PERSONAL NOTES

ENGINEERING THERMODYNAMICS

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2023

Sept. 26, 2023. — (1 week-1) Date. No.

- 1st & 2nd laws of thermodynamics.

. analyze thermo-system based on laws

⇓

energy-conversion system.

↗ energy density → mass. volume, → efficiency

* 1st law for control mass & control volume systems.

➤ canvas - main platform.

➤ Gradescope - grading

➤ piazza - discussion.

Advanced Thermodynamics for Engineers.

— Kenneth Wark.

(#) Thermodynamics — An Engineering Approach.

Physical understanding + Math derivation

Date.
No.

Tools : MATLAB + Cantera

Grading : HWs. 50%
Midterm 30%.
Project. 20%

Syllabus.

- 1st & 2nd law Thermodynamics
- exergy analysis. 1st + 2nd law
- ideal → real gas : $f(p, v, T) \Rightarrow$ EoS.
- thermodynamic property relations. ~~xxx~~ → computation
  - $f(p, v, T)$ → prop. of interest.
- Equilibrium & multicomponent &
- ↑ multiphase mixtures : Gibbs. f.e.
- Chemical thermodynamics. $A+B \rightarrow C+D$

no chemical reactions.
physically mixing. → phase change.

⑱ < 6 ↪ 5

Date.
No.

Thermodynamics – heat & power.
↳ energy transformation & conv.

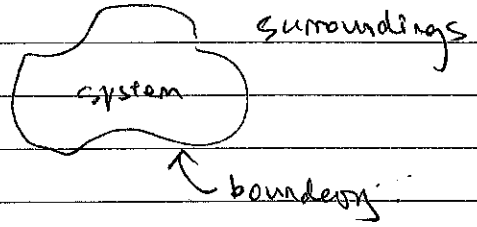
Energy list.

- kinetic
- chemical
- electrical
- nuclear. ← . (nuclear interactions).
- thermal
- magnetic.

potential.	chemical.	✓
kinetic.	thermal.	↑ ✓
electrical	nuclear	×
magnetic.	latent	✓
elastic		
external	internal	
(mass)	(Molecular.)	

$\underbrace{E}_{KE + PE}$ + U ← ✱ associated w/ individual molecules/atoms.

— define a system.



∘ Control mass — closed system.

∘ Control volume — ~~close~~ open system

m
V
T →
P
ρ

vs. { Intensive → non-depend on mass,
extensive → depend on mass

(divide by mass)

— Equilibrium states.

T, P, → represent the whole system.

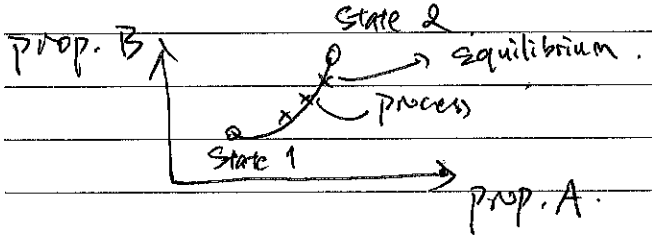
— State Postulate.

$$\begin{cases} u=u(T,v). \\ p=p(T,v). \end{cases} \qquad pv=RT.$$

☆ in order to describe the system, we only need two variables.

mixtures → bring more variables in there

— Process.



{ - process
- path.
- quasi-equilibrium process.

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First Law of Thermodynamics

Production Accounting.

Accumulation( ) = inflow( ) - outflow( ) + production( ).

$\Downarrow$

(change of ( ) of system)

$\Delta m_{sys} = m_{in} - m_{out}$.

$\Delta E_{sys} = E_{in} - E_{out}$.

$\Delta S_{sys} = S_{in} - S_{out} + S_{gen}$.

$\Delta X_{sys} = X_{in} - X_{out} - X_{des}$.

$$\frac{dE_{sys}}{dt} = \underbrace{\dot{E}_{in} - \dot{E}_{out}}$$

work
heat
mass

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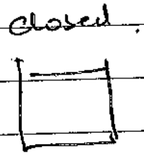
No.

$\Delta E_{sys} =$.



mass - 2kg.

600kPa — 800kPa
P 200°C. T
T

det: init. vol. ; work ; heat transfer.

$\frac{P}{T}$ = const.

$P_{init} \to P_{end}$ $T \equiv 200\,°C \to 473.15\,K$.

$P_{init} V_{init} = P_{end} V_{end}$?

mass — V_{end}: $\rho V = m$

$V = \frac{m}{\rho}$.

$V_{init} = \frac{\cancel{8}}{\cancel{6}} \frac{4}{30} V_{end}$

$\frac{4}{30} = \frac{2}{\rho_{air}}$

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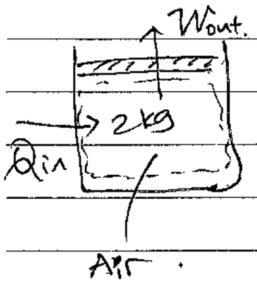
☆ - Isothermal : $u=h$
- control Mass: $\Delta U=0$
- isentropic $\Delta S=0$



Given: $T_1=T_2=200°C$.

$P_1=600$ kPa, $P_2=80$ kPa

$P_1 v_1 = RT_1$.

$P_1 \frac{V_1}{M} = RT_1$.

$V_1 = \frac{mRT_1}{P_1}$.

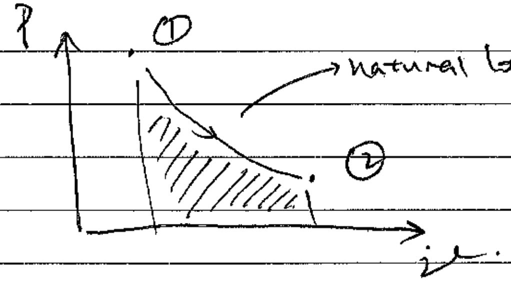
$\Delta E = E_{in} - E_{out}$.

$U_2 - U_1 = Q_{in} - W_{out}$.

$m(u_2-u_1) =$

$mC_v(T_2-T_1) \longrightarrow Q_{in} - W_{out}$.

0.



const T → Pv → const

- Abiadic $Q=0$
- Isobaric $\Delta P=0$

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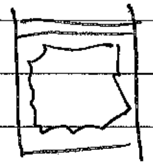
Preview.

Ex: CM

$$\boxed{ds=\frac{C dT}{T_v}}$$



closed system.

$$\boxed{S=CT}$$

$$S=\frac{Q}{T}.$$

↓

we get Q.

$T_1 = 100°C \to 373K$.

Consider entropy: $ds = \frac{du}{T} + \frac{Pdv}{T}$.

heat trans. → work

$$T ds - \underset{U}{du} = Pdv.$$

$S = U + W$, Q

Const. pressure & Temperature → P, T

$\overset{\Delta}{P}v = R\overset{\Delta}{T}$

determine W & Q.

cannot use $Q=\Delta U + W$.

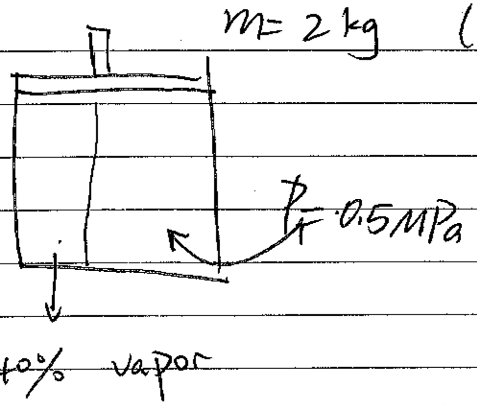
$v = \frac{RT}{P}$.

$S=\frac{Q}{T}$ $Q = ST$. $PdV = \boxed{TdS - dU}$ $\boxed{cdT}$

HW.

Problem #1.   Control volume problem

$m = 2\,kg$ (H_2O)



$P_2 = 2MPa$.

multiphase → state postulate : P. T. ✓

Calculate: ① volume V

② heat transfer Q.

③ T-s process

1st law: Work: $W = \int_{V_1}^{V_2} pdV$ ↳ V fixed.

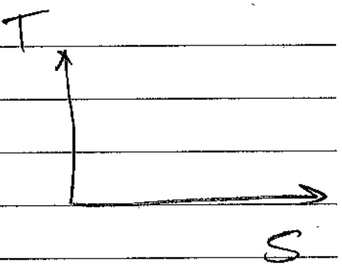
⇓

$Q = \Delta U + W_{\to 0}$.

control volume → zero work wrong

$dW = -pdV$

$\cancel{d}Q = \Delta U + W$



$P_1 \to P_2$

0.5MPa   2MPa

Control mass: → $\Delta U = 0$

$Q = W$ we know V_1

$Q = \int_{V_1}^{V_2} -pdV$

$= \cancel{-p\ln\left(\frac{V_2}{V_1}\right)}$. $-\overset{\checkmark}{p}(V_2 - \overset{\checkmark}{V_1})$

$ds = \frac{dh}{T} - \frac{vdP}{T}$. $-p\Delta V = Q$.

$ds = \frac{du}{T} + \frac{pdV}{T}$. $T = (U+W)\frac{1}{S}$.

$S = \frac{U}{T} + \frac{W}{T} = \frac{U+W}{T}$

To conclude.

① – 1st law & control Mass

$$Q = -p\Delta V$$

② – EoS:

Van der Waals.

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

Solve for V → Q.

③ $S = \frac{U + W}{T} = \frac{\quad}{T}$

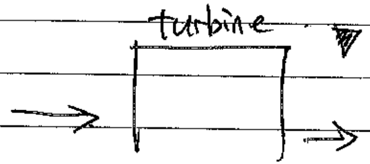
$$dS = \frac{1}{T}(\cancel{dU} + pdV).$$

$$S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

Subs. T.

Problem #2.

▼ Control volume
(mass flow).



▼ isentropic.
↳ $dS = 0$

$P_1 = 10$ bar

$T_1 = 800$k.

$P_2 = 0.2$ bar.

Calculate: ① Work.

② thermodynamic state of fluid i.t.o. quality & temp.

③ plot P–h.

assump.
- ○ steady-flow
- ○ $A_1 = A_2$
- ○ ideal gas

$$\Delta E = \Delta m \cdot e + \Delta W.$$

$$\Delta E - \Delta m e = \Delta W.$$

$$\frac{\delta E}{\delta m} = h + pe + ke$$

① mass balance.
$P_1V_1 = P_2V_2$ ✓

② ideal gas T_1

③ ~~ener balance~~.

~~Q~~ $W = nRT\ln\left(\frac{V_2}{V_1}\right)$

③. Energy balance.

~~$\dot{Q}_{in} + \dot{W}_{in} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right)$~~

~~$= \dot{Q}_{out} + \dot{W}_{out} + \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right).$~~

~~$\frac{\delta E}{\delta m} = h + pe + ke.$~~

second law : $ds = \frac{dh}{T} - \frac{v\,dP}{T}.$

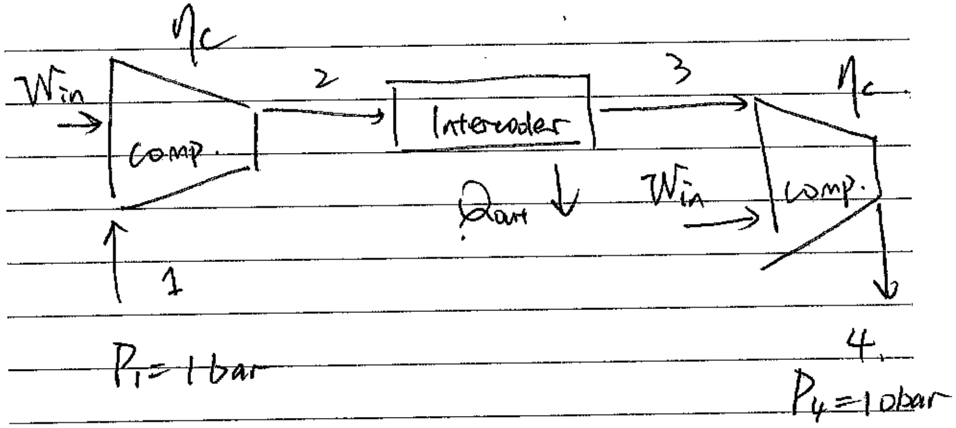
because isentropic → $ds = 0$

$$\frac{dh}{T} = \frac{v\,dP}{T}$$

$$h = \int_{P_1}^{P_2} v\,dP = v(P_2 - P_1)$$

Problem #3

(ambient temp. : 300k).



- Dry air (ideal gas).
- effectiveness $\varepsilon = 0.85$ · (intercooler).
- isentropic efficiency $\eta_c = 70\%$.

↓

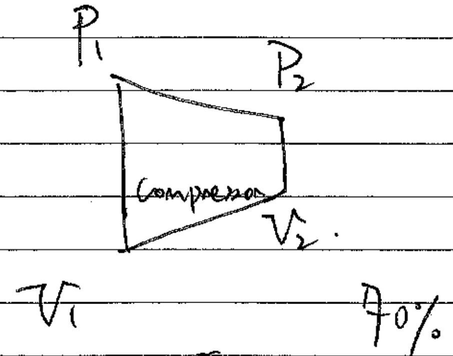
$\Delta S = 0$

determine : $\frac{P_2}{P_1}$

→ for min. $\frac{W}{\dot{m}}$.

~~Compressor 1: $Q = \Delta U + W$~~

Compressor 1



ideal gas: $\frac{P_1}{P_2} = \frac{V_2}{V_1}$ | mass balance $P_1 V_1 A_1 = P_2 V_2 A_2$

$$\begin{cases} P_1 V_1 = nRT_1 \\ P_2 V_2 = nRT_2 \end{cases}$$

- energy balance:

$$\dot{Q}_{in} + \dot{W}_{in} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right)$$

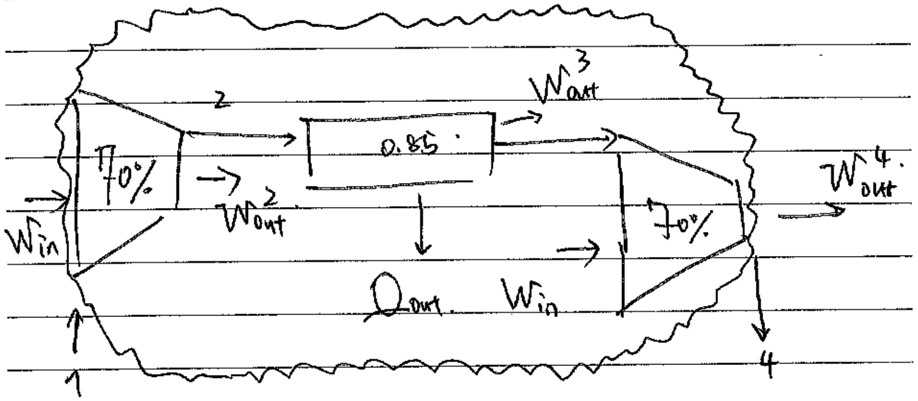
$$= \dot{Q}_{out} + \dot{W}_{out} + \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right).$$

- isentropic

$$ds = \frac{du}{T} + \frac{P\,dV}{T} = 0$$

$$dU = -P\,dV$$

Work: $W = -\int p\,dV$



$$\dot{Q}_{in} + \dot{W}_{in} = \dot{Q}_{out} + \dot{W}_{out}$$

For compressor 1:

$$Q_{out} - Q_{in} = 0.3 W_{in}.$$

- isentropic $ds = \frac{du}{T} + \frac{P\,dv}{T} = 0.$

Work = internal energy change

Date.
No. Sept 28, 2023. - (1 Week - 2)

1st law for control volume system.

▷ write laws in the rate form

$$\left.\begin{array}{l} \frac{dm_{sys}}{dt} = \dot{m}_{in} - \dot{m}_{out} \\ \frac{dE_{sys}}{dt} = \dot{E}_{in} - \dot{E}_{out} \end{array}\right\} \text{steady state}$$

→ time concept

$\frac{d}{dt} = 0$

$E_{sys} = m_{sys}(u + \frac{v^2}{2} + gz)$.

$\dot{E}_{in} - \dot{E}_{out}$ ↓ transfer across boundary.

⇓

$\dot{m}_{in} = \dot{m}_{out}$

$\dot{E}_{in} = \dot{E}_{out}$

equilibrium

↓

spatial concept $\begin{cases} \text{mass} \rightarrow \dot{m}(h + \frac{v^2}{2} + gz) \\ \text{heat} \rightarrow \dot{Q}_{in}, \dot{Q}_{out} \\ \text{work} \rightarrow \dot{W}_{in}, \dot{W}_{out} \end{cases}$

☆ { steady state
equilibrium

$$\dot{m}(u + \frac{v^2}{2} + gz + \underbrace{pv}_{\text{flow work}}).$$

Enthalpy: $h\,\cancel{\phi} = u + pv$ (internal ener. + flow work)

Date.
No.

Example

$\dot{m}_1 = 70kg/s$.

in: $T_1 = 480K$; $P_1 = 1atm$.

out: $T_2 = 400K$;

in: $T_1' = 298K$; $P_1' = 7.5kPa$.

$\dot{m}_1' = 2kg/s$

- abiadic :
- kinetic & potential ener. → 0.

$E = U + \cancel{KE + PE}$

$C_p = 1.02kJ/(kg \cdot K)$

- ① power produced
- ②. turbine inlet. temp., const press.
- ③. econ. (efficiency).

$\frac{\delta E}{\delta m} = h = $ ~~dst~~

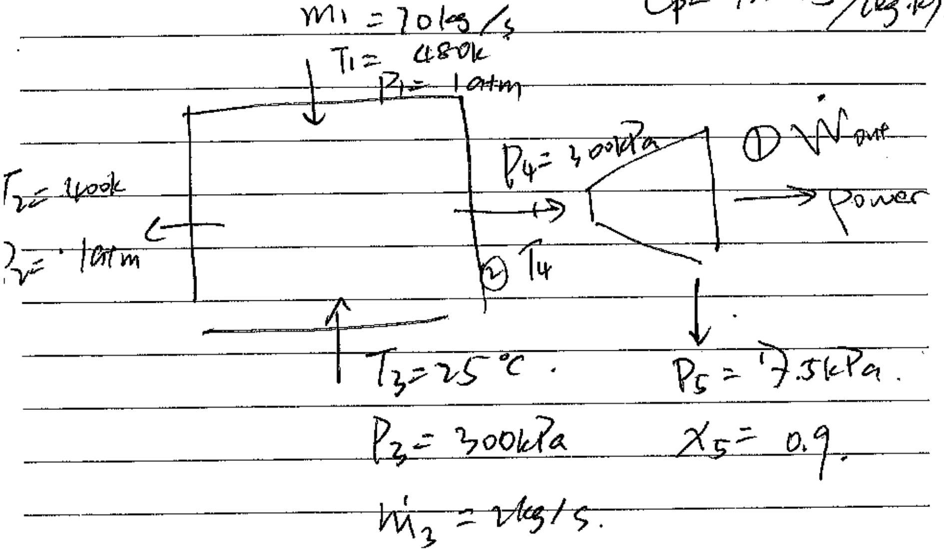
$$\cancel{\dot{Q}_{in}} + \dot{W}_{in} + \dot{m}_i \left(h + \frac{V_i^2}{2}\right) + \dot{m}_i \left(h + \frac{V_i^2}{2}\right)$$

$C_p \Delta T$

$$= \cancel{\dot{Q}_{out}} + \dot{W}_{out}$$

$C_p \Delta T$

$C_p = 1.02\,\mathrm{kJ}/(\mathrm{kg \cdot K})$.



quality: $\frac{\text{vapor}}{\text{liquid}}$.

Assume: $\dot{Q} = 0$; $\Delta KE, \Delta PE = 0$

1st step: choose system,

2nd step: energy balance

mass balance.

$\dot{E}_{in} = \dot{E}_{out}$;

$\dot{m}_1 h_1 + \dot{m}_3 h_3 = \dot{m}_2 h_2 + \dot{m}_5 h_5 + \dot{W}_{out}$

$\dot{W}_{out} = \dot{m}_1 (h_1 - h_2) + \dot{m}_3 (h_3 - h_5)$

$= \dot{m}_1 C_p (T_1 - T_2) + \dot{m}_3 (h_3 - h_5)$

$\boxed{= 1255.22\,\mathrm{kW}}$

additional notes

IG: $du = C_v dT$

$dh = C_p dT$

→ ability for molecules to store energy

3rd IG law

1st step. (re) chose system..

2nd step. $\dot{m}_1 h_1 + \dot{m}_3 \underset{?}{h_3} = \dot{m}_2 h_2 + \dot{m}_4 h_4$.

$h_4, P_4 \rightarrow \boxed{T_4 = 247\,°\mathrm{C}}$.

Cantera.

Date.
No.

