# 4200:225 Equilibrium Thermodynamics 

Unit I. Earth, Air, Fire, and Water

Chapter 4. Thermodynamics of Processes

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## I. Energy and Entropy



## The Carnot Cycle


$\eta \equiv-W / Q_{H} \quad$ General Formula for the Thermal Efficiency
Entire process is reversible: $\Delta S_{1 \rightarrow 1=0} \Rightarrow \frac{Q_{H}}{T_{H}}+\frac{Q_{L}}{T_{L}}=O \Rightarrow Q_{L}=-\frac{T_{L}}{T_{H}} Q_{H}$
But $-\mathrm{W}=\mathrm{QH}+\mathrm{QL}=\mathrm{QH}\left(1-\mathrm{T}_{\mathrm{L}} / \mathrm{T}_{\mathrm{H}}\right)$
$\eta=\frac{-W}{Q_{H}}=\frac{T_{H}-T_{L}}{T_{H}} \Rightarrow$ Control efficiency by controlling temperature difference.

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## The Basic Rankine Cycle



Advantages:

1. Less wear on turbine and compressor.
2. Compression of liquid is cheap and easy (negligible in most cases).

Disadvantages:

1. Lower thermodynamic efficiency than Carnot or Stirling. This can be somewhat compensated by multiple stages and regeneration.

## Example 4.1 Power plant based on the ordinary Rankine cycle

The steam power installation in a chemical plant must satisfy the following requirements:

1) $500^{\circ} \mathrm{C}$ maximum temperature from the boiler.
2) 0.025 MPa saturated vapor from the turbine.
3) 1 MW net power output.

Determine:
a) The operating pressure of the boiler
b) The thermal efficiency
c) The circulation rate

a) Interpolating on the pressure at $500^{\circ} \mathrm{C}$ and $S=7.8314, P=0.869 \mathrm{Mpa}$
b) The enthalpy at state 3 is interpolated at $500^{\circ} \mathrm{C}$ and $0.869 \mathrm{MPa}, H=3480$
$W_{\mathrm{T}}=2618-3480=-862 \mathrm{~J} / \mathrm{g} ; W_{\mathrm{p}}=\int V \mathrm{~d} P=V \Delta P=0.79 \mathrm{~J} / \mathrm{g}$
$W_{\text {net }}=W_{\mathrm{T}}+W_{\mathrm{p}}=-861 \mathrm{~J} / \mathrm{g} ; Q_{\mathrm{L}}=2618-273=2345 ; \eta=861 /(2345+861)=27 \%$

## Example 4.3. Power plant based on a Rankine cycle with reheat

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Consider the same outlet conditions as above, but interject an extra stage for the pressure drop. That is, consider the case depicted above with stream 3 being at $434^{\circ} \mathrm{C}$ and 6 MPa and stream 5 at $500^{\circ} \mathrm{C}$ and 0.8 MPa . Compute the thermal efficiency in this case.
$434^{\circ} \mathrm{C}, 6 \mathrm{MPa} \Rightarrow H_{3}=3262 \mathrm{~J} / \mathrm{g} ; S_{3}=6.6622 \mathrm{~J} / \mathrm{g}-\mathrm{K}$; State $4^{\prime}$ ' is SatV, $0.8 \mathrm{MPa} \Rightarrow H_{4}=2769$ State 5 is same as previous problem $\Rightarrow H_{5}=3480 \mathrm{~J} / \mathrm{g}, H_{6}=2618 \mathrm{~J} / \mathrm{g}, H_{7}=272$.
The pump work has increased because the pressure has increased $\Rightarrow W_{\mathrm{p}}=6 \mathrm{~J} / \mathrm{g}, H_{8}=278$
$W_{\text {net }}=\left(H_{4}-H_{3}\right)+\left(H_{6}-H_{5}\right)+W_{\mathrm{p}}=(2769-3262)+(2618-3480)+6=-1349$
$Q_{\text {tot }}=\left(H_{3}-H_{8}\right)+\left(H_{5}-H_{4}\right)=(3262-278)+(3480-2769)=3695 \mathrm{~J} / \mathrm{g}$
$\eta=36.7 \%$
This compares to $27 \%$ for the cycle without reheat.
Note: The Carnot cycle gives the upper limit of $\eta_{\text {carnot }}=(500-65) / 773=56 \%$

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## Refrigeration

$\mathrm{COP}=Q_{L} / W_{\text {net }} \Rightarrow \quad$ For Carnot: $\mathrm{COP}=\left(Q_{H} / W_{\text {net }}\right) *\left(Q_{L} / Q_{H}\right)=T_{L} /\left(T_{H}-T_{L}\right)$ But the Carnot cycle is not always practical.

