Equations of State

ReadingProblems $3-6, 3-7, 4-3 \rightarrow 4-5$ 3-54, 3-64, 3-80, 4-25, 4-39, 4-426-6 $7-3, 7-4, 7-7 \rightarrow 7-10$ 7-43, 7-116, 7-166, 7-193

Ideal Gas

- When is the ideal gas assumption viable?
 - for a low density gas where:
 - * the gas particles take up negligible volume
 - * the intermolecular potential energy between particles is small
 - * particles act independent of one another
 - Under what conditions can it be used?
 - * low density
 - * high temperatures considerably in excess of the saturation region
 - * at very low pressures
- for any gas whose equation of state is exactly

$$Pv = RT$$

the specific internal energy depends only on temperature

u = u(T)

• the specific enthalpy is given by

$$h = u + Pv$$

where

$$h(T) = u(T) + RT$$

Note: Since u = u(T), and R is a constant, enthalpy is only a function of temperature.

• for a ideal gas

$$c_v = rac{du}{dT} \Rightarrow c_v = c_v(T) \ only$$

$$c_p \;\;=\;\; {dh\over dT} \;\;\Rightarrow\;\; c_p = c_p(T) \;\; only$$

From the equation for enthalpy,

$$RT = h(T) - u(T)$$

If we differentiate with respect to T

$$R=rac{dh}{dT}-rac{du}{dT}$$
 $R=c_p-c_v$

Is Water Vapor an Ideal Gas?

- Figure 3-49 can be used to determine the regions where water vapor behaves as an ideal gas
 - YES at pressures below 10 kPa regardless of temperature
 - NO at high pressure
 - what about at atmospheric pressure and temperature ($P_{atm} \approx 100 \ kPa$ and $T_{atm} < 50 \ ^{\circ}C$)? Figure 3-49 would indicate YES
 - * look at the T-s diagram for water: h pprox constant for atmospheric conditions
 - * for an ideal gas: h = h(T) since h only varies with respect to T, it must behave like an ideal gas

In Summary

For an ideal gas with constant c_p and c_v

 $egin{array}{rcl} Pv &=& RT \ u_2 - u_1 &=& c_v(T_2 - T_1) \ h_2 - h_1 &=& c_p(T_2 - T_1) \end{array}$

There are 3 forms of a change in entropy as a function of T & v, T & P, and P & v.

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$
$$= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$
$$= c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{P_2}{P_1}$$

$$R = c_p - c_v$$

Isentropic and Polytropic Processes for Ideal Gases

Gibb's equation can be written as

$$Tds = du + Pdv = c_v dT + Pdv = 0 \tag{1}$$

The definition of enthalpy is

$$h = u + Pv$$

Taking the derivative yields

$$dh = \underbrace{du + Pdv}_{\equiv Tds} + vdP$$

$$dh = Tds + vdP \Rightarrow Tds = 0 = dh - vdP$$

$$c_p dT - v dP = 0 \tag{2}$$

Equating Eqs. (1) and (2) through the dT term gives

$$\frac{dP}{P} = -\frac{c_p}{c_v} \frac{dv}{v} \tag{3}$$

Integrating (3) from its initial state to a final state

$$egin{array}{rcl} \ln P ig|_1^2 &=& -k \ln v ig|_1^2 \ \ln P_1 - \ln P_2 &=& k [\ln v_2 - \ln v_1] \ \ln \left(rac{P_1}{P_2}
ight) &=& \ln \left(rac{v_2}{v_1}
ight)^k \end{array}$$

take exp of each side

$$P_2v_2^k = P_1v_1^k$$

where $k=rac{c_p}{c_v}$

The product of $P \cdot v^k$ 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

$$\boxed{rac{T_2}{T_1} = \left(rac{v_1}{v_2}
ight)^{k-1} = \left(rac{P_2}{P_1}
ight)^{(k-1)/k}}$$

Relative Pressure and Relative Specific Volume

- typically we assume specific heat to be constant with respect to temperature
- but when temperature swings are significant, this assumption can lead to inaccuracies, i.e.

$T\left(K ight)$	$c_p \left(kJ/kg \cdot K ight)$	% difference	
300	1.0057		
1000	1.1417	13.5	
2500	1.688	67.8	

- the relative pressure and relative volume tables (C&B Table A-17), provide an accurate way of including the temperature effects on specific heat for ideal gases during isentropic processes
- note: the specific heat ratio term given by $k = c_p/c_v$ will also be influenced by temperature
- Procedure:
 - given T_1, P_1 and P_2 for an isentropic process
 - determine P_{r1} at T_1 from Table A-17
 - calculate P_{r2} , where

$$\left(\frac{P_2}{P_1}\right)_{s=const} = \frac{P_{r2}}{P_{r1}}$$

- read T_2 from Table A-17 for the calculated value of P_{r2}
- use a similar procedure if volume is known instead of pressure, where

$$\left(rac{v_2}{v_1}
ight)_{s=const} = rac{v_{r2}}{v_{r1}}$$

Sign Convention

There are many potential sign conventions that can be used.

Cengel Approach

Heat Transfer: heat transfer to a system is positive and heat transfer from a system is negative.Work Transfer: work done by a system is positive and work done on a system is negative.



Culham Approach

Anything directed into the system is positive, anything directed out of the system is negative.



Incompressible Liquids

- a substance whose volume cannot be changed
- no substance is truly incompressible, but this model is good for most liquids and solids

State Postulate

- the number of independent intensive thermodynamic properties is equal to the number of relevant <u>reversible</u> work modes plus one.
- the "plus one" is for the independent control on energy through heat transfer
- we know that for a *simple* (has only one work mode), *compressible* (the work mode is *Pdv* work) substance
 - 2 thermodynamic properties will fix the rest
 - * list of intensive properties includes, T, u, P, v, s
 - * state postulate says two will fix the rest, i.e. if u and v are known, the equations of state are

$$egin{array}{rcl} T &=& T(u,v) \ P &=& P(u,v) \ s &=& s(u,v) \end{array}$$

Hence, if the substance is assumed to be incompressible, then its internal energy, for example, cannot be varied independently by work transfer \longrightarrow but it can be varied by heat transfer at constant volume, i.e. Pdv = 0 since dv = constant. There are no reversible work modes.

