

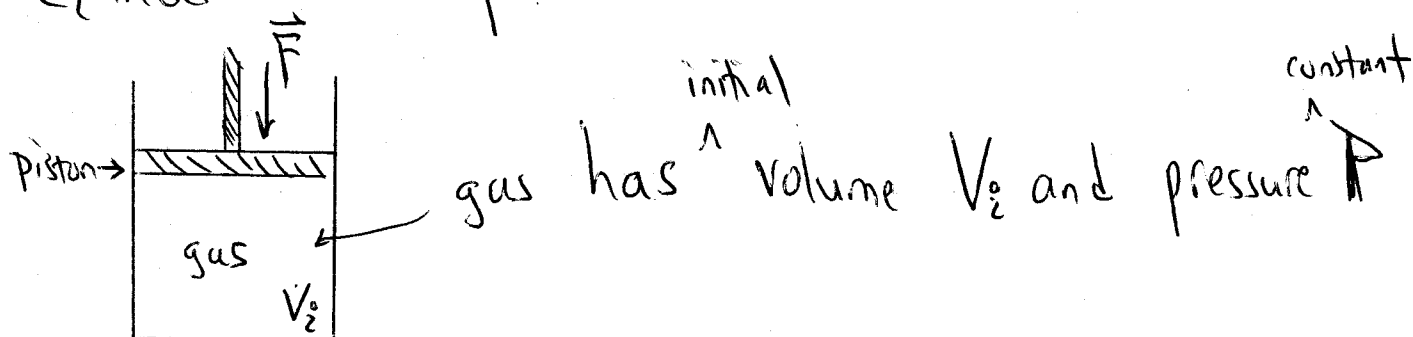
Thermodynamics

Unit #12

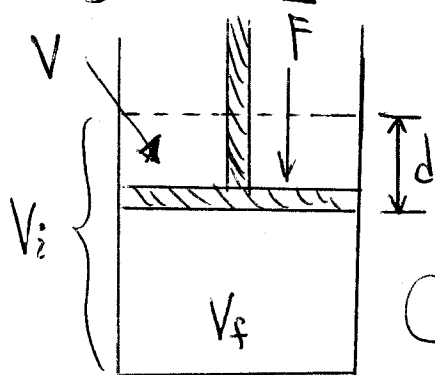
①

Work:

Let's examine the work done on a gas enclosed in a cylinder with a piston:



Applying a force to the piston does work on the gas when the piston moves by an amount d :



$$\text{Work} = F \cdot d$$

$$\text{but Pressure} = P = \frac{F}{A} \Rightarrow F = PA$$

$$\text{Then: Work} = PAd = P \cdot V$$

Volume moved through by piston

Note: $V + V_f = V_i$ (initial volume)

$$V = V_i - V_f = -(V_f - V_i) = -\Delta V$$

Then, $Work = W = -P\Delta V$ (constant pressure)

↑
minus sign because volume inside the cylinder decreases (ΔV is negative)

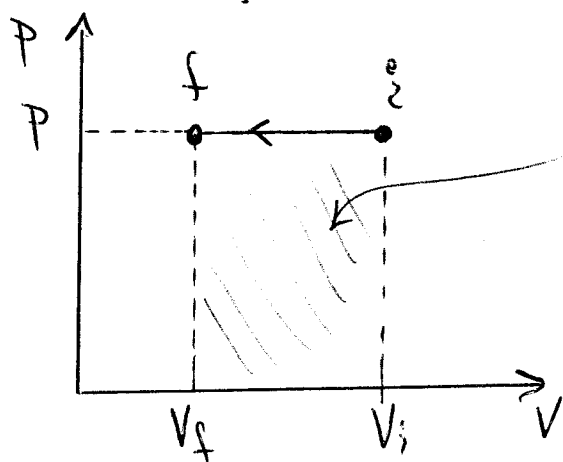
$$Work \text{ done on gas} = W_{on \text{ gas}} = -P\Delta V = \text{positive}^\#$$

$$Work \text{ done by gas} = W_{by \text{ gas}} = +P\Delta V = \text{negative}^\#$$

when decreases

$$W_{on \text{ gas}} = -W_{by \text{ gas}}$$

This is an isobaric process since the pressure is always constant.



$$Area = \text{base} \times \text{height}$$

$$= (V_i - V_f) \cdot P$$

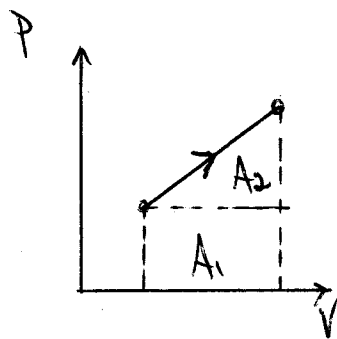
$$= |P\Delta V| = |W_{on \text{ gas}}|$$

$$\text{Magnitude of work done on gas} = |W_{on \text{ gas}}|$$

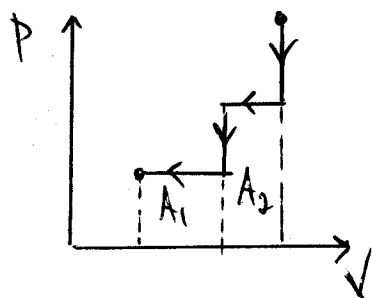
$$= \text{Area under the } P \text{ vs. } V \text{ curve}$$

$W_{\text{on gas}} = + \text{Area}$ if Volume decreases
(arrow goes to the left)

$W_{\text{on gas}} = - \text{Area}$ if volume increases
(arrow goes to the right)



$$W_{\text{on gas}} = -(A_1 + A_2)$$



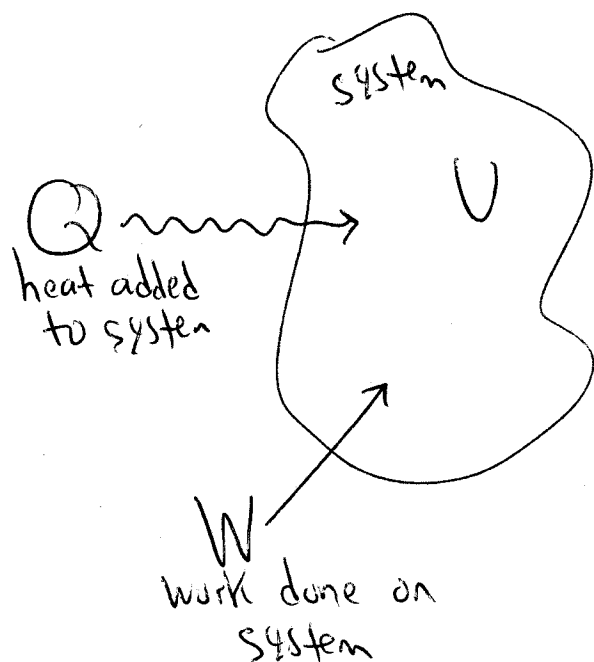
$$W_{\text{on gas}} = +(A_1 + A_2)$$

Positive Work: I push on gas in cylinder with piston and the gas compresses $\rightarrow$ I am doing positive work on gas.

