Module 7
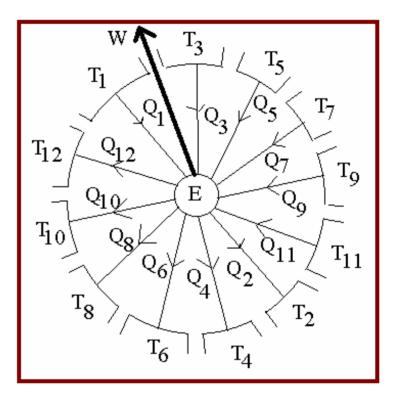
Entropy

Clausius Inequality

Suppose we have an engine that receives from several heat reservoirs and rejects heat to several reservoirs, we still have the equation valid.
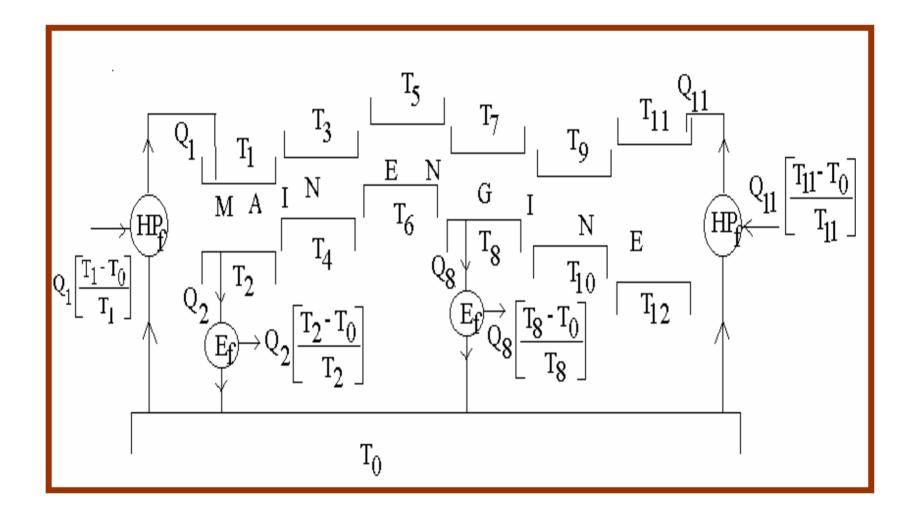
Clausius Inequality (contd…)

❖ With reference to previous fig,

➢ Assume that reservoir at T_1 gets its Q_1 with the help of a fictitious heat pump operating between a source T_0 and T_1. The same for 3,5,7….

➢ Similarly, assume that reservoir at T_2 rejects the heat Q_2 through a fictitious heat engine to the sink at T_0. The same for 4,6,8….

Clausius Inequality (contd...)

Clausius Inequality (contd…)

➢ Sum of work inputs for = $-Q_1 - Q_3 \ldots\ldots + Q_1 T_0 / T_1 + Q_3 T_0 / T_3 \ldots$

All fictitious heat pumps

➢ Sum of work outputs of = $Q_2 + Q_4 \ldots\ldots - Q_2 T_0 / T_2 - Q_4 T_0 / T_4 \ldots$

All fictitious heat engines

❖ *[Note that the sign convention for work is already taken into account]*

Clausius inequality (contd…)

❖ The net of work inputs + work outputs of all the fictitious units

$$= -Q_1 - Q_3 \ldots + Q_2 + Q_4 \ldots + T_o [Q_1/T_1 + Q_3/T_3 \ldots - Q_2/T_2 - Q_4/T_4 \ldots]$$

But we know that for the main engine at the centre

❖ $W = Q_1 + Q_3 \ldots - Q_2 - Q_4 \ldots$ [after taking the sign into account]

Clausius Inequality (Contd…)

➢ If we consider the entire system consisting of all the reservoirs 1-12 and the fictitious source at T_0, the work output of our main engine must be compensated by the works of fictitious engines (Otherwise the overall system will be delivering work by interaction with a single source at T_0).

