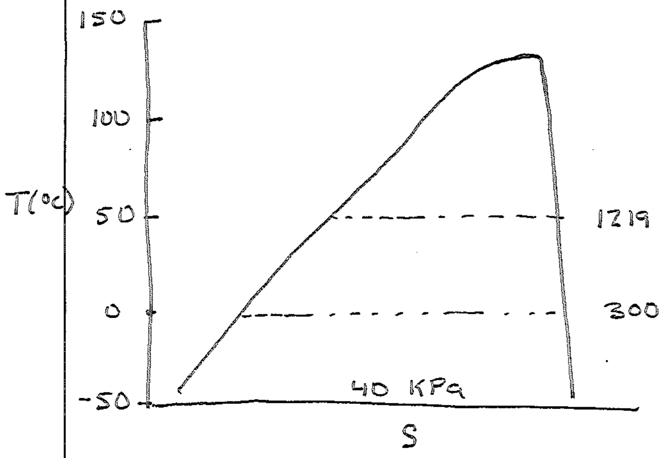
Talk about refrigerant selection:

$\boxed{\text{R-12}}$ CCl_2F_2 ⇒ Methane with Cl, F.



- Want evap > 100 KPa to avoid air inleakage
  - ⇒ R-12 100 KPa = -30°C
- Want high Tcrit, so condenser is in dome.
  - ⇒ Keep T for Q_{out} constant
  - ⇒ Boil and condense have high heat transfer coeficients — Keep areas low.
- Is steep shape of dome on right benificial?
  - ⇒ Keeps overtemp out of compressor down.

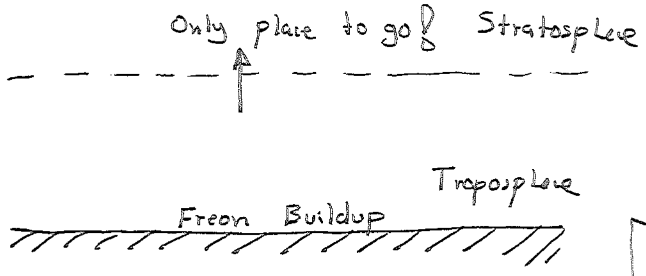
Original refrigerants:

- Air: Poor β
- Water: Forms ice below 0°C ⇒ Plugs system.
- NH_3: Still used in industrial systems, but toxic.
- Propane: ~~What about~~ Flammable

} Which would you prefer in your car?

- SO_2 - home units.

⇒ Freons developed to be inert & non-toxic ⇒ Too inert!



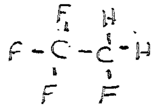
- In stratosphere you have enough short wavelength UV so

$$CCl_2F_2 + \text{photon} \rightarrow CClF_2 + Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

Always there.

Some replacements: R-22; $CHClF_2$ - Less inert.
R-134a;

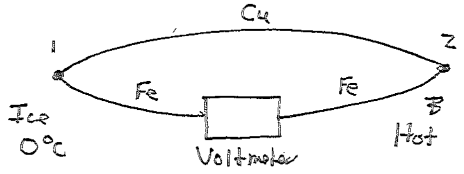


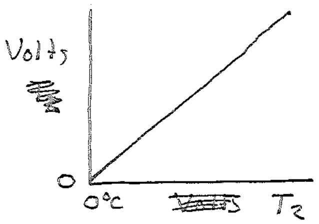
CF_3-CH_2F

Final Topic - Thermoelectric cooling -

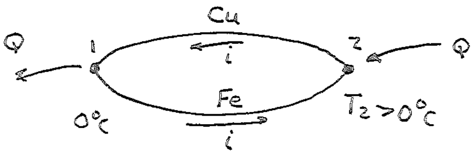
① Thermocouple:

Pt/Rh → 2200°C!





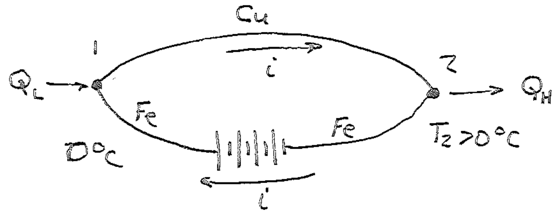
② Now short out voltmeter



- Sets up a current flow.
- Q absorbed at hot junction
- Q released at cold.

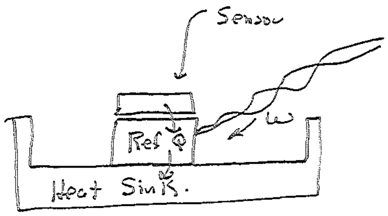
⇒ Could add motor to make heat engine!

③ Now use voltage source to force current into reverse.



First law: $Q_H = Q_L + W_{Battery}$

Application: Cooling IR Sensor:



Chapter 11 - Prop. Relations.

~~Goal~~:

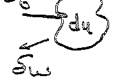
Idea: Can measure T, P, v easily.
Can also get C_p, C_v

No meters for u, h, s ... so need to get from measurable properties. How to make the tables?

⇒ Advanced thermo allow us to get these.

- Thermo
- Partial derivative ⇒ dh, du, ds
  ⇒ Integrate these.

Start at the begining:



1^{st} Law: $\delta q - \delta w = du$

Definition of entropy $dS \equiv \left(\frac{\delta q}{T}\right)_{reversible.}$ ⇒ $(\delta q)_{rev} = Tds$

Reversible process: $\delta w = Pdv$ ⇒ $TdS - Pdv = du$

or $\boxed{du = TdS - Pdv}$ First Gibbs.

Next: $h \equiv u + Pv$ $dh = du + Pdv + vdP$

$dh = [TdS - Pdv] + Pdv + vdP$ ⇒ $\boxed{dh = TdS + vdP}$ 2^{nd} Gibbs.

Define Helmboltz energy $A \equiv u - Ts$ $dA = du - Tds - sdT$

$dA = [TdS - Pdv] - TdS - sdT$ ⇒ $\boxed{dA = -Pdv - sdT}$ 3^{rd} Gibbs.

(Oct. 26) Define Gibbs energy $g \equiv u + Pv - Ts = h - Ts$ ⇒ $dg = dh - TdS - sdT$

$dg = [TdS + vdP] - TdS - sdT$ ⇒ $\boxed{dg = vdP - SdT}$ 4^{th} Gibbs.

Now let's review partial derivatives:

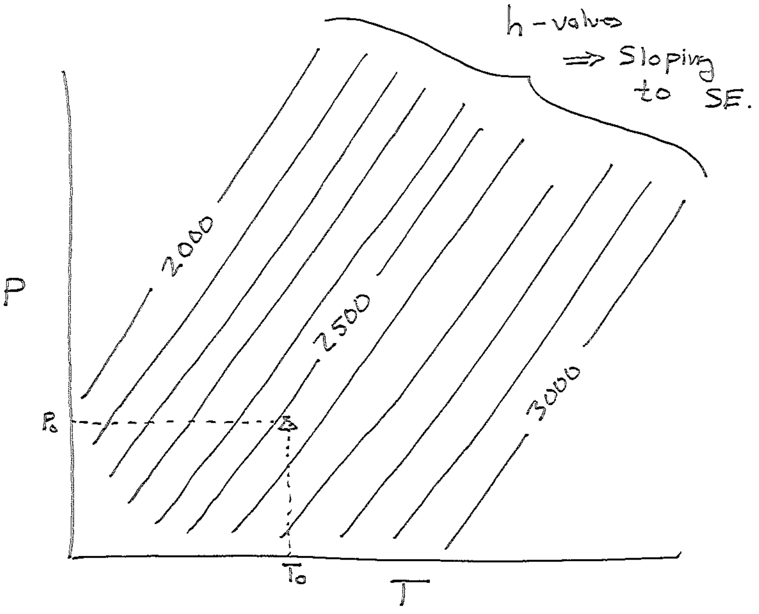
State postulate: Any two independent properties are sufficient to establish a state.

$$h = h(P, T)$$ in superheat region.