Negative Work: I push on gas in cylinder with piston and the gas expands! $\rightarrow$ I am doing negative work on the gas since it is not doing what I want it to do $\rightarrow$ it should compress.

(4)

1st law of thermodynamics:



$$\Delta U = U_f - U_i = Q + W$$

$$Q + W = \Delta U$$

heat + $W_{\text{on system}}$ = change in internal energy of the system

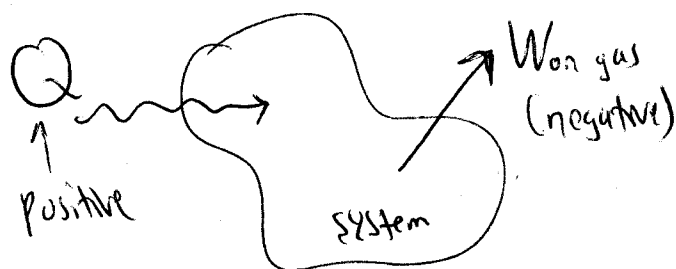
$\Delta U = W + Q \rightarrow$ when heat flows into system

$\Delta U = W - Q \rightarrow$ when heat flows out of system

$W_{\text{on system}}$ = positive (if volume decreases)

$W_{\text{on system}}$ = negative (if volume increases)

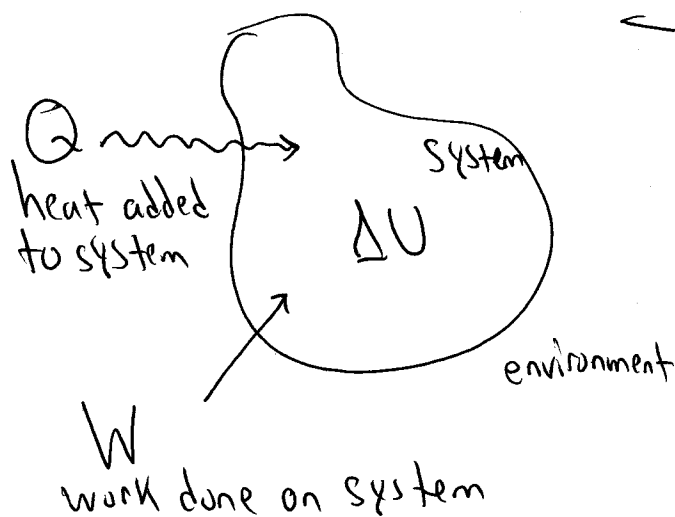
Example: An idea gas absorbs $5 \times 10^3 \text{ J}$ of energy while doing $2 \times 10^3 \text{ J}$ of work on the environment.



$$\begin{aligned} \Delta U &= Q + W_{\text{on gas}} \\ &= (5 \times 10^3 \text{ J}) - (2 \times 10^3 \text{ J}) \\ &= 3 \times 10^3 \text{ J} \end{aligned}$$

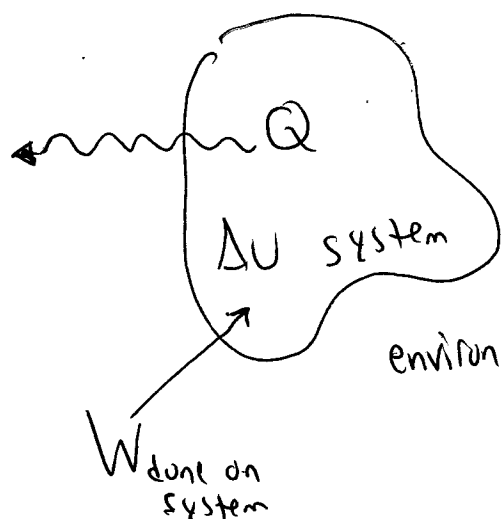
1st Law of Thermodynamics:

④



The Conservation of Energy is :

$$\underbrace{W + Q}_{\text{(energy added to the system)}} = \underbrace{\Delta U}_{\text{(energy inside the system)}}$$



Conservation of Energy in this case is

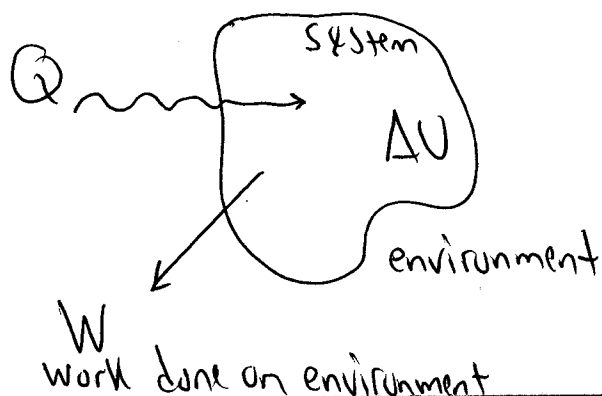
$$\underbrace{W}_{\text{(energy added to system)}} = \underbrace{\Delta U + Q}_{\text{(energy inside the system)}}$$

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

minus sign for when heat leaves the system

Notice: $W = W_{\text{done on system}}$

If the system does work on the environment then:



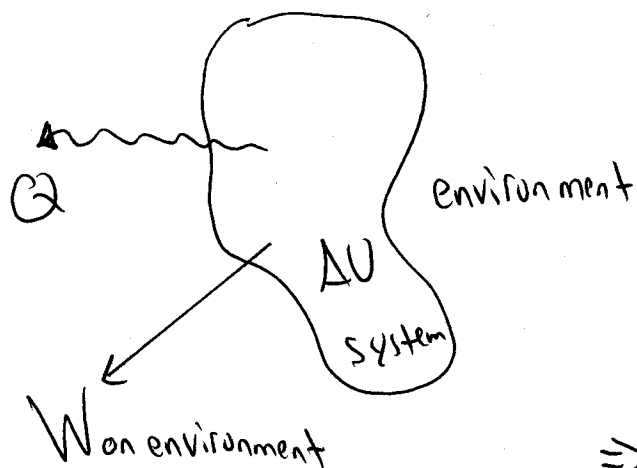
Conservation of Energy

$$\underbrace{Q}_{\text{(energy added to system)}} = \underbrace{\Delta U + W}_{\text{(energy inside the system)}}$$

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

(5)

Thus, $W_{\text{done on system}} = -W_{\text{system does on environment}}$



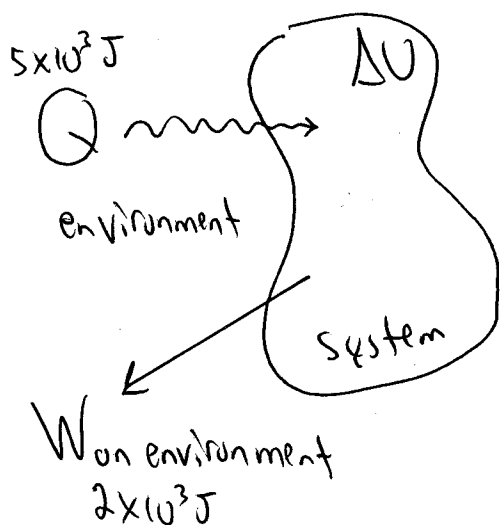
Conservation of Energy

$$0 = \Delta U + W + Q$$

(Energy added to system) = (Energy inside the system)

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

Example: An ideal gas absorbs $5 \times 10^3 \text{ J}$ of energy while doing $2 \times 10^3 \text{ J}$ of work on the environment.



