## Review of the Fundamentals



## Reading

## Problems

Review Chapter 3 and property tables
More specifically, look at:
$3.2 \rightarrow 3.4,3.6,3.7,8.4,8.5,8.6,8.8$

## Thermal Sciences

The thermal sciences involve the storage, transfer and conversion of energy.


Thermodynamics: the study of energy, energy transformations and its relation to matter. The analysis of thermal systems is achieved through the application of the governing conservation equations, namely Conservation of Mass, Conservation of Energy (1st law of thermodynamics), the 2 nd law of thermodynamics and the property relations.

Heat Transfer: the study of energy in transit including the relationship between energy, matter, space and time. The three principal modes of heat transfer examined are conduction, convection and radiation, where all three modes are affected by the thermophysical properties, geometrical constraints and the temperatures associated with the heat sources and sinks used to drive heat transfer.

Fluid Mechanics: the study of fluids at rest or in motion. While this course will not deal extensively with fluid mechanics we will be influenced by the governing equations for fluid flow, namely Conservation of Momentum and Conservation of Mass.

## Examples of Energy Conversion


solar energy
(photo-thermal conversion)

## windmills <br> (kinetic energy)



## Other Examples

- power plants
- refrigeration systems
- automotive engines
- jet engines
- heating, ventilation and air conditioning
- human body

Modelling \& Analysis of Thermodynamic Systems


# Modelling and Analysis of Thermodynamic Systems 

Step 1: System Identification
Step 2: Assumptions
Step 3: System Model
Step 4: Governing Equations
Step 5: Properties
Step 6: Solution Procedure
Step 7: Process Identification

We need a good understanding of Thermodynamics fundamentals (as presented in ME250: Thermodynamics 1) in order to proceed with our system modeling and analysis.

## Thermodynamic Fundamentals

We will need to characterize the thermophysical properties of the three distinct homogeneous phases of materials as they move through a range of temperature, pressure and volume.

- ME250: Thermodynamics 1 looked at equations of state, thermophysical properties and property relationships
- we will review the various sources for determining material properties


## Gases

Thermodynamic relations are generally given in three different forms:

Tables: $\quad$ water (Tables B.1.1 $\rightarrow$ B.1.5), Ammonia (Table B.2.1), R134a (Tables B.5.1 $\rightarrow$ B.5.2)
Graphs: water (Figures E. 1 \& E. 4 [psychrometric chart])
Equations: (Appendix D)

## Ideal Gases

- gases that adhere to a pressure, temperature, volume relationship

$$
P v=R T \quad \text { or } \quad P V=m R T
$$

are referred to as ideal gases

For an ideal gas with constant $\boldsymbol{c}_{\boldsymbol{p}}$ and $\boldsymbol{c}_{\boldsymbol{v}}$

$$
\begin{aligned}
P v & =R T \\
u_{2}-u_{1} & =c_{v}\left(T_{2}-T_{1}\right) \\
h_{2}-h_{1} & =c_{p}\left(T_{2}-T_{1}\right)
\end{aligned}
$$

There are 3 forms of a change in entropy as a function of $\boldsymbol{T} \& \boldsymbol{v}, \boldsymbol{T} \& \boldsymbol{P}$, and $\boldsymbol{P} \& \boldsymbol{v}$.

$$
\begin{aligned}
& s_{2}-s_{1}=c_{v} \ln \frac{T_{2}}{T_{1}}+R \ln \frac{v_{2}}{v_{1}} \\
&=c_{p} \ln \frac{T_{2}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}} \\
&=c_{p} \ln \frac{v_{2}}{v_{1}}+c_{v} \ln \frac{P_{2}}{P_{1}} \\
& R=c_{p}-c_{v}
\end{aligned}
$$

## What can be done when the ideal gas assumption in not viable?

## Compressibility Factor

- provides a quantitative procedure for determining the suitability of the ideal gas assumption
- the compressibility factor is given as

$$
Z=\frac{P v}{R T}
$$

where $Z=1$ for an ideal gas and any deviation from 1 is a measure of the suitability of the ideal gas assumption

- if we "reduce" the properties with respect to the values at the critical point, i.e.

$$
\begin{aligned}
\text { reduced pressure } & =\boldsymbol{P}_{r}=\frac{\boldsymbol{P}}{\boldsymbol{P}_{\boldsymbol{c}}}
\end{aligned} \quad \boldsymbol{P}_{c}=\text { critical pressure }
$$

- Table A. 2 lists the critical pressure and critical temperature for various gases


## Is Water Vapor an Ideal Gas?

- Figure E. 1 can be used to determine the regions where water vapor behaves as an ideal gas


## Isentropic and Polytropic Processes for Ideal Gases

Given:

- constant specific heats over a wide range of temperature
- $d s=0$
- $d u=c_{v} d T \equiv c_{v}=\left(\frac{\partial u}{\partial T}\right)_{V}$
- $d h=c_{p} d T \equiv c_{p}=\left(\frac{\partial h}{\partial T}\right)_{P}$

The product of $\boldsymbol{P} \cdot \boldsymbol{v}^{k}$ remains constant for an ideal gas when:

- specific heats are constant
- the gas undergoes an isentropic process $\rightarrow$ reversible + adiabatic

Combining this result with the ideal gas equation of state

$$
\frac{T_{2}}{T_{1}}=\left(\frac{v_{1}}{v_{2}}\right)^{k-1}=\left(\frac{P_{2}}{P_{1}}\right)^{(k-1) / k}
$$

The isentropic process is a special case of a more general process known as a polytropic process where $\rightarrow \boldsymbol{P} \boldsymbol{v}^{\boldsymbol{n}}=\boldsymbol{c o n s t a n t}$ and $\boldsymbol{n}$ is any number.

## Special Cases

$$
\begin{array}{ll}
n=1 & P v=R T=\text { constant } \Rightarrow \text { isothermal process } \\
n=0 & P v^{0}=\text { constant }=P \Rightarrow \text { isobaric process (constant pressure) } \\
n=k & P v^{k}=\text { constant } \Rightarrow \text { isentropic process }\left(k=c_{p} / c_{v}\right) \\
n=\infty & P v^{\infty}=\text { constant } \Rightarrow \text { isochoric process (constant volume) }
\end{array}
$$

## Relative Pressure and Relative Specific Volume

## - Procedure:

- given $\boldsymbol{T}_{\mathbf{1}}, \boldsymbol{P}_{\mathbf{1}}$ and $\boldsymbol{P}_{\mathbf{2}}$ for an isentropic process
- determine $\boldsymbol{P}_{\boldsymbol{r} 1}$ at $\boldsymbol{T}_{\mathbf{1}}$ from Table A.7.2
- calculate $\boldsymbol{P}_{\boldsymbol{r} 2}$, where

$$
\left(\frac{\boldsymbol{P}_{2}}{\boldsymbol{P}_{1}}\right)_{s=c o n s t}=\frac{\boldsymbol{P}_{\boldsymbol{r} 2}}{\boldsymbol{P}_{\boldsymbol{r} 1}}
$$

$-\operatorname{read} \boldsymbol{T}_{\mathbf{2}}$ from Table A-7.2 for the calculated value of $\boldsymbol{P}_{\boldsymbol{r} \mathbf{2}}$

- use a similar procedure if volume is known instead of pressure, where

$$
\left(\frac{\boldsymbol{v}_{2}}{\boldsymbol{v}_{1}}\right)_{s=c o n s t}=\frac{\boldsymbol{v}_{r 2}}{\boldsymbol{v}_{r 1}}
$$

## Liquids

## $\underline{T-v}$ Diagram for a Simple Compressible Substance

- consider an experiment in which a substance starts as a solid and is heated up at constant pressure until it all becomes as gas

- depending on the prevailing pressure, the matter will pass through various phase transformations. At $\boldsymbol{P}_{0}$ :

1. solid
2. mixed phase of liquid and solid
3. sub-cooled or compressed liquid
4. wet vapor (saturated liquid-vapor mixture)
5. superheated vapor

## Properties of Saturated Mixtures

- all the calculations done in the vapor dome can be performed using Tables.
- in Table B.1.1, the properties are listed under Temperature
- in Table B.1.2, the properties are listed under Pressure


## Properties of Superheated Vapor

- superheated means $\boldsymbol{T}>\boldsymbol{T}_{\text {sat }}$ at the prevailing $\boldsymbol{P}$, eg. water at $100 \boldsymbol{k P a}$ has a saturation temperature of $T_{s a t}(P)=99.63{ }^{\circ} C$.
- Table B.1.3 for superheated water


## Properties of Sub-cooled (Compressed) Liquid

- sub-cooled liquid means $\boldsymbol{T}<\boldsymbol{T}_{\text {sat }}$ at the prevailing $\boldsymbol{P}$, eg. water at $20^{\circ} \boldsymbol{C}$ and $100 \boldsymbol{k P a}$ has a saturation temperature of $T_{s a t}(P)=99.63{ }^{\circ} C$.
- Table B.1.4 for compressed liquid water (if not available, you can use the approximations listed above)


## Reference Values for $u, h, s$

- values of enthalpy, $\boldsymbol{h}$ and entropy, $\boldsymbol{s}$ listed in the tables are with respect to a datum where we arbitrarily assign the zero value. For instance:

Tables B.1.1, B.1.2: saturated liquid - the reference for both $\boldsymbol{h}_{f}$ and $s_{f}$ is taken as $0^{\circ} \boldsymbol{C}$. This is shown as follows:

$$
\begin{aligned}
u_{f}(@ T & \left.=0^{\circ} C\right)
\end{aligned}=0 \mathrm{~kJ} / \mathrm{kg} \mathrm{C}=0 \mathrm{~kJ} / \mathrm{kg} .
$$

Tables B.5.1, B.5.2: saturated R134a - the reference for both $\boldsymbol{h}_{\boldsymbol{f}}$ and $s_{f}$ is taken as $-40^{\circ} \boldsymbol{C}$.
This is shown as follows:

$$
\begin{aligned}
& h_{f}\left(@ T=-40^{\circ} C\right)=0 \mathrm{~kJ} / \mathrm{kg} \\
& h_{f}\left(@ T=-40^{\circ} C\right)=0 \mathrm{~kJ} / \mathrm{kg} \\
& s_{f}\left(@ T=-40^{\circ} \mathrm{C}\right)=0 \mathrm{~kJ} / \mathrm{kg} \cdot \mathrm{~K}
\end{aligned}
$$

## Guidelines to Solve Thermodynamic Problems

1. Read the problem carefully and understand the requirements.
(a) hi-lite or underline specific conditions and/or information requested
2. Sketch the necessary diagrams.
(a) System diagram: indicate the system components/stages
(b) Process diagram: indicate the states
3. State assumptions and idealizations.
4. Apply the laws of thermodynamics (1st and 2nd laws, conservation of mass).
5. Simplify the general equations based on assumptions and idealizations.
6. Obtain the necessary thermodynamic properties from figures and tables or using the equations of state.
(a) clearly indicate where you obtained the information
7. Solve the problem.
8. Clearly label your final answer.
9. Give comments if you have any.

## PROBLEM STATEMENT:

Two rigid, $0.03 \mathrm{~m}^{\mathbf{3}}$ tanks are connected by a valve. Initially tank $\boldsymbol{A}$ contains argon gas at $400 \mathrm{~K}, 2 \mathrm{~atm}$ and tank $\boldsymbol{B}$ is a vacuum. The valve is opened and argon flows from tank $\boldsymbol{A}$ to tank $\boldsymbol{B}$ until the tanks each reach the same pressure. Each tank is adiabatic.
a) Determine the final pressure. [atm]
b) Assuming that the gas that remains in tank $\boldsymbol{A}$ underwent a reversible, adiabatic process, determine the temperature $[\boldsymbol{K}]$ and mass $[\mathbf{k g}]$ at state A2
c) Determine the mass $[\boldsymbol{k g}]$ and temperature $[\overline{\boldsymbol{K}]}$ at state B 2 .
d) Determine the entropy produced $[\mathbf{k J} / \mathbf{k g} \cdot \boldsymbol{K}]$ in the process


## Conservation Equations

|  |  |  |
| :--- | :--- | :--- |

## Definitions

SYSTEM:

- any specified collection of matter under study.


## WORK \& HEAT TRANSFER:

- thermodynamics deals with these properties of matter as a system interacts with its surroundings through work and heat transfer



## CONSERVATION OF MASS



$$
\begin{aligned}
& \left\{\begin{array}{c}
\text { rate of increase } \\
\text { of mass within } \\
\text { the } C V
\end{array}\right\}=\left\{\begin{array}{c}
\text { net rate of } \\
\text { mass flow } \\
I N
\end{array}\right\}-\left\{\begin{array}{c}
\text { net rate of } \\
\text { mass flow } \\
\text { OUT }
\end{array}\right\} \\
& \frac{d}{d t}\left(m_{C V}\right)=\dot{m}_{I N}-\dot{m}_{O U T}
\end{aligned}
$$

where:

$$
\begin{aligned}
m_{C V} & =\int_{V} \rho d V \\
\dot{m}_{I N} & =\left(\rho v^{*} A\right)_{I N} \\
\dot{m}_{O U T} & =\left(\rho v^{*} A\right)_{O U T}
\end{aligned}
$$

with $\boldsymbol{v}^{*}=$ average velocity

## First Law of Thermodynamics

What is the difference between a closed and an open system?