Think about this like a 3-D surface:

{ P & T are y & x
{ h = elevation
→ like a topo map.

h increases with T
h decreases with P
(a little).



Assume I am standing at △

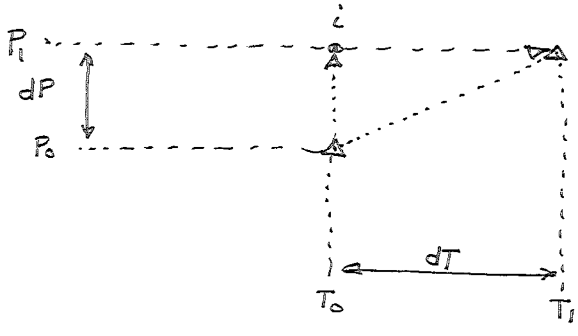
How would I measure $\left(\frac{\partial h}{\partial P}\right)_T \overset{?}{=}$
- Look north
- lay a tangent line ~~on slope~~ going N-S
- Measure the slope.

Or: $$\lim_{\Delta P \to 0} \left[\frac{h(P_o + \Delta P, T_o) - h(P_o, T_o)}{\Delta P} \right] \equiv \left(\frac{\partial h}{\partial P}\right)_T$$

If I want $\left(\frac{\partial h}{\partial T}\right)_P$ ⇒ Measure slope of tangent in e-w direction.

$$\equiv \lim_{\Delta T \to 0} \left[\frac{h(P_o, T_o + \Delta T) - h(P_o, T_o)}{\Delta T} \right]$$

Now, how do we find how h changes going in any direction?



Do this in two steps:

$$dh_{0\to 1} = dh_{0\to i} + dh_{i \to 1}$$

(get the same "elevation" change no matter which way you go).

$$dh = \left[\text{Slope}\right]_{0\to i} dP + \left[\text{Slope}\right]_{i\to 1} dT$$

$$\boxed{dh = \left(\frac{\partial h}{\partial P}\right)_T dP + \left(\frac{\partial h}{\partial T}\right)_P dT}$$

Total derivative:
You give me dP, dT, $h(P,T)$
$\Longrightarrow$ I'll give you dh.

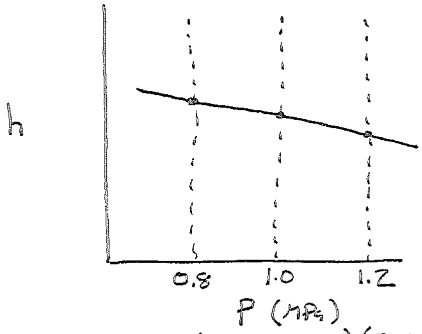
Lets run a numerical example: (steam)

$$\left.\begin{matrix} P_0 = 1\text{ MPa} \\ T_0 = 500°\text{C} \end{matrix}\right\} h = 3478.5 \text{ KJ/Kg}.$$

$\Longrightarrow$ Get Δh for 1.2 MPa, 400°C.

$$\Delta h \cong \left(\frac{\partial h}{\partial P}\right)_T \Delta P + \left(\frac{\partial h}{\partial T}\right)_P \Delta T$$

(all @ 500°C) (North/South Profile)

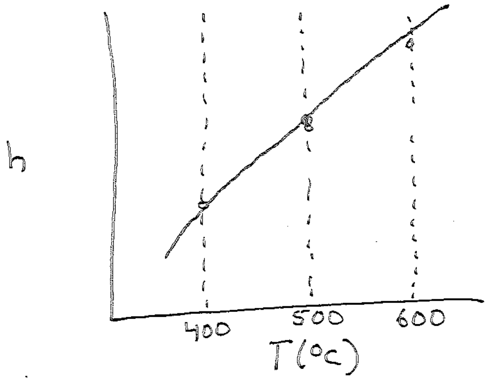


$$\left(\frac{\partial h}{\partial P}\right)_T \cong \frac{h(1.2\text{ MPa}, 500°\text{C}) - h(0.8\text{ MPa}, 500°\text{C})}{\Delta P\ (= \cancel{\text{or}}\ 400\text{ KPa})}$$

$$= \frac{3476.3 - 3480.6 \text{ KJ/Kg}}{400 \text{ KPa}}$$

$$= \boxed{-0.01075 \frac{\text{KJ}}{\text{Kg-KPa}}}$$

(all @ 1 MPa)(East/West Profile)



$$\left(\frac{\partial h}{\partial T}\right)_P \cong \frac{h(1\text{ MPa}, 600°\text{C}) - h(1\text{ MPa}, 400°\text{C})}{\Delta T\ (= 200°\text{C})}$$

$$= \frac{3697.9 - 3263.9 \text{ KJ/Kg}}{200 \text{ K}}$$

$$= \boxed{+2.17 \text{ KJ/Kg-K}}$$

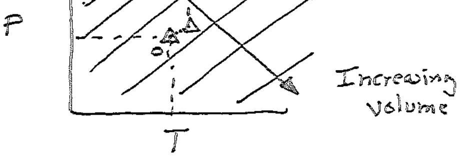
$$\Delta h \cong \left[-0.01075 \frac{\text{KJ}}{\text{Kg-KPa}}\right](+200\text{ KPa}) + \left[+2.17 \frac{\text{KJ}}{\text{Kg-K}}\right]\left[-100\text{ K}\right] = -219.15 \text{ KJ/Kg}$$

Actual Δh from table: -217.80 KJ/Kg. (<1% off).

Second major approach is to work from equations:

$v = v(P,T)$ for an ideal gas.

$$v = \frac{RT}{P}$$



$$dv = \left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT$$

$\left(\frac{\partial v}{\partial P}\right)_T \overset{?}{=}$

① Write operative equation $Pv = RT$

② Solve for dependent variable

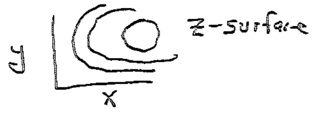
$$v = \frac{RT}{P}$$

③ Take derivative treating T as constant.

$$\left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2} \quad \Rightarrow \quad \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$\Rightarrow \boxed{dv = \left[-\frac{RT}{P^2}\right]dP + \left[\frac{R}{P}\right]dT}$$

Now, math of <u>exact</u> <u>differentials</u>.



$z = z(x,y) \quad \Rightarrow \quad$ ~~dz~~

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Let $M \equiv \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

$$\Rightarrow \quad dz = M\,dx + N\,dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x \qquad \left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

But order of differentiation is immaterial, so those are equal.

So: $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

This means if I can write: ⟶ $dz = M\,dx + N\,dy$

~~Then~~

Then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Now return to the 4 Gibbs relations

	Z	M	X	N	Y
$du = T\,ds - P\,dv$	u	T	s	$-P$	v
$dh = T\,ds + v\,dP$	h	T	s	v	P
$da = -P\,dv - s\,dT$	a	$-P$	v	$-s$	T
$dg = v\,dP - s\,dT$	g	v	P	$-s$	T

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T$$

⇒ Four Maxwell relations

⇒ Useful here for clearing s out of expressions.