Clausius Inequality (Contd…)

This is possible only when

- $T_o [Q_1 /T_1 + Q_3 /T_3 ... - Q_2 /T_2 - Q_4 /T_4 ..] = 0$

- which implies that $Q_1/T_1 + Q_3 /T_3 ... - Q_2/T_2 - Q_4/T_4 .. = 0$

- In general, $S(Q/T) = 0$ provided the engine is perfectly reversible.

  If it is not $S(Q/T) < 0$

  Therefore in general $S(Q/T) \leq 0$

  Since, summation can be replaced by an integral $(\delta Q /T) \leq 0$.

Clausius Inequality (contd…)

➢ The cyclic integral is to remind us that II Law holds only for a cycle.

➢ Note: Equality holds when the cycle is reversible. < sign will be the most probable one for real cycles.

➢ Just as we had dW= p dV

➢ Can we guess that there is something emerging to define Q?
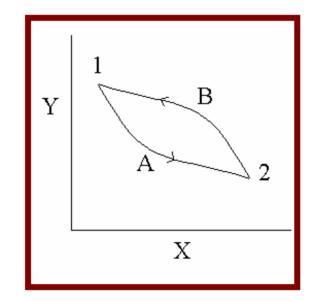
Clausius Inequality (contd…)

✓ Is there (something) which is = dQ/T? Or dQ = T. (something) ???

✓ In W, p, V relation on the right hand side p and V are properties.

✓ Is this (something) also a property?

✓ For an adiabatic process we said dQ = 0. Does that (something) remain invariant during an adiabatic process?

The Concept Of Entropy

❖ Consider a reversible cycle constructed as shown. Since we will be integrating $\int \delta Q /T$ over the entire process say 1-2 along A or B, processes A and B need not be isothermal.

The Concept of Entropy (contd…)

➢ $(\delta Q /T) = \int \delta Q /T \Big|_{\text{along } 1A2} + \int \delta Q /T \Big|_{\text{along } 2B1} = 0$

➢ If A and B are reversible and <0 if they are not.

➢ $\int \delta Q /T \Big|_{\text{along } 1A2} = -\int \delta Q /T \Big|_{\text{along } 2B1}$

➢ $\int \delta Q /T \Big|_{\text{along } 1A2} = \int \delta Q /T \Big|_{\text{along } 1B2}$

The Concept of Entropy (contd…)

❖ In other words the integral remains the same no matter what the path is. It can be simply written as S_2-S_1. The value depends only on the end states and not on the path followed. So it is a state function or a property.

❖ Like energy entropy (s) is also an extensive property. It will have the units of J/K. Similar to energy where we converted it into specific property, specific entropy (lower case s) will have units of J/kg K (same as specific heat)
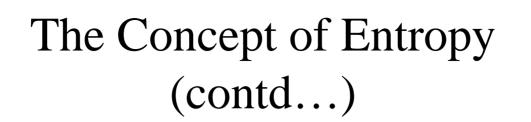
The Concept of Entropy (contd…)

$$\int_2^1 \delta Q / T = S_2 - S_1 \quad \text{or} \quad \int_2^1 \delta q / T = s_2 - s_1 \quad | \quad \delta q / T = \delta s \text{ or } \delta q = T \delta s$$
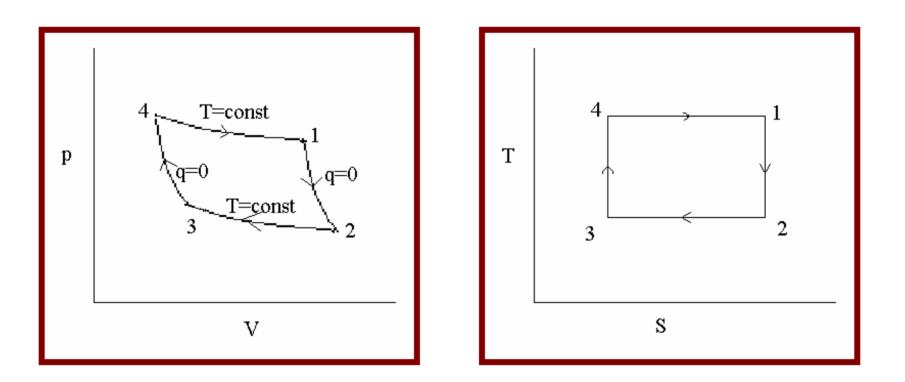
❖ Lesson learnt:

