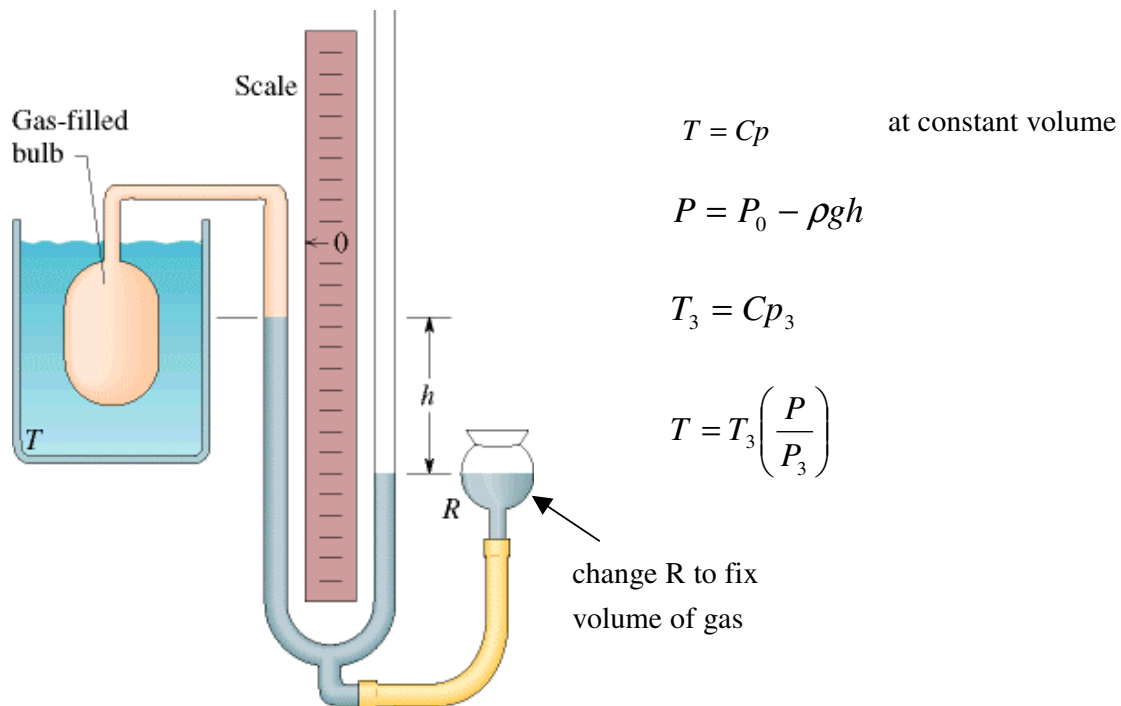
If A , B are each in thermal equilibrium with C at T , then they are in thermal equilibrium with each other.

Measuring temperature



phase diagram of water

The Constant-Volume Gas Thermometer



A constant-volume gas thermometer, its bulb immersed in a liquid whose [temperature](#) T is to be measured.

$$T = 273.16 \left(\lim_{m \rightarrow 0} \frac{P}{P_3} \right)$$

The Celsius and Fahrenheit Scales

$$T_C = T - 273.15$$

$$T_F = \frac{9}{5} T_C + 32$$

Thermal Expansion



(a) A bimetal strip, consisting of a strip of brass and a strip of steel welded together, at temperature T_0 . (b) The strip bends as shown at temperatures above this reference temperature. Below the reference temperature the strip bends the other way. Many thermostats operate on this principle, making and breaking an electrical contact as the temperature rises and falls.

$$\Delta L = \alpha L \Delta T \quad \alpha = \frac{\Delta L / L}{\Delta T} \quad \text{coefficients of linear expansion}$$

$$\Delta V = \beta V \Delta T \quad \beta = 3\alpha$$

pf.

$$\Delta L_x = \alpha L_x \Delta T$$

$$\Delta L_y = \alpha L_y \Delta T$$

$$\Delta L_z = \alpha L_z \Delta T$$

$$\Delta V = (L_x + \Delta L_x)(L_y + \Delta L_y)(L_z + \Delta L_z) - L_x L_y L_z$$

$$\cong \Delta L_x L_y L_z + \Delta L_y L_x L_z + \Delta L_z L_x L_y$$

$$= \alpha(\Delta L_x L_y L_z) \Delta T + \alpha(\Delta L_y L_x L_z) \Delta T + \alpha(\Delta L_z L_x L_y) \Delta T$$

$$= (3\alpha)V \Delta T \cong \beta V \Delta T \quad \beta = 3\alpha$$

On a hot day in Las Vegas, an oil trucker loaded 37,000 L of diesel fuel. He encountered cold weather on the way to Payson, Utah, where the temperature was 23.0 K lower than in Las Vegas, and where he delivered his entire load. How many liters did he deliver? The coefficient of volume expansion for diesel fuel is $9.50 \times 10^{-4}/\text{C}^\circ$, and the coefficient of linear expansion for his steel truck tank is $11 \times 10^{-6}/\text{C}^\circ$.

SOLUTION:

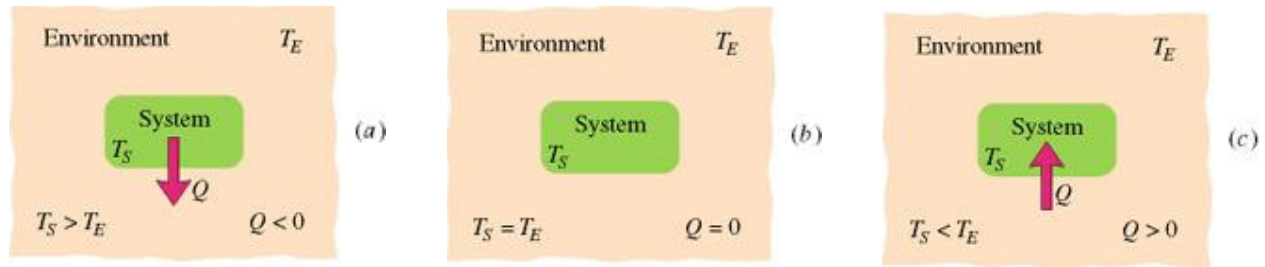
The **Key Idea** here is that the volume of the diesel fuel depends directly on the temperature. Thus, because the temperature decreased, the volume of the fuel did also. From Eq. [19-10](#), the volume change is

$$\begin{aligned}\Delta V &= V \beta \Delta T \\ &= (37,000 \text{ L})(9.50 \times 10^{-4} / \text{C}^\circ)(-23.0 \text{ K}) = -808 \text{ L}.\end{aligned}$$

Thus, the amount delivered was

$$\begin{aligned}V_{\text{del}} &= V + \Delta V = 37,000 \text{ L} - 808 \text{ L} \\ &= 36,190 \text{ L}.\end{aligned}$$

Temperature and Heat



If the **temperature** of a system exceeds that of its environment as in (a), **heat** Q is lost by the system to the environment until thermal equilibrium (b) is established. (c) If the temperature of the system is below that of the environment, heat is absorbed by the system until thermal equilibrium is established.

heat is a form of energy

$$1 \text{ cal} = 3.969 \times 10^{-3} \text{ Btu} = 4.186\text{J}$$

heat for 1 lb water 1°F increase in temperature = 1 Btu

Heat capacity (C)

$$Q = C(T_f - T_i)$$

$$c \propto m \text{ (mass)} \quad \left(\frac{\text{J}}{\text{K}}\right)$$

define $C = cm$

molar specific heat

$$Q = cm(T_f - T_i) \quad \left(\frac{\text{J}}{\text{kg} \cdot \text{K}}\right) \rightarrow \text{J}/\text{mol} \cdot \text{K}$$

C_v : specific heat at constant volume

C_p : specific heat at constant pressure

for an ideal gas $C_p = C_v + Nk$

When heat is absorbed,



(1) temperature : vibration or translation more violently

(2) phase transitions : define L as heat of transformation

$$Q = L m$$

For example, heat of vaporization L_v of water (liquid \leftrightarrow gas)

$$L_v = 539 \text{ cal/g} = 40.7 \text{ KJ/mol} = 2256 \text{ KJ/kg}$$

heat of fusion L_f (liquid \leftrightarrow solid)

$$L_f = 79.5 \text{ cal/g} = 6.01 \text{ KJ/mol} = 333 \text{ KJ/kg}$$

A copper slug whose mass m_c is 75 g is heated in a laboratory oven to a temperature T of 312°C. The slug is then dropped into a glass beaker containing a mass $m_w = 220$ g of water. The heat capacity C_b of the beaker is 45 cal/K. The initial temperature T_i of the water and the beaker is 12°C. Assuming that the slug, beaker, and water are an isolated system and the water does not vaporize, find the final temperature T_f of the system at thermal equilibrium.