Conservation of Energy

$$\Delta U + W = Q$$

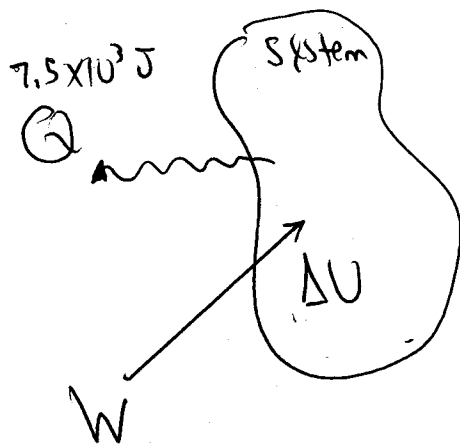
$$\Delta U = Q - W$$

$$= (5 \times 10^3 \text{ J}) - (2 \times 10^3 \text{ J})$$

$$= 3 \times 10^3 \text{ J}$$

Example: If the internal energy drops by $4.5 \times 10^3 \text{ J}$ and $7.5 \times 10^3 \text{ J}$ is expelled from the system, what is the change in volume? Assume the pressure is constant at $1.01 \times 10^5 \text{ Pa}$. (atmospheric pressure)

(6)



Conservation of Energy

$$\Delta U + Q = W$$

$$(U_f - U_i)$$

$$= -4.5 \times 10^3 \text{ J}$$

Since the internal energy decreases

$$U_f < U_i$$

$$-P\Delta V$$

$$\Delta U + Q = -P\Delta V$$

$$\Delta V = \frac{-(\Delta U + Q)}{P} = - \frac{[-4.5 \times 10^3 \text{ J} + 7.5 \times 10^3 \text{ J}]}{1.01 \times 10^5 \text{ Pa}}$$

$$= -2.97 \times 10^{-2} \text{ m}^3$$

↑
the volume decreases

Internal Energy:

If an atom was moving only in the x-direction, its kinetic energy is related to its temperature by

$$\left(\text{Ave. kinetic energy} \right) = \left(\frac{1}{2} m v_x^2 \right)_{\text{ave}} = \frac{1}{2} k_B T$$

for motion in the y & z-directions:

$$\left(\frac{1}{2} m v_y^2 \right)_{\text{ave}} = \frac{1}{2} k_B T$$

$$\left(\frac{1}{2} m v_z^2 \right)_{\text{ave}} = \frac{1}{2} k_B T$$

Thus, there is

$$\frac{1}{2} k_B T$$

for each degree of freedom

(movement in the x, y, z-dir.)

$$\text{Since } (v^2)_{\text{ave}} = (v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}} \quad (7)$$

$$\text{Then, } \left(\frac{1}{2} m v^2\right)_{\text{ave}} = \frac{1}{2} K_B T + \frac{1}{2} K_B T + \frac{1}{2} K_B T \\ = \frac{3}{2} K_B T$$

The internal energy is then, $U = \frac{3}{2} K_B T$

If there are N atoms, the total internal energy is

$$U = (\text{Total Kinetic energy}) = N \left(\frac{1}{2} m v^2\right)_{\text{ave}} = \frac{3}{2} N K_B T$$

Using the relation: $K_B = R/N_A$ and $n = N/N_A$ allows us to write U as:

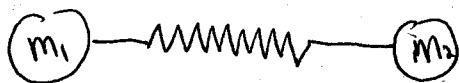
$$U = \frac{3}{2} N K_B T = \frac{3}{2} n R T$$

Internal energy monatomic ideal gas.

If the temperature changes an amount ΔT , then we have the change in internal energy:

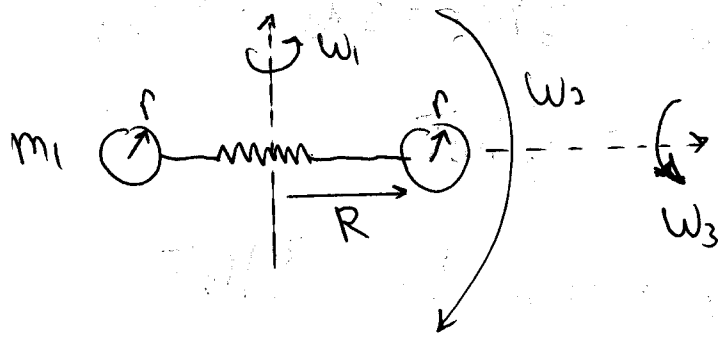
$$\Delta U = \frac{3}{2} n R \Delta T$$

Let's examine the internal energy of a diatomic gas:



bond between atoms

A diatomic gas has additional degrees of freedom (ways to move) ⑧



It can rotate about 3 different axes. Each rotation adds rotational kinetic energy to the total internal energy : $KE = \frac{1}{2} I \omega^2$

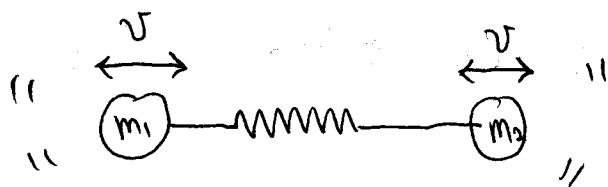
Notice that $I_1 = (m_1 + m_2) R^2$
 $I_2 = (m_1 + m_2) R^2$
 $I_3 = (m_1 + m_2) r^2$ } Since $r = \text{radius of atom}$
 $r \ll R \approx \frac{1}{2} (\text{bond length})$

Since $r \ll R$, we can ignore I_3 and only consider 2 more degrees of freedom added to the internal energy:

$$\Delta U = \left(\frac{3}{2} + \frac{1}{2} + \frac{1}{2} \right) n R \Delta T$$

$$\Delta U = \frac{5}{2} n R \Delta T \Rightarrow \text{for a diatomic molecule}$$

Let us now consider vibrations of the bond between the atoms in the diatomic molecule:



The atoms m_1 and m_2 can now move due to vibrations of the molecular bond. ⑨

There is now spring potential energy that adds to the internal energy : $U_{\text{spring}} = \frac{1}{2} K x^2$

Also, since the atoms now have additional motion relative to each other, there is additional kinetic energy $\frac{1}{2} (m_1 + m_2) v^2$

These two energies adds two more degrees of freedom:

$$\Delta U = \left(\frac{5}{2} + \frac{1}{2} + \frac{1}{2} \right) n R \Delta T$$

$$\Delta U = \frac{7}{2} n R \Delta T \quad \left. \vphantom{\Delta U} \right\} \begin{array}{l} \text{diatomic molecule} \\ \text{(translations} \\ \text{rotations} \\ \text{vibrations)} \end{array} \text{ included}$$

Molar Specific Heat:

For an ideal monatomic gas : $\Delta U = \frac{3}{2} n R \Delta T$

The molar specific heat at constant volume is defined as $C_v = \frac{3}{2} R$

Then, $\Delta U = n C_v \Delta T$

For ideal gases, this expression is valid even when the volume is not constant.

