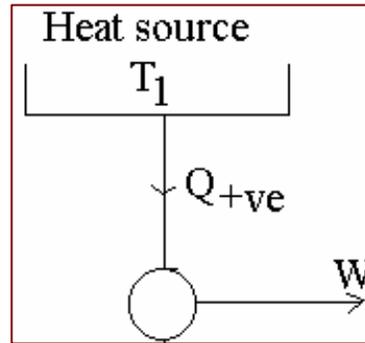# Chapter 6
Second Law of Thermodynamics

Leads Up To Second Law Of Thermodynamics

It is now clear that we can't construct a heat engine with just one +ve heat interaction.

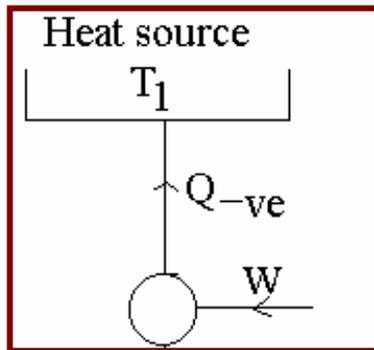
The above engine is not possible.

Second Law Of Thermodynamics (contd…)

Is it possible to construct a heat engine with only one -ve heat interaction?
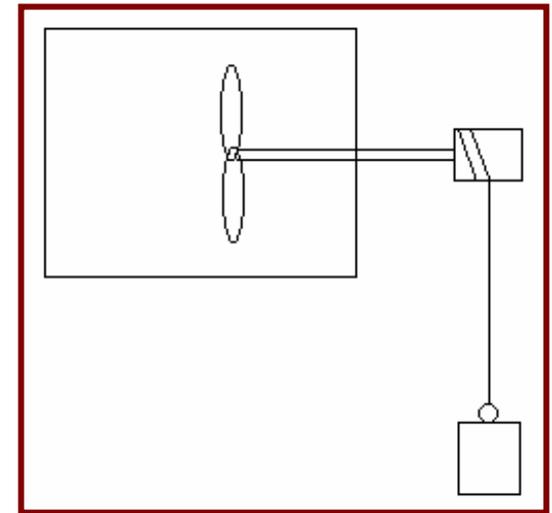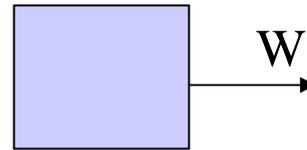
Is the following engine possible?

The answer is <u>yes</u>, because
This is what happens in a
stirrer

Second Law Of Thermodynamics (contd…)

Perpetual motion machine of the second kind is not possible.

Perpetual motion machine of the first kind violates I LAW (It produces work without receiving heat)

W

Enunciation of II Law of Thermodynamics

Statement 1: It is impossible to construct a device which operating in a cycle will produce no effect other than raising of a weight and exchange of heat with a single reservoir.

Note the two underlined words.

II Law applies only for a cycle - not for a process!! (We already know that during an isothermal process the system can exchange heat with a single reservoir and yet deliver work)

!!There is nothing like a 100% efficient heat engine!!

Enunciation of
II Law of Thermodynamics

❖ To enunciate the II law in a different form

➢ !!! We have to appreciate some ground realities !!!

➢ All processes in nature occur unaided or spontaneously in one direction. But to make the same process go in the opposite direction one needs to spend energy.
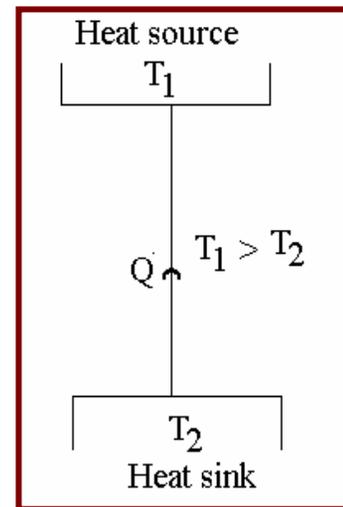
Common sense tells us that

1Heat flows from a body at higher temperature to a body at lower temperature
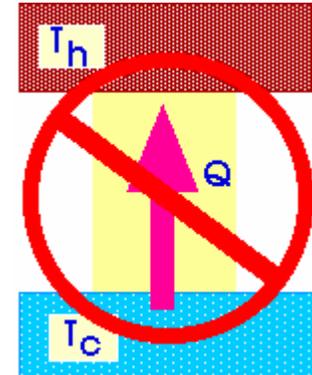
A hot cup of coffee left in a room becomes cold. We have to expend energy to rise it back to original temperature
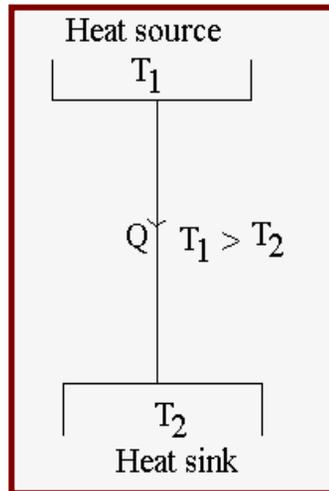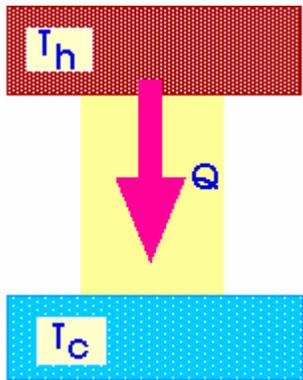
Possible