➢ Just as we can represent work interactions on P-V plane

➢ we can represent heat interactions on T-S plane.

➢ Naturally, T will be the ordinate and S will be the abscissa.

➢ All constant temperature lines will be horizontal and constant entropy lines vertical. So Carnot cycle will be just a rectangle.

The Concept of Entropy (contd…)

❖Integrals under P-V plane give work interaction
❖Integrals under T-S plane give heat interactions

Calculations

- Let us invoke the I law for a process namely $\delta q = \delta w + du$

- Substitute for $\delta q = Tds$ and $\delta w = p\, dv$ $Tds = pdv + du$

- For a constant volume process we have $Tds = du\ldots$ (1)

- We have by definition $h = u + pv$

- Differentiating $dh = du + pdv + vdp$

                                    $dh = Tds + vdp$

- For a constant pressure process $Tds = dh\ldots.$ (2)

Calculations (contd…)
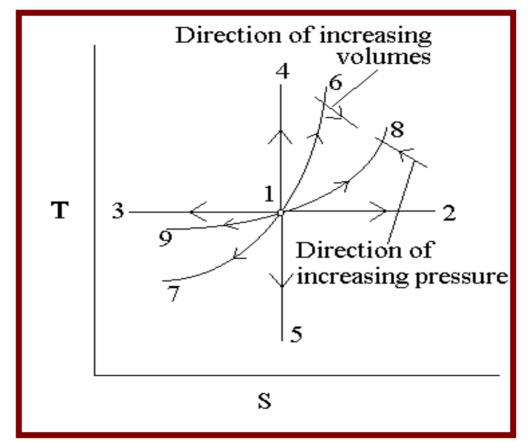
❖ **For a perfect gas** $du = c_v dT$ and $dh = c_p dT$

Substitute for du in (1) and dh in (2)

for v=const $Tds = c_v dT$ or $dT/ds\big|_{v=const} = T / c_v$

for p=const $Tds = c_p dT$ or $dT/ds\big|_{p=const} = T / c_p$

1. Since $c_p > c_v$ a constant pressure line on T-s plane will be flatter than a constant volume line.

2. The both (isobars and isochores) will have +ve slopes and curve upwards because the slope will be larger as the temperature increases

Calculations (contd…)

7-1-6   Const V line

9-1-8   Const. p line
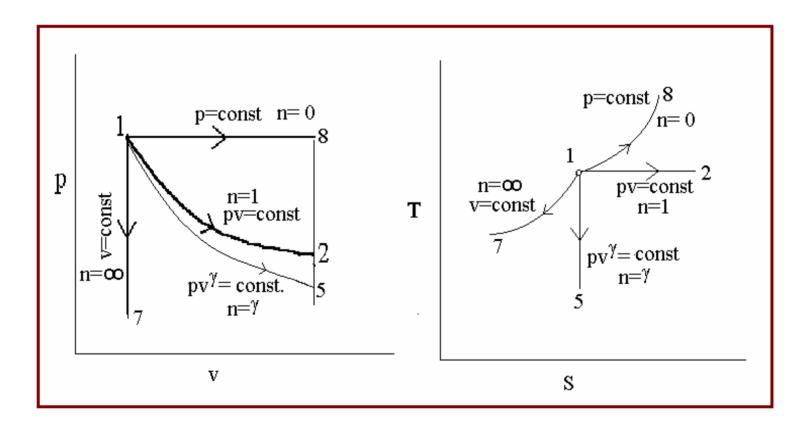
Calculations (contd…)

	s	T	p	v
1-2 Isothermal expansion	↑	—	↓	↑
1-3 Isothermal compression	↓	—	↑	↓
1.4 Isentropic compression	—	↑	↑	↓
1-5 Isentropic expansion	—	↓	↓	↑
1-6 Isochoric heating	↑	↑	↑	—
1-7 Isochoric cooling	↓	↓	↓	—
1-8 Isobaric heating/expansion	↑	↑	—	↑
1-9 Isobaric cooling/compression	↓	↓	—	↓