2nd Law.

entropy - disorder.

$$\boxed{\star\ h = u + pv}$$

☆ Gibbs equation - Tds relation.

$$\begin{cases} ds = \dfrac{dh}{T} \cancel{+} - \dfrac{v\,dp}{T} \\ ds = \dfrac{du}{T} + \dfrac{p\,dv}{T} \end{cases} \qquad \begin{cases} T\,dS = du + p\,dv \\ T\,dS = dh - v\,dp. \end{cases}$$

Ideal gas. → $pv = RT$.

$$T\,ds = c_v\,dT + p\,dv$$

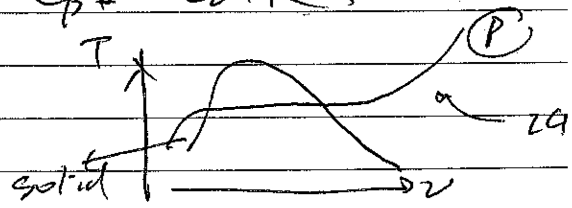
$$T\,ds = c_v\,dT + \frac{RT}{v}\cdot dv$$

$$ds = \frac{c_v}{T}\,dT + \frac{R}{v}\,dv.$$

$$s_2 - s_1 = \int ds = C_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right).$$

$$k = \frac{c_p}{c_v} \rightarrow c_p = c_v + R.$$

☆ phase diagram.



Date.
No.

Incompressible substance: v = const.

$$T\,dS = du + p\,dv.$$

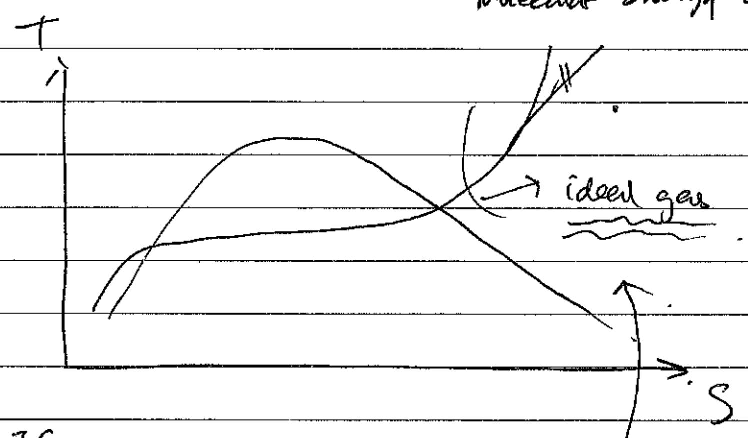
ICS (liquid, solid)

$$T\,ds = du + \nearrow$$

$$T\,dS = c\,dT. \quad (c_p \approx c_v)$$ → pressing a rock

$$dS = c\,\frac{dT}{T}.$$ ← solid.

molecular energy discussion.



IG:

$$\frac{ds}{dT} = \frac{c_p}{T} \rightarrow \overset{\text{slope}}{\left(\frac{dT}{ds}\right)} = \frac{T}{c_p}$$

Date.
No.

Entropy balance.

transfer entropy : mass + heat

× work

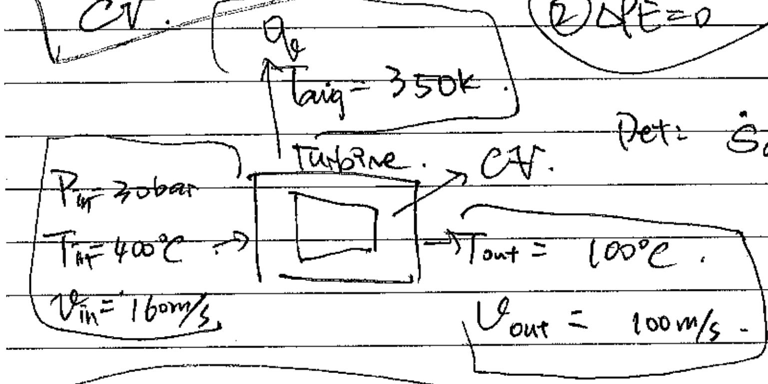
~~$S_{in} - S_{out} + S_{gen} = \Delta S_{sys}$.~~

mass: $\dot{m}s$. → $s = s_{in}$ or s_{out}.

heat : $\dot{Q}/T$.

~~CM~~ Example

CV.



② $\Delta PE = 0$

Det: $\dot{S}_{gen}$

① Steady State : $\frac{d}{dt} = 0$. → assume

$W = 540kJ/kg$.

Date.
No.

~~$Tds = dh - vdp$.~~

① system

② mass & energy & entropy balance.

$\dot{E}_{in} = \dot{E}_{out}$

$\cancel{\dot{m}}\left(h_1 + \frac{V_1^2}{2}\right) = \cancel{\dot{m}}\left(h_2 + \frac{V_2^2}{2}\right) + \frac{\dot{W}_{out}}{\dot{m}} + \frac{\dot{Q}_{out}}{\dot{m}}$

$\frac{\dot{Q}_{out}}{\dot{m}}$ ⇒ to be solved

$0 = \dot{S}_{in} - \dot{S}_{out} + \underset{\uparrow \text{to be solved}}{\dot{S}_{gen}}$

$= \dot{m}s_1 - \dot{m}s_2 - \frac{\dot{Q}_{out}}{T_b} + \dot{S}_{gen}$

Input Mechanism

Self-contained ⟵ {
- gri30.yaml → water
- liquidvapor.yaml ⟵ mixture.
- air.yaml.

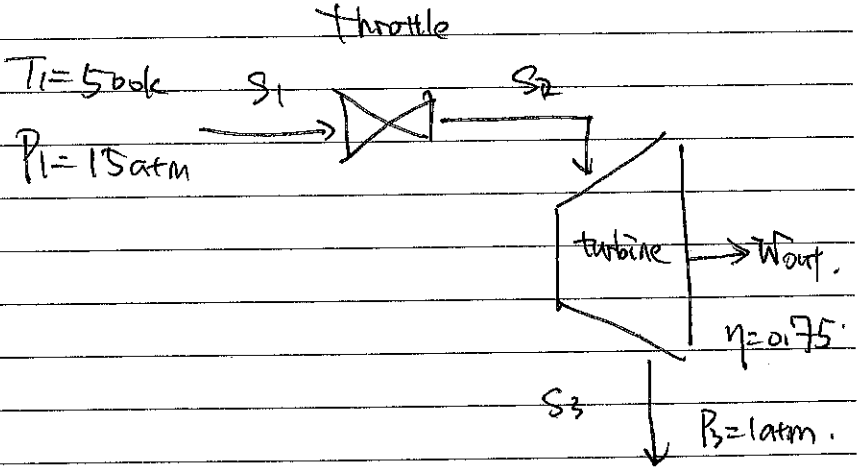
}

Do not use ".cti" & ".xml".

Solution()
Air(). — mechanism.

Set() ↦ define properties.

Example



Compressor: $W_{real} = W_{isen} / \eta$

Turbine: $W_{real} = W_{isen} \cdot \eta$

Efficiencies: $\varepsilon = (h_{out} - h_{in}) / (h_{out,ideal} - h_{in})$.

— define object.

⇓

conduct state changes.

① Set(). → Set state properties.

↓

record all thermodynamical properties of interest.

② Set(). → throttle.

→ we do not know the pressure, a good practice is to guess

walk around known path
↑
apply efficiency

③ Set() → turbine

write a "for loop"
⇓
plot it

isotropic → known path

P_3: $P_2=P_3$

Iterate to find solution

P_4: $P_2=P_3=P_4$.

$P_5=P_6=P_7=P_0$.

☆ Value = subs (a, [c d e], [1 0 3]).

↓

a=a(c, d, e)

Value = double (Value).

Pset 3. : Subs. syms ← func.

↓

get results ← Solve for symbol

from "for" loops.

```
classdef dog < handle
```

```
properties.
        family = "    "
          ears = "    "
        speaks = "    "
end.

methods.
        speak (self)
              self. speaks = true;
end
```

Date.
No.

Week 2 - 1

Exergy – Combination of 1st & 2nd law

1 Exergy : X.

2. fixed mass ϕ, flowing mass ψ.

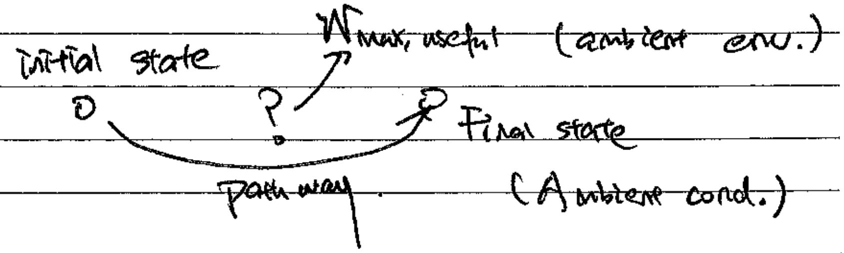
3. Exergy balance → CM & CV.

4. Second law efficiency.

ambient condition: exergy is zero

Definition: . A measure of work potential.

The maximum useful work that can be obtained from the system at a given state in a specified env.



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Exergy does not depend on the process

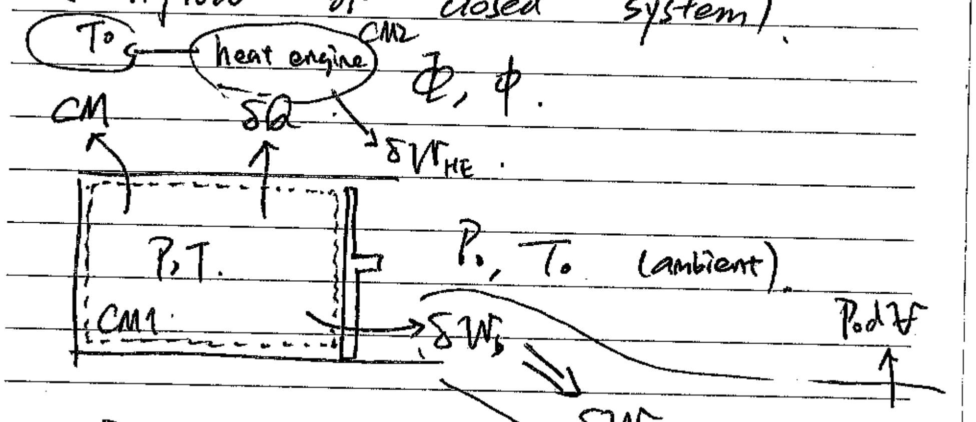
↓

is a state property.

In real-world app., actual exergy depends on the device chosed.

Exergy of a fixed mass

(non-flow or closed system).



$(P, T) \rightarrow (P_0, T_0)$

↓

$W_{max, useful}$.

"Imaginary Carnot Cycle"

Date.
No.

ambient : dead state

$$X = \Phi_{\text{fixed mass}} = \int_{i.s.}^{d.s} (\delta W_{b,\text{useful}} + \delta W_{HE})$$

CM₁:

$$dU = -\delta Q - \delta W_b .$$

dU ↓ state properties ↓ (don't know what's in between)

δQ, δW_b → path functions

$$\delta W_b = P\, dV = \delta W_{b,\text{useful}} + P_0\, dV .$$

$$\Rightarrow \delta W_{b,\text{useful}} = \delta W_b - P_0\, dV .$$

$$= -\delta Q - dU - P_0\, dV$$

$$CM_2: \quad 1 - \frac{T_0}{T} = \frac{\delta W_{HE}}{\delta Q} .$$

$$\Rightarrow \delta W_{HE} = \delta Q \left(1 - \frac{T_0}{T}\right).$$

Date.
No.

↓ Substituting the work changes

$$X = \int_{is}^{ds} \left(-\delta Q - dU - P_0\, dV + \delta Q - \delta Q \frac{T_0}{T}\right)$$

$$= \int_{is}^{ds} \left(-dU - P_0\, dV - \delta Q \frac{T_0}{T}\right)$$

$$CM_1: \quad \underbrace{dS}_{\text{entropy change}} = -\frac{\delta Q}{T} \Rightarrow \delta Q = -T\, dS$$

↓ substitute back:

$$X = \int_{is}^{ds} \left(-dU - P_0\, dV \underbrace{- \delta Q \frac{T_0}{T}}_{+T_0 dS}\right).$$

$$\Phi = (U - U_0) + P_0 (V - V_0) - T_0 (S - S_0)$$

$$+ \frac{m}{2} v^2 + mgz$$

⇑

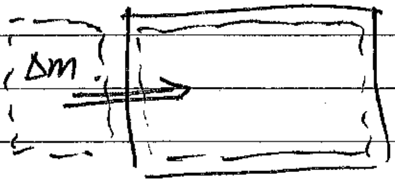
for a fixed mass.

Date.

No.

The exergy of a flow mass

ψ, Ψ



* flow work: $h = u + Pv$

$X_{flow,useful} = Pv - P_0 v$

$\psi_{flow mass} = \Phi_{fix mass} + X_{useful\ flow\ work}$

$= (U - U_0) + P_0(V - V_0)$

$- T_0(S - S_0)$

$+ \underbrace{(P - P_0)V}_{\text{useful part}} + \frac{mV^2}{2} + mgz$

$= \overset{H}{U} - \overset{H_0}{U_0} + P_0V - P_0V_0 - T_0S + T_0S_0$

$+ PV - P_0V + \frac{mV^2}{2} + mgz$

Date.

No.

$= H - H_0 + \cancel{P_0(V - V)} - T_0(S - S_0) + \sim$

$= (H - H_0) - T_0(S - S_0) + \sim$

Exergy Balance (is not conserved).

$\Delta X_{sys} = X_{in} - X_{out} - X_{des}$

$\frac{d X_{sys}}{dt} = \underbrace{\dot{X}_{in} - \dot{X}_{out}}_{\text{mass, work, heat}} - \dot{X}_{des}$

fixed mass comes in here

$\Phi_{fixed mass}$

flow mass crossing b.

$\psi_{flow mass}$.

∘ exergy transfer by heat:

$X_{heat} = Q\left(1 - \frac{T_0}{T_b}\right)$

∘ exergy transfer by work:

for moving boundary work.

$$X_{work} = \begin{cases} W - W_{surr} = W - P_0(V_2 - V_1) \\ W : \text{other forms of work} \end{cases}$$

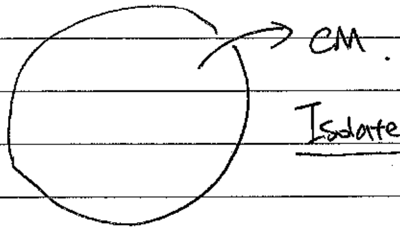
exergy destroyed:

$$X_{des} = T_0 \, \Delta S_{gen} .$$

Example

$$X_{des} = T_0 S_{gen} \qquad (\geq 0)$$

{irreversible
 reversible



Isolated System

$$\Delta E_{sys} = E_{in} - E_{out} , \quad E_1 = E_2 .$$

$$\Delta S_{sys} = S_{in} - S_{out} + S_{gen} , \quad S_2 - S_1 = S_{gen} .$$

$$\Delta X_{sys} = X_{in} - X_{out} - X_{des}.$$

$$X_2 - X_1 = - X_{des}$$

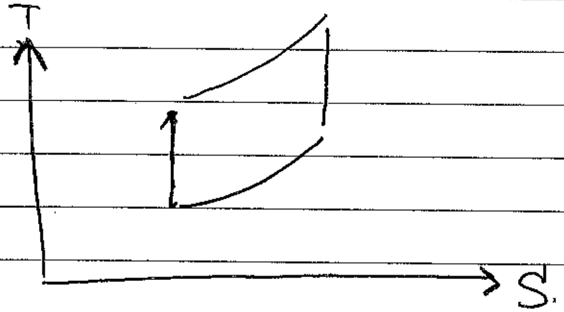
$$X_{des} = X_1 - X_2$$

$$= (E_1 - E_2) + P_0(V_1 - V_2)$$

isolated system

$$- T_0(S_1 - S_2).$$

$$= 0 + 0 + T_0 S_{gen}$$



Tutorial

maximum - reversible work
(no entropy generation)

exergy review:

KE

PE

Work $W - W_{surr}$ (if boundary).

Heat $= Q(1 - \frac{T_{sink}}{T_{medium}})$ → environment; → system

mass $= (u - u_0) + \underline{P_0(v - v_0)} - T_0(s - s_0)$ → boundary work.

mass-flow $= (h - h_0) - T_0(s - s_0)$

☆: we have to do temp. in K.

Exergy destroyed

$X_{loss} = I = T_0 S_{gen}$.

↳ if ask for min work $I = 0$

exergy balance.

~

{ reversible
{ irreversible

$(W_{u,rev})_{max} = \Phi_1$ (CM)

$(W_{u,rev})'_{max} = \Psi_1$ (CV)

$(W_u^{12})_{rev} = \Phi_{12}$ (CM) or Ψ_1 (CV)

$W_u^{12} = (W_u^{12})_{rev} - I_{12}$

no exergy destroyed, minimum amount work

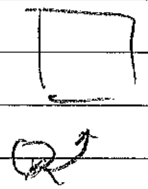
frictionless case

↓

work become a variable

$\Delta X = U_2 - U_1$ ~~[illegible]~~

not all reversible are isentropic.

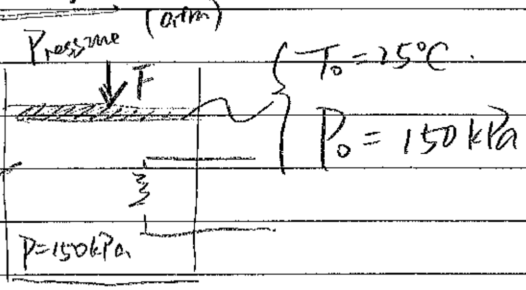


slowly → reversible ✓ isentropic ✗

$$\eta_{II} = 1 - \frac{X_{des}}{X_{supplied}}$$

$$\eta_{II} = \frac{W_u}{W_{rev}}$$

Example 1.



2L ✓

$T_0 = 25°C$

$P_0 = 150 kPa$

insulated → no heat exchange.

$Q = 0.$

- 2L water
- saturated
- $x = 0.$
- $P_{sat} = 150kPa$ ← force from the piston

begin ↑

First & Second law

1st law: $E_{in} - E_{out} = \Delta E_{sys}.$

$\quad\quad Q \quad\quad W_{out}$

$$2200kJ - P_0(V_2 - V_1) = U_2 - U_1$$

$$2200kJ = \underbrace{U_2 + P_0 V_2}_{enthalpy} - U_1 - P_0 V_1$$

$$2200kJ = h_2 - h_1$$

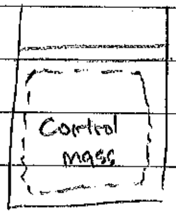
State = Thermostate (Water)

S1 = State. updateState ('P, Liquid', [ ])

$h_2 = 2200 \times 10^3 + S1.h$

→ find state 2 using 1st law:

S2 = S1. updateState ('P, H', [ ])



Using 2nd law:

$$\Delta S_{sys} = \cancel{S_{in}} - \cancel{S_{out}} + S_{gen}$$

↳ $S_{gen} = \Delta S$

code

Sgen_12 = S2.s - S1.s .

minimum work <-> max reversible work

$\cancel{\Delta X} = \cancel{X_{in}} - \cancel{X_{out}} - \cancel{X_{des}}$

a → b ⇒ State 1 and State 2

$W_e = (u_2 - u_1) + P_0(v_2 - v_1) - T_0\underbrace{(S_2 - S_1)}_{S_{gen}}$

no heat transfer

⇓

isentropic

reversible

↓

Should be no entropy

↓

no $\cancel{X_{des}}$ (S_{gen})

$\underbrace{h_2 - h_1}_{W_{e,actual}} - T_0(S_2 - S_1)$

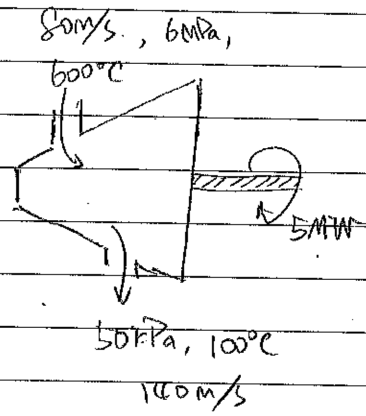
---

molecular motion, vapor, multiphase vibration, etc. $\boxed{\text{caused entropy}}$!

$W_{min} = 2200 \times 1e3 - (25 + 273.15) \times S_{gen,12}$

$W_{actual} - W_{rev.} = I$

Example



first: First & Second law → Pull in Matlab

$h_{in} + KE_{in} - h_{out} - KE_{out} - W_{out} = 0$

$X_{in} - X_{out} - \cancel{X_{des}} \xrightarrow{} 0 = 0.$

$\Delta KE + \cancel{\Delta X} + W = 0$

$KE_{in} = KE_{out} + h_{in} - h_{out} - \overbrace{T_0(S_{in} - S_{out})}^{\text{part from control volume}} - W = 0$

during ideal case

leave it as a var.

↓

assume no entropy generate to find max W

$\eta_{II} = \frac{W_{useful}}{W_{max,rev}}$ → W_{actual}

‖

maximum, reversible

‖

what we solve for

Date.
No.

$W_{irreversible} = W_{rev} + T_0 S_{gen}$

entropy { mass flow
heat

no other forms carry entropy

Date.
No.

