ENTROPY – an introduction

$\mathcal{S}$ entropy $\qquad d\mathcal{S} \equiv \left(\frac{\delta Q}{T}\right)_{rev}$

$$\mathcal{S}_2 - \mathcal{S}_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} \qquad \text{units } \frac{kJ}{K} \text{ or } \frac{Btu}{°R}$$

$$s \equiv \frac{\mathcal{S}}{m} \qquad \text{units } \frac{kJ}{kg\,K} \text{ or } \frac{Btu}{lb\,°R}$$

s is an intensive T-D state property like v, u, & h

$s = s_f + x(s_g - s_f)$ for a mixture of sat liq & sat vap

Some T-D Relations

$$d\mathcal{S} \equiv \left(\frac{\delta Q}{T}\right)_{rev} \implies Td\mathcal{S} = \delta Q$$

remember $\delta Q = dU + \delta W$

and $\delta W = pdV$

giving,

$$\boxed{Td\mathcal{S} = dU + pdV} \qquad \div m \Rightarrow Tds = du + pdv$$

$$\div n \Rightarrow Td\bar{s} = d\bar{u} + pd\bar{v}$$

Now, remember,

$$H = U + pV \implies dH = dU + pdV + Vdp$$

$$\text{or } \quad dU = dH - pdV - Vdp$$

substituting into the boxed equation,

$$Td\mathcal{S} = (dH - pdV - Vdp) + pdV$$

$$\boxed{Td\mathcal{S} = dH - Vdp} \qquad \div m \Rightarrow Tds = dh - vdp$$

$$\div n \Rightarrow Td\bar{s} = d\bar{h} - \bar{v}dp$$

Where $s \equiv \frac{\mathcal{S}}{m}$, $h \equiv \frac{H}{m}$, $u \equiv \frac{U}{m}$, $v \equiv \frac{V}{m}$ $\qquad$ m - mass

$\bar{s} \equiv \frac{\mathcal{S}}{n}$, $\bar{h} \equiv \frac{H}{n}$, $\bar{u} \equiv \frac{U}{n}$, $\bar{v} \equiv \frac{V}{n}$ $\qquad$ n - # moles

MORE ENTROPY

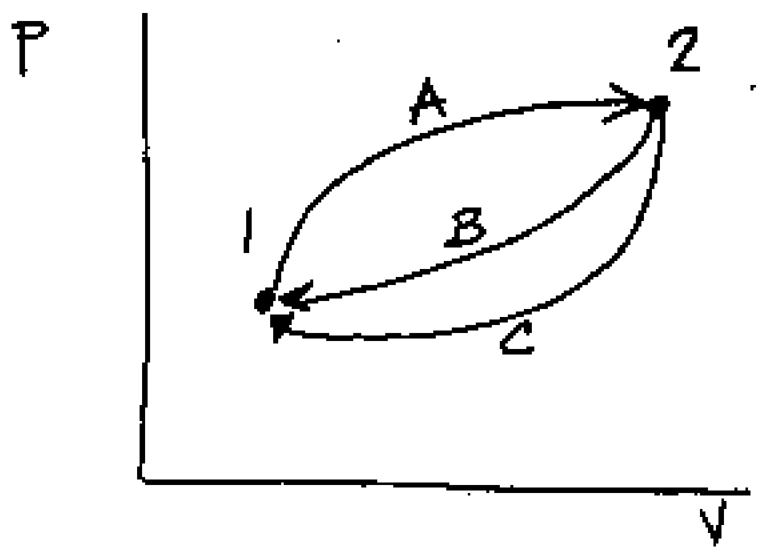
Inequality of Clausius

$\oint \frac{\delta Q}{T} \leq 0$ for the system (we'll look at the surroundings later)

$\oint \frac{\delta Q}{T} = 0$ for ______________ processes

$\oint \frac{\delta Q}{T} < 0$ for ______________ processes

Similar to our derivation for dU $[dU = \delta Q - \delta W]$



for a reversible process, $\oint \frac{\delta Q}{T} = 0$

$\boxed{1\text{-}A\text{-}2\text{-}B\text{-}1}\ 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B$