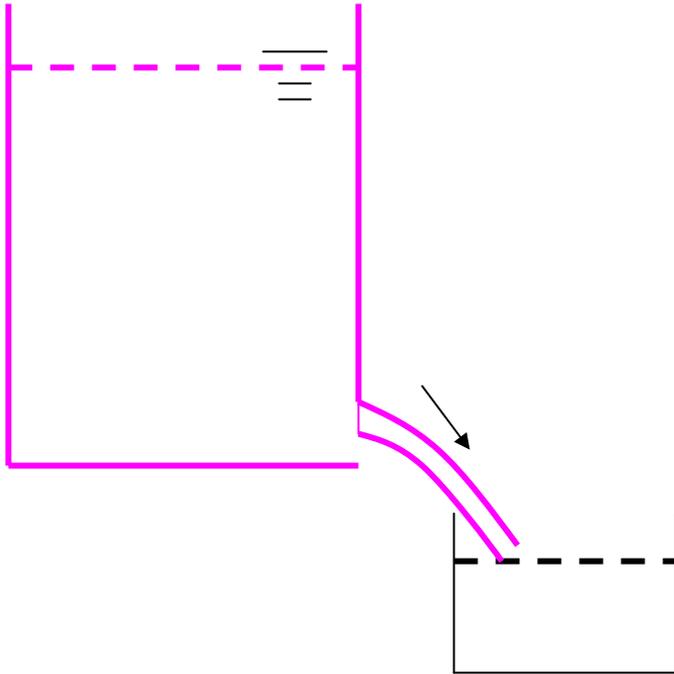Not possible

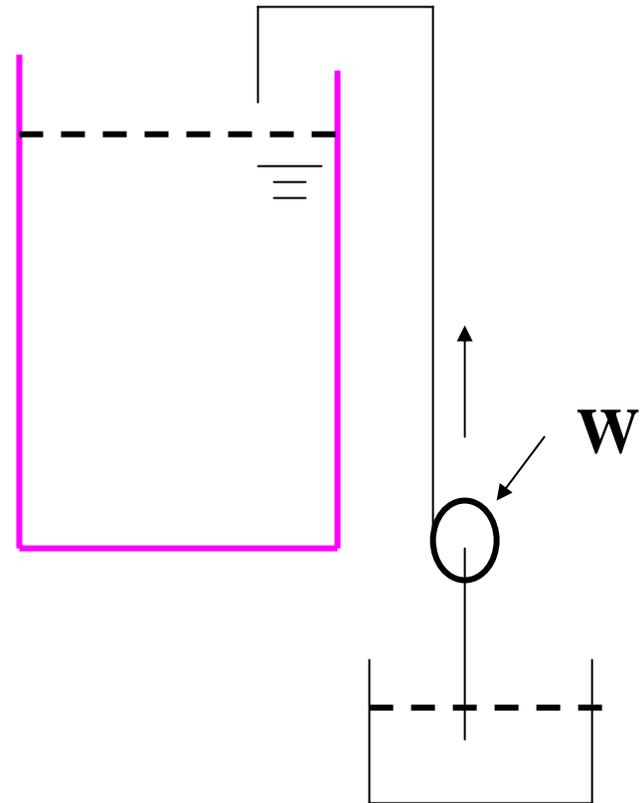*(you can't make room heat up your coffee!!)*

Common sense tells us that

2.Fluid flows from a point of higher pressure or potential. to a lower one

Water from a tank can flow down To get it back to the tank you have to use a pump i.e, you spend energy

W

Possible

Common sense tells us that

3.Current flows from a point of higher potential to lower one

Battery can discharge through a resistance, to get the charge

4. You can mix two gases or liquids. But to separate them you have to spend a lot of energy. (You mix whisky and soda without difficulty - but can't separate the two - Is it worthwhile?)

5. All that one has to say is "I do". To get out of it one has to spend a lot of money

6. When you go to a bank and give 1US$ you may get Rs 49. But if you give Rs 49 to the bank they will give you only 95 US cents (*if you are lucky !!*). You spend more.

Common sense tells us that

6. When you go to a bank and give 1US$ you may get Rs 49. But if you give Rs 49 to the bank they will give you only 95 US cents (if you are lucky !!). You spend more.

7. You can take tooth paste out of the tube but can't push it back!!

Moral:

All processes such as 1-7 occur unaided in one direction

but to get them go in the other direction there is an

expenditure - money, energy, time, peace of mind? ….

They are called irreversible processes

Definitions of Reversible Process

❖A process is reversible if after it, means can be found to restore the system and surroundings to their initial states.

Some reversible processes:

➢Constant volume and constant pressure heating and cooling - the heat given to change the state can be rejected back to regain the state.
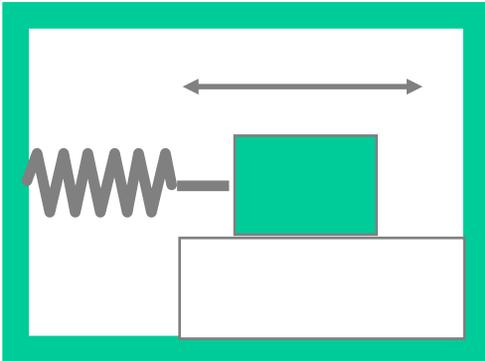
Reversible Process (contd…)

➢ Isothermal and adiabatic processes -the work derived can be used to compress it back to the original state