In summary

$$egin{array}{rcl} u_2 - u_1 &=& \overline{c} \; (T_2 - T_1) \ h_2 - h_1 &=& (u_2 - u_1) + v(P_2 - P_1) \ s_2 - s_1 &=& \overline{c} \; \ln(T_2/T_1) \ c_p = c_v = \overline{c} \end{array}$$

Review of First and Second Laws of Thermodynamics



WORK & HEAT TRANSFER:

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



First Law of Thermodynamics

Control Mass (Closed System)

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:

$$\left\{egin{array}{c} Initial \ Energy \ Energy \ E_1 \end{array}
ight\} + \left\{egin{array}{c} Energy \ energy \ loss \ Q_{1-2} \end{array}
ight\} = \left\{egin{array}{c} Final \ Energy \ E_2 \end{array}
ight\}$$

$$E_1 + W_{1-2} - Q_{1-2} = E_2$$

Control Volume Analysis (Open System)

CONSERVATION OF MASS:



CONSERVATION OF ENERGY:

The 1st law states:

$$E_{CV}(t) + \Delta Q + \Delta W_{shaft} + (\Delta E_{IN} - \Delta E_{OUT}) + (\Delta W_{IN} - \Delta W_{OUT}) = E_{CV}(t + \Delta t) \quad (1)$$

What is flow work?

$$\Delta m_{IN} \;=\;
ho_{IN} \overbrace{A_{IN} \, v_{IN}^* \, \Delta t}^{volume}$$



$$egin{array}{rcl} \Delta W_{IN} &=& F \, \cdot \, distance \ &=& \displaystyle \underbrace{P_{IN} \, A_{IN}}_{F} \, \cdot \, \underbrace{v_{IN}^{*} \, \Delta t}_{\Delta s} \ &=& \displaystyle rac{P_{IN} \, \Delta m_{IN}}{
ho_{IN}} \end{array}$$

with

$$v = \frac{1}{
ho}$$

 $\Delta W_{IN} = (P \ v \ \Delta m)_{IN} \quad \rightarrow \text{flow work}$ (2)

Similarly

$$\Delta W_{OUT} = (P \ v \ \Delta m)_{OUT} \tag{3}$$

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

$$E_{CV}(t + \Delta t) - E_{CV}(t) = \Delta Q + \Delta W_{shaft} + \Delta m_{IN}(e + Pv)_{IN} - \Delta m_{OUT}(e + Pv)_{OUT}$$
(4)



Equation 4 can also be written as a rate equation ightarrow divide through by Δt and take the limit as $\Delta t
ightarrow 0$

$$rac{d}{dt}E_{CV}=\dot{Q}+\dot{W}_{shaft}+[\dot{m}(e+Pv)]_{IN}-[\dot{m}(e+Pv)]_{OUT}$$

where:

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

Note that:

$$egin{array}{rcl} e+Pv &=& \underbrace{u+Pv}_{}+rac{(v^*)^2}{2}+gz \ &=& h(enthalpy)\,+\,KE\,+\,PE \end{array}$$

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).

$$egin{array}{rcl} {\cal P}_m&=&m_2-m_1=0~{
m (conservation of mass)} \ {\cal P}_E&=&E_2-E_1=0~{
m (conservation of energy)}
ightarrow 1{
m st}~{
m law} \ {\cal P}_S&=&S_2-S_1\geq 0~
ightarrow 2{
m nd}~{
m law} \end{array}$$

The second law states:

 $(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0$

where $\Delta \equiv final - initial$

- 3. **Reference:** In a prefect crystal of a pure substance at T = 0 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 S = 0. That is, there is no uncertainty about the microscopic state.
- 4. *Heat:* Energy transfer as heat takes place as work at the microscopic level but in a random, <u>disorganized</u> way. This type of energy transfer carries with it some chaos and thus results in entropy flow in or out of the system.
- 5. Work: Energy transfer by work is microscopically organized and therefore entropy-free.

Second Law Analysis for a Control Volume



where:

FR	-	fluid reservoir
TER	-	thermal energy reservoir
MER	-	mechanical energy reservoir

For the isolated system

$$egin{aligned} & (\Delta S)_{sys} + (\Delta S)_{sur} = \mathcal{P}_{S_{1-2}} \geq 0 \ & \ & \Delta S_{CV} - s_A m^A_{1-2} + s_B m^B_{1-2} - rac{Q^A_{1-2}}{T^A_{TER}} + rac{Q^B_{1-2}}{T^B_{TER}} = \mathcal{P}_{S_{1-2}} \end{aligned}$$

or as a rate equation

$$\left(rac{dS}{dt}
ight)_{CV} = \left(s\dot{m} + rac{\dot{Q}}{T_{TER}}
ight)_{IN} - \left(s\dot{m} + rac{\dot{Q}}{T_{TER}}
ight)_{OUT} + \dot{\mathcal{P}}_S$$

This can be thought of as

accumulation = IN - OUT + generation

Availability



Second Law Analysis of Systems

AVAILABILITY:

- the theoretical maximum amount of work that can be obtained from a system at a given state P_1 and T_1 when interacting with a reference atmosphere at the constant pressure and temperature P_0 and T_0 .
- also referred to as "exergy".

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 the temperature and pressure of the dead state.
- 3. Availability of a system is 0 at its **dead state** when $T = T_0$ and $P = P_0$.
- 4. Unless otherwise stated, assume the dead state to be:

 $P_0 = 1 atm$ $T_0 = 25^{\circ}C$

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

$$\underbrace{REVERSIBLE WORK}_{W_{rev}} = \underbrace{USEFUL WORK}_{W_{useful}} + \underbrace{IRREVERSIBILITY}_{X_{des}}$$





Control Mass Analysis



• we know

$$W_{rev} = W_{useful} + X_{des}$$

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

$$W_{actual} = W_{useful} + W_{sur}$$

• where W_{sur} is the part of the work done against the surroundings to displace the ambient air

$$W_{sur} = P_0(V_2 - V_1) = -P_0(V_1 - V_2)$$

this is unavoidable → this is not useful work. Nothing is gained by pushing the atmosphere away.