Lets use these to work a couple of examples before moving ahead:

① Estimate Δs for steam: from P-v-T data.
$$\left.\begin{matrix}500°C\\ 1.0\,MPa\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}500°C\\ 1.2\,MPa\end{matrix}\right.$$

Last one looks good!

$$\left(\frac{\partial v}{\partial T}\right)_P \cong \left(\frac{\Delta v}{\Delta T}\right)_P = \frac{v(600°C,\ 1.0\,MPa) - v(400°C,\ 1.0\,MPa)}{200\,K}$$

Oct. 29

$$= \frac{0.4011 - 0.3066\ m^3/kg}{200\,K} = 4.73E{-3}\ m^3/kg\text{-}K.$$

$$\overbrace{-\left(\frac{\partial v}{\partial T}\right)_P}^{\text{Know}} = \left(\frac{\partial s}{\partial P}\right)_T \cong \left(\frac{\Delta s}{\Delta P}\right)_T$$

$$\Rightarrow \quad \Delta s \cong \left[-\left(\frac{\partial v}{\partial T}\right)_P\right]\Delta P = \left[-4.73E{-3}\ \frac{m^3}{kg\text{-}K}\right]\left[200\ kPa\right] = -0.0945\ \frac{kJ}{kg\text{-}K}$$

$$\text{Tables} = -0.0863\ \frac{kJ}{kg\text{-}K}.$$

Difference due to finite differencing, and basing $\left(\frac{\partial v}{\partial T}\right)_P$ @ 1 MPa (Should be 1.1 MPa).

---

② Ideal gas: Const T, $P_1 \rightarrow P_2$.

(a) $\left(\frac{\partial v}{\partial T}\right)_P$

$$Pv = RT \Rightarrow v = \frac{RT}{P}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

(b)
$$-\frac{R}{P} = \left(\frac{\partial s}{\partial P}\right)_T \quad \Rightarrow \quad ds = -\frac{R}{P}dP$$

$$\boxed{\Delta s = -R\ln\frac{P_2}{P_1}}$$

$$\Delta s = \overset{0 \text{ for } \Delta T = 0}{\cancel{s_2^0 - s_1^0}} - R\ln\frac{P_2}{P_1}$$

Now get general relationships for u, h, s.

$u = u(T, v)$ or (P, v) or $\boxed{(P, T)}$ ⟶ don't choose because P, T not independent in dome.

$$du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{\equiv C_v} dT + \left(\frac{\partial u}{\partial v}\right)_T dv = C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

We're stuck, so lets go to Gibbs for du.

$$du = T\underbrace{ds}_{\text{Expand}} - P dv$$

$$s = s(T, v) \qquad ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Now there's hope! dT, dv appear.

Substituting:

$$du = T\left[\left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv\right] - P\,dv$$

Collect like differentials:

$$du = \underset{\updownarrow}{T\left(\frac{\partial s}{\partial T}\right)_v} dT + \left[\underset{\updownarrow}{T\left(\frac{\partial s}{\partial v}\right)_T} - P\right]dv \quad \Rightarrow \boxed{C_v = T\left(\frac{\partial s}{\partial T}\right)_v}$$

(later).

but $$du = C_v\,dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$\Rightarrow$ So indicated terms are equal!

$$du = C_v dT + \left[T\underbrace{\left(\frac{\partial s}{\partial v}\right)_T}_{\to\ =\ \left(\frac{\partial P}{\partial T}\right)_v} - P\right]dv$$

via 3rd Maxwell.

$$\boxed{\cancel{du = C_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right]dv}}$$

$$\boxed{du = C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv}$$

Air table suggests that for an ideal gas, $u = u(T)$ only.

$$Pv = RT \Rightarrow P = \frac{RT}{v} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\Rightarrow \left[T\frac{R}{v} - P\right]dv$$ but $\frac{RT}{v} = P \Rightarrow$ Bracket goes to zero!

Can integrate:

$$\boxed{u_2 - u_1 = \int_{T_1}^{T_2} C_v\,dT + \int_{v_1}^{v_2}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv}$$

Once you have this, can get $\boxed{h_2 - h_1 = u_2 - u_1 + P_2v_2 - P_1v_1}$

Now look at $s = s(T, v) \Rightarrow$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \underbrace{\left(\frac{\partial s}{\partial v}\right)_T}_{\to \left(\frac{\partial P}{\partial T}\right)_v} dv$$

via 3rd Maxwell.

From above: $C_v = T\left(\frac{\partial s}{\partial T}\right)_v \Rightarrow \left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$

$$\Rightarrow \boxed{ds = \frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_v dv}$$

or

$$\boxed{s_2 - s_1 = \int_{T_1}^{T_2}\frac{C_v}{T}dT + \int_{v_1}^{v_2}\left(\frac{\partial P}{\partial T}\right)_v dv}$$

Lets apply the latter to get S_{fg} for steam @ 100°C.

$$\Delta S = \underbrace{\int_{T_1}^{T_2} \frac{C_v}{T}\,dT}_{=0 \text{ for phase change}} + \int_{v_1}^{v_2} \underbrace{\left(\frac{\partial P}{\partial T}\right)_v}\,dv$$

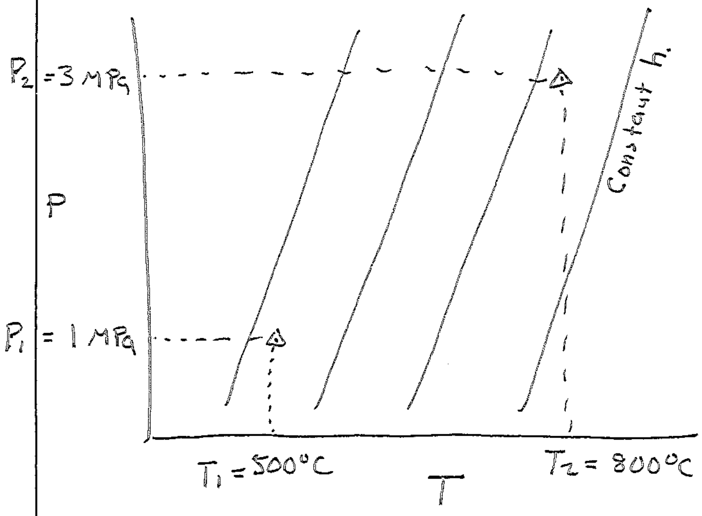
$$\left(\frac{\partial P}{\partial T}\right)_v \overset{\text{Two-phase mix}}{=} \left.\frac{dP}{dT}\right)_{sat}.$$

$$\left.\frac{dP}{dT}\right)_{sat} \cong \frac{\Delta P}{\Delta T} = \frac{P_{sat} @ 105°C - P_{sat} @ 95°C}{10\,K} = \frac{120.82 - 84.55\ kPa}{10\,K} = 3.63\ \frac{kPa}{K}$$

$$\Delta S = \int_{v_1}^{v_2}\left[3.63\ \frac{kPa}{K}\right]dv = \left[3.63\ \frac{kPa}{K}\right]\left[\underset{\uparrow\,1.6729}{v_g} - \underset{\uparrow\,1.044E\text{-}3\ m^3/kg}{v_f}\right] = 6.07\ \frac{kJ}{kg\text{-}K}$$

Table = 6.05 !

Now, lets apply to a real problem.



Find Δh from P-v-T data
Cp, Cv data

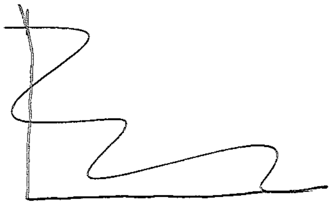
① $h_2 - h_1 = u_2 - u_1 + P_2 v_2 - P_1 v_1$

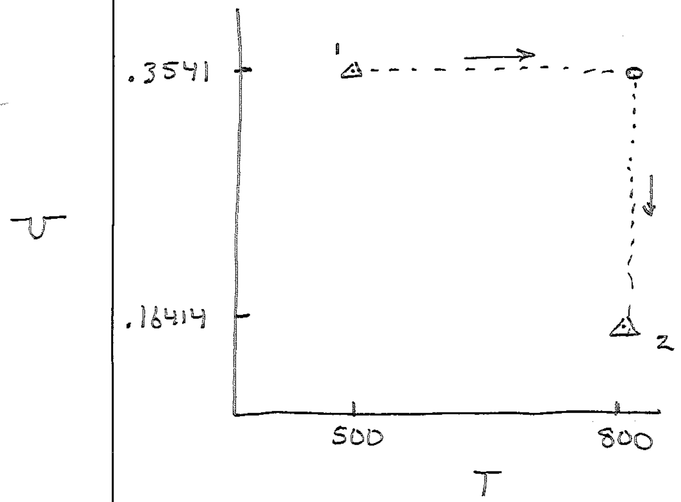
$$u_2 - u_1 = \int_{T_1}^{T_2} C_v\,dT + \int_{v_1}^{v_2}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