➢ Evaporation and condensation

➢ Elastic expansion/compression (springs, rubber bands)
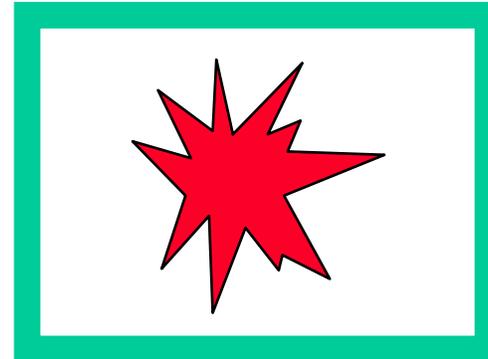
❖ *Lending money to a friend (who returns it promptly)*
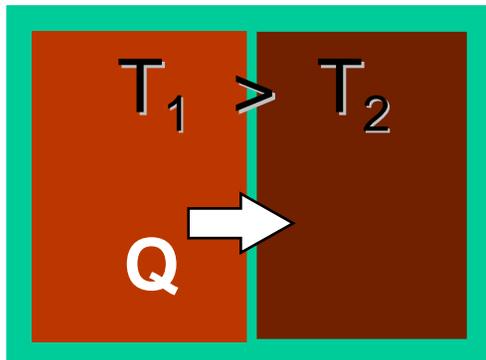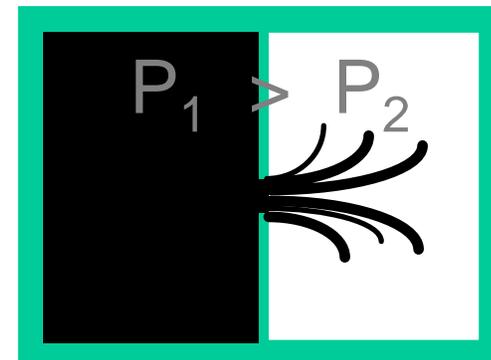
Some Irreversible Process

motion with friction

spontaneous chemical reaction

unrestrained expansion

heat transfer
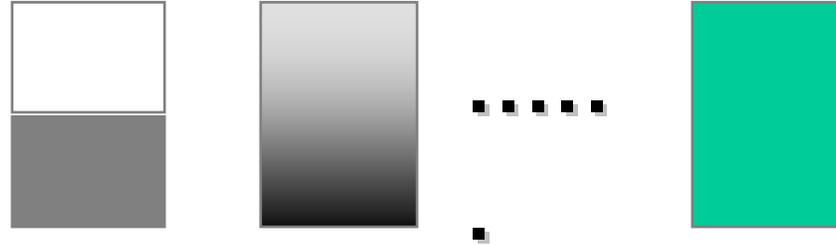

$$T_1 > T_2$$

Q

$$P_1 > P_2$$

Irreversible Process (contd…)

mixing

Flow of current through a resistance - when a battery discharges through a resistance heat is dissipated. You can't recharge the battery by supplying heat back to the resistance element!!

Pickpocket

!!!Marriage!!!!

Reversible Cycle

➢A cycle consisting of all reversible processes is a reversible cycle. Even one of the processes is irreversible, the cycle ceases to be reversible.
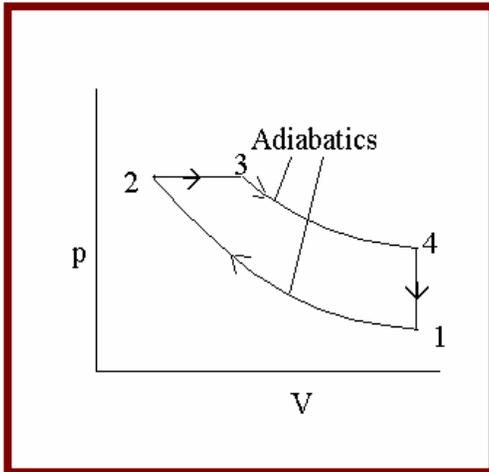
Otto, Carnot and Brayton cycles are all reversible.
A reversible cycle with clockwise processes produces work with a given heat input. The same while operating with counter clockwise processes will reject the same heat with the same work as input.
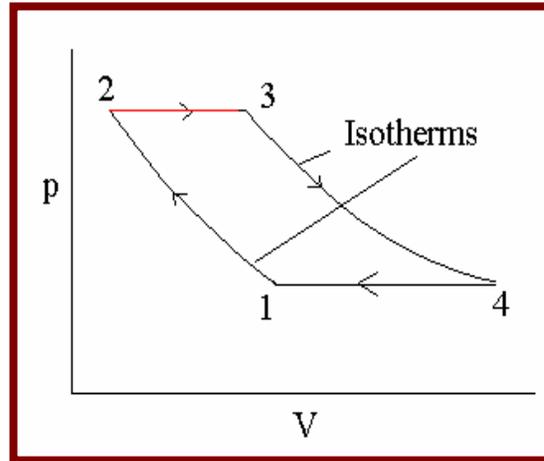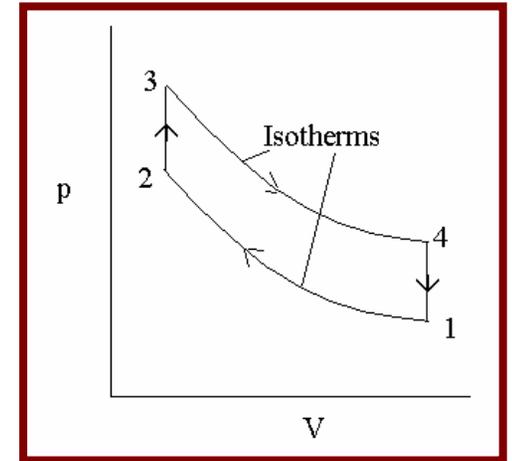
Other reversible cycles:

Diesel cycle   **Ericsson cycle**   Stirling cycle

Clausius Statement of II Law of Thermodynamics

It is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

❖ Yes, you can transfer heat from a cooler body to a hotter body by expending some *energy*.

# Clausius Statement (contd…)

➢ *Note : It is not obligatory to expend work, even thermal energy can achieve it.*

➢ Just as there is maximum +ve work output you can derive out of a heat engine, there is a *minimum work* you have to *supply* (-ve) *to a device* achieve transfer of thermal energy from a cooler to a hotter body.