- is there mass crossing the system boundary? YES: open system NO: closed system


## Control Mass (Closed System)

conservation of mass is inherently satisfied

## CONSERVATION OF ENERGY:

- the energy content of an isolated system is constant
energy entering - energy leaving = change of energy within the system

Example: A Gas Compressor


Performing a 1st law energy balance:

$$
\left\{\begin{array}{c}
\text { Initial } \\
\text { Energy } \\
E_{1}
\end{array}\right\}+\left\{\begin{array}{c}
\text { Energy gain } W_{1-2} \\
\text { Energy loss } Q_{1-2}
\end{array}\right\}=\left\{\begin{array}{c}
\text { Final } \\
\text { Energy } \\
E_{2}
\end{array}\right\}
$$

## Control Volume Analysis (Open System)

CONSERVATION OF ENERGY:


The 1st law states:

$$
\begin{align*}
E_{C V}(t)+\Delta Q+\Delta W_{\text {shaft }}+ & \left(\Delta E_{I N}-\Delta E_{\text {OUT }}\right)+ \\
& \left(\Delta W_{I N}-\Delta W_{O U T}\right)=E_{C V}(t+\Delta t) \tag{1}
\end{align*}
$$

where:

$$
\Delta E_{I N}=e_{I N} \Delta m_{I N}
$$

$\Delta E_{\text {OUT }}=e_{\text {OUT }} \Delta m_{\text {OUT }}$
$\Delta \boldsymbol{W}=$ flow work

$$
e=\frac{E}{m}=\underbrace{u}_{\text {internal }}+\underbrace{\frac{\left(v^{*}\right)^{2}}{2}}_{\text {kinetic }}+\underbrace{g z}_{\text {potential }}
$$

## What is flow work?



$$
\begin{aligned}
& \Delta m_{I N}=\rho_{I N} \overbrace{A_{I N} v_{I N}^{*} \Delta t}^{\text {volume }} \\
& \Delta W_{I N}=F \cdot \text { distance }=\underbrace{P_{I N} A_{I N}}_{F} \cdot \underbrace{v_{I N}^{*} \Delta t}_{\Delta s}=\frac{P_{I N} \Delta m_{I N}}{\rho_{I N}}
\end{aligned}
$$

with $v=1 / \rho$

$$
\begin{equation*}
\Delta W_{I N}=(P v \Delta m)_{I N} \quad \rightarrow \text { flow work } \tag{2}
\end{equation*}
$$

Similarly

$$
\begin{equation*}
\Delta W_{O U T}=(P v \Delta m)_{O U T} \tag{3}
\end{equation*}
$$

Substituting Eqs. 2 and 3 into Eq. 1 gives the 1st law for a control volume

$$
\begin{align*}
E_{C V}(t+\Delta t)-E_{C V}(t)= & \Delta Q+\Delta W_{s h a f t}+\Delta m_{I N}(e+P v)_{I N} \\
& -\Delta m_{O U T}(e+P v)_{O U T} \tag{4}
\end{align*}
$$

Equation 4 can also be written as a rate equation $\rightarrow$ divide through by $\Delta t$ and take the limit as $\Delta t \rightarrow \mathbf{0}$

$$
\frac{d}{d t} E_{C V}=\dot{Q}+\dot{W}_{s h a f t}+[\dot{m}(e+P v)]_{I N}-[\dot{m}(e+P v)]_{O U T}
$$

where:

$$
\dot{m}=\rho v^{*} A
$$

## Second Law of Thermodynamics

## Fundamentals

1. Like mass and energy, every system has entropy.

Entropy is a measure of the degree of microscopic disorder and represents our uncertainty about the microscopic state.
2. Unlike mass and energy, entropy can be produced but it can never be destroyed. That is, the entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

$$
\begin{aligned}
& \mathcal{P}_{m}=m_{2}-m_{1}=0(\text { conservation of mass }) \\
& \mathcal{P}_{E}=E_{2}-E_{1}=0(\text { conservation of energy }) \rightarrow 1 \text { st law } \\
& \mathcal{P}_{S}=S_{g e n}=S_{2}-S_{1} \geq 0 \rightarrow 2 \text { nd law }
\end{aligned}
$$

The second law states:
$(\Delta S)_{\text {system }}+(\Delta S)_{\text {surr } .} \geq 0$
where $\Delta \equiv$ final - initial
3. Reference: In a prefect crystal of a pure substance at $\boldsymbol{T}=\mathbf{0} \boldsymbol{K}$, the molecules are completely motionless and are stacked precisely in accordance with the crystal structure. Since entropy is a measure of microscopic disorder, then in this case $\boldsymbol{S}=0$. That is, there is no uncertainty about the microscopic state.
4. Relationship to Work: For a given system, an increase in the microscopic disorder (that is an increase in entropy) results in a loss of ability to do useful work.
5. Heat: Energy transfer as heat takes place as work at the microscopic level but in a random, disorganized way. This type of energy transfer carries with it some chaos and thus results in entropy flow in or out of the system.
6. Work: Energy transfer by work is microscopically organized and therefore entropy-free.

## Definitions

## Example: Slow adiabatic compression of a gas



Reversible Process: A process $1 \rightarrow 2$ is said to be reversible if the reverse process $2 \rightarrow 1$ restores the system to its original state without leaving any change in either the system or its surroundings.
$\rightarrow$ idealization where $S_{2}=S_{1} \Rightarrow S_{g e n}=0$
Adiabatic Process: A process is adiabatic where there is no energy in the form of heat crossing the boundary.

Isentropic Process: An isentropic process exhibits no change in the entropy of the state between an initial and final condition. Note: since entropy can be produced as well as transferred, it is important to asses the net result of both mechanisms.
$\underbrace{\text { Reversible }}_{S_{g e n}=0}+\underbrace{\text { Adiabatic Process }}_{Q=0} \Rightarrow \underbrace{\text { Isentropic Process }}_{S_{1}=S_{2}}$

But does:

Isentropic Process $\Rightarrow$ Reversible + Adiabatic

## Second Law Analysis for a Control Mass



- control mass is uniformly at $\boldsymbol{T}_{\boldsymbol{T E R}}$ at all times
- control mass has a fixed size ( $V=$ constant $)$

From Gibb's equation

$$
T_{T E R} d S=d U+P d V^{0}
$$

From the 1st law

$$
d U=d Q
$$

Therefore for a reversible process

$$
d S=\frac{d Q}{T_{T E R}}
$$

We integrate to give

$$
S_{2}-S_{1}=\frac{Q_{1-2}}{T_{T E R}}
$$

and for a non-reversible process

$$
d S=\frac{d Q}{T_{T E R}}+d S_{g e n}
$$

We integrate to give

$$
S_{2}-S_{1}=\frac{Q_{1-2}}{T_{T E R}}+S_{g e n ~ 1-2}
$$

## Second Law Analysis for a Control Volume



For the isolated system

$$
\begin{aligned}
& (\Delta S)_{s y s}+(\Delta S)_{s u r}=S_{g e n} \geq 0 \\
& \Delta S_{C V}-s_{A} m_{1-2}^{A}+s_{B} m_{1-2}^{B}-\frac{Q_{1-2}^{A}}{T_{T E R}^{A}}+\frac{Q_{1-2}^{B}}{T_{T E R}^{B}}=\mathcal{P}_{S_{1-2}}=S_{g e n}
\end{aligned}
$$

or as a rate equation

$$
\left(\frac{d S}{d t}\right)_{C V}=\left(s \dot{m}+\frac{\dot{Q}}{T_{T E R}}\right)_{I N}-\left(s \dot{m}+\frac{\dot{Q}}{T_{T E R}}\right)_{O U T}+\dot{S}_{g e n}
$$

## PROBLEM STATEMENT:

A bicycle tire has a volume of $1200 \mathrm{~cm}^{3}$ which is considered to be constant during "inflation". Initially the tire contains air at atmospheric conditions given as $P_{0}=100 \mathrm{kPa}$ and $\boldsymbol{T}_{0}=20^{\circ} \mathrm{C}$. A student then hooks up a bicycle pump and begins to force air from the atmosphere into the tire. After pumping stops and a new equilibrium is reached, the tire pressure is $600 \boldsymbol{k P a}$ and the air temperature in the tire is $20^{\circ} \mathrm{C}$.
a) Determine the mass [ $\mathbf{k g}$ ] of air added to the tire.
b) Determine the minimum amount of work $[k J]$ required to reach this end state.
c) If more than the minimum work is actually used, where does this extra energy go? That is what becomes of the extra energy?


## Availability

|  | Reading $10.1 \rightarrow 10.4$ | Problems <br> 10.59, 10.65, 10.66, 10.67 <br> $10.69,10.75,10.81,10.88$ |
| :---: | :---: | :---: |

## Second Law Analysis of Systems

## AVAILABILITY:

- the theoretical maximum amount of reversible work that can be obtained from a system at a given state $\boldsymbol{P}_{\mathbf{1}}$ and $\boldsymbol{T}_{\mathbf{1}}$ when interacting with a reference atmosphere at the constant pressure and temperature $\boldsymbol{P}_{\mathbf{0}}$ and $\boldsymbol{T}_{\mathbf{0}}$.

What do we mean by work potential of a system?
Notice that:


$$
\eta=\frac{\dot{W}}{\dot{Q}}=1-\frac{T_{0}}{T_{T E R}}
$$

Therefore

$$
\dot{W}=\dot{Q}\left(1-\frac{T_{0}}{T_{T E R}}\right)
$$

This term represents the work potential (availability) of a given TER with respect to the surroundings (dead state) at $T_{0}$.

The following observations can be made about availability:

1. Availability is a property - since any quantity that is fixed when the state is fixed is a property.
2. Availability is a composite property - since its value depends upon an external datum
3. Availability of a system is $\mathbf{0}$ at its dead state when $\boldsymbol{T}=\boldsymbol{T}_{0}$ and $\boldsymbol{P}=\boldsymbol{P}_{0}$.
4. Unless otherwise stated, assume the dead state to be:

$$
\begin{aligned}
P_{0} & =1 \mathrm{~atm} \\
T_{0} & =25^{\circ} \mathrm{C}
\end{aligned}
$$


5. The maximum work is obtained through a reversible process to the dead state.

$$
\underbrace{R E V E R S I B L E W O R K}_{W_{r e v}}=\underbrace{U S E F U L W O R K}_{W_{u s e f u l}}+\underbrace{I R R E V E R S I B I L I T Y}_{I}
$$

## Control Mass Analysis



- we know

$$
W_{\text {rev }}=W_{u s e f u l}+I
$$

but as shown in the figure, the actual work of the process is divided into two components

$$
W_{\text {actual }}=W_{u s e f u l}+W_{s u r}
$$

- where $\boldsymbol{W}_{\text {sur }}$ is the part of the work done against the surroundings to displace the ambient air

$$
W_{s u r}=P_{0}\left(V_{2}-V_{1}\right)=-P_{0}\left(V_{1}-V_{2}\right)
$$

To find $\boldsymbol{W}_{\text {actual }}$, from the 1st law

$$
E_{1}-Q-W_{\text {actual }}=E_{2} \quad \rightarrow \quad Q=E_{1}-E_{2}-W_{\text {actual }}
$$

From the 2nd law

$$
\begin{aligned}
S_{g e n} & =\Delta S_{\text {system }}+\Delta S_{\text {sur }} \geq 0 \\
& =S_{2}-S_{1}+\frac{Q}{T_{0}}
\end{aligned}
$$

But from the 1st law balance we know

$$
\frac{Q}{T_{0}}=\frac{E_{1}-E_{2}-W_{\text {actual }}}{T_{0}}
$$

and when we combine this with the 2nd law

$$
S_{g e n}=S_{2}-S_{1}+\frac{E_{1}-E_{2}-W_{a c t u a l}}{T_{0}}
$$

which leads to

$$
W_{a c t u a l}=\left(E_{1}-E_{2}\right)+T_{0}\left(S_{2}-S_{1}\right)-T_{0} S_{g e n}
$$

or by reversing the order of $\boldsymbol{S}_{\mathbf{2}}$ and $\boldsymbol{S}_{\mathbf{1}}$

$$
W_{\text {actual }}=\left(E_{1}-E_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)-T_{0} S_{g e n}
$$

But we also know that

$$
W_{u s e f u l}=W_{\text {actual }}-W_{\text {sur }}
$$

therefore

$$
W_{u s e f u l}=\left(E_{1}-E_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)+\underbrace{P_{0}\left(V_{1}-V_{2}\right)}_{-W_{s u r}}-T_{0} S_{g e n}
$$

and

$$
\begin{aligned}
\boldsymbol{W}_{\text {rev }} & =\boldsymbol{W}_{\text {useful }}+\boldsymbol{I} \\
& =\boldsymbol{W}_{\text {actual }}-\boldsymbol{W}_{\text {sur }}+\boldsymbol{I}
\end{aligned}
$$

where

$$
I=T_{0} S_{g e n}
$$

Therefore

$$
W_{\text {rev }}=\left(E_{1}-E_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)+P_{0}\left(V_{1}-V_{2}\right)
$$

Define

$$
\begin{aligned}
\Phi & =C O N T R O L M A S S \text { AV AILABILITY } \\
& =W_{\text {rev }} \text { (in going to the dead state) } \\
& =\left(E-E_{0}\right)-T_{0}\left(S-S_{0}\right)+P_{0}\left(V-V_{0}\right)
\end{aligned}
$$

where the specific availability is defined as

$$
\phi=\frac{\Phi}{m}
$$

The availability destroyed is

$$
I=W_{r e v}-W_{u s e f u l}=T_{0} S_{g e n}=T_{0} S_{g e n}
$$

This can be referred to as: irreversibilities, availability destruction or loss of availability.