Need to change independent variable: $[P, T] \rightarrow [T, v]$

1 MPa, 500°C] $v_1 = 0.3541\ m^3/kg$

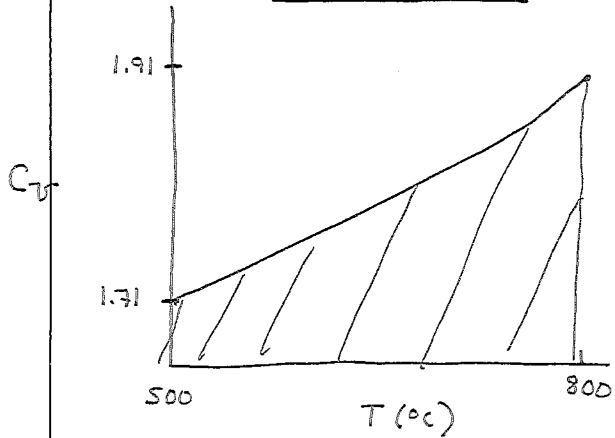
3 MPa, 800°C] $v_2 = 0.16414\ m^3/kg$.





- Since properties are independent of path, go 500 → 800°C at constant v_1.
- Then go $v_1 \rightarrow v_2$ at constant T.

$v = 0.3541\ m^3/kg$



$$\int_{500}^{800} C_v dT = 539\ kJ/kg$$

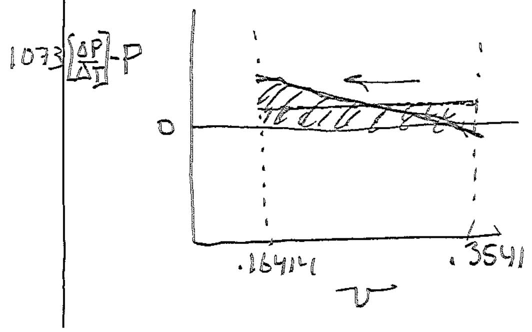
$$\int_{v_1}^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$T = 800°C = 1073\ K$

Oct. 31

$(1073)(1.28) - 1395.27$

T	v	P(800°C)	P(801°C)	$(\Delta P/\Delta T)_v$	$T\left[\frac{\partial P}{\partial T}\right]_v - P$
800°C	.3541	1395.27	1396.~~49~~55	1.28	—
"	.35	1411.91	1413.22	1.31	—
"	.34	↓	↓	↓	
"	.33				
	⋮				
	.17				
	.16414				



$= -\overset{4.16}{\cancel{3.84}}\ kJ/kg.$

$\Rightarrow \Delta u = 539 + (\overset{-4.16}{\cancel{-3.84}}) = 535.16\ kJ/kg$

$\Delta h = \Delta u + P_2 v_2 - P_1 v_1$

$= 535.16 + (3000)(0.16414) - (1000)(0.3541)$

$\boxed{\Delta h = 673.48\ kJ/kg}$

Book ⇒ 669.6
→ 0.5% error.

Finish up with two specialized properties:

Clapeyron equation - Getting h_{fg}

From before: $$\Delta S = \underbrace{\int_{T_1}^{T_2} \frac{C_v}{T} dT} + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv$$

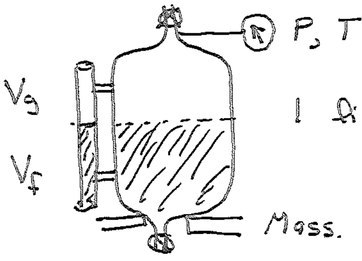
Phase change ? $$= 0 + \left(\frac{dP}{dT}\right)_{sat} (v_g - v_f)$$

2nd Gibbs: $dh = Tds + \cancel{vdP}^{\,0}$ for phase change.

$$\boxed{h_{fg} = T s_{fg} = T\left[\frac{dP}{dT}\right]_{sat}\left[v_g - v_f\right]}$$

How to get? h_{fg} for NH_3 @ 0 °C.

① Get v_g, v_f



Could fill with all liquid $\Rightarrow m_f, V_f \Rightarrow v_f$

" vapor $\Rightarrow v_g$

But hitting the saturated state with only one phase would be hard.

Instead: 0°C, part liquid, part vapor m_1, $V_{f,1}$, $V_{g,1}$

Note: $m_1 = m_f + m_g = \frac{V_{f,1}}{v_f} + \frac{V_{g,1}}{v_g} \Rightarrow$ Two unknowns.

Next, bleed some refrigerant off
$\rightarrow$ mass decreases
$\rightarrow V_f$ down
$\rightarrow V_g$ up.

$$m_2 = \frac{V_{f,2}}{v_f} + \frac{V_{g,2}}{v_g} \Rightarrow \text{Same two unknowns!}$$

$\Rightarrow$ ~~B~~

	V_f		V_g		m (g)
1	10 cc	(1.E-5 m^3)	990 cc	(0.99E-3 m^3)	9.805
2	5 cc	(5. E-6 m^3)	995 cc	(0.995E-3 m^3)	6.630

$\Rightarrow v_g = 0.2895\ m^3/kg$, $v_f = 0.001566\ m^3/kg$.

② $\left(\frac{dP}{dT}\right)_{sat}$ What experiment do I run?

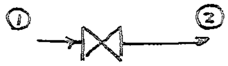
T (°C)	P (kPa)
-2	398.27
0	429.44
2	462.49

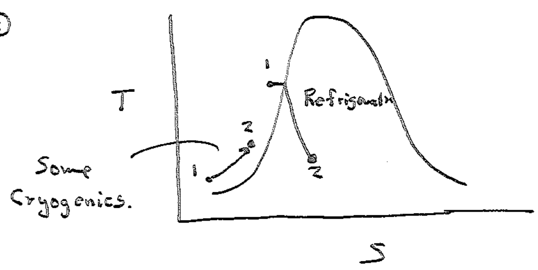
$$\left(\frac{dP}{dT}\right)_{sat} \cong \frac{462.49 - 398.27\ kPa}{4\ K} = 16.06\ \frac{kPa}{K}.$$

$$h_{fg} = T\left(\frac{dP}{dT}\right)_{sat} v_{fg} = \begin{array}{c|c|c} 273.15\ K & 16.06\ kPa & 0.2879\ m^3 \\ \hline & K & kg \end{array} = 1262.6\ \frac{kJ}{kg}$$

Table: 1262.8 kJ/kg.

Other example: Joule-Thompson Coefficient.





$$\mu \cong \left(\frac{\Delta T}{\Delta P}\right)_h$$ up or down?

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

For ideal gas: $v = \frac{RT}{P}$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P} \Rightarrow \left[T\left(\frac{R}{P}\right) - \underset{\frac{RT}{P}}{\underset{\downarrow}{v}}\right] \Rightarrow \boxed{\mu = 0}$$

Goals: $\delta q - \delta w = du$

rev → $T ds - P dv = du$ 1st Gibbs

$h \equiv u + Pv \Rightarrow dh = du + Pdv + vdP = TdS + vdP$ 2nd Gibbs

$a \equiv$ 3rd

$g \equiv$ 4th

Then $dz = Mdx + Ndy$

$\Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

- 4 Maxwell relations

$\Rightarrow du = f(P, v, T \text{ only})$

$dh =$

$ds =$

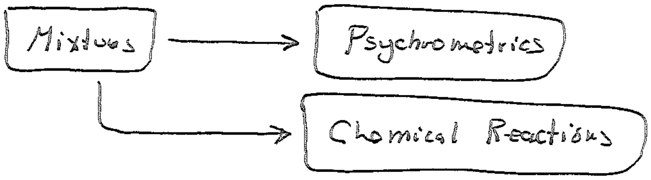
⇒ Mechanics of evaluating partial derivatives
- From tables
- From equations.

