

# Chapter 21

## Entropy & The 2<sup>nd</sup> Law of Thermo

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see sections  
1-5

irreversible process - a process that cannot be reversed

ex: break an egg, drop a glass ← these would never spontaneously reassemble

slide a box along a floor =

↑ friction converts KE into thermal energy.

However heat would never convert spontaneously into KE...

These irreversible events have a one-way nature that is a consequence of the entropy postulate:

If an irreversible process occurs in a closed system, then the system's entropy  $S$  always increases.

The fact that  $\Delta S \geq 0$  provides direction to the arrow of time.

Ex: dropping an egg changes its entropy  $S$  by  $\Delta S > 0$ ,  
likewise, a broken egg that reassembles itself  
would have  $\Delta S < 0$ , which would never happen.

# Entropy Changes $\Delta S$ :

formal definition of entropy:

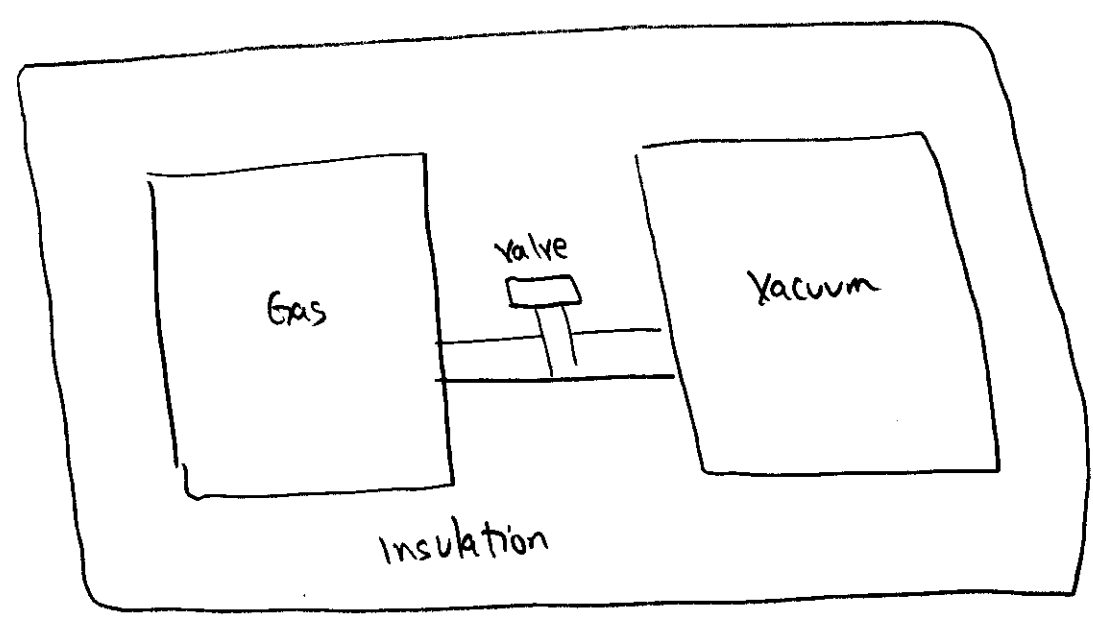
$$\Delta S = S_{\text{final}} - S_{\text{initial}} \equiv \int_{\text{initial state}}^{\text{final state}} \frac{dQ}{T}$$

note that S has units of energy/temp or J/K

= change in a system's entropy as it evolves from initial  $\rightarrow$  final state

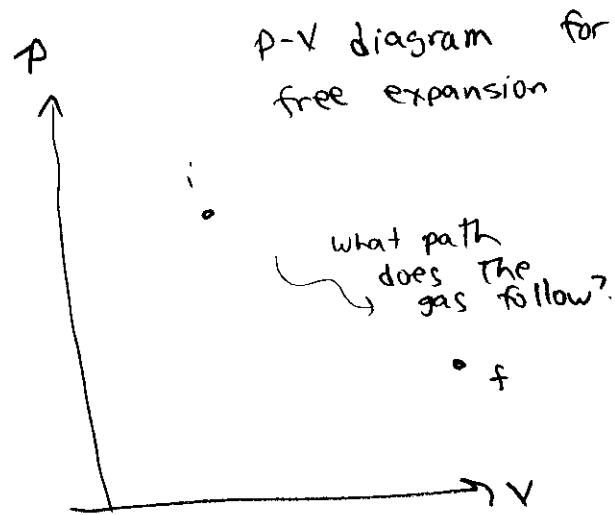
Note that  $\Delta S$  does not depend on the particular path you use to drive the system from i  $\rightarrow$  f. (important! - we will use this later...)

let's calculate  $\Delta S$  for a free expansion of a gas:



Is this process reversible?