## Control Volume Analysis

Consider a steady state, steady flow (SS-SF) process


From the 1st law

$$
\begin{equation*}
\frac{d E_{c v_{z}}}{d t^{\prime}}=-\dot{W}_{a c t u a l}-\dot{Q}+\left[\dot{m}\left(h+\frac{\left(v^{*}\right)^{2}}{2}+g z\right)\right]_{i n}-\left[\dot{m}\left(h+\frac{\left(v^{*}\right)^{2}}{2}+g z\right)\right]_{o u t} \tag{1}
\end{equation*}
$$

From the 2nd law

$$
\begin{equation*}
\frac{d S_{c v_{7}}}{d t}=\left(\dot{m} s+\frac{\dot{Q}^{00}}{T_{T E R}}\right)_{i n}-\left(\dot{m} s+\frac{\dot{Q}}{T_{0}}\right)_{o u t}+\dot{S}_{g e n} \tag{2}
\end{equation*}
$$

Combining (1) and (2) through the $\dot{\boldsymbol{Q}}$ term, leads to the actual work output of the turbine, given as

$$
\begin{align*}
\dot{W}_{\text {actual }} & =\left[\dot{m}\left(h+\frac{\left(v^{*}\right)^{2}}{2}+g z-T_{0} s\right)\right]_{i n}-\left[\dot{m}\left(h+\frac{\left(v^{*}\right)^{2}}{2}+g z-T_{0} s\right)\right]_{o u t}-T_{0} \dot{S}_{g e n} \\
& =\dot{m}\left[-T_{0} \Delta s+\Delta h+\Delta K E+\Delta P E\right]-\left(T_{0} \dot{S}_{g e n}\right) \tag{3}
\end{align*}
$$

$\dot{W}_{\text {actual }}$ is the actual work output of the turbine.
The specific flow availability, $\boldsymbol{\psi}$, is given as

$$
\begin{equation*}
\psi=-T_{0}\left(s-s_{0}\right)+\left(h-h_{0}\right)+\left(\frac{\left(v^{*}\right)^{2}}{2}-\frac{\left(v_{0}^{* 0}\right)^{2}}{2}\right)+g\left(z-z \sigma^{\pi^{0}}\right) \tag{4}
\end{equation*}
$$

For a steady state, steady flow process where we assume $\mathrm{KE}=\mathrm{PE}=0$

$$
\begin{align*}
\dot{W}_{r e v} & =(\dot{m} \psi)_{i n}-(\dot{m} \psi)_{o u t}  \tag{5}\\
\dot{I} & =\dot{W}_{r e v}-\dot{W}_{a c t u a l}=T_{0} \dot{S}_{g e n}=T_{0} \dot{S}_{g e n}  \tag{6}\\
\psi & =\left(h-h_{0}\right)-T_{0}\left(s-s_{0}\right) \tag{7}
\end{align*}
$$

## The Exergy Balance Equation



From the 1st law

$$
\begin{equation*}
\frac{d E_{c v}}{d t}=\dot{W}_{i n}-\dot{W}_{o u t}-\dot{Q}_{0}+\dot{Q}_{1}-\dot{Q}_{2}+[\dot{m}(e+P v)]_{i n}-[\dot{m}(e+P v)]_{o u t} \tag{1}
\end{equation*}
$$

From the 2nd law

$$
\begin{equation*}
\frac{d S_{c v}}{d t}=\left(\dot{m} s-\frac{\dot{Q_{0}}}{T_{0}}+\frac{\dot{Q}_{1}}{T_{1}}\right)_{i n}-\left(\dot{m} s+\frac{\dot{Q}_{2}}{T_{2}}\right)_{o u t}+\dot{S}_{g e n} \tag{2}
\end{equation*}
$$

Multiply (2) by $\boldsymbol{T}_{\mathbf{0}}$ and subtract from (1) to eliminate $\boldsymbol{Q}_{\mathbf{0}}$, which leads to the generalized exergy equation

$$
\frac{d}{d t}\left(E-T_{0} S\right)_{C V}=\dot{W}_{i n}-\dot{W}_{o u t}+\left[\dot{m}\left(e+P v-T_{0} s\right)\right]_{i n}
$$

$$
\begin{align*}
& {\left[\dot{m}\left(e+P v-T_{0} s\right)\right]_{o u t}+\left(\dot{Q}_{1}-\frac{T_{0} \dot{Q}_{1}}{T_{1}}\right)_{i n}} \\
& -\left(\dot{Q}_{2}-\frac{T_{0} \dot{Q}_{2}}{T_{2}}\right)_{o u t}-T_{0} \dot{S}_{g e n} \tag{3}
\end{align*}
$$

We can rewrite Eq. (3) in a generalized form by introducing the definitions of $\boldsymbol{X}$ and $\boldsymbol{\psi}$.

$$
\begin{aligned}
\frac{d \Phi}{d t}= & P_{0} \frac{d V_{C V}}{d t}+\left[\dot{W}+\dot{m} \psi+\dot{Q}\left(1-\frac{T_{0}}{T_{T E R}}\right)\right]_{i n} \\
& -\left[\dot{W}+\dot{m} \psi+\dot{Q}\left(1-\frac{T_{0}}{T_{T E R}}\right)\right]_{o u t}-\dot{I}
\end{aligned}
$$

where

$$
\begin{aligned}
\dot{I} & =T_{0} \dot{S}_{g e n} \\
& =\text { exergy destruction rate } \\
\Phi & =\left[\left(E-E_{0}\right)+P_{0}\left(V-V_{0}\right)-T_{0}\left(S-S_{0}\right)\right] \\
& =\text { non-flow exergy } \\
\psi & =\left(h-h_{0}\right)-T_{0}\left(s-s_{0}\right)+\frac{1}{2}\left[\left(v^{*}\right)^{2}-\left(v_{0}^{*}\right)^{2}\right]+g\left(z-z_{0}\right) \\
& =\text { flow exergy } \\
\dot{W}_{u s e f u l} & =(\underbrace{\dot{W}_{\text {in }}-\dot{W}_{\text {out }}}_{\dot{W}_{\text {actual }}})-\underbrace{\left(P_{0} \frac{d V_{C V}}{d t}\right)}_{W_{\text {sur }}}
\end{aligned}
$$

## Efficiency and Effectiveness

1. First law efficiency (thermal efficiency)

$$
\eta=\frac{\text { net work output }}{\text { gross heat input }}=\frac{W_{n e t}}{Q_{i n}}
$$

Carnot cycle

$$
\eta=\frac{Q_{H}-Q_{L}}{Q_{H}}=1-\frac{T_{L}}{T_{H}}
$$

2. Second Law Efficiency (effectiveness)

$$
\eta_{2 n d}=\frac{\text { net work output }}{\text { maximum reversible work }}=\frac{\text { net work output }}{\text { availability }}
$$

Turbine $\rightarrow \quad \eta_{2 n d}=\frac{\dot{W} / \dot{m}}{\psi_{e}-\psi_{i}}$
Compressor $\rightarrow \quad \eta_{2 n d}=\frac{\psi_{e}-\psi_{i}}{\dot{W} / \dot{m}}$
Heat Source $\rightarrow \quad \eta_{2 n d}=\frac{\dot{W} / \dot{m}}{\dot{Q} / \dot{m}\left[1-\frac{T_{0}}{T_{T E R}}\right]}$
3. Isentropic efficiency (process efficiency)
(a) adiabatic turbine efficiency

$$
\eta_{T}=\frac{\text { work of actual adiabatic expansion }}{\text { work of reversible adiabatic expansion }}=\frac{W_{a c t}}{W_{S}}
$$

(b) adiabatic compressor efficiency

$$
\eta_{C}=\frac{\text { work of rever sible adiabatic compression }}{\text { work of actual adiabatic compression }}=\frac{W_{S}}{W_{a c t}}
$$

## PROBLEM STATEMENT:

2 kg of air in a piston-cylinder device is expanded reversibly and isothermally from 700 kPa and $250^{\circ} \mathrm{C}$ to a pressure of 125 kPa . During the process, heat is added from a thermal energy reservoir at $250^{\circ} \mathrm{C}$. Assume the dead state conditions to be $\boldsymbol{T}_{0}=25^{\circ} \mathrm{C}$ and $\boldsymbol{P}_{0}=101.325 \mathrm{kPa}$.
a) Determine the amount of work transfer $[k J]$ to the piston and the amount of heat transfer $[k J]$ from the source.
b) Determine the availability transfer $[k J]$ due to work and heat.
c) Determine the increase in availability $[k J]$ of the air in the cylinder.
d) Physically, how do you explain that, although the internal energy of the air did not change, its availability did?


## Rankine Cycle



## Reading

$11.1 \rightarrow 11.7$

## Problems

11.29, 11.36, 11.43, 11.47, 11.52,
$11.55,11.58,11.74$

## Definitions

- working fluid is alternately vaporized and condensed as it recirculates in a closed cycle
- the standard vapour cycle that excludes internal irreversibilities is called the Ideal Rankine Cycle


Analyze the Process

Device 1st Law Balance

| Boiler | $h_{2}+q_{H}=h_{3}$ | $\Rightarrow q_{H}=h_{3}-h_{2} \quad$ (in) |
| :--- | :--- | :--- | :--- |
| Turbine | $h_{3}=h_{4}+w_{T}$ | $\Rightarrow w_{T}=h_{3}-h_{4} \quad$ (out) |
| Condenser | $h_{4}=h_{1}+q_{L}$ | $\Rightarrow q_{L}=h_{4}-h_{1} \quad$ (out) |
| Pump | $h_{1}+w_{P}=h_{2}$ | $\Rightarrow w_{P}=h_{2}-h_{1} \quad$ (in) |

The Rankine efficiency is

$$
\begin{aligned}
\eta_{R} & =\frac{\text { net work output }}{\text { heat supplied to the boiler }} \\
& =\frac{\left(h_{3}-h_{4}\right)+\left(h_{1}-h_{2}\right)}{\left(h_{3}-h_{2}\right)}
\end{aligned}
$$

## Effects of Boiler and Condenser Pressure

We know the efficiency is proportional to

$$
\eta \propto 1-\frac{T_{L}}{T_{H}}
$$

The question is $\rightarrow$ how do we increase efficiency $\Rightarrow \boldsymbol{T}_{\boldsymbol{L}} \downarrow$ and/or $\boldsymbol{T}_{\boldsymbol{H}} \uparrow$.

## 1. INCREASED BOILER PRESSURE:



- an increase in boiler pressure results in a higher $\boldsymbol{T}_{\boldsymbol{H}}$ for the same $\boldsymbol{T}_{\boldsymbol{L}}$, therefore $\boldsymbol{\eta} \uparrow$.
- but $4^{\prime}$ has a lower quality than 4
- wetter steam at the turbine exhaust
- results in cavitation of the turbine blades
- $\boldsymbol{\eta} \downarrow$ plus $\uparrow$ maintenance
- quality should be $>80-90 \%$ at the turbine exhaust


## 2. LOWER $T_{L}$ :

- we are generally limited by the $\boldsymbol{T} \boldsymbol{E} \boldsymbol{R}$ (lake, river, etc.)
eg. lake @ $15{ }^{\circ} C+\underbrace{\Delta T=10^{\circ} C}_{\text {resistance to } H T}=25{ }^{\circ} C$
$\Rightarrow P_{\text {sat }}=3.169 \mathrm{kPa}$.
- this is why we have a condenser
- the pressure at the exit of the turbine can be less than atmospheric pressure


## 3. INCREASED $T_{H}$ BY ADDING SUPERHEAT:



- the average temperature at which heat is supplied in the boiler can be increased by superheating the steam
- dry saturated steam from the boiler is passed through a second bank of smaller bore tubes within the boiler until the steam reaches the required temperature
- The value of $\bar{T}_{\boldsymbol{H}}$, the mean temperature at which heat is added, increases, while $\overline{\boldsymbol{T}_{L}}$ remains constant. Therefore the efficiency increases.