Solution:

energy conserved for the system of water + beaker + copper slug

water : $Q_w = m_w c_w (T_f - T_i)$

$$Q_b = C_b (T_f - T_i)$$

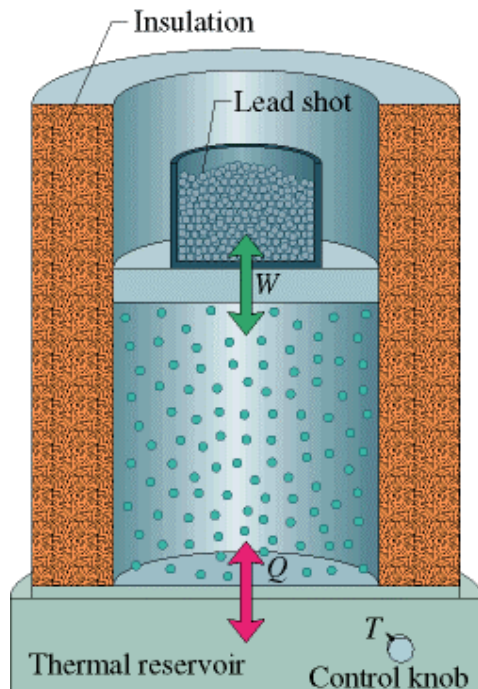
$$Q_c = m_c c_c (T_f - T)$$

$$Q_w + Q_b + Q_c = 0$$

$$m_w c_w (T_f - T_i) + C_b (T_f - T_i) + m_c c_c (T_f - T) = 0$$

$$T_f = \frac{m_c c_c T + m_w c_w T_i + C_b T_i}{m_w c_w + C_b + m_c c_c} = \frac{5332.8}{271.9} \cong 19.6^\circ \text{C}$$

Heat and Work



initial state i

$$V_i, P_i, T_i$$

final state f

$$V_f, P_f, T_f$$

$$F = P \cdot A$$

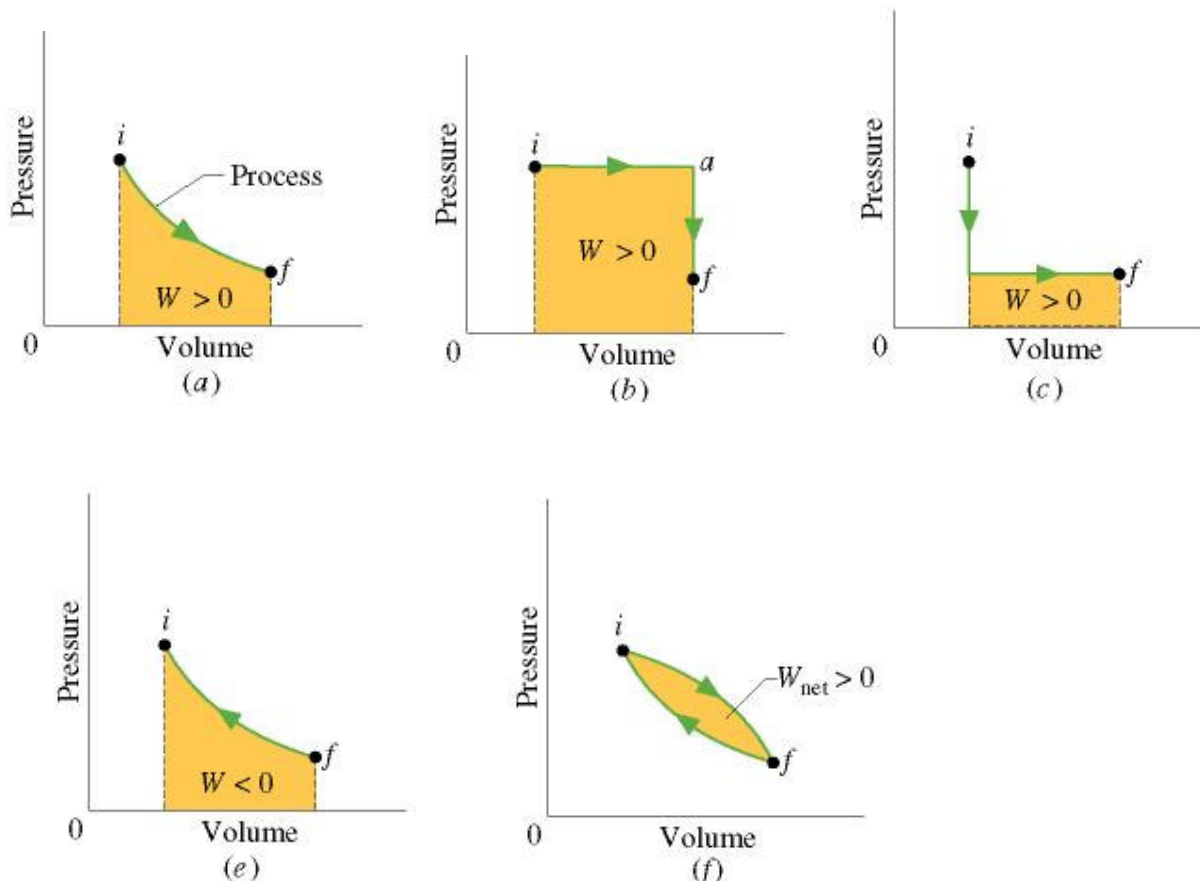
let $W < F$ piston move

A gas is confined to a cylinder with a movable piston. Heat Q can be added to, or withdrawn from, the gas by regulating the temperature T of the adjustable thermal reservoir. Work W can be done by the gas by raising or lowering the piston.

Work done by the gas

$$dW = F \cdot ds = PAd s = p dv$$

$$W = \int_i^f dw = \int_i^f p dv$$



(a) The shaded area represents the work W done by a system as it goes from an initial state i to a final state f . **Work** W is positive because the system's volume increases. (b) W is still positive, but now greater. (c) W is still positive, but now smaller. (d) W can be even smaller (path $icdf$) or larger (path $ighf$). (e) Here the system goes from state f to state i , as the gas is compressed to less volume by an external force. The work W done by the system is now negative. (f) The net work W_{net} done by the system during a complete cycle is represented by the shaded area.

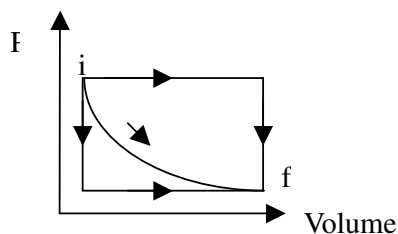
The First Law of Thermodynamics

$Q-W$ is the same for all processes if initial state and final state are not changed. It is independent of path.

$Q-W$ is the intrinsic property of the system, we call it internal energy

$$\Delta E_{int} = E_f - E_i = Q - W$$

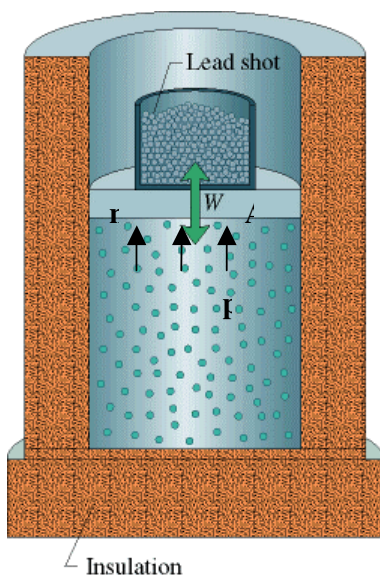
For an infinitesimal change $dE = dQ - dW$



(1) Adiabatic processes

no heat transferred $Q = 0$

$$\Delta E_{\text{int}} = -W$$



If $mg < pA$, gas expand, $W > 0$

$$\Delta E_{\text{int}} < 0$$

If $mg > pA$, gas compressed, $W < 0$

$$\Delta E_{\text{int}} > 0$$

An adiabatic expansion can be carried out by slowly removing lead shot from the top of the piston. Adding lead shot reverses the process at any stage.