Open the valve & gas rushes in, so  
 $P$ ,  $V$ , and  $T$  in an unpredictable way.



what is  $\Delta S = \int_i^f \frac{dq}{T(\omega)}$

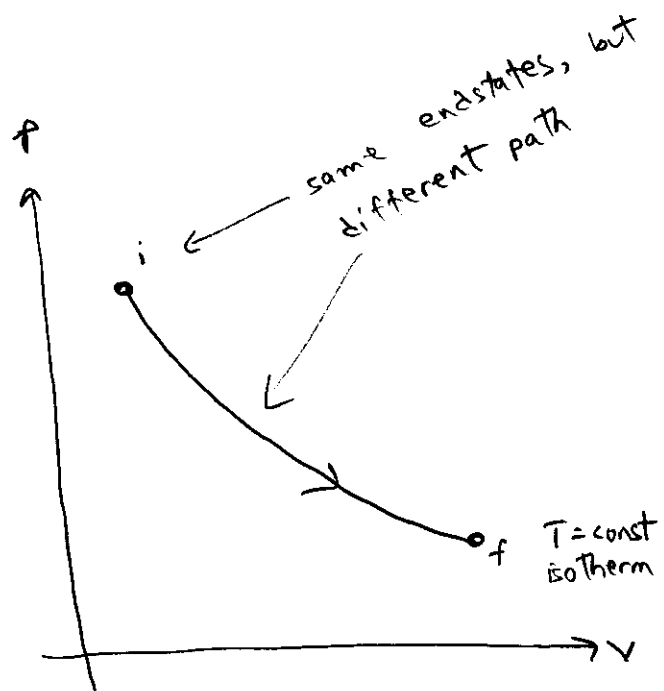
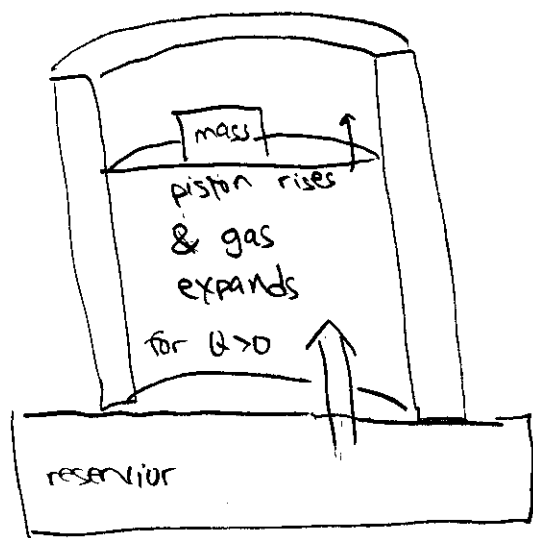
what is  $T(\omega)$ ?

Recall that  $\Delta S = \int_i^f \frac{dq}{T}$  depends only on

the endstates of the process. It does NOT depend on the choice of a particular path.

Also recall that the free expansion of a gas occurs at constant temperature  $T_i = T_f = T$ .

So we can instead consider the isothermal expansion of the gas:



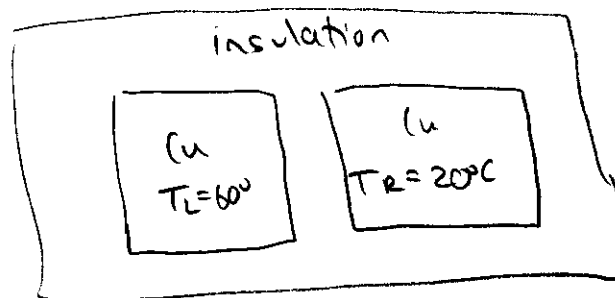
$$\text{so } \Delta S = \frac{1}{T} \int_i^f dq = \frac{Q}{T} = \frac{\text{heat added}}{\text{gas temp.}}$$

In summary:

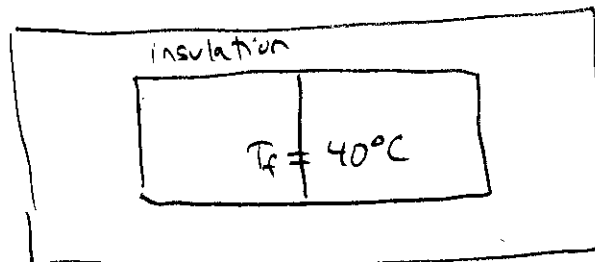
To calculate  $\Delta S$  for an irreversible process in a closed system, replace that process with any other reversible process that also connects the same initial  $\leftrightarrow$  final states.