$\boxed{1\text{-}A\text{-}2\text{-}C\text{-}1}\ 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_C$

we see, $\int_2^1 \left(\frac{\delta Q}{T}\right)_B = \int_2^1 \left(\frac{\delta Q}{T}\right)_C$

the $\int \frac{\delta Q}{T}$ is independent of path AS LONG AS THE PROCESS IS REVERSIBLE

This gives us the state property

ENTROPY S $\quad dS \equiv \left(\frac{\delta Q}{T}\right)_{rev} \quad \frac{kJ}{K}$

change in entropy $\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$

ΔS for a SUBSTANCE is independent of path (whether reversible or irreversible)

This tells us how to find the DIFFERENCE in entropy, (not the actual entropy)

HOWEVER, we define $S = 0$ @ $T = 0\,K$ for pure substances.

$\mathcal{S}$ is an extensive property

$s \equiv \frac{\mathcal{S}}{m}$ $\frac{kJ}{kg\,K}$ is the intensive property

$\therefore \Delta s = \frac{1}{m}\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$

and joins the ranks of our other intensive T-D state prop.

p, v, T, x, u, h, s or p, u, s, h, T, v, x

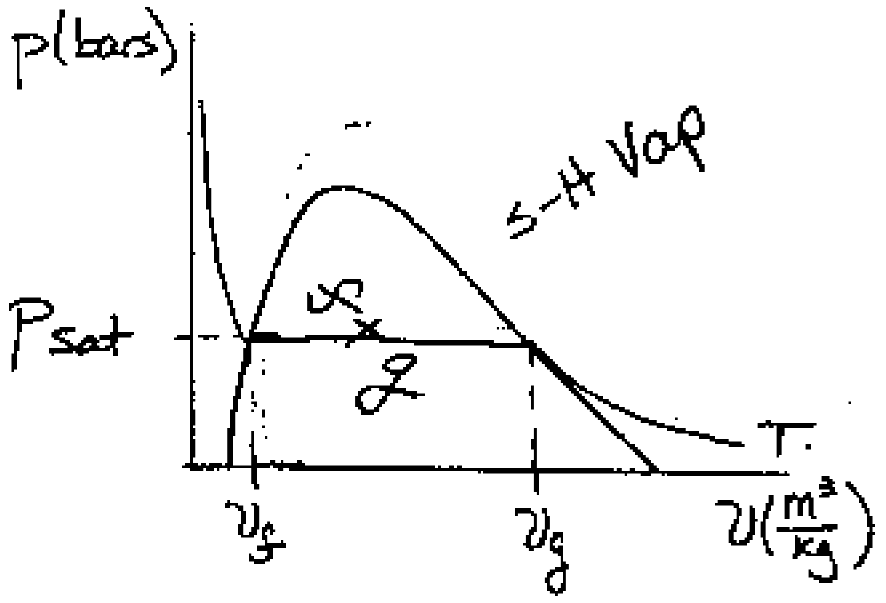
Any 2 independent intensive T-D state properties will specify the state of the system (and you can find the others)

