# SECOND LAW OF THERMODYNAMICS – INTRODUCTION AND CYCLES

You could say that the 2<sup>nd</sup> Law was developed because physicists observed that there were phenomena that were not explained by the 1<sup>st</sup> law.

There are various formulations and applications of the 2<sup>nd</sup> Law. We will study two of them that relate to important cycles using pure substances in simple compressible systems.

1. An electric resistance heater has current (work) passed through a resistance (wire) and produces heat continuously..

heat

electricity (work)

Neglecting changes to the wire, the 1<sup>st</sup> law for the heater is:

$$\mathbf{Q} = \mathbf{W}$$

The 1<sup>st</sup> Law does not say anything about the direction of the energy transfer. In fact, according to the 1<sup>st</sup> law, we could reverse the arrows, heat the wire, and produce electricity. However, you know from experience that this cannot be done. **So there are some kinds of energy transfers allowed by the 1<sup>st</sup> law that do not occur in nature, and continuously producing work from heat is one**. (You can produce work once by adding heat to a piston cylinder, but the process will stop when the piston reaches the top of the cylinder.)

2. If you place a cold can of soda in a warm room, it is easy to predict that heat will be transferred from the warmer surroundings to the soda. The 1<sup>st</sup> law statement for the soda in this passive process (no work) is:

$$Q = \Delta U$$
  
e and the system gains energy.  
 $20 ^{\circ}C$   
 $Q$   
 $5 ^{\circ}C$ 

Where Q is positive and the system gains energy. However, the 1<sup>st</sup> law does not say that the process could not be reversed with heat transfer from the can to the room and decrease in the energy of the soda. But we know from experience that heat is never transferred spontaneously from a cold system to warm surroundings.

These are examples of two principles addressed by the 2<sup>nd</sup> Law of Thermodynamics:

- 1. SOME PROCESSES CAN OCCUR SPONTANEOUSLY ONLY IN ONE DIRECTION. HEAT TRANSFER IS A DIRECTIONAL PROCESS, AND **HEAT WILL ONLY BE TRANSFERRED FROM HIGH TEMPERATURE TO LOW TEMPERATURE.**
- 2. ENERGY HAS A HIERARCHY. WORK (MECHANICAL, ELECTRICAL, CHEMICAL, ETC.) IS HIGHER QUALITY ENERGY THAN HEAT. FURTHERMORE, THE QUALITY OF ENERGY ALWAYS <u>DECREASES</u> IN THERMODYNAMIC PROCESSES. THIS MEANS THAT WORK CAN ALWAYS BE CONVERTED TO HEAT, BUT HEAT CANNOT BE CONVERTED DIRECTLY TO WORK.

All thermodynamic processes must satisfy both the 1<sup>st</sup> and 2<sup>nd</sup> Laws.

# **DEFINITION**

# THERMAL RESERVOIR

A thermal reservoir is a body that can supply or absorb heat without changing temperature.

- a) Could be a large mass with high heat capacity  $(mC_p)$ : ocean, atmosphere
- b) Could be a smaller two-phase system that boils/condenses or freezes/melts at constant temperature

# **HIGH TEMPERATURE RESERVOIR IS A SOURCE** THAT CAN SUPPLY HEAT TO A SYSTEM WHILE IT STAYS AT A CONSTANT TEMPERATURE

LOW TEMPERATURE RESERVOIR IS A <mark>SINK</mark> THAT CAN ABSORB HEAT WITHOUT CHANGING TEMPERATURE.

# WE WILL STUDY TWO CYCLES FOR SIMPLE COMPRESSIBLE SYSTEMS CONTAINING PURE SUBSTANCES RELATED TO THE TWO PRINCIPLES STATED BEFORE ABOUT HEAT TRANSFER DIRECTION AND ENERGY QUALITY.

# 1. HEAT ENGINES 2. REFRIGERATORS

## 1. HEAT ENGINES ARE CYCLES FOR CONVERTING HEAT TO NET WORK CONTINUOUSLY.

Characteristics of heat engines:

- a) a heat engine receives heat from a high temperature reservoir or SOURCE (furnace, sun, fission reaction, etc)
- b) A fraction of the heat input is converted to NET WORK (mechanical directly)
- c) The remaining fraction of the heat input <u>must</u> be rejected to a low temperature reservoir or SINK.
- d) Heat engines operate in a cycle so the 1<sup>st</sup> law statement for the heat engine cycle is:

$$Q_{\rm NET} = W_{\rm NET}$$

e) the medium in a heat engine process is a fluid, called the "working fluid." Working fluid can be water/steam, air, R-134a, etc.

Analysis of Heat Engines

Net work = 
$$W_{\text{NET}} = W_{\text{OUT}} - W_{\text{IN}}$$

Since a heat engine is a cyclic process, the change in energy of the working fluid = 0.