Comparison Between p-v and T-s Planes

Comparison Between p-v and T-s Planes (contd…)

➢ A similar comparison can be made for processes going in the other direction as well.

➢ Note that n refers to general index in pv^n=const.

   Note:

➢ For $1 < n < g$ the end point will lie between 2 and 5

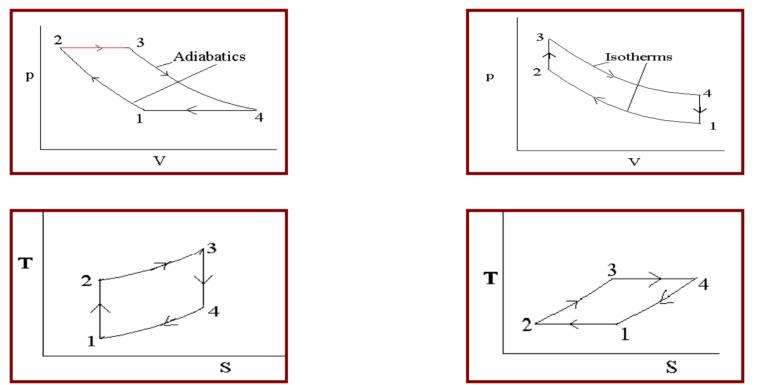➢ For $n > g$ the end point will lie between 5 and 7

Comparison Between
P-v and T-s Planes (contd…)
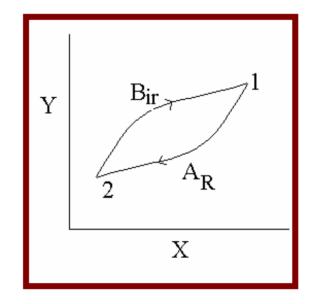
Brayton cycle

Stirling cycle

Note: All work producing cycles will have a clockwise direction
even on the T-s plane

Consider the Clausius inequality

$$\int \delta Q / T \leq 0$$

In the cycle shown let A be a reversible process (R) and B an irreversible one (ir), such that 1A2B1 is an irreversible cycle.

❖ Applying Clausius inequality

$$\delta Q /T \big|_{\text{along } 1A2} + \int \delta Q /T \big|_{\text{along } 2B1} < 0$$

(because the cycle is irreversible < sign applies)

Since A is reversible $\int \delta Q /T \big|_{\text{along } 1A2} = S_2 - S_1$

$$S_2 - S_1 + \int \delta Q /T \big|_{\text{along } 2B1} < 0$$

- Implying that $\int \delta Q /T \big|$ along 2B1 $< S_1 - S_2$

- Or $S_1 - S_2 > \int \delta Q /T \big|$ along 2B1

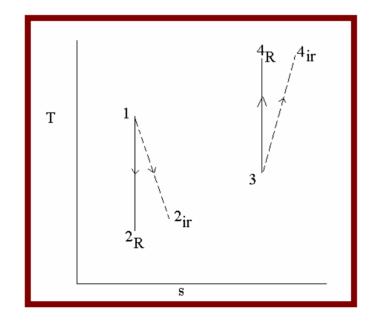- Had <u>B</u> also been <u>reversible</u> $\int \delta Q/T \big|$ along 2B1 would have been <u>equal</u> to <u>S_1-S_2</u>

Moral 1

$(S_1-S_2)_{irreversible} > (S_1-S_2)_{reversible}$

An irreversible process generates more entropy than a reversible process.