(2) Constant-volume processes

$$W = 0 \quad Q > 0 \quad \Delta E_{\text{int}} > 0$$

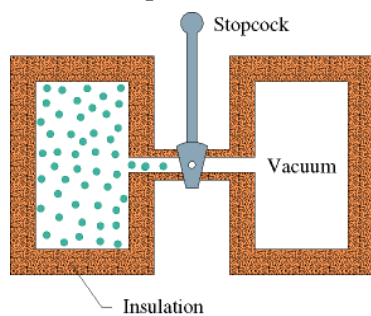
$$\Delta E_{\text{int}} = Q \quad Q < 0 \quad \Delta E_{\text{int}} < 0$$

(3) Cyclical processes

$$\Delta E_{\text{int}} = 0$$

$$Q = W$$

(4) Free expansions.

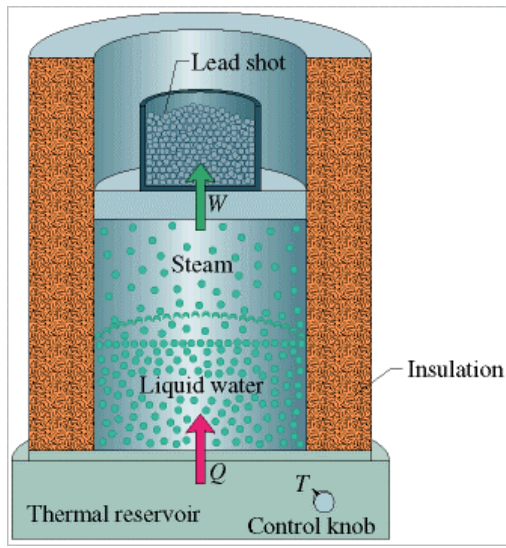


$$Q = W = 0$$

$$\Delta E = 0$$

The initial stage of a free-expansion process. After the stopcock is opened, the gas fills both chambers and eventually reaches an equilibrium state.

Let 1.00 kg of liquid water at 100°C be converted to steam at 100°C by boiling at standard atmospheric [pressure](#) (which is 1.00 atm or 1.01×10^5 Pa) in the arrangement of Fig. [19-17](#) . The volume of that water changes from an initial value of 1.00×10^{-3} m³ as a liquid to 1.671 m³ as steam.



Water boiling at constant [pressure](#). Energy is transferred from the thermal reservoir as [heat](#) until the liquid water has changed completely into steam. [Work](#) is done by the expanding gas as it lifts the loaded piston.

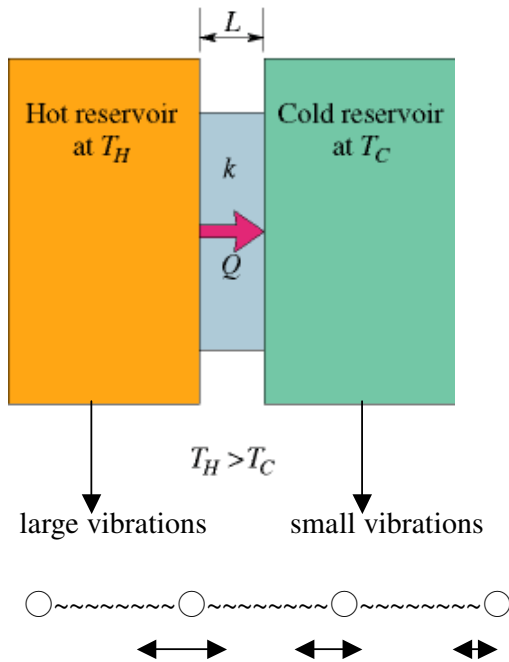
$$\begin{aligned}
 \text{(a) } W &= \int_i^f p dv = p(V_f - V_i) \\
 &= 1.01 \times 10^5 \times (1.671 - 10^{-3}) \\
 &= 1.69 \times 10^5 \text{ J}
 \end{aligned}$$

$$\text{(b) } Q = L_v m = 2260 \text{ kJ/kg} \cdot 1 \text{ kg} = 2260 \text{ kJ}$$

$$\text{(c) } \Delta E = Q - W = 2090 \text{ (kJ)}$$

Heat Transfer Mechanisms

conduction, convection, and radiation



Thermal **conduction**. Energy is transferred as **heat** from a reservoir at **temperature** T_H to a cooler reservoir at temperature T_C through a conducting slab of thickness L and thermal conductivity k .

$$H = \frac{Q}{t} = KA \frac{(T_H - T_C)}{L}$$

↑
↘

thermal
∇ T

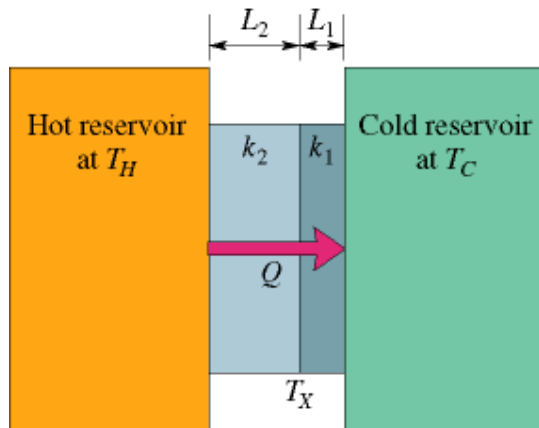
conductivity

Thermal resistance to conduction

$$R = \frac{L}{K}$$

$$H = A \cdot \frac{T_H - T_C}{R}$$

Conduction through a composite slab



Heat is transferred at a steady rate through a composite slab made up of two different materials with different thicknesses and different thermal conductivities. The steady-state temperature at the interface of the two materials is T_X .

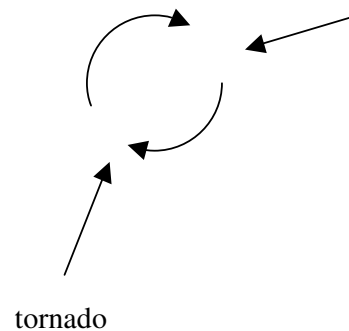
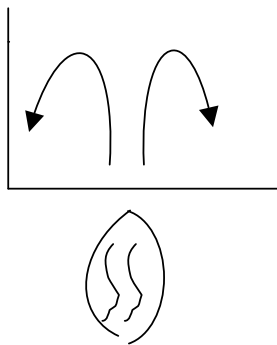
$$H = \frac{k_2 A (T_H - T_X)}{L_2} = \frac{k_1 A (T_X - T_C)}{L_1}$$

$$T_X = \frac{k_1 L_2 T_C + k_2 L_1 T_H}{k_1 L_2 + k_2 L_1}$$

$$H = \frac{A(T_H - T_C)}{L_1/k_1 + L_2/k_2} = \frac{A(T_H - T_C)}{R} = \frac{A(T_H - T_C)}{\sum R_i}$$

$$R = R_1 + R_2$$

Convection



Radiation

thermal radiation rate

$$P_r = \sigma \epsilon A T^4 \quad \sigma = 5.67 \times 10^{-8} \left(\frac{\text{W}}{\text{m}^2 \text{K}^4} \right)$$

ϵ : emissivity

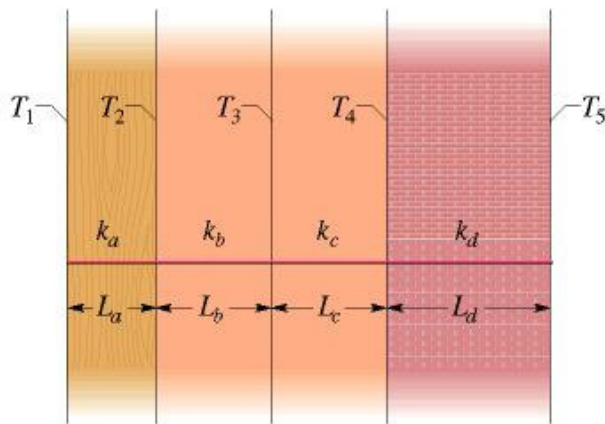
absorption from the environment

$$P_a = \sigma \epsilon A T_{env}^4$$

$$P_n = P_a - P_r = \sigma \epsilon A (T_{env}^4 - T^4)$$

$\epsilon_{black} > \epsilon_{white}$
if $T_{env} > T$
 $P_n^b > P_n^w$

Figure below shows the cross section of a wall made of white pine of thickness L_a and brick of thickness $L_d (= 2.0L_a)$, sandwiching two layers of unknown material with identical thicknesses and thermal conductivities. The thermal conductivity of the pine is k_a and that of the brick is $k_d (= 5.0k_a)$. The face area A of the wall is unknown. Thermal conduction through the wall has reached the steady state; the only known interface temperatures are $T_1 = 25^\circ\text{C}$, $T_2 = 20^\circ\text{C}$, and $T_3 = -10^\circ\text{C}$. What is interface temperature T_4 ?