### Sample Problem 21-2

Have 2 insulated copper blocks of mass  $m = 1.5 \text{ kg}$ , one at  $T_L = 60^\circ\text{C}$  and another at  $T_R = 20^\circ\text{C}$



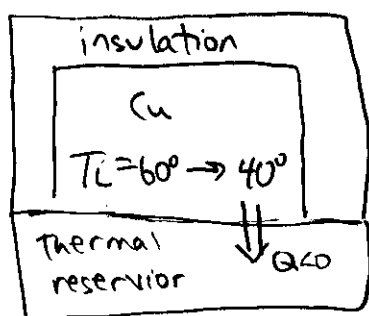
bring blocks into contact



Is this a reversible or irreversible process?

What is the net entropy change  $\Delta S$ ?

To simplify this calculation of  $\Delta S$ ,  
 Instead consider 2 separate, reversible  
 processes:



$$\Delta T = -20^\circ\text{C}$$

$$Q = cm\Delta T = cm(T - T_i) \quad (\text{Eqn 19-14})$$

$\uparrow$  mass specific heat of copper =  $386 \text{ J/kg}\cdot\text{K}$

so  $dQ = cm dT =$  heat needed to change block  
 temp by small  $dT$

$$\begin{aligned} \Rightarrow \Delta S_L &= \int_{T_i=60^\circ\text{C}}^{T_f=40^\circ\text{C}} \frac{cm dT}{T} = cm \ln T \Big|_{T_i}^{T_f} \\ &= cm \ln (T_f/T_i) \\ &= \text{entropy change of left block} \end{aligned}$$

Should I use  $T_f = 40^\circ\text{C}$  and  $T_i = 60^\circ\text{C}$ ?

No! These temps must have units of Kelvins!

$$T_i = 60^\circ\text{C} + 273 = 333\text{K}$$

$$T_f = 40 + 273\text{K} = 313\text{K}$$

$$\text{so } \Delta S_L = cm \ln(T_f/T_i) = -35.86\text{J/K}$$

$$\text{Likewise, } \Delta S_R = \int_{T_i=20^\circ\text{C}}^{T_f=40^\circ\text{C}} \frac{dQ}{T} = cm \ln(T_f/T_i)$$

$$\text{where } T_i = 20^\circ\text{C} + 273 = 293\text{K}$$

$$T_f = 313\text{K}$$

$$\Rightarrow \Delta S_R = +38.23\text{J/K}$$

The system's total change in entropy is

$$\Delta S = \Delta S_L + \Delta S_R = 2.37$$

which is positive, as expected.

## Entropy for an ideal gas

Recall  $dE_{int} = dQ - dW$   $\leftarrow$  differential form of 1<sup>st</sup> law of thermo  
 $= n C_V dT$