## Rankine Cycle with Reheat

- the wetness at the exhaust of the turbine should be no greater that $10 \%$ - this can result in physical erosion of the turbine blades
- but high boiler pressures are required for high efficiency - tends to lead to a high wetness ratio
- to improve the exhaust steam conditions, the steam can be reheated with the expansion carried out in two steps




## Rankine Cycle with Regeneration

- Carnot cycle has efficiency: $\boldsymbol{\eta}=1-\boldsymbol{T}_{L} / \boldsymbol{T}_{\boldsymbol{H}}$
- add $\boldsymbol{Q}_{\boldsymbol{H}}$ at as high a $\boldsymbol{T}_{\boldsymbol{H}}$ as possible
- reject $Q_{L}$ at as low a $\boldsymbol{T}_{L}$ as possible
- the Rankine cycle can be used with a Feedwater Heater to heat the high pressure sub-cooled water at the pump exit to the saturation temperature
- most of the heat addition $\left(\boldsymbol{Q}_{\boldsymbol{H}}\right)$ is done at high temperature



## Feedwater Heaters

There are two different types of feedwater heaters

1. OPEN FWH: the streams mix $\rightarrow$ high temperature steam with low temperature water at constant pressure
2. CLOSED FWH: a heat exchanger is used to transfer heat between the two streams but the streams do not mix. The two streams can be maintained at different pressures.

## OPEN FWH:

- working fluid passes isentropically through the turbine stages and pumps
- steam enters the first stage turbine at state 5 and expands to state 6 - where a fraction of the total flow is bled off into an open feedwater heater
- the rest of the steam expands into the second stage turbine at state point 7 - this portion of the fluid is condensed and pumped as a saturated liquid to the FWH at state 2
- a single mixed stream exists the FWH at state point 3


CLOSED FWH: two variations exist
Case 1: pump the condensate back to the high pressure line


- a steam trap is inserted in the condensed steam line that allows only liquid to pass
- liquid is passed to a low pressure region such as the condenser or a low pressure heater


Case 2: the incoming feedwater does not mix with the extracted steam

- both streams flow separately through the heater
- the two streams can have different pressures



## Binary Cycle

- involves two Rankine cycles running in tandem with different working fluids such as mercury and water
- why:
- typically a boiler will supply energy at $1300-1400^{\circ} \mathrm{C}$
- but $\boldsymbol{T}_{\text {critical }}$ for water is $374.14{ }^{\circ} \mathrm{C}$
* most energy is absorbed below this temperature
* high $\boldsymbol{\Delta T}$ between the boiler source and the water leads to a major source of irreversibilities
- $T_{\text {critical }}$ for mercury is about $1500^{\circ} \mathrm{C}$
* no need for superheating




## PROBLEM STATEMENT:

Water is the working fluid for a Rankine cycle process where the turbine and the pump have isentropic efficiencies of $85 \%$ and $70 \%$, respectively. Superheated vapor enters the turbine at 8 MPa and $500^{\circ} \mathrm{C}$. The condenser pressure is $7.5 k P a$. The net power output of the cycle is $100 M W$. Determine for the cycle:
a) the mass flow rate of the steam $[\mathrm{kg} / \mathrm{s}]$, for a net power output of 100 MW .
b) the rate of heat transfer $[M W]$ to the working fluid passing through the steam generator.
c) the thermal efficiency.
d) the mass flow rate of the condenser cooling water $[\mathbf{k g} / \mathrm{h}]$, if the cooling water enters the condenser at $15{ }^{\circ} \mathrm{C}$ and exits at $35^{\circ} \mathrm{C}$, with negligible pressure change.


## Refrigeration Cycle



## Definitions

- refrigeration cycles may be classified as
- vapour compression
- gas compression
- refrigerators and heat pumps have a great deal in common. The primary difference is in the manner in which heat is utilized.

- the Carnot cycle can serve as the initial model of the ideal refrigeration cycle

$$
\begin{aligned}
Q_{L} & =T_{L}\left(s_{3}-s_{2}\right) \\
Q_{H} & =T_{H}\left(s_{4}-s_{1}\right) \\
W_{i n} & =Q_{n e t}=Q_{H}-Q_{L} \\
& =\left(T_{H}-T_{L}\right)\left(s_{3}-s_{2}\right)
\end{aligned}
$$

The coefficient of performance $(\boldsymbol{\beta})$ is given by

$$
\beta=\frac{b e n e f i t}{\operatorname{cost}}
$$



$$
\beta_{r e f r i g}=\frac{T_{L}}{T_{H}-T_{L}}
$$

$$
\beta_{\text {heat pump }}=\frac{T_{H}}{T_{H}-T_{L}}
$$

## Vapour Compression Refrigeration Cycle




## Refrigeration Process

Process Description

1-2s: A reversible, adiabatic (isentropic) compression of the refrigerant. The saturated vapour at state 1 is superheated to state 2 .

$$
\Rightarrow \quad w_{c}=h_{2 s}-h_{1}
$$

2s-3: An internally, reversible, constant pressure heat rejection in which the working substance is desuperheated and then condensed to a saturated liquid at 3 . During his process, the working substance rejects most of its energy to the condenser cooling water.

$$
\Rightarrow \quad q_{H}=h_{2 s}-h_{3}
$$

3-4 An irreversible throttling process in which the temperature and pressure decrease at constant enthalpy.

$$
\Rightarrow \quad h_{3}=h_{4}
$$

4-1 An internally, reversible, constant pressure heat interaction in which the working fluid is evaporated to a saturated vapour at state point 1 . The latent enthalpy necessary for evaporation is supplied by the refrigerated space surrounding the evaporator. The amount of heat transferred to the working fluid in the evaporator is called the refrigeration load.

$$
\Rightarrow \quad q_{L}=h_{1}-h_{4}
$$

The thermal efficiency of the cycle can be calculated as

$$
\eta=\frac{q_{\text {evap }}}{w_{\text {comp }}}=\frac{h_{1}-h_{4}}{h_{2 s}-h_{1}}
$$

## Common Refrigerants

There are several fluorocarbon refrigerants that have been developed for use in VCRC.

| $\mathbf{R} 11$ |  |  |
| :---: | :---: | :---: |
| R12 | $\mathrm{CCl}_{2} \mathrm{~F}_{2}$ | dichlorodifluoromethane <br> - used for refrigeration systems at higher temperature levels <br> - typically, water chillers and air conditioning |
| $\mathbf{R 2 2}$ | $\mathrm{CHClF}_{2}$ | has less chlorine, a little better for the environment than R12 <br> - used for lower temperature applications |
| R134a | $\mathrm{CFH}_{2} \mathrm{CF} 3$ | tetrafluorethane - no chlorine <br> - went into production in 1991 <br> - replacement for R12 |
| R141b | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{FCl}_{2}$ | dichlorofluoroethane |
| Ammonia | $\mathrm{NH}_{3}$ | corrosive and toxic <br> - used in absorption systems |
| R744 | $\mathrm{CO}_{2}$ | behaves in the supercritical region - low efficiency |
| R290 | propane | combustible |

## How to Choose a Refrigerant

Many factors need to be considered

- ozone depletion potential
- global warming potential
- combustibility
- thermal factors


## Ozone Depletion Potential

- chlorinated and brominated refrigerants act as catalysts to destroy ozone molecules
- reduces the natural shielding effect from incoming ultra violet B radiation


## Global Warming Potential

- gases that absorb infrared energy
- gases with a high number of carbon-fluorine bonds
- generally have a long atmospheric lifetime


## Combustibility

- all hydro-carbon fuels, such as propane


## Thermal Factors

- the heat of vaporization of the refrigerant should be high. The higher $\boldsymbol{h}_{f g}$, the greater the refrigerating effect per $\boldsymbol{k g}$ of fluid circulated
- the specific heat of the refrigerant should be low. The lower the specific heat, the less heat it will pick up for a given change in temperature during the throttling or in flow through the piping, and consequently the greater the refrigerating effect per $\boldsymbol{k g}$ of refrigerant
- the specific volume of the refrigerant should be low to minimize the work required per $\mathbf{k g}$ of refrigerant circulated
- since evaporation and condenser temperatures are fixed by the temperatures of the surroundings - selection is based on operating pressures in the evaporator and the condenser

| Designation | Chemical Formula | Ozone Depletion Potential ${ }^{1}$ | Global Warming Potential ${ }^{2}$ |
| :---: | :---: | :---: | :---: |
| Ozone Depleting \& Global Warming Chemicals |  |  |  |
| CFC-11 | $\mathrm{CCl}_{3} \mathrm{~F}$ | 1 | 3,400 |
| CFC-12 | $\mathrm{CCl}_{2} \mathrm{~F}_{2}$ | 0.89 | 7,100 |
| CFC-13 | $\mathrm{CClF}_{3}$ |  | 13,000 |
| CFC-113 | $\mathrm{C}_{2} \mathrm{~F}_{3} \mathrm{Cl}_{3}$ | 0.81 | 4,500 |
| CFC-114 | $\mathrm{C}_{2} \mathrm{~F}_{4} \mathrm{Cl}_{2}$ | 0.69 | 7,000 |
| CFC-115 | $\mathrm{C}_{2} \mathrm{~F}_{5} \mathrm{Cl}_{1}$ | 0.32 | 7,000 |
| Halon-1211 | $\mathrm{CF}_{2} \mathrm{ClBr}$ | 2.2-3.5 |  |
| Halon-1301 | $\mathrm{CF}_{3} \mathrm{Br}$ | 8-16 | 4,900 |
| Halon-2402 | $C_{2} F_{4} B r_{2}$ | 5-6.2 |  |
| carbon tetrachloride | $\mathrm{CCl}_{4}$ | 1.13 | 1,300 |
| methyl chloroform | $\mathrm{CH}_{3} \mathrm{CCl}_{3}$ | 0.14 |  |
| nitrous oxide | $\mathrm{N}_{2}$ |  | 270 |
| Ozone Depleting \& Global Warming Chemicals - Class 2 |  |  |  |
| HCFC-22 | $\boldsymbol{C H F} \mathrm{F}_{2} \mathrm{Cl}$ | 0.048 | 1,600 |
| HCFC-123 | $\mathrm{C}_{2} \mathrm{H} \mathrm{F}_{3} \mathrm{Cl}_{2}$ | 0.017 | 90 |
| HCFC-124 | $\mathrm{C}_{2} \mathrm{HF} \mathrm{F}_{4} \mathrm{Cl}$ | 0.019 | 440 |
| HCFC-125 | $\mathrm{C}_{2} \mathrm{H} \mathrm{F}_{5}$ | 0.000 | 3,400 |
| HCFC-141b | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{FCl}_{2}$ | 0.090 | 580 |
| HCFC-142b | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~F}_{2} \mathrm{Cl}$ | 0.054 | 1800 |
| Global Warming, non-Ozone Depleting Chemicals |  |  |  |
| carbon dioxide | $\mathrm{CO}_{2}$ | 0 | 1 |
| methane | $\mathrm{CH}_{4}$ | 0 | 11 |
| HFC-125 | $\mathrm{CHF}_{2} \mathrm{CF}_{3}$ | 0 | 90 |
| HFC-134a | $\mathrm{CFH}_{2} \mathrm{CF}_{3}$ | 0 | 1,000 |
| HFC-152a | $\mathrm{CH}_{3} \mathrm{CHF} \mathrm{F}_{2}$ | 0 | 2,400 |
| perfluorobutane | $C_{4} F_{10}$ | 0 | 5,500 |
| perfluoropentane | $C_{5} F_{12}$ | 0 | 5,500 |
| perfluorohexane | $C_{6} \boldsymbol{F}_{14}$ | 0 | 5,100 |
| perfluorotributylamine | $N\left(C_{4} F_{9}\right)_{3}$ | 0 | 4,300 |

1 - relative to R 11
2 - relative to $\mathrm{CO}_{2}$

## Cascade Refrigeration System



- two or more vapour compression refrigeration cycles are combined
- used where a very wide range of temperature between $T_{L}$ and $T_{H}$ is required
- the condenser for the low temperature refrigerator is used as the evaporator for the high temperature refrigerator


## Advantages

- the refrigerants can be selected to have reasonable evaporator and condenser pressures in the two or more temperature ranges
$\beta=\frac{Q_{L}(\uparrow)}{W_{\text {net }}(\downarrow)} \operatorname{overall}(\uparrow)$



## Absorption Refrigeration System

Differences between an absorption refrigeration system and a VCRC

VCRC

- vapour is compressed
between the evaporator and the condenser
- process is driven by work

Absorption RS

- the refrigerant is absorbed by an absorbent material to form a liquid solution
- heat is added to the process
to retrieve the refrigerant vapour from the liquid solution
- process is driven by heat


## Common Refrigerant/Absorber Combinations

| Refrigerant | Absorber |  |
| :--- | :---: | :---: |
| 1. | ammonia | water |
| 2. | water | lithium bromide <br> lithium chloride |

## Process



- the compressor is replaced by an absorber, pump, generator, regenerator and a valve
- in the absorber, ammonia vapour is absorbed by liquid water
- the process is exothermic (gives off heat)
- ammonia vapour is absorbed into the water at low $\boldsymbol{T}$ and $\boldsymbol{P}$ maintained by means of $Q_{L}^{*}$
- absorption is proportional to $1 / \boldsymbol{T} \Rightarrow$ the cooler the better
- in the generator, ammonia is driven out of the solution by the addition of $\boldsymbol{Q}_{\boldsymbol{H}}^{*}$, (endothermic reaction)
- a regenerator is used to recoup some of the energy from the weak ammonia water solution passed back to the absorber. This energy is transferred to the solution pumped to the generator. This reduces the $Q_{H}^{*}$ required to vapourize the solution in the generator. It also reduces the amount of $Q_{L}^{*}$ that needs to be removed from the solution in the absorber.