Carnot Cycle for a Refrigerator/heat Pump

Heat sink

T_1

Q_1

W

$T_1 > T_2$

T_2 Q_2

Heat source

Fig. 1. Refrigerator/Heat Pump.
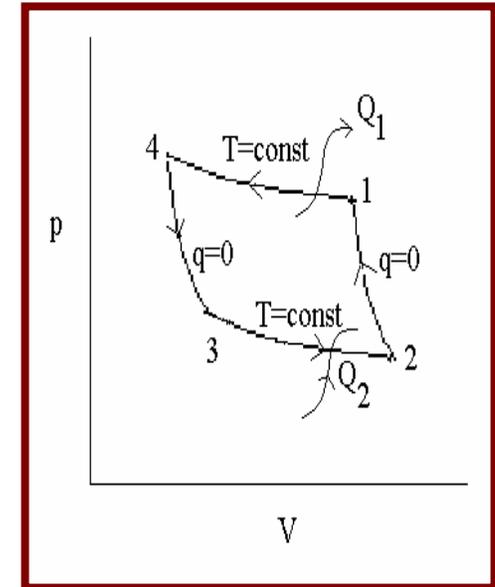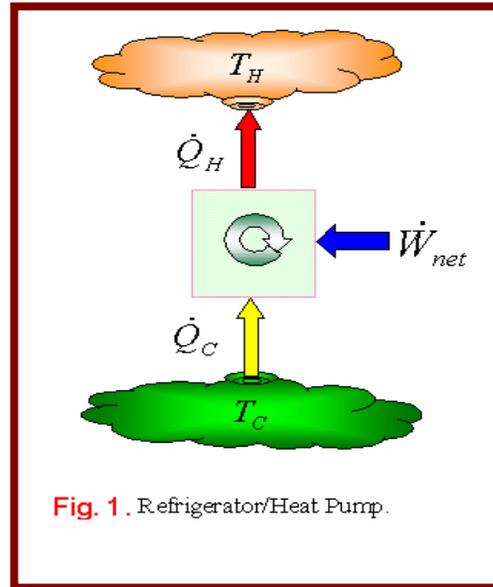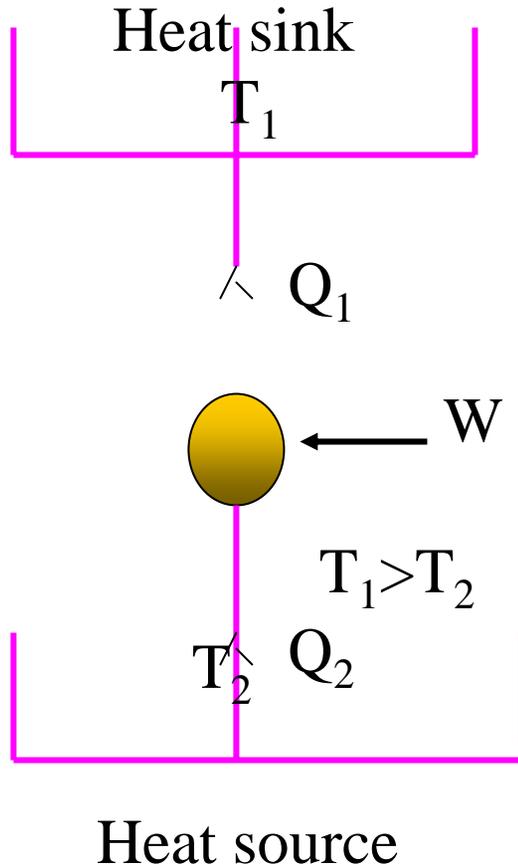
$T_H = T_1$

$T_C = T_2$

Heat pump

❖*A device which transfers heat from a cooler to a warmer body (by receiving energy) is called a heat pump.* A refrigerator is a special case of heat pump.

Just as efficiency was defined for a heat engine, for a heat pump the coefficient of performance (COP) is a measure of how well it is doing the job.

Heat Pump (contd…)

❖ A heat pump

- Invoke the definition: what we have achieved ، what we spent for it

- COP_{HP} = heat given out ، work done = $\frac{1}{2}Q_1/W\frac{1}{2}$

- Note : The entity of interest is how much heat could be realised. Work is only a penalty.

Heat Pump (contd…)

Reverse cycle air conditioners used for winter heating do the above. Heat from the ambient is taken out on a cold day and put into the room.

The heat rejected at the sink is of interest in a heat pump , ie., Q_1.

In a refrigerator the entity of interest id Q_2.

In this case $COP_R = \left| Q_2/W \right|$

NOTE: η ,COP_{HP} COP_R are all positive numbers $\eta < 1$ but COPs can be $>$ or < 1

Heat Pump (contd…)

Relation between η and COP_{HP}

It is not difficult to see that $\eta\ COP_{HP} = 1$

Apply I law to Carnot cycle as a heat pump/refrigerator:

$-Q_1 + Q_2 = -W$ or $Q_1 = Q_2 + W$

Divide both sides with W $\qquad Q_1/W = Q_2/W + 1$

or $\qquad COP_{HP} = COP_R + 1$

The highest COP_{HP} obtainable therefore will be $T_1/(T_1-T_2)$

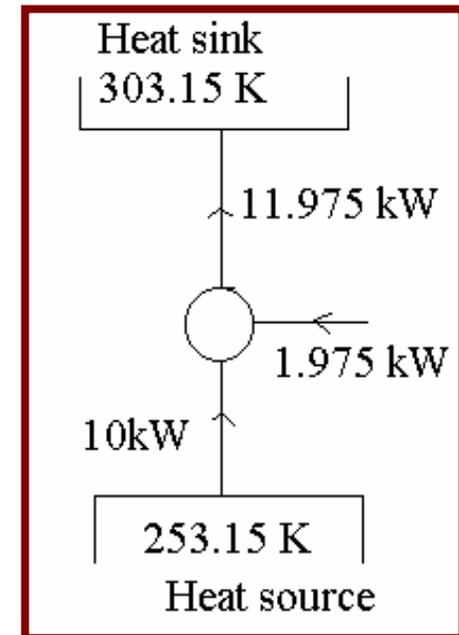and highest COP_R obtainable therefore will be $T_2/(T_1-T_2)$

Examples

Eg: If 10 kw of heat is to be removed from a cold store at -20°Cand rejected to ambient at 30°C.