To find W_{actual} , from the 1st law

$$E_1-Q-W_{actual}=E_2 \ \
ightarrow \ \ Q=E_1-E_2-W_{actual}$$

From the 2nd law

$$egin{array}{rcl} S_{gen}&=&\Delta S_{system}+\Delta S_{sur}\geq 0 \ &=&S_2-S_1+rac{Q}{T_0} \end{array}$$

But from the 1st law balance we know

$$rac{Q}{T_0} = rac{E_1 - E_2 - W_{actual}}{T_0}$$

and when we combine this with the 2nd law

$$S_{gen}=S_2-S_1+rac{E_1-E_2-W_{actual}}{T_0}$$

which leads to

$$W_{actual} = (E_1 - E_2) + T_0(S_2 - S_1) - T_0S_{gen}$$

or by reversing the order of $old S_2$ and $old S_1$

$$W_{actual} = (E_1 - E_2) - T_0(S_1 - S_2) - T_0S_{gen}$$

But we also know that

$$W_{useful} = W_{actual} - W_{sur}$$

therefore

$$W_{useful} = (E_1 - E_2) - T_0(S_1 - S_2) + \underbrace{P_0(V_1 - V_2)}_{-W_{sur}} - T_0S_{gen}$$

and

$$egin{array}{rll} W_{rev} &=& W_{useful} + X_{des} \ &=& W_{actual} - W_{sur} + X_{des} \end{array}$$

where

$$X_{des} = T_0 S_{gen}$$

Therefore

$$W_{rev} = (E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)$$

In summary

$$egin{array}{rll} W_{actual}&=&(E_1-E_2)-T_0(S_1-S_2)-T_0S_{gen}\ W_{useful}&=&(E_1-E_2)-T_0(S_1-S_2)+P_0(V_1-V_2)-T_0S_{gen}\ X&=W_{rev}&=&(E_1-E_2)-T_0(S_1-S_2)+P_0(V_1-V_2) \end{array}$$

Define

$$X = CONTROL MASS AVAILABILITY$$
$$= W_{rev} (in going to the dead state)$$
$$= (E - E_0) - T_0(S - S_0) + P_0(V - V_0)$$

where the specific availability is defined as

$$\phi = rac{X}{m}$$

Control Volume Analysis

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



From the 1st law

$$\frac{dE_{cv,0}}{dt} = -\dot{W}_{actual} - \dot{Q} + \left[\dot{m}(h + \frac{(v^*)^2}{2} + gz)\right]_{in} - \left[\dot{m}(h + \frac{(v^*)^2}{2} + gz)\right]_{out}$$
(1)

From the 2nd law

$$\frac{dS_{cv,0}}{dt} = \left(\dot{m}s + \frac{\dot{Q}^{0}}{T_{TER}}\right)_{in} - \left(\dot{m}s + \frac{\dot{Q}}{T_0}\right)_{out} + \dot{S}_{gen}$$
(2)

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

$$\dot{W}_{actual} = \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz - T_0 s \right) \right]_{in} - \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz - T_0 s \right) \right]_{out} - T_0 \dot{S}_{gen}$$

$$= \dot{m} \left[-T_0 \Delta s + \Delta h + \Delta KE + \Delta PE \right] - (T_0 \dot{S}_{gen})$$
(3)

The specific flow availability, ψ , is given as

$$\psi = -T_0(s - s_0) + (h - h_0) + \left(\frac{(v^*)^2}{2} - \frac{(v_0^{*30})^2}{2}\right) + g(z - z_0^{*0})$$
(4)

Efficiency and Effectiveness

1. First law efficiency (thermal efficiency)

$$\eta = rac{net \ work \ output}{gross \ heat \ input} = rac{W_{net}}{Q_{in}}$$

Carnot cycle

$$\eta = rac{Q_H-Q_L}{Q_H} = 1 - rac{T_L}{T_H}$$

2. Second Law Efficiency (effectiveness)

 $\eta_{2nd} = rac{net \ work \ output}{maximum \ reversible \ work} = rac{net \ work \ output}{availability}$

Turbine
$$ightarrow \ \eta_{2nd} = rac{\dot{W}/\dot{m}}{\psi_e - \psi_i}$$

Compressor
$$\rightarrow \quad \eta_{2nd} = rac{\psi_e - \psi_i}{\dot{W}/\dot{m}}$$

Heat Source
$$\rightarrow \eta_{2nd} = \frac{\dot{W}/\dot{m}}{\dot{Q}/\dot{m}\left[1 - \frac{T_0}{T_{TER}}\right]}$$

- 3. Isentropic efficiency (process efficiency)
 - (a) adiabatic turbine efficiency

$$\eta_T = rac{work \ of \ actual \ adiabatic \ expansion}{work \ of \ reversible \ adiabatic \ expansion} = rac{W_{act}}{W_S}$$

(b) adiabatic compressor efficiency

$$\eta_{C} = rac{work \ of \ reversible \ adiabatic \ compression}{work \ of \ actual \ adiabatic \ compression} = rac{W_{S}}{W_{act}}$$

Carnot Cycle



• based on a fully reversible heat engine - it does not include any of the irreversibilities associated with friction, viscous flow, etc.



Process	State Points	Description
Pump	$1 \rightarrow 2$	isentropic compression from $T_L o T_H$
Heat Supply	$2 \rightarrow 3$	to return vapour to a liquid state heat is supplied at constant temperature and pressure
Work Output	$3 \rightarrow 4$	the vapour expands isentropically from the high pressure and temperature
Condenser	$4 \rightarrow 1$	to the low pressure the vapour which is wet at 4 has to be cooled to state point 1

Practical Problems

- at state point 1 the steam is wet at T_L and it is difficult to pump water/steam (two phase) to state point 2
- can we devise a Carnot cycle to operate outside the wet vapour region



- between state points 2 and 3 the vapour must be isothermal and at different pressures this is difficult to achieve
- the high temperature and pressure at 2 and 3 present metallurgical limitations

The net effect is that the Carnot cycle is <u>not</u> feasible for steam power plants.