(a)

$$H_a = k_a A \frac{T_1 - T_2}{L_a}$$

$$H_d = k_d A \frac{T_4 - T_5}{L_d}$$

$$H_a = H_d \Rightarrow T_4 = \frac{k_a L_d}{k_d L_a} (T_1 - T_2) + T_5$$

$$\cong -8.0^\circ\text{C}$$

(b)

$$k_b A \frac{T_2 - T_3}{L_b} = k_c A \frac{T_3 - T_4}{L_c}$$

$$k_b = k_c \quad L_b = L_c$$

$$T_2 - T_3 = T_3 - T_4$$


$$T_3 = \frac{T_2 + T_4}{2} = 6^\circ\text{C}$$

The Kinetic Theory of Gases

1 mole is the number of atoms in a 12 g sample of carbon 12.

$N_a = 6.02 \times 10^{23} \text{ mol}^{-1}$: Avogadro's number

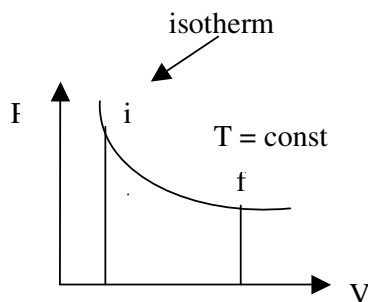
number of moles $n = \frac{N}{N_a} = \frac{M_{sam}}{mN_A} = \frac{M_{same}}{M}$



molar mass

ideal gas eg. of state

$pV = nRT$ (experiment first) $R = 8.31 \text{ J}/(\text{mole K})$ gas constant



$$W = \int p dv = \int \frac{nRT}{V} dv$$

$$= nRT \log\left(\frac{V_f}{V_i}\right) \quad (\text{isothermal processes})$$

constant volume processes $W = 0$

constant pressure process $W = \int p dv = p(V_f - V_i) = p\Delta V$

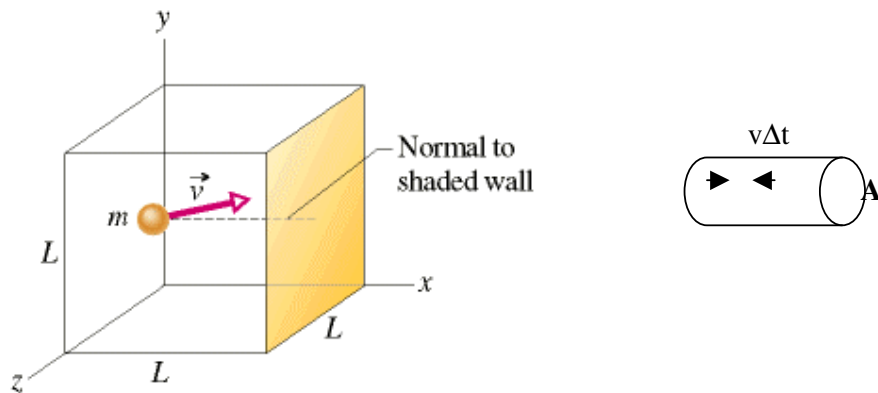
A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

Solution:

$$\frac{pV}{T} = nR = \text{const} \quad \frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

$$p_f = p_i \cdot \frac{V_i}{V_f} \cdot \frac{T_f}{T_i} = 22 \text{ atm}$$

Pressure, Temperature, and RMS Speed



A cubical box of edge L , containing n moles of an ideal gas. A molecule of mass m and velocity \vec{v} is about to collide with the shaded wall of area L^2 . A normal to that wall is shown.

$$\Delta p_x = -mv_x - mv_x = -2mv_x$$

$$\frac{\left[\left(\frac{N}{V} \right) (A \cdot v_x \Delta t) / 2 \right] \cdot 2mv_x}{\Delta t} = F$$

$$\frac{F}{A} = p = \frac{Nmv_x^2}{V} = \frac{nMv_x^2}{V}$$

$$p = \frac{nM}{V} (v_{x1}^2 + \dots + v_{xN}^2) / N$$

$$= \frac{nM}{V} v_x^2 = \frac{nM}{3V} v^2 = \frac{nM}{3V} v_{rms}^2$$

$$pV = \frac{nM}{3} v_{rms}^2 = nRT$$

$$\frac{M}{3} v_{rms}^2 = RT \quad v_{rms}^2 = \sqrt{\frac{3RT}{M}}$$

at $T = 300\text{K}$ 4300 (mi/h)

| Gas | v_{rms} (m/s) |
|--------------------------------------|-----------------|
| Hydrogen (H_2) | 1920 |
| Helium (He) | 1370 |
| Water vapor (H_2O) | 645 |
| Carbon dioxide (CO_2) | 412 |

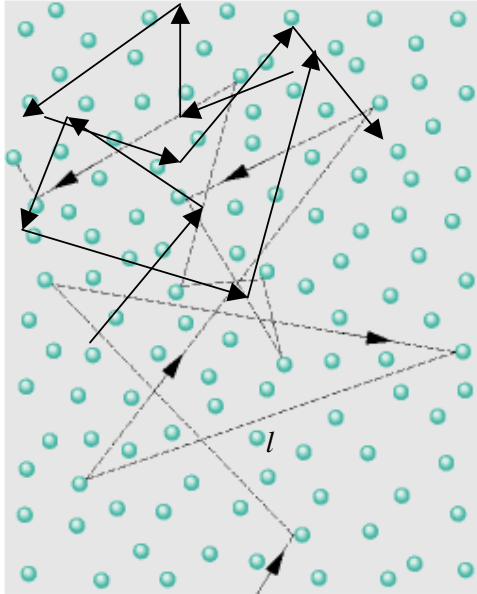
Translational Kinetic Energy

$$\bar{K} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m \bar{v}_2 = \frac{1}{2} m v_{rms}^2$$

$$\bar{K} = \frac{3}{2} kT \quad k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K}$$

(Boltzmann constant)

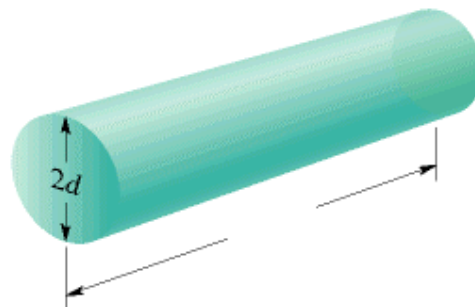
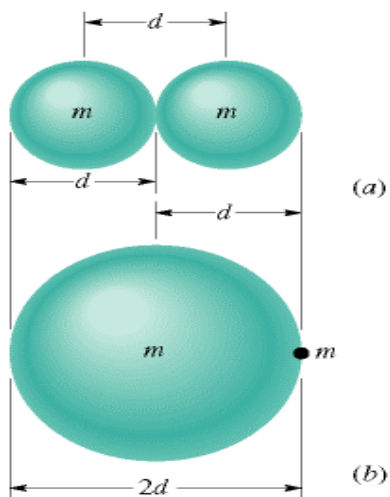
Mean free path



A molecule traveling through a gas, colliding with other gas molecules in its path. Although the other molecules are shown as stationary, they are also moving in a similar fashion.

$\langle l \rangle = \lambda$: mean free path

$$\lambda \propto \frac{1}{\left(\frac{N}{V}\right)} \quad \lambda \propto \frac{1}{(\tau d^2)} \quad d: \text{molecular size}$$



(a) A collision occurs when the centers of two molecules come within a distance d of each other, d being the molecular diameter.

(b) An equivalent but more convenient representation is to think of the moving molecule as having a radius d and all other molecules as being points. The condition for a collision is unchanged.

In time Δt the moving molecule effectively sweeps out a cylinder of length $v \Delta t$ and radius d .

$r_{cm} < d$: collision

τ : mean collision time

$$(\pi d^2 \cdot v \tau) \cdot \frac{N}{V} = 1$$

consider all others are at rest $\lambda = \frac{1}{\pi d^2 \left(\frac{N}{V}\right)}$

in fact, all molecules are moving $\lambda = \frac{1}{\sqrt{2} \pi d^2 \left(\frac{N}{V}\right)}$

ex.

(a) What is the mean free path λ for oxygen molecules at temperature $T = 300$ K and pressure $p = 1.0$ atm? Assume that the molecular diameter is $d = 290$ pm and the gas is ideal. (b) Assume the average speed of the oxygen molecules is $v = 450$ m/s. What is the average time t between successive collisions for any given molecule? At what rate does the molecule collide; that is, what is the frequency f of its collisions?

