

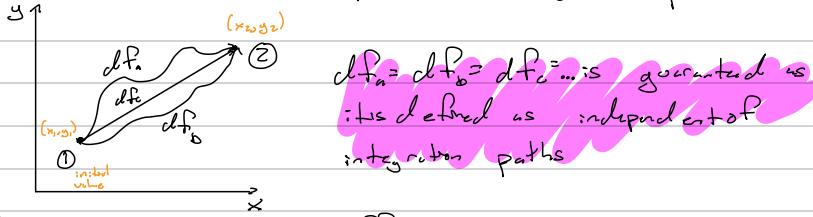


Midterm Exam 1



Math Review

① **Differentials** \equiv an infinitesimal change in a function or variable
 ex: If $f = f(x, y)$, then the total differential of f is $df = P(x, y)dx + Q(x, y)dy$
 and is exact and independent of integration paths



② **Partial Derivatives** \equiv the differential change in one variable with respect to a differential change in another variable, while holding other variables fixed/constant

ex: Let $f(x, y) = x^2y + xy + \sin x \sin y$.

$$\begin{aligned} \text{Diff. change in } f & \text{ (} \frac{\partial f}{\partial x} \text{)} @ \text{constant } y = \left(\frac{\partial f}{\partial x} \right) \\ \text{Diff. change in } x & \text{ (} \frac{\partial x}{\partial x} \text{)} \end{aligned}$$

then $\left(\frac{\partial f}{\partial x} \right) = 2xy + \sin y + \cos x \sin y \leftarrow P$

Similarly $\left(\frac{\partial f}{\partial y} \right) = x^2 + x \cos y + \sin x \cos y \leftarrow Q$

Now note that for our total differential, $df = P(x, y)dx + Q(x, y)dy$
 \rightarrow if y is held constant and hence $dy = 0$, $df = P(x, y)dx \Rightarrow \left(\frac{\partial f}{\partial x} \right)_y = P(x, y)$
 \rightarrow similarly for constant x , then $\left(\frac{\partial f}{\partial y} \right)_x = Q(x, y)$

③ **Integration** \equiv continuous sum over differential changes

$$\int f(x) dx$$

Integral \uparrow Differential

1. **Indefinite Integral:** No upper/lower bounds

$$\text{ex: } \int (A + BT + CT^2 + \frac{D}{T} + \frac{E}{T^2}) dT \quad \text{where } A, B, C, D, E \text{ are constants, } T \text{ is temperature}$$

$$= AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 + DT - \frac{E}{T} + (\text{constant})$$

2. **Definite Integral:** Specified lower & upper bounds (no constant of integration)

$$\int_{T_0}^{T_1} (A + BT) dT = \left[AT + \frac{B}{2}T^2 \right]_{T=T_0}^{T=T_1} = A(T_1 - T_0) + \frac{B}{2}(T_1^2 - T_0^2)$$

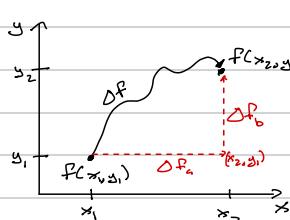
Summary - Common points of confusion!

① **Differential:** infinitesimal changes denoted df

② **Derivative:** change in one variable with respect to another (\approx differential / another differential)
 ex: $\frac{df}{dx}, \frac{df}{dt}, \frac{df}{dx}_y$

③ **Integral:** Continuous sum over differential changes
 ex: $f = f(x)$: $f(x_b) - f(x_a) = \int_{x_a}^{x_b} df$ problem: Need to integrate w.r.t. variable in our bounds of integration $= \int_{x_a}^{x_b} \left(\frac{df}{dx} \right) dx$ derivative!

ex: $f = f(x, y)$:



$$f(x_2, y_2) - f(x_1, y_1) = \Delta f = \Delta f_a + \Delta f_b$$

$$= \int_{x_1}^{x_2} \left(\frac{\partial f}{\partial x} \right)_{y=y_1} dx + \int_{y_1}^{y_2} \left(\frac{\partial f}{\partial y} \right)_{x=x_2} dy$$

We can do this bc the differential is independent of path

* Math no-no!

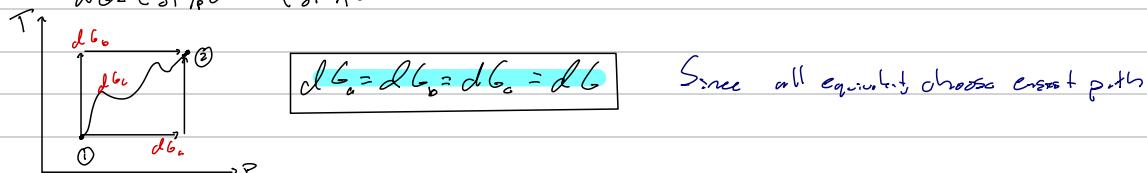
$\times \Rightarrow \int \frac{df}{dx} dx$ cannot be evaluated! Missing the differential!

\hookrightarrow Must integrate over differential changes

$\checkmark \Rightarrow \int \left(\frac{df}{dx} \right) dx$ is allowed!