Rankine Cycle



Definitions

• the standard vapour cycle that excludes internal irreversibilities is called the **Ideal Rankine Cycle**



Effects of Boiler and Condenser Pressure

1. INCREASED BOILER PRESSURE:

- an increase in boiler pressure results in a higher T_H for the same T_L , therefore $\eta \uparrow$.
- but 4' has a lower quality than 4
 - wetter steam at the turbine exhaust
 - results in cavitation of the turbine blades
 - $\eta \downarrow$ plus \uparrow maintenance
- quality should be > 80 90% at the turbine exhaust



2. LOWER T_L :

• we are generally limited by the *TER* (lake, river, etc.)

eg. lake @ 15 °C + $\Delta T = 10$ °C = 25 °C resistance to HT

 $\Rightarrow P_{sat} = 3.2 \, kPa.$

- this is why we have a condenser
 - the pressure at the exit of the turbine can be less than atmospheric pressure
 - the closed loop of the condenser allows us to use treated water on the cycle side
 - but if the pressure is less that atmospheric pressure, air can leak into the condenser, preventing condensation



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 advantage is

$$\eta = rac{W_{net}\uparrow}{Q_{H}\uparrow} \;\; overall\uparrow$$

The value of \overline{T}_H , the mean temperature at which heat is added, increases, while \overline{T}_L remains constant. Therefore the efficiency increases.

- the quality of the turbine exhaust increases, hopefully where x > 0.9
- with sufficient superheating the turbine exhaust can fall in the superheated region.

Rankine Cycle with Reheat

• to improve the exhaust steam conditions, the steam can be reheated with the expansion carried out in two steps



- modern boilers can handle up to 30 MPa and a maximum temperature of $T_{max} \approx 650 \ ^\circ C$.
- newer materials, such as ceramic blades can handle temperatures up to $750 \,^{\circ}C$.

Rankine Cycle with Regeneration

- 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 (Q_H) 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.

Other Topics

"IDEAL" RANKINE CYCLE:

- too expensive to build
- requires multiple reheat and regeneration cycles
- approaches Carnot efficiency

TOPPING CYCLE (BINARY CYCLE):



• involves two Rankine cycles running in tandem with different working fluids such as mercury and water











Refrigeration Cycle



Reading $11-1 \rightarrow 11-7, 11-9$

Problems 11-11, 11-46, 11-49, 11-103

Definitions

- the 1st law of thermodynamics tells us that heat flow occurs from a hot source to a cooler sink, therefore, energy in the form of work must be added to the process to get heat to flow from a low temperature region to a hot temperature region.
- 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 coefficient of performance (COP) is given by

$$COP = rac{benefit}{cost}$$

where the benefit for a refrigeration process is the cooling load given as Q_L . This is the net benefit, i.e. heat is removed from the cold space. For a heat pump, the benefit is the heat added to the hot space, i.e. Q_H .

$$\begin{aligned} COP_{refrig} &= \frac{Q_L}{W_{in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} = \frac{1}{\frac{T_H(s_4 - s_1)}{T_L(s_3 - s_2)} - 1} \\ &= \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_L}{T_H - T_L} \end{aligned}$$

$$\begin{aligned} COP_{heat\ pump} &= \ \frac{Q_H}{W_{in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} = \frac{1}{1 - \frac{T_L}{T_H}} \\ &= \ \frac{T_H}{T_H - T_L} \end{aligned}$$

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. $\Rightarrow w_c = h_{2s} - h_1$			
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. $\Rightarrow q_H = h_{2s} - h_3$			
3-4	An irreversible throttling process in which the temperature and pressure decrease at constant enthalpy. $\Rightarrow h_3 = h_4$			
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. $\Rightarrow q_L = h_1 - h_4$			

$$\Rightarrow q_L = h_1 - h_4$$

Common Refrigerants

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

R11		
R12	CCl_2F_2	 dichlorofluoromethane used for refrigeration systems at higher temperature levels typically, water chillers and air conditioning
R22	$CHClF_2$	has less chlorine, a little better for the environment than R12used for lower temperature applications
R134a	CFH_2CF3	tetrafluorethane - no chlorine - went into production in 1991 - replacement for R12
R141b	$C_2H_3FCl_2$	dichlorofluoroethane
Ammonia	NH_3	corrosive and toxic - used in absorption systems
R744	CO_2	behaves in the supercritical region - low efficiency
R290	propane	combustible

Designation	Chemical	Ozone Depletion	Global Warming				
	Formula	Potential ¹	Potential ²				
Ozone Depleting & Global Warming Chemicals							
CFC-11	CCl_3F	1	3,400				
CFC-12	CCl_2F_2	0.89	7,100				
CFC-13	$CClF_3$		13,000				
CFC-113	$C_2F_3Cl_3$	0.81	4,500				
CFC-114	$C_2F_4Cl_2$	0.69	7,000				
CFC-115	$C_2F_5Cl_1$	0.32	7,000				
Halon-1211	CF_2ClBr	2.2-3.5					
Halon-1301	CF_3Br	8-16	4,900				
Halon-2402	$C_2F_4Br_2$	5-6.2					
carbon tetrachloride	CCl_4	1.13	1,300				
methyl chloroform	CH_3CCl_3	0.14					
nitrous oxide	N_2O		270				
Ozone Depleting & Global Warming Chemicals - Class 2							
HCFC-22	CHF_2Cl	0.048	1,600				
HCFC-123	$C_2HF_3Cl_2$	0.017	90				
HCFC-124	C_2HF_4Cl	0.019	440				
HCFC-125	C_2HF_5	0.000	3,400				
HCFC-141b	$C_2H_3FCl_2$	0.090	580				
HCFC-142b	$C_2H_3F_2Cl$	0.054	1800				
Global Warming, non-Ozone Depleting Chemicals							
carbon dioxide	CO_2	0	1				
methane	CH_4	0	11				
HFC-125	CHF_2CF_3	0	90				
HFC-134a	CFH_2CF_3	0	1,000				
HFC-152a	CH_3CHF_2	0	2,400				
perfluorobutane	C_4F_{10}	0	5,500				
perfluoropentane	C_5F_{12}	0	5,500				
perfluorohexane	C_6F_{14}	0	5,100				
perfluorotributylamine	$N(C_4F_9)_3$	0	4,300				

1 - relative to R11

2 - relative to $CO_{\mathbf{2}}$

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

Advantages

• the refrigerants can be selected to have reasonable evaporator and condenser pressures in the two or more temperature ranges

$$COP = rac{Q_L(\uparrow)}{W_{net}(\downarrow)} \; overall(\uparrow)$$



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 <u>work</u>

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 <u>heat</u>

Process



Internal Combustion Engines



IC Engines

• although most gas turbines are also IC engines, the name is usually applied to reciprocating IC engines



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 c_p and c_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.