Week 3 - 1

Equation of State

- EOS for ideal fluids
  - ideal gas & incompressible subs
- EOS for real gases & fluids
  - → Van der Waals
  - → corresponding principles
  - → Virial state eq.
    - ↪ taylor exp → $Pv = RT$

☆ accurate thermodynamic calculations

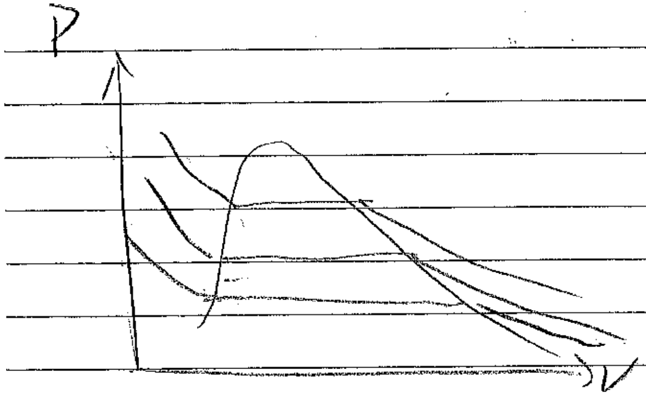
nondimensionalized number

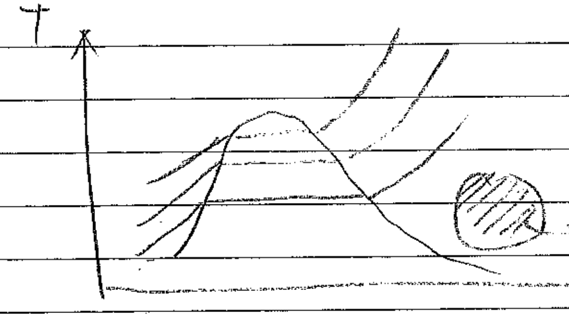
{ van der Waals
Benedict - Webb - Rubin

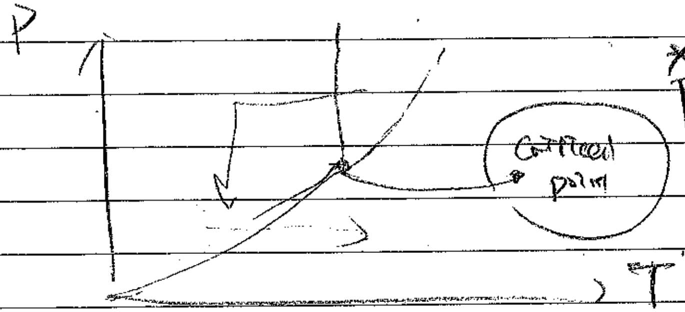
Corresponding principles.

$$Z = \frac{Pv}{RT} \quad Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$$

$$P = \sum_{n=1}^{9} \frac{a_n}{v^n} + e^{(-v_c/v)^2} \sum_{n=10}^{15} \frac{a_n}{v^{2n-17}}$$







* Supercritical fluid enhance the transport property

EOS

Ideal Gases

EOS → $Pv = RT$.

Ideal fluid: incompressible substances

⇓

assumption: volume does not change

$du = C_v\,dT$.

$\Delta u = u_2 - u_1 = \int_1^2 c(T)\,dT$.

$h = u + Pv$.

$dh = du + v\,dP + \underset{\to 0}{P\,dv}$

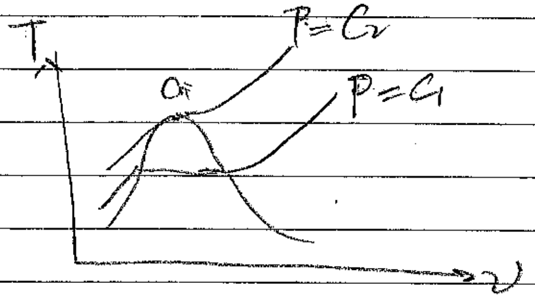
pressure can change the enthalpy

---

real gases?

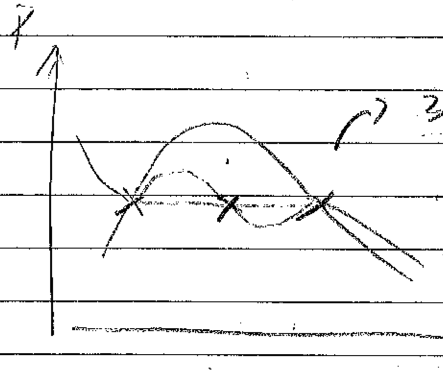
vdW Eq. $\underbrace{\left(P + \frac{a}{v^2}\right)}_{\text{intermolecular forces}} \underbrace{(v-b)}_{\text{size effect}} = RT.$ → cubic equation of state

← fit a, b.



$$\begin{cases}\left(\frac{\partial P}{\partial v}\right)_{T_c}=0\\ \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c}=0\end{cases}$$

→ Substitute these conditions, one can solve for a & b.



3 solutions

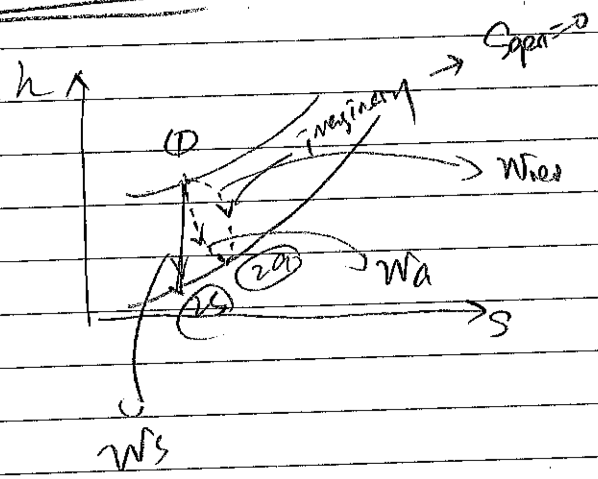
↳ van der Waals equation is not accurate

Take A_{23} for a, b for lc steps.

the corresponding principle

reduced pressure, $P_s = \frac{P}{P_c}$

Week 3 -2



1st law efficiency : $\frac{W}{W_{in}}$

could be heat

$$\left(P+\frac{a}{v^2}\right)(v+b)=RT$$

force correction

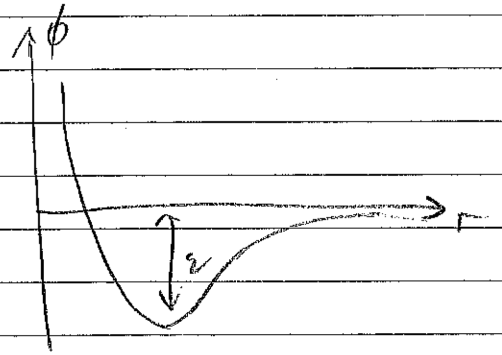
Volume correction

$$\begin{cases}P_c,\ T_c\\ \left(\frac{\partial P}{\partial v}\right)_{T_c}=0\\ \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c}=0\end{cases}$$

Date.

No.

— corresponding principles



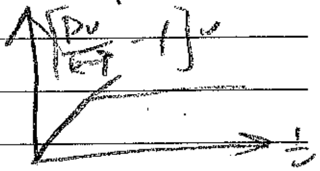
$$Z = \frac{Pv}{RT}$$ Lee-Kesler

$$Z_1(T_r, P_r, \omega) = \underbrace{Z_1^{(0)}(T_r, P_r)}_{\Downarrow \ \text{2-parameter}} + \underbrace{\omega Z_1^{(1)}(T_r, P_r)}_{\downarrow \ \text{3-parameter}}$$

Virial Equation of State.

$$Z_1 = \frac{Pv}{RT} = 1 + \underbrace{\frac{B(T)}{v} + \frac{C(T)}{v^2} \ \ldots}_{\text{virial coefficients}}$$

$$\left(\frac{Pv}{RT} - 1\right)v = B(T) + \frac{C(T)}{v}$$



Date.

No.

Thermodynamic Property Relations

function $(P, v, T) \rightarrow$ other properties

h, u, s, c_v, c_p, g

Maxwell eq.

Gibbs eq. (Tds relation)

other than first & second law

Four Maxwell Relations.

$$\begin{cases} \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \\ \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \end{cases}$$

Partial differential Relations

① $du = Tds - pdv$.

② $dh = Tds + vdp$

for ①: $\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial p}{\partial s}\right)_v$

for ②: $\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$

Gibbs function: $g = h - Ts$
Helmholtz function: $a = u - Ts$
} $g = a + pv$

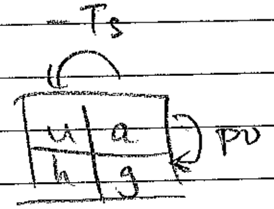
③ $dg = dh - Tds - sdT$
$= vdp - sdT$

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

$\boxed{pvTs}$

④ $da = du - Tds - sdT$
$= -pdv - sdT$

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



* physical understanding of h)

Using Maxwell equation to show $s = a + b\ln v$ for ideal gas

$\left(\frac{\partial s}{\partial v}\right)_T = b\frac{1}{v}$

$pv = RT$

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

$\frac{\partial p}{\partial T} = \frac{R}{v}$

Internal energy change, du,

$u = u(T, v)$.

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

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

$s = s(T, v)$

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

$= \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial T}\right)_v dv$

Date.
No.

Subs.

Gibbs: $du = Tds - pdv$

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

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

fundamental relation

properties are measurable

$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$$\begin{matrix}u\\h\end{matrix} = f\left(C_v, C_p, \begin{matrix}P\\v\\T\end{matrix}\right)$$

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$$

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

Date.
No.

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_v$$

Volume expansion coefficient:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$ → thermal expansion

Isothermal coefficient of compressibility

$$\alpha \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$ → bulk compressibility

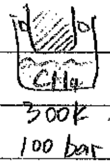
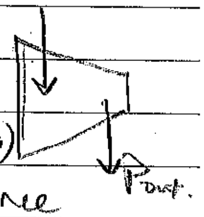
$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$ ← incompressible

$$C_p > C_v$$

Mayer Relation

Date.
No.

Tutorial – Week 4

CM. (u)	CV (h)
piston J 	Turbine, compressor, HX, J / kg fluid.
χ_1. $\underbrace{T_0, P_0}$ dead state	$\psi_2 - \psi_1 =$ $(h_2 - h_1) - T_0(s_2 - s_1)$ 
absolute exergy.	exergy difference

$$\phi = (u - u_0) + v(P - P_0) - T_0(s - s_0) + \ldots \quad + P_0(v - v_0)$$

either is zero

☆ Thermodynamics. consider sth not in equilibrium and move it into environmental equilibrium.

$S_2 \quad S_1 \quad S_0$

$\underbrace{S_2 \quad S_1}_{CV}\underbrace{\quad \text{dead}}_{CM}$

$\chi_2 - \chi_1 = 0$ — for control volume system

$\chi_2 - \chi_1$

⇓

χ_1 becomes dead state for CM.

Date.
No.

P4. $(v_2 - v_1) P_0$ → work done

Equation of State.

- why only P, v, T ? → we can measure (experimentally)
- simplest EOS → ideal gas: $P_{ideal} = \frac{RT}{v}$

empirically, we care about:

air	water	refridgerator
ideal	not	not

- small molecules, non-polar, high T, low P
  ⇓
  fewer collisions

Var der Waals Eq.

$$P_{actual} = \frac{RT}{v} - \frac{a}{v^2}$$

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$\frac{a}{v^2}$ → intermolecular forces

b → the volume taken up by molecules

a, b can be found in tables

Redlich-Kwong Equation

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

Corresponding State Principal

$$Z_1 = \frac{V_{actual}}{V_{ideal}}, \quad Pv = Z_1RT$$

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}$$

$\Downarrow$

what Lee-Keslar Table is about!

▶ Two-parameter: $Z_1(T_r, P_r) = Z_1^0(T_r, P_r)$

▶ Three-parameter: $Z_1(T_r, P_r, \omega)$
$= Z_1^0(T_r, P_r) + \omega Z_1^1(T_r, P_r)$

$\downarrow$

non-sphericity of molecules

CO_2 $\dot{m} = 2kg/s$

$T_1 = 500K$, $P_1 = 3$ MPa.

$\downarrow$

$T_2 = 450K$

For Ideal Gas:

$T_r \gg 1$,

$P_r \ll 1$.

Date.
No.

Week 4 - 1

Maxwell: P, v, T, x

↳ Meyer relation

du for vdW Gas:

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

Gibbs : $\boxed{\text{MEMORIZE}}$!!!

$$\rightarrow u_2 - u_1 = C_v(T_2 - T_1) + \int\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

$$\text{vdW} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

$$\frac{RT}{v-b} - P = \frac{a}{v^2}$$

$$du = C_v\,dT + \left[\frac{a}{v^2}\right]dv$$

$$= C_v\,dT + \frac{a}{v^2}dv$$

$$= (C_1 + C_2T)\,dT + \frac{a}{v^2}dv$$

$$u_2 - u_1 = C_1(T_2 - T_1) + \frac{C_2}{2}(T_2^2 - T_1^2) + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$$

Date.
No.

Mayer relation:

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

at absolute zero temp. $\underbrace{C_p \equiv C_v \equiv 0}$

molecules cannot store energy
||
☆ not moving

The Δh, Δu & Δs of real gases → residual functions

$$h^R = h^* - h$$

h^*: Ideal gas.

h: Real Gas.

residual function.

$$h_2 - h_1 = (h_2^* - h_2^R) - (h_1^* - h_1^R)$$

$$= \underbrace{(h_2^* - h_1^*)}_{\text{Ideal Gas version equations of use}} - \underbrace{(h_2^R - h_1^R)}_{h^{R(0)}(T_r, P_r) + \omega h^{R(1)}(T_r, P_r)}$$

Date.

No.

$T ds = dh - v dP$ P_0 same

$h_2 - h_1$

residual function vs departure function

$\parallel$

different terms in diff. textbooks

residual functions

$$\underbrace{h^R = h^*(T,P) - h(T,P)}_{\text{hard to imagine}}$$

departure function

$$h^D = h^*(T,P_0) - h(T,P)$$

if ideal gas

h same

$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$$h^D = \underbrace{h^*(T,0) - h(T,P)}_{\text{two diff. states}}$$

$$= \cancel{\int_T^T C_p dT} + \int_P^0 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Date.

No.

$$Z = \frac{Pv}{RT}. \quad v = \frac{ZRT}{P}$$

↳ subs. → $\frac{\partial v}{\partial T}$

h^R

$\parallel$

$$h^D = RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}$$

$$\frac{h^R}{RT_c} = T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} d(\ln P_r)$$

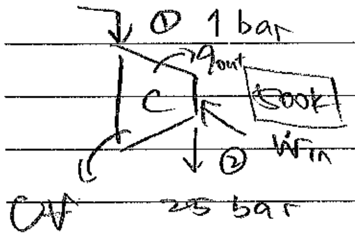
$h^D \equiv h^R$

↳ do the calculation from h^D

to get h^R

$\boxed{\text{residual}}$

$$\frac{h^R}{RT_c} = \left(\frac{h^R}{RT_c}\right)^{(0)}(T_r, P_r) + \omega \left(\frac{h^R}{RT_c}\right)^{(1)}(T_r, P_r)$$



reversibly & isothermally, steady state

Find $\dot{W}_{in}$, $\dot{q}_{out}$

Date.
No.

energy & entropy balance

energy balance

$$\frac{dE}{dt} = 0 = \dot{E}_{in} - \dot{E}_{out}$$

$$\cancel{\frac{\dot{Q}_1}{\dot{m}}} + \frac{\dot{W}_1}{\dot{m}} + \cancel{\dot{m}_1} h_1 = \frac{\dot{Q}_2}{\dot{m}} + \cancel{\frac{\dot{W}_2}{\dot{m}}} + h_2$$

$$\frac{\dot{W}_1}{\dot{m}} + h_1 = \frac{\dot{Q}_2}{\dot{m}} + h_2$$

entropy balance

$$\frac{dS}{dt} = S_{in} - S_{out} + \overset{0}{\cancel{S_{gen}}} = 0$$

$$= \int \frac{dh_{in} - v\,dP_{in}}{T} - \int \frac{dh_{out} - v\,dP_{out}}{T}$$

$$= 0$$

$$\begin{cases} T\,ds = dh - v\,dP \\ T\,ds = du + p\,dv \end{cases}$$

Date.
No.

$$\dot{q}_{out} = T_b (S_1 - S_2)$$

$$\dot{W}_{in} = (h_2 - h_1) + \dot{q}_{out}$$

$$= T_b \left[(S_1^* - S_2^*) - (S_1^R - S_2^R) \right]$$

$$= T_b \left[R \ln \frac{P_2}{P_1} - (\underline{\underline{S_1^R}} - \underline{\underline{S_2^R}}) \right]$$

figure out

$$\underbrace{T_{r_1} = \frac{T_1}{T_c}, \quad P_{r_1} = \frac{P_1}{P_c}}$$

$$\frac{S^R}{R} = (\quad)^{(0)} + \omega(\quad)^{(1)}$$

☆☆☆

$$\frac{dS}{dt} = \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen}$$

universally applied

↓

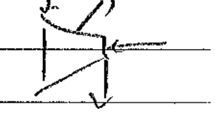
0 → steady state

‖

$$\dot{S}_1 - \dot{S}_2 - \frac{\dot{q}_{out}}{T_b} + 0$$

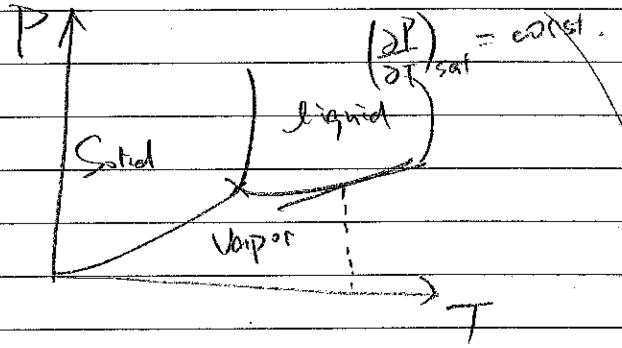
[Work does not generate entropy)

four arrows



Usefulness of Maxwell Equation

Clapeyron Equation



$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T v_{fg}}.$$

$$\Downarrow$$

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T v_{12}}$$

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

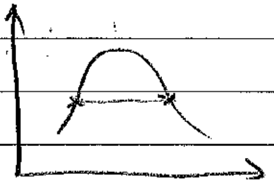
During phase change, $P_{sat} = P_{sat}(T_{sat})$.

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{s_{fg}}{v_{fg}}\right) = \frac{s_g - s_f}{v_g - v_f}.$$

use like to approximate

Use Gibbs: $dh = Tds + vdp$.

$$\int_f^g dh = \int_f^g Tds + vdp$$



$h_{fg} = T s_{fg} \longrightarrow$ put it back

$$\boxed{\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T v_{fg}}.}$$

$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T v_{12}}$ (1, 2 refer to two phases.)

Clausius-Clapeyron Equation (Vapor)

$v_{12} = v_g - v_f$

v_f

$v_{12} = v_g = \frac{RT}{P}$

$$\left(\frac{dP}{dT}\right)_{sat} \approx \frac{h_{fg}}{T\frac{RT}{P}} = \frac{P h_{fg}}{RT^2}$$

$$\left(\frac{dP}{P}\right)_{sat} = \left(\frac{h_{fg}}{RT^2} dT\right)_{sat}$$

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

Date.

No. Week 4-2

Rev. Clapeyron Eq.

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T v_{fg}}.$$

$$" \left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T v_{12}} "$$

↳ general form.

↳ using ideal gas relation

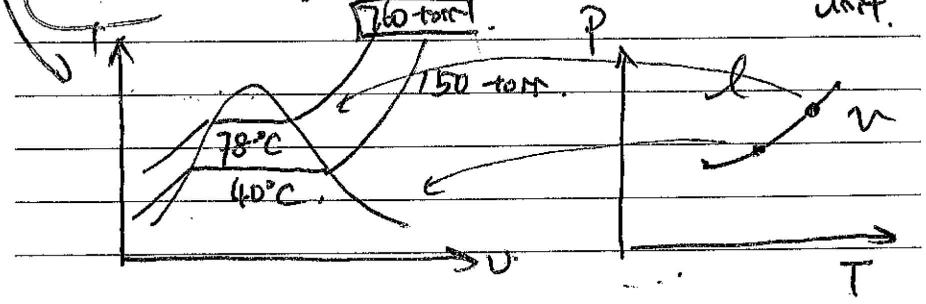
$$\ln\left(\frac{P_2}{P_1}\right)_{sat} = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

"Clausius-Clapeyron Relation"

Calculate enthalpy vaporization ethanol.

vapor pressure 40°C → 150 torr.

normal boiling → 78°C. → 1 atm. 760 torr. ↳ pressure unit.



Date.

No.

Using the Clausius-Clapeyron Eqn.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

$$\ln\left(\frac{760}{150}\right) = \frac{h_{fg}}{8.314}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(universal)

$$\Delta H_{vap} = \bar{h}_{fg} = 39.0\ kJ/mole$$

Calculate pressure required to melt ice at 7°C, latent heat of fusion for water is 334 kJ/kg.

$$\Delta v_{sf} = -0.905 \times 10^{-5}\ m^3/kg$$

No vapor → no Clausius-Clapeyron

↳ just use Clapeyron;

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{sf}}{T v_{sf}}.$$

ice → 1 atm 0°C.