(a)

$$d = 2.9 \times 10^{-10}$$

$$V = \frac{nRT}{p} = \frac{1 \times 8.31 \times 300}{1(\text{atm}) \times 10^5 \left(\frac{\text{Pa}}{\text{atm}}\right)} = 2.5 \times 10^{-2} \text{ m}^3$$

$$\frac{N}{V} = \frac{6 \times 10^{23}}{2.5 \times 10^{-2}} = 2.4 \times 10^{25} \left(\frac{\text{molecules}}{\text{m}^3}\right)$$

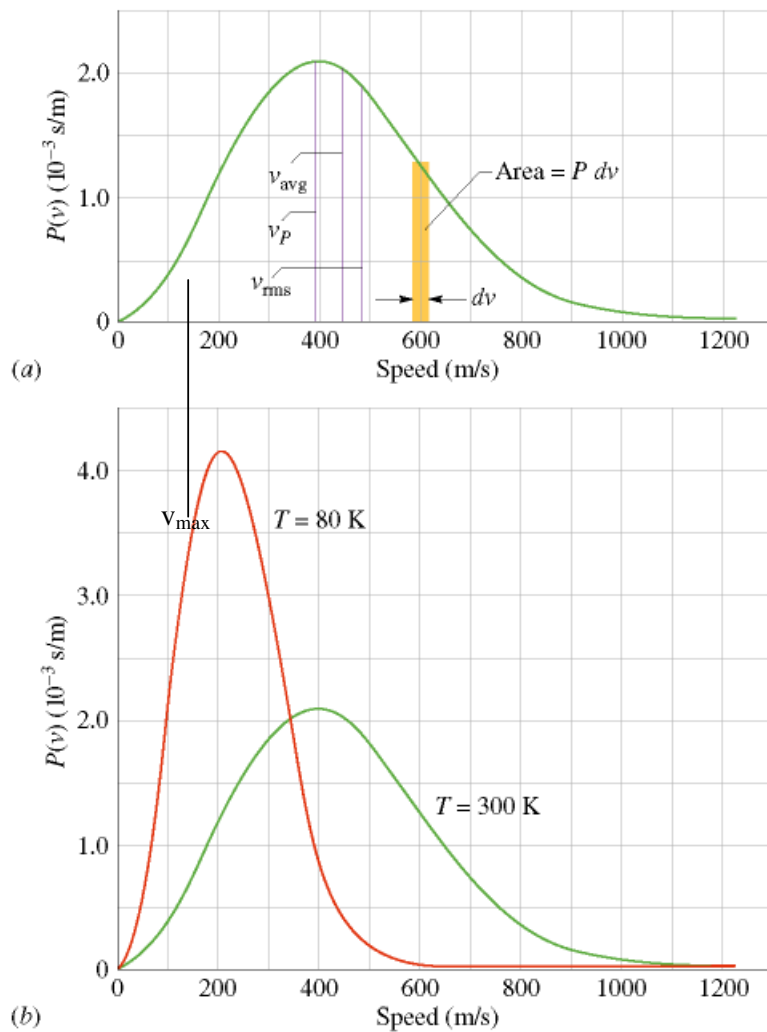
$$\lambda = \frac{1}{\sqrt{2} \pi d^2 \left(\frac{N}{V}\right)} = 1.1 \times 10^{-7} \text{ (m)}$$

(b)

$$\tau = \frac{\lambda}{v_{rms}}$$

$$\tau^{-1} = \frac{v_{rms}}{\lambda} = 4 \times 10^9 \text{ (s}^{-1}\text{)}$$

Boltzmann distribution



a) The Maxwell speed distribution for oxygen molecules at $T = 300\text{ K}$. The three characteristic speeds are marked. (b) The curves for 300 K and 80 K . Note that the molecules move more slowly at the lower [temperature](#). Because these are probability distributions, the area under each curve has a numerical value of unity.

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT} \right)$$

$$\frac{2P(v)}{2v^2} = 0 \Rightarrow \exp\left(-\frac{Mv^2}{2RT} \right) - \frac{M}{2RT} v_{\text{max}}^2 \exp\left(-\frac{Mv^2}{2RT} \right) = 0$$

$$v_{\text{max}}^2 = \frac{2RT}{M} \quad v_{\text{max}} = \sqrt{\frac{2RT}{M}}$$

$$\begin{aligned}
\langle v^2 \rangle &= \int 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^4 \exp\left(-\frac{Mv^2}{2RT}\right) dv \\
&= \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot 4\pi \int v^2 e^{-\alpha v^2} dv \\
&= \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot 4\pi \left(\frac{d^2}{d\alpha^2} \int e^{-\alpha v^2} dv \right) \\
&= \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot 2\pi \frac{d^2}{d\alpha^2} \cdot \sqrt{\frac{\pi}{\alpha}} \\
&= \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot 2\pi \cdot \left(\frac{-1}{2} \right) \left(\frac{-3}{2} \right) \frac{\sqrt{\pi}}{\alpha^{\frac{5}{2}}} \\
&= \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \cdot \frac{3}{2} \cdot \left(\sqrt{\frac{2RT}{M}} \right)^{\frac{5}{2}} = \frac{3}{2} \cdot \frac{2RT}{M} = \frac{3RT}{M}
\end{aligned}$$

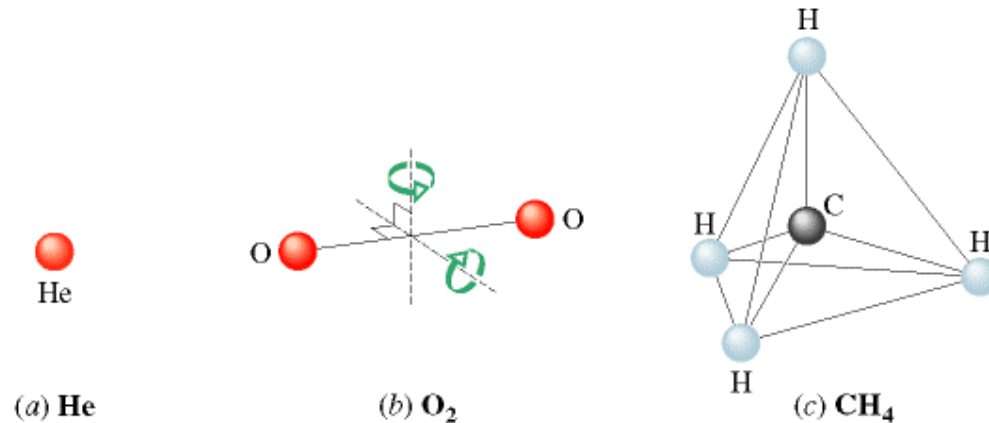
$$\sqrt{\langle v^2 \rangle} = v_{rms} = \sqrt{\frac{3RT}{M}}$$

Internal energy E_{int}

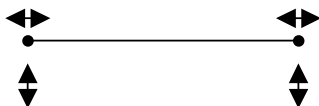
$$E_{int} = n \cdot N_A \cdot (K) = n \cdot N_A \cdot \frac{3}{2} kT = \frac{3}{2} nRT \quad (\text{monatomic ideal gas})$$

$$E_{int} = \frac{f}{2} nRT \quad f = \# \text{ of degrees of freedom}$$

ex.



Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.