COP_R= 253.15/(303.15-253.15)= 5.063

W= Q_2/ COP_R ; Q_2= 10 kW

Therefore W= 10/5.063 = 1.975 kW

Examples (contd…)

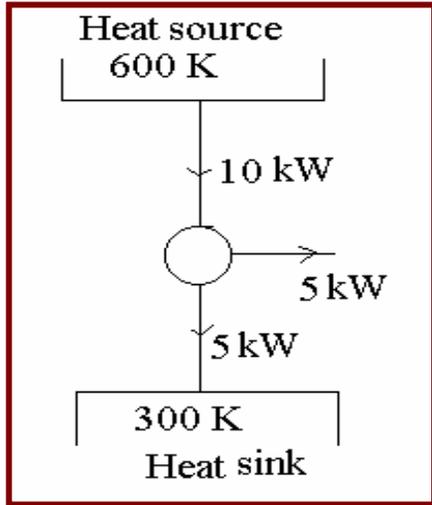❖Another example: Let us say that the outside temperature on a hot summer day is 40°C. We want a comfortable 20°C inside the room. If we were to put a 2 Ton (R) air conditioner, what will be its power consumption?

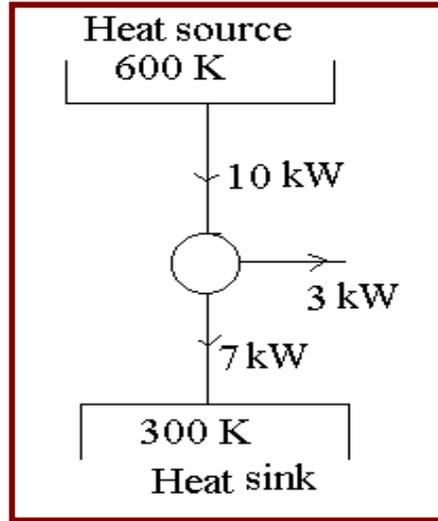Answer: 1 Ton (R) = 3.5 kw. Therefore Q_2=7 kW

COP_R= 293.15/(313.15-293.15)= 14.66 ie., W=7/14.66 =0.47 kW

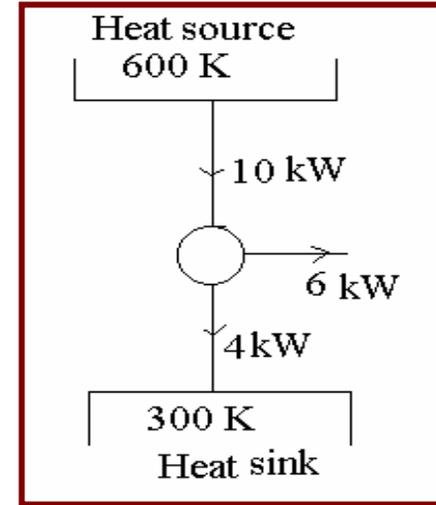Actually a 2 Ton air-conditioner consumes nearly 2.8 kW (much more than an ideal cycle!!)
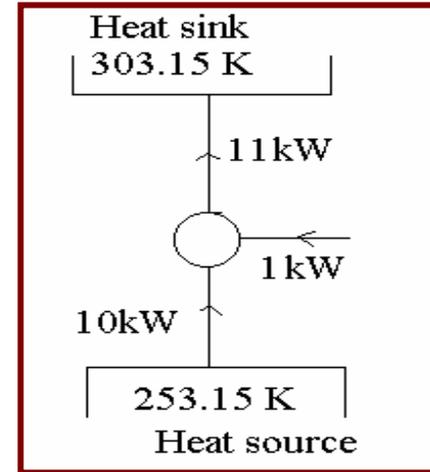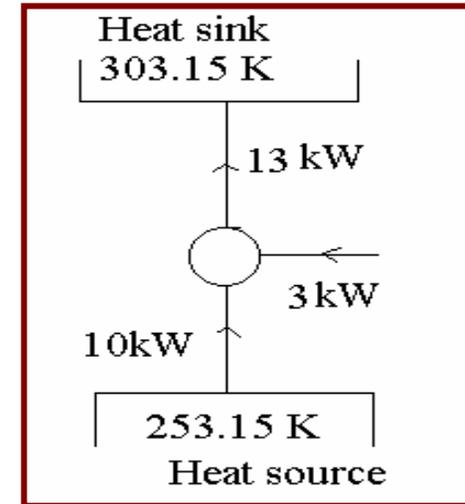
Ideal but possible | Real and possible | Not possible

HEAT ENGINE

Heat source 600 K	Heat source 600 K	Heat source 600 K
10 kW	10 kW	10 kW
5 kW	3 kW	6 kW
5 kW	7 kW	4 kW
300 K Heat sink	300 K Heat sink	300 K Heat sink