also recall that  $W = \int P dV \Rightarrow dW = P dV$

so  $dQ = n C_V dT + P dV$

where  $PV = nRT$   
 is ideal gas law  
 so  $\frac{P}{T} = \frac{nR}{V}$

or  $\frac{dQ}{T} = n C_V \frac{dT}{T} + \frac{P dV}{T}$

$$= n C_V \frac{dT}{T} + nR \frac{dV}{V}$$

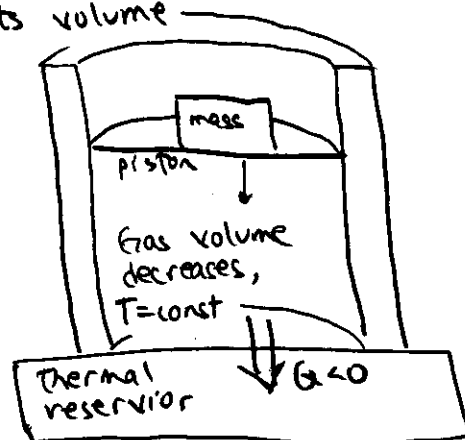
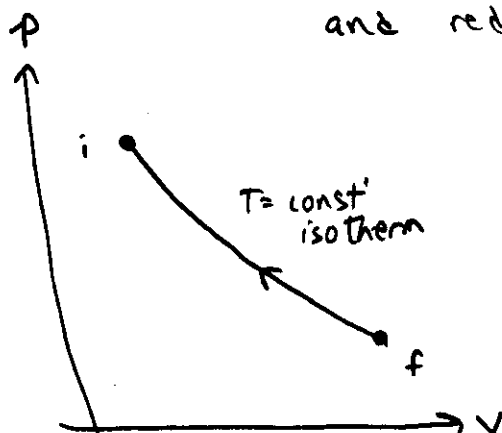
so  $\int_i^f \frac{dQ}{T} = \Delta S = n C_V \int_i^f \frac{dT}{T} + nR \int_i^f \frac{dV}{V}$

$$\Rightarrow \Delta S = S_f - S_i = n C_V \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)$$

= entropy change of ideal gas  
 that results when  $V_i, T_i \rightarrow V_f, T_f$



Now let's consider isothermal contraction of a gas,  
which occurs as we remove heat ( $Q < 0$ )  
and reduce its volume.



Is this a reversible process?

$$\text{Note that } \Delta S_{\text{gas}} = \int_i^f \frac{dQ}{T} = \frac{Q}{T} = -\frac{|Q|}{T}$$

Did we violate our entropy postulate?

No: that postulate says that  $\Delta S > 0$  for irreversible processes  
(we have not yet talked about  $\Delta S$  for reversible processes...)

Note that the thermal reservoir also gained heat  $+|Q|$   
during the isothermal contraction, so its entropy  
changed by

$$\Delta S_{\text{res}} = \frac{+|Q|}{T}$$

What is the entropy change of our entire system  
(gas + reservoir)?

2<sup>nd</sup> Law of Thermo :  $\Delta S \geq 0$

ie, an irreversible process occurring in a closed system has  $\Delta S > 0$ , while a reversible process has  $\Delta S = 0$ .

### Entropy & Heat Engines

A heat engine (or engine for short) = device that extracts heat (energy) from the environment, and does work.

All heat engines utilize some working substance (w/s)  
= the stuff that makes the engine go

(ie, gas-air mixture in an auto engine,  
steam in a steam engine, etc)

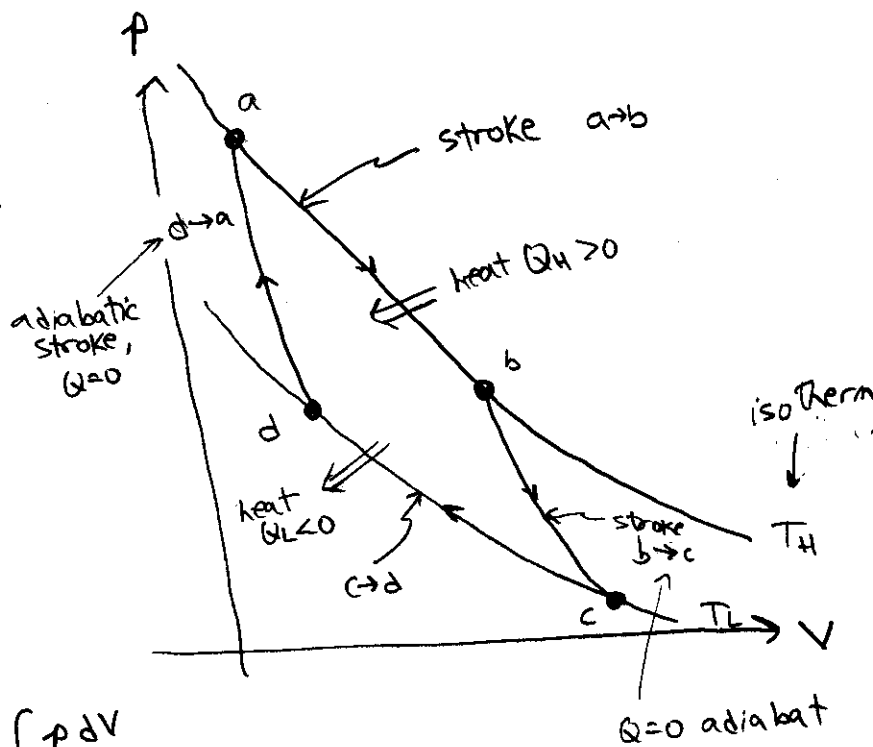
To do sustained work, the engine's activity must be cyclic:

each cycle of the engine causes its WS to pass through a sequence of thermodynamic process (called strokes) that repeat