## PROBLEM STATEMENT:

A computer facility in the Sahara Desert $\left[T_{0}=40^{\circ} C\right.$ ] is to be maintained at $15^{\circ} C$ by a vapourcompression refrigeration system that uses water as the refrigerant. The water leaves the evaporator as a saturated vapour at $10^{\circ} \boldsymbol{C}$. The compressor is reversible and adiabatic. The pressure in the condenser is $0.01 M P \boldsymbol{P a}$ and the water is saturated liquid as it leaves the condenser.
i) determine the coefficient of performance for the cycle
ii) determine the second law efficiency of the system
iii) briefly explain what factors in this system lead to the destruction of exergy?


## Internal Combustion Engines



## The Gasoline Engine

4-stroke engine


- conversion of chemical energy to mechanical energy
- can obtain very high temperatures due to the short duration of the power stroke


## Air Standard Cycle

A closed cycle model for the IC engine, such as the gasoline or diesel cycle. Some assumptions must be made in order to model this complex process.

## ASSUMPTIONS:

- air is an ideal gas with constant $\boldsymbol{c}_{\boldsymbol{p}}$ and $\boldsymbol{c}_{\boldsymbol{v}}$
- no intake or exhaust processes
- the cycle is completed by heat transfer to the surroundings
- the internal combustion process is replaced by a heat transfer process from a TER
- all internal processes are reversible
- heat addition occurs instantaneously while the piston is at TDC


## Definitions

Mean Effective Pressure (MEP): The theoretical constant pressure that, if it acted on the piston during the power stroke would produce the same net work as actually developed in one complete cycle.

$$
M E P=\frac{\text { net work for one cycle }}{\text { displacement volume }}=\frac{W_{n e t}}{V_{B D C}-V_{T D C}}
$$

The mean effective pressure is an index that relates the work output of the engine to it size (displacement volume).

## Otto Cycle

- the theoretical model for the gasoline engine
- consists of four internally reversible processes
- heat is transferred to the working fluid at constant volume


## Otto Cycle Efficiency

$$
\begin{aligned}
& \eta=\frac{W_{n e t}}{Q_{H}}=\frac{Q_{H}-Q_{L}}{Q_{H}}=1-\frac{Q_{L}}{Q_{H}}=1-\frac{Q_{4-1}}{Q_{2-3}} \\
& Q_{H}=m c_{v}\left(T_{3}-T_{2}\right) \quad(\text { intake }) \\
& Q_{L}=m c_{v}\left(T_{4}-T_{1}\right) \quad(\text { exhaust })
\end{aligned}
$$

Therefore

$$
\eta=1-\frac{\left(T_{4}-T_{1}\right)}{\left(T_{3}-T_{2}\right)}=1-\left(\frac{T_{1}}{T_{2}}\right) \frac{\left(\frac{T_{4}}{T_{1}}-1\right)}{\left(\frac{T_{3}}{T_{2}}-1\right)}
$$



Since processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are isentropic, we know that

$$
\begin{aligned}
& P V^{k}=\text { constant } \\
& \frac{m R T_{1}}{V_{1}} V_{1}^{k}=\frac{m R T_{2}}{V_{2}} V_{2}^{k}
\end{aligned}
$$

and

$$
\frac{T_{2}}{T_{1}}=\left(\frac{V_{1}}{V_{2}}\right)^{k-1}=\left(\frac{V_{4}}{V_{3}}\right)^{k-1}=\frac{T_{3}}{T_{4}}
$$

We can make this equality since

$$
\frac{V_{1}}{V_{2}}=\frac{V_{4}}{V_{3}}=\text { compression ratio }=r
$$

Therefore

$$
\frac{T_{3}}{T_{2}}=\frac{T_{4}}{T_{1}}
$$



Substituting into the equation for $\boldsymbol{\eta}$ gives

$$
\eta=1-\frac{T_{1}}{T_{2}}=1-\left(\frac{V_{2}}{V_{1}}\right)^{k-1}=1-\left(\frac{V_{1}}{V_{2}}\right)^{1-k}
$$

If we let

$$
r=\frac{V_{1}}{V_{2}}=\frac{V_{4}}{V_{3}}=\text { compression ratio }
$$

Then

$$
\eta_{O t t o}=1-r^{1-k}
$$

## Diesel Cycle

- an ideal cycle for the compression ignition engine (diesel engine)

- all steps in the cycle are reversible
- heat is transferred to the working fluid at constant pressure
- heat transfer must be just sufficient to maintain a constant pressure


## Diesel Cycle Efficiency

$$
\begin{equation*}
\eta=1-\frac{c_{v}\left(T_{4}-T_{1}\right)}{c_{p}\left(T_{3}-T_{2}\right)}=1-\left(\frac{1}{k}\right)\left(\frac{T_{1}}{T_{2}}\right) \frac{\left(\frac{T_{4}}{T_{1}}-1\right)}{\left(\frac{T_{3}}{T_{2}}-1\right)} \tag{1}
\end{equation*}
$$


where

$$
k=\frac{c_{p}}{c_{v}}
$$

If we let

$$
\begin{aligned}
r & =\frac{V_{1}}{V_{2}}=\text { compression ratio }=\frac{V_{4}}{V_{2}} \\
r_{v} & =\frac{V_{3}}{V_{2}}=\text { cutoff ratio } \rightarrow \text { injection period }
\end{aligned}
$$

From the Otto cycle analysis we know

$$
\begin{equation*}
\frac{T_{2}}{T_{1}}=\left(\frac{V_{1}}{V_{2}}\right)^{k-1}=r^{k-1} \tag{2}
\end{equation*}
$$

and for an isentropic process

$$
\frac{T_{3}}{T_{4}}=\left(\frac{V_{4}}{V_{3}}\right)^{k-1}=\left(\frac{V_{4}}{V_{2}} \cdot \frac{V_{2}}{V_{3}}\right)^{k-1}=\left(\frac{r}{r_{v}}\right)^{k-1}
$$

From this, we can write

$$
\frac{T_{3}}{T_{4}}=\frac{r^{k-1}}{r_{v}^{k-1}}=\frac{T_{2} / T_{1}}{r_{v}^{k-1}}
$$

and

$$
\frac{T_{2}}{T_{1}}=\frac{T_{3}}{T_{4}} r_{v}^{k-1}
$$

or

$$
\begin{equation*}
\frac{T_{4}}{T_{1}}=\frac{T_{3}}{T_{2}} r_{v}^{k-1} \tag{3}
\end{equation*}
$$

From the ideal gas law

$$
\begin{equation*}
P_{3}=\frac{R T_{3}}{V_{3}}=\frac{R T_{2}}{V_{2}}=P_{2} \quad \Rightarrow \quad \frac{T_{3}}{T_{2}}=\frac{V_{3}}{V_{2}}=r_{v} \tag{4}
\end{equation*}
$$

Substituting (2), (3), and (4) into (1)

$$
\eta_{\text {Diesel }}=1-\frac{1}{r^{k-1}}\left(\frac{1}{k}\right)\left(\frac{r_{v}^{k}-1}{r_{v}-1}\right)
$$

## Dual Cycle (Limited Pressure Cycle)

- better representation of the combustion process in both the gasoline and the diesel engines



## Dual Cycle Efficiency

Given

$$
\begin{aligned}
r & =\frac{V_{1}}{V_{2}}=\text { compression ratio } \\
r_{v} & =\frac{V_{4}}{V_{3}}=\text { cutoff ratio } \\
r_{p} & =\frac{P_{3}}{P_{2}}=\text { pressure ratio }
\end{aligned}
$$

$$
\eta_{D u a l}=1-\frac{r_{p} r_{v}^{k}-1}{\left[\left(r_{p}-1\right)+k r_{p}\left(r_{v}-1\right)\right] r^{k-1}}
$$

Note: if $r_{p}=1$ we get the diesel efficiency.

## Atkinson and Miller Cycles

Similar to the Otto cycle but with constant pressure heat rejection that allows for a higher expansion ratio (more work extraction) compared to the compression ratio and in turn a higher cycle efficiency.



The Atkinson Cycle


## Atkinson Cycle Efficiency

If we let

$$
\begin{aligned}
r & =\frac{V_{1}}{V_{2}}=\text { compression ratio } \\
r_{\alpha} & =\frac{V_{4}}{V_{3}}=\text { expansion ratio (larger than the compression ratio) }
\end{aligned}
$$

$$
\begin{aligned}
\eta & =1-k \cdot r^{1-k} \cdot \frac{\left[\frac{r_{\alpha}}{r}-1\right]}{\left[\frac{r_{\alpha}^{k}}{r^{k}}-1\right]} \\
& =1-k\left[\frac{r_{\alpha}-r}{r_{\alpha}^{k}-r^{k}}\right]
\end{aligned}
$$

## Stirling Cycle


heat the regenerator by pushing the hot gas through it

$$
\text { (4) } \rightarrow \text { (1) }
$$

constant volume process

move both pistons to the left to get back to state 1.
During this process the regenerator cools down by giving off energy to the gas

- reversible regenerator used as an energy storage device
- possible to recover all heat given up by the working fluid in the constant volume cooling process
- all the heat received by the cycle is at $\boldsymbol{T}_{\boldsymbol{H}}$ and all heat rejected at $\boldsymbol{T}_{\boldsymbol{L}}$
- $\eta_{\text {Stirling }}=1-T_{L} / T_{H} \quad$ (Carnot efficiency)


## PROBLEM STATEMENT:

An air-standard Diesel cycle has a compression ratio of 15 and the heat transferred to the working fluid per cycle is $1600 \mathrm{~kJ} / \mathrm{kg}$. At the beginning of the compression process, the pressure is 0.1 MPa and the temperature is $17^{\circ} \mathrm{C}$. Assuming variable specific heats for air, determine:
a) the pressure and temperature at each point in the cycle
b) the thermal efficiency


## Brayton Cycle



## Introduction

The gas turbine cycle is referred to as the Brayton Cycle or sometimes the Joule Cycle. The actual gas turbine cycle is an open cycle, with the intake and exhaust open to the environment.

- can use different fuels
- simple in construction, easy to maintain
- can handle large volumes of gases
- small weight-to-power ratio


## Definitions

Back Work Ratio: the ratio of the compressor work to the turbine work

## Open Cycle Gas Turbine Engines



- compressor power requirements vary from $40-80 \%$ of the power output of the turbine (remainder is net power output), i.e. back work ratio $=0.4 \rightarrow 0.8$
- high power requirement is typical when gas is compressed because of the large specific volume of gases in comparison to that of liquids


## Idealized Air Standard Brayton Cycle



- closed loop
- constant pressure heat addition and rejection
- ideal gas with constant specific heats



## Brayton Cycle Efficiency

The efficiency of the cycle is given by the benefit over the cost or

$$
\eta=\frac{W_{n e t}}{Q_{H}}=1-\frac{Q_{L}}{Q_{H}}=1-\frac{\dot{m} c_{p}\left(T_{4}-T_{1}\right)}{\dot{m} c_{p}\left(T_{3}-T_{2}\right)}=1-\frac{T_{1}}{T_{2}} \frac{\left(\frac{T_{4}}{T_{1}}-1\right)}{\left(\frac{T_{3}}{T_{2}}-1\right)}
$$

If we use the isentropic equations with the ideal gas law, we see that

$$
\frac{T_{2}}{T_{1}}=\left(\frac{P_{2}}{P_{1}}\right)^{(k-1) / k}=\left(\frac{P_{3}}{P_{4}}\right)^{(k-1) / k}=\frac{T_{3}}{T_{4}} \Rightarrow \frac{T_{4}}{T_{1}}=\frac{T_{3}}{T_{2}}
$$

and

$$
\eta=1-\frac{T_{1}}{T_{2}}=1-\frac{T_{4}}{T_{3}}
$$

If we define the pressure ratio as:

$$
r_{p}=\frac{P_{2}}{P_{1}}=\frac{P_{3}}{P_{4}}
$$

$$
\eta=1-\left(r_{p}\right)^{(1-k) / k}
$$



## Maximum Pressure Ratio

Given that the maximum and minimum temperature can be prescribed for the Brayton cycle, a change in the pressure ratio can result in a change in the work output from the cycle.