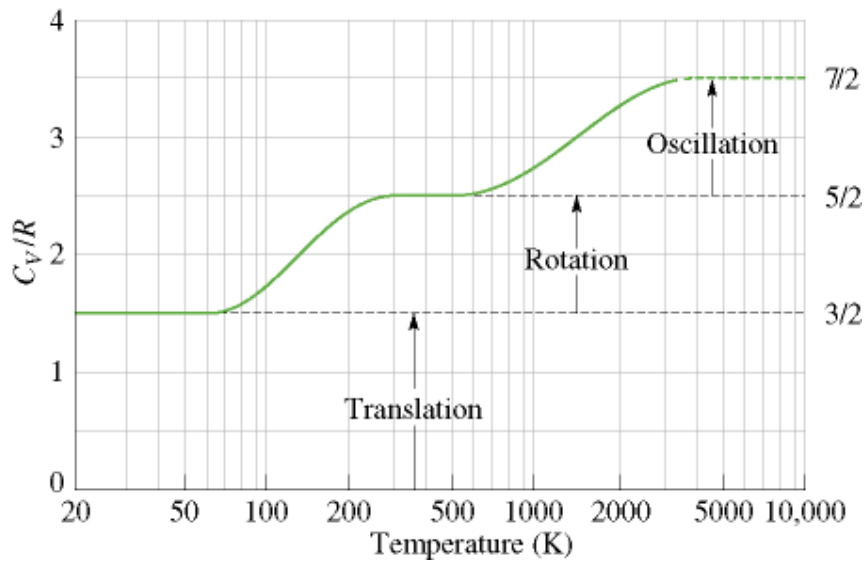
$$f = 3$$

$$f = 3 + 2 = 5 \quad (\text{translation} + \text{rotation})$$

$$f = 3 + 2 + 2 = 7 \quad (\text{translation} + \text{rotation} + \text{vibration})$$

Degrees of Freedom for Various Molecules

| Molecule | Example | Degrees of Freedom | | | Predicted Molar Specific Heats | |
|------------|-----------------|--------------------|------------|---------------|------------------------------------|-----------------|
| | | Translational | Rotational | Total (f) | C_V (Eq. 20-51) | $C_p = C_V + R$ |
| Monatomic | He | 3 | 0 | 3 | $\frac{3}{2}R$ | $\frac{5}{2}R$ |
| Diatomic | O ₂ | 3 | 2 | 5 | $\frac{5}{2}R$ | $\frac{7}{2}R$ |
| Polyatomic | CH ₄ | 3 | 3 | 6 | $3R$ | $4R$ |



A plot of C_V/R versus [temperature](#) for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.

Molar Specific Heats at constant volume

initial state i : p, T, V

↓ ΔQ

final state f : $p + \Delta p, T + \Delta T, V$

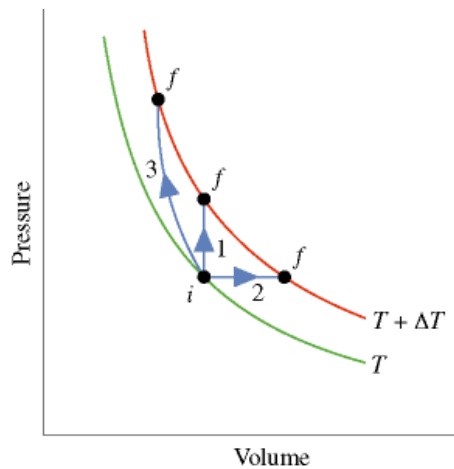
$$\Delta Q = nC_v \Delta T$$

$$\Delta E = \Delta Q - \Delta W = nC_v \Delta T \quad (\Delta W = 0)$$

$$C_v = \frac{1}{n} \cdot \frac{\Delta E_{\text{int}}}{\Delta T} = \frac{3}{2} R$$

$$E_{\text{int}} = nC_v T$$

$$\Delta E = nC_v \Delta T$$



1 · constant volume process

2 · constant pressure process

3 · adiabatic process

Since final state property doesn't depend on path, it can always be obtained from path 1, $\Delta E_{\text{int}} = nC_v \Delta T$ and then by eg. of state $pV = nRT$

Molar Specific Heat at Constant Pressure

$$\Delta Q = nC_p \Delta T$$

$$\Delta E = \Delta Q - \Delta W = \Delta Q - p\Delta V$$

$$= \Delta Q - nR\Delta T$$

$$= (nC_p - nR)\Delta T$$

$$n(C_p - R) = nC_v \quad C_p = C_v + R = \frac{5}{2} R$$

$$H_e \quad C_v = \frac{3}{2} R \quad C_p = \frac{5}{2} R$$

$$O_2 \text{ (rotation)} \quad C_v = \frac{5}{2} R \quad C_p = \frac{7}{2} R$$

$$\text{(vibration)} \quad C_v = \frac{7}{2} R \quad C_p = \frac{9}{2} R$$

Adiabatic expansion of an ideal gas

$$pV^\gamma = \text{const} \quad \gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

Pf :

$$dE = dQ - pdv$$

$$nC_v dt - pdV$$

$$pV = nRT$$

$$pdV + Vdp = nRdT$$

$$\frac{C_v}{R}(pdV + Vdp) = -pdV$$

$$\frac{C_v}{C_p - C_v}(pdV + Vdp) = -pdV$$

$$C_p pdV + VC_v dp = 0$$

$$C_p \frac{dV}{V} + C_v \frac{dp}{p} = 0$$

$$\frac{dp}{p} = -\frac{C_p}{C_v} \cdot \frac{dV}{V} = -\gamma \frac{dV}{V}$$

$$\ln p = -\gamma \ln V + \text{const}$$

$$= \ln V^{-\gamma} + \text{const}$$

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

$$pV = nRT$$

$$\left(\frac{nRT}{V}\right)V^\gamma = \text{const}$$

$$TV^{\gamma-1} = \text{const}$$

free expansion

$$\Delta Q = 0 \quad \Delta W = 0 \quad \Rightarrow \Delta E = 0$$

$$T_f = T_i$$

$$p_i V_i = p_f V_f$$

Entropy and the Second Law of Thermodynamics

Entropy S measures the degree of disorder of a system which is a function of the state of system.

The experience tells us that the entropy S increases for an irreversible process of a closed system 2nd

law of thermodynamics $\Delta S \geq 0$

Kelvin statement :

The entropy of a system increases when it receives heat decreases when it loses heat. $\Delta S \propto \Delta Q$

Clausius statement :

the higher the temperature of the system from which heat is transferred , the less entropy change occurs in that