Nov 1 - Exam

Nov 2

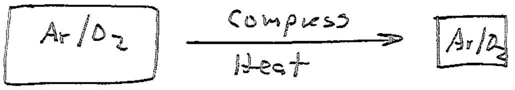
Properties of Gas Mixtures

New start:

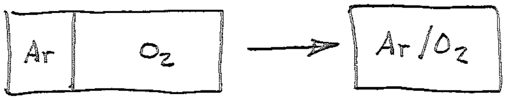


Goal is two things:

① Find change in u, h, s when you change P, T, v for mixture.



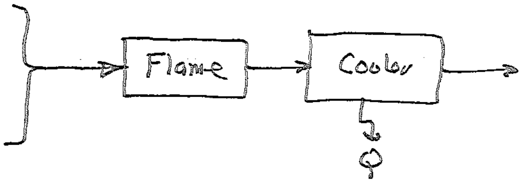
② Create a mixture



$\Delta u, \Delta h, \Delta s$

Need to define terms: Use an example:

1 Kmole CH_4 + Stoichiometric Air



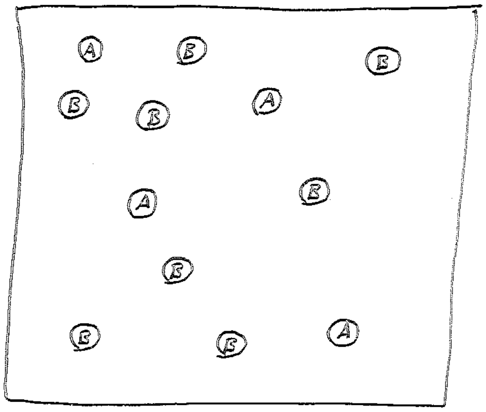
Products @ 600 K

1 Kmole CO_2
2 Kmoles H_2O
7.52 Kmoles N_2

n_i = Kmoles of species "i" in mixture
n = total Kmoles in mixture = $\sum_i n_i$
~~m_i~~ = M_i = molar mass or molecular weight of "i"
m_i = mass of species "i" in mix = $n_i M_i$ (units help)
m = total mass in mix = $\sum_i m_i$
M = average molecular weight of mix = $m/n = 290.6/10.52 = 27.62$ Kg/Kmole
y_i = mole fraction of i = n_i/n
mf_i = mass fraction of i = m_i/m

	n_i (Kmoles)	M_i (Kg/Kmole)	m_i (Kg)	y_i	mf_i	P_i (KPa)	V_i m^3
CO_2	1	44	44	0.10	0.15	10	52.5
H_2O	2	18	36	0.19	0.12	19	99.7
N_2	7.52	28	210.6	0.71	0.73	71	372.6
	n = 10.52 Kmoles		m = 290.6 Kg	1	1	100	524.8 m^3

Partial Pressure: Dalton model.



- Negligible interaction with other molecules
- Volume occupied is small
  $\longrightarrow$ Each component acts as if it's in isolation.

Partial pressure $= P_i =$ pressure exerted by n_i moles if they were alone in the box.

$$\boxed{P_i \equiv \frac{n_i \bar{R} T}{V}}$$

i.e., as if we were only counting strikes by Ⓐ on walls.

$$\frac{P_i}{P} = \frac{\frac{n_i \bar{R} T}{V}}{\frac{n \bar{R} T}{V}} = \frac{n_i}{n} = y_i \Rightarrow \boxed{P_i = y_i P}$$

Partial Volume: Amagat model.

- Each component occupies a volume that corresponds to what it would occupy by itself at same P and T. (i.e., divide the mixture up into separate volumes).

$$\boxed{V_i \equiv \frac{n_i \bar{R} T}{P}} \qquad \frac{V_i}{V} = \frac{\frac{n_i \bar{R} T}{P}}{\frac{n \bar{R} T}{P}} = \frac{n_i}{n} = y \Rightarrow V_i = y_i V$$

$$V = \frac{n\bar{R}T}{P} = \frac{10.52\ \text{Kmols}}{} \left| \frac{8.314\ \text{KPa-m}^3}{\text{Kmols-K}} \right| \frac{600\ \text{K}}{100\ \text{KPa}} = 524.8\ m^3$$

Properties of Gas Mixtures:

	Mass units	Mix	Mole units	Mix
Internal Energy	u	$u = \sum_i mf_i\, u_i$	$\bar{u}$	$\bar{u} = \sum y_i \bar{u}_i$
Others	h	All the same.		
	s			
	c_p			
	c_v			

Two Key points: ① ***Never*** mix mass and mole units (i.e., carry your units to stay out of trouble!)

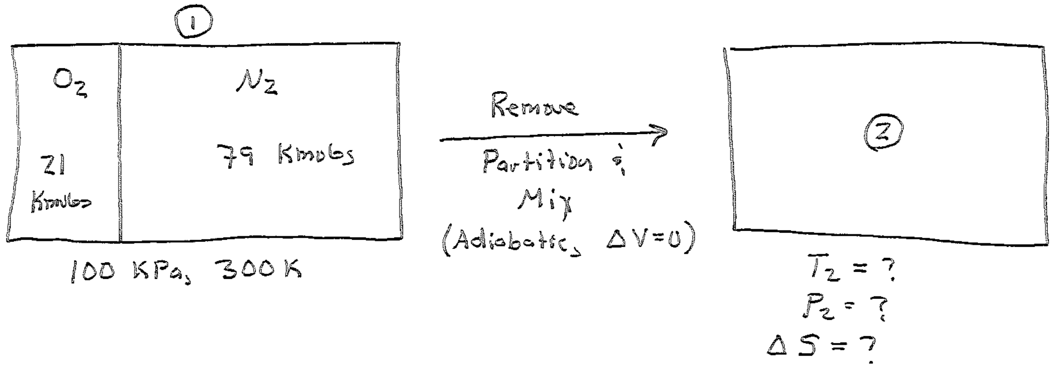
② s_i, $\bar{s}_i$ change when in a mixture.

e.g.: Pure CO_2 - 600 K, 100 KPa $\Big\}$ $s_{CO_2} = 5.527\ \frac{KJ}{Kg_{CO_2}\text{-}K}$.

In our mix $y_{CO_2} = 0.1$ 600 K, 100 KPa $\Big\}$ $s_{CO_2} = 5.962\ \frac{KJ}{Kg\,CO_2\text{-}K}$

This has to do with mixing being irreversible. Same 1 Kg CO_2 in mix has higher S] Will follow up later.

Walk through a simple example:



First Law: $\overset{0}{\cancel{Q}} - \overset{0}{\cancel{W}} = \Delta U$ (closed system).

$$0 = \Delta U = \Big[\sum_i \overset{n_i}{\cancel{m_i}}\,\bar{u}_i\Big]_2 - \Big[\sum_i \overset{n_i}{\cancel{m_i}}\,\bar{u}_i\Big]_1$$

$$= \Big[\overset{n_{O_2}}{\cancel{m_{O_2}}}\,\bar{u}_{O_2} + \overset{n_{N_2}}{\cancel{m_{N_2}}}\,\bar{u}_{N_2}\Big]_2 - \Big[\overset{n_{O_2}}{\cancel{m_{O_2}}}\,\bar{u}_{O_2} - \overset{n_{N_2}}{\cancel{m_{N_2}}}\,\bar{u}_{N_2}\Big]_1$$

$$= \overset{n_{O_2}}{\cancel{m_{O_2}}}\left(\bar{u}_{O_2,2} - \bar{u}_{O_2,1}\right) + \overset{n_{N_2}}{\cancel{m_{N_2}}}\left(\bar{u}_{N_2,2} - \bar{u}_{N_2,1}\right)$$

$$= \overset{n_{O_2}}{\cancel{m_{O_2}}}\,\overline{c_{v,O_2}}\,(T_2 - T_1) + \overset{n_{N_2}}{\cancel{m_{N_2}}}\,\overline{c_{v,N_2}}\,(T_2 - T_1)$$

$$0 = \Big[\overset{n_{O_2}}{\cancel{m_{O_2}}}\,\overline{c_{v,O_2}} + \overset{n_{N_2}}{\cancel{m_{N_2}}}\,\overline{c_{v,N_2}}\Big](T_2 - T_1) \quad \Rightarrow \quad \boxed{T_2 = T_1}$$

If $T_{1,O_2} \neq T_{1,N_2}$, substitute here and solve for T_2.