HEAT PUMP

Heat sink 303.15 K	Heat sink 303.15 K	Heat sink 303.15 K
11.975 kW	13 kW	11 kW
1.975 kW	3 kW	1 kW
10 kW	10 kW	10 kW
253.15 K Heat source	253.15 K Heat source	253.15 K Heat source
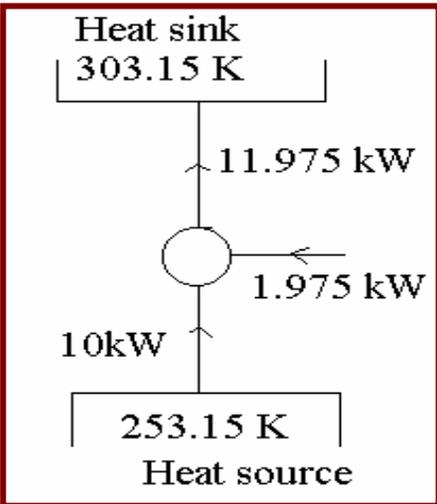
This is the best that can happen

This is what happens in reality

You derive work > what is thermodynamic maximum nor can You expend work < what is thermodynamic minimum
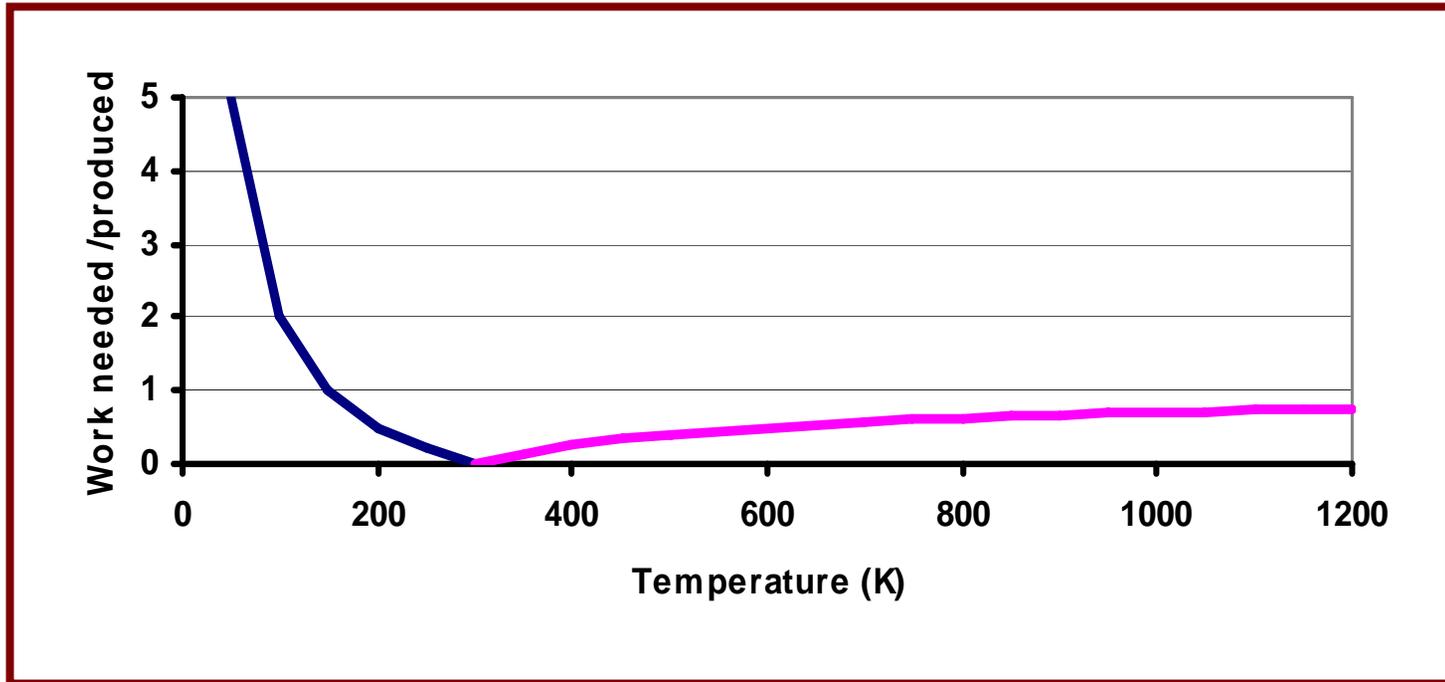
Examples (contd…)

Suppose the ambient is at 300 K. We have heat sources available at temperatures greater than this say 400, 500, 600…..K. How much work ca you extract per kW of heat ? Similarly, let us say we have to remove 1 kW of heat from temperatures 250, 200, 150 …. K. How much work should we put in?

Examples (contd…)

Some Interesting Deductions

➢Firstly, there isn't a meaningful temperature of the source from which we can get the full conversion of heat to work. Only at ∞ temp. one can dream of getting the full 1 kW work output.

Some Interesting Deductions

❖ Secondly, more interestingly, there isn't enough work available to produce 0 K. In other words, 0 K is unattainable. This is precisely the III LAW.

❖ Because, we don't know what 0 K looks like, we haven't got a starting point for the temperature scale!! That is why all temperature scales are at best empirical.

Summation of 3 Laws

You can't get something for nothing

> To get work output you must give some thermal energy

You can't get something for very little

> To get some work output there is a minimum amount of thermal energy that needs to be given

You can't get every thing

> However much work you are willing to give 0 K can't be reached.

Violation of all 3 laws: try to get everything for nothing

Equivalence of Kelvin-Planck and Clausius statements

II Law basically a negative statement (*like most laws in society*). The two statements look distinct. We shall prove that violation of one makes the other statement violation too.