For a mixture of sat liq & sat vap $s = s_f + x(s_g - s_f)$

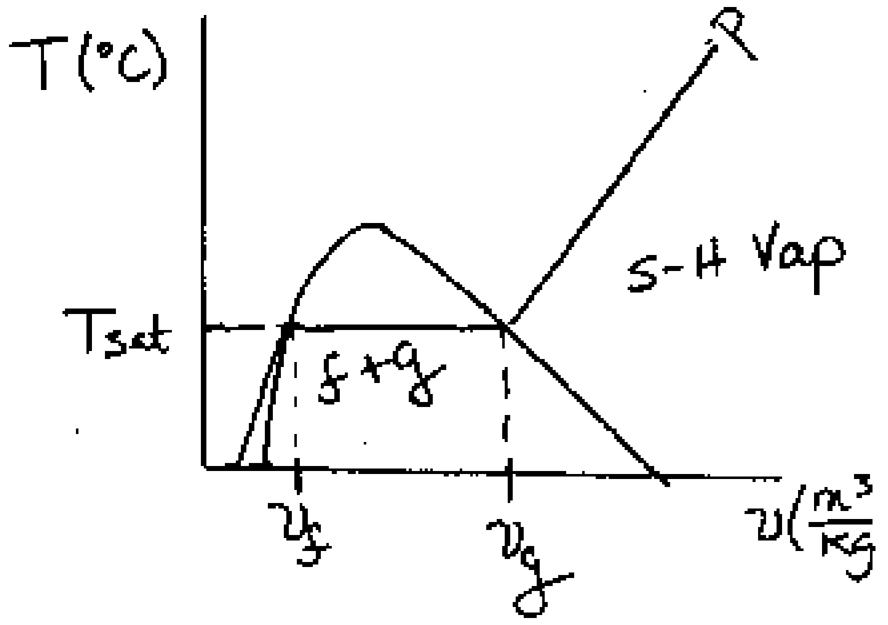
or $s = s_f + x\,s_{fg}$

in general we use the following plots

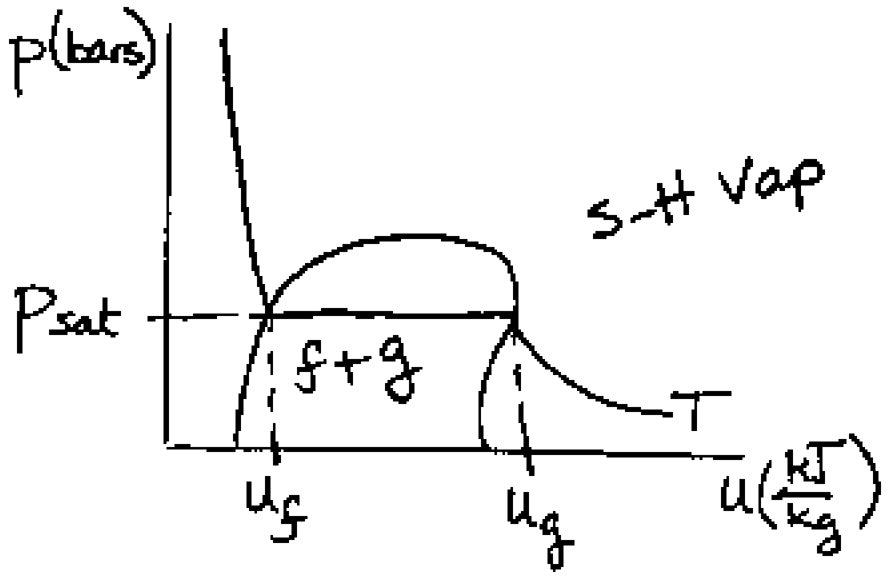
p-v



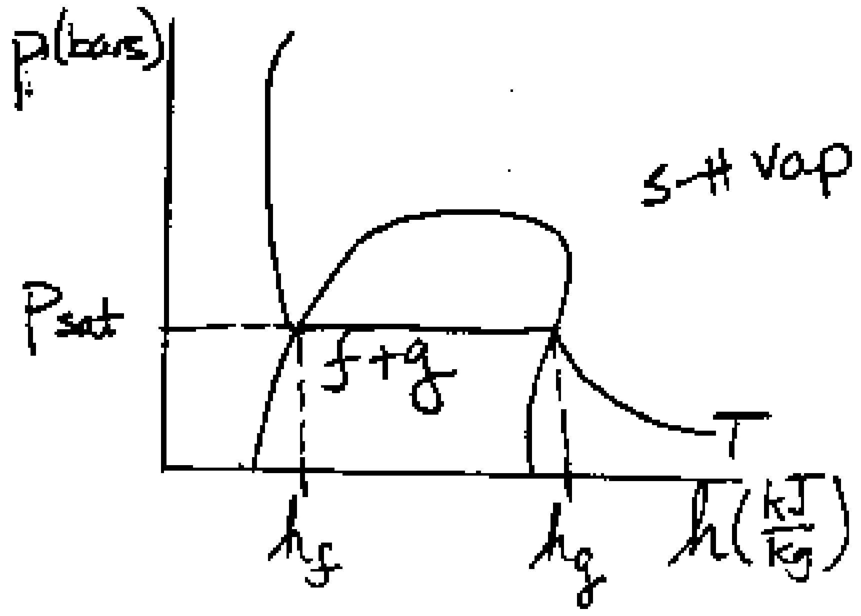
T-v



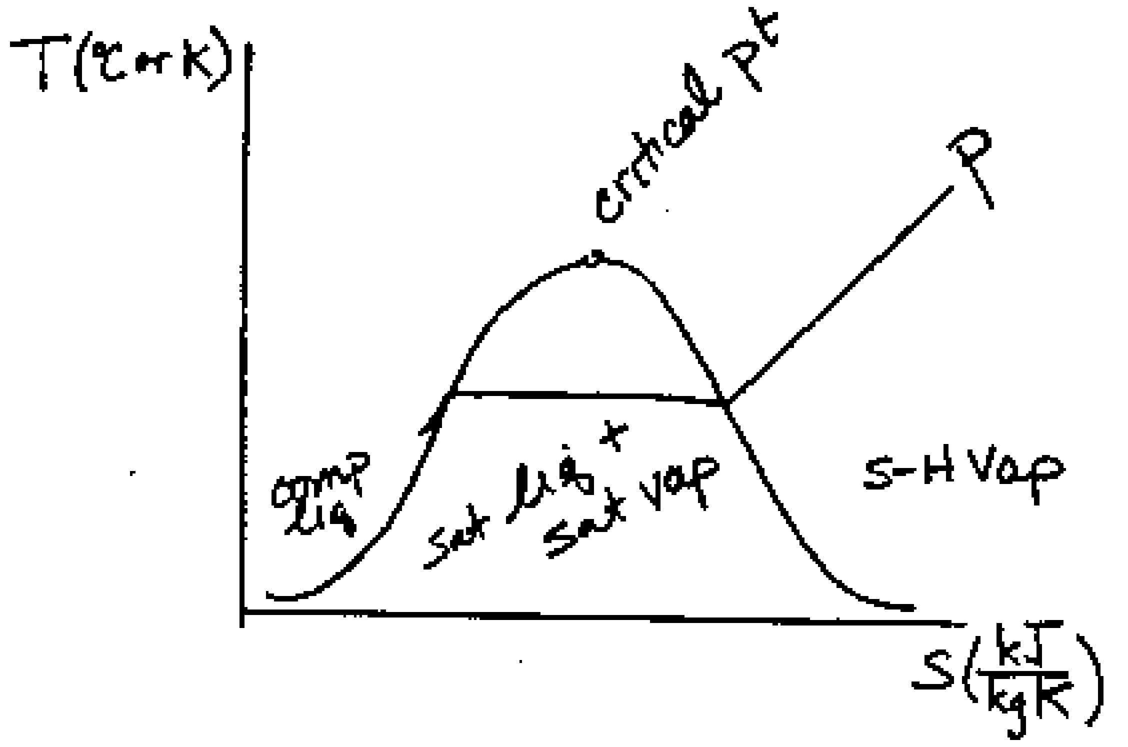
p-u



p-h



We now have a T-s plot



note the shape of vapordome

fig 8.5 (pg 257)
shows T-s w/ lines of
const p
const h
const v
const x

fig 8.6 (pg 258)
shows h-s w/lines of
const P
const T
const x

for most substances,

$s_{comp\,liq} \approx s_f$ @ same temperature

so the "const p" line lies on the sat liq line below T_{sat}.