Isobaric Process: Constant Pressure $\Rightarrow P = \text{constant}$ (10)

$$\begin{array}{ccc} \Delta U = Q + W & & \\ \downarrow & & \downarrow \\ \frac{3}{2} n R \Delta T & & -P \Delta V \\ \text{(monatomic gas)} & & \end{array}$$

$$\Rightarrow Q = \Delta U - W = \frac{3}{2} n R \Delta T + P \Delta V$$

From the ideal gas law: $PV = nRT$

$$\begin{array}{ccc} \Delta(PV) = \Delta(nRT) & \longrightarrow & P \Delta V = n R \Delta T \\ \uparrow \text{constant} & \uparrow \text{constants} & \uparrow \text{pressure is constant} \end{array}$$

Then,

$$Q = \frac{3}{2} n R \Delta T + P \Delta V$$

$$Q = \frac{3}{2} n R \Delta T + n R \Delta T$$

$$Q = \frac{5}{2} n R \Delta T \longrightarrow \left(\begin{array}{c} \text{monatomic} \\ \text{gas} \end{array} \right) \left(\begin{array}{c} \text{for an} \\ \text{isobaric} \\ \text{process} \end{array} \right)$$

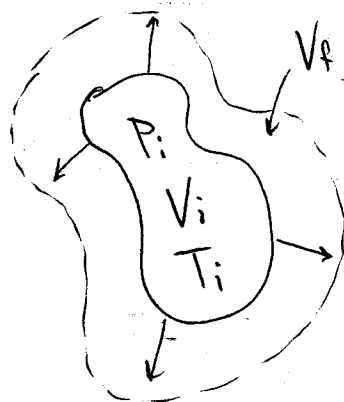
Define $C_p = \frac{5}{2} R$ = molar specific heat at constant pressure

Then, $Q = n C_p \Delta T$

Note: since $C_v = \frac{3}{2} R \Rightarrow \boxed{C_p = C_v + R}$

Example: 12.4 in Serway: A monatomic ideal gas at $2 \times 10^5 \text{ Pa}$ and initial temperature 293°K slowly expands at constant pressure from a volume of 1 L to 2.5 L . (11)

(a) Find the work done on the environment



$$\left\{ \begin{array}{l} P_i = 2 \times 10^5 \text{ Pa} \\ V_i = 1 \text{ L} \\ T_i = 293^\circ \text{K} \end{array} \right\} \quad \left\{ \begin{array}{l} V_f = 2.5 \text{ L} \\ P_f = 2 \times 10^5 \text{ Pa} \end{array} \right\}$$

$$W_{\text{done on system}} = -P \Delta V = -P(V_f - V_i) = -(2 \times 10^5 \text{ Pa})(2.5 \text{ L} - 1 \text{ L})$$

$$= -3 \times 10^5 \text{ Pa} \times \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) = -300 \text{ J}$$

$$W_{\text{done by system}} = -W_{\text{done on system}} = -(-300 \text{ J}) = 300 \text{ J}$$

(b) Find the change in internal energy of the gas.

$$\Delta U = \frac{3}{2} n R \Delta T = \frac{3}{2} n R (T_f - T_i)$$

we do not know "n" or "T_f"

Use the Ideal gas law to find "n":

$$P_i V_i = n R T_i \Rightarrow n = \frac{P_i V_i}{R T_i} \rightarrow \text{we know } P_i, V_i, T_i \text{ we can calculate } n$$

Use Ideal Gas law to find T_f :

(12)

$$\left\{ \begin{array}{l} P_i V_i = n R T_i \\ P_f V_f = n R T_f \end{array} \right\} \rightarrow T_f = \frac{P_f V_f}{n R} = \frac{P_f V_f}{\underbrace{\left(\frac{P_i V_i}{R T_i} \right) \cdot R}} = \frac{V_f T_i}{V_i}$$

note: $P_i = P_f$

Then,

$$\Delta U = \frac{3}{2} n R (T_f - T_i) = \frac{3}{2} \left(\frac{P_i V_i}{R T_i} \right) R \left[\frac{V_f T_i}{V_i} - T_i \right]$$

$$\Delta U = \frac{3}{2} \frac{P_i V_i}{T_i} \cdot T_i \left(\frac{V_f}{V_i} - 1 \right)$$

$$\Delta U = \frac{3}{2} P_i V_i \left(\frac{V_f}{V_i} - 1 \right)$$

$$\Delta U = \frac{3}{2} P_i (V_f - V_i)$$

$$\boxed{\Delta U = \frac{3}{2} P \Delta V}$$

← a nice relationship was discovered

$$\begin{aligned} \Delta U &= \frac{3}{2} (2 \times 10^5 \text{ Pa}) (2.5 \text{ L} - 1.5 \text{ L}) \\ &= \frac{3}{2} (300 \text{ J}) \rightarrow \text{from Part (a)} \\ &= 450 \text{ J} \end{aligned}$$

(c) Use the first law to obtain the energy transferred by heat:

$$\Delta U = Q + W_{\text{on system}} \Rightarrow Q = \Delta U - W_{\text{on system}}$$

$$Q = 450 \text{ J} - (-300 \text{ J}) = 750 \text{ J}$$

(13)