Let us suspect the Clausius statement-it *may be* possible to transfer heat from a body at colder to a body at hotter temperature without supply of work

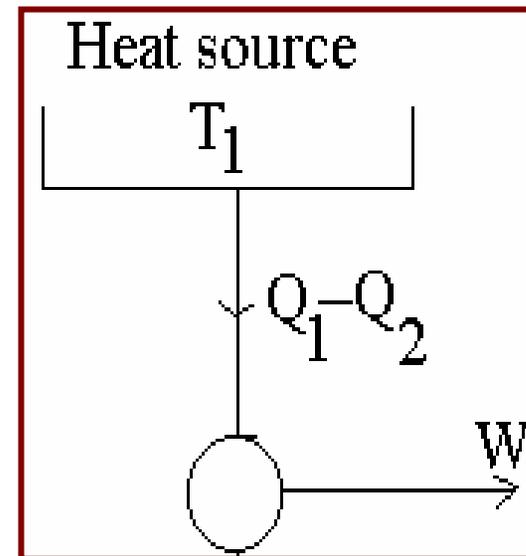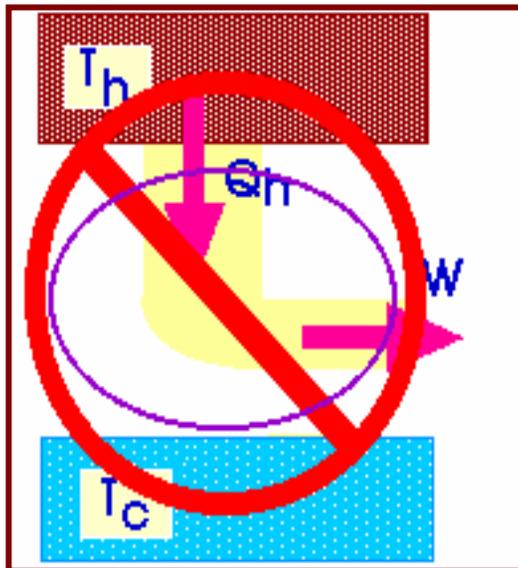# Equivalence of Kelvin-Planck and Clausius statements
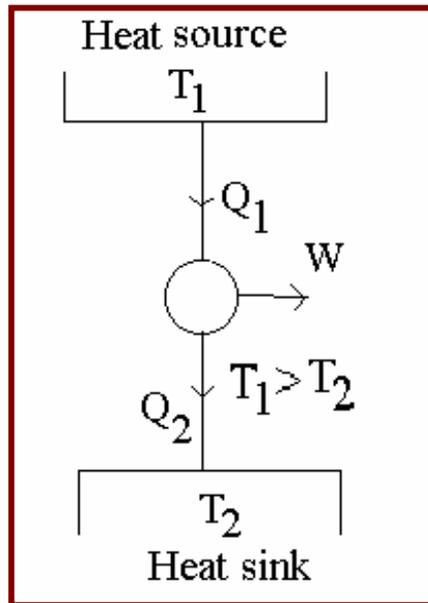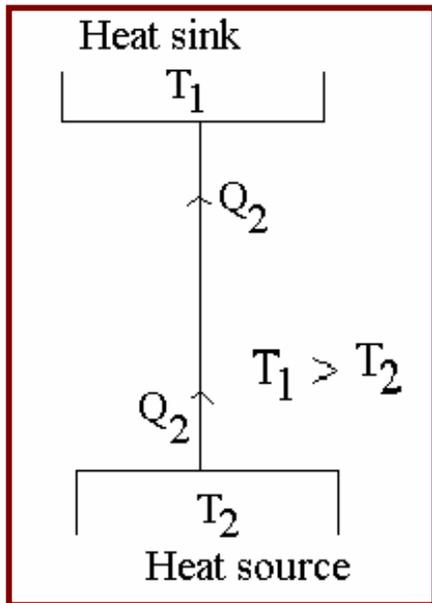
Let us have a heat engine operating between T_1 as source and T_2 as a sink. Let this heat engine reject exactly the same Q_2 (as the pseudo-Clausius device) to the reservoir at T_2. To do this an amount of Q1 needs to be drawn from the reservoir at T_1. There will also be a $W = Q_1 - Q_2$

Equivalence of Kelvin-Planck and Clausius statements

Combine the two. The reservoir at T_2 has not undergone any change (Q_2 was taken out and by pseudo-Clausius device and put back by the engine). Reservoir 1 has given out a net Q_1-Q_2. We got work output of W. Q_1-Q_2 is converted to W with no net heat rejection. This is violation of Kelvin-Planck statement.
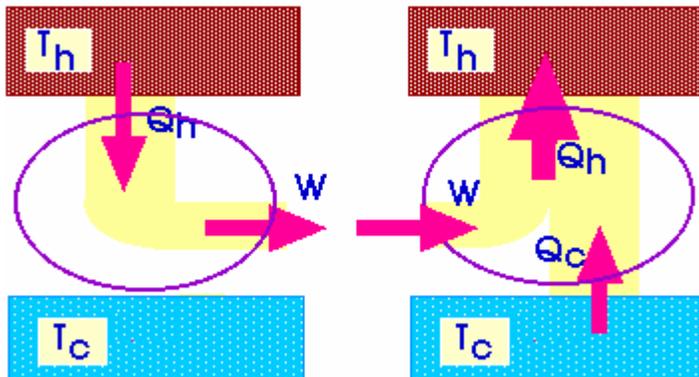
Equivalence of Kelvin-Planck and Clausius statements

- Let us assume that Clausius statement is true and suspect Kelvin-Planck statement
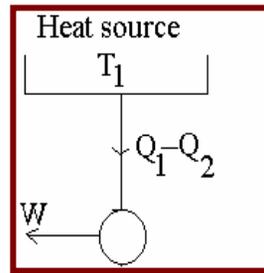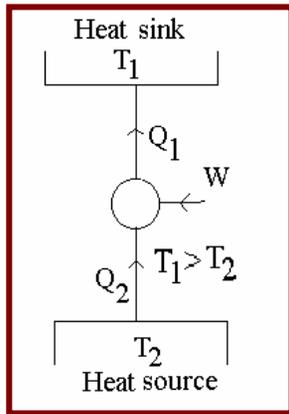
May be possible?