Lets consider the <u>CARNOT CYCLE</u>

2 reversible isothermal steps
2 reversible adiabatic steps

hmmmmm...

reversible adiabatic, $Q=0$, $\delta Q = 0$

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$$

if $\delta Q = 0$ & reversible, $\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} = 0 \rightarrow S_2 - S_1 = 0$

$S_2 = S_1$ or $\Delta S = 0$

A reversible adiabatic process
reversible, $Q=0$
$\Delta S = 0$ ($\Delta s = 0$)
is an ISENTROPIC PROCESS

<u>REVIEW</u>
isothermal – T const
isobaric – p const
isochoric – V const
adiabatic – $Q=0$
Isentropic – $\Delta S = 0$, $\Delta s = 0$, reversible, adiabatic

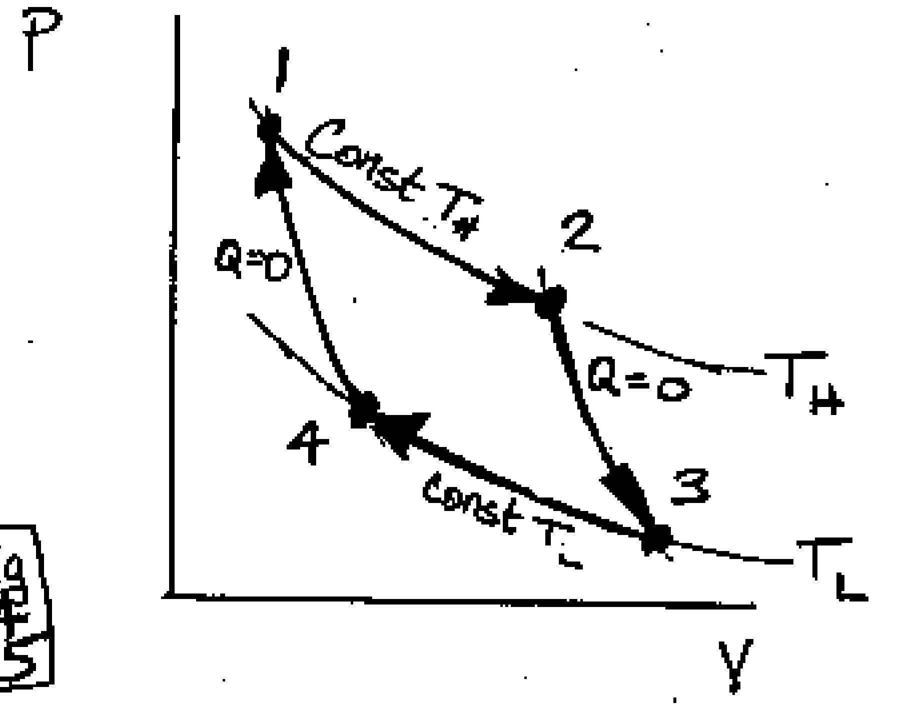
Back to the Carnot Cycle

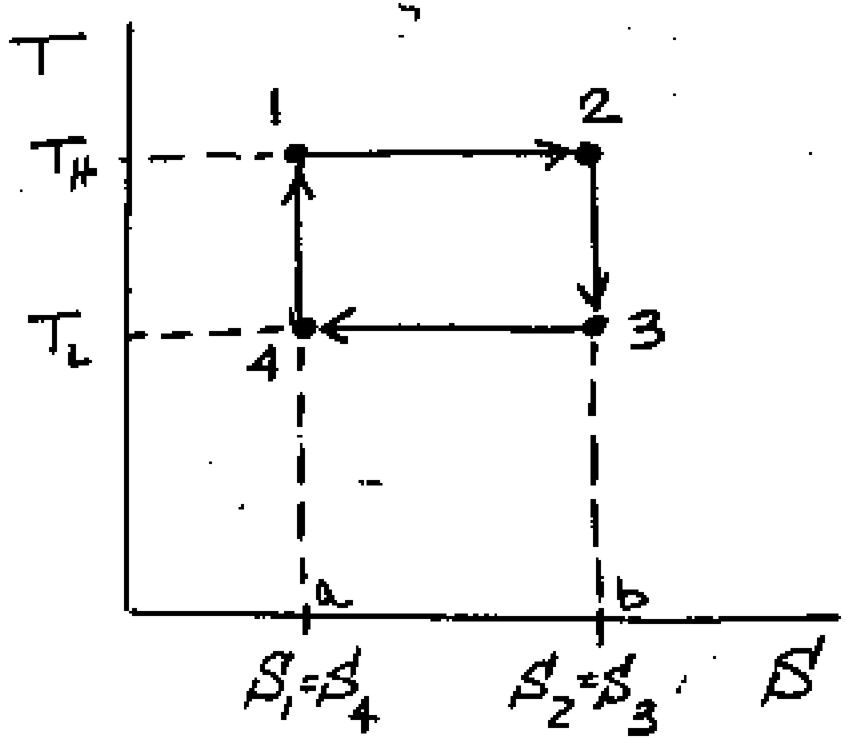
reversible, 2 isothermal
2 adiabatic

See pg for adiabatic & isothermal

See fig 8.8 Pg. 259

See fig 7.24 pg 235





What do the areas on a T-s represent?

isothermal $1 \to 2$ $\quad S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$ $\quad$ T const @ T_H, can pull thru $\int$

$$= \frac{1}{T_H}\int_1^2 \delta Q = \frac{{}_1Q_2}{T_H}$$

$$S_2 - S_1 = \frac{{}_1Q_2}{T_H} \Longrightarrow T_H(S_2 - S_1) = {}_1Q_2 = Q_H$$

adiabatic $2 \to 3$ $\quad \Delta S = 0 \Longrightarrow S_2 = S_3$

isothermal $3 \to 4$ $\quad S_4 - S_3 = \int_3^4 \frac{\delta Q}{T}$ $\quad$ T const @ T_L

$$= \frac{1}{T_L}\int_3^4 \delta Q = \frac{{}_3Q_4}{T_L}$$

$$(S_4 - S_3)T_L = {}_3Q_4 = Q_L$$