Moral 2:

If process B is adiabatic but irreversible $S_1-S_2 > 0$ or $S_1 > S_2$

❖ In general we can say ds $\geq \delta Q / T$ or $\delta Q \leq T\,ds$

   (equality holding good for reversible process)

1-2$_R$ Isentropic expansion (reversible)

1-2$_{ir}$ Non-isentropic expansion (irreversible)

3-4$_R$ Isentropic compression (reversible)

3-4$_{ir}$ Non-isentropic compression (irreversible)

An irreversible engine can't produce more work than a reversible one.

❖ *An irreversible heat pump will always need more work than a reversible heat pump.*

• An irreversible expansion will produce less work than a reversible expansion

❖ *An irreversible compression will need more work than a reversible compression*

Calculation of change in entropy during various reversible processes for perfect gases

Starting point of equation $\quad\quad\quad\quad\quad\quad\quad\quad \delta q - \delta w = du$

Rewritten as $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Tds = pdv + c_v dT$

1. Constant volume process $\quad dv=0 \quad\quad ds = c_v dT/T$

which on integration yields $\quad\quad\quad\quad\quad s_2 - s_1 = c_v \ln(T_2/T_1)$

2. For constant pressure process $\quad\quad\quad\quad ds = c_p dT/T$

which on integration yields $\quad\quad\quad\quad\quad s_2 - s_1 = c_p \ln(T_2/T_1)$

3. Constant temperature process $(dT=0) \quad Tds = pdv$

But $p = RT/v \quad\quad\quad\quad\quad\quad\quad\quad\quad ds = Rdv/v$

Which on integration yields $\quad s_2 - s_1 = R \ln(v_2/v_1) = R \ln(p_1/p_2)$

Starting point of equation $\qquad \delta q - \delta w = du$

Rewritten as $\qquad Tds = pdv + cvdT$

1. Constant volume process $\quad dv = 0 \qquad ds = c_v dT/T$

   which on integration yields $\qquad s_2 - s_1 = c_v \ln(T_2/T_1)$

2. For constant pressure process $\qquad ds = c_p dT/T$

   which on integration yields $\qquad s_2 - s_1 = c_p \ln(T_2/T_1)$

4. General equation $ds = p\,dv/T + c_v dT/T = R\,dv/v + c_v dT/T$

Which on integration yields $s_2 - s_1 = R\ln(v_2/v_1) + c_v\ln(T_2/T_1)$

Using $Tds = c_p dT - vdp$ (see slide 130) $s_2 - s_1 = c_p\ln(T_2/T_1) - R\ln(p_2/p_1)$

5. Throttling $dT = 0$ $p = RT/v$ from which $s_2 - s_1 = R\ln(p_1/p_2)$

Since $p_2 < p_1$, throttling is always irreversible
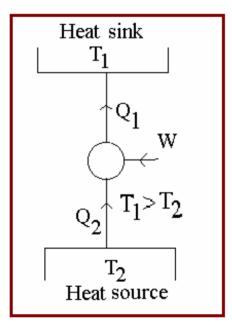
Refrigeration Processes

- As per II law we need to put in work to transfer heat from a colder system to a warmer one.

- We need to put in work to remove moisture from air (unmixing is an energy intensive process).

- Therefore, refrigeration and air conditioning are energy intensive processes

Refrigeration Processes (contd…)

To take Q_2 out of source at T_2 we need a medium. This is the refrigerant

The same medium (refrigerant) will reject Q_1 to sink at T_1.