system. $\Delta S \propto 1/T$

$$\Delta S = \frac{\Delta Q}{T} \quad \text{or} \quad dS = \frac{dQ}{T}$$

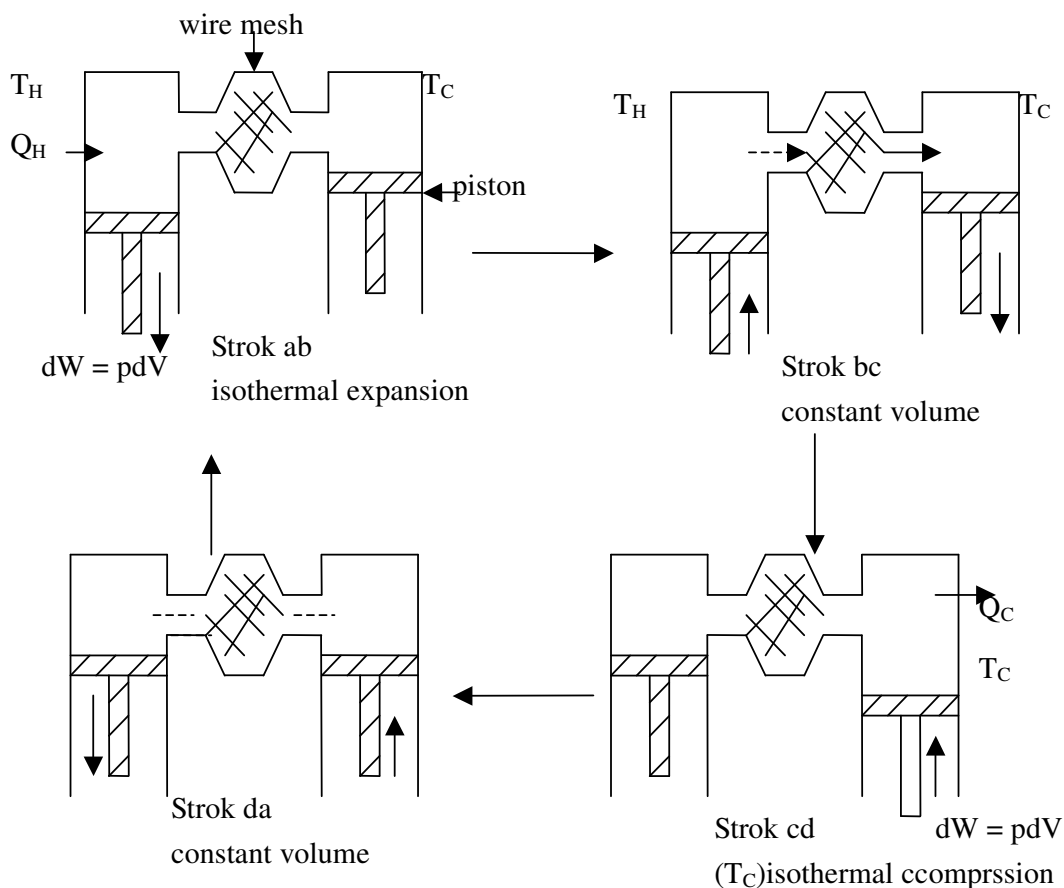
$$dQ = dE + dW$$

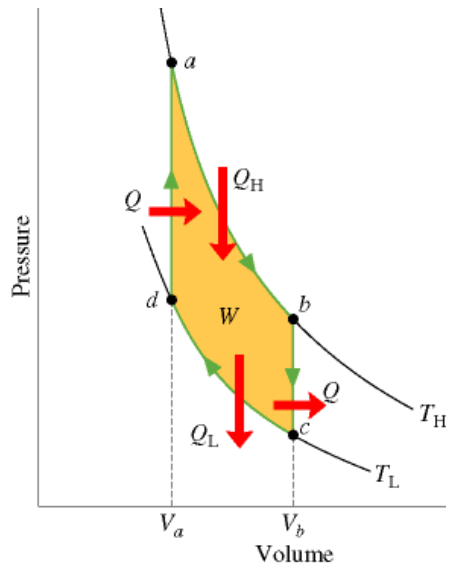
$$= nC_v dT + pdV$$

$$\int \frac{dQ}{T} = \int \frac{nC_v dT}{T} + \int \frac{nRTdV}{VT}$$

$$S_f - S_i = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Engines





Efficiency

$$\varepsilon = \frac{W}{Q_H}$$

$$W = Q_H - Q_C \quad (\text{since } \Delta E = 0)$$

$$\text{For a reversible process } \Delta S = 0 = \left(\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \right)$$

i.e.

$$\frac{Q_H}{T_H} = -\frac{Q_L}{T_L} \quad \frac{Q_L}{Q_H} = -\frac{T_L}{T_H}$$

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

For an irreversible process $\Delta S > 0$

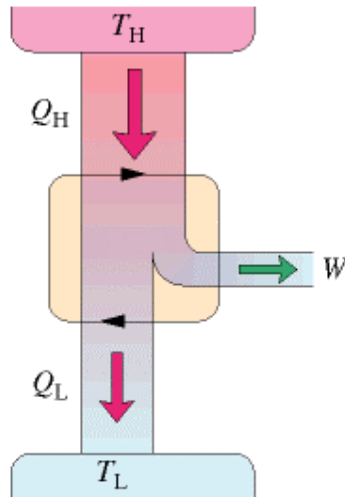
$$\frac{Q_H}{T_H} < -\frac{Q_C}{T_C} \quad \text{or} \quad \frac{Q_C}{Q_H} > \frac{T_C}{T_H}$$

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

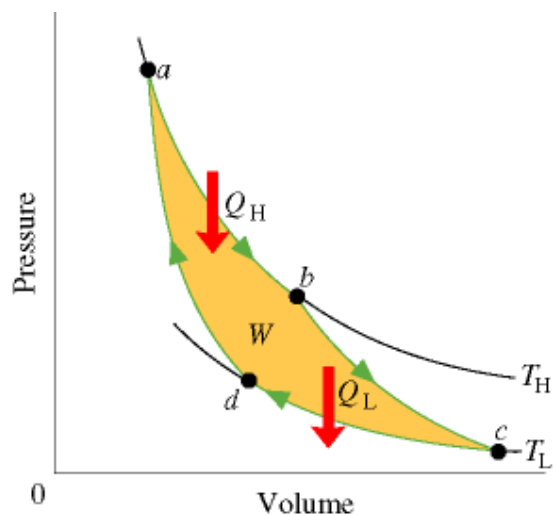
$$\varepsilon \leq 1 - \frac{T_C}{T_H}$$

A Carnot Engine

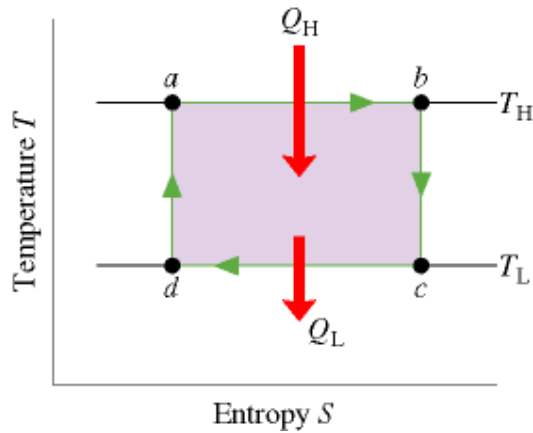
We shall focus on a particular ideal [engine](#) called a **Carnot engine** after the French scientist and engineer N. L. Sadi [Carnot](#) (pronounced “car-no”), who first proposed the engine's concept in 1824. This ideal engine turns out to be the best (in principle) at using energy as [heat](#) to do useful work. Surprisingly, Carnot was able to analyze the performance of this engine before the first law of [thermodynamics](#) and the concept of [entropy](#) had been discovered.



The elements of an engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p - V plot. Energy $|Q_H|$ is transferred as [heat](#) from the high-temperature reservoir at [temperature](#) T_H to the working substance. Energy $|Q_L|$ is transferred as heat from the working substance to the low-temperature reservoir at temperature T_L . Work W is done by the [engine](#) (actually by the working substance) on something in the environment.



A pressure–volume plot of the cycle followed by the working substance of the [Carnot engine](#). The cycle consists of two isotherm (ab and cd) and two adiabatic processes (bc and da). The shaded area enclosed by the cycle is equal to the work W per cycle done by the Carnot engine.



The [Carnot](#) cycle plotted on a temperature–entropy diagram. During processes *ab* and *cd* the [temperature](#) remains constant. During processes *bc* and *da* the [entropy](#) remains constant.

The Work:

To calculate the net work done by a [Carnot engine](#) during a cycle, let us apply Eq. 19-26, the first law of [thermodynamics](#) ($\Delta E_{\text{int}} = Q - W$), to the working substance. That substance must return again and again to any arbitrarily selected state in the cycle. Thus, if X represents any state property of the working substance, such as [pressure](#), [temperature](#), volume, internal energy, or [entropy](#), we must have $\Delta X = 0$ for every cycle. It follows that $\Delta E_{\text{int}} = 0$ for a complete cycle of the working substance. Recalling that Q in Eq. 19-26 is the [net heat](#) transfer per cycle and W is the [net work](#), we can write the first law of thermodynamics for the Carnot cycle as

$$W = |Q_H| - |Q_L|.$$

Entropy Changes:

In a [Carnot engine](#), there are *two* (and only two) reversible energy transfers as heat, and thus two changes in the [entropy](#) of the working substance—one at [temperature](#) T_H and one at T_L . The net entropy change per cycle is then

$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} + \frac{|Q_L|}{T_L}.$$

Here ΔS_H is positive because energy $|Q_H|$ is *added to* the working substance as [heat](#) (an increase in entropy) and ΔS_L is negative because energy $|Q_L|$ is *removed from* the working substance as heat (a decrease in entropy). Because entropy is a state function, we must have $\Delta S = 0$ for a complete cycle. Putting $\Delta S = 0$ in Eq. 21-7 requires that

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}.$$

Note that, because $T_H > T_L$, we must have $|Q_H| > |Q_L|$; that is, more energy is extracted as heat from the high-temperature reservoir than is delivered to the low-temperature reservoir.

We shall now use Eqs. [21-6](#) and [21-8](#) to derive an expression for the efficiency of a [Carnot engine](#).

Efficiency of a Carnot Engine

The purpose of any [engine](#) is to transform as much of the extracted energy Q_H into work as possible. We measure its success in doing so by its **thermal efficiency** ϵ , defined as the work the engine does per cycle (“energy we get”) divided by the energy it absorbs as [heat](#) per cycle (“energy we pay for”):

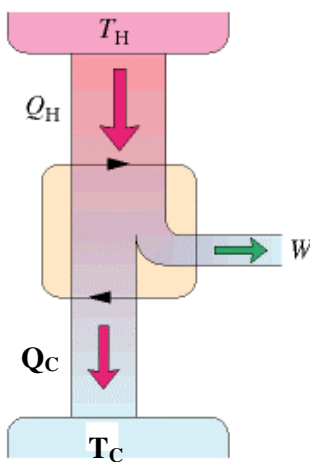
$$\epsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} \quad (\text{efficiency, any engine}).$$

For a [Carnot engine](#) we can substitute for W from Eq. [21-6](#) to write Eq. 21-9 as

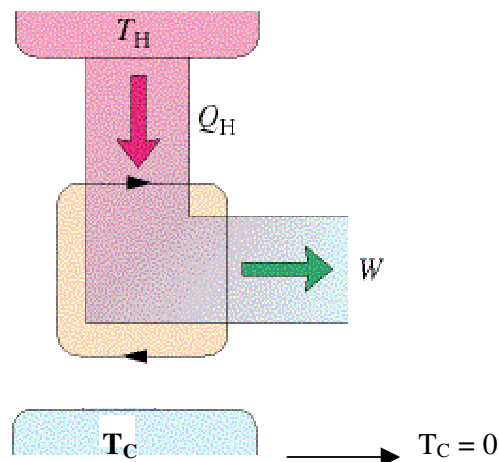
$$\epsilon = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}.$$

Using Eq. [21-8](#) we can write this as

$$\epsilon = 1 - \frac{T_L}{T_H} \quad (\text{efficiency, Carnot engine}).$$



perfect engine



Ex.