Nov. 5

$$P_2 = \frac{n_2 \bar{R} T_2}{V_2} \qquad V_2 = V_{O_2,1} + V_{N_2,1}$$

$$V_{O_2,1} = \frac{n_{O_2}\bar{R}T_1}{P_1} = \frac{21 \text{ Kmoles}}{} \left| \frac{8.314 \text{ KPa-m}^3}{\text{Kmole - K}} \right| \frac{300 \text{ K}}{100 \text{ KPa}} = 523.8 \text{ m}^3$$

$V_{N_2,1}$ = same with 79 Kmoles $= \underline{1970.4 \text{ m}^3}$

$V_2 = 2494.2 \text{ m}^3$

$$P_2 = \frac{100 \text{ Kmoles}}{} \left| \frac{8.314 \text{ KPa-m}^3}{\text{Kmole - K}} \right| \frac{300 \text{ K}}{2494.2 \text{ m}^3} = \underline{\underline{100 \text{ KPa}}} \; !$$

$$\Delta S = S_2 - S_1 = \Big[\sum_i n_i \bar{s}_i\Big]_2 - \Big[\sum_i n_i \bar{s}_i\Big]_1$$

$$= \Big[n_{O_2}\bar{s}_{O_2} + n_{N_2}\bar{s}_{N_2}\Big]_2 - \Big[n_{O_2}\bar{s}_{O_2} + n_{N_2}\bar{s}_{N_2}\Big]_1$$

$$= n_{O_2}\Big[\bar{s}_{O_2,2} - \bar{s}_{O_2,1}\Big] + n_{N_2}\Big[\bar{s}_{N_2,2} - \bar{s}_{N_2,1}\Big]$$

P_i (KPa)
$\frac{21}{100}$
$\frac{79}{100}$

$$\bar{s}_{O_2,2} - \bar{s}_{O_2,1} = \overset{0}{\cancel{\bar{s}^{\circ}_{O_2,2} - \bar{s}^{\circ}_{O_2,1}}} - \bar{R}\ln\frac{P_{O_2,2}}{P_{O_2,1}}$$

$$\bar{s}_{N_2,2} - \bar{s}_{N_2,1} = \overset{0}{\cancel{\bar{s}^{\circ}_{N_2,2} - \bar{s}^{\circ}_{N_2,1}}} - \bar{R}\ln\frac{P_{N_2,2}}{P_{N_2,1}}$$

$$\Delta S_{O_2} = -\left[8.314 \frac{KJ}{Kmole\text{-}K}\right]\ln\left[\frac{21}{100}\right] = 12.98 \frac{KJ}{Kmole\text{-}K}$$

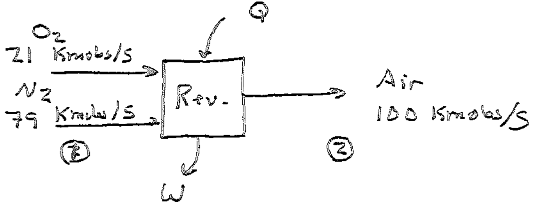
$$\Delta S_{N_2} = -\left[8.314 \frac{KJ}{Kmole\text{-}K}\right]\ln\left[\frac{79}{100}\right] = 1.96 \frac{KJ}{Kmole\text{-}K}$$

$$\Delta S = [21 \text{ Kmoles}]\left[12.98 \frac{KJ}{Kmole\text{-}K}\right] + [79 \text{ Kmoles}]\left[1.96 \frac{KJ}{Kmole\text{-}K}\right] = 427.4 \frac{KJ}{K}$$

$$\text{or} \quad 4.274 \frac{KJ}{Kmole\text{-}K}$$

OK, what gives here?

- ⇒ Mixing is irreversible [once you make air, you cannot separate it].
- ⇒ To unmix requires work.
- ⇒ Means we could get work out of mixing process!
- ⇒ Can figure without knowing anything about process!



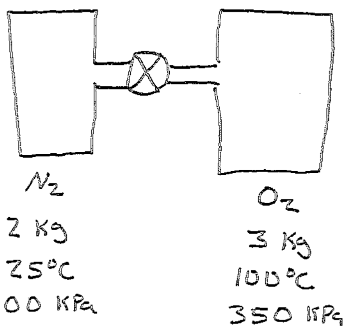
$$W_{max} = \overset{0}{\cancel{h_2 - h_1}} - T_0(S_2 - S_1) = [293\text{ K}]\left[\left(21 \frac{Kmoles}{s}\right)\left(12.98 \frac{KJ}{Kmole\text{-}K}\right) + \left(79 \frac{Kmoles}{s}\right)\left(1.96 \frac{KJ}{Kmole\text{-}K}\right)\right]$$

$$\boxed{W_{max} = 125{,}200 \text{ KW}}$$ ⇐ This is also the minimum amount of work needed to <u>unseparate</u> air into O_2 and N_2!

$2.9 \frac{\text{tons air}}{s}$ requires energy in 1.5 gal of gasoline

Nov 7

Now try a more challenging example:



- Adiabatic
- Open valve and mix
- Find
  - (a) Final T
  - (b) Final P
  - (c) ΔS

(a) Look at 1st law: $\overset{0}{\cancel{Q}} - \overset{0}{\cancel{W}} = \Delta U = \left[\sum_i m_i u_i\right]_2 - \left[\sum_i m_i u_i\right]_1 = 0$

$$0 = m_{O_2} C_{v,O_2}\left[T_2 - T_{1,O_2}\right] + m_{N_2} C_{v,N_2}\left[T_2 - T_{1,N_2}\right]$$

Move over N_2 term and consolidate

$$\underbrace{\frac{m_{N_2} C_{v,N_2}}{m_{O_2} C_{v,O_2}}}_{=B}\left[T_{1,N_2} - T_2\right] = \left[T_2 - T_{1,O_2}\right] \Rightarrow T_2 = \frac{BT_{1,N_2} + T_{1,O_2}}{1+B}$$

$$B = \frac{(2\text{ Kg})(0.743\ \text{KJ/Kg-K})}{(3\text{ Kg})(0.658\ \text{KJ/Kg-K})} = 0.753$$

$$T_2 = \frac{(0.753)(25°\text{C}) + 100°\text{C}}{1 + 0.753} = 68.78°\text{C}$$ ⇒ Note that nothing depends on P!