 $MEP = rac{ ext{net work for one cycle}}{ ext{displacement volume}} = rac{W_{net}}{V_{BDC} - V_{TDC}}$

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

Otto Cycle



The Otto cycle consists of four internally reversible processes in series

- $1 \rightarrow 2$ isentropic compression or air as the piston moves from BDC to TDC
- $2 \rightarrow 3$ constant volume heat addition to the fuel/air mixture from an external source while the piston is at TDC (represents the ignition process and the subsequent burning of fuel)
- $3 \rightarrow 4$ isentropic expansion (power stroke)
- $4 \rightarrow 1$ constant volume heat rejection at BDC

$$\eta_{Otto} = 1 - r^{1-k}$$





Why not go to higher compression ratios?

- there is an increased tendency for the fuel to detonate as the compression ratio increases
- the pressure wave gives rise to engine knock
- can be reduced by adding tetraethyl lead to the fuel
- not good for the environment



Diesel Cycle

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



Aside: The Air Standard Diesel Cycle



• assumes heat addition occurs during a constant pressure process that starts with the piston at TDC

First, look at Q_L . From the 1st law

$$rac{U_4}{m}-rac{U_1}{m}=rac{Q_L}{m}=c_v(T_4-T_1)$$

Next look at Q_H

Diesel Cycle Efficiency

$$\eta_{Diesel} = 1 - rac{1}{r^{k-1}} \left(rac{1}{k}
ight) \left(rac{r_v^k - 1}{r_v - 1}
ight)$$

Where we note

$$\eta_{Diesel} = 1 - rac{1}{r^{k-1}} \underbrace{\left(rac{1}{k}
ight) \left(rac{r_v^k - 1}{r_v - 1}
ight)}_{=1 \; in \; the \; Otto \; Cycle}$$

Comparison of the Otto and the Diesel Cycle

- $\eta_{Otto} > \eta_{Diesel}$ for the same compression ratio
- <u>but</u> a diesel engine can tolerate a higher ratio since only air is compressed in a diesel cycle and spark knock is not an issue
- direct comparisons are difficult

Dual Cycle (Limited Pressure Cycle)

• this is a better representation of the combustion process in both the gasoline and the diesel engines



- 1 2 isentropic compression
- 2 3 constant volume fuel injection and initial combustion \rightarrow modelled as a reversible, constant volume heat addition
- 3 4 isobaric expansion as the fuel burns \rightarrow modelled as a reversible, isobaric heat addition
- 4 5 isentropic expansion
- 5 1 exhausting of spent gases \rightarrow modelled as a constant volume heat rejection process

Dual Cycle Efficiency

Given

$$egin{array}{rcl} r &=& rac{V_1}{V_2} = compression\ ratio \ r_v &=& rac{V_4}{V_3} = cutoff\ ratio \ r_p &=& rac{P_3}{P_2} = pressure\ ratio \end{array}$$

$$\eta_{Dual} = 1 - rac{r_p r_v^k - 1}{\left[(r_p - 1) + k r_p (r_v - 1)
ight] r^{k-1}}$$

Note: if $r_p = 1$ we get the diesel efficiency.

Stirling Cycle





Ericsson Cycle



- hardware is not complicated
- but it is very difficult to operate turbines and compressors isothermally
- can approach isothermal conditions by repeated intercooling (compressor) and repeated reheating (turbines)
- $\eta_{Ericsson} = 1 T_L/T_H$ (Carnot efficiency)



Brayton Cycle



Problems 9-100, 9-105, 9-131

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.

Some examples that typically use a closed cycle version of the gas turbine cycle are:

- power plants
- nuclear reactors

They generally see limited application because of the cost associated with moving a fluid with a high specific volume

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 Brayton cycle efficiency can be written as



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.



The **maximum temperature** in the cycle (T_3) is limited by metallurgical conditions because the turbine blades cannot sustain temperatures above 1300 K. Higher temperatures (up to 1600 K can be obtained with ceramic turbine blades). The **minimum temperature** is set by the air temperature at the inlet to the engine.

Brayton Cycle with Reheat



- turbine outlet temperature is increased with reheat $(T_6 > T_4')$, therefore potential for regeneration is enhanced
- when reheat and regeneration are used together the thermal efficiency can increase significantly

Compression with Intercooling



- 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
- but the lower temperature at the compressor exit enhances the potential for regeneration i.e. a larger ΔT across the heat exchanger

How Can We Improve Efficiency?

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

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

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

$$rac{\dot{W}}{\dot{m}} = \int_{in}^{out} v \ dP \ \Rightarrow \ ext{keep} \ v \uparrow \ ext{in turbine, keep} \ v \downarrow \ ext{in compressor}$$

This can be achieved through the use of intercooling and reheating.

Compressor
$$\longrightarrow \eta = \frac{\dot{W}_T - \dot{W}_C(\downarrow)}{\dot{Q}_{H,Total}(\uparrow)}$$
, overall (\downarrow)

Turbine
$$\longrightarrow \eta = rac{\dot{W}_T(\uparrow) - \dot{W}_C)}{\dot{Q}_{H,Total}(\uparrow)}$$
, overall (\downarrow)

The conclusion is the intercooling and/or reheating by themselves will lower η . We have to find a way to reduce \dot{Q}_H

Brayton Cycle with Regeneration



• a regenerator (heat exchanger) is used to reduce the fuel consumption to provide the required \dot{Q}_H

$$\eta = 1 - \left(rac{T_{min}}{T_{max}}
ight) (r_p)^{(k-1)/k}$$

• for a given T_{min}/T_{max} , the use of a regenerator above a certain r_p will result in a reduction of η



Regenerator Effectiveness

$$\epsilon = rac{\dot{Q}_{reg,actual}}{\dot{Q}_{reg,ideal}} = rac{h_5 - h_2}{h_5' - h_2} = rac{h_5 - h_2}{h_4 - h_2} = rac{T_5 - T_2}{T_4 - T_2}$$

Typical values of effectiveness are ≤ 0.7

Repeated intercooling, reheating and regeneration will provide a system that approximates the Ericsson Cycle which has Carnot efficiency $\left(\eta = 1 - \frac{T_L}{T_H}\right)$.