"approximation"

$$\frac{P - 1atm}{T_2 - T_1} = \frac{-334 \times 10^5\ J/kg}{273\ K \times 9.05 \times 10^{-5}\ m^3/kg}$$

↳ 7 K

Solve for pressure:

$P = 946$ atm.

definition V_{sf} : liquid - solid

↓

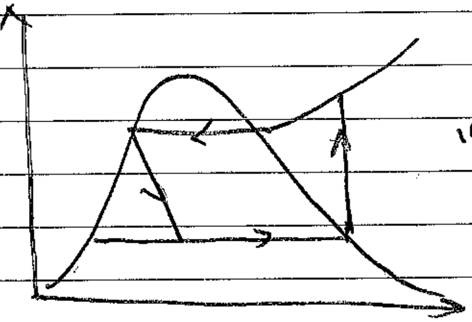
"melting requires high pressure

⇒ could be concentration happened locally"

§ Joule - Thompson Coefficient.

☆ heat pump → coefficient > 1

(not efficiency),



"how temperature changes thru values"

Energy balance:

$$h_2 \simeq h_1$$

$$u_1 + P_1 v_1 = u_2 + P_2 v_2$$

Control the flow in heat pump

↓

use friction

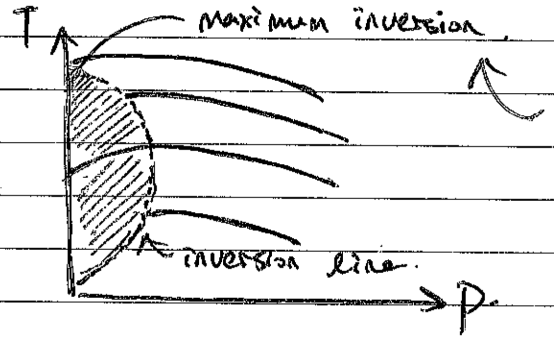
↓

generate entropy.

J-T coefficient.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \leftarrow \text{const. enthalpy.}$$

$$\mu \begin{cases} > 0 & \text{temperature increase} \\ = 0 & \text{remains const.} \\ < 0. & \text{temperature decrease} \end{cases}$$



H_2: $T_{max, inversion}$ $= -68°C$

The Goal: Calculate J-T coefficient.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$$

$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dP$$

Date.
No.

$$\mu_{JT} = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right].$$

⇗

assumes $dh=0$

for ideal gas

$$pv = RT$$

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

$$\mu_{JT} = \frac{1}{C_p}\left[\frac{TR}{P} - v\right]$$

ideal gas

$\mu = 0$

$$= \frac{1}{C_p}\cdot 0 = 0.$$

$$Z = \frac{Pv}{RT} \qquad v = \frac{ZRT}{P}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P}\,\frac{\partial (ZT)}{\partial T}\Big|_p.$$

$$= \underbrace{\frac{R}{P}\left[T\left(\frac{\partial Z}{\partial T}\right)_p + Z\overset{1}{\left(\frac{\partial T}{\partial T}\right)_p}\right]}_{\text{subs back to } \mu_{JT}.}$$

$$\mu_{JT} = \frac{1}{C_p}\left\{\frac{RT}{P}\left[T\left(\frac{\partial Z}{\partial T}\right)_p + Z\right] - v\right\}$$

Date.
No.

$$= \frac{1}{C_p}\left[\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_p + \cancel{\frac{ZRT}{P} - v}\right]$$

Cancelled out.

$$= \frac{1}{C_p}\left[\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_p\right].$$

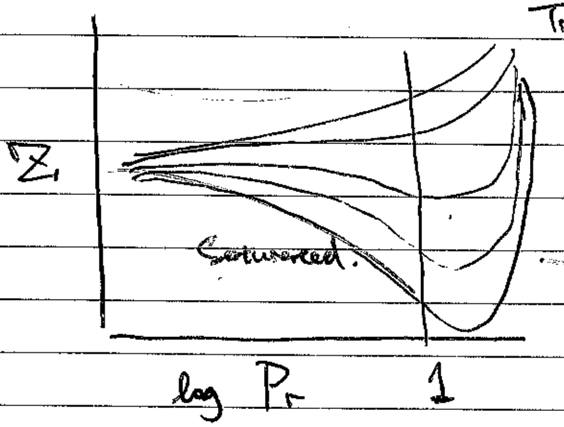
↳ cooling: hoped to be positive.

Cooling thru a value:

$$\left(\frac{\partial Z}{\partial T}\right)_p > 0. \qquad Z(T_v, P_v)$$

↖ check chart for Z value.

Then look at the Lee-Kesler table.

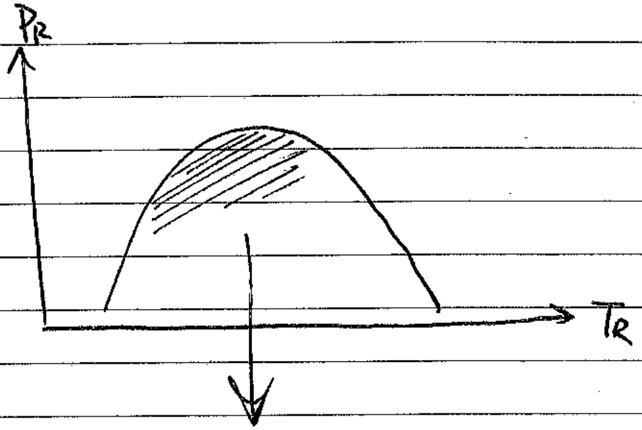


bigger $\left(\frac{\partial Z}{\partial T}\right)_p$

▲ better cooling

→ is Z increasing w T.

Date.
No.



only have cooling within this region

we can get P_c, T_c, T_{max}.

↓

Maximum inversion temperature

⇓

More than T_{max} cannot cool it.

☆ Departure & Residual function

Date.
No.

Determine.

1. T_r^2, T_r^1,
P_r^2, P_r^1

2. Residual properties.

3. Calculate y_2^D, y_1^D.

> multiply residual properties by R

- $y^D = y_R^{(0)} + \omega \cdot y_R^{(1)}$

4.

5

Enthalpy. Entropy.

$$\begin{tikzcd}
\text{Real } ① \arrow[r] \arrow[d] & & ② \text{ Real} & ① \arrow[rr] \arrow[d] & & ② \\
\text{ideal } ① \arrow[r, "\text{Isobaric}"'] & ①' \arrow[r, "\text{Isothermal}"'] & ② \text{ ideal} \arrow[u] & ① \arrow[r] & ①' \arrow[r] & ② \arrow[u]
\end{tikzcd}$$

$Pv = RT.$

$h = u + Pv$

$$h = u + RT.$$

$$\downarrow$$

$$u = h - ZRT$$

$$\Downarrow.$$

$$\Delta u = h_2 - RZ_2T_2 - (h_1 - RZ_1T_1)$$

$$= \Delta h - R(Z_2T_2 - Z_1T_1)$$

$Z(T_r, P_r).$

$$\downarrow$$

$$T_r = \frac{T_0}{T_c}, \quad P_r = \frac{P_0}{P_c}.$$

Clausius Clapeyron

$$\left(\frac{\partial P}{\partial T}\right)_{sat.} = \frac{\Delta h}{T\Delta v}.$$

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = -\frac{h_{fg}}{R}\left(\frac{1}{T_2^{sat}} - \frac{1}{T_1^{sat}}\right)$$

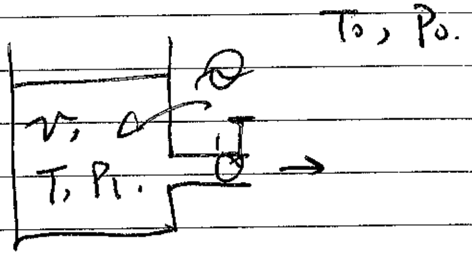
small dT: $\Delta h = c$

(assume)

Q3. Maxwell Eqn.

$$\begin{cases} a = 8bP_c \\ b = \frac{27}{64}T_c \end{cases}$$

☆ $\left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial P}{\partial v}\right)_T = -1.$



mass balance. $\dot{m}_1 = \dot{m}_2$

$$m_1 - m_{exit} = m_2$$

$$PV = mRT \quad \text{(ideal gas)}$$

$$V = \frac{mRT}{P}$$

$$V_2 = V/2$$

$$m_2 \frac{RT}{P} = \frac{1}{2} \frac{m_1 RT}{P}$$

$$m_2 = \frac{1}{2} m_1$$

$$\frac{1}{2} m_1 = m_2 = m_{exit}.$$

1^{st} law

$$W_{in} + Q_{in} + \cancelto{0}{m h_{in}} - \cancelto{0}{W_{out}} - Q_{out} - m h_{out}$$

$$= m_2 u_2 - m_1 u_1.$$

$$W_{in} + Q_{net.} - m_e h_{exit}$$

$$= m_2 u_2 - m_1 u_1$$

$$P_B(m_2 v_2 - m_1 v)$$

$$\downarrow$$

300kPa.

$$u + Pv = h$$

$$Q_{net} - m_{exit} h_{exit}$$

$$= m_2 h_2 - m_1 h_1$$

$$Q_{net} - (m_1 - m_2) h_e = m_2 h_2 - m_1 h_1$$

$$h_e = h_2 = h_1.$$

$Q_{net} - \cancel{(m_1 - m_2)}h_e = \cancel{(m_2 - m_1)}h_e$

$Q_{net} = 0$

2nd law

Only heat & mass carry entropy.

$-m_e S_e + S_{gen} = m_2 S_2 - m_1 S_1$

$S_{gen} = 0$

$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$

$\lim_{v \to \infty} \mu = 0$

$\lim_{P \to 0} \mu = 0.$

L'hopital's Rule

Week 5 - 1.

Review: 1st & 2nd law

Energy.

↓

heat & flow work.

Atmosphere boundary (non-useful).

⇓

Equation of State.

corresponding states

virial relationship

Maxwell relationship

↓

residual/departure function.

Clapeyron equation

Joule - Thompson equation.

Simple compressible systems

Date.
No.

⇒ Multiphase → calculate properties.

⇓

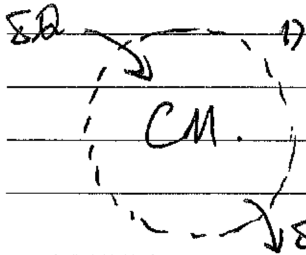
overall mass.

- criteria for equilibrium.
- phase equilibrium
- homogeneous mixture equilibrium
- mixture phase equilibrium.

2nd law → $S_{gen} \geq 0$.

$$\left\{ \begin{array}{l} - \text{ isolated systems, } U, \forall = \text{const,} \\ - \ T, P = \text{const.} \\ - \ T, \forall = \text{const.} \end{array} \right.$$

General equilibrium conditions. (Subject to constraints).



1). P, T = const.

1st law: $dU = \delta Q_{in} - Pd\forall$

2nd law: $dS = \frac{\delta Q_{in}}{T} + \delta S_{gen}$

$\delta W = pd\forall$.

Date.
No.

$$\Rightarrow T\delta S_{gen} = TdS - (dU + pd\forall) \geq 0$$

(there's no assumptions here) (*)

$G = H - TS$ ★ Memorize.

$= U + P\forall - TS$

$$dG_{T,P} = dU + Pd\forall - TdS.$$

@ const T, P:

$\boxed{dG_{T,P} \leq 0}$ At equilibrium.

$G = G_{min}$.

(T, P = const)

- - - - - - - - - - - - - - - -

@ const. T, ∀: Helmholtz.

$A = U - TS$

$dA_{T,\forall} = dU - TdS$.

Date.
No.

$$T\delta S_{gen} = -dA_{T,V} - p\,dV \geq 0.$$

$$= -dA_{T,V} \geq 0.$$

@ Equilibrium const T, V,

$$dA_{T,V} \leq 0.$$

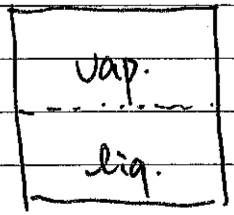
$$A = A_{min}.$$

V, U = const. ⇒ $T\delta S_{gen} = T\,dS \geq 0$

$$dS_{sys} \geq 0$$

Equilibrium applies to multicomponent. multiphase scenarios

phase equilibrium → Clapeyron Eqn.



$$G = m_L g^L + m_v g^v$$

T, p = const.

Date.
No.

$$dG_{T,p} = g^L dm_L + g^v dm_v.$$

mass conservation: $dm_L = -dm_v$.

$$dG_{T,p} = (g^L - g^v)\,dm_L.$$

Equilibrium: $dG_{T,p} = 0 \Rightarrow g^L = g^v$.

phase boundary: $g^L = g^v = g^s$ (mass)

or $\hat{g}^L = \hat{g}^v = \hat{g}^s$ (molar)

$g^L = g^v$, $dg^L = dg^v$. $g = h - Ts$.

$$d(h^L - Ts^L) = d(h^v - Ts^v).$$

$$d(h - Ts) = dh - T\,ds - s\,dT.$$

plug in: $T\,ds = dh - v\,dp$.

$$= v\,dp - s\,dT.$$

$$v^L dp - s^L dT = v^v dp - s^v dT.$$

Date.
No.

rearrange this:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{s^v - s^l}{v^v - v^l}.$$

$$= \frac{h^v - h^l}{T(v^v - v^l)} = \frac{h_{fg}}{T v_{fg}}.$$

$\because g = h - Ts.$

$$h^l - Ts^l = h^v - Ts^v.$$

$$\Downarrow$$

$$s^v - s^l = \frac{h^v - h^l}{T}.$$

Evaluation of $\hat{g}$ for ideal gas:

(1cMp).

$$g = h - Ts \rightarrow dg = dh - Tds - sdT$$

$$= vdP - sdT.$$

At constant T, $dg_T = vdP$. (*)

Ideal gas, $Pv = RT$.

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

Date.
No.

$$dg_T = \frac{RT}{P}dP = RT\, d\ln P \;.\cdots(1)$$

Integrate Eqn (1). from (T, P_0) to (T, P).

$$g(T,P) - g(T,P_0) = RT\ln\left(\frac{P}{P_0}\right).$$

$$g(T,P) = g(T,P_0) + RT\ln\left(\frac{P}{P_0}\right).$$

molar-based:

$$\hat{g}(T,P) = \hat{g}(T,P_0) + \hat{R}T\ln\left(\frac{P}{P_0}\right).$$

for ideal gas. the partial pressure

- - - - - - - - - - - - - - - -

Starting from Eqn (*):

$$dg_T = vdP \xrightarrow{IG} RT\, d\ln P.$$

$$\Downarrow \text{RG}.$$

$$dg_T = RT\, d\ln f. \rightarrow \text{fugacity}.$$

unit pressure

$$\Downarrow$$

$$dg_T = RT\, d\ln(P\phi).$$

Fugacity coefficient

$$\phi \equiv f/P.$$

Two ways of doing this:

$\log(\phi) = (\log\phi)^0 + \omega(\log\phi)^1$

use real gas EOS.

vdW Eqn.

$$d\ln f = \frac{v}{RT}\,dp,$$

$$\ln f = \frac{b}{v-b} + \ln\left(\frac{RT}{v-b}\right) - \frac{2a}{RTv}.$$

proposed by Gilbert Lewis.

Week 5 -2

real fluid. like HW problem

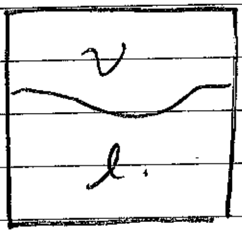
× Camera. Energy.

* balance equation correctly

get the number from table.

uploaded on Canvas.

M_c/M_p.



$g^v = g^l$.

Recall vdW Eqn

$$d\ln f = \frac{v}{RT}\,dp.$$

$$\ln f = \frac{b}{v-b} + \ln\left(\frac{RT}{v-b}\right) - \frac{2a}{RTv}$$

$$\phi = \frac{f}{P}.$$

$$\begin{cases} d\ln\phi = d\ln f - d\ln P \\ d\ln\phi = \frac{v}{RT}\, d\ln P - d\ln P \end{cases}$$

$$d g_T = v\,dP$$

$$\downarrow \qquad \Rightarrow \qquad v\,dP = RT\,d\ln f.$$

$$dg_T = RT\,d\ln f. \qquad d\ln f = \frac{v}{RT}\,dP.$$

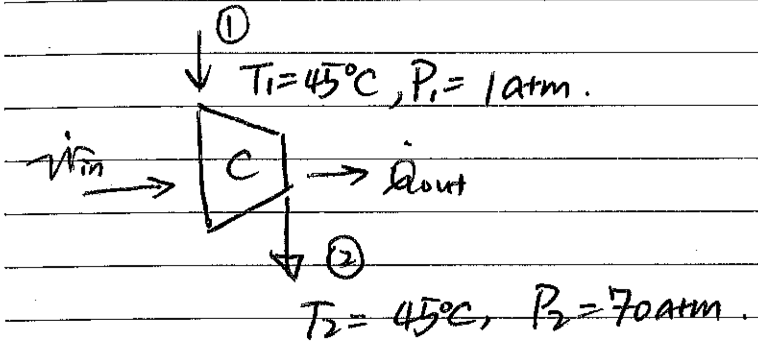
$$= \left(\frac{vP}{RT} - 1\right) d\ln P$$

$$= (Z-1)\, d\ln P$$

$$\ln\phi = \int_0^{P_r} (Z-1)\, d\ln P_r$$

$\boxed{\text{Example:}}$ Use of fugacity.

Isothermal compression of CH_4: Steady state



Find: $\frac{\dot{W}_{in}}{\dot{m}}$. internally reversible.

Control volume: $\frac{dE_{sys}}{dt} = \dot{E}_{in} - \dot{E}_{out}$

$$\underbrace{\dot{m} h_1 + \dot{W}_{in} = \dot{m} h_2}_{\text{assume const. mass flow}} + \dot{Q}_{out} \text{ (Energy balance)}$$

$$\dot{m}(s_1 - s_2) - \frac{\dot{Q}_{out}}{T} + \cancel{S_{gen}} = 0 \text{ (Entropy balance)}$$

(IR).

$$\frac{\dot{W}_{in}}{\dot{m}} = (h_2 - T_2 s_2) - (h_1 - T_1 s_1)$$

$$= g_2 - g_1$$

$$\Downarrow$$

$$dg_T = RT\,d\ln f \rightarrow P\phi.$$

$$= RT \ln\left(\frac{P_2\phi_2}{P_1\phi_1}\right)$$

CH_4, P_c, T_c $\Rightarrow$ T_{r_1}, P_{r_1} $\Rightarrow$ ϕ_1, ϕ_2

(look up to the table)

$$\frac{W_{in}}{\dot{m}} = (518\,J/kg\cdot K) \times 318K \times \ln\left(\frac{70\times 0.86}{1\times 1}\right)$$

$$= 675\ kJ/kg.$$

$$\eta_{FC} = \frac{\Delta G}{\Delta H}.$$

$$\log\phi = \underset{\text{table A-31}}{\underset{\downarrow}{(\log\phi)^0}} + \omega \underset{\text{table A-32}}{\underset{\downarrow}{(\log\phi)'}}$$

$$d\hat{g}_T = v\,dp = RT\,d\ln f.$$

$$d\ln f = \frac{v}{RT}\,dP.$$

v small

$$\int_{sat} d\ln f = \int_{sat} \frac{v}{RT}\,dP.$$

when $P \approx P_{sat}$, ≈ 0

$$\rightarrow \ln\left(\frac{f(T,p)}{f_{sat}(T)}\right) \approx \frac{v}{RT}(P - P_{sat}).$$

$$f^L(T,p) \approx f^L_{sat}(T).$$

---

pure liquid @ equilibrium with vapor.

$$f^l_{eq} = f^v_{eq} \Rightarrow f^v_{sat}(T) = f^l_{sat}(T).$$

the way we approximate liquid:

$$f^{liq}(T,P) \approx f^{liq}_{sat}(T) = \underbrace{f^{vap}_{sat}(T)}_{\uparrow \text{ real gas}}$$

Mixtures.

$$\Delta G = \Delta H - T\Delta S < 0.$$

↳ High-entropy mat.

Fundamental property relationships & chemical potential.

Simple compressible system, (fixed chemical

Date.
No.

composition). $\nearrow + \sum_i \mu_i \, dN_i$

$$\boxed{\begin{aligned} dU &= TdS - pdV. \\ dH &= TdS + VdP. \\ dG &= Vdp - SdT. \\ dA &= -pdV - SdT. \end{aligned}}$$

Homogeneous mixture (no reaction).

$Y = Y(T, P, N_1, N_2, \ldots N_i)$.

$G = G(T, P, N_1, N_2, \ldots, N_i)$.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, N_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T, N_i} dp + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_j} dN_i$$

$$dG = Vdp - SdT + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i$$

$\rightarrow + \sum_i [\ ] \, dN_i$

Define chemical potential:

$$\boxed{\bar{\mu}_i \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}} \Rightarrow \text{partial molal property.}$$

(intensive property)

Date.
No.

$$dU = TdS - pdV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j} dN_i.$$

$$G = H - TS = U + PV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT.$$

$$dU = TdS - pdV + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_j} dN_i.$$

Meaning of chemical potential. $\bar{\mu}_i$.

$$dG = Vdp - SdT + \sum_i \bar{\mu}_i \, dN_i$$

At equilibrium @ const T, P. 2 components.

$$\bar{\mu}_1 dN_1 + \bar{\mu}_2 dN_2 = 0$$

$$(\bar{\mu}_1 - \bar{\mu}_2) dN_1 = 0$$

Equilibrium: $\bar{\mu}_1 = \bar{\mu}_2$

If not equilibrium yet:

$\bar{\mu}_1 > \bar{\mu}_2$: $dG < 0$

↳ driving force for chem. composition change.