Carnot Engine - hypothetical engine (which is a sequence of thermodynamic processes) proposed by N. L. Sadi Carnot in 1824. This engine is the most efficient in its use of heat to do work.

use a p-V diagram to illustrate each stroke occurring during 1 cycle of a Carnot engine:

How much work is done by 1 cycle of this engine? Recall  $W = \int p dV$



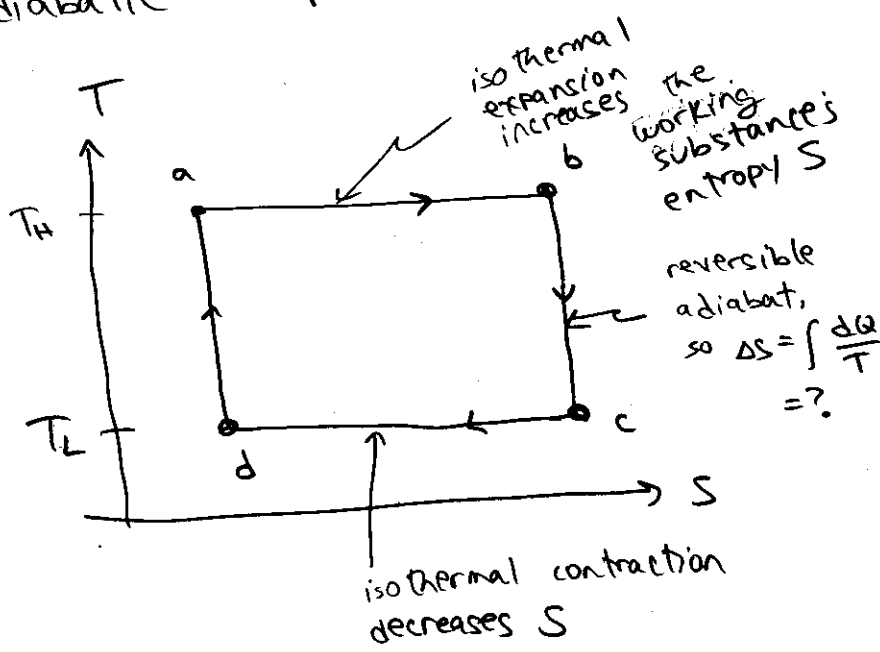
stroke a → b: results in the isothermal expansion of the working substance at the temp  $T_H =$  temp of some hot thermal reservoir. Does the working substance lose/gain heat  $Q_H$  from the hot reservoir? (Yes,  $Q_H > 0$ )

Next, stroke b → c: The working substance expands adiabatically ( $Q=0$ ). Evidently this stroke is insulated, and this process lowers the temp of the WS to  $T=T_L$

stroke c → d: isothermal contraction of the gas, the engine loses heat, so  $Q_L < 0$ .

stroke d → a: adiabatic compression of the gas,  $T \rightarrow T_H$

A temp-entropy diagram of a Carnot cycle:



What is the net change in the system's entropy occurring over 1 cycle?

Calculate the work done during one cycle of engine

1<sup>st</sup> Law. what is  $\Delta E_{int} = Q - W$  during one cycle of this cyclic process?

$$\Delta E_{int} = 0 = Q - W \quad \text{during 1 cycle}$$

$$\Rightarrow \text{work done during one cycle} \quad W = Q = \text{total heat exchanged during 1 cycle}$$

$$= Q_H + Q_L$$

$$= |Q_H| - |Q_L|$$

The system's  
total change in entropy is:

$$\Delta S = \Delta S_H + \Delta S_L = 0$$

↑  
 entropy change during  
 stroke  $a \rightarrow b$ , isothermal  
 expansion:

$$\Delta S_H = \int_i^f \frac{dQ}{T} = \frac{1}{T_H} \int_i^f dQ = \frac{Q_H}{T_H}$$

Likewise, 
$$\Delta S_L = \frac{Q_L}{T_L} = - \frac{|Q_L|}{T_L}$$

Since 
$$\Delta S = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L} = 0$$

$$\Rightarrow \left| \frac{Q_L}{Q_H} \right| = \frac{T_L}{T_H} < 1$$

more heat is extracted from the high-T  
 reservoir than is delivered to the low-T  
 reservoir ... why?