Brayton Cycle With Intercooling, Reheating and Regeneration

Compressor and Turbine Efficiencies

Isentropic Efficiencies

(1)
$$\eta_{comp} = \frac{h_{2,s} - h_1}{h_2 - h_1} = \frac{c_p(T_{2,s} - T_1)}{c_p(T_2 - T_1)}$$

(2)
$$\eta_{turb} = \frac{h_3 - h_4}{h_3 - h_{4,s}} = \frac{c_p(T_3 - T_4)}{c_p(T_3 - T_{4,s})}$$

(3)
$$\eta_{cycle} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{c_p(T_4 - T_1)}{c_p(T_3 - T_2)}$$

Given the turbine and compressor efficiencies and the maximum (T_3) and the minimum (T_1) temperatures in the process, find the cycle efficiency (η_{cycle}) .

(4) Calculate T_{2s} from the isentropic relationship,

Get T_2 from (1).

- (5) Do the same for T_4 using (2) and the isentropic relationship.
- (6) substitute T_2 and T_4 in (3) to find the cycle efficiency.

Jet Propulsion



Gas Turbines for Aircraft Propulsion

- gas turbines are well suited to aircraft propulsion because of their favorable power-to-weight ratio
- 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

$$rac{d(Mom)_{x,cv}}{dt} = (\dot{M}om)_{x,in} - (\dot{M}om)_{x,out} + \sum F_x$$

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

$$\dot{m}_iv_i^*-\dot{m}_ev_e^*+F_T+P_iA_i-P_eA_e=0$$

Since the air-fuel mass ratio is high

 $\dot{m}_{fuel} << \dot{m}_i \qquad \Rightarrow \dot{m}_i pprox \dot{m}_e$

and

$$P_e pprox P_i pprox P_{atm}$$

Therefore

$$egin{array}{rcl} F_T &=& \dot{m}_e v_e^* - \dot{m}_i v_i^* - \underbrace{P_{atm}(A_i - A_e)}_{negligible} \ &=& \dot{m}_i (v_e^* - v_i^*) \end{array}$$

Specific Impulse:
$$I = rac{F_T}{\dot{m}_i} = v_e^* - v_i^* = rac{ ext{thrust}}{ ext{mass}}$$

Propulsive Power: $\dot{W}_T = F_T \, v_i^* pprox \dot{m}_i (v_e^* - v_i^*) v_i^*$

Propulsive Efficiency: $\eta = rac{\dot{W}_T}{\dot{Q}_{in}}$

Turbojet Engine



Sections

- a-1: diffuser
 - decelerates the incoming flow relative to the engine
- 1-4: gas generator
 - compressor, combustor and turbine
 - * 1-2: isentropic compression
 - * 2-3: constant pressure heat addition
 - * 3-4: isentropic expansion through the turbine during which work is developed
 - turbine power just enough to drive the compressor
- **4-5**: nozzle
 - isentropic expansion through the nozzle, air accelerates and the pressure deceases
 - gases leave the turbine significantly higher in pressure than atmospheric pressure
 - gases are expanded to produce a high velocity, $v_e^{st} >> v_i^{st}$ results in a thrust

Afterburner



- similar to a reheat device
- produces a higher temperature at the nozzle inlet, $T_5 > T_4$
- results in an increase in velocity



Other Types of Engines

1. Turbo-Prop Engine



- gas turbine drives the compressor and the propeller
- most of the thrust is from the propeller
- works by accelerating large volumes of air to moderate velocities
- propellers are best suited for low speed (< 300 mph) flight
- new turbo-props are suitable for velocities up to 500 mph
- by-pass ratio of 100:1 or more
- 2. Turbo-Fan Engine (Ducted Turbo-Prop Engine)



- by-pass ratio can be adjusted
- typical by-pass ratios are 5-6

3. Ramjet



• compression is achieved by decelerating the high-speed incoming air in the diffuser

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
- uses a shutter-type valve for damper control
Non-Reacting Gas Mixtures



Formulations

• the total mass of a mixture, *m* is the sum of the masses of its components

$$m=m_1+m_2+\ldots+m_j={\displaystyle\sum_{i=1}^j}m_i$$

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

$$X_i = rac{m_i}{m} \qquad \Rightarrow \qquad \sum_{i=1}^j X_i = 1$$

• the total number of moles in a mixture, *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

$$Y_i = rac{n_i}{n} \qquad \Rightarrow \qquad \sum_{i=1}^j Y_i = 1$$

• m_1 and n_i are related by the molecular weight $ilde{M}_i$

$$m_i = n_i M_i$$

Therefore the total mass is

$$m = {\sum\limits_{i=1}^{j}} n_i ilde{M}_i$$

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

$$ilde{M} = rac{m}{n} = rac{\sum\limits_{i=1}^{j} n_i ilde{M}_i}{n} = \sum\limits_{i=1}^{j} Y_i ilde{M}_i$$

• X_i and Y_i are also related by the molecular weights

$$rac{X_i}{Y_i} = rac{(m_i/m)}{(n_i/n)} = \left(rac{m_i}{n_i}
ight) \left(rac{n}{m}
ight) = \left(ilde{M}_i
ight) \left(rac{1}{ ilde{M}}
ight)$$

Therefore

$$rac{X_i}{Y_i} = rac{ ilde{M}_i}{ ilde{M}} ~
ightarrow X_i = Y_i egin{bmatrix} ilde{M}_i \ ilde{\sum}_{i=1}^j Y_i ilde{M}_i \end{bmatrix}$$

P-V-T Relationships for Ideal Gas Mixtures

Amagat Model (law of additive volumes)

• the volume of a mixture is the sum of the volumes that each constituent gas would occupy if each were at the pressure, *P* and temperature, *T*, of the mixture



• the volume that n_i moles of a component i would occupy at P and T is called the partial volume, V_i

$$V_i = rac{n_i \mathcal{R} T}{P}$$

• dividing through by the total volume gives

$$\frac{V_i}{V} = \left(\frac{n_i \mathcal{R} T / P}{n \mathcal{R} T / P}\right) \Rightarrow \frac{n_i}{n} = Y_i \qquad (1)$$

which leads to

$$\sum_{i=i}^{j} V_i = \sum_{i=1}^{j} Y_i V = V \sum_{\substack{i=1 \ i=1}}^{j} Y_i$$

where the sum of the mole fractions is 1.