Date.
No.

Part 1 : 1st & 2nd law

1st law : wording $\square \to \square$

C.M: $\Delta E_{sys} = Q + W = \Delta U + \Delta KE + \Delta PE$

C.V.: $\dot{Q} + \dot{W} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right)$

$\qquad - \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right) = \frac{dE_{sys}}{dt}$.

pos : work in

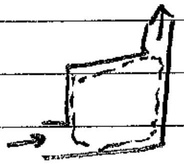
neg : work out.

uniform flow : $Q + W = \sum_{out} mh - \sum_{in} mh + \underbrace{(m_2u_2 - m_1u_1)_{sys}}_{\text{state 1 \& 2}}$.

↓

unsteady state problem, no kinetic, no pot., m equal.

Common relations :



ideal gas
$$\begin{cases} h = u + Pv. \\ \Delta h = C_p \Delta T. \\ \Delta u = C_v \Delta T. \\ C_p - C_v = R \\ k = C_p / C_v \end{cases}$$

Date.
No.

Gibbs Eqn.

$Tds = du + Pdv.$

$Tds = dh - vdP.$

ideal gas
$$\begin{cases} \to s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ \to s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}. \end{cases}$$

isentropic relation

$$\left(\frac{T_2}{T_1}\right)_s = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} = \left(\frac{v_1}{v_2}\right)^{k-1}.$$

$C_p, C_v \equiv$ const. . . . second term?

Entropy Balance

boundary temperature ⇓ $\boxed{350}$ 300 ↓ avg

C.M.: $\Delta S = \sum_{i=1}^{n} \frac{Q_i}{T_i} + S_{gen}$.

C.V.: $\frac{dS_{cv}}{dt} = \sum_{i=1}^{n} \frac{\dot{Q}_i}{T_i} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s + \dot{S}_{gen}$

Part 2: Exergy

Exergy balance

C.M.: $\Delta X_{sys} = X_{in} - X_{out} - X_{des}$.

er mass) $\phi = (u-u_0) + P_0(v-v_0) - T_0(s-s_0)$

$+ \frac{V^2\ V_0^2}{2} + g(z-z_0)$.

C.V.: $\frac{dX_{sys}}{dt} = \dot{X}_{in} - \dot{X}_{out} - \dot{X}_{des}$

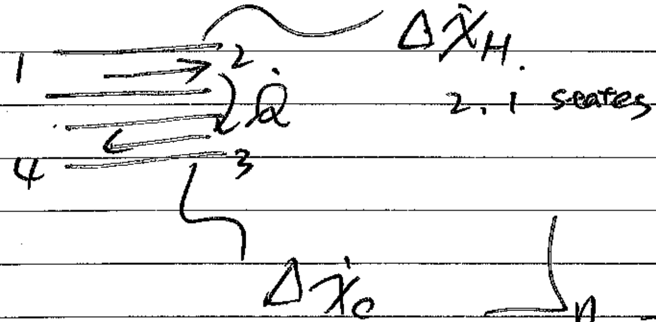
$\psi = (h-h_0) - T_0(s-s_0) + \frac{V^2}{2} + gz$.

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

$\eta_{I} = \frac{W_{net}}{Q_{in}}$

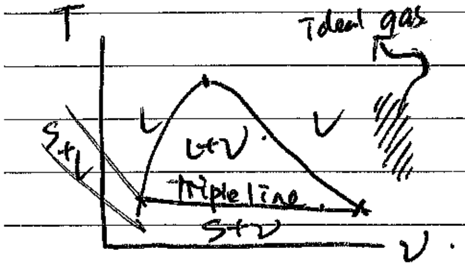
Def.

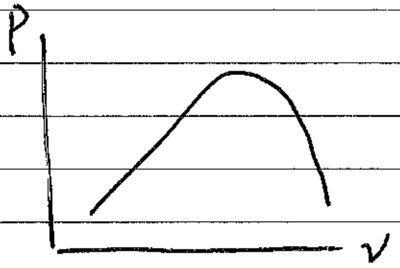
$\eta_{II} = \frac{\text{exergy recovered}}{\text{exergy supplied}}$ ☆

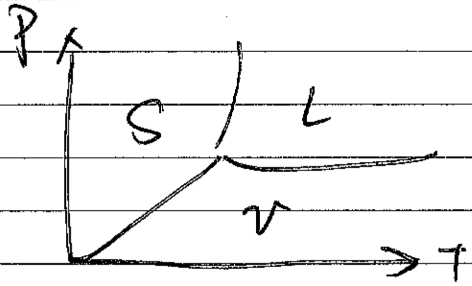


$\eta_{II} = \frac{\Delta\dot{X}_c}{\Delta\dot{X}_H}$

Part 3: EOS







Real gas: $Pv = ZRT$ $\quad Z = \frac{v_{actual}}{v_{ideal}}$

$Z^{(0)} + \omega Z^{(1)}$.

Table A-2
(Wark). ↳ A-24, A-25

Van der Waals:

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

$$a=\frac{9RT_c v_c}{8}$$

$$b=\frac{v_c}{3}$$

Part 4: Thermodynamic Property Relations

Maxwell Eqns.

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

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

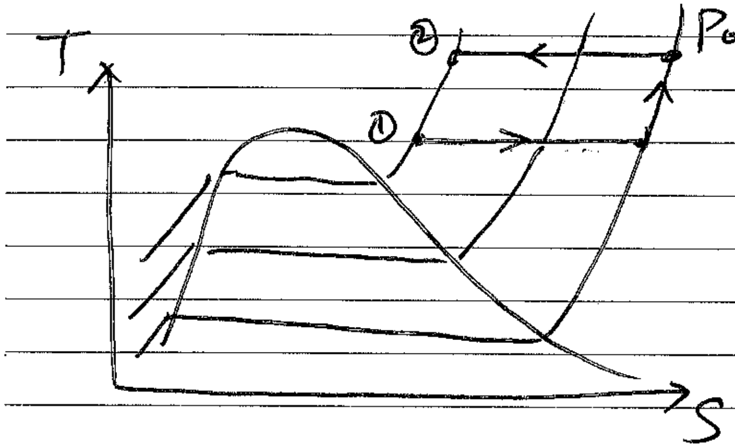
$$\left(\frac{\partial T}{\partial P}\right)_s=\left(\frac{\partial v}{\partial s}\right)_P$$

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

$$\Rightarrow h_2-h_1=u_2-u_1+(P_2v_2-P_1v_1).$$

look up Lee-kesler.

Residual Functions



$$h_2-h_1=\underbrace{(h_2-h_2^*)}_{\text{Lee-kesler}}+\underbrace{(h_2^*-h_1^*)}_{\text{ideal}}+\underbrace{(h_1^*-h_1)}_{\text{Lee-kesler.}}$$

$$\text{Lee-kesler} = \frac{h^*-h}{RT_c}$$

Date.
No.

Clapeyron Eq.

$$\ln\left(\frac{P_{2,sat}}{P_{1,sat}}\right) \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

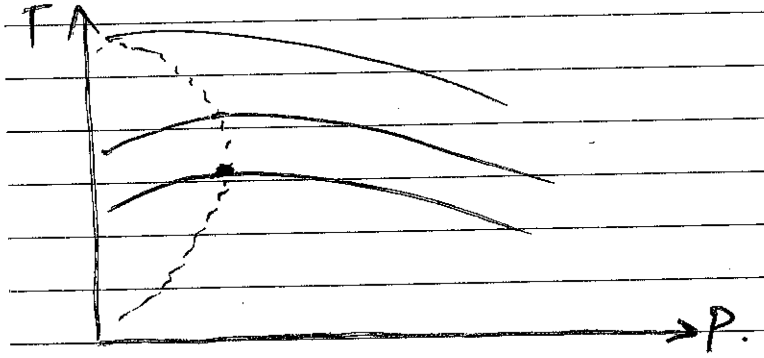
↓

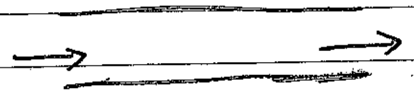
specific or universal

depends on h

Joule-Thomson Coefficient.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right].$$





$h_1 = h_2$.

Date.
No.

as $P\downarrow$ $\begin{cases} >0 : T\uparrow \\ <0 : T\searrow \\ =0 : \text{same } T. \end{cases}$

$s_1 = s_2$ $\quad$ $S_{gen} = 0$.

isentropic $\quad$ reversible.

due to mos,

$(s_2 - s_1) = 0$.

usually given in assumption

1st & 2nd law

Questions / Confirmations:

$$\eta_{II} = \frac{W_{real}}{x_2 - x_1}$$

1) two-parameter : $Z^{(0)}$

three-param. $Z^{(0)} + wZ^{(1)}$.

2). $y = y_1 + (x - x_1)\frac{(y_2 - y_1)}{x_2 - x_1}$. ... interp.?

3) exergy recovered, supplied.
useful work.

4) reversible work — exergy difference
useful → $S_{gen} = 0$

Date.
No.

Week 6-2

Fundamental property relationships.

chemical potential;

$$dG = \bar{V}dP - \bar{S}dT + \underbrace{\sum_i \left(\frac{\partial G}{\partial N_i}\right)_{T.P.V_i} dN_i}$$

partial molal ← $\bar{\mu}_i$: chemical potential.

Chemical reaction: $2H_2 + O_2 = 2H_2O$.

burning hydrogen ↗

$$\frac{dN_{H_2}}{2} = \frac{dN_{O_2}}{1} = -\frac{dN_{H_2O}}{2} = d\lambda.$$

At equilibrium: const. T & P :

$$\sum_i \bar{\mu}_i \, dN_i = 0.$$

$$\bar{\mu}_{H_2} dN_{H_2} + \bar{\mu}_{O_2} dN_{O_2} + \bar{\mu}_{H_2O} dN_{H_2O} = 0$$

Date.
No.

$$(2\bar{\mu}_{H_2} + 1\bar{\mu}_{O_2} - 2\bar{\mu}_{H_2O})\,d\lambda = 0.$$

$$2\bar{\mu}_{H_2} + 1\bar{\mu}_{O_2} = 2\bar{\mu}_{H_2O}$$

↓

ideal gas.

react — product → Δ "achieve balance"

$$K_p = \exp\left(-\frac{\Delta \hat{G}_R^0(T)}{\hat{R}_u T}\right)$$

→ Gibbs free energy of reactants.

Chemical Potential.

▽ Mixture rules: partial molal vs. partial molar properties

▽ Property of Mixing.

↳ ▽ Ideal Sol'n (Properties are interdependent)

Mixture rules:

Single-phase homogeneous multicomponent mixtures, ...

Extensive property : $Y = Y(T, p, N_i)$

↳ # of moles of component i.

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{p,N_i} dT + \left(\frac{\partial Y}{\partial p}\right)_{T,N_i} dp + \sum_{i=1}^{c} \left(\frac{\partial Y}{\partial N_i}\right)_{T,p,N_{j\neq i}} dN_i$$

partial molal property : $\bar{y}_i = \left(\frac{\partial Y}{\partial N_i}\right)_{T,p,N_{j\neq i}}$

$$\boxed{Y^{mixture}(T,p) = \sum_i \bar{y}_i N_i} \rightarrow \text{Contribution from each components.}$$

↳ mixture rule.

Coupled property ‖ depends on other portion of mixture.

$$y^{mixture} = \sum_i \bar{y}_i x_i$$

↳ mole fraction.

1. "Molal" → property not only depends on component i, but also all the other components in the mixture.

$\bar{y}_i$ is not an independent property of component i.

- - - - - - - - - - - - - - - - - - -

If assuming "Ideal Mixtures" :

$$Y(T,p) = \sum_i \hat{y}_i N_i .$$

$$\hat{y}^m = \sum_i \hat{y}_i x_i .$$

→ partial molar property only depends on component i.

Gibbs-Duhem Equation.

$$\sum_i N_i \, d\mu_i = 0 \quad \text{or} \quad \sum_i x_i \, d\mu_i = 0$$

Notes: ① for a given T & P, only (c-1) of all the components have independent chemical potentials, the last one is determined from G-D.

Derivation:

$$dG = vdP - \bar S dT + \sum_i \bar\mu_i dN_i$$

$$G = \sum_i \bar\mu_i N_i$$

$$\Downarrow$$

$$dG = \sum_i \bar\mu_i dN_i + \sum_i N_i d\bar\mu_i$$

At equilibrium: for const T, p:

↳ $dG = 0$, $dT = 0$, $dp = 0$.

$$\Downarrow$$

$$\sum_i N_i d\bar\mu_i = 0$$

$\bar y$ – molal

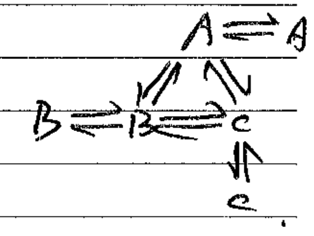
$\hat y$ – molar

y^m mixture

$\hat y^*$ – single component molar

Ideal Mixtures

(no interactions among N_i,
similar interactions



Mixing rule → linear relations.

$$\hat y^m(T,p) = \sum_i x_i \bar y_i \text{ (any mixture)}$$

$$\overset{\text{ideal}}{\underset{\text{mix}}{=}} \sum_i x_i \hat y_i(T, \underset{\text{pressure imposed on } i}{p_i}).$$

Ideal mixture of ideal gases.

$$\hat S^m(T,p) = \sum_i x_i \hat S_i(T,p_i)$$

$$= \sum_i x_i \left[\hat S_i^*(T,p) - \hat R \ln \underset{\text{mole fraction}}{\frac{p_i}{p}}\right].$$

Ideal gas: $\boxed{\hat S(T,P_1) = \hat S(T,P_2) - \hat R \ln \frac{P_1}{P_2}}$

$$= \sum_i \underset{\text{mole fraction}}{x_i} \left[\overset{\text{pure component}}{\hat S_i^*}(T,p) - \hat R \ln x_i\right]$$

(mixture) molar entropy

$$\hat{S}^{air}_v(T,p) = 0.21\left[\hat{S}_{O_2}(T,p) - \hat{R}\ln 0.21\right] + 0.79 * \left[\hat{S}_{N_2}(T,p) - \hat{R}\ln 0.79\right]$$

given Gibbs. $\hat{g}_i(T,P_i) = \hat{g}(T,p) + \hat{R}T\ln\frac{P}{P_i}$

$g^m(T,p) = x_1 g_1^m + x_2 g_2^m$

Gibbs of the mixture equals.

$$\hat{g}^m(T,p) = \sum_i x_i\left[\hat{g}_i^*(T,p) + \hat{R}T\ln x_i\right]$$

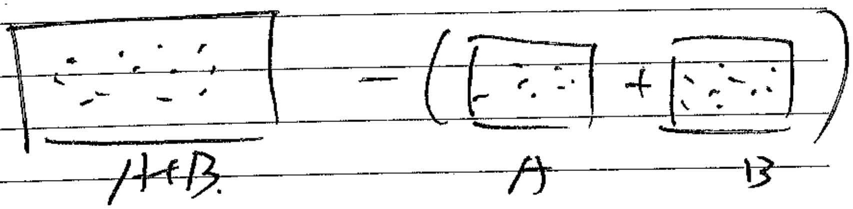
$$\hat{h}^m(T,p) = \sum_i x_i \hat{h}_i^*(T,p)$$

$$h^m = g^m + Ts$$

#property of mixing.

$$\Delta Y_{mixing} = Y_{mixture} - (Y_1 + Y_2 \cdots Y_n)$$

@ same T, P.



T, P.

$$\Delta\hat{y}_{mixing} = \sum_i x_i \bar{y}_i - \sum_i x_i \hat{y}_i^*(T,p)$$

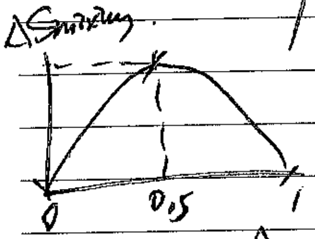
$$= \sum_i x_i\left[\bar{y}_i - \hat{y}_i^*(T,p)\right]$$

Ideal mixture of IG.

$$\Delta\hat{S}_{mixing} = \hat{S}^m(T,p) - \sum_i x_i \hat{S}_i^*(T,p)$$

$$= \sum_i x_i\left[\hat{S}_i(T,p) - \hat{R}\ln x_i\right]$$

$$- \sum_i x_i \hat{S}_i^*(T,p)$$



$$\Delta\hat{S}_{mixing} = -\hat{R}\sum_i x_i \ln x_i$$

$\hookrightarrow > 0.$

$$\Delta\hat{g}_{mixing} = \hat{R}T\sum_i x_i \ln x_i$$

Ideal mixtures. → linear mixing rules.

Ideal gas mixtures:

$$\hat{g}_i(T, P_i) = \hat{g}_i(T,p) + \hat{R}T\ln X_i.$$

Def'n: ideal solution. for a single phase mixture.

$$\bar{\mu}_i(T,p) = \hat{\mu}_i^*(T,p) + \hat{R}T\ln X_i.$$

satisfied ⇓ ideal mixture.

mole fraction of i

partial molal chemical potential of i in the mixture.

chemical potential of pure component i @ (T, p) of mixture

$\Delta\hat{h}_{mixing} = 0$, $\Delta\hat{v}_{mixing} = 0$

ideal gas

no change of intermolecular forces.

$\Delta\hat{S}_{mixing}$ → exact required in mixing)

$$= -\hat{R}\sum_i x_i \ln x_i.$$

$$\Delta\hat{g}_{mixing} = \hat{R}T\sum_i x_i \ln x_i.$$

#Calculation:

$$\Delta\hat{g}_{mixing} = \sum_i x_i \bar{g}_i - \sum_i x_i \hat{g}_i^*$$

$$= \sum_i x_i\left[\hat{g}_i^*(T,p) + \hat{R}T\ln x_i - \hat{g}_i^*(T,p)\right]$$

Lewis-Randall Rule (Fugacity).

For ideal mixing & ideal solutions,

$$\bar{f}_i = x_i f_i^*(T,p) \text{ (single-phase).}$$

partial molal fugacity of i in mixture.

fugacity of pure component i @ $(T,p)_{mix}$.

Date.
No.

Ideal mixture: $\bar{\mu}_i(T,p) = \mu_i^*(T,p) + \hat{R}T \ln x_i$. (*)

$$d\bar{\mu}_{i,T} = d\bar{g}_{i,T} = \hat{R}T\, d\ln \bar{f}_i$$

$$d\ln x_i = d\ln f_i.$$

same

$\boxed{\text{Ref, P295-302}}$

$$d\bar{\mu}_i = \hat{R}T\, d\ln x_i.$$

$x_i = 1$ (pure component) to x_i.

$$\int_1^{x_i} d\ln x_i = \int_{f_i^*(T,p)}^{\bar{f}_i} d\ln \bar{f}_i$$

$$\boxed{\bar{f}_i(T,p) = x_i f_i^*(T,p)}$$ L-R rule

Date.
No.

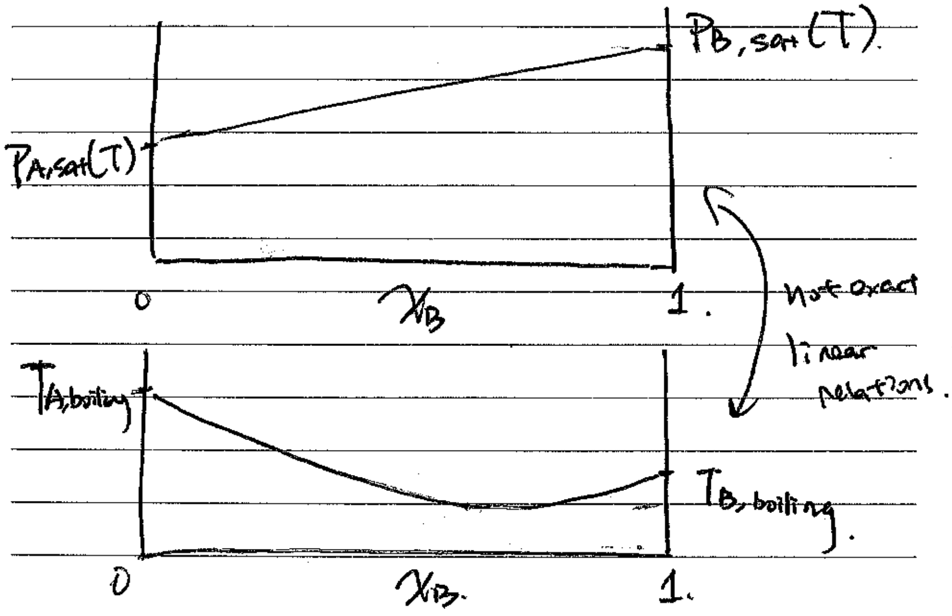
Raoult's law

$$P_A^V = x_A^L\, P_{A,sat}(T).$$

$$P_A^V = x_A^V \cdot P_V \text{ (system's pressure)}.$$

$$\left.\begin{aligned} x_A^L \cdot P_{A,sat}(T) &= x_A^V \cdot P. \\ x_B^L \cdot P_{B,sat}(T) &= x_B^V \cdot P. \end{aligned}\right\} \text{suppose 2 components A \& B}$$

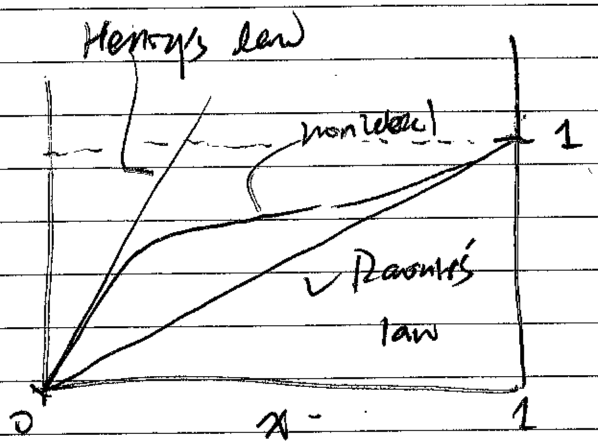
Diagram:

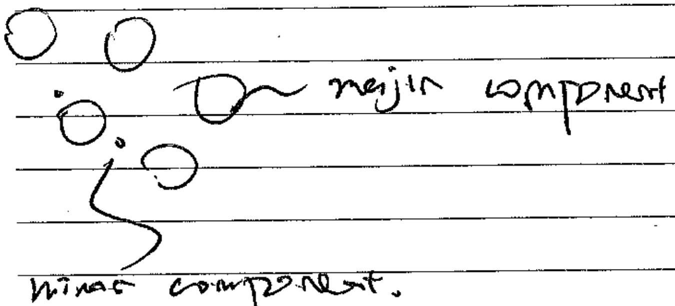


Date.
No.