## Brayton Cycle with Reheat




- total work is increased
- but additional heat input is required
- net efficiency may or may not increase


## Compression with Intercooling



- the work required to compress in a steady flow device can be reduced by compressing in stages
- cooling the gas reduces the specific volume and in turn the work required for compression
- by itself compression with intercooling does not provide a significant increase in the efficiency of a gas turbine because the temperature at the combustor inlet would require additional heat transfer to achieve the desired turbine inlet temperature



## How Can We Improve Efficiency?

We know the efficiency of a Brayton cycle engine is given as

$$
\eta=\frac{\dot{W}_{\text {net }}}{\dot{Q}_{H}}=\frac{\dot{W}_{\text {turbine }}-\dot{\boldsymbol{W}}_{\text {compressor }}}{\dot{Q}_{H}}
$$

There are several possibilities, for instance we could try to increase $\dot{W}_{\text {turbine }}$ or decrease $\dot{\boldsymbol{W}}_{\text {compressor }}$. Recall that for a SSSF, reversible compression or expansion

$$
\frac{\dot{W}}{\dot{m}}=\int_{i n}^{o u t} v d P \Rightarrow \operatorname{keep} v \uparrow \text { in turbine, keep } v \downarrow \text { in compressor }
$$

This can be achieved through the use of intercooling and reheating.
Compressor $\longrightarrow \boldsymbol{\eta}=\frac{\dot{\boldsymbol{W}}_{T}-\dot{W}_{C}(\downarrow)}{\dot{Q}_{H, \text { Total }}(\uparrow)}$, overall $(\downarrow)$

Turbine $\longrightarrow \quad \eta=\frac{\left.\dot{W}_{T}(\uparrow)-\dot{W}_{C}\right)}{\dot{Q}_{H, \text { Total }}(\uparrow)}$, overall $(\downarrow)$

The conclusion is the intercooling and/or reheating by themselves will lower $\boldsymbol{\eta}$. We have to find a way to reduce $\dot{Q}_{H}$

## Brayton Cycle with Regeneration



- a regenerator is used to reduce the fuel consumption to provide the required $\dot{Q}_{H}$
- the efficiency with a regenerator can be determined as:

$$
\eta=1-\left(\frac{T_{\min }}{T_{\max }}\right)\left(r_{p}\right)^{(k-1) / k}
$$

- for a given $\boldsymbol{T}_{\min } / \boldsymbol{T}_{\max }$, the use of a regenerator above a certain $\boldsymbol{r}_{\boldsymbol{p}}$ will result in a reduction of $\boldsymbol{\eta}$



## Brayton Cycle With Intercooling, Reheating and Regeneration



## Compressor and Turbine Efficiencies

Isentropic Efficiencies
(1) $\quad \eta_{c o m p}=\frac{h_{2, s}-h_{1}}{h_{2}-h_{1}}=\frac{c_{p}\left(T_{2, s}-T_{1}\right)}{c_{p}\left(T_{2}-T_{1}\right)}$
(2) $\quad \eta_{t u r b}=\frac{h_{3}-h_{4}}{h_{3}-h_{4, s}}=\frac{c_{p}\left(T_{3}-T_{4}\right)}{c_{p}\left(T_{3}-T_{4, s}\right)}$
(3) $\eta_{\text {cycle }}=\frac{W_{n e t}}{Q_{H}}=\frac{Q_{H}-Q_{L}}{Q_{H}}=1-\frac{Q_{L}}{Q_{H}}=1-\frac{c_{p}\left(T_{4}-T_{1}\right)}{c_{p}\left(T_{3}-T_{2}\right)}$
(4) Calculate $\boldsymbol{T}_{2 s}$ from the isentropic relationship,

$$
\frac{T_{2, s}}{T_{1}}=\left(\frac{P_{2}}{P_{1}}\right)^{(k-1) / k}
$$

Get $\boldsymbol{T}_{\mathbf{2}}$ from (1).
(5) Do the same for $\boldsymbol{T}_{\mathbf{4}}$ using (2) and the isentropic relationship.
(6) substitute $\boldsymbol{T}_{\mathbf{2}}$ and $\boldsymbol{T}_{4}$ in (3) to find the cycle efficiency.

## PROBLEM STATEMENT:

Air enters the compressor of a gas-turbine power plant, at $290 \mathrm{~K}, 0.1 \mathrm{MPa}$. The ratio of the maximum to minimum pressure in the cycle is 4.0 and the maximum cycle temperature is 1200 K . Compressor and turbine isentropic efficiencies are $\mathbf{0 . 8 5}$. The compression process occurs in two stages, each having a pressure ratio of 2.0 with intercooling to $300 K$ in between. A $75 \%$ effective regenerator reduces fuel costs.
a) Determine the net work transfer $[k J / k g]$
b) Determine the thermal (first law) efficiency.


## Jet Propulsion



## Gas Turbines for Aircraft Propulsion

- gas turbines are well suited to aircraft propulsion because of their favorable power-to-weight ratio
- gases are expanded in the turbine to a pressure where the turbine work is just equal to the compressor work plus some auxiliary power for pumps and generators i.e. the net work output is zero
- typically operate at higher pressure ratios, often in the range of 10 to 25


## Conservation of Momentum


where $v_{i}^{*}$ is the velocity of the aircraft

$$
\frac{d(\text { Mom })_{x, c v}}{d t}=(\dot{M o m})_{x, \text { in }}-(\dot{\text { Mom }})_{x, o u t}+\sum F_{x}
$$

for steady flow $\Rightarrow \frac{d}{d t}=0$ and

$$
\dot{m}_{i} v_{i}^{*}-\dot{m}_{e} v_{e}^{*}+F_{T}+P_{i} A_{i}-P_{e} A_{e}=0
$$

Since the air-fuel mass ratio is high

$$
\dot{m}_{\text {fuel }} \ll \dot{m}_{i} \quad \Rightarrow \dot{m}_{i} \approx \dot{m}_{e}
$$

and

$$
P_{e} \approx P_{i} \approx P_{a t m}
$$

Therefore

$$
\begin{aligned}
F_{T} & =\dot{m}_{e} v_{e}^{*}-\dot{m}_{i} v_{i}^{*}-\underbrace{P_{a t m}\left(A_{i}-A_{e}\right)}_{\text {negligible }} \\
& =\dot{m}_{i}\left(v_{e}^{*}-v_{i}^{*}\right)
\end{aligned}
$$

Specific Impulse: $\quad I=\frac{F_{T}}{\dot{m}_{i}}=v_{e}^{*}-v_{i}^{*}=\frac{\text { thrust }}{\text { mass }}$

Propulsive Power: $\quad \dot{W}_{T}=F_{T} v_{i}^{*} \approx \dot{m}_{i}\left(v_{e}^{*}-v_{i}^{*}\right) v_{i}^{*}$

Propulsive Efficiency: $\quad \eta=\frac{\dot{W}_{T}}{\dot{Q}_{i n}}$

## Turbojet Engine



## Sections

- a-1: diffuser
- decelerates the incoming flow relative to the engine
- 1-4: gas generator
- compressor, combustor and turbine
- turbine power just enough to drive the compressor
- $\boldsymbol{P}_{\boldsymbol{T}} \gg \boldsymbol{P}_{\text {atm }}$
- 4-5: nozzle
- gases are expanded to produce a high velocity, $v_{e}^{*} \gg v_{i}^{*}$ results in a thrust
- $\boldsymbol{v}_{1}^{*} \ll \boldsymbol{v}_{a}^{*} \quad v_{1}^{*}$ is negligible
- $\boldsymbol{v}_{4}^{*} \ll \boldsymbol{v}_{5}^{*} \quad \boldsymbol{v}_{4}^{*}$ is negligible


## Afterburner



- similar to a reheat device
- produces a higher temperature at the nozzle inlet, $\boldsymbol{T}_{5}>\boldsymbol{T}_{\mathbf{4}}$
- exit velocity proportional to $v_{e}^{*} \propto \sqrt{2 c_{p}\left(T_{4}-T_{e}\right)}$
- afterburner is used to increase $\boldsymbol{T}_{4}$ to $\boldsymbol{T}_{5}$
- similar to a reheat device
- produces a higher temperature at the nozzle inlet



## Other Types of Engines

## 1. Turbo-Prop Engine



- gas turbine drives the compressor and the propeller
- works by accelerating large volumes of air to moderate velocities
- propellers are best suited for low speed $(<300 \mathrm{mph})$ flight
- by-pass ratio of 100:1 or more
- by-pass ratio defined as:
bypass ratio $=\frac{\text { mass flow bypassing the combustion chamber }}{\text { mass flow through the combustion chamber }}$

2. Turbo-Fan Engine (Ducted Turbo-Prop Engine)


- high speed exhaust gases are mixed with the lower speed air in the by-pass resulting in a considerable noise reduction
- typically used for speeds up to 600 mph
- typical by-pass ratios are 5-6


## 3. Ramjet



## Flame holder

- compression is achieved by decelerating the high-speed incoming air in the diffuser
- aircraft must already be in flight at a high speed


## 4. Pulse Jet Engine

- similar to a ram jet but lets in a slug of air at a time and then closes a damper during the combustion stage
- used in German V1 missile
- the combustion firing rate was approximately 40 cycles/sec with a maximum flight velocity of 600 mph


## PROBLEM STATEMENT:

An airplane is flying at $950 \mathrm{~km} / \mathrm{h}$ at an altitude where the pressure is 74.26 kPa and the temperature is $\mathbf{- 2 3 . 1 5}{ }^{\circ} \mathrm{C}$. The airplane is powered by a jet engine having a maximum cycle pressure of 280 kPa and a maximum cycle temperature of $1090^{\circ} \mathrm{C}$. The air flow rate is $100 \mathrm{~kg} / \mathrm{s}$. Determine the maximum propulsive force that can be produced by the engine. Assume that the velocities at the entrance to the compressor and the exit of the turbine are negligible.


## Non-Reacting Gas Mixtures



## Introduction

- homogeneous gas mixtures are frequently treated as a single compound
- the individual properties of inert gases tend to behave as a single pure substance


## Definitions

$\boldsymbol{m}$ - total mass of a mixture
$m_{i} \quad$ - mass of the i'th component of the mixture
n - total number of moles of a mixture
$n_{i} \quad-\quad$ number of moles of the i'th component of the mixture
$\boldsymbol{X}_{\boldsymbol{i}}$ - mass fraction of the i'th component of the mixture
$\boldsymbol{Y}_{i} \quad$ - mole fraction of the i'th component of the mixture
$\tilde{M} \quad$ - molecular weight of the mixture (molar mass)
$\tilde{M}_{i}-\quad$ molecular weight of the i'th component of the mixture
$\mathcal{R} \quad$ - universal gas constant $\equiv 8.3145 \mathrm{~kJ} / \mathrm{kmole} \cdot \boldsymbol{K}$
$\boldsymbol{R}$ - gas constant for a particular gas
$\boldsymbol{R}_{\boldsymbol{i}} \quad-\quad$ gas constant of the i'th component of the mixture
$\boldsymbol{P}$ - mixture pressure
$\boldsymbol{P}_{\boldsymbol{i}} \quad-\quad$ partial pressure of the i'th component of the mixture
$\boldsymbol{V}$ - mixture volume
$\boldsymbol{V}_{\boldsymbol{i}} \quad$ - partial volume of the i'th component of the mixture
$\boldsymbol{u} \quad$ - specific internal energy of the mixture
$\boldsymbol{u}_{\boldsymbol{i}} \quad-\quad$ specific internal energy of the i'th component of the mixture
$\overline{\boldsymbol{u}}$ - specific internal energy of the mixture per mole of the mixture (same as for $h, s, c_{\boldsymbol{p}}$ and $\boldsymbol{c}_{\boldsymbol{v}}$ )

## Formulations

- the total mass of a mixture, $\boldsymbol{m}$ is the sum of the masses of its components

$$
m=m_{1}+m_{2}+\ldots+m_{j}=\sum_{i=1}^{j} m_{i}
$$

- the relative amounts of the components present in the mixture can be specified in terms of mass fractions

$$
X_{i}=\frac{m_{i}}{m} \quad \Rightarrow \quad \sum_{i=1}^{j} X_{i}=1
$$

- the total number of moles in a mixture, $\boldsymbol{n}$ is the sum of the number of moles of each of the components

$$
n=n_{1}+n_{2}+\ldots+n_{j}=\sum_{i=1}^{j} n_{i}
$$

- the relative amounts of the components present in the mixture can be specified in terms of mole fractions

$$
Y_{i}=\frac{n_{i}}{n} \quad \Rightarrow \quad \sum_{i=1}^{j} Y_{i}=1
$$

- $m_{1}$ and $n_{i}$ are related by the molecular weight $\tilde{M}_{\boldsymbol{i}}$

$$
m_{i}=n_{i} \tilde{M}_{i}
$$

Therefore the total mass is

$$
m=\sum_{i=1}^{j} n_{i} \tilde{M}_{i}
$$

- the mixture molecular weight can be calculated as a mole fraction average of the component molecular weights

$$
\tilde{M}=\frac{m}{n}=\frac{\sum_{i=1}^{j} n_{i} \tilde{M}_{i}}{n}=\sum_{i=1}^{j} Y_{i} \tilde{M}_{i}
$$

- $\boldsymbol{X}_{\boldsymbol{i}}$ and $\boldsymbol{Y}_{\boldsymbol{i}}$ are also related by the molecular weights

$$
\frac{X_{i}}{Y_{i}}=\frac{\left(m_{i} / m\right)}{\left(n_{i} / n\right)}=\left(\frac{m_{i}}{n_{i}}\right)\left(\frac{n}{m}\right)=\left(\tilde{M}_{i}\right)\left(\frac{1}{\tilde{M}}\right)
$$

Therefore

$$
\frac{X_{i}}{Y_{i}}=\frac{\tilde{M}_{i}}{\tilde{M}} \quad \rightarrow \quad X_{i}=Y_{i}\left[\frac{\tilde{M}_{i}}{\sum_{i=1}^{j} Y_{i} \tilde{M}_{i}}\right]
$$

## P-V-T Relationships for Ideal Gas Mixtures

## Amagat Model (law of additive volumes)

The volume of the gas mixture is equal to the sum of the volumes each gas would occupy if it existed at the mixture temperature and pressure.

$$
V=\sum_{i=1}^{j} V_{i}
$$

## Dalton Model (law of additive pressures)

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at $\boldsymbol{T}$ and $\boldsymbol{V}$.