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 mixture of gases is the sum of the pressures of its components when each alone occupies the volume of the mixture, V, at the temperature, T, of the mixture

$$egin{array}{cccc} V,T \ m_A,n_A,P_A \end{array} + egin{array}{cccc} V,T \ m_B,n_B,P_B \end{array} = egin{array}{cccc} V,T \ m_C = m_A + m_B \ n_C = n_A + n_B \ P_C = P_A + P_B \end{array}$$

- for a mixture of ideal gases the pressure is the sum of the partial pressures of the individual components
- the individual components do not exert the mixture pressure, P, but rather a partial pressure

$$P_i = rac{n_i \mathcal{R} T}{V}$$

• dividing through by the total pressure

$$\frac{P_i}{P} = \frac{n_i \mathcal{R} T / V}{n \mathcal{R} T / V} = \frac{n_i}{n} = Y_i \qquad (2)$$

From (2)

$$\sum_{i=1}^{j} P_i = \sum_{i=1}^{j} Y_i P = P \underbrace{\sum_{i=1}^{j} Y_i}_{=1}$$

For a mixture of ideal gases the pressure is the sum of the partial pressures of the individual components

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

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

$$\boxed{\frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n}}$$

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

Mixture Properties

Extensive properties such as U, H, c_p, c_v and S can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

$$egin{array}{rcl} U = \sum U_i &=& \sum m_i u_i = m \sum X_i u_i = m u \ &=& \sum n_i \overline{u}_i = n \sum Y_i \overline{u}_i = n \overline{u} \end{array}$$

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

ig u	=	$\sum X_i u_i$
h	=	$\sum X_i h_i$
c_v	=	$\sum X_i c_{v_i}$
c_p	=	$\sum X_i c_{p_i}$
s	=	$\sum X_is_i$

Changes in internal energy and enthalpy of mixtures

$$\begin{aligned} u_2 - u_1 &= \sum X_i (u_2 - u_1)_i = \int_{T_1}^{T_2} c_v \, dT = c_v (T_2 - T_1) \\ h_2 - h_1 &= \sum X_i (h_2 - h_1)_i = \int_{T_1}^{T_2} c_p \, dT = c_p (T_2 - T_1) \\ s_2 - s_1 &= \sum X_i (s_2 - s_1)_i = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \end{aligned}$$

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

$$egin{array}{rcl} \Delta S &=& -\left(m_A R_A \ln rac{P_A}{P} + m_B R_B \ln rac{P_B}{P} + \cdots
ight) \ &=& -\sum\limits_{i=1}^j m_i R_i \ln rac{P_i}{P} \ &=& -\mathcal{R} \sum\limits_{i=1}^j n_i \ln Y_i \end{array}$$

Psychrometrics

- studies involving mixtures of dry air and water vapour
- used in the design of air-conditioning systems, cooling towers and most processes involving the control of vapour content in air
- for $T \leq 50^{\circ}C$ $(P_{sat} \leq 13 \ kPa) \Rightarrow h \approx h(T)$
 - water vapour can be treated as an ideal gas



Total Pressure

$$egin{array}{rcl} P &=& P_a + P_w \ P_a &=& rac{m_a R_a T}{V} \ P_w &=& rac{m_w R_w T}{V} \end{array}$$

where P_a is the partial pressure of air and P_w is the partial pressure of water vapour. Typically $m_w << m_a$.

Relative Humidity - ϕ

$$\phi = \frac{P_w(T)}{P_{sat}(T)} = \frac{\text{vapour pressure at the prevailing T}}{\text{saturation pressure at the prevailing T}}$$

If $P_w = P_{sat}(T)$ the mixture is said to be saturated.

Specific Humidity (Humidity ratio) - ω

$$\omega = \frac{m_w}{m_a} = \frac{\text{mass of water vapour}}{\text{mass or air}}$$
$$= \frac{\tilde{M}_w n_w}{\tilde{M}_a n_a} = \frac{\tilde{M}_w (P_w V/\mathcal{R}T)}{\tilde{M}_a (P_a V/\mathcal{R}T)}$$
$$= \left(\frac{\tilde{M}_w}{\tilde{M}_a}\right) \left(\frac{P_w}{P_a}\right)$$
$$= 0.622 \left(\frac{P_w}{P_a}\right)$$

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

<u>Sling Psychrometer</u> - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. T_{DB} and T_{WB} are sufficient to fix the state of the mixture.

$P_{W} = 1 \text{ atm}^{\phi = 100\%}$ $P_{W} = \frac{m_{W}}{m_{a}}$ $\omega = \frac{m_{W}}{m_{a}}$ T_{db}

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?



• the adiabatic saturator is used to measure humidity

Adiabatic Saturator Analysis

Conservation of Mass

$$\dot{m}_{a,1} = \dot{m}_{a,3}$$
 air (1)
 $\dot{m}_{w,1} + \dot{m}_{w,2} = \dot{m}_{w,3}$ water (2)

Conservation of Energy

$$(\dot{m}h)_{a,1} + (\dot{m}h)_{w,1} + (\dot{m}h)_{w,2} = (\dot{m}h)_{a,3} + (\dot{m}h)_{w,3}$$
 (3)

By definition

$$\omega_{1} = \left(\frac{\dot{m}_{w}}{\dot{m}_{a}}\right)_{1} \qquad (4)$$
$$\omega_{3} = \left(\frac{\dot{m}_{w}}{\dot{m}_{a}}\right)_{3} \qquad (5)$$

From (2) and (1)

$$igg(rac{\dot{m}_{w,2}}{\dot{m}_{a,1}}igg) = igg(rac{\dot{m}_{w,3}}{ec{m}_{a,1}}igg) - igg(rac{\dot{m}_{w,1}}{\dot{m}_{a,1}}igg) = \omega_3 - \omega_1$$

Dividing (3) by $\dot{m}_{a,1}$ and noting $m_{a_1}=m_{a_3}$ and $\dfrac{m_{w_2}}{m_{a_1}}=\omega_3-\omega_1$

$$h_{a,1} + \omega_1 h_{w,1} + (\omega_3 - \omega_1) h_{w,2} = h_{a,3} + \omega_3 h_{w,3}$$
(6)

$$\omega_1 = rac{(h_{a,3}-h_{a,1})+\omega_3~(h_{w,3}-h_{w,2})}{(h_{w,1}-h_{w,2})}$$



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

 $fuel + oxidizer \rightarrow products$

Fuels:

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
 - liquids \rightarrow gasoline octane, C_8H_{18}
 - gases \rightarrow methane, CH_4
 - solids \rightarrow coal

Combustion Air:

- oxygen is required in every combustion reaction
- in most combustion reactions air provides the needed oxygen
- dry air is considered to be

21% oxygen 79% nitrogen } on a molar basis

$$molar\ ratio = rac{n_{N_2}}{n_{O_2}} = rac{0.79}{0.21} = 3.76$$

1 *mole* of air can then be written as $[0.21 O_2 + 0.79 N_2]$ For convenience, we typically refer to air as $[O_2 + 3.76 N_2]$ which is actually 4.76 moles of air.