Therefore, we apply the


ORDINARY VAPOR COMPRESSION (OVC) CYCLE


COP for ordinary vapor compression cycle
$\mathrm{COP}=Q_{L} / W ; Q_{L}=\left(H_{2}-H_{1}\right)$
Energy balance: $W=\Delta H_{2} \rightarrow 3=\left(H_{3}-H_{2}\right)$
$\Rightarrow \mathrm{COP}=\left(\mathrm{H}_{2}-\mathrm{H}_{1}\right) /\left(\mathrm{H}_{3}-\mathrm{H}_{2}\right)=\left(\mathrm{H}_{2}-\mathrm{H}_{4}\right) /\left(\mathrm{H}_{3}-\mathrm{H}_{2}\right)$

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## Example 4.5 Refrigeration by vapor-compression cycle

A cold storage room is to be maintained at $-15^{\circ} \mathrm{C}$ and the available cooling water exits the evaporator at 298 K . The refrigerant temperature exiting the condenser is to be $30^{\circ} \mathrm{C}$. The refrigeration capacity is to be $120,000 \mathrm{Btu} / \mathrm{hr}(126,500 \mathrm{~kJ} / \mathrm{hr})$. (This is the cooling rate required to freeze ten tons of $32^{\circ} \mathrm{F}$ water to $32^{\circ} \mathrm{F}$ ice in a 24 hr period. It is known in the trade as ten "tons" of refrigeration.) Freon-134a will be used for the vapor compression cycles. Calculate the COP and recirculation rate (except part a for the following cases:
a) Carnot cycle
b) Ordinary vapor compression cycle.
c) Vapor compression cycle with expansion engine $1 \quad 241.5$--- $\quad$ Throttle from 4
d) Ordinary vapor compression cycle 1, 235.0 1.1428 Tur from 4, $q=.29$
for which compressor is $80 \%$ efficient. $2 \quad 386.5$ 1.7414 $\quad$ Sat V, 253 K
(a) Carnot $\quad 3 \prime \quad 424 \quad 1.7414 \quad S_{3}=S_{2}$, read chart
$\begin{array}{llllll}T_{L} \\ \left(T_{H} T_{L}\right.\end{array}=\frac{253}{(303}=5.06 \quad 4 \quad 241.5 \quad 1.1428 \quad$ Sat L, 303K
(b) OVC cycle $\Rightarrow C O P=\frac{\left(H_{2}-H_{1}\right)}{\left(H_{3}-H_{2}\right)}=\frac{\left(H_{2}-H_{4}\right)}{\left(H_{3}-H_{2}\right)}=\frac{386.5-241.5}{424-386.5}=3.87$
$\dot{m}=\frac{126,500}{386.5-241.5}=872 \frac{\mathrm{~kg}}{\mathrm{hr}}$
(c) VC cycle with turbine expansion
$q S_{I}{ }^{V}+(1-q) S_{l}{ }^{L}=S_{4}{ }^{L}=1.1428=q(1.7414)+(1-q) 0.8994 \Rightarrow q=0.289 \Rightarrow H_{1}{ }^{\prime}=235$
$\Rightarrow C O P=\frac{\left(H_{2}-H_{1}^{\text {rev }}\right)}{\left(H_{3}-H_{2}\right)+\left(H_{1}^{\prime}-H_{4}\right)}=\frac{386.5-235.0}{(424-386.5)+(235.0-241.5)}=4.89$
$\dot{m}=\frac{126,500}{386.5-235.0}=835 \frac{\mathrm{~kg}}{\mathrm{hr}}$
(d) States (1), (2) \& (4) are the same as in (b)

The only difference is that $W=(424-386.5) / 0.8=46.9$
$\Rightarrow C O P=\frac{H_{2}-H_{4}}{H_{3}-H_{2}}=\frac{386.5-241.5}{46.9}=3.09$ and $m=872 \mathrm{~kg} / \mathrm{hr}$
Note: Choice of refrigerant dictated by
(1) Toxicity (Freon-12, 22 are bad for (4) high heat of vaporization per unit mass ozone and is being phased out) (5) small $C p / C v$
(2) vapor pressure > atmospheric @ $T_{\text {fridge }}$
(3) vapor pressure not too high @ $T_{H}$
(6) high heat transfer coefficients in vapor and liquid

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## Example 4.6. Liquefaction of methane by the Linde process.