adiabatic $4 \to 1$ $\quad \Delta S = 0 \Longrightarrow S_4 = S_1$

for carnot cycle $\quad Q_H - Q_L = W$

$$|\text{area } 1\text{-}2\text{-}b\text{-}a\text{-}1| - |\text{area } 4\text{-}3\text{-}b\text{-}a\text{-}4| = W$$

area bounded by cycle = W

remember $T\,dS = dU + p\,dV$

ENTROPY CHANGES in solids, liquids & Ideal Gases & poly tropic processes

remember,

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{rev} \Rightarrow T\,dS \equiv \delta Q$$

for isothermal, reversible process

for reversible adiabatic process

$$T\,dS = dU + p\,dV \quad \Longrightarrow$$

$$T\,dS = dH - V\,dp \quad \Longrightarrow$$

for solids & liquids

$$dS = \frac{dU}{T} + \frac{p\,dV}{T}$$

or

$$ds = \frac{du}{T} + \frac{p\,dv}{T}$$

solids, liquids fairly incompressible $\therefore dv \approx 0$

$$ds = \frac{du}{T} \qquad \text{and} \qquad du = C\,dT$$

$$ds = \frac{C\,dT}{T}$$

$$s_2 - s_1 = \int_1^2 C \frac{dT}{T}$$

assume C is constant w/ T

$$s_2 - s_1 = \boxed{C \ln\frac{T_2}{T_1} = \Delta S}$$

C values can be found in tables A-3 & A-4

$$\uparrow$$

C_p

for ideal gases

$$Tds = du + pdv$$

$$ds = \frac{du}{T} + \frac{P}{T}dv \qquad \text{and for I.G.} \quad du = C_{vo}dT$$

Substituting

$$pv = RT \Longrightarrow \frac{P}{T} = \frac{R}{v}$$

$$ds = \frac{C_{vo}dT}{T} + \frac{R}{v}dv$$

$$s_2 - s_1 = \int_1^2 \left[\frac{C_{vo}dT}{T} + \frac{Rdv}{v}\right]$$

$$\boxed{s_2 - s_1 = \left[\int_1^2 C_{vo}\frac{dT}{T}\right] + R\ln\frac{v_2}{v_1}}$$