Air-Fuel Ratio:

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

$$AF = ar{AF}\left(rac{ ilde{M}_{air}}{ ilde{M}_{fuel}}
ight)$$

where:

AF - air fuel ratio on a mass basis

AF - air fuel ratio on a molar basis

 \tilde{M}_{air} = 28.97 kg/kmole

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
- normally the amount of air supplied is given as a percentage of the theoretical value i.e. $150\% = 1.5 \times$ the theoretical air
 - referred to as 50% excess air, 150% stoichiometric

Equivalence Ratio:

• defined as

$$equivalence\ ratio = rac{AF_{actual}}{AF_{theoretical}}$$

• 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
 → differences cannot be calculated for all substances involved
- it is necessary to establish a common base to account for differences in composition
- h = 0 assigned to elements in their most stable form i.e. $O_2, N_2, C, etc.$
- Enthalpy of Formation: the energy released or absorbed when a compound is formed from its stable elements at STP



where \overline{h}_{f}^{o} is the enthalpy of formation.

Taking an energy balance over the combustion chamber shown above, we obtain

$$\underbrace{a \ \overline{h}^o_A + b \ \overline{h}^o_B + c \ \overline{h}^o_C}_{generally=0} + \overline{h}^o_f \ \longrightarrow \ \overline{h}^o_{ABC}$$

In general

$$\overline{h}^{o}_{f} = \overline{h}^{o}_{comp} - \sum \overline{n}_{i}\overline{h}^{o}_{i} ~~(kJ/kmole)$$

where

 \overline{n}_i = # of moles of i'th elemental substance in forming a single mole of compound (unitless)

Effects of Non-Standard Temperature

$$\overline{h}(T,P) = \overline{h}_{f}^{o} + \underbrace{(\overline{h}_{T,P} - \overline{h}_{T=25\ ^{o}C,\ P=\ 1\ atm})}_{\Delta \overline{h}\ at\ known\ temperatures}$$

where

- \overline{h}^o_f is the heat resulting from a chemical change at $T=25~^\circ C$ and P=1~atm
- $\Delta \overline{h}$ is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $T_{ref} = 25 \ ^{\circ}C$

Effects of Non-Standard Pressure

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

but for an ideal gas

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

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

$$\Delta h \ at \ known \ temperatures$$

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

$$Q = \sum (mh)_P - \sum (mh)_R = \underbrace{H_P(T_P) - H_R(T_R)}_{H_{RP}}$$
$$Q = \sum (n\overline{h})_P - \sum (n\overline{h})_R = \underbrace{\overline{H}_P(T_P) - \overline{H}_R(T_R)}_{\overline{H}_{RP}}$$

where

 $\overline{h}_{c} = H_{RP}/kmole \ of \ fuel$



Heating Value

- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion when products are returned to the state of the reactants
- 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

$$egin{array}{rcl} HHV &=& LHV + rac{(m \, \cdot \, h_{fg})_{H_2O}}{kmole \ of \ fuel} \ &=& LHV + (ilde{M} \ \cdot \ h_{fg})_{H_2O} \ \cdot \ rac{n_{H_2O}}{n_{fuel}} \end{array}$$

where

$$egin{array}{rcl} h_{fg}(25\ ^{
m o}C) &=& 2,442.3\ kJ/kg \ && ilde{M}_{H_{2}O} &=& 18.015\ kg/kmole \end{array}$$

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

$$egin{aligned} &H_P(T_{ad})=H_R(T_R)\ &\sum_P n_P\,(\overline{h}_f^o+\underbrace{\overline{h}}_{\Delta\overline{h}}-\overline{h}^0)_P=\sum_R n_R\,(\overline{h}_f^o+\underbrace{\overline{h}}_{\Delta\overline{h}}-\overline{h}^0)_R \end{aligned}$$

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 T_{ad} .

$$\sum_{P} \underbrace{n_{P}(\bar{h})_{P}}_{sensible \ heat}_{function \ of \ T_{ad}} = \sum_{R} \underbrace{n_{R}(\bar{h} - \bar{h}^{o})_{R} - \left(-\sum_{P} n_{P}(\bar{h}^{o})_{P}\right)}_{sensible \ heat}_{function \ of \ T_{R} \ or \ T_{ref}} + \sum_{R} \underbrace{n_{R}(\bar{h}^{o}_{f})_{R} - \sum_{P} n_{P}(\bar{h}^{o}_{f})_{P}}_{chemical \ heat}_{function \ of \ T_{R} \ or \ T_{ref}}$$

Step 1: Calculate the right hand side based on known values of T_R and T_{ref} .

Step 2: Calculate the left hand side based on a guessed value of T_{ad} .

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

Evaluation of Entropy for Reacting Systems

The 2nd law entropy equation can be written as

 $\underbrace{S_{in} - S_{out}}_{due \ to \ heat \ \& \ mass \ transfer} + \underbrace{S_{gen}}_{generation} = \underbrace{\Delta S_{system}}_{change \ in \ entropy}$

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

$$\sum rac{Q_i}{T_i} + S_{gen} = S_P - S_R$$

- absolute entropy at 1 atm and temperature T is denoted as $s^o(T)$ or $\overline{s}^o(T)$ for a per unit mass or per mole basis
- while \overline{h} was only a function of temperature for ideal gases, we must account for the effects of both T and P in entropy
- the entropy at any value of *T* and *P* can be calculated as

$$\overline{s}(T,P) = \underbrace{\overline{s}^o(T)}_{tables} - \mathcal{R} \ln \left(rac{P_i}{P_{ref}}
ight)$$

• the partial pressure P_i can also be written as

$$P_i = Y_i P$$

and

$$\overline{s}(T,P_i) = \overline{s}^o_i(T) - \mathcal{R} \ln \left(rac{Y_i P}{P_{ref}}
ight)$$

where P is the mixture pressure and Y_i is the mole fraction of the i'th component.