In other words, there is a need for an "agent" to collect heat from one source to transfer it over to the other source.
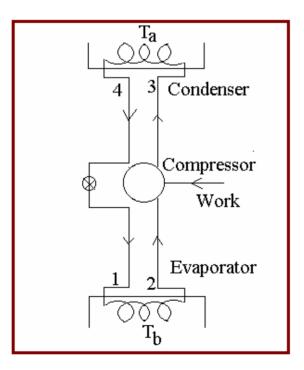
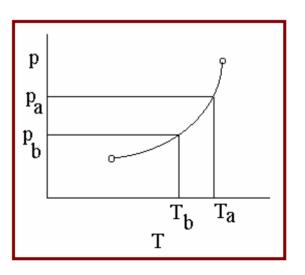One of the easiest ways of transferring heat at constant temperature is by evaporation and condensation.

Refrigeration Processes (contd…)

Technically we should have refrigerant evaporating at T2 and condensing at T1. The only way to do this is to raise the pressure.

Vapour pressure curve

Refrigeration Processes (contd…)

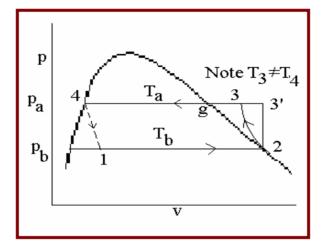Raising of the pressure occurs in the compressor which receives work.

What options are available?

i) Constant volume heating

ii) polytropic compression $pv^n = const$

Refrigeration Processes (contd…)

Option 1: $T_{3'} > T_a$

We like to get the state 3 as close as possible to the saturated vapour (g) state at p_a.

Ideally the process should follow the path 2-g.

We are left with no choice but to use polytropic compression. Ideally we like to have $n = \gamma$.

Refrigeration Processes (contd…)

➢ The process 4-1 is a pressure reduction process. Possibilities are polytropic or isentropic expansion. State 4 is saturated liquid.

➢ In practice, it is extremely difficult to compress or expand liquids.

➢ What happens in an actual refrigeration cycle is the liquid at 4 is throttled from pressure p4 to p1. But throttling is an irreversible process. Consequently, the cycle is irreversible.

➢ As a convention we depict irreversible processes by dashed lines.

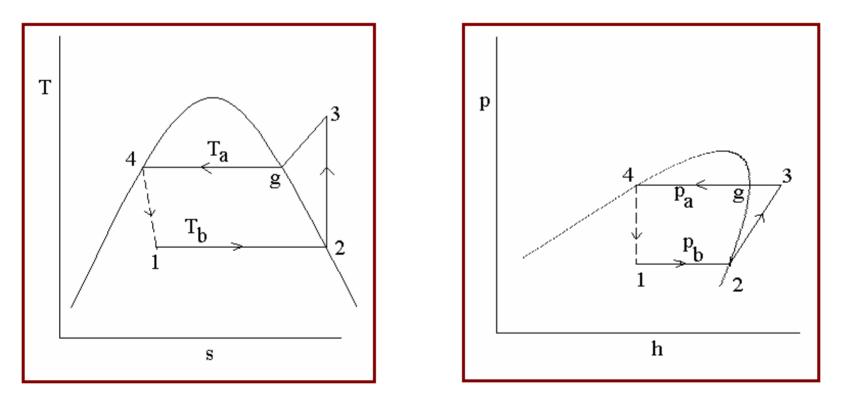➢ The above cycle is called vapour compression refrigeration cycle.

Refrigeration Processes (contd…)

➢ The working fluid that goes through those cycle changes is called a refrigerant.

➢ Ammonia (NH_3), CO_2, SO_2, methyl chloride were some of the early refrigerants.

➢ Chlorofluorocarbons (commonly called as freons) revolutionalised the refrigeration industry from about late 30's.

➢ There is a rethinking on them because of their ozone depletion potential.

➢ General trend is to use naturally occurring substances eg: NH_3, CO_2

Refrigeration Processes (contd…)

The vapour compression refrigeration cycle is seldom analyzed on the p-V plane. T-s is slightly better. p-h is the best.

Refrigeration Processes (contd…)

⬟ Selection criteria for refrigerants:

✓ p_b > atm. pr. or else if there is a leak atmospheric air will enter the system.

✓ Heat of vaporization at T_b (or p_b) should be large - so that we can circulate only the minimal amount of refrigerant

✓ p_a/p_b should be small so that the work of compression is the least.