Henry's law

↳ dilute solution.





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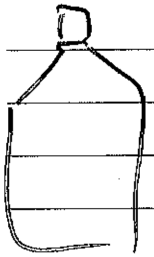
Week 7 -2

Multicomponent / Multiphase

Raoult's law / Henry's law (Review):

Binary Phase Diagram.

- Bubble vs. dew points
- The lever rule.



2% → component (mole)

↓

98% H_2O.

$$P^V_{H_2O} = x^L_{H_2O} \cdot P_{sat}(\overset{100^\circ C}{T})$$

$$P^L_{H_2O} = 0.98 \text{ atm.}$$

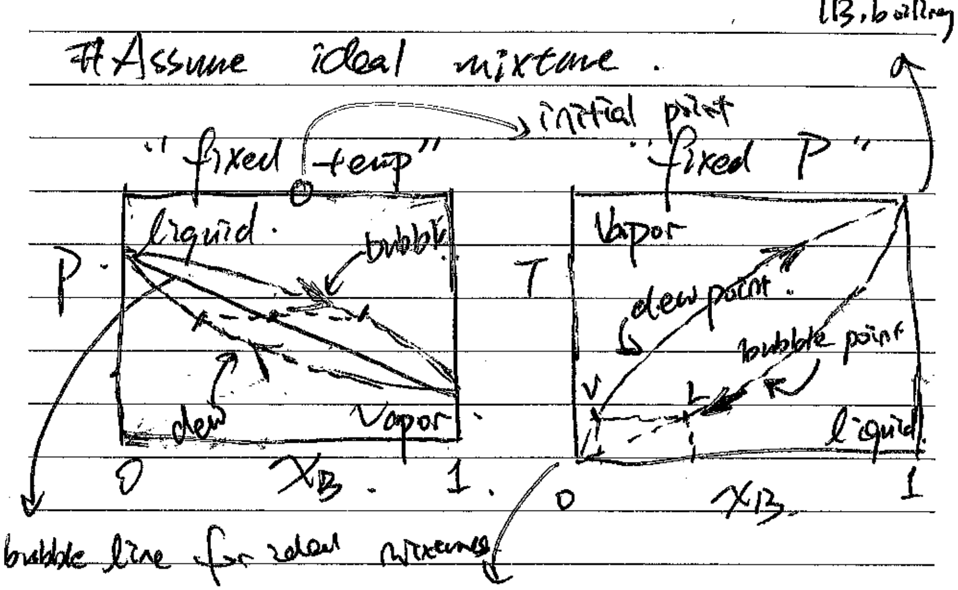
→ Clausius - Clapeyron Equation.

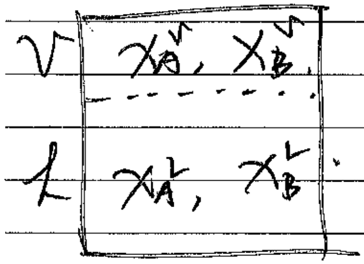
Colligative properties.

Bubble point: L → V.

Dew Point: V → L.

*Assume ideal mixture.





*Derive the bubble point. (L → V).

Assume: Ideal mixture → Raoult's law.

Initially, liquid mixture @ P.

$x^L_{A,ini}$, $x^L_{B,ini}$.

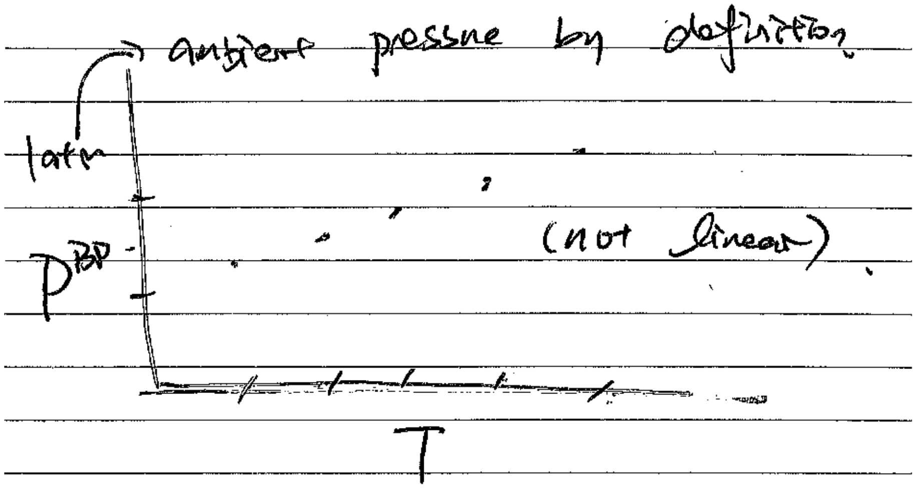
$$\left\{\begin{array}{l} x_A^v \cdot P' = x_A^L \cdot P_{A} \cdot sat(T) \quad ① \\ \quad \swarrow \\ (P', \text{the } P \text{ in the figure}) \\ x_B^v \cdot P = x_B^L \cdot P_{B,sat(T)} \quad ② \end{array}\right.$$

→ ☆ equilibrium.

$$①+②: \; P = x_A^L \cdot P_{A,sat}(T) + x_B^L \cdot P_{B,sat}(T).$$

$$P^{BP} = x^L_{A,ini} \cdot P_{A,sat(T)} + x^L_{B,ini} \cdot P_{B,sat(T)}$$

boiling temp.: find P = 1 atm
Calculate T.



... bubble point

Derive the dew point.

now, start from the vapor side.

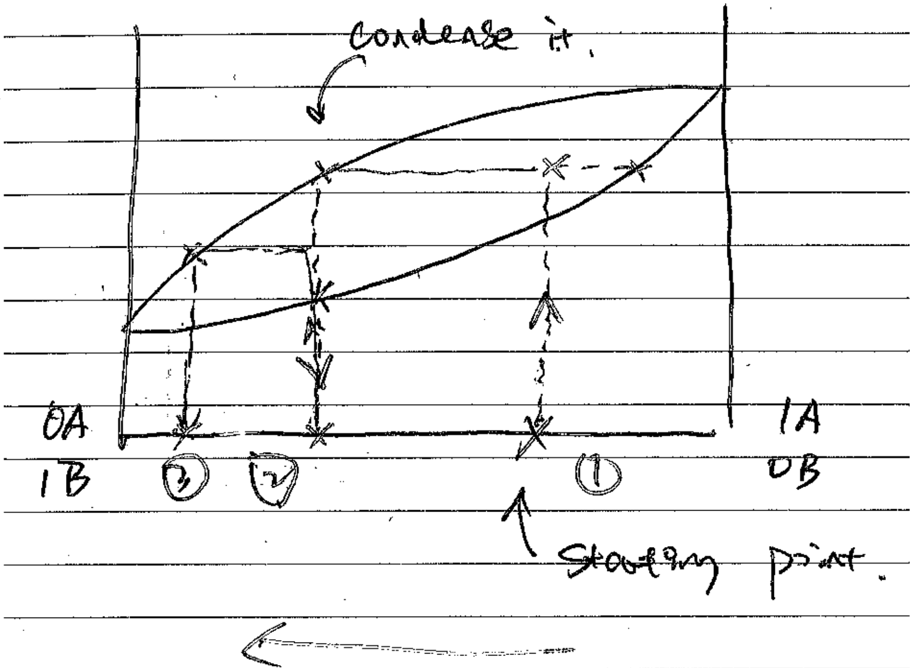
we know $x_A^L + x_B^L = 1$,

①+②: $\left[\frac{x_A^V}{P_{A,sat(T)}} + \frac{x_B^V}{P_{B,sat(T)}}\right] P^{DP} = 1$.

I want to solve for P

(By def.) dew point.

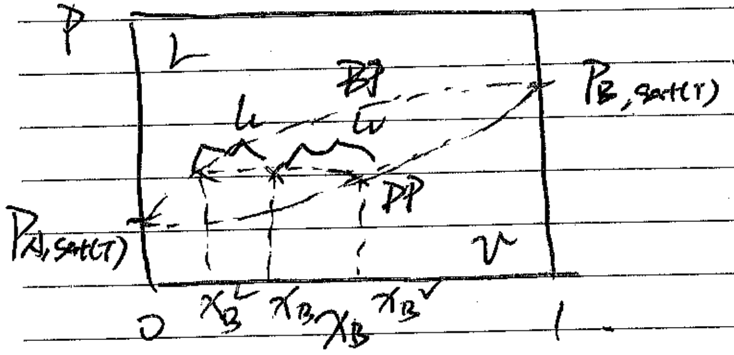
$$\therefore \frac{1}{P^{DP}} = \frac{x^V_{A,ini}}{P_{A,sat(T)}} + \frac{x^V_{B,ini}}{P_{B,sat(T)}}$$



The lever rule.

$$\frac{n^L_{(A+B)}}{n^V_{(A+B)}} = ?$$

@ given T.



#the def'n of BP & DP depends on the volatility of A / B.

$n_B = n_L x_B^L + n_V x_B^V$.

↓

$n_B = (n_L + n_V) x_B$.

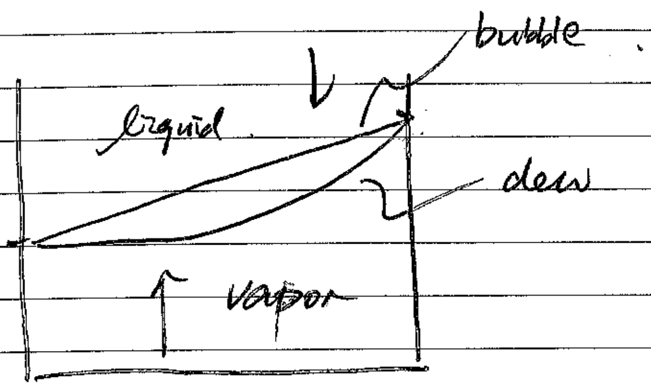
$n_L x_B^L + n_V x_B^V = n_L x_B + n_V x_B$

$n_L (x_B - x_B^L) = n_V (x_B^V - x_B)$

$n_L \cdot L_L = n_V \cdot L_V$.

$$\frac{n_V}{n_L + n_V} = \frac{L_L}{L_L + L_V}$$

Week 8 -1.



- Equilibrium Condition.

Mc/Mp Equilibrium. ↲

(Subjected to constraint).

const. T, P. : $dG_{T,P} \le 0$.

↓

@ Equilibrium : $G = G_{min}$.

Conservation of mass.

$N_i = \sum_i N_{ij} \rightarrow$ phases. $i = 1, 2, \ldots$

species (components)

Final Conclusion

(cond.).

$$\bar{g}_{ij} = \lambda_i$$

↑ Gibbs free energy is a const.

$$\left(\bar{g}_{i1} = \bar{g}_{i2} = \bar{g}_{i3} = \cdots \right)$$

Method of Lagrange multipliers:

→ ways to determine extreme (optimal) of a function under constraints

$$h = G(T, P, N_{ij}) + \sum_i \lambda_i \underbrace{\left(N_i - \sum_j N_{ij}\right)}_{\text{constraint}}$$

Use the mixture rule:

$$= \sum_i \sum_j \bar{g}_{ij} N_{ij} + \sum_i \lambda_i \left(N_i - \sum_j N_{ij}\right)$$

$$\left(\frac{\partial h}{\partial N_{ij}}\right)_{T,P} = 0 = \bar{g}_{ij} - \lambda_i .$$

⇓

write out:

$$\lambda_A = \bar{g}_{A1} = \bar{g}_{A2} = \cdots$$

$$\lambda_B = \bar{g}_{B1} = \bar{g}_{B2} = \cdots$$

Gibbs Phase rule. (Non-reacting system).

Final Conclusion:

$$\underset{\text{Degree of freedom of the system}}{DOF} = \underset{\text{component number}}{C} - \underset{\text{phase number}}{P} + 2.$$

# of components: C.

# of phases: P,

⇒ equilibrium

For each phase j: T_j, P_j, x_{ij}.

$(i=1,2,\dots,C-1)$

last are calculated.

For each phase,

unknown: C+1

Total numbers of unknown: $P(C+1)$.

relations: $T_1 = T_2 = \dots = T_P \xrightarrow{} P-1$ eqns.

$P_1 = P_2 = \dots = P_P$.

$$\underbrace{\left.\begin{array}{l}\bar{g}_{i1} = \bar{g}_{i2} = \dots = \bar{g}_{iP} \quad (P-1) \\ \vdots \end{array}\right\}}_{C(P-1)}$$

the summation: $(C+2)(P-1)$

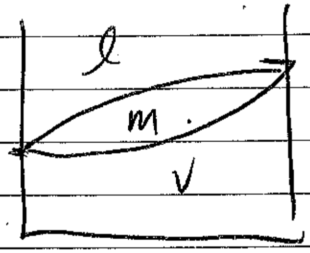
DoF = # unknowns − # relations.

$= P(C+1) - (C+2)(P-1)$

$= C-P+2$

↑

Gibbs Phase rule.



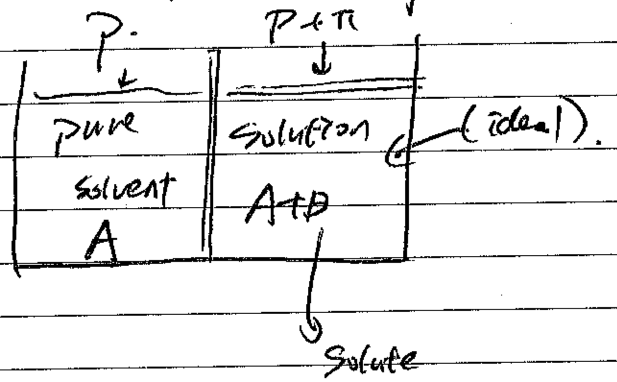
mixture single component

$$\text{Ideal solution}: \bar{\mu}_i(T,p) = \hat{\mu}_i^*(T,p)$$

$$+\hat{R}T\ln x_i.$$

molal. properties

Osmotic Pressure of an ideal soln:



$$\hat{\mu}_A^*(T,p) = \bar{\mu}_A(T,p+\pi, x_A),$$

$$\hat{\mu}_A^*(T,p) = \hat{\mu}_A^*(T,p+\pi) + \hat{R}T\ln x_A. \quad \cdots ①.$$

$$d\hat{g} = \hat{s}\,dT + \hat{v}\,dp \quad \cdots \text{Gibbs}.$$

$$dT = 0 \rightarrow T = \text{const}.$$

$$\int_p^{p+\pi} d\hat{g} = \int_p^{p+\pi} \hat{v}\,dp.$$

$$\hat{g}(T,p+\pi) - \hat{g}(T,p) = \hat{v}\pi$$

$$\hat{\mu}_A^*(T,p) + \hat{v}\pi.$$

$$\underline{\pi = -\frac{\hat{R}T}{\hat{v}_A}\ln x_A.}$$

relies on mole fraction.

does not depend on chemical composition.

$$\pi = -\frac{\hat{R}T}{\hat{V}_A}\ln(1-x_B)$$

↑

mole fraction of solute

$$\pi_{\text{diluted solution}} \approx \frac{\hat{R}T}{\hat{V}_A} x_B .$$

$$= \frac{\hat{R}T}{V_A/N_A} \cdot \frac{N_B}{\underbrace{N_A+N_B}_{\sim N_A}}$$

↑

$N_B << N_A$

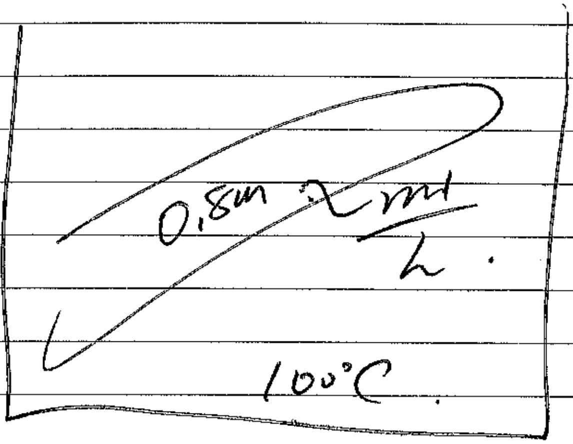
(diluted case).

$$= \frac{\hat{R}T}{V} \cdot N_B = \hat{R}T \cdot \frac{N_B}{V}$$

↓

Concentration of B.

$$= \hat{R}T\frac{N_B}{V}$$



$\pi = 25$ atm.

Date.
No. Week 8-2

McMp- wrap up!

→ Raoult & Henry

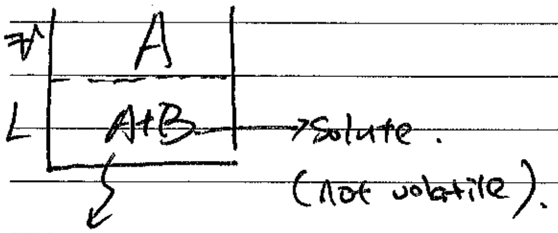
→ Binary Phase

→ Colligative (Bubble & dew).

→ Equilibrium - Gibbs phase.

* the idea of the derivation.

elevation of T_{bp}.



$$\hat{\mu}_A^V(T,p) = \hat{\mu}_A^L(T,p,x_A).$$

$$\overset{\text{ideal soln}}{=} \hat{\mu}_A^L(T,p) + RT\ln x_A.$$

Date.
No.

$$\ln x_A = \frac{\hat{\mu}_A^V(T,p) - \hat{\mu}_A^L(T,p)}{\hat{R}T}$$

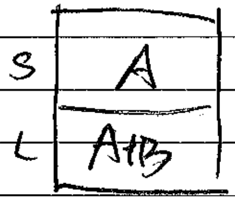
Gibbs free energy difference

(of the evaporation).

$$\rightarrow \frac{d\ln x_A}{dT} = \frac{1}{\hat{R}}\frac{d}{dT}\left(\frac{\Delta_{vap}G}{\hat{R}T}\right).$$

Work Book P_{247}.

Depression of T_{FP}.

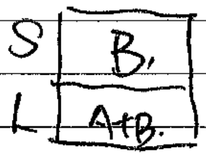


$$\hat{\mu}_A^S(T,P) = \hat{\mu}_A^L(T,P,x_A).$$

$$\hat{\mu}_B^S(T,P) = \hat{\mu}_B^L(T,P,x_B).$$

$$= \hat{\mu}_B^L(T,P) + \hat{R}T\ln x_B.$$

Solubility



Date.
No.

Derive it: $\ln x_B = \frac{\Delta_{fus} H}{\hat{R}}\left(\frac{1}{T_{melt}} - \frac{1}{T}\right)$

- Mass conservation.

stoichiometric coeff.

species

$$\sum_{i=1}^{S} \nu_i A_i \rightleftharpoons \sum_{i=1}^{S} \nu_i' A_i .$$

e.g., a simple reaction.

$$\underbrace{CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O}_{\text{elemt. conservation}}.$$

$a_j = \sum_i N_{ij} \nu_i$ num. moles

num. j atoms in species i.

- Equivalence ratio.

Date.
No.

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O.$$

everything fully oxidized (full comb.)

$\Downarrow$

In this case, we call them

"stoichiometry".