By combining the results of the Amagat and Dalton models i.e. (1) and (2), we obtain for ideal gas mixtures

$$
\frac{P_{i}}{P}=\frac{V_{i}}{V}=\frac{n_{i}}{n}
$$

Therefore, Amagat's law and Dalton's law are equivalent to each other if the gases and the mixture are ideal gases.

## Ideal Gas Law for a Mixture

The gas constant can be expressed as

$$
R=\sum_{i=1}^{j} X_{i} R_{i}
$$

The mixture molecular weight can be written as

$$
\tilde{M}=\sum_{i=1}^{j} \boldsymbol{Y}_{i} \tilde{M}_{i}
$$

and

$$
\begin{aligned}
& \frac{X_{i}}{\boldsymbol{Y}_{i}}=\frac{\tilde{M}_{i}}{\tilde{M}} \\
& X_{i} \boldsymbol{R}_{i}=Y_{i} \frac{\tilde{M}_{i}}{\tilde{M}} R_{i}=Y_{i} \frac{\mathcal{R}}{\tilde{M}}=Y_{i} \boldsymbol{R}
\end{aligned}
$$

The relative mass fractions and mole fractions can be related in terms of the gas constant as

$$
Y_{i}=X_{i}\left\{\frac{R_{i}}{\sum_{i=1}^{j} X_{i} R_{i}}\right\}
$$

## Mixture Properties

Extensive properties such as $\boldsymbol{U}, \boldsymbol{H}, \boldsymbol{c}_{\boldsymbol{p}}, \boldsymbol{c}_{\boldsymbol{v}}$ and $\boldsymbol{S}$ can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

$$
\begin{aligned}
U=\sum U_{i} & =\sum m_{i} u_{i}=m \sum X_{i} u_{i}=m u \\
& =\sum n_{i} \bar{u}_{i}=n \sum \boldsymbol{Y}_{i} \bar{u}_{i}=n \bar{u}
\end{aligned}
$$

where $\bar{u}$ is the specific internal energy of the mixture per mole of the mixture.

$$
\begin{aligned}
\boldsymbol{u} & =\sum \boldsymbol{X}_{i} \boldsymbol{u}_{i} \\
\boldsymbol{h} & =\sum \boldsymbol{X}_{i} \boldsymbol{h}_{i} \\
\boldsymbol{c}_{\boldsymbol{v}} & =\sum \boldsymbol{X}_{i} \boldsymbol{c}_{v_{i}} \\
\boldsymbol{c}_{p} & =\sum \boldsymbol{X}_{i} \boldsymbol{c}_{p_{i}} \\
\boldsymbol{s} & =\sum \boldsymbol{X}_{i} \boldsymbol{s}_{i}
\end{aligned}
$$

Changes in internal energy and enthalpy of mixtures

$$
\begin{aligned}
u_{2}-u_{1} & =\sum X_{i}\left(u_{2}-u_{1}\right)_{i}=\int_{T_{1}}^{T_{2}} c_{v} d T=c_{v}\left(T_{2}-T_{1}\right) \\
h_{2}-h_{1} & =\sum X_{i}\left(h_{2}-h_{1}\right)_{i}=\int_{T_{1}}^{T_{2}} c_{p} d T=c_{p}\left(T_{2}-T_{1}\right) \\
s_{2}-s_{1} & =\sum X_{i}\left(s_{2}-s_{1}\right)_{i}=c_{p} \ln \frac{T_{2}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}}
\end{aligned}
$$

These relationships can also be expressed on a per mole basis.

## Entropy Change Due to Mixing of Ideal Gases

- when ideal gases are mixed, a change in entropy occurs as a result of the increase in disorder in the systems
- if the initial temperature of all constituents are the same and the mixing process is adiabatic
- temperature does not change
- but entropy does

$$
\begin{aligned}
\Delta S & =-\left(m_{A} R_{A} \ln \frac{P_{A}}{P}+m_{B} R_{B} \ln \frac{P_{B}}{P}+\cdots\right) \\
& =-\sum_{i=1}^{j} m_{i} R_{i} \ln \frac{P_{i}}{P} \\
& =-\mathcal{R} \sum_{i=1}^{j} n_{i} \ln Y_{i}
\end{aligned}
$$

## Psychrometrics

- studies involving mixtures of dry air and water vapour
- for $T \leq 50^{\circ} C \quad\left(P_{\text {sat }} \leq 13 k P a\right) \Rightarrow h \approx h(T)$
- water vapour can be treated as an ideal gas



## Definitions

## Moist Air

- a mixture of dry air and water vapour where dry air is treated as if it were a pure component
- the overall mixture is given as $\Rightarrow P=\frac{m R T}{V}$


## Total Pressure

$$
\begin{aligned}
P & =P_{a}+P_{w} \\
P_{a} & =\frac{m_{a} R_{a} T}{V} \\
P_{w} & =\frac{m_{w} R_{w} T}{V}
\end{aligned}
$$

where $\boldsymbol{P}_{\boldsymbol{a}}$ is the partial pressure of air and $\boldsymbol{P}_{\boldsymbol{w}}$ is the partial pressure of water vapour. Typically $\boldsymbol{m}_{\boldsymbol{w}} \ll \boldsymbol{m}_{\boldsymbol{a}}$.

## Relative Humidity - $\phi$

$$
\phi=\frac{P_{w}(T)}{P_{s a t}(T)}=\frac{\text { vapour pressure at the prevailing } \mathrm{T}}{\text { saturation pressure at the prevailing } \mathrm{T}}
$$

If $\boldsymbol{P}_{\boldsymbol{w}}=\boldsymbol{P}_{\text {sat }}(\boldsymbol{T})$ the mixture is said to be saturated.

## Specific Humidity (Humidity ratio) - $\omega$

$$
\begin{aligned}
\omega & =\frac{m_{w}}{m_{a}}=\frac{\text { mass of water vapour }}{\text { mass or air }} \\
& =\frac{\tilde{M}_{w} n_{w}}{\tilde{M}_{a} n_{a}}=\frac{\tilde{M}_{w}\left(P_{w} V / \mathcal{R} T\right)}{\tilde{M}_{a}\left(P_{a} V / \mathcal{R} T\right)} \\
& =\left(\frac{\tilde{M}_{w}}{\tilde{M}_{a}}\right)\left(\frac{P_{w}}{P_{a}}\right) \\
& =0.622\left(\frac{P_{w}}{P_{a}}\right)
\end{aligned}
$$

In addition $\boldsymbol{\omega}$ can be written as

$$
\omega=0.622\left(\frac{P_{w}}{P_{a}}\right)=0.622\left(\frac{P_{w}}{P-P_{w}}\right)=0.622\left(\frac{\phi P_{s a t}}{P-\phi P_{s a t}}\right)
$$

which can be rearranged in terms of relative humidity

$$
\phi=\frac{P \omega}{P_{s a t}\left(\omega+\frac{\tilde{M}_{w}}{\tilde{M}_{a}}\right)}=\frac{P \omega}{P_{s a t}(\omega+0.622)}
$$

Dry Bulb Temperature - the temperature measured by a thermometer placed in a mixture of air and water vapour

## Wet Bulb Temperature

- thermometer surrounded by a saturated wick
- if air/water vapour mixture is not saturated, some water in the wick evaporates and diffuses into the air $\rightarrow$ cooling the water in the wick
- as the temperature of the water drops, heat is transferred to the water from both the air and the thermometer

- the steady state temperature is the wet-bulb temperature

Sling Psychrometer - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. $\boldsymbol{T}_{\boldsymbol{D}}$ and $\boldsymbol{T}_{\boldsymbol{W}}$ are sufficient to fix the state of the mixture.

## The Psychrometric Chart


where the dry bulb temperature is the temperature measured by a thermometer place in the mixture and the wet bulb temperature is the adiabatic saturation temperature.

## An Adiabatic Saturator

How can we measure humidity?


## Conservation of Mass

$$
\begin{align*}
\dot{m}_{a, 1} & =\dot{m}_{a, 3} & & \text { air }  \tag{1}\\
\dot{m}_{w, 1}+\dot{m}_{w, 2} & =\dot{m}_{w, 3} & & \text { water } \tag{2}
\end{align*}
$$

## Conservation of Energy

$$
\begin{equation*}
(\dot{m} h)_{a, 1}+(\dot{m} h)_{w, 1}+(\dot{m} h)_{w, 2}=(\dot{m} h)_{a, 3}+(\dot{m} h)_{w, 3} \tag{3}
\end{equation*}
$$

By definition

$$
\begin{align*}
& \omega_{1}=\left(\frac{\dot{m}_{w}}{\dot{m}_{a}}\right)_{1}  \tag{4}\\
& \omega_{3}=\left(\frac{\dot{m}_{w}}{\dot{m}_{a}}\right)_{3} \tag{5}
\end{align*}
$$

From (2) and (1)

$$
\left(\frac{\dot{m}_{w, 2}}{\dot{m}_{a, 1}}\right)=\left(\begin{array}{c}
\underbrace{\frac{\dot{m}_{w, 3}}{\dot{m}_{a, 1}}}_{\dot{m}_{a, 3}})-\left(\frac{\dot{m}_{w, 1}}{\dot{m}_{a, 1}}\right)=\omega_{3}-\omega_{1} .
\end{array}\right.
$$

Dividing (3) by $\dot{m}_{a, 1}$ and noting $m_{a_{1}}=m_{a_{3}}$ and $\frac{m_{w_{2}}}{m_{a_{1}}}=\omega_{3}-\omega_{1}$

$$
\begin{align*}
& h_{a, 1}+\omega_{1} h_{w, 1}+\left(\omega_{3}-\omega_{1}\right) h_{w, 2}=h_{a, 3}+\omega_{3} h_{w, 3}  \tag{6}\\
& \omega_{1}=\frac{\left(h_{a, 3}-h_{a, 1}\right)+\omega_{3}\left(h_{w, 3}-h_{w, 2}\right)}{\left(h_{w, 1}-h_{w, 2}\right)}
\end{align*}
$$



If we assume:
i) air is an ideal gas and $\left(h_{a, 3}-h_{a, 1}\right)=c_{p_{a}}\left(T_{3}-T_{1}\right)$
ii) $\quad\left(h_{w, 3}-h_{w, 2}\right)=h_{g}-h_{f}=h_{f g}\left(T_{3}\right)$
iii) $\quad h_{w, 1} \approx h_{g}\left(T_{1}\right)$
iv) $\quad h_{w, 2}=h_{f}\left(T_{2}\right)=h_{f}\left(T_{3}\right)$
then we can write $\boldsymbol{\omega}_{1}$ as a function of $\boldsymbol{T}_{\mathbf{1}}$ and $\boldsymbol{T}_{\mathbf{3}}$ only

$$
\omega_{1}=\frac{c_{p_{a}}\left(T_{3}-T_{1}\right)+\omega_{3} h_{f g}\left(T_{3}\right)}{h_{g}\left(T_{1}\right)-h_{f}\left(T_{3}\right)}
$$

## PROBLEM STATEMENT:

Outdoor air at $\boldsymbol{T}_{1}=10{ }^{\circ} \mathrm{C}$ and $\phi=30 \%$ is first to be heated to $\boldsymbol{T}_{2}=22{ }^{\circ} \mathrm{C}$ and then humidified to $\boldsymbol{T}_{3}=25^{\circ} \mathrm{C}$ and $\phi_{3}=60 \%$ at atmospheric pressure. The volumetric flow rate is $\dot{V}=45 \mathrm{~m}^{3} / \mathrm{min}$.
i) find the heating requirement, $\dot{Q}$
ii) find the mass flow rate of steam, $\dot{m}_{\text {steam }}$ required to complete the process.
iii) what would you expect if liquid water was sprayed instead of steam?


## PROBLEM STATEMENT:

A mixture of 5 kg carbon dioxide and 10 kg nitrogen is at $27^{\circ} \mathrm{C}$ and 101.325 kPa . Determine:
a) the volumetric analysis [ $\%$ by volume] of this mixture
b) the specific heat of the mixture, $c_{v}, c_{p}[k J / k g \cdot K]$ and $\bar{c}_{v}, \bar{c}_{p}[k J / k m o l \cdot K]$
c) the heat transfer $[k J]$ to reduce the temperature to $0^{\circ} C$,
if the mixture is confined in a rigid tank
d) the increase in availability $[\boldsymbol{k J}]$ of the mixture during this cooling process

## Reacting Gas Mixtures



## Definitions

## Combustion Process:

- a fuel made up of hydrocarbons is said to have burned completely if:
- all the carbon present in the fuel is burned to carbon dioxide
- all the hydrogen is burned to water
- if the conditions are not fulfilled the combustion process is incomplete


## Combustion Reactions:

reactants $\rightarrow$ products
or
fuel + oxidizer $\rightarrow$ products

- in all cases the mass is conserved
mass of products $=$ mass of reactants

Fuels:

- hydrocarbon fuels exist as liquids, gases and solids
- liquids $\rightarrow$ gasoline - octane, $\mathrm{C}_{8} \mathrm{H}_{18}$
- gases $\rightarrow$ methane, $\boldsymbol{C H}_{4}$
- solids $\rightarrow$ coal


## Combustion Air:

- oxygen is required in every combustion reaction
- dry air is considered to be

$$
\left.\begin{array}{c}
21 \% \text { oxygen } \\
79 \% \text { nitrogen }
\end{array}\right\} \text { on a molar basis } \quad \begin{aligned}
& \text { molar ratio }=\frac{n_{N_{2}}}{n_{O_{2}}}=\frac{0.79}{0.21}=3.76
\end{aligned}
$$

1 mole of air can then be written as $\left[0.21 \mathrm{O}_{2}+0.79 \mathrm{~N}_{2}\right]$
For convenience, we typically refer to air as $\left[O_{2}+3.76 N_{2}\right]$ which is actually 4.76 moles of air.