Chapter 1 - Thermodynamic Properties

Thermodynamic Properties are state functions that do not depend on path and have exact differentials.
 ex: $G = G(T, P)$ Gibbs Free Energy
 $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$



Inexact Differentials are path functions (i.e., they do depend on path)

ex: work (w) and heat (Q)

→ dW and dQ do depend on path

→ use notation δQ and δW to denote an inexact differential

What is Thermodynamics?

↳ A self-contained, logically consistent theory that can be expressed in two laws:

• First Law: Conservation of Energy

$\Delta E_{\text{univ}} = 0$ for any process

• Second Law: Entropy increases

$\Delta S_{\text{univ}} \geq 0$ for any process

• Two benefits of the 2nd Law

(i) Is our process consistent with 2nd Law?

(ii) Entropy of system + surroundings should reach a maximum over time.

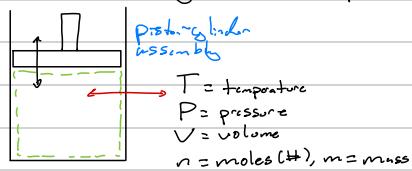
① System and Surroundings



• Three Types of Systems

| | "closed" | "open" | "isolated" |
|-----------------|----------|--------|------------|
| energy transfer | yes | yes | No |
| mass transfer | No | yes | No |

② Thermodynamic Properties of Fluids (mostly gases & liquids, only some solids)



Types of Properties

- (i) extensive = varies w/ size of system
- (ii) intensive = independent of system size

Q: Which of the following thermodynamic properties are intensive? (out of P, T, n, V, ρ)

$$\textcircled{1} P, T, n$$

$$\textcircled{3} V, n$$

$\textcircled{2} P, T, \rho$ None of these depend on how large the system is,
or how much stuff is in it!

| | | | |
|--|--|----------|----------|
| P | V | T | n |
| ↑ intensive (C_{int}) | ↑ extensive (C_{ext}) | ↑ int | ↑ ext |

density

We can convert ext quantities to int ones:

extensive = "specific property" ← lowercase with or w/o
mass → intensive quantity normalized by mass

$$\text{ext: } \frac{\text{Volume}}{\text{mass}} = \frac{V}{m} = \frac{1}{\rho} \quad \text{specific volume}$$

extensive = "molar property" ← lowercase w/ subscript m
moles → intensive

$$\text{ext: } \frac{\text{Volume}}{\text{moles}} = V_m \quad \begin{array}{l} \text{relation for ext of} \\ \text{readily & easily} \\ \text{is distinct from textbook} \end{array}$$

③ "State" of a System

- The "state" of a system depends on its thermodynamic properties
↳ can be described by the Gibbs phase rule:

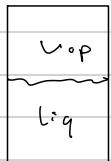
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑
degrees of freedom
↑
of chemical species
↑
of phases

o Degrees of Freedom \Rightarrow # of intensive properties that must be specified to constrain properties of system

- To fully specify a state, also need to know amount of material

Example: Vapor-liquid mixture of H_2O



$$m=1 \quad \pi=2 \quad \Rightarrow f=1$$

↓
molar of H_2O

↓
molar of H_2O

$$V_{\text{tot}} = V = V_{m,L} n_L + V_{m,V} n_V \quad \rightarrow \text{divide by } n_{\text{tot}} = n_L + n_V$$

$$\Rightarrow \frac{V}{n} = V_m = (1-x) V_{m,L} + x V_{m,V}$$

↑
average molar volume

x ≈ "quality"

We can't for example specify V_m for each phase

→ constrains all other intensive properties

Also need to specify total amount in each phase

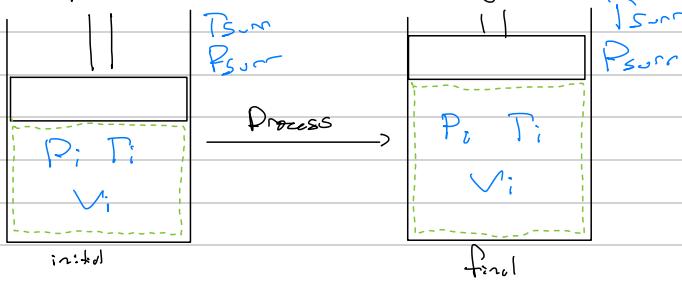
$$\rightarrow V_{\text{tot}} = V_{\text{liq}} + V_{\text{vap}}$$

$Q_{\text{liq}} = \text{mole or mass fraction of } \text{H}_2\text{O}$

$$\text{Also: } \beta = (1-x) \beta_2 + x \beta_1$$

④ Processes

- A process is a change in the system



4 Special Types of Processes

- Isothermal** $\rightarrow \text{const } T$
- Isobaric** $\rightarrow \text{const } P$
- Isochoric** $\rightarrow \text{const } V$
- Adiabatic** $\rightarrow \text{No heat transfer to/from sum}$
↳ can also be described as well-insulated

⑤ Equilibrium

- A system does not change @ equilibrium and there is no driving force for change

→ Examples:

(i) Thermal Equilibrium $\rightarrow T_{\text{sys}} = T_{\text{sum}}$ (also btwn phases)

(ii) Force/mechanical $\rightarrow P_{\text{sys}} = P_{\text{sum}}$

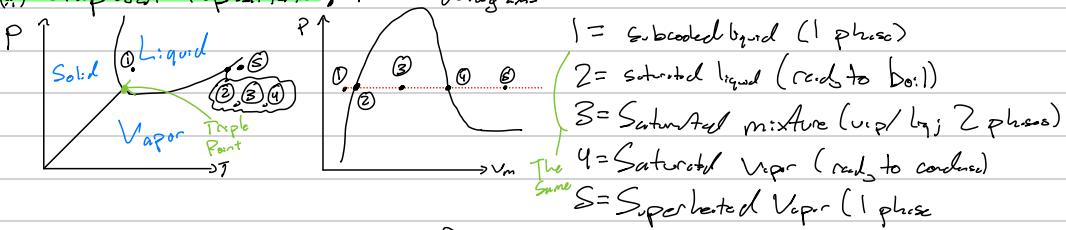
(iii) Phase Equilibrium \rightarrow Composition of phases is constant

(iv) Chemical Equilibrium \rightarrow No mass transfer into/out of a phase, or no net chemical reaction

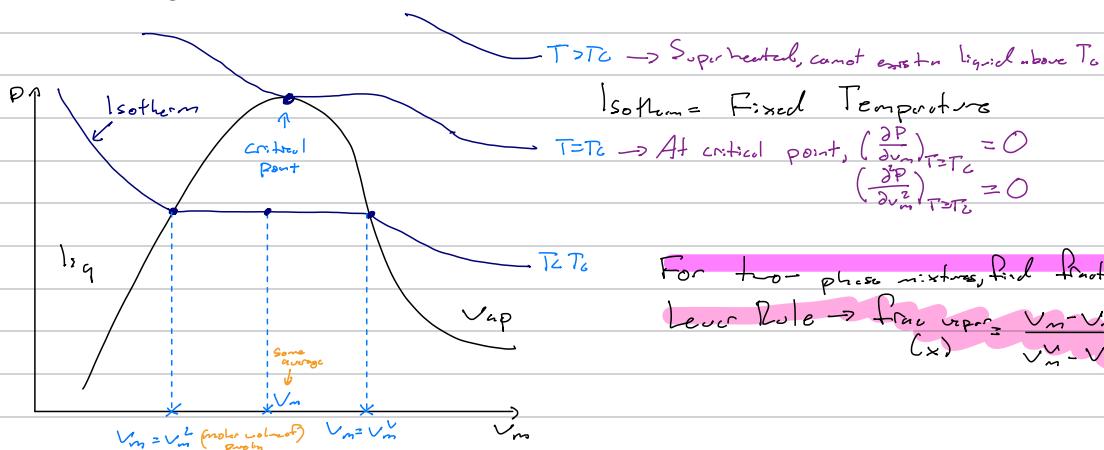
Thermodynamic Property Sources

(i) Experiment $\rightarrow P, T, V, \dots$

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



For two-phase mixtures, find fraction of vapor using mass balance
Lever Rule \rightarrow frac vapor $= \frac{V_m - V_m^L}{V_m - V_m^V}$ (Derivation on Canvas)

(iii) Thermodynamic Tables (ex. steam tables \rightarrow Appendix B of Kotz et al.)

• Always use steam tables for water

• Linear interpolation required for conditions between values in the table

(iv) Equations of State

\rightarrow ideal gas law, $PV_m = RT$

\rightarrow van der Waals...

(v) Statistical Mechanics (molecular calculations)

\hookrightarrow not focused on in this course

Final Notes about (Potentially) 2-phase systems

- If $V \geq V_{i,c}^{sat}$ you have pure vapor
- If $V_{i,c}^{sat} > V > V_{i,l}^{sat}$ you have a mixed phase
- If $V_{i,l}^{sat} \geq V$ you have pure liquid

Similar ideas work for any specific (or master) property: v_m, u_m, h_m, \dots

Example A rigid 100L container w/ saturated water @ 100°C. If the initial reaches the critical point.

a) Draw the process on a P-v diagram.

initial (i)

$$V_i = 100L$$

$$T_i = 100^\circ C$$

saturated

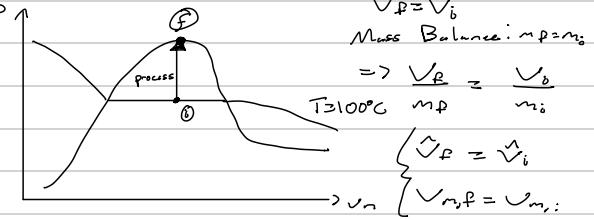
final (f)

$$V_f = 100L = V_i$$

$$T_f = T_c$$

$$P_f = P_c$$

process reaches
at critical point



b) Find the mass and initial quality.