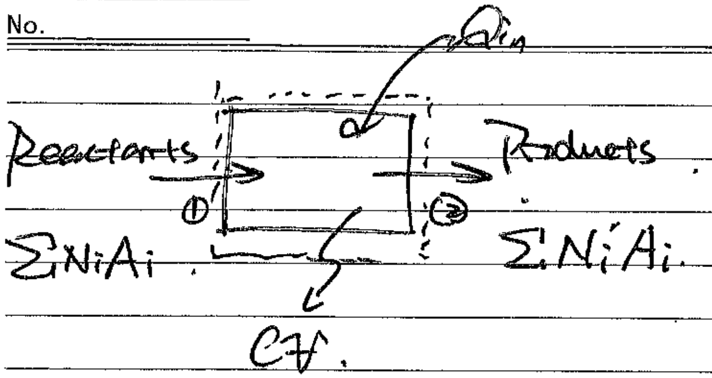
$$\Phi = \frac{(F/O)_{mixture}}{(F/O)_{stoichiometry}}.$$

$$\Phi = \frac{1/1}{1/2} = 2$$

$$\Phi \begin{cases} =1 \rightarrow \text{stoichiometry. (perfect).} \\ >1 \rightarrow \text{more fuel. (fuel-rich)} \\ <1 \rightarrow \text{more. oxidizer (fuel-lean).} \end{cases}$$

1st law of reacting system.

Date.
No.



Steady state reactor.

$\dot{E}_{in} = \dot{E}_{out}$

$\dot{Q}_{in} + \dot{H}_R = \dot{H}_p$

$\underbrace{\dot{Q}_{in} = \dot{H}_p - \dot{H}_R}_{\text{the real diff.}}$

how to calculate?

$H_R = \sum_i N_i h_i$.

↓

chemical bonds are considered!

$\hat{h}_i = (\hat{h}_i)_{sensible} + \underbrace{(\hat{e}_i)_{chemical}}_{\text{the new concept.}}$

$\Delta \hat{H}^{\circ}_{f_i}$ \

Date.
No.

↘ enthalpy of formation.

two common references.

① $T_{ref} = 0$ K.

Atomic species (O, N, H)

NASA tables ... ↗ ↖ reference spe.

② $T_{ref} = 298$K. } ref pressure ... 1 bar?

Stable diatomic species.

↳ O_2, N_2, H_2

Janaf tables. ∈ ↳ C.

e.g., h_{CO_2} (700K)

Sensible { ↓

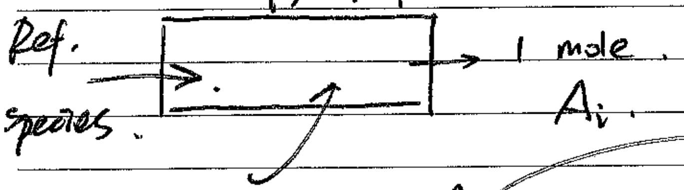
h_{CO_2} (298K). $\underbrace{\qquad}_{P_{ref}}$ → reference part. re. h_{O_2}.

Chemical Energy / Datum.

Heat of Formation. (Standard).

(Enthalpy).

T_{ref}, P_{ref}.

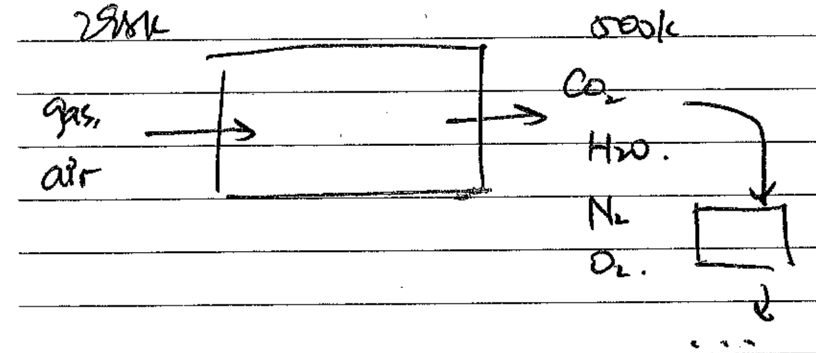


$$Q_{in} = \Delta\hat{H}^{\circ}_{f,i}(T_{ref}).$$

reference pressure

$$\hat{h}_{CO_2}(1500K) = \hat{h}_{gas}\Big|_{298.15}^{1500}$$

$$+\Delta\hat{H}^{\circ}_{f,}(298.15K).$$



$$\frac{ds}{d\tau} = \int \frac{dh_1 - v dP_1}{T} - \int \frac{dh_2 - v dP_2}{T}$$

$$= 0$$

$$\int \frac{dh_1 - v dP_1}{T} = \int \frac{dh_2 - v dP_2}{T}$$

$\underline{h_1 - v}$

$$\frac{h_1 - vP_1}{T} = \frac{h_2 - vP_2}{T}$$

$$h_1 - h_2 = v(P_2 - P_1)$$

$$v(P_2 - P_1) = Q - W$$

$$\Delta S = 0$$

Stoichiometric

Problem 1. Calculate K_p.

$CO + H_2O \rightleftharpoons CO_2 + H_2$

$\Delta_f G^\circ$ method

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right).$$

$$\Delta G^\circ = \sum_i (\nu_i' - \nu_i)\, \Delta_f \hat{G}_i^\circ (T)$$

$\Delta_f \hat{G}_{CO_2} = -396.3$ kJ/mol

$\Delta_f \hat{G}_{H_2} = 0$

$\Delta_f \hat{G}_{CO} = -252.3$ kJ/mol.

$\Delta_f \hat{G}_{H_2O} = -158.6$ kJ/mol.

$$= 1(-396.3 \text{ kJ/mol}) - (-252.3 \text{ kJ/mol}) - (-158.6 \text{ kJ/mol}).$$

$= 14.6$ kJ/mol.

$$K_p = \exp\left(\frac{-14.6 \text{ kJ/mol}}{\left(\frac{831.4}{1000}\right) 1600\text{K}}\right)$$

$= 0.3337.$

b). K_{pf} method.

$$\log_{10} K_p = \sum_i (\nu_i' - \nu_i) \log_{10} K_{pfi}$$

$\log_{10} K_{fCO_2} = 12.939.$

$\log_{10} K_{pfH_2} = 0.$

$\log_{10} K_{pfCO} = 82.36.$

$\log_{10} K_{pfH_2O} = 5.179.$

$\log_{10} K_p = (12.939) - (8.236) - (5.179)$

$K_p = 0.3342.$

Date.
No.

Problem 2 Calculate the equilibrium mole fraction of CO, CO_2, H_2O and H_2 in the problem of combustion of a $\phi = 1.5$ CH_4-air mixture at 1600 K, 1 bar.

$C_xH_y + Z(O_2 + 3.76N_2)$

(major product assump.)

Stoichiometric: $Z = \frac{y}{4} + x$.

$C_2H_6 \Rightarrow Z = 3.5$.

assume major product only:

$aCO_2 + bH_2O + cCO + dN_2$

Date.
No.

$1.5CH_4 + 2(O_2 + 3.76N_2) \rightarrow$

$aCO_2 + bCO + cH_2O + dH_2 + 7.52N_2$.

atom balancing

C: $1.5 = a + b$.

H: $6 = 2c + 2d$.

O: $4 = 2a + b + c$.

$CO + H_2O \rightleftharpoons CO_2 + H_2$

$$K_p = \frac{\left(\frac{P_{CO_2}}{P_0}\right)\left(\frac{P_{H_2}}{P_0}\right)}{\left(\frac{P_{H_2O}}{P_0}\right)\left(\frac{P_{CO}}{P_0}\right)} = \frac{X_{CO_2}X_{H_2}}{X_{H_2O}X_{CO}} = \frac{ad}{bc}$$

Subs. $K_p = 0.3342$.

Date.
No.

Week 8

1st law of reacting system.

$$\hat{h}_i(T) = \left[\hat{h}_i(T) - \hat{h}_i(T_{ref})\right]_{sensible}$$

$$+ \Delta_f \hat{H}^\circ(T_{ref})$$

CO_2 1000K $\hat{h}_{CO_2}$ (1000K).

↓ ↓

CO_2 298K

298K, C, O_2, N_2, --

IG. 1 bar

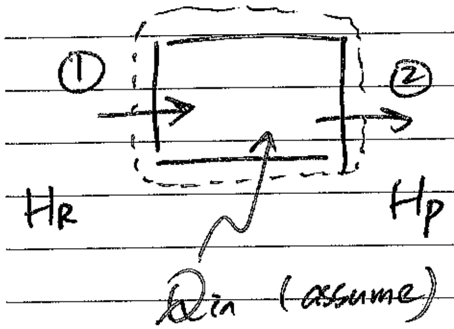
$$\hat{u}_i(T) = \hat{h}_i(T) - pv = \hat{h}_i(T) - \hat{R}_u T$$

$$= \int_{T_{ref}}^{T} \hat{c}_{v,i}(T)\,dT + \Delta_f \hat{H}_f^\circ(T_{ref})$$

$$- \hat{R}_u T_{ref}.$$

Date.
No.

Heat of Reaction.



$$\Delta H_{react} = H_p - H_R$$

$$E_{in} = E_{out}.$$

$$H_R + Q_{in} = H_p.$$

↳ $Q_{in} = H_p - H_R. = \Delta H_{react}.$

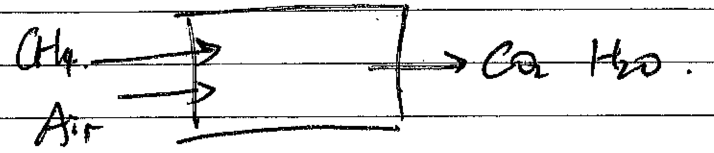
Standard Heat of Reaction.

(T_{ref}, P_{ref}).

$$\Delta G_R = W. = IV. = nF\forall.$$

Subset of H_{react} → Heat of Combustion

Heat of Combustion



$\phi=1$. $= -\Delta H_R$

water can stay in the v/l.

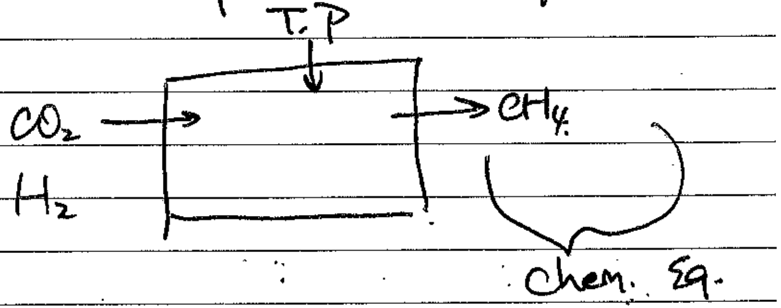
thats why we have

LHV & HHV.

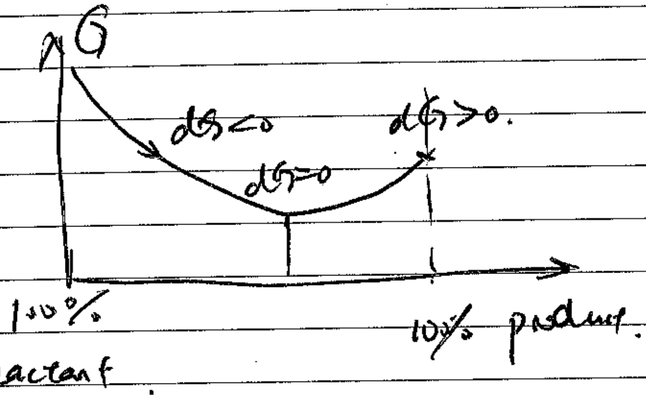
liquid phase → LHV.

vapor phase → HHV

2nd law for reactive systems.



☆ we are not saying the products & reactants are at chemical equilibrium. we are saying the reactants (i.e. CH_4, ...).



assume a general reaction

$$\sum_{i=1}^{c} \nu_i A_i \rightleftharpoons \sum_{i=1}^{c} \nu_i' A_i$$

Equilibrium : T, P (const.)

$$\sum_{i=1}^{c} (\nu_i' - \nu_i)\bar{\mu}_i = 0$$

ideal gas: Gibbs

non-ideal gas: fugacity } .

→ assume ideal gas, ideal mixture

$$\bar{\mu}_i = \hat{g}_i(T, P_i)$$

$$= \hat{g}_i(T, P_0) + \underbrace{\hat{R}_u T \ln\frac{P_i}{P_0}}$$

↓

Subs. into the equilibrium condition

$$\underbrace{\sum_i (\nu_i' - \nu_i)\,\hat{g}_i(T, P_0)}_{G_P - G_R} + \sum_i (\nu_i' - \nu_i)\,\hat{R}_u T \ln\frac{P_i}{P_0} = 0$$

$G_P - G_R$.

(at standard pressure).

⇓

$\Delta G_R^\circ(T, P_0)$: the Gibbs of reaction.

↓

$$\hat{R}_u T \sum_i (\nu_i' - \nu_i) \ln\frac{P_i}{P_0}$$

$$\sum_i (\nu_i' - \nu_i) \ln\frac{P_i}{P_0} = -\frac{\Delta G_R^\circ(T, P_0)}{\hat{R}_u T}.$$

$$\underbrace{\prod_i \left(\frac{P_i}{P_0}\right)^{(\nu_i' - \nu_i)}}_{\text{defined as } K_p.} = \exp\left[-\frac{\Delta G_R^\circ(T, P_0)}{\hat{R}_u T}\right]$$

example $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$

$$K_p = \frac{\left(\frac{P_{CO}}{P_0}\right)^1 \left(\frac{P_{O_2}}{P_0}\right)^{\frac{1}{2}}}{\left(\frac{P_{CO_2}}{P_0}\right)^1}$$

$$= \frac{\left(\frac{P \cdot X_{CO}}{P_0}\right)^1 \left(\frac{P \cdot X_{O_2}}{P_0}\right)^{\frac{1}{2}}}{\left(\frac{P}{P_0} \cdot X_{CO_2}\right)^1}$$

$$= K_x \left(\frac{P}{P_0}\right)^{1+\frac{1}{2}-1}.$$

reverse react.

Date.

No. tutorial

$$K_p = K_p(P_{ij}, \ldots).$$

$$Pv = ZnRT$$

$$\phi = \frac{F}{P} = \phi(T_r, P_r)$$

$$\log_{10}(\phi).$$

Example #1

$$H_2O + CO_2 \rightleftharpoons H_2CO_3.$$

$$K_p = \frac{H_2CO_3}{H_2O\,CO_2} \cdot \left(\quad \right).$$

$$K_p = \exp\left(-\frac{G^*}{R_u \cdot \Delta T}\right)^{\nearrow x}_{\text{ideal}}$$

$$\phi = \frac{F}{P} \rightarrow F = \phi P.$$

Date.

No.

$$\frac{P_i}{P_0} = \frac{\phi P_{i(\text{ideal})}}{P_0}$$

$$\underset{\uparrow}{H_2O + CO_2 \rightleftharpoons H_2CO_3}$$

figure out Gibbs.

$$+\left[\begin{array}{l} CO_2 = C + O_2. \\ H_2O = H_2 + \tfrac{1}{2}O_2. \\ H_2 + C + \tfrac{3}{2}O_2 = H_2CO_3. \end{array}\right] \begin{array}{l} \Delta G_1 \\ \Delta G_2 \\ \Delta G_3 \end{array}$$

$$K_p = \frac{[\quad]}{[\ 7r\ ]} \cdot \left(\frac{\phi_{H_2CO_3}}{\phi_{H_2O}\,\phi_{CO_2}}\right)$$

Entropy of mixing.

$$\Delta S_{tot} = \Delta S_{chem} + \Delta S_{mixing}.$$

$$S_i(T, P_i) = S_i(T, P_0)_{\text{unmixed}} - R \ln x_i$$

Date.
No.

1000 moles

Example $A+B \rightleftharpoons C$.

Find K_p : $(T,P) \rightarrow \Delta G_R < 0$. ↑ JANAF

Equiv: $\Delta G_{forward} = \Delta G_{backward}$.

$$\parallel$$

$$\Delta G_R - R\ln x_A - R\ln x_B$$

$$\Delta G_{backward} = -\Delta G_R - R\ln x_2$$

$$\Delta G_R - R\ln x_R - R\ln x_A = X_R - TR\ln X$$

$$\ln x_c - \ln x_A - \ln x_B = -\frac{\Delta G}{RT}$$

$$\ln\left(\frac{x_c}{x_A x_B}\right) = -\frac{\Delta G}{RT}$$

$$X = (H_p - H_R) - T(S_p - S_r)$$

Date.
No.

Final Week.

K_p calculation.

$$\frac{d(\ln K_p)}{dT} = \frac{\bar{h}_R(T)}{R_u T^2}$$

Van't Hoff equation.

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H_R^0(T)}{\hat{R}_u T^2} \quad \cdots (\dagger)$$

$$\ln K_p = -\frac{\Delta G_R^0(T,P_0)}{\hat{R}_u T}$$

$$= -\frac{\Delta H_R^0(T) - T\Delta S_R^0(T,P_0)}{\hat{R}_u T}$$

$$\frac{d(\ln K_p)}{dT} = \cancel{\frac{\Delta H_R^0(T) - T\Delta S_R^0(T,P_0)}{\hat{R}_u T^2}}$$

$$-\frac{1}{\hat{R}_u T}\left[\frac{d(\Delta H_R^0(T))}{dT} - \cancel{\Delta S_R^0(T,P_0)} - T\cdot\frac{d\Delta S_R^0}{dT}\right]$$

$$= \frac{\Delta H_R^\circ(T)}{\hat{R}_u T^2} - \frac{1}{\hat{R}_u T}\left[\frac{d(\Delta H_R^\circ(T))}{dT}\right.$$

$$\left. + \frac{1}{\hat{R}_u T} T \frac{d[\Delta S_R^\circ(T,P)]}{dT}\right]$$

Gibbs: $dh = Tds - vdP$.

@ const. P: $dh = Tds$.

$$d[\Delta H_R^\circ(T)] - T d[\Delta S_R^\circ(T,P)] = 0$$

In the end we arrive at (4)

→ Evaluation of K_p.

$$K_p = \exp\left[-\Delta G_R^\circ(T)/\hat{R}_u T\right]$$

$$\Delta G_R^\circ(T) = \sum_i (\nu_i' - \nu_i)\hat{g}_i(T, P_0).$$

$\sum' \nu_i A_i = \sum \nu_i' A_i$.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$\Delta G_R^\circ(T) = \hat{g}^\circ_{CO_2}(T) + \hat{g}^\circ_{H_2}(T)$$

$$- \hat{g}^\circ_{CO}(T) - \hat{g}^\circ_{H_2O}(T)$$

$$C_{(s)} + \tfrac{1}{2}O_2 \rightleftharpoons CO. \quad ①$$ $K_{p1} \leftarrow$ formation reaction

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \quad ②$$

$$C_{(s)} + O_2 \rightleftharpoons CO_2 \quad ③$$

$$H_2 \rightleftharpoons H_2 \quad ④$$

$$K_p = \frac{\left(\frac{P_{CO_2}}{P_0}\right)\left(\frac{P_{H_2}}{P_0}\right)}{\left(\frac{P_{CO}}{P_0}\right)\left(\frac{P_{H_2O}}{P_0}\right)} \Longleftrightarrow K_p = \frac{K_{p_3} \cdot K_{p_4}}{K_{p_1} \cdot K_{p_2}}$$

$$\log_{10} K_p(T) = \sum_i (\nu_i' - \nu_i) \log_{10} K_{f,i}(T).$$

$$K_p = \exp\left(-\frac{\Delta G_R^\circ(T)}{\hat{R}_u T}\right) = \exp\left[-\frac{\sum_i(\nu_i' - \nu_i)\Delta_f \hat{G}}{\hat{R}_u T}\right]$$

Condensed phase. (solid, liquid)

$$P_{condense} = P_0$$

$$\sum_i (\nu_i' - \nu_i)\hat{g}_i(T, P_i) = 0$$

$$\hat{g}(T,P) \approx \hat{g}(T,P_0).$$

$\hat{g}(T,P) - \hat{g}(T,P_0) \triangleq v(P - P_0)$

Maxwell Relations $dg = vdP - sdT$.

For const. temp: $dg = vdP$

Date.
No.

Gibbs ener.

$C(s) + O_2 \rightleftharpoons CO_2$

$$K_p = \frac{\left(\frac{P_{CO_2}}{P_0}\right)}{\left(\frac{P_{O_2}}{P_0}\right)\cdot\underbrace{\left(\frac{P_0}{P_0}\right)}_{\to 1}} = \exp\left[\sim\right]$$

K_p, K_x, K_c.

C_i → molar concentration. mole/cm³. $c_i = n_i/V$.

x_i → mole fraction. ↳ $x_i = P_i/P$

$2NH_3 \rightleftharpoons N_2 + 6H_2$.

$$K_c = \frac{\left[\frac{C_{N_2}}{C_0}\right]\cdot\left[\frac{C_{H_2}}{C_0}\right]^3}{\left[\frac{C_{NH_3}}{C_0}\right]^2} \; ; \quad K_x = \frac{x_{N_2}\, x_{H_2}^3}{x_{NH_3}^2}$$

↑ liquid phase

molar concen.

IG: $P_i = x_i P$.

$$K_p = \prod_i \left(\frac{x_i P}{P_0}\right)^{\nu_i'-\nu_i} = \prod_i x_i^{(\nu_i'-\nu_i)} \prod_i \left(\frac{P}{P_0}\right)^{\nu_i'-\nu_i}$$

$P_i = c_i \hat{R}_u T$.