Refrigeration Processes (contd…)

⬟ Components of a refrigeration system

➢ The compressor is the heart - Process 2-3 occurs in this. It is here that we meet the II law requirement of giving the work input. This is the "black box" at the rear bottom of your domestic refrigerator. This is the one which makes noise while running

➢ The evaporator - or the freezer is where process 1-2 occurs. This is where we get the cooling. This is the unit inside your refrigerator and on which a lot of frost forms. This serves the role of the low temperature heat source.

Refrigeration Processes (contd…)

- The condenser - where the process 3-4 occurs. It is the black painted serpentine tube with grill on it at the rear of the refrigerator. Usually it feels warm. This serves the purpose of high temperature sink. (In the modern refrigerator it is embedded beneath outer surface of the refrigerator - so don't be surprised if you don't physically see one!!)

- The expansion device - where process 4-1 occurs. It takes the form of a capillary tube (a small diameter tube) in domestic refrigerators. In large cold rooms it takes the from of a valve (on which you may see a lot of frost). The capillary is usually attached to the end of the condenser tube at the rear of the refrigerator. (In many units you may not see it as it passes through the body)
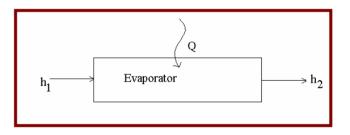
Application of SFEE to the evaporator yields

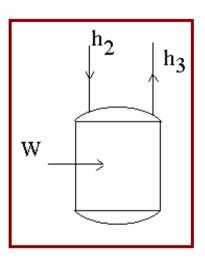Heat taken out of the source at T_b

$Q_b = m (h_2 - h_1)$

This is the area under the line 1-2 in the T-s diagram $m T_b(s_2 - s_1)$

Application of SFEE to the evaporator yields (contd…)

Application of SFEE to the compressor (assuming it to be insulated) yields $\quad -W = m(h_3 - h_2)$

$$COP_R = \left| Q/W \right| = (h_2 - h_1)/(h_3 - h_2)$$

Application of SFEE to the condenser yields

$$Q_a = m(h_4 - h_3)$$

(which will be negative because $h_4 < h_3$ or condenser rejects heat)

Application of SFEE to the evaporator yields (contd…)

The above aspects are easy to determine from the p-h plane. It is not difficult to see that $(h_2-h_1)+(h_3-h_2)=h_3-h_1$ (mathematically and on the p-h diagram)

Further, since $h_4=h_1$ (for the throttling process)

$h_3-h_1 =h_3-h_4$ (which is exactly the heat rejected in the condenser)

Moral: The condenser has to reject the heat taken in from the evaporator and the work put in at the compressor
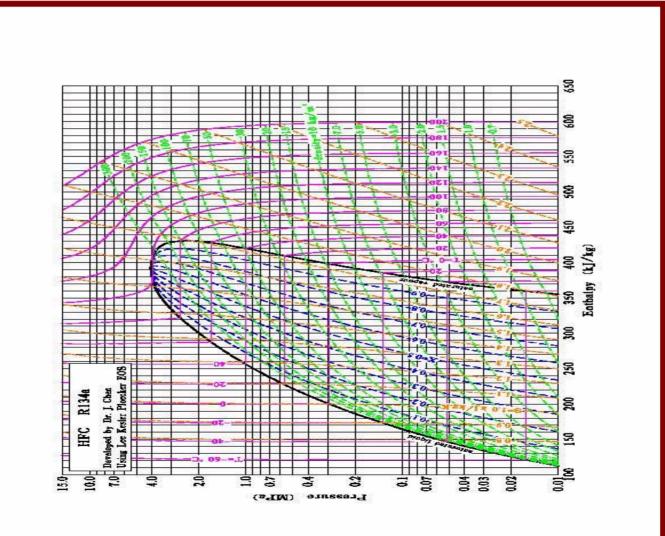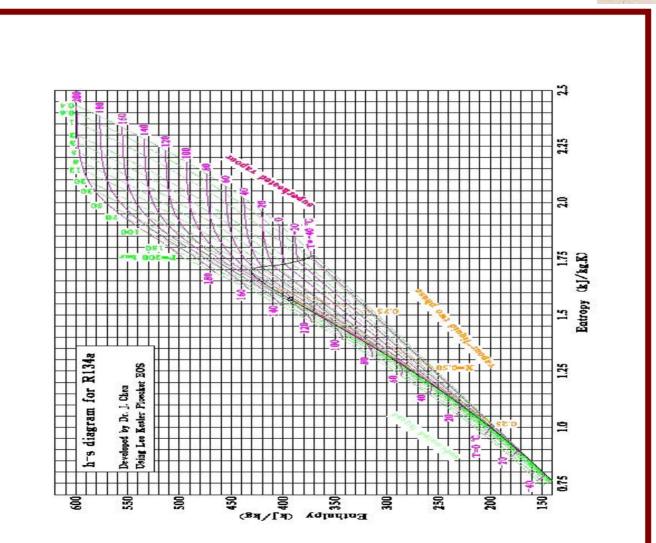
What the thermal engineer should be able to do