C_{vo} is a funct. of T

if instead we use

$$Tds = dh - vdp$$

$$ds = \frac{dh}{T} - \frac{vdp}{T} \qquad \text{and for I.G.} \quad dh = C_{po}dT$$

$$pv = RT \Longrightarrow \frac{v}{T} = \frac{R}{P}$$

Substituting,

$$ds = \frac{C_{po}dT}{T} - \frac{Rdp}{P}$$

$$\boxed{s_2 - s_1 = \left[\int_1^2 C_{po}\frac{dT}{T}\right] - R\ln\frac{P_2}{P_1}}$$

C_p is a funct of T

in order of increasing accuracy

1) assuming const C_{vo}, C_{po} (Table A-5)

$$s_2 - s_1 = C_{vo}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$s_2 - s_1 = C_{po}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

2) using equation in table A-6 & integrating

$$s_2 - s_1 = \left[\int_1^2 \frac{C_{vo}dT}{T}\right] + R\ln\frac{v_2}{v_1}$$

$$s_2 - s_1 = \left[\int_1^2 \frac{C_{po}dT}{T}\right] - R\ln\frac{P_2}{P_1}$$

3) using values in Tables A.7.1, A.8 & A.9

$$s_T^\circ = \int_{T_o}^{T_1} \frac{C_{po}}{T}dT \qquad \text{Ref temp } T_o = 0K,\ p = 1\text{ bar}$$

$$s_2 - s_1 = (s_{T2}^\circ - s_{T1}^\circ) - R\ln\frac{P_2}{P_1}$$

More nifty ideal gas stuff

Specific heat ratio

$$k = \frac{C_{po}}{C_{vo}}$$

and remember,

$$C_{po} = C_{vo} + R$$

for I.G. $k = \frac{C_{po}}{C_{vo}} = \frac{C_{vo} + R}{C_{vo}}$

$k = 1 + \frac{R}{C_{vo}}$

or $\boxed{C_{vo} = \frac{R}{k-1}}$

Also

$k = \frac{C_{po}}{C_{vo}} = \frac{C_{po}}{C_{po} - R}$ leads to

$\boxed{C_{po} = \frac{kR}{k-1}}$

Ideal gases & the reversible adiabatic process

$\Delta s = 0$, $ds = 0$

$Tds = du + pdv = C_{vo}dT + pdv = 0$

$pv = RT$

$T = \frac{pv}{R} \Longrightarrow dT = \frac{1}{R}(pdv + vdp)$

substituting for dT in

$C_{vo}dT + pdv = 0$

leads to

$\frac{C_{vo}}{R}(pdv + vdp) + pdv = 0$

using $C_{vo} = \frac{R}{k-1} \Longrightarrow \frac{C_{vo}}{R} = \frac{1}{k-1}$ & substituting

gives $\frac{1}{k-1}(pdv + vdp) + pdv = 0$ collecting terms gives

$\frac{1}{k-1}(kpdv + vdp) = 0$ either $\frac{1}{k-1} = 0$ (not the case)

OR

$kpdv + vdp = 0$ ÷ by pv

$k\frac{dv}{v} + \frac{dp}{p} = 0$

integrating gives $\boxed{pv^k = \text{const} \Longrightarrow \text{isentropic process for I.G}}$

getting back to I.G. & the reversible adiabatic process

$pv^k = \text{const}$, $pV^k = \text{const}$ $\qquad k = \frac{c_{p0}}{c_{v0}}$

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^k$$

and $$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\left(\frac{k-1}{k}\right)} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

$${}_1W_2 = \frac{p_2V_2 - p_1V_1}{1-k} = \frac{mR}{1-k}(T_2 - T_1)$$

remember, for I.G.
$pV = mRT$

SUMMARIZING reversible polytropic processes for I.G. $pV^n = \text{const}$

(see also fig 8.17 pg 279)

process	n	const?	work

Irreversible Processes

for δQ (heat trans. to/from control vol)

$$dS = \left(\frac{\delta Q}{T}\right)_{rev}$$

for a fixed δQ, if the process has any irreversibilities

$$dS > \left(\frac{\delta Q}{T}\right)_{irr} \qquad dS \geq \frac{\delta Q}{T}$$

for the same "process" (final & initial states)

$$dS_{irr} > dS_{rev}$$

There is some additional entropy generated

δS_{gen}, or σ_{cv} due to friction
unrestrained expansion
transfer of energy
(the irreversible things)