Method #2 to find Q :

$$Q = nC_p \Delta T = \frac{5}{2} nR \Delta T \rightarrow \text{monatomic ideal gas}$$

$$= \frac{5}{2} \left(\frac{P_i V_i}{RT_i} \right) R (T_f - T_i) = \frac{5}{2} \left(\frac{P_i V_i}{T_i} \right) \left(\frac{V_f T_i}{V_i} - T_i \right)$$

$$= \frac{5}{2} P_i (V_f - V_i) = \frac{5}{2} P \Delta V$$

$$= \frac{5}{2} (300 \text{ J}) \rightarrow \text{since } P \Delta V = 300 \text{ J} \text{ from Part (a)}$$

$$= 750 \text{ J} \checkmark \text{ checks with 1st law of thermodynamics}$$

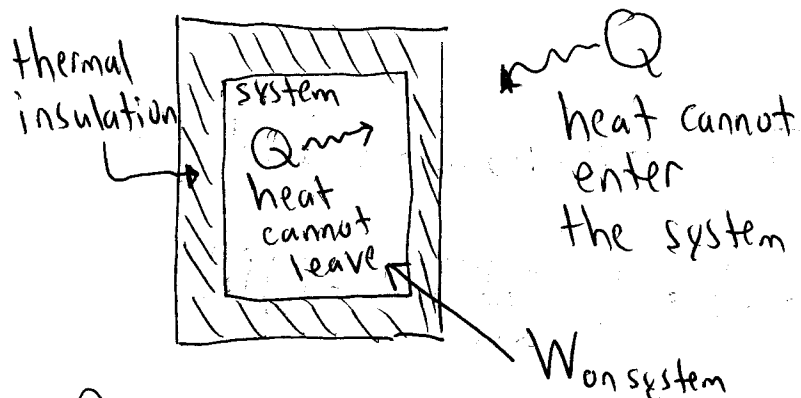
If the gas was diatomic, we must add two more degrees of freedom (ignoring vibrational degrees of freedom)

$$\Delta U = \left(\frac{3}{2} + \frac{1}{2} + \frac{1}{2} \right) P \Delta V = \frac{5}{2} P \Delta V = \frac{5}{2} (300 \text{ J}) = 750 \text{ J}$$

$$Q = \left(\frac{5}{2} + \frac{1}{2} + \frac{1}{2} \right) P \Delta V = \frac{7}{2} P \Delta V = \frac{7}{2} (300 \text{ J}) = 1050 \text{ J}$$

adding $\frac{1}{2} k_B T$ for each degree of freedom

Adiabatic Process: $Q = 0$



For an adiabatic process: $Q = 0$
no heat is able to enter the system

The 1st law of thermodynamics is then

$$\Delta U = \cancel{Q} + W$$

$$\Delta U = W \quad \text{for an adiabatic process}$$

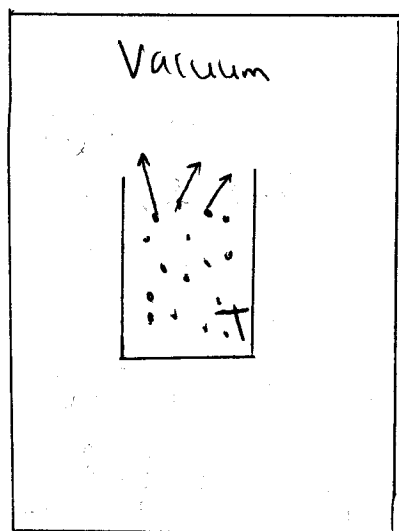
Example 12.5 (Serway) Find the work done by the gas on a piston in a car's cylinder during an adiabatic expansion of 0.1 moles of monatomic gas that goes from 1200°K to 900°K during the expansion:

$$W_{\text{on system (gas)}} = \Delta U = \frac{3}{2} n R \Delta T = \frac{3}{2} (0.1 \text{ mole}) \left(\frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}} \right) (900 - 1200) \text{ K} = -997 \text{ J}$$

$$W_{\text{by system (gas)}} = -W_{\text{on system (gas)}} = +997 \text{ J}$$

Example: Adiabatic Free Expansion of a Gas

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What is the change in internal energy, ΔU , for adiabatic free expansion of a gas?

For example. The gas is contained in an insulated container and allowed to expand in a vacuum.

Because there is nothing for the gas to push against, the work done by the gas is zero:

$$\Delta U = W = 0$$

The internal energy does not change. Since the internal energy varies with temperature, the temperature of the system does not change.

$$T = \text{Constant} \quad \left(\begin{array}{l} \text{even though} \\ \text{the gas expands!} \end{array} \right)$$

Isovolumetric Process [Isochoric]: Constant Volume (16)

Since $V = \text{constant}$

$$W = -P\Delta V = 0 \quad \left(\begin{array}{l} \text{no work is done on or} \\ \text{by the system} \end{array} \right)$$

$$\Delta U = Q + W$$

$$\Rightarrow \Delta U = Q \quad \left. \vphantom{\Delta U = Q} \right\} \text{ for an isochoric process}$$

For an ideal monatomic gas: $\Delta U = \frac{3}{2} nR\Delta T$

$$\text{Then, } Q = \frac{3}{2} nR\Delta T$$

Example: 12.7 (Serway) A monatomic gas has a temperature of 300°K and a constant volume of 1.5L . There are 5 moles of gas.

(a) How much thermal energy must be added to raise the temperature to 380°K ?

$$\begin{aligned} Q &= \frac{3}{2} nR\Delta T = \frac{3}{2} nR(T_f - T_i) = \frac{3}{2} (5 \text{ moles}) \left(\frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}} \right) (380^\circ\text{K} - 300^\circ\text{K}) \\ &= 4986 \text{ J} \end{aligned}$$

(b) What is the change in pressure, ΔP ?

Use the Ideal Gas Law: $PV = nRT$

$$\Delta(PV) = nR\Delta T$$

Note: $\Delta(PV) = P\Delta V + V\Delta P \rightarrow V\Delta P$ if $V = \text{constant}$

(17)

Then,

$$\Delta(PV) = V\Delta P = nR\Delta T$$

$$\Delta P = \frac{nR\Delta T}{V} = \frac{(5 \text{ moles})(8.31 \frac{\text{J}}{\text{mol K}})(380^\circ\text{K} - 300^\circ\text{K})}{1.5 \times \left(\frac{10^{-3} \text{ m}^3}{1 \text{ K}}\right)}$$

$$= 2.216 \times 10^6 \text{ Pa}$$

(c) For a diatomic gas $\rightarrow$ add 2 more degrees of freedom

$$Q = \left(\frac{3}{2} + \frac{1}{2} + \frac{1}{2}\right) nR\Delta T = \frac{5}{2} nR\Delta T = \frac{5}{2} (5 \text{ moles})(8.31 \frac{\text{J}}{\text{mol K}})(380^\circ\text{K} - 300^\circ\text{K})$$

$$= 8310 \text{ J}$$

 ΔP does not change since

$$\Delta P = \frac{nR\Delta T}{V} \text{ holds for all ideal gases}$$

$\rightarrow$ it comes from the Ideal Gas Law

 $\Delta P = 2.216 \times 10^6 \text{ Pa}$ for diatomic gas as well

Isothermal Process (Constant Temperature)

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If T is constant, the internal average kinetic energy is constant, and thus the internal energy is constant

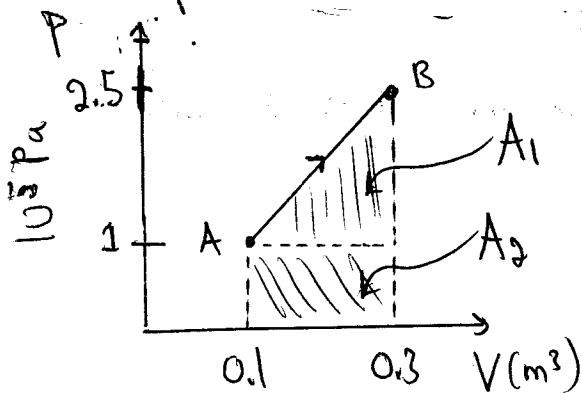
$$U = \text{constant} \rightarrow \Delta U = 0$$

For a monatomic ideal gas: $\Delta U = \frac{3}{2} n R \Delta T = 0$
↑
since $T = \text{constant}$

~~$\Delta U = Q + W$~~

$\Rightarrow W = -Q$ } for an isothermal process

Example: General Case Serway Example 12.9



1 moles of a monatomic ideal gas expands from an initial volume of 0.1 m^3 to a final volume of 0.3 m^3 and pressure of $2.5 \times 10^5 \text{ Pa}$.