Net heat transfer =  $Q_{\text{NET}} = Q_{\text{IN}} - Q_{\text{OUT}}$ 

From the  $1^{st}$  Law:  $Q_{NET} = W_{NET}$ 

From the 2nd law: Q<sub>OUT</sub> > 0

$$\eta = \frac{net \ work \ produced}{heat \ input} = \frac{W_{net}}{Q_{in}}$$

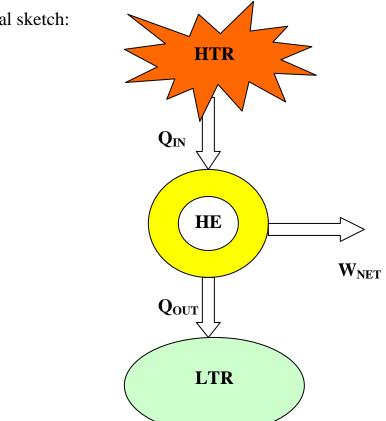
However,  $W_{NET} = Q_{NET} = Q_{IN} - Q_{OUT}$  and substituting into above

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

$$0 < \eta < 1$$

If only the 1<sup>st</sup> law controlled,  $\eta$  could equal 1. However, by the 2<sup>nd</sup> law, since  $Q_{OUT} > 1$ , then  $\eta < 1$ .

 $Q_{IN}$  is the heat input from the high temperature reservoir (HTR), and  $Q_{OUT}$  is the heat rejected to the low temperature reservoir (LTR).



Conceptual sketch:

#### EXAMPLE 1

A steam power plant receives 280 GJ/hr from a furnace. Heat is rejects at the rate of 145 GJ/hr and there is an additional 8 GJ loss through the pipes of the plant.

a) What is the net power output from the plant?

$$\dot{W}_{net} = \dot{Q}_{net} = 280 - 145 - 8(GJ/jr)$$
  
 $\dot{W}_{net} = 127 \frac{GJ}{hr} * \frac{10^3 \frac{MJ}{GJ}}{3600 \frac{s}{hr}} = 35.3 MW$ 

b) What is the plant efficiency,  $\eta$ ?

$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{127 \text{GJ} / \text{hr}}{280 \text{GJ} / \text{hr}} = 0.45$$
OR
$$\eta = 1 - \frac{\dot{Q}_{out}}{\dot{Q}_{in}} = 1 - \frac{(145 + 8)}{280} = 0.45$$

#### EXAMPLE 2

A solar power plant has an efficiency of 0.03 and a net power output of 100 kw. At what rate must solar heat be collected for this plant?

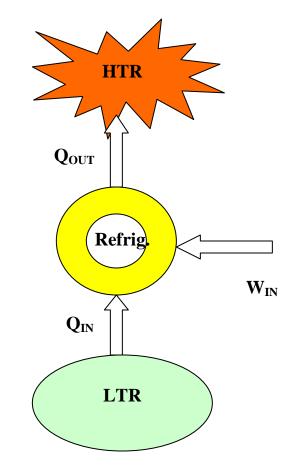
$$\dot{Q}_{IN} = \dot{Q}_{H} = \frac{W_{NET}}{\eta} = \frac{100 \text{kw}}{0.03} = 3,333 \text{kw}$$

At what rate is heat rejected?

$$\dot{W}_{NET} = \dot{Q}_{IN} - \dot{Q}_{OUT} = \dot{Q}_{H} - \dot{Q}_{L}$$
  
 $\dot{Q}_{L} = 3,333 - 100 \text{kw} = 3,233 \text{kw}$ 

KELVIN-PLANCK STATEMENT OF THE 2<sup>ND</sup> LAW PERTAINING TO HEAT ENGINES: It is impossible for any device operating in a cycle to receive heat from only one reservoir and produce a net amount of work.

## 2. REFRIGERATOR (OR HEAT PUMP) IS A DEVICE TO TRANSFER HEAT FROM A LOW TEMPERATURE MEDIUM TO A HIGH TEMPERATURE MEDIUM.