(b) $P = \dfrac{n\bar{R}T}{V}$ Got T, ~~need~~ can get n, need V,,, how to get?

	m_i (Kg)	M_i (Kg/Kmols)	n_i (Kmols)	$y_i = n_i/n$
N_2	2	28	0.0714	0.43
O_2	3	32	0.0938	0.57
			n = 0.1652	

$$V_{O_2} = \frac{n_{O_2}\bar{R}T}{P} = \frac{0.0938\ \text{Kmols} \;\big|\; 8.314\ \text{KPa-m}^3 \;\big|\; 373\text{K}}{\big|\; \text{Kmols-K} \;\big|\; 350\ \text{KPa}} = 0.83\ \text{m}^3$$

$$V_{N_2} = \frac{0.0714 \;\big|\; 8.314 \;\big|\; 298}{\big|\;\big|\; 100} = 1.77\ \text{m}^3 \qquad V = \Sigma V_i = 2.60\ \text{m}^3$$

$$P = \frac{0.1652\ \text{Kmols} \;\big|\; 8.314\ \text{KPa-m}^3 \;\big|\; (273 + 67.8)\text{K}}{\big|\; \text{Kmols-K} \;\big|} = 180\ \text{KPa}$$

(c) Entropy: $$\Delta S = (\Sigma m_i s_i)_2 - (\Sigma m_i s_i)_1$$
$$= m_{O_2}\Delta s_{O_2} + m_{N_2}\Delta s_{N_2}$$

$$\Delta s_{O_2} = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$
$$= (0.918)\ln\left[\frac{340.8}{373}\right] - \frac{8.314}{32}\ln\left[\frac{102.6}{350}\right] = 0.24\ \frac{\text{KJ}}{\text{Kg-K}}$$

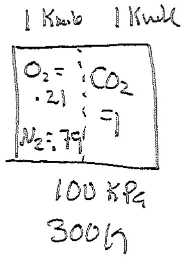
$$P_{2,O_2} = y_{O_2}P = (0.57)(180\ \text{KPa}) = 102.6\ \text{KPa}$$

$$\Delta s_{N_2} = 1.039\ln\left[\frac{340}{298}\right] - \frac{8.314}{28}\ln\left[\frac{77.4}{100}\right] = 0.22\ \frac{\text{KJ}}{\text{Kg-K}}$$

$$P_{2,N_2} = y_{N_2}P = (0.43)(180\ \text{KPa}) = 77.4\ \text{KPa}$$

$$\Delta S = (2\text{ Kg})(0.22\ \text{KJ/Kg-K}) + (3\text{ Kg})(0.24\ \text{KJ/Kg-K}) = 1.16\ \frac{\text{KJ}}{\text{K}}$$

What if:



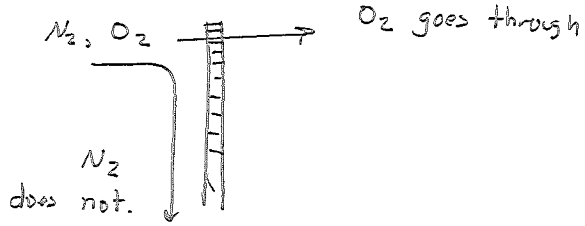
$$\Delta\bar{s}_{O_2} = -\bar{R}\ln\left[\frac{P_{O_2,2}}{P_{O_2,1}}\right] =$$

10.5 KPa

21 KPa

- Mixing is irreversible
- Unmixing takes work.

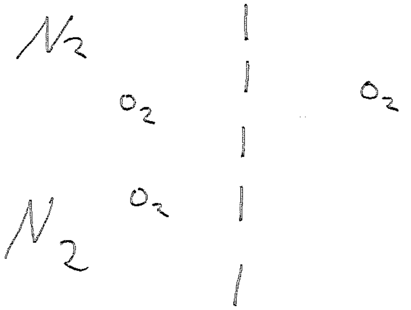
⇒ Look at making O_2 with membrane.



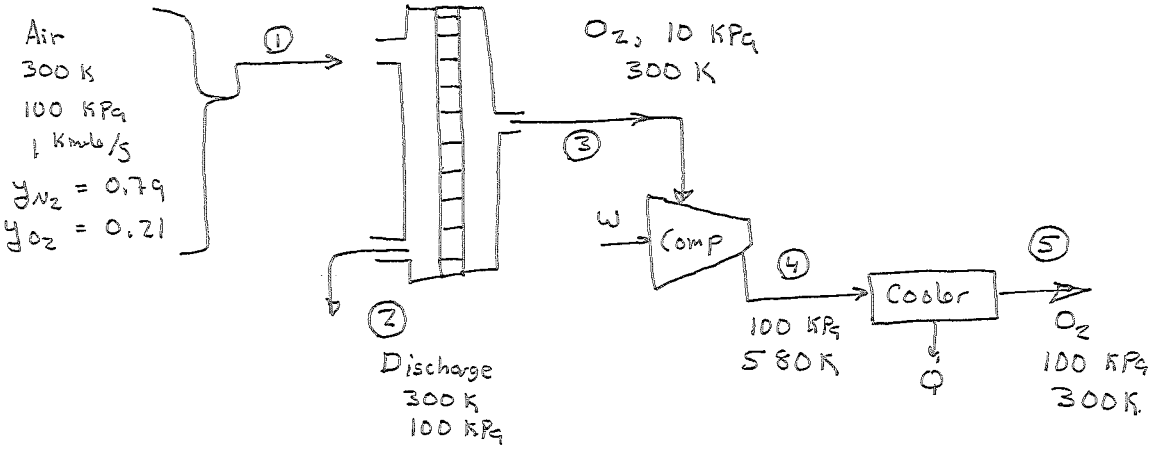
Does this get us around the work requirement?

Key Point: O_2 flows only if $P_{O_2,1} > P_{O_2,2}$ ⇒ Otherwise, O_2 goes other way.

$\underbrace{\text{(Membrane doesn't recognize } N_2\text{)}}_{\text{Membrane counts } O_2 \text{ strikes.}}$



How to make it work:



At ② what is the best we can do? Pure N_2? No!

$P_{\cancel{2,O_2}\,O_2,2} = 10$ KPa. If less, O_2 flows the other way.

$$\Rightarrow y_{\cancel{2,O_2}\,O_2,2} = \frac{P_{O_2,2}}{P} = \frac{10}{100} = 0.1$$

Now find out how much O_2 is in stream ②

$$0.1 = \frac{\dot{n}_{O_2}}{\dot{n}_{N_2} + \dot{n}_{O_2}} = \frac{\dot{n}_{O_2}}{0.79\,\frac{\text{Kmoles}}{\text{s}} + \dot{n}_{O_2}} \Rightarrow \dot{n}_{O_2} = 0.088\,\frac{\text{Kmoles}}{\text{s}}$$

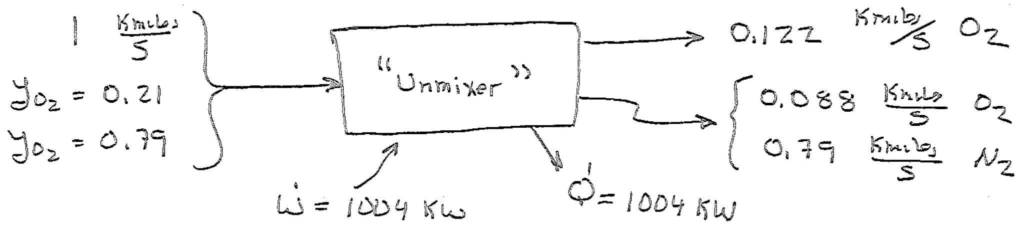
$$\dot{n}_{O_2,3} = 0.21 - 0.088 = 0.122\,\frac{\text{Kmoles}}{\text{s}}$$

Nov 8

$$\dot{W}_{comp} = \dot{n}_{O_2,3}\,\overline{C}_{P,O_2}\,(T_4 - T_3) = \frac{0.122\ \text{Kmoles}}{\text{s}}\Big|\frac{29.38\ \text{KJ}}{\text{Kmole-K}}\Big|\,580-300\text{K} = \underline{\underline{1004\text{KW}}}$$

$$\dot{Q}_{cooler} = \dot{n}_{O_2,3}\,\overline{C}_{P,O_2}\,(T_4 - T_5) = 1004\text{KW}.$$

So overall the system looks like:



2nd Law balance sheet ⇒ Increase in order or utility of gas streams
≤ Decrease in quality of energy going from organized (work) to thermal (heat).