(a) Find the work done on the gas.

$W = \text{Area under the curve} = - (A_1 + A_2)$

↑
minus sign since the volume increases as pressure increases
→ not what we expect

(19)

$$A_1 = \frac{1}{2}bh = \frac{1}{2}(0.3-0.1)m^3(2.5-1)10^5 Pa = 1.5 \times 10^4 J$$

$$A_2 = bh = (0.3-0.1)m^3(1-0) \times 10^5 Pa = 2 \times 10^4 J$$

$$W = -(A_1 + A_2) = -(1.5 + 2) \times 10^4 J = -3.5 \times 10^4 J$$

(b) What is the change in the internal energy of the gas?

$$\Delta U = \frac{3}{2}nRT = \frac{3}{2}nR(T_f - T_i)$$

Use Ideal Gas equation to find T_i, T_f

$$P_i V_i = nRT_i \Rightarrow T_i = \frac{P_i V_i}{nR} \quad \text{and} \quad T_f = \frac{P_f V_f}{nR}$$

$$\Rightarrow \Delta U = \frac{3}{2}nR \left(\frac{P_f V_f}{nR} - \frac{P_i V_i}{nR} \right) = \frac{3}{2} (P_f V_f - P_i V_i)$$

$$= \frac{3}{2} [(2.5 \times 10^5 Pa)(0.3 m^3) - (1 \times 10^5 Pa)(0.1 m^3)]$$

$$= 9.75 \times 10^4 J$$

(c) What is the thermal energy transferred to the gas?

$$\Delta U = Q + W$$

$$\Rightarrow Q = \Delta U - W = 9.75 \times 10^4 J - (-3.5 \times 10^4 J)$$

$$= 1.325 \times 10^5 J$$

Heat Engines

(20)

Drop a ball on the floor:

$\Rightarrow$ (gravitational potential energy) $\xrightarrow{\text{converted to}}$ (Kinetic energy) + (Heat)

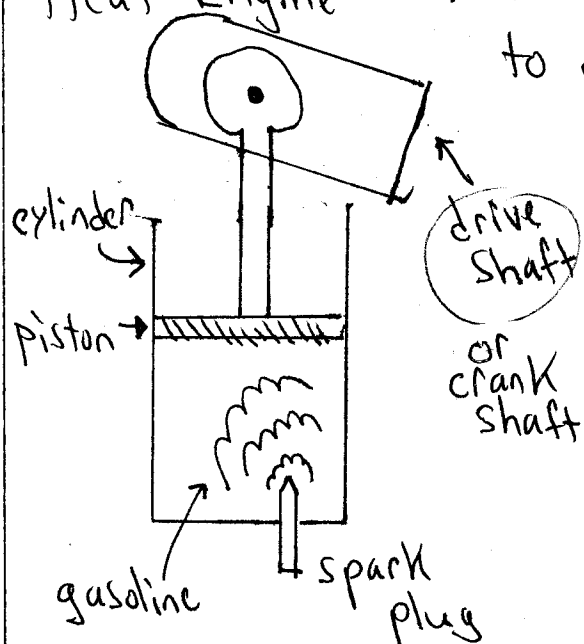
Slide a book across the table:

$\Rightarrow$ (Work) $\xrightarrow{\text{converted to}}$ (Kinetic energy) + (Heat)

All these processes create thermal energy (Heat). We can also go in the opposite direction:

Convert Thermal energy into Kinetic energy or other forms of energy

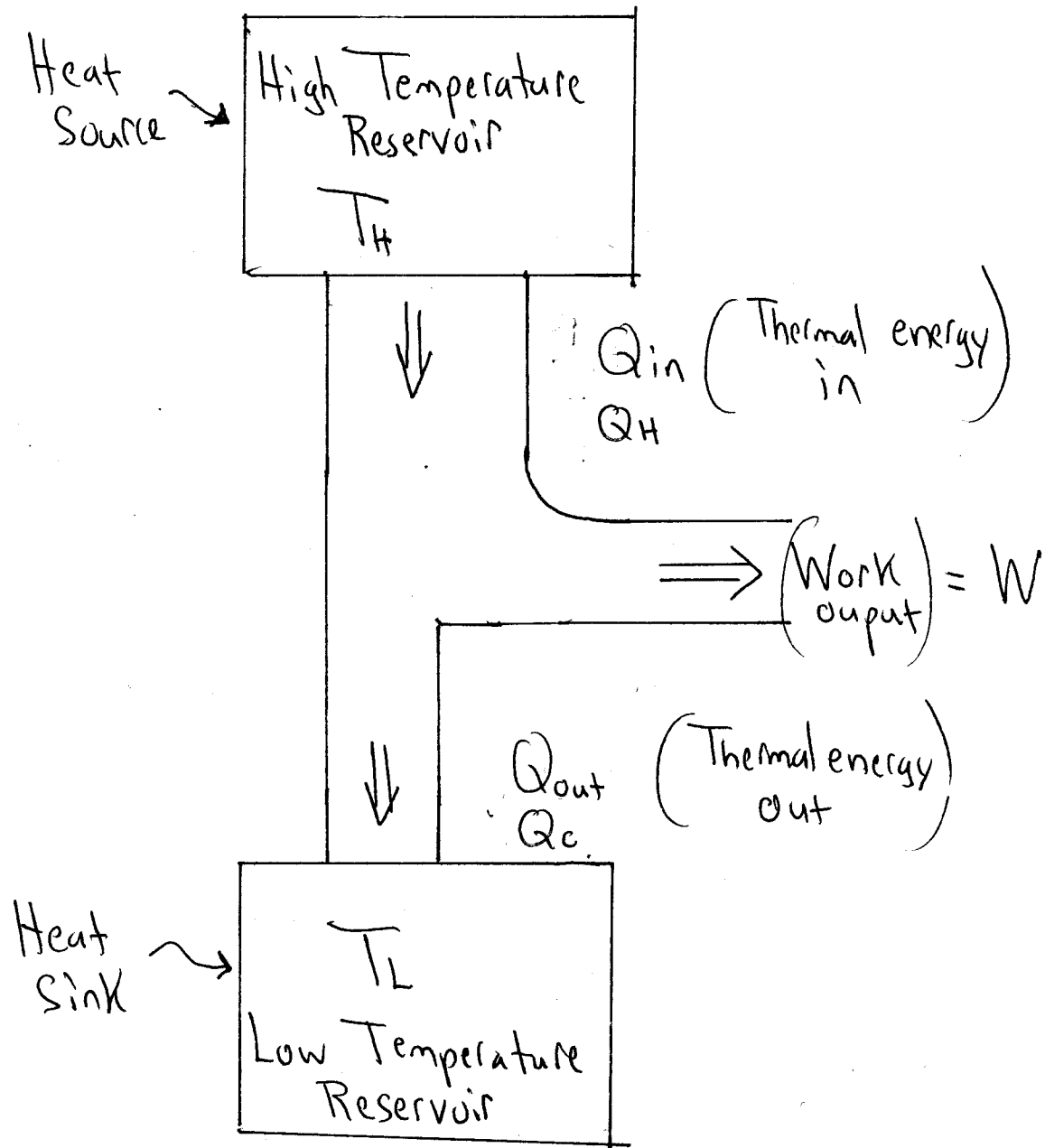
Heat Engine $\rightarrow$ is a device that uses thermal energy to do work (example: an automobile engine)