## **Characteristics of Refrigerators/Heat Pumps**

- a) Refrigerator/heat pump receives heat from a low temperature medium (ice box of refrigerator, outdoor air, etc.
- b) Heat is rejected to a high temperature medium (room air).
- c) Cycle requires work input
- d) 1<sup>st</sup> Law statement

$$W_{IN} = Q_{OUT} - Q_{IN}$$

e) Working fluid is special chemical that boils at low temperatures and near atmospheric pressures (R-134a)

### **Analysis of Refrigerators/Heat Pumps**

The term to describe the performance of refrigerators is the COEFFICIENT OF PERFORMANCE (COP)

$$COP = \frac{desired output}{required input}$$

for a refrigerator, the desired output is the heat removed from the cold medium and the required input is work:

$$COP_{R} = \frac{Q_{in}}{W_{in}}$$

but

$$W_{in} = Q_{out} - Q_{in}$$

$$COP_{R} = \frac{Q_{in}}{Q_{out} - Q_{in}} = \frac{1}{\frac{Q_{out}}{Q_{in}} - 1} = \frac{1}{\frac{Q_{H}}{Q_{L}} - 1}$$

$$1 < \frac{Q_{H}}{Q_{L}} \text{ and often } < 2$$

then typically,  $COP_R > 1$  (different from  $\eta$ )

 $(Q_H = heat rejected to high temperature medium and Q_L = heat input from low temperature medium.)$ 

NOTE THAT <u>AIR CONDITIONERS ARE REFRIGERATORS</u>, THE DESIRED OUTPUT IS THE HEAT REMOVED FROM THE LOW TEMPERATURE ROOM AIR AND REJECTED INTO THE WARMER OUTDOORS AIR. for a heat pump, the desired output is the heat rejected into the warm medium and the required input is work.

$$COP_{HP} = \frac{Q_{out}}{W_{in}}$$
but
$$W_{in} = Q_{out} - Q_{in}$$

$$COP_{HP} = \frac{Q_{out}}{Q_{out} - Q_{in}} = \frac{1}{1 - \frac{Q_{in}}{Q_{out}}} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

$$1 > \frac{Q_L}{Q_H}$$

 $\text{COP}_{\text{HP}} > 1$  also

In fact,  $COP_{HP} = COP_R + 1$ 

You can show this as below

$$COP_{R} + 1 = \frac{1}{\frac{Q_{H}}{Q_{L}} - 1} + 1 = \frac{1 + \frac{Q_{H}}{Q_{L}} - 1}{\frac{Q_{H}}{Q_{L}} - 1} = \frac{\frac{Q_{H}}{Q_{L}}}{\frac{Q_{H}}{Q_{L}} - 1} = COP_{R} + 1 = \frac{1}{1 - \frac{Q_{L}}{Q_{H}}} = COP_{HP}$$

CLAUSIUS STATEMENT OF THE 2<sup>ND</sup> LAW PERTAINING TO REFRIGERATORS. IT IS IMPOSSIBLE TO CONSTRUCT A DEVICE THAT OPERATES IN A CYCLE AND PRODUCES NO EFFECT OTHER THAN TRANSFER OF HEAT FROM A LOW TEMPERATURE BODY TO A HIGHER TEMPERATURE BODY WITH NO WORK INPUT.

# EXAMPLE 1

The compressor of a refrigerator runs 6 hours per day in order to continuously remove heat (24 hours/day) from the cold box at a rate of 1,200 kJ/hr. The coefficient of performance ( $COP_R$ ) is 2.5.

Find the required power input.

Solution:

$$COP_{R} = \frac{\dot{Q}_{in}}{\dot{W}_{in}} = \frac{\dot{Q}_{in} * 24hr / d}{\dot{W}_{in} * 6hr / d}$$
$$\dot{W}_{in} = \frac{\dot{Q}_{in}}{COP_{R}} * \frac{24}{6} = \frac{1,200kJ / hr * 4}{2.5} = 1,920kJ / hr$$
$$\frac{1,920kJ / hr}{3600s / hr} = 0.533kw$$

# EXAMPLE 2

A house is to be cooled by an air conditioner with a  $\text{COP}_{\text{R}} = 2.5$ . The house contains 800 kg air at an initial temperature of 32 °C. The house air is to be cooled to 20 °C in 15 minutes.

a) Find the required power input to the compressor.

Solution:

Write the 1<sup>st</sup> Law on the house air:

 $Q = \Delta U = mC_v(T_2-T_1) = 800 \text{ kg}(0.72 \text{ kJ/kg-K})(20-32)\text{K} = -6,912 \text{ kw}$ 

 $Q_L = 6,912$  kw heat <u>input</u> to air conditioner. The rate of heat transfer required is:

$$\dot{Q}_{L} = \frac{6,915 \text{kJ}}{15 \text{ min}} * \frac{1 \text{ min}}{60 \text{s}} = 7.68 \text{kw}$$
  
 $\dot{W}_{IN} = \frac{\dot{Q}_{L}}{\text{COP}_{R}} = \frac{7.68 \text{kw}}{2.5} = 3.07 \text{kw}$ 

c) What is the rate at which heat is rejected to the outdoors?

 $W_{IN} = Q_H - Q_L$ 7.68 kw = Q<sub>H</sub> - 3.07 kw Q<sub>H</sub> = 10.8 kw