Natural gas, assumed here to be pure methane, is liquefied in a simple Linde process. Compression is to 60 bar and precooling is to 300 K . The separator is maintained at a pressure of 1 bar and unliquefied gas at this pressure leaves the cooler at 295 K .

Solution

a) Bottom half E-Bal: $\mathrm{H}_{3}-\left[q H_{8}+(1-q) H_{6}\right]=0$

$$
\begin{aligned}
\Rightarrow q & =\frac{H_{3}-H_{6}}{H_{8}-H_{6}}=\frac{H(60,300)-H(1, S A T L)}{H(1,295)-H(1, S A T L)} \\
& =\frac{1130-284}{1195-284}=0.9286 \Rightarrow 7.14 \% \text { liquefied }
\end{aligned}
$$

b) E-Bal around HXER: $\mathrm{H}_{4}-\mathrm{H}_{3}=q\left(\mathrm{H}_{8}-\mathrm{H}_{7}\right)$
$=.9286(1195-796.1)=-370.5$
$\Rightarrow H_{4}=780 @ 60 \mathrm{BAR} \Rightarrow$ chart gives 203 K

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Example 4.8 Thermal Efficiency of the Otto Engine

Determine the thermal efficiency of the air-standard Otto cycle as a function of the specific heat ratio $\gamma(=C p / C v)$ and the compression ratio $r=V 1 / V 2$.
Solution:


$$
Q H=C v(T 3-T 2)
$$

$$
Q L=C v(T 1-T 4)
$$

$$
W=Q H+Q L=C v(T 3-T 2+T 1-T 4)
$$

$$
\eta=C v(T 3-T 2+T 1-T 4) /[C v(T 3-T 2)]+1-(T 3-T 2) /(T 3-T 2)=
$$

$$
1+(T 1-T 4) /(T 3-T 2)
$$

$\Rightarrow \mathrm{T} 4=\mathrm{T} 3 r^{-R / C v} ; \mathrm{T} 1=\mathrm{T} 2 r-R / C v$

$$
\frac{T_{2}}{T_{1}}=\left(\frac{V_{1}}{V_{2}}\right)^{R / C_{v}} ; \frac{T_{4}}{T_{3}}=\left(\frac{V_{3}}{V_{4}}\right)^{R / C_{v}}=\left(\frac{V_{2}}{V_{1}}\right)^{R / C_{v}}
$$

$\eta=1-r-R / C v \quad=1-r(1-\gamma)$

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In a large refrigeration plant it is necessary to compress a fluid which we will assume to be an ideal gas with constant heat capacity, from a low pressure P1 to a much higher pressure P2. If the compression is to be done in two stages, first compressing the gas from P1 to $\mathrm{P}^{*}$, then cooling the gas at constant pressure down to the compressor inlet temperature T 1 , and then compressing the gas to P 2 , what should the value of the intermediate pressure be to accomplish the compression with minimum work?
Solution:
E-Bal: $\Delta H=Q+W=W=C p \Delta T$
S-Bal: $\Delta S=0 \Rightarrow T^{*} / T_{1}=\left(P^{*} / P_{1}\right) \mathrm{R} / \mathrm{Cp} ; T_{2} / T_{1}=\left(\mathrm{P}_{2} / \mathrm{P}^{*}\right) \mathrm{R} / \mathrm{Cp}$
$W_{\text {tot }}=C p\left(T_{2}-T_{1}\right)+C p\left(T^{*}-T_{1}\right)=C p T_{1}\left\{\left[\left(P_{2} / P^{*}\right)^{R / C_{P}}-1\right]+\left[\left(P^{*} / P_{1}\right)^{R / C_{p}}-1\right]\right.$
To maximize function, set derivative to zero.

$$
\begin{aligned}
& \frac{d W}{d P^{*}}=C p T_{1}\left\{\frac{-R / C p}{P^{*}}\left(\frac{P_{2}}{P^{*}}\right)^{R / C_{p}}+\frac{R / C p}{P^{*}}\left(\frac{P^{*}}{P_{1}}\right)^{R / C_{p}}\right\}=0 \\
& \left(\frac{P_{2}}{P^{*}}\right)^{R / C_{p}}=\left(\frac{P^{*}}{P_{1}}\right)^{R / C_{p}} \Rightarrow P^{*}=\sqrt{P_{2} P_{1}}
\end{aligned}
$$

Note: Equal compression ratios per stage is optimal for multistage compressors also.