## Air-Fuel Ratio:

$$
\frac{\text { mass of air }}{\text { mass of fuel }}=\frac{\text { moles of air } \times \tilde{M}_{\text {air }}}{\text { moles of fuel } \times \tilde{M}_{\text {fuel }}}
$$

$$
A F=\overline{A F}\left(\frac{\tilde{M}_{a i r}}{\tilde{M}_{f u e l}}\right)
$$

where:

$$
\begin{array}{ll}
\boldsymbol{A F} & \text { - air fuel ratio on a mass basis } \\
\overline{\boldsymbol{A F}} & \text { - air fuel ratio on a molar basis } \\
\tilde{\boldsymbol{M}}_{\text {air }} & =28.97 \mathrm{~kg} / \mathrm{kmol}
\end{array}
$$

## Theoretical or Stoichiometric Air:

- the minimum amount of air that supplies sufficient oxygen for complete combustion of all carbon and hydrogen in the fuel - referred to as stoichiometric, $100 \%$ stoichiometric or theoretical


## Equivalence Ratio:

- defined as

$$
\Phi=\frac{F A_{\text {actual }}}{F A_{\text {theoretical }}}=\frac{A F_{\text {theoretical }}}{A F_{\text {actual }}}
$$

mass of air theoretical

$$
=\frac{\text { mass of fuel }}{\frac{\text { mass of air actual }}{\text { mass of fuel }}}
$$

$$
=\frac{\text { mass of air theoretical }}{\text { mass of air actual }}
$$

- if the equivalence ratio is:
$-<1 \rightarrow$ lean mixture (excess air)
$->1 \rightarrow$ rich mixture (not enough air)


## Conservation of Energy for Reacting Systems

## Enthalpy of Formation

- when chemical reactions occur, reactants disappear and products are formed $\rightarrow$ differences cannot be calculated for all substances involved
- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure
$-T_{r e f}=25^{\circ} \mathrm{C} \rightarrow 298 \mathrm{~K}$
- $P_{r e f}=1 \mathrm{~atm}$
- $h=0$ assigned to elements in their most stable form i.e. $\mathrm{O}_{2}, \mathrm{~N}_{2}, C$, etc.
- Enthalpy of Formation: the energy released or absorbed when a compound is formed from its stable elements at STP

where $\bar{h}_{f}^{o}$ is the enthalpy of formation.
Taking an energy balance over the combustion chamber shown above, we obtain

$$
\underbrace{a \bar{h}_{A}^{o}+b \bar{h}_{B}^{o}+c \bar{h}_{C}^{o}}_{\text {generally }=0}+\bar{h}_{f}^{o} \longrightarrow \bar{h}_{A B C}^{o}
$$

The left side of the equation is typically zero because $\boldsymbol{h}=\mathbf{0}$ for elements in their stable form. The sign of $\bar{h}_{f}^{o}$ indicates the direction of heat flow; +ve is endothermic and -ve is exothermic.

In general

$$
\bar{h}_{f}^{o}=\bar{h}_{c o m p}^{o}-\sum \bar{n}_{i} \bar{h}_{i}^{o} \quad(k J / k m o l)
$$

where

$$
\begin{aligned}
\bar{n}_{i}= & \# \text { of moles of i'th elemental substance in } \\
& \text { forming a single mole of compound (unitless) }
\end{aligned}
$$

## Effects of Non-Standard Temperature

$$
\bar{h}(T, P)=\bar{h}_{f}^{o}+\underbrace{\left(\bar{h}_{T, P}-\bar{h}_{T=25{ }^{\circ} C, P=1 \mathrm{~atm}}^{o}\right)}_{\Delta \bar{h} \text { at known temperatures }}
$$

where
$\bar{h}_{f}^{o} \quad$ is the heat resulting from a chemical change at $T=25^{\circ} C$ and $P=1 \mathrm{~atm}$
$\Delta \bar{h}$ is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $\boldsymbol{T}_{\text {ref }}=25^{\circ} \mathrm{C}$

## Effects of Non-Standard Pressure

$$
\bar{h}(T, P)=\bar{h}_{f}^{o}+\bar{h}_{T, P}-\bar{h}_{T=25{ }^{\circ} C}^{o}-P \bar{v}
$$

but for an ideal gas

$$
P \bar{v}=\mathcal{R} T
$$

This allows us to write the pressure in terms of temperature.

$$
\bar{h}(T, P)=\bar{h}_{f}^{o}+\underbrace{\left(\bar{h}_{T, P}-\bar{h}_{T=25{ }^{\circ} C}^{o}-\mathcal{R} T\right)}_{\Delta \bar{h} \text { at known temperatures }}
$$

## Enthalpy of Combustion

- Enthalpy of Combustion: the difference between the enthalpy of the products and the enthalpy of the reactants where complete combustion occurs at a given temperature and pressure

$$
\begin{aligned}
Q & =\sum(m h)_{P}-\sum(m h)_{R}=\underbrace{H_{P}\left(T_{P}\right)-H_{R}\left(T_{R}\right)}_{H_{R P}} \\
Q & =\sum(n \bar{h})_{P}-\sum(n \bar{h})_{R}=\underbrace{\bar{H}_{P}\left(T_{P}\right)-\bar{H}_{R}\left(T_{R}\right)}_{\bar{H}_{R P}}
\end{aligned}
$$

where

$$
\bar{h}_{c}=H_{R P} / \text { kmol of fuel }
$$


with:

$$
\begin{aligned}
& +v e Q \Rightarrow \text { endothermic } \\
& -v e Q \Rightarrow \text { exothermic }
\end{aligned}
$$

## Heating Value

- two values are used
- HHV: higher heating value - obtained when all the water formed by combustion is a liquid at the reference temperature
- LHV: lower heating value - obtained when all the water formed by combustion is a vapour as an ideal gas in the mixture of the products
- the HHV exceeds the LHV by the energy required to vaporize the liquid formed
- Table 15.3 lists HHV and LHV for commonly used fuels

$$
\begin{aligned}
H H V & =L H V-\frac{m_{H_{2} \mathrm{O}}}{m_{f u e l}} \cdot\left(h_{f g}\right)_{\mathrm{H}_{2} \mathrm{O}} \\
& =L H V-\cdot \frac{(n \cdot \tilde{M})_{\mathrm{H}_{2} \mathrm{O}}}{(n \cdot \tilde{M})_{f u e l}} \cdot\left(h_{f g}\right)_{\mathrm{H}_{2} \mathrm{O}}
\end{aligned}
$$

where

$$
\begin{aligned}
h_{f g}\left(25^{\circ} C\right) & =2,442.3 \mathrm{~kJ} / \mathrm{kg} \\
\tilde{M}_{\mathrm{H}_{2} \mathrm{O}} & =18.015 \mathrm{~kg} / \mathrm{kmol}
\end{aligned}
$$

## Adiabatic Flame Temperature



- if the system is perfectly insulated it cannot dispose of the LHV and the LHV goes into heating the products above the reference temperature
- under adiabatic conditions, the maximum temperature attained by the products when combustion is complete is called the adiabatic flame or adiabatic combustion temperature

$$
\begin{aligned}
& H_{P}\left(T_{a d}\right)=H_{R}\left(T_{R}\right) \\
& \sum_{P} n_{P}(\bar{h}_{f}^{o}+\underbrace{\overline{\boldsymbol{h}}-\bar{h}^{0}}_{\Delta \bar{h}})_{P}=\sum_{R} n_{R}(\bar{h}_{f}^{o}+\underbrace{\overline{\boldsymbol{h}}-\bar{h}^{0}}_{\Delta \bar{h}})_{R}
\end{aligned}
$$

We need to collect terms based on what we know or can readily calculate and what we do not know, i.e. terms that are a function of $\boldsymbol{T}_{a d}$.

$$
\begin{aligned}
\sum_{P} \underbrace{n_{P}(\bar{h})_{P}}_{\begin{array}{c}
\text { sensible heat } \\
\text { function of } T_{a d}
\end{array}}= & \sum_{R} \underbrace{n_{R}\left(\bar{h}-\bar{h}^{o}\right)_{R}-\left(-\sum_{P} n_{P}\left(\bar{h}^{o}\right)_{P}\right)}_{\begin{array}{c}
\text { sensible heat } \\
\text { function of } T_{R} \text { or } T_{r e f}
\end{array}} \\
& +\sum_{R} \underbrace{n_{R}\left(\bar{h}_{f}^{o}\right)_{R}-\sum_{P} n_{P}\left(\bar{h}_{f}^{o}\right)_{P}}_{\begin{array}{r}
\text { chemical heat } \\
\text { function of } T_{R} \text { or } T_{r e f}
\end{array}}
\end{aligned}
$$

Step 1: Calculate the right hand side based on known values of $\boldsymbol{T}_{\boldsymbol{R}}$ and $\boldsymbol{T}_{\boldsymbol{r e f}}$.

Step 2: Calculate the left hand side based on a guessed value of $\boldsymbol{T}_{\boldsymbol{a d}}$.

Step 3: Repeat Step 2, until LHS = RHS.

## Dew Point

- since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapour in the form of gaseous products can be significant
- if the gaseous products of combustion are cooled at constant mixture pressure the dew point temperature is reached when water vapour begins to condense
- since corrosion of duct work, mufflers etc. can occur, the knowledge of dew point temperature is important


## Evaluation of Entropy for Reacting Systems

The 2nd law entropy equation can be written as

$$
\underbrace{S_{i n}-S_{\text {out }}}_{\text {due to heat \& mass transfer }}+\underbrace{S_{g e n}}_{\text {generation }}=\underbrace{\Delta S_{\text {system }}}_{\text {change in entropy }}
$$

For a closed system, such as a combustion process, the entropy balance on the system can be written as

$$
\sum \frac{Q_{i}}{T_{i}}+S_{g e n}=S_{P}-S_{R}
$$

- a common datum must be used to assign entropy values for each substance involved in the reaction
- an entropy of 0 for pure crystalline substances is obtained at absolute zero
- the entropy relative to this datum is called absolute entropy
- absolute entropy at 1 atm and temperature $\boldsymbol{T}$ is denoted as $\boldsymbol{s}^{o}(\boldsymbol{T})$ or $\overline{\boldsymbol{s}}^{o}(\boldsymbol{T})$ for a per unit mass or per mole basis
- while $\bar{h}$ was only a function of temperature for ideal gases, we must account for the effects of both $\boldsymbol{T}$ and $\boldsymbol{P}$ in entropy
- the entropy at any value of $\boldsymbol{T}$ and $\boldsymbol{P}$ can be calculated as

$$
\bar{s}(T, P)=\underbrace{\bar{s}^{o}(T)}_{\text {tables }}-\mathcal{R} \ln \left(\frac{P_{i}}{P_{\text {ref }}}\right)
$$

where

$$
\begin{aligned}
P_{r e f} & =1 \mathrm{~atm} \\
P_{i} & =\text { partial pressure of } i^{\prime} \text { th component } \\
\mathcal{R} & =8.31451 \mathrm{~kJ} / \mathrm{kmol} \cdot K
\end{aligned}
$$

- the partial pressure $P_{i}$ can also be written as

$$
\boldsymbol{P}_{i}=\boldsymbol{Y}_{i} \boldsymbol{P}
$$

and

$$
\bar{s}\left(T, P_{i}\right)=\bar{s}_{i}^{o}(T)-\mathcal{R} \ln \left(\frac{Y_{i} P}{P_{r e f}}\right)
$$

where $\boldsymbol{P}$ is the mixture pressure and $\boldsymbol{Y}_{\boldsymbol{i}}$ is the mole fraction of the $\boldsymbol{i}^{\prime} \boldsymbol{t} \boldsymbol{h}$ component.

## PROBLEM STATEMENT:

Liquid octane $\left(\boldsymbol{C}_{8} \boldsymbol{H}_{18}\right)$ enters a steady-flow combustion chamber at $25^{\circ} \mathrm{C}$ and 1 atm at a rate of $0.4 \mathrm{~kg} / \mathrm{min}$. It is burned with $\mathbf{5 0 \%}$ excess air that also enters at $25^{\circ} \mathrm{C}$. If it is assumed that $T_{0}=298 \mathrm{~K}$, the products leave the combustion chamber at 1 atm , the combustion process is complete and that all the $\mathrm{H}_{2} \mathrm{O}$ in the products is in liquid form. Determine the entropy generation rate $[k J /(\min \cdot K)]$ and the irreversibility $[\boldsymbol{k W}]$