## Efficiency of a Carnot engine:

the efficiency of a heat engine is

$$\Sigma = \frac{\text{payoff}}{\text{cost}} = \frac{\text{work done by engine}}{\text{energy supplied to engine}} = \frac{|W|}{|Q_H|}$$

$$= \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \left| \frac{Q_L}{Q_H} \right|$$

so  $\Sigma = 1 - \frac{T_L}{T_H} < 1$  ← in units of K or C?

⇒ Even though a Carnot engine is the most efficient engine ever invented, it is never 100% efficient

Any engine that converts heat (from some thermal reservoir) into work must also 'throw away' some heat energy, thus  $\Sigma < 1$

Note: real engines have additional inefficiencies (due to friction), and are less efficient than a Carnot engine.

Ex - Nuclear power plant described in

Fig 21-11. It generates  $P = 900 \text{ MW}$  of electrical power, <sup>so</sup>  $W = P\Delta t =$  work done in time  $\Delta t$ , and discharges  $|Q_L| = 2100 \text{ MW}$

into a nearby river.

$1 \text{ mwg-watt} = \text{energy per time}$

since  $W = |Q_H| - |Q_L|$

$\Rightarrow |Q_H| = W + |Q_L| = (3000 \text{ MW}) \times \Delta t = \text{heat consumed in time } \Delta t$

so  $\epsilon = \frac{W}{|Q_H|} = \frac{900 \text{ MW } \Delta t}{3000 \text{ MW } \Delta t} = 30\%$

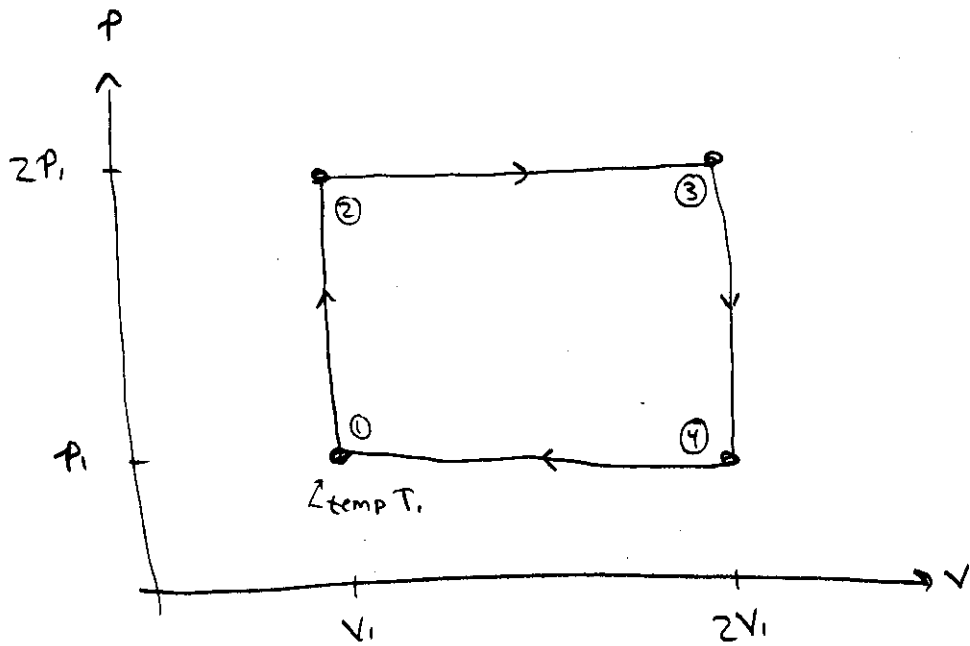
is the power plant's efficiency.

please read Section 21-5 on Carnot Refrigerator



Example :

Consider 1 cycle of the hypothetical heat engine.  
The working substance is a polyatomic ideal gas.