$\delta S_{gen} > 0$ for ______________ processes

$\delta S_{gen} = 0$ for ______________ processes

for the same "process"

$$\delta Q_{irr} = \delta Q_{rev} + T\delta S_{gen}$$

$$\delta Q_{irr} = dU + \delta W_{irr}$$

& $\delta W_{irr} < \delta W_{rev}$ because some of the energy was lost

$$\delta W_{irr} = p\,dV - \underbrace{T\delta S_{gen}}_{\text{lost work (lost opportunity to extract work)}}$$

$$S_2 - S_1 = \int_1^2 dS = \underbrace{\int_1^2 \frac{\delta Q}{T}}_{\text{reversible part}} + \underbrace{{}_1S_{2\,gen}}_{\text{irreversible part}}$$

Major Points regarding entropy

- There are 2 ways to increase the entropy of a system
  1.
  2.
- There is only 1 way to decrease the entropy of a system
  1.
- There is an increase in entropy associated w/ irreversibilities
- Irreversibilities cause work to be smaller than reversible work.

$$dS_{cm} \geq \frac{\delta Q}{T}$$

$$dS_{surr} = -\frac{\delta Q}{T_o}$$

heat transferred TO system
is transferred FROM surroundings

$$dS_{net} = dS_{cm} + dS_{surr}$$

note: $S_{net} = \sigma$ (in text)

→

→

→

$$\boxed{\Delta S_{net} = \Delta S_{sys} + \Delta S_{surr}}$$

The 2nd law of thermo, Entropy, & SSSF systems

Similar to our derivation of the 1st law for open systems

$$\dot{Q}-\dot{W} = \sum_e \left(h_e+\frac{V_e^2}{2}+gz_e\right)\dot{m}_e - \sum_i \left(h_i+\frac{V_i^2}{2}+gz_i\right)\dot{m}_i + \frac{dE_{cv}}{dt}$$

and for SSSF

where $\frac{dm_{cv}}{dt}=0$, $\frac{dE_{cv}}{dt}=0$ and

$$\dot{Q}-\dot{W} = \sum_e \left(h_e+\frac{V_e^2}{2}+gz_e\right)\dot{m}_e - \sum_i \left(h_i+\frac{V_i^2}{2}+gz_i\right)\dot{m}_i$$

we can derive an equation for entropy

beginning with $dS = \frac{\delta Q}{T} + \delta S_{gen}$

and ending up with

$$\boxed{\sum_e s_e\dot{m}_e - \sum_i s_i\dot{m}_i + \frac{dS_{cv}}{dt} = \sum_{c.v.} \frac{\dot{Q}_{c.v.}}{T} + \dot{S}_{gen}}$$

the term $\sum_{cv} \frac{\dot{Q}_{cv}}{T}$ because heat can be transferred across many boundaries.

- each T is the Temp of the SURROUNDINGS

for SSSF

$$\frac{dS_{cv}}{dt}=0$$

leaving $\sum_e s_e\dot{m}_e - \sum_i s_i\dot{m}_i = \sum_{cv} \frac{\dot{Q}_{cv}}{T} + \dot{S}_{gen}$

for an adiabatic process with 1 inlet & 1 outlet

$\dot{Q}_{cv}=0$, $\dot{m}_e=\dot{m}_i$

$$s_e\dot{m}_e - s_i\dot{m}_i = \dot{S}_{gen}$$

$$\dot{m}(s_e-s_i) = \dot{S}_{gen} \geq 0$$

$$s_e - s_i \geq 0$$

$s_e \geq s_i$ = if rev. adiabatic; isentropic

\> if irrev. adiabatic.