Spark plug ignites gasoline which burns rapidly and produces heat. This heat causes the gas in the cylinder to expand and thus push the piston up. This does work on the drive shaft and moves the car.

Schematic representation of a Real Heat Engine

(21)



Work can be found through conservation of energy:

$$\underbrace{Q_{in}}_{\text{input energy}} = W + \underbrace{Q_{out}}_{\text{output energy}}$$

$$\Rightarrow W = Q_{in} - Q_{out} = \text{Work done by the engine} \\ (\text{work done by gas in a gas engine})$$

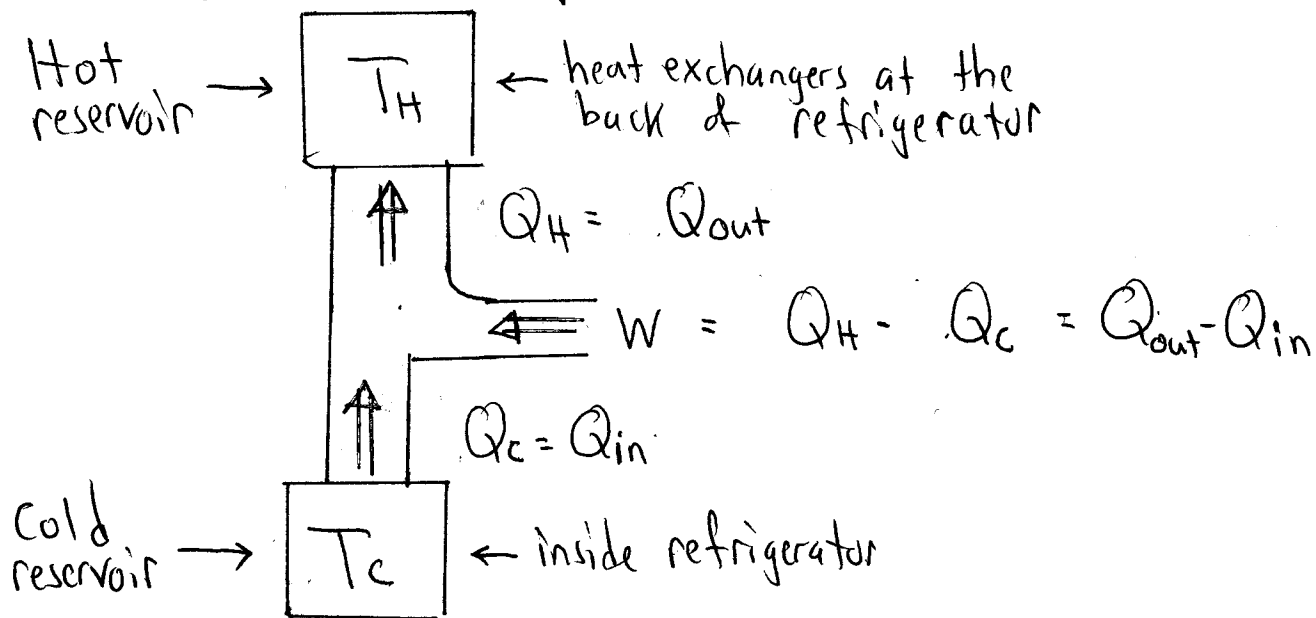
The efficiency of a real heat engine is defined as (22)

$$\text{efficiency} = e = \frac{\text{Work that we get out}}{\text{energy that we put in}} = \frac{W}{Q_{in}}$$

We can also write this as:

$$e = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

A refrigerator is a heat engine that works in reverse: it uses work to extract heat from a cold source and moves it to a higher temperature place (the heat sink).



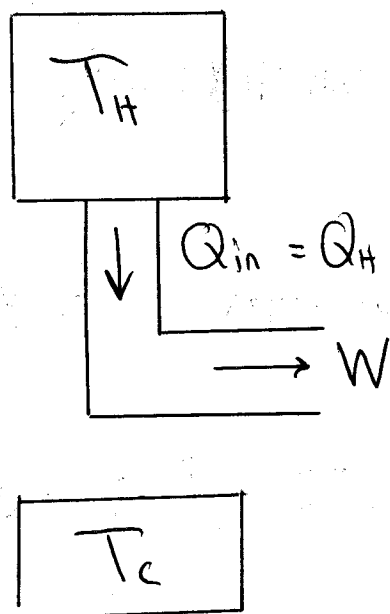
Notice that the efficiency for a heat engine

$$e = 1 - \frac{Q_{out}}{Q_{in}}$$

$$e = 100\% \text{ if } Q_{out} = 0$$

Thus, a heat engine can be 100% efficient if no heat is expelled out. This is impossible, and thus leads to the

2nd Law of Thermodynamics (stated as the law of heat engines): Any process that uses thermal energy as the input to do work must also have a thermal energy output, or exhaust.



This heat engine violates the 2nd law of Thermodynamics since $Q_{out} = 0$.

This is a perpetual motion machine of the 2nd kind

$\Rightarrow$ it is a perfect refrigerator $\rightarrow$ it could freeze ice cream as well as turn the crank.