- a.) What is  $P, V, T$  after each of the 4 strokes of this cycle, in terms of  $P_1, V_1, T_1$ ?
- b.) What is the efficiency of this cycle?

a). at point ①,  $P = P_1, V = V_1,$   
while ideal gas law says  $P_1 V_1 = n R T_1$

②:  $P_2 = 2P_1, V_2 = V_1$  so ideal gas law:  $P_2 V_2 = 2P_1 V_1 = 2n R T_1 = n R T_2$

$$\Rightarrow T_2 = 2T_1$$

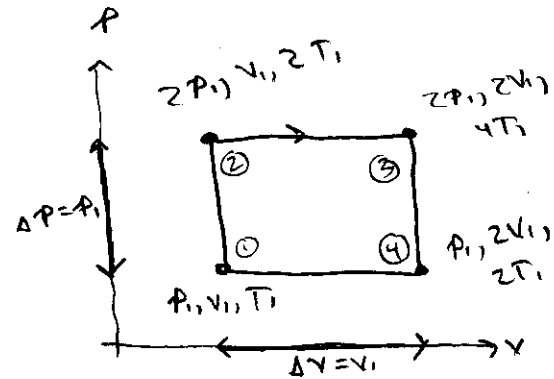
$$\textcircled{3}: 2P_1 \cdot 2V_1 = 4nRT_1 = nRT_3$$

$$\Rightarrow T_3 = 4T_1$$

\textcircled{4}

$$P_1 \cdot 2V_1 = 2nRT_1 = nRT_4$$

$$\Rightarrow T_4 = 2T_1$$



b.) The engines efficiency  $\Sigma = \frac{\text{work } W \text{ done by gas}}{\text{input heat } Q_{in} \text{ that the engine removes from the environment}}$

$$\text{where } W = \int P dV = ?$$

$$= \Delta P \Delta V =$$

$$= P_1 V_1 = nRT_1$$

The total heat extracted by engine from the environment is

$$Q = Q_{12} + Q_{23} + Q_{34} + Q_{41}$$

↑  
heat extracted  
during stroke 1 → 2

← stroke  
2 → 3

Use 1<sup>st</sup> Law to calculate  $Q_{12}$ :

$$\Delta E_{12} = Q_{12} - W_{12}$$

↑  
change in  
internal energy  
during stroke 1→2

↑  
what is this

but  $\Delta E_{12} = n C_V \Delta T_{12}$  for any ideal gas

what is  $C_V$  for this gas?

$C_V = \frac{f}{2} R$  for ideal gas, where a  
polyatomic gas has  $f=6$  degrees of  
freedom

$$\text{so } \Delta E_{12} = 3nR \Delta T_{12}$$

$$\text{where } \Delta T_{12} = T_2 - T_1 = T_1$$

$$\text{so } Q_{12} = \Delta E_{12} = 3nRT_1$$

Calculate  $Q_{23}$ :

$$\Delta E_{23} = Q_{23} - W_{23} = 3nR\Delta T_{23}$$

$$\text{where } \Delta T_{23} = T_3 - T_2 = 2T_1$$

What is  $W_{23}$ ?

$$W_{23} = \int P dV = \int_{V_1}^{2V_1} 2P_1 dV = 2P_1 V_1 = 2nRT_1$$

$$\text{so } Q_{23} = W_{23} + 6nRT_1 = 8nRT_1$$

Likewise you can show that

$$\left. \begin{array}{l} Q_{34} = -6nRT_1 \\ Q_{41} = -4nRT_1 \end{array} \right\} \text{please confirm this yourself!}$$

$Q_{34} < 0$  since the gas cooled off

So  $Q_{12} = 3nRT_1$

$$Q_{23} = 8nRT_1$$

$$Q_{34} = -6nRT_1$$

$$Q_{41} = -4nRT_1$$

How much heat did the engine withdraw from the environment?

$$Q_{in} = Q_{12} + Q_{23} = 11nRT_1$$

How much heat was thrown away as 'waste heat'?

$$Q_{waste} = Q_{34} + Q_{41} = -10nRT_1$$

The engine's efficiency is

$$\Sigma = \frac{W}{Q_{in}} = \frac{1}{11} = 9\%$$

ie, 9% of  $Q_{in}$  gets converted to useful work, while 91% of  $Q_{in}$  'goes out the tailpipe' as wasted energy.

Note that we didn't need to know  $P_1, V_1, T_1$  to calculate  $\Sigma$ .