An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is this possible?

$$(a) \quad \varepsilon \leq 1 - \frac{T_C}{T_H} = 1 - \frac{273}{100 + 273} = 27\%$$

(b) another check

change of entropy of high T reservoir

$$\Delta S_H = \frac{-Q_H}{T_H}$$

change of entropy of low T reservoir

$$\Delta S_C = \frac{-Q_C}{T_C}$$

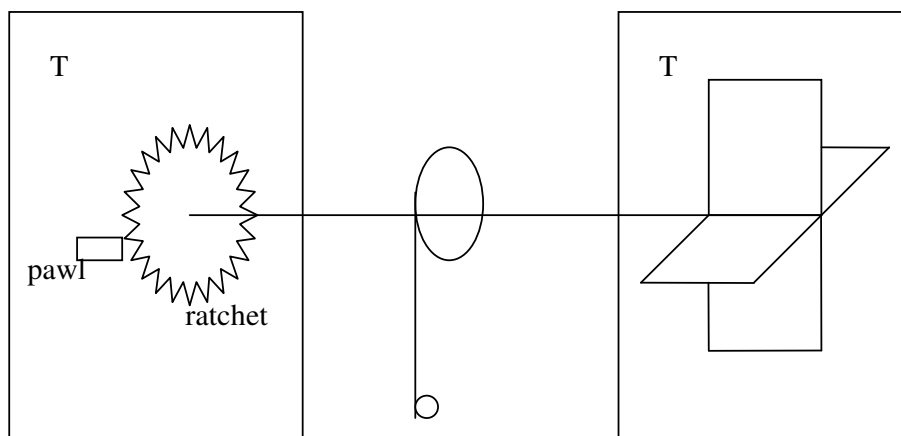
$$\varepsilon = 1 - \frac{Q_C}{Q_H} \quad Q_C = (1 - \varepsilon)Q_H$$

$$\Delta S = \Delta S_H + \Delta S_C + \Delta S_{w.s}$$

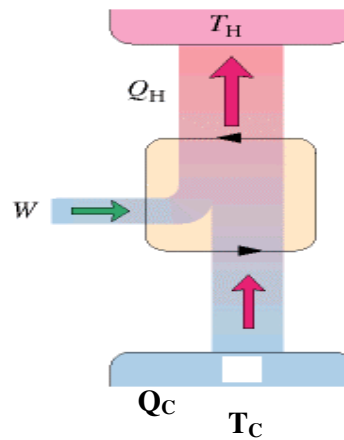
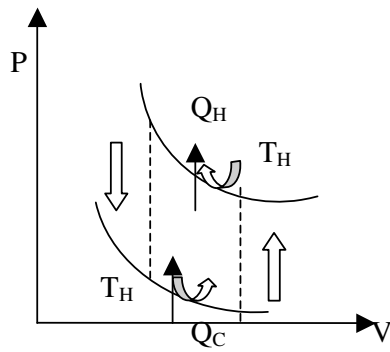
$$= -\frac{Q_H}{T_H} + \frac{(1 - \varepsilon)Q_H}{T_C}$$

$$\text{for } \varepsilon = 0.75 \quad \Delta S = -0.0018 \quad Q_H < 0 \quad \text{unphysical}$$

Brownian Ratchet



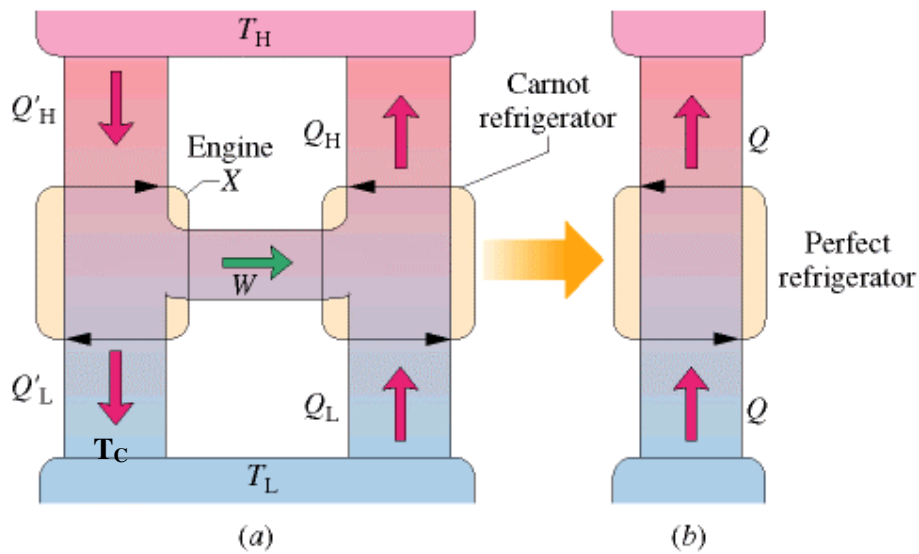
refrigerator



performance

$$K = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{T_C}{T_H - T_C}$$

perfect refrigerator



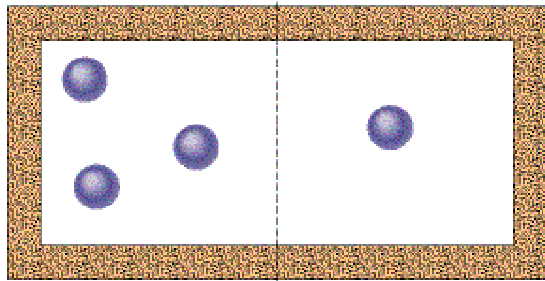
(a) Engine X drives a Carnot refrigerator. (b) If, as claimed, engine X is more efficient than a Carnot engine, then the combination shown in (a) is equivalent to the perfect refrigerator shown here. This violates the second law of thermodynamics, so we conclude that engine X *cannot* be more efficient than a Carnot engine.

$$\Delta S = -\frac{Q}{T_C} + \frac{Q}{T_H} = -Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) < 0 \quad \text{impossible}$$

$K \cong 2.5$ for typical airconditioner

$K \cong 5$ for household refrigerator

A Statistical View of Entropy



L

R

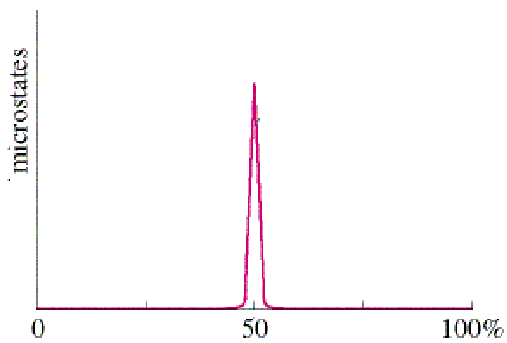
consider for molecules in a container

| | configuration | probability |
|-----------|---------------|-------------|
| 4 at left | 1 | 1/16 |
| 3 at left | $C_1^4 = 4$ | 4/16 |
| 2 at left | $C_2^4 = 6$ | 6/16 |
| 1 at left | 4 | 4/16 |
| 0 at left | 1 | 1/16 |

of microstates

$$W = \frac{N!}{n_L! n_R!} \quad n_L + n_R = N$$

$$S = k \ln W$$



stirling's formula $\ln N! = N \ln N - N$

ex.

When n moles of an ideal gas doubles its volume in a free expansion, the entropy increase from the initial state i to the final state f is $S_f - S_i = nR \ln 2$. Derive this result with statistical mechanics.

$$W_i = \frac{N!}{N!0!} = 1 \quad S_i = 0$$

$$W_f = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}$$

$$S_f = k \ln W_f$$

$$= k \left(\ln N! - 2 \ln \left(\frac{N}{2}\right)! \right)$$

$$= k \left(N \ln N - N - N \ln \frac{N}{2} + N \right)$$

$$= kN \ln 2$$

$$= nR \ln 2$$

$$\Delta S = nR \ln 2$$