Pseudo Kelvin Planck engine requires only Q_1-Q_2 as the heat interaction to give out W (because it does not reject any heat) which drives the Clausius heat pump

Combining the two yields:

- The reservoir at T_1 receives Q_1 but gives out Q_1-Q_2 implying a net delivery of Q_2 to it.
- Q_2 has been transferred from T_2 to T_1 without the supply of any work!!
- *A violation of Clausius statement*

Equivalence of Kelvin-Planck and Clausius statements

Moral: If an engine/refrigerator violates one version of II Law,

it violates the other one too.

All reversible engine operating between the same two fixed temperatures will have the same η and COPs.

If there exists a reversible engine/ or a refrigerator which can do better than that, it will violate the Clausius statement.
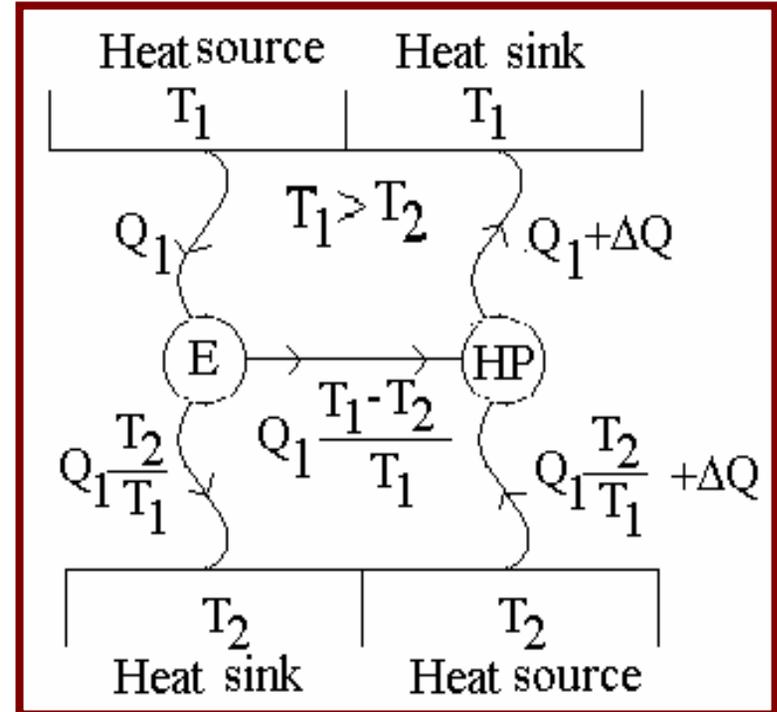
Equivalence of Kelvin-Planck and Clausius statements

Let us presume that the HP is super efficient!!

For the same work given out by the engine E, it can pick up an extra DQ from the low temperature source and deliver over to reservoir at T1. The net effect is this extra DQ has been transferred from T2 to T1 with no external work expenditure. *Clearly, a violation of Clausius statement!!*
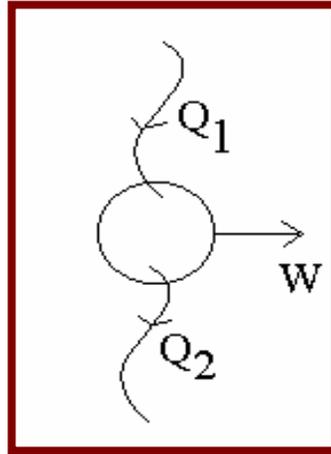
Equivalence of Kelvin-Planck and Clausius statements (contd…)

SUM UP

- ➢ Heat supplied = Q_1; Source temperature = T_1 ;Sink temperature= T_2
- ➢ Maximum possible efficiency = $W/Q_1 = (T_1-T_2)/T_1$
- ➢ Work done = $W = Q_1(T_1-T_2)/T_1$

Equivalence of Kelvin-Planck and Clausius statements (contd…)

Applying I Law
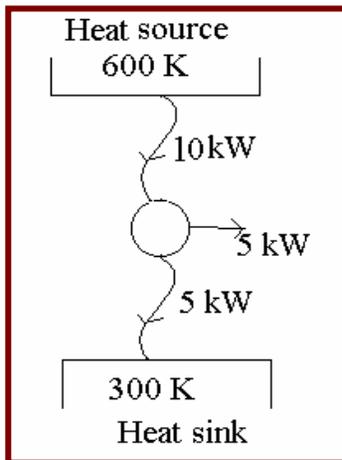
Sum of heat interactions = sum of work interactions

$Q_1 + Q_2 = W = Q_1 (T_1 - T_2)/T_1$

Q_1 is +ve heat interaction; Q_2 is -ve heat interaction

Equivalence of Kelvin-Planck and Clausius statements

➤ Heat rejected = -ve heat interaction = $-Q_2 = (Q_1-W) = Q_1T_2/T_1$
➤ For a reversible heat engine operating in a cycle $Q_1/T_1 + Q_2/T_2 = 0$
➤ or $S(Q/T) = 0$

Ideal engine

$10,000/600 + (-5000/300) = 0$

Not so efficient engine

$10,000/600 + (-7000/300) < 0$

Heat source
600 K
10kW
5 kW
5 kW
300 K
Heat sink

Heat source
600 K
10kW
3 kW
7 kW
300 K
Heat sink