A perpetual motion machine of the 1st kind is where a heat engine gets more work output than energy input

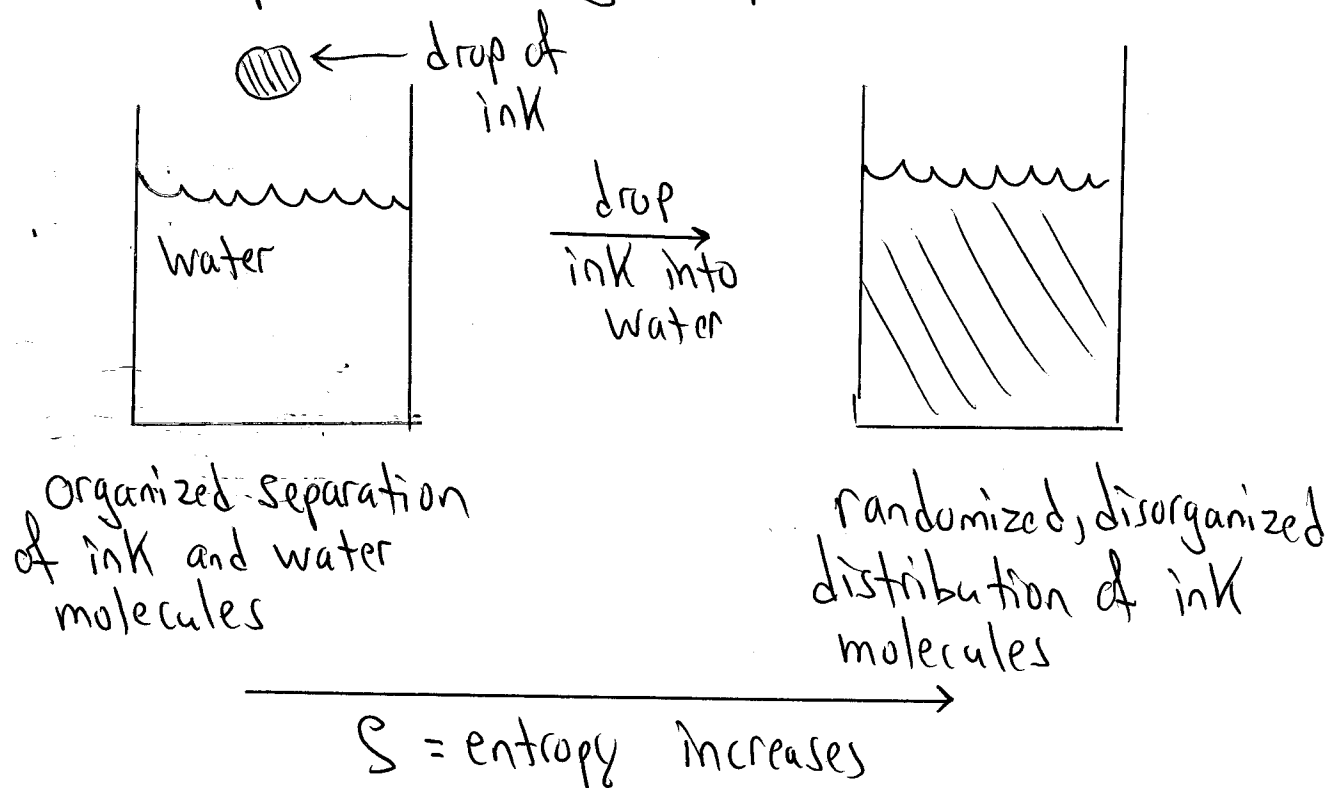
Entropy:

(24)

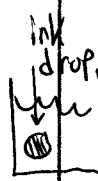
Entropy is a measure of the disorder in a system.

An example of increasing entropy: Your room gradually becomes more messy (disorganized) as time goes on.

Another example of increasing entropy:



The 2nd Law of Thermodynamics (Law of increasing entropy): The total entropy of all the participants in any physical process must either increase or remain unchanged $\rightarrow$ it cannot decrease.

The law of increasing entropy states that most processes are irreversible $\rightarrow$ they cannot proceed in the opposite direction (like the ink in water cannot group into an ink drop) 

Entropy is defined as

(25)

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

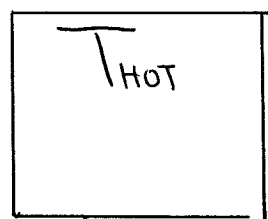
← Units of T must be °K

Q_{in}
↑
thermal

What a heat engine does is to take (disorganized) thermal energy and transform it into (organized) work energy.

→ were it not for the exhaust (Q_{out}), entropy would decrease and the heat engine would violate the law of increasing entropy.

Heat
Source



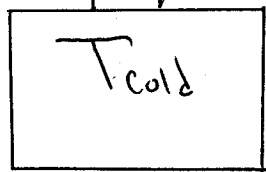
$Q_{in} = Q_H =$ disorganized thermal energy input

$W = Q_{in} - Q_{out} = Q_H - Q_C$
= organized output work

$Q_{out} = Q_C$

= disorganized thermal energy out

Heat
Sink



when heat flows out of hot source, the entropy of the hot source decreases

Entropy decrease of Heat Source = $\Delta S_{in} = -\frac{Q_{in}}{T_H} = -\frac{Q_H}{T_H}$

Entropy increase of Heat Sink = $\Delta S_{out} = +\frac{Q_{out}}{T_C} = +\frac{Q_C}{T_C}$

For an ideal reversible heat engine:

$$\Delta S_{in} + \Delta S_{out} = 0$$

Then,

$$\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_C} \Rightarrow \frac{Q_{out}}{Q_{in}} = \frac{T_C}{T_H}$$

Then the efficiency is:

$$e = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H}$$

Example: A heat engine accepts 900 cal of heat from a heat source having a temperature of 450°K. Some heat goes into work and some is released as waste heat dumped into a heat sink having a temperature of 300°K.

(a) What is the entropy associated with accepting heat from the heat source?

$$\Delta S_{in} = \frac{Q_{in}}{T_H} = \frac{900 \text{ cal}}{450^\circ \text{K}} = 2 \text{ cal/}^\circ \text{K} = \text{entropy decrease of heat source}$$

(b) How much heat must be dumped into the heat sink if this entropy decrease is to be balanced by an equal increase of entropy due to the heat flow at the lower temperature?

$$-\Delta S_{in} = \Delta S_{out} = \frac{Q_{out}}{T_C}$$

$$Q_{\text{out}} = T_c \Delta S_m = (300^\circ\text{K})(2\text{cal/K})$$

= 600 cal entropy of heat sink increases
entropy of the engine decreases by -2cal/K

(c) What is the efficiency of the heat engine?

$$e = 1 - \frac{T_c}{T_H} = 1 - \frac{300^\circ\text{K}}{450^\circ\text{K}} = 0.83$$

$$\Rightarrow e = 33\%$$

For a real^{heat} engine (rather than an ideal heat engine)
the efficiency is always less than this value.

$$(e)_{\text{real engine}} < (e)_{\text{ideal engine}} \rightarrow \text{reversible heat engine}$$

$$(e)_{\text{real engine}} < \left(1 - \frac{T_c}{T_H}\right)$$

this is the maximum possible
efficiency of a real engine