① Sources of irreversibility?
② Run in reverse to get $\dot{W}_{out}$

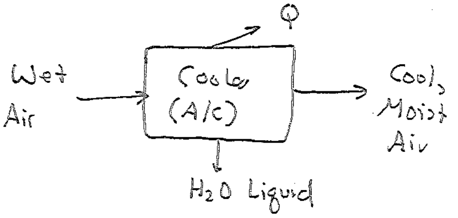
Summary: Know how to go from mole ⇄ mass compositions.

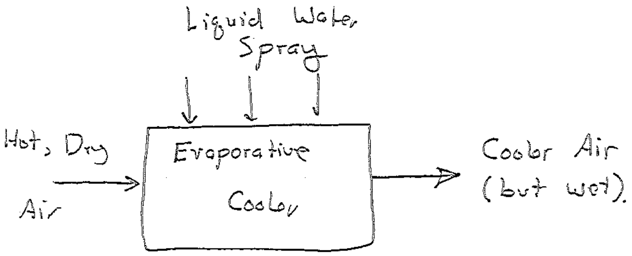
Prop ⇒ $u = \sum mf_i u_i$ ⇒ Don't mix mole and mass.

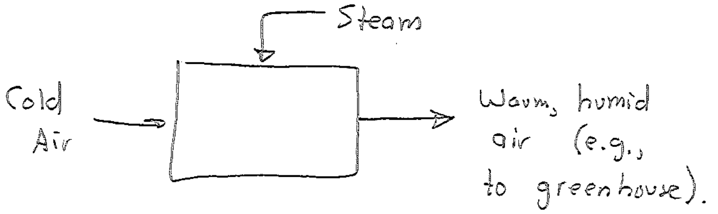
For entropy $s = \sum mf_i s_i$, but s_i changes when gas is in mix at same overall P, T.

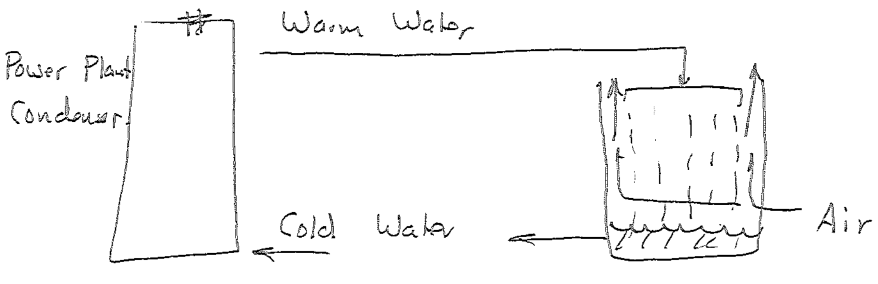
Next – **Air/Water Systems** –

Kinds of problems –





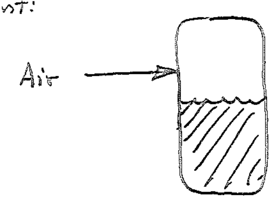




Cooling Tower –
- Each drop evaporates
  → Cools
  → Remaining water is cooled

Specialized area with its own nomenclature.

Thought experiment:



- ~~Sta~~ Water liquid/vapor mix @ 20°C
  $P = P_{sat} = 2.34$ KPa ≅ 0.02 atm.
- Now add air to the vapor space until $P = 100$ KPa, 20°C.

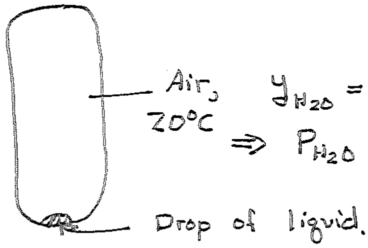
⇒ Liquid water will still want to see $P_{H_2O} = 2.34$ KPa over its surface, and will ignore the air.

- ~~Partial~~ Pressure of water = 2.34 KPa
- " " air = 97.66 KPa

This is the $\boxed{\text{Vapor Pressure}}$ — ~~Eq~~
- Saturated P_{H_2O} the liquid wants to see at its surface.
- Also, most water vapor air can hold

$\Rightarrow P_g = P_g(T)$ ⟶ A thermo property ... look it up in steam table.

Now, assume



$y_{H_2O} = 0.01$

$\Rightarrow P_{H_2O} = y_{H_2O} P = 1$ KPa

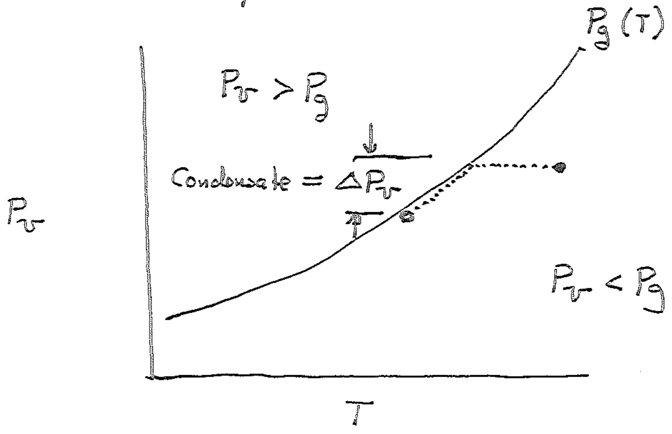
What happens over time? ⟶ Drop evaporates; Why?

Water wants to see $P_g = 2.34$ KPa over its surface, but since it sees only 1 KPa, it dries out trying to bring volume to P_g.

- The 1 KPa is the $\boxed{\text{Partial Pressure}}$ ⇒ A measure of composition

$$P_v = y_{H_2O} P$$

- Think of a plot:



Experiment.
- Car sits out overnight
- Get covered in condensate.

⇒ Why?
- Car cools, reaches P_g.

⟶ Air cannot hold excess water, so it condenses.

⇒ An aside; Air ~~[illegible]~~ doesn't get foggy because car get cooler than air ⟶ car radiates to space

Although we can work problem via the mixture ideas from before, a special nomenclature has grown up around this area:

Ways of describing amount of water in air:

$$\boxed{\text{Humidity Ratio}} \equiv \frac{\text{mass water}}{\text{mass } \underline{\underline{\underline{\text{dry}}}} \text{ air}} = \frac{m_v}{m_a} \equiv \omega \quad \text{(omega).}$$

(sometimes called absolute humidity)

Note that this is not a mass fraction, [why not?]

$$mf_v = \frac{m_v}{m_a + m_v}, \text{ but it's possible for } \omega > 1.$$

Working equation for $\omega = \omega(P_v)$

$$\omega = \frac{m_v}{m_a} = \frac{M_v n_v}{M_a n_a} = \frac{M_v P_v}{M_a P_a} = \frac{\overset{18}{M_v} P_v}{\underset{29}{M_a}(P - P_v)} = \frac{0.622 P_v}{P - P_v}$$

$$\text{but} \quad \left.\begin{aligned} n_v &= \frac{P_v V}{\bar{R} T} \\ n_a &= \frac{P_a V}{\bar{R} T} \end{aligned}\right]$$

- So now you can go $P_v \rightleftarrows \omega$

$$\boxed{\text{Relative Humidity}} \equiv \frac{P_v}{P_g} \equiv \phi$$

(what you hear on weather channel).

- Get ϕ from ω.

$$\omega = \frac{0.622 P_v}{P - P_v}, \text{ but } P_v = \phi P_g \Rightarrow \omega = \frac{0.622 \phi P_g}{P - \phi P_g}$$

$$\text{or} \quad \phi = \frac{\omega P}{(0.622 + \omega) P_g}$$

So we have 3 variables to represent humidity: P_v, ω, ϕ; Can relate as follows:

	P_v	ω	ϕ
P_v		$P_v = \frac{\omega P}{0.622 + \omega}$	$P_v = \phi P_g$
ω	$\omega = \frac{0.622 P_v}{P - P_v}$		$\omega = \frac{0.622 \phi P_g}{P - \phi P_g}$
ϕ	$\phi = \frac{P_v}{P_g}$	$\phi = \frac{\omega P}{(0.622 + \omega) P_g}$	