(outcomes)

→ mass balance: $m_f = m_i$

rigid: $V_f = V_i = V$

$$\rightarrow V_f = V_i = V$$

Steam Tables

because P_c , T_c state is a crit point

$$V_p = V_i = V_c = 0.0033155 \frac{m^3}{kg}$$

$$V = 0.0033155 \frac{m^3}{kg}$$

bottom of tube

↳ of temp → $V_{i,g} = 0$

$$M = \frac{V}{V} = \frac{100 L}{0.0033155 \frac{m^3}{kg}} \times \frac{1000 L}{1000 L} = 316.6 \text{ kg}$$

(continued)

$$V_i = V_{i,L}^{sat} (1-x) + V_{i,V}^{sat} x$$

$$x = \frac{V_i - V_{i,L}^{sat}}{V_{i,V}^{sat} - V_{i,L}^{sat}} = 0.0015 \quad (\text{nearly all liquid})$$

S + Steam @ 100°C

$$V_{i,L}^{sat} = 0.001047 \frac{m^3}{kg}$$

$$V_{i,V}^{sat} = 1.4194 \frac{m^3}{kg}$$

$$\rightarrow V_{i,L}^{sat} < V < V_{i,V}^{sat} \Rightarrow L/V mix$$

Chapter 2 - The First Law of Thermodynamics

- First Law: $\Delta E_{\text{univ}} = 0$ or $E_{\text{univ}} = \text{constant}$

Q: What is E_{univ} ?

1) Macroscopic Kinetic Energy ($E_k = \frac{1}{2} m (v)^2$)

2) Macroscopic Potential Energy ($E_p = mg$)

3) Internal Energy (U_m): all energy at molecular level
 $\rightarrow U_m$ includes:

- molecular kinetic energy $\rightarrow T$

- molecular potential energy (attractions/repulsions between molecules)

o Changes in U_m come from:

First part of the class - changes in T, P , or other properties

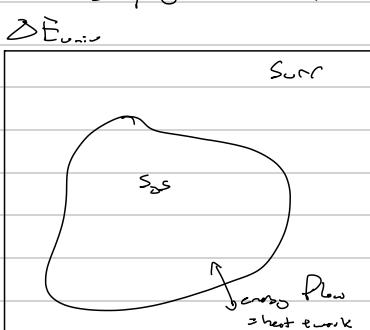
- phase changes

- chemical reactions (breaking/forming chemical bonds)

Note: An ideal gas by definition has no (0) potential energy between molecules

$U_m = U_m(T)$ only true for ideal gases

- We can simplify 1st Law (for closed systems):



$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}} = Q + W$$

heat
work

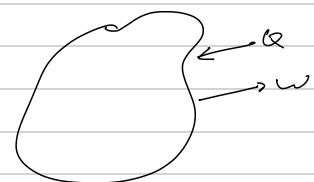
Q: Heat and work are flowing across the system boundary. What can we say about Q and W ?

1) both $Q & W > 0$

2) $Q > 0, W < 0$

3) $Q < 0, W > 0$

4) both $Q & W < 0$



Recall $\Delta E = \text{internal} + \text{kinetic} + \text{potential}$

$$\Delta E_{\text{sys}} = \Delta U + \Delta E_k + \Delta E_p$$

Leave off "sys" for convenience

so, exterior: $\Delta U + \Delta E_k + \Delta E_p = Q + W$ First Law for closed systems

interior: $\Delta U + \Delta E_{\text{int}} + \Delta E_{\text{p,int}} = Q + W$

And for small processes, $\Delta u \rightarrow du$

$$du + dE_{\text{int}} + dE_{\text{p,int}} = \delta Q + \delta W \leftarrow Q \text{ and } W \text{ are moment differentials for path functions}$$

Accumulation

How do we calculate variables in the first law?

Not currently focused on
 in this course → ECHE360

① Heat (Q): energy transferred across system boundaries by Temperature gradients (conduction, radiation, etc.)

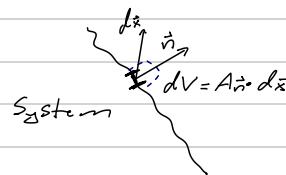
② Work (W): this class!

a) System boundary moves against an external force

$$\rightarrow \text{From physics, } W = \int_{\text{path}} \vec{F}_E \cdot d\vec{x}$$

where $\vec{F}_E = -P_E \vec{A}$

$$\text{so then, } W = - \int_{\text{path}} P_E \vec{A} \cdot d\vec{x} = - \int P_E dV \quad \text{"PV work"}$$



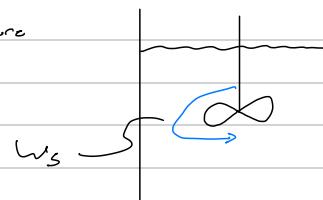
→ Calculating PV work requires us to know external pressure

* P_E does not always equal P_{ext}

b) Shaft Work (W_s)

example: propeller in fluid (macroscopic, not PV)

$$\therefore W = W_s - \int P_E dV$$



Work (and Heat) can be transferred either reversibly or irreversibly.