Fugacity Equilibrium const. for reaction involving real gas

Date.
No.

$$K_f^* = K_p K^*_{\phi(T,P)} = \exp\left[-\frac{\Delta\hat{G}_R^0(T,P_0)}{\hat{R}_u T}\right]$$

↳ $f = \frac{\phi}{P}$. assume $K_\phi^* \approx 1$ ...?

$\sum_i \nu_i A_i \rightleftharpoons \sum_i \nu_i' A_i$.

Equilibrium cond.: $\sum_i (\nu_i' - \nu_i)\,\bar{\mu}_i(T,P) = 0$ ...①

↑ still an ideal mixture

For ideal mixture.

$\bar{\mu}_i(T,P) = \hat{\mu}_i^*(T,P) + \hat{R}_u T \ln x_i$ ...②

↖ pure component.

For real gas: (pure component).

$d\hat{\mu}_{i,T} = \hat{R}_u T\, d\ln f_i$.

$$\hat{\mu}_i^*(T,P) = \hat{\mu}_i^*(T,P_0) + \hat{R}_u T \ln\frac{f_i^*(T,P)}{\underset{\Downarrow\; P_0}{f_i(T,P_0)}}$$ ...③

③→②, ②→①

$$\bar{\mu}_i(T,P) = \hat{\mu}_i^*(T,P_0) + \hat{R}_u T \ln\left[\frac{x_i f_i^*(T,P)}{P_0}\right]$$

$f_i^* = P\cdot\phi^*(T,P)$, $x_i = P_i/P$.

$$\prod_i \left[\frac{P_i}{P_0}\cdot\phi^*(T,P)\right]^{(\nu_i'-\nu_i)} = \exp\left[-\frac{\Delta\hat{G}_R^0(T,P)}{\hat{R}_u T}\right]$$

Date.

No.

$$K_p \cdot K_{\phi^*(T,p)} = \exp\left[\frac{\Delta \hat{G}^\circ_R(T,P_0)}{\hat{R}_u T} \right]$$

Lewis-Randall Rule (ideal mixture).

$$f_i(T,p) = \chi_i \cdot f_i^*(T,p)$$

$$K_f = \prod_i \left(\frac{f_i(T,p)}{f_0} \right)^{\nu_i' - \nu_i} = K_p \cdot K_{\phi^*}$$

$$= \exp\left[- \frac{\Delta \hat{G}^\circ_R(T,P_0)}{\hat{R}_u T} \right]$$

adiabatic flame temperature (oxidation).

$$\phi C_3H_8 + 5(O_2 + 3.76 N_2) \rightarrow$$

$$\phi = \frac{(F/O)_{mix}}{(F/O)_{st}} = \frac{\phi/5}{1/5} = \phi.$$ ✓ 1.2 in HW.

satisfied eq.).

① $\phi < 1$, $\overset{\text{Major}}{CO_2, H_2O, N_2, O_2}$. (Minor products $H, O, H_2, \ldots$)

$\frac{1}{2}N_2 + O_2 = NO_2$

② $\phi > 1$. CO_2, H_2O, CO, H_2, N_2 $\quad K_p = \frac{\chi_{CO_2} \cancel{\chi} \chi_{H_2}}{\chi_{CO} \chi_{H_2O}}$

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Additional Notes: Thermodynamics

Chapter Summary Collections

Chapter 3: Pure substances.

- Definition of quality: $x = \frac{m_{vapor}}{m_{total}}$.

- average value of intensive property y: $y = y_f + x y_{fg}$.

Saturated liquid.

where $y \simeq y_{f@T}$ Saturated vapor

↳ y could be v, u or h.

- Ideal gas: $Pv = RT$.

- real gas: $Z = \frac{Pv}{RT}$ or $\frac{v_{actual}}{v_{ideal}}$.

↳ Same at same reduced temp. & pressure.

defined as:

$$T_R = \frac{T}{T_{cr}} \quad \& \quad P_R = \frac{P}{P_{cr}}.$$

→ known as "Principle of corresponding states".

pseudo-reduced specific volume: $v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$

Three best known P-v-T relations:

vdW: $\left(P+\frac{a}{v^2}\right)(v-b)=RT$.

$$a=\frac{27R^2T_{cr}^2}{64P_{cr}}, \quad b=\frac{RT_{cr}}{8P_{cr}}.$$

B-B: $P=\frac{R_uT}{\bar{v}^2}\left(1-\frac{c}{\bar{v}T^3}\right)(\bar{v}+B)-\frac{A}{\bar{v}^2}$

$$A=A_0\left(1-\frac{a}{\bar{v}}\right), \quad B=B_0\left(1-\frac{b}{\bar{v}}\right)$$

B-W-B:

$$P=\frac{R_uT}{\bar{v}}+\left(B_0R_uT-A_0-\frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2}+\frac{bR_uT-a}{\bar{v}^3}$$

$$+\frac{a\alpha}{\bar{v}^6}+\frac{c}{\bar{v}^3T^2}\left(1+\frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

Chapter 4: Closed Systems

Work: Area under process curve for a P-v diagram

- General: $W_b=\int_1^2 P\,dV$.
- Isobaric process: $W_b=P_0(V_2-V_1)$
  $$\downarrow$$
  $$P_0=P_1=P_2=\text{const}.$$
- Polytropic process: $W_b=\frac{P_2V_2-P_1V_1}{1-n}$. $(PV^n=\text{const.})$.
- Isothermal process for ideal gas:

$$\underbrace{W_b=P_1V_1\ln\frac{V_2}{V_1}=mR\underset{\text{because isothermal.}}{T_0}\ln\frac{V_2}{V_1}}_{\text{Important.}}$$

$E_{sys}=E_{in}-E_{out}$. or $\dot{E}_{sys}=\dot{E}_{in}-\dot{E}_{out}$

- The energy balance for closed system:

$$Q-W=\Delta U+\Delta KE+\Delta PE.$$

→ where

$$W = W_{other} + W_b.$$

$$\Delta U = m(u_2 - u_1).$$

$$\Delta KE = \frac{1}{2} m (V_2^2 - V_1^2)$$

$$\Delta PE = mg(z_2 - z_1).$$

☆ For constant-pressure process,

$$W_b + \Delta U = \Delta H \quad \ldots ?$$

Hence,

$$Q - W_{other} = \Delta H + \Delta KE + \Delta PE.$$

Specific heat at constant volume C_v
& constant pressure C_p:

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v \quad ; \quad C_p = \left(\frac{\partial h}{\partial T}\right)_p.$$

For ideal gases: u, h, C_v & C_p are functions of temperature alone.

The Δu & Δh of ideal gases are expressed as:

$$\Delta u = u_2 - u_1 = \int_1^2 C_v(T)\,dT$$

$$\simeq C_{v,avg}(T_2 - T_1).$$

$$\Delta h = h_2 - h_1 = \int_1^2 C_p(T)\,dT$$

$$\simeq C_{p,avg}(T_2 - T_1).$$

For ideal gases, C_p & C_v are related:

$C_p = C_v + R$. → specific gas constant.

→ Specific heat ratio k is defined as:

$$k = \frac{C_p}{C_v}$$

↳ usually $\simeq 1.4$

For incompressible (fluids & solids).

$$C_p = C_v \equiv C.$$

- Δu & Δh of [incompressible] substances:

$$\Delta u = \int_1^2 C(T)\,dT = C_{avg}(T_2 - T_1)$$

$$\Delta h = \Delta u + v\Delta P$$

Chapter 5. Control Volume

- conservation of mass:

$$m_{in} - m_{out} = \Delta m_{sys} \quad \& \quad \frac{dm_{sys}}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

- mass flow rate:

$$\dot{m} = \rho \underset{\hookrightarrow \text{velocity}}{V} \underset{}{A} \rightarrow \text{area.}$$

- Volume flow rate: $\dot{V} = VA = \frac{\dot{m}}{\rho}$.

★★ - Work required to push a unit mass of fluid into or out of a control volume:

flow work or flow energy.

↳ expressed as: $w_{flow} = Pv$.

- Total energy of flowing fluid:

$$\theta = \underbrace{h}_{Pv + e} + ke + pe$$

$e \rightarrow$ close system. (internal)

- mass energy transport:

$$E_{mass} = mh \quad \text{(or rate form).}$$

- general energy balance.

$$\Delta E_{sys} = E_{in} - E_{out} \quad \text{or} \quad \frac{dE_{sys}}{dt} = \dot{E}_{in} - \dot{E}_{out}$$

- conservation of mass & energy equations for steady-flow processes:

$$\sum_{in} \dot{m} = \sum_{out} \dot{m}$$

★★

$$\dot{Q} - \dot{W} = \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right) - \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right)$$

For single stream systems (mechanical eng.)

$$\dot{m}_1 = \dot{m}_2 \rightarrow \frac{1}{v_1} V_1 A_1 = \frac{1}{v_2} V_2 A_2.$$

$$\hookrightarrow \dot{Q} - \dot{W} = \dot{m}\left[\underbrace{h_2 - h_1 + \frac{V_2^2 - V_1^1}{2} + g(z_2 - z_1)}_{\text{mass flow energy}}\right]$$

→ mass & energy relations for a uniform-flow system:

$$m_{in} - m_{out} = \Delta m_{sys}.$$

$$Q - W = \sum_{out} mh - \sum_{in} mh + (m_2u_2 - m_1u_1)_{sys}$$

where $Q = Q_{net,in} = Q_{in} - Q_{out}$. is the net heat input &

$$W = W_{net,out} = \underbrace{W_{out} - W_{in}}_{\text{net work output.}}$$

It is recommended to use the general form:

$$\Delta E_{sys} = E_{in} - E_{out}.$$

Chapter 6 Second law

- thermal efficiency of heat engine

$$\eta_{th} = \frac{W_{net,out}}{Q_H} = 1 - \frac{Q_L}{Q_H}.$$

- Special cases for refrigerators & pumps:

$$COP_R = \frac{Q_L}{W_{net,in}} = \frac{1}{Q_H/Q_L - 1}$$

$$COP_{HP} = \frac{Q_H}{W_{net,in}} = \frac{1}{1 - Q_L/Q_H}.$$

- Carnot cycle states the relationship for reversible device:

$$\left(\frac{Q_H}{Q_L}\right)_{\underline{rev}} = \frac{T_H}{T_L}$$ reversible is important

= For Carnot heat engine, thermal efficiency writes:

$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}.$$

- COPs for reversible refrigerator & Heat pump

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1} \; ; \; COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

Chapter 7: Entropy

- entropy is defined as:

$$dS = \left(\frac{dQ}{T}\right)_{int\_rev.}$$

↳ For internally reversible process:

$$\Delta S = \frac{Q}{T_0}.$$

- inequality part of Clausius inequality

→ increase of entropy principle:

$$\underbrace{S_{gen}}_{\text{entropy generated during process.}} \geq 0.$$

entropy-change & isentropic relations for a process:

1. pure substance:

any process: $\Delta S = S_2 - S_1$.

Isentropic process: $S_2 = S_1$.

2. Incompressible substances:

Any process: $s_2 - s_1 = C_{avg} \ln \frac{T_2}{T_1}$.

Isentropic process: $T_2 = T_1$

3. Ideal gases:

→ "constant specific heats"

Any process: $s_2 - s_1 = c_{v,avg} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$.

$$s_2 - s_1 = c_{p,avg} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.$$

Isentropic process:

$$\left(\frac{T_2}{T_1}\right)_{s=const.} = \left(\frac{v_1}{v_2}\right)^{k-1}.$$

$$\left(\frac{T_2}{T_1}\right)_{s=const.} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}.$$

$$\left(\frac{P_2}{P_1}\right)_{s=const.} = \left(\frac{v_1}{v_2}\right)^{k}$$

→ Variable specific heats:

Any process:

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R\ln\frac{P_2}{P_1}$$

Isentropic process:

$$s_2^\circ = s_1^\circ + R\ln\frac{P_2}{P_1}$$

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

$$\left(\frac{v_2}{v_1}\right)_{s=\text{const.}} = \frac{v_{r2}}{v_{r1}}$$

→ P_r is the relative pressure and v_r is the relative specific volume. The function s° depends on temperature only.

- Steady-flow work for a reversible process can be expressed:

$$W_{rev} = -\int_1^2 v\,dP - \Delta ke - \Delta pe$$

For incompressible substances ($v = \text{const.}$).

$$\rightarrow W_{rev} = -v(P_2 - P_1) - \Delta ke - \Delta pe.$$

Work done during a steady-flow process is proportional to the specific volume.

- reversible work input to a compressor:

Isentropic: $W_{comp,in} = \dfrac{kR(T_2 - T_1)}{k-1}$

$$= \frac{kRT_1}{k-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$$

Polytropic: $W_{comp,in} = \dfrac{nR(T_2 - T_1)}{k-1}$

$$= \frac{nRT_1}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$$

Isothermal: $W_{comp,in} = RT\ln\dfrac{P_2}{P_1}$.

For steady-flow devices:

We consider turbine, compressor, nozzles:

- $\eta_T = \dfrac{\text{Actual turbine}}{\text{Isentropic turbine}} \simeq \dfrac{h_1 - h_{2a}}{h_1 - h_{2s}}$

- $\eta_C = \dfrac{\text{Isentropic comp.}}{\text{Actual comp.}} \simeq \dfrac{h_{2s} - h_1}{h_{2a} - h_1}$

- $\eta_N = \dfrac{\text{Actual KE @ noz.}}{\text{Isentropic KE @ noz.}} \simeq \dfrac{h_1 - h_{2a}}{h_1 - h_{2s}}$

entropy balance for any system:

$$S_{in} - S_{out} + \dot{S}_{gen} = \Delta S_{sys}.$$

or in rate form:

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{sys}$$

For general steady flow process:

$$\dot{S}_{gen} = \sum_e \dot{m}_e s_e - \sum_i \dot{m}_i s_i - \sum_k \frac{\dot{Q}_k}{T_k}.$$

Chapter 8: Exergy

- Irreversibility I or exergy destroyed:

$$I = X_{des} = T_0 S_{gen}$$
$$= W_{rev,out} - W_{u,out}$$
$$= W_{u,in} - W_{rev,in}.$$

- Second-law efficiency:

$$\eta_{II} = \frac{\eta_{th}}{\eta_{th,rev}} = \frac{W_u}{W_{rev}}.$$

- For heat engines & other work-producing dev.:

$$\eta_{II} = \frac{COP}{COP_{rev}} = \frac{W_{rev}}{W_u}.$$

- For refrigerators, heat pumps, & other

$$\eta_{II} = \frac{\text{Exergy recovered}}{\text{Exergy supplied}} = 1 - \frac{\text{Exergy destroyed}}{\text{Exergy supplied}}$$

- The exergies of a fixed mass / flow stream

Non-flow exergy:

$$\phi = \underbrace{(u-u_0) + P_0(v-v_0)} - T_0(s-s_0) + \frac{V^2}{2} + gz.$$

Flow exergy:

$$\psi = (h-h_0) - T_0(s-s_0) + \frac{V^2}{2} + gz.$$

☆ - The exergy change as "it" undergoes from state 1 ⟶ state 2:

$$\Delta X = X_2 - X_1 = m(\phi_2 - \phi_1)$$

$$= (E_2 - E_1) + P_0(V_2 - V_1) - T_0(S_2 - S_1)$$

$$= (U_2 - U_1) + P_0(V_2 - V_1) - T_0(S_2 - S_1) + m\frac{V_2^2 - V_1^2}{2} + mg(Z_2 - Z_1).$$

$$\Delta \psi = \psi_2 - \psi_1 = (h_2 - h_1) - T_0(S_2 - S_1) + \frac{V_2^2 - V_1^2}{2} + g(Z_2 - Z_1).$$

Exergy transfer by heat:

$$X_{heat} = \left(1 - \frac{T_0}{T}\right) Q.$$

Exergy transfer by work:

$$X_{work} = \begin{cases} W - W_{surr} \nearrow P_0 & (\text{boundary w.}) \\ W & (\text{other forms}) \end{cases}.$$

Exergy transfer by mass:

$$X_{mass} = m\psi.$$

The exergy of an isolated system during a process always decrease.

$$\Delta X_{iso} \leq 0. \rightsquigarrow \text{Clausius statement}.$$

Exergy balance for any system undergoes any proc.

General: $X_{in} - X_{out} - X_{des} = \Delta X_{sys}.$

rate form: $\dot{X}_{in} - \dot{X}_{out} - \dot{X}_{des} = \frac{dX_{sys}}{dt}.$

unit-mass: $(x_{in} - x_{out}) - x_{des} = \Delta x_{sys}$

where:

$$\dot{X}_{heat} = \left(1-\frac{T_0}{T}\right)\dot{Q}$$

☆ $\dot{X}_{work} = \dot{W}_{useful}$ $\rightsquigarrow$ used in calculating efficiency.

$\dot{X}_{mass} = \dot{m}\psi$.

For reversible process, no "X_{des}"

general exergy balance:

$$\sum \left(1-\frac{T_0}{T_k}\right)Q_k - \left[W - P_0(V_2 - V_1)\right] + \sum_{in} m\psi - \sum_{out} m\psi - X_{des} = X_2 - X_1.$$

$$\sum \left(1-\frac{T_0}{T_k}\right)\dot{Q}_k - \left(\dot{W} - P_0\frac{dV_{cv}}{dt}\right) + \sum_{in} \dot{m}\psi - \sum_{out} \dot{m}\psi - \dot{X}_{des} = \frac{dX_{cv}}{dt}.$$

Chapter 12. Thermodynamic Property

four Gibbs equations:

$$\begin{cases} du = Tds - Pdv. \\ dh = Tds + vdP. \\ da = -sdT - Pdv. \\ dg = -sdT + vdP. \end{cases}$$

the Maxwell relations:

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

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

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

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

the Clapeyron equation → enthalpy change associated with phase change:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{Tv_{fg}}$$

liquid-vapor & solid-vapor @ low pressures:

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)_{sat}$$

The changes in internal energy, enthalpy, entropy of simple compressible subs.

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

$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

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

or

$$ds = \frac{C_p}{T}dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

- The general relations for specific heats:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

$$C_{p,T} - C_{p0,T} = -T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T$$

$$C_p - C_v = \frac{vT\beta^2}{\alpha} \rightarrow \text{general.}$$

β: volume expansivity,

α: isothermal compressibility.

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \& \quad \alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

The temperature behavior of a fluid during a throttling (h = const.) is described by the Joule-Thomson coefficient:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$$

during a const. enthalpy process.

$$\mu_{JT} = -\frac{1}{C_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]$$

The enthalpy, internal energy, & entropy changes of real gases:

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1)_{ideal} - R_u T_{cr}(Z_{h_2} - Z_{h_1})$$

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u(Z_2T_2 - Z_1T_1)$$

$$\bar{s}_2 - \bar{s}_1 = (\bar{s}_2 - \bar{s}_1)_{ideal} - R_u(Z_{s_2} - Z_{s_1})$$

Practice Midterm.

1. N_2. $v_1 = 0.005 m^3/kg$, $T_1 = 200K$.

Determine the pressure using two-parameter corresponding state principle.

look up $Z_1^{(0)}, Z_1^{(1)}, w$

$$Z_1 = Z_1^{(0)} + w Z_1^{(1)}.$$

$$pv_1 = Z_1 R T_1$$

---

2. exergy of CO_2: $m = 10kg$.

rigid tank; critical point

environmental conditions: $P = 1$ bar, $T = 300K$.

Recall the exergy of a closed system:

$$\phi = (u-u_0) + P_0(v-v_0) - T_0(s-s_0)$$

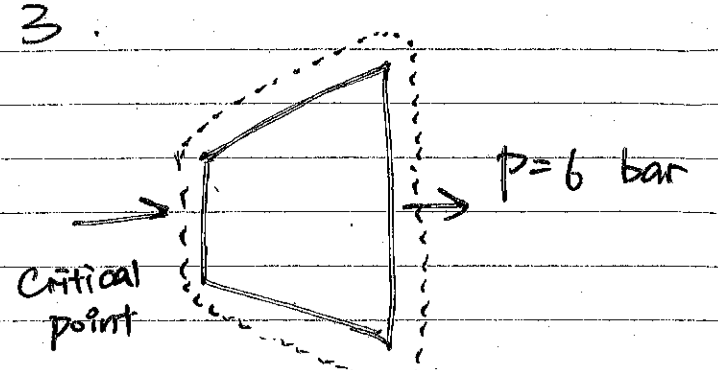
From tables A-21 & A-22

One knows @ Critical point:

$T = 304.21$ K, $P = 73.825$.

One gets u_1, u_0; v_1; v_0; s_1, s_0

3.



Isothermal

↓

$T_2 = T_1 = 200K$

↓

$T_R = 1$

$P_{cr} = 60$ bar

$T_{cr} = 200K$.

$\omega = 0.5$

↳ corresponding principle.

$$P_R = \frac{P}{P_{cr}} = 0.1.$$

↓

$$Z^{(0)} = 0.9659$$

$$Z^{(1)} = -0.0069.$$

$$Z = Z^{(0)} + wZ^{(1)}$$

$$= 0.9659 + 0.5\cdot(-0.0069).$$

$$Pv = ZRT.$$

For isothermal process: $W = P_1V_1 \ln\frac{V_2}{V_1}$