1. Identify any process or series of processes including components of cyclic processes
2. Select control masses or volumes as appropriate
3. Identify interactions between subsystems
4. Sketch a diagram showing control surfaces and interactions and a process diagram showing state changes
5. Obtain all necessary properties at each state given independent properties – u, v, h, s, T, P, composition
6. Calculate interactions directly where possible
7. Apply the 1st Law to any process or set of processes
8. Calculate the behavior of an isentropic process or a non-isentropic process given the isentropic efficiency (s_1 and s_2 related)
9. Put it all together and solve the system of algebraic equations
10. Estimate the system performance

HFC R134a

Developed by Dr. J. Chen
Using Lee Kesler Ploecker EOS

h-s diagram for R134a

Developed by Dr. J. Chen
Using Lee Kesler Plowcket EOS

Irreversibility

❑ The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

The second law states:

$(\Delta S)_{system} + (\Delta S)_{surr}$. where Δ = *final - initial*

> 0 *irreversible* (*real world*)

$= 0$ *reversible* (*frictionless, ideal*)

Irreversibility (contd…)

❑ In an ideal case if Q is the heat supplied from a source at T, its availability or the maximum work it can deliver is Q(1-T0/T) where T0 is the temperature of the surroundings. Invariably it will be less than this value. The difference is termed as irreversibility

Availability = Maximum possible work-Irreversibility

$$W_{useful} = W_{rev} - I$$

Irreversibility (contd…)

➢ Irreversibility can also be construed as the amount of work to be done to restore the system to the original state.

➢ Eg: If air at 10 bar is throttled to 1 bar, the irreversibility will be

➢ pv ln (10) which is the work required to get 10 bar back. Here p is 1 bar and v is the specific volume at this condition.

Irreversibility (contd…)

- Note that the system has been restored to the original state but not the surroundings Therefore increase in entropy will be
- R ln 10.
- Combining I & II laws
- TdS $\geq \Delta u + \delta W$
- equality sign being for the reversible process. It implies that the amount of heat energy to be supplied in a real process is larger than the thermodynamic limit.

Second Law of Thermodynamics

✓ Irreversible Processes increase the entropy of the universe
✓ Reversible Processes do not effect the entropy of the universe
✓ Impossible Processes decrease the entropy of the universe

   $\Delta S \ universe = 0$

Entropy Generation in the universe is a measure of lost work

ΔS Universe $= \Delta S$ System $+ \Delta S$ Surroundings

The losses will keep increasing

The sin keeps accumulating

Damage to environment keeps increasing

❑ When the entropy of the universe goes so high, then some one has to come and set it right. HE SAYS HE WILL COME. Every religion confirms this. Let us all wait.

   Cheer up, things are not that bad yet!!