Reversible Processes - Characteristics & overview

- a) Slow → never more than differentially away from equilibrium
- b) Driven by small changes in forces (or pressures)
- c) Can be reversed at any point
- d) No friction or dissipation → highly idealized process

New
Rec'd
T_{ip} Brovo
21
7

Ex

Reversible work for ideal gas expansion under isothermal conditions.



- isothermal → T is constant
- ideal gas → $PV_m = RT$
- work → PV work → $W = - \int P_E dV$
- mole balance → $n = \text{constant}$ (closed sys)

• reversible → $P_E \approx P$

$$\text{Thus, } W = - \int P_E dV \stackrel{\text{rev.}}{\approx} - \int P dV \\ \stackrel{\text{IGL}}{=} - \int \frac{RT}{V_m} d(V_{m,f} - V_{m,i})$$

n is constant

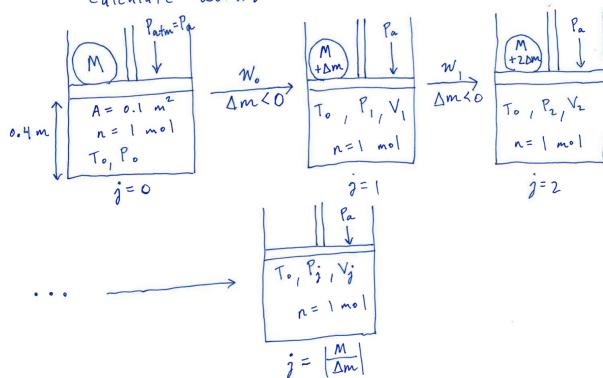
$$\frac{W}{n} = w_m = - RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

$$w_m = - RT_i \ln \left(\frac{V_{m,f}}{V_{m,i}} \right)$$

reversible work,
isothermal,
ideal gas

ex: ideal gas in a piston expands isothermally in increments of changes in external pressure.

calculate work.



• mole balance: $n = \text{const} = 1 \text{ mol}$

• final mass = 0

• ideal gas: $nRT_0 = P_0V_0 = P_1V_1 = P_2V_2 = \dots = P_jV_j$

• isothermal: $T = \text{const} = T_0$

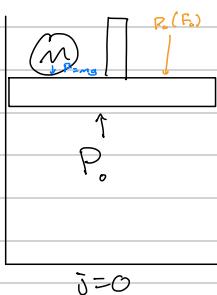
• PV work def'n → $W = - \int P_E dV$ external pressure

↳ what is P_E ?

• At eq. P_E should equal P_{eq}

• pressure / force balance:

Pressure / Force Balance



$$\text{initial } (j=0): A P_0 = A P_{E,0} \Rightarrow A \left(\frac{Mg}{A} + P_0 \right)$$

cross-section area of piston

$$\rightarrow P_0 = P_{atm} + \frac{Mg}{A}$$

$$\text{Similarly } (j=1): P_1 = P_{E,1} = \left(\frac{(M+\Delta m)g}{A} + P_0 \right)$$

$\Delta m < 0$ for this problem (given)

$$W_0 = - \int_{V_0}^{V_1} P_{E,1} dV = - P_1 \int_{V_0}^{V_1} dV = - P_1 (V_1 - V_0) = - P_1 \left(\frac{P_0 V_0}{P_1} - V_0 \right) = - V_0 (P_0 - P_1)$$

from $j=0$ to $j=1$

$P_{E,1} = P_1$

Subd. g.s.law

$P_1 V_1 = P_0 V_0$

$$\text{Now, sub } P's \text{ from force balance} = -V_0 \left[(P_0 + \frac{Mg}{A}) - (P_0 + \frac{Mg}{A} + \frac{\Delta mg}{A}) \right] = +V_0 \cdot \frac{\Delta mg}{A} < 0$$

negative indicates S_{down} class work

$$\text{Similarly, } W_1 = - P_{E,2} \Delta V = - P_2 (V_2 - V_1) = - P_2 V_2 \left(1 - \frac{V_1}{V_2} \right) = - P_0 V_0 \left(1 - \frac{V_1}{V_2} \right) = - P_0 V_0 \left(1 - \frac{P_2}{P_1} \right)$$

$(V_1 \text{ to } V_2)$

$$= - P_0 V_0 \left(\frac{P_1 - P_2}{P_1} \right)$$

$$\rightarrow \text{use force balance} = -V_0 \left(P_{atm} + \frac{Mg}{A} \right) \left(\frac{(-\Delta mg)}{P_0 + \frac{Mg}{A} + \frac{\Delta mg}{A}} \right)$$

P_0

$$\Rightarrow W_1 = \frac{V_0 \Delta mg}{A} \cdot \frac{P_0 + \frac{Mg}{A}}{P_0 + \frac{Mg}{A} + \frac{\Delta mg}{A}} < 0$$

Expansion $\rightarrow S_{downward}$

Example Continued

$$W_2 = -P_3(V_3 - V_2) = \frac{V_0 \Delta mg}{A} \frac{\frac{mg}{A}}{P_a + \frac{mg}{A} + \frac{\Delta mg}{A}} \text{ etc...}$$

(from $j=2$
to $j=3$)

so, total work done is:

$$W_{\text{tot}} = \sum_{j=0}^{j=1 \text{ to } j-1} W_j = \sum_{j=0}^{j=1 \text{ to } j-1} \left[\frac{V_0 \Delta mg}{A} \cdot \frac{\frac{mg}{A}}{P_a + \frac{mg}{A} + j \frac{\Delta mg}{A}} \right]$$

What happens w/ different $\Delta m's$? Suppose $M = 1020 \text{ kg}$

| Final State | $\Delta m (\text{kg})$ | $W_{\text{tot}} (\text{J})$ |
|-------------|------------------------|-----------------------------|
| $j=1$ | -1020 | -4000 |
| $j=2$ | -510 | -4666 |
| $j=3$ | -340 | -4928 |
| : | : | : |

Thermodynamic properties (i.e., path independent quantities) like T, P, V do not change between initial and final states between scenarios.

→ But work is not a thermodynamic property.
It is path dependent

As we increase the number of steps w/ smaller changes per step, magnitude of work done by the system on the surroundings increases

The Limit? $\lim_{\Delta m \rightarrow 0}$ = reversible process w/ max work done by system on surroundings

($P_E \approx P_{\text{sys}}$ for all steps j)

$$\text{Reversible: } W = - \int_{V_0}^{V_F} P_B dV = - \int_{V_0}^{V_F} P dV$$

$P_B = P$ for a reversible process
changes happening very slowly, so
 $P \approx P_E$ (small changes)

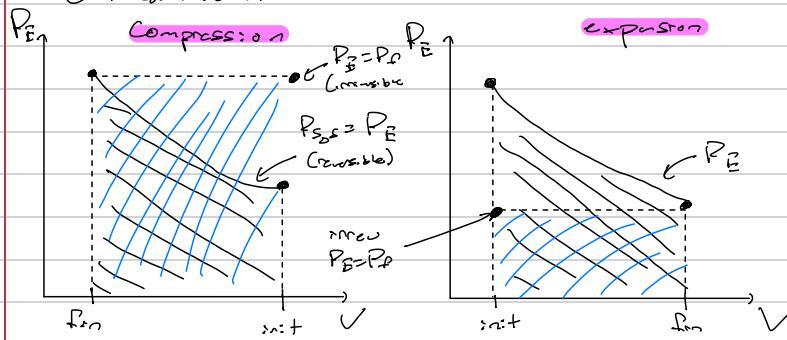
This is a reason why assuming a reversible process can be convenient. $W_{\text{re}} = -5545 \text{ J}$

We've shown that, for closed systems that undergo an isothermal reversible change in Volume, that:

$$W_{\text{isoth}} = -RT \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

→ If a process were reversible and $V_F < V_i$:

- ① $|W_{\text{min,rev}}| > |W_{\text{max,rev}}|$ This is compression $P_E > P$
- ② $|W_{\text{min,rev}}| < |W_{\text{max,rev}}|$ True for expansion
- ③ $|W_{\text{min,rev}}| = |W_{\text{max,rev}}|$
- ④ Need more information



$$|W_{\text{min,rev}}| > |W_{\text{max,rev}}| \quad |W_{\text{min,rev}}| < |W_{\text{max,rev}}|$$

$$W = - \int P_E dV$$

Internal Energy

• How do we calculate ΔU (dU)?

→ Several Options:

(i) Property tables (NIST, steam tables)

(ii) Specific (molar) heat capacities

a) Ideal Gas: $U_m = U_m(T)$ only (Combining of Temperature)
 $\rightarrow \text{Thus, } C_{v,m} = \frac{dU_m(T)}{dT}$ for ideal gas only

Typically correlations are used: $C_{v,m}(T) = A + BT + CT^2 + \frac{D}{T^2} + ET^3$ where $A-E$ are constants for the gas

Reminder: $C_{v,m} = \left(\frac{\partial U_m}{\partial T} \right)_{V_m} = \frac{dU_m(T)}{dT}$
 \uparrow constant volume
 \uparrow generally true
 \uparrow ideal gas only

Similarly,
 $C_{p,m} = \left(\frac{\partial h_m}{\partial T} \right)_P = \frac{dh_m(T)}{dT}$
 \uparrow constant pressure
 \uparrow generally true
 \uparrow ideal gas only

Enthalpy (h_m)

• Mathematically: $h_m = U_m + PV_m$ (general defn)

→ For ideal gas, $PV_m = RT$

$$\therefore h_m = U_m(T) + RT \Rightarrow h_m = h_m(T) \text{ only for an ideal gas}$$

Note that heat capacities are defined for a single phase.

How to Measure $C_{p,m}$

→ closed system, calorimeter, system @ const P

const P → $P_E = P$ (force balance)

1st Law: $dU_m = dq_m - Pdv_m$ ($P_E = P$)

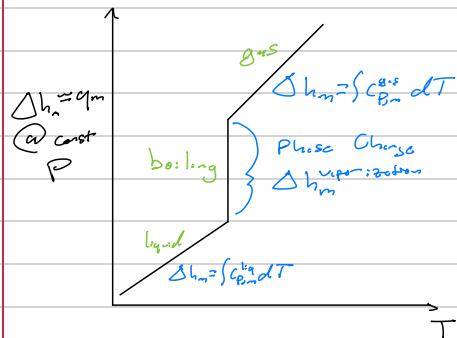
$dU_m = dq_m - d(PV_m)$ can make this more only bc Pressure P is constant

$$dU_m + d(PV_m) = dq_m$$

$$\underbrace{d(U_m + PV_m)}_{h_m} = dH_m = C_{p,m}dT = dq_m \quad \leftarrow \text{measure } q_m \text{ @ const } P$$

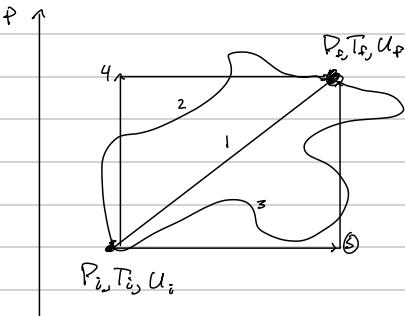
\leftarrow measure T to determine h_m & $C_{p,m}$

③ Latent Heat \equiv enthalpy (or internal energy) of a phase change



Calculation Paths

Used to calculate changes in thermodynamic properties as these do not depend on path ($T, P, V_m, U_m, h_m, \dots$)

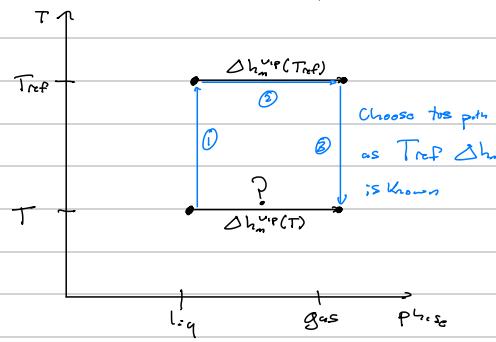


$$\Delta U = U_f - U_i$$

$$= \Delta U_1 = \Delta U_2 = \Delta U_3 = \Delta U_f$$

True for any process!

We can use calculation path to find $\Delta h_m^{vp}(T)$



* T_{ref} is usually 298K

Solution:

$$\Delta h_m^{vp}(T) = \Delta h_m^v + \Delta h_m^g + \Delta h_m^s$$

$$\textcircled{1} \text{ Sink phase heating/cooling } \Delta h_{m,1} = \int_{T_{ref}}^{T_f} C_{P,m}^{l,g} dT$$

$$\textcircled{2} \text{ Phase change @ } T_{ref}; \Delta h_{m,2} = \Delta h_m^{vp}(T_{ref})$$

$$\textcircled{3} \text{ Sink phase cooling/heating } \Delta h_{m,3} = \int_{T_{ref}}^T C_{P,m}^{s,s}(T) dT$$

$$\therefore \Delta h_m^{vp}(T) = \Delta h_m^{vp}(T_{ref}) + \int_{T_{ref}}^T [C_{P,m}^{s,s}(T) - C_{P,m}^{l,g}(T)] dT$$

Example 1st Law w/ Property Tables

A rigid container has sat'd water @ 2 bar and quality of $x=0.42$. The water is heated to 540°C. Find the final pressure and the $\Delta \hat{U}, \hat{q}$, and \dot{m} for the process.

| initial | final |
|--|---|
| $\text{Sat'd } H_2O$ $x = 0.42$ $P = 2 \text{ bar}$ V_i | $T_f = 540^\circ\text{C}$ $\xrightarrow{\text{Process: Closed System, Constant volume}}$ $V_f = V_i (\text{rigid})$ |

- initial state is sat'd water, $x = 0.42$
- rigid $\rightarrow V_f = V_i$, and $\dot{V}_f = \dot{V}_i = 0$
- closed system $\rightarrow m_i = m_f$ From mass balance
- water is heated $\rightarrow q \neq 0$
- $\dot{W}_s = 0$ no moving parts or mixing
- $\dot{W} = - \int_{V_i}^{V_f} P_B dV = 0$ (no volume change)
- $\rightarrow KE, PE / mg$ small and negligible

$$1^{\text{st}} \text{ Law: } \Delta \hat{U} = \hat{q} + \dot{W}$$

$$\Delta \hat{U}: \text{initial} \rightarrow \text{sat'd water @ } P_{s,t} = 2 \text{ bar (0.2 MPa)}$$

| | |
|--|---|
| $\text{Table B.2: } \begin{cases} \hat{u}_i = 504.47 \frac{\text{kJ}}{\text{kg}} \\ \hat{v}_i = 0.001061 \frac{\text{m}^3}{\text{kg}} \end{cases}$ | $\hat{u}_f = 2529.5 \frac{\text{kJ}}{\text{kg}}$ $\hat{v}_f = 0.8857 \frac{\text{m}^3}{\text{kg}}$ |
|--|---|

$$\text{Recall: } \hat{u}_i = x \hat{u}_w + (1-x) \hat{u}_l$$

\uparrow
orange

$$\hat{v}_i = x \hat{v}_w + (1-x) \hat{v}_l$$

$$\Rightarrow \begin{cases} \hat{u}_i = 1385 \frac{\text{kJ}}{\text{kg}} \\ \hat{v}_i = 0.373 \frac{\text{m}^3}{\text{kg}} \end{cases}$$

$$\text{Final: Known } T_f = 540^\circ\text{C}, V_f = 0.373 \frac{\text{m}^3}{\text{kg}} \text{ (rigid)}$$

Table B.2 shows $T_f > T_c \rightarrow$ superheated steam

- Interpolate superheated water vapor tables (B4)
 $\rightarrow P_s = 10 \text{ bar (1 MPa)}$

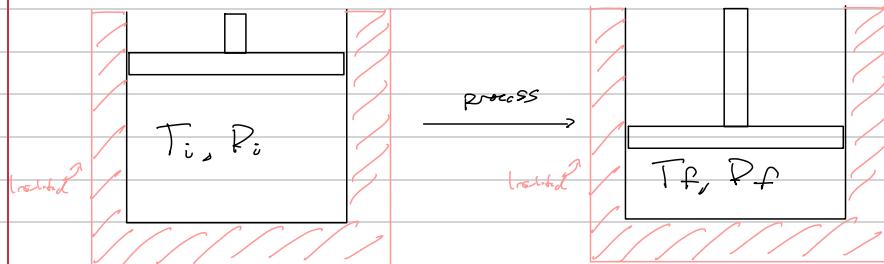
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

$$1^{\text{st}} \text{ Law: } \Delta \hat{U} = \hat{q}$$

$$\Delta \hat{U} = \hat{u}_f - \hat{u}_i = 1839 \frac{\text{kJ}}{\text{kg}}$$

| |
|---|
| $P_f = 10 \text{ bar}$ |
| $\Delta \hat{U} = \hat{q} = 1839 \frac{\text{kJ}}{\text{kg}}$ |
| $\dot{m} = 0$ |

Example: Reversible adiabatic expansion/compression of an ideal gas with $C_{v,m} = \text{constant}$.
Relate P_i, P_f, V_i, V_f



- closed, mass/mol fixed: $nF = n$
- 1st Law: $dU = \delta Q + \delta W$
- ideal gas $\nabla C_{v,m}dT$
- $P_B dV$ (defn of P_{bulk})

Reversible
 $P_B = P$

$$\rightarrow n C_{v,m} dT = -P_B dV$$

$$n C_{v,m} dT = -P dV$$

$$\rightarrow n C_{v,m} dT = -\frac{n RT}{V} dV$$

$$\int_{T_0}^{T_f} \frac{C_{v,m}}{T} dT = \int_{V_i}^{V_f} -\frac{R}{V} dV$$

$$\rightarrow \text{If } C_{v,m} = \text{const} \Rightarrow C_{v,m} \ln\left(\frac{T_f}{T_i}\right) = -R \ln\left(\frac{V_f}{V_i}\right)$$

$$\text{take exp: } \left(\frac{T_f}{T_i}\right)^{C_{v,m}} = \left(\frac{V_f}{V_i}\right)^{-R}$$

$$\Rightarrow C_{p,m} = C_{v,m} + R \quad (\text{notes to follow})$$

$$P_f V_f^{\frac{C_{p,m}}{C_{v,m}}} = P_i V_i^{\frac{C_{p,m}}{C_{v,m}}}$$

ideal gas, constant $C_{v,m}$, reversible
and adiabatic

Final Notes on Ideal Gas Heat Capacities

$$\Delta h_m = \int_{h_{m,1}}^{h_{m,2}} dh_m = \int_{T_1}^{T_2} C_{p,m} dT \quad (\text{always true for ideal gas})$$

$$\text{Because } h_m \equiv U_m + PV_m = U_m + RT$$

$$\frac{dh_m}{dT} = \frac{dU_m}{dT} + R$$

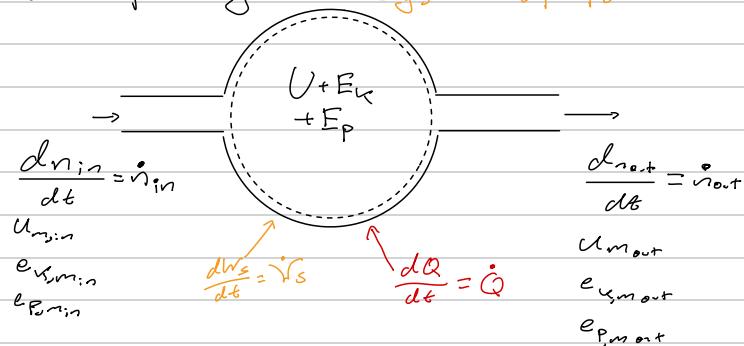


$$C_{p,m} = C_{v,m} + R$$

↑ function of T
only
↑ function of
T only

(for ideal gas)

Skip §2.8.2.1 1st Law Open Systems e.g. turbines, pumps, reactors...



* Important Calculus Note:

$$\dot{\nu}_{in} = \frac{d\dot{m}_{in}}{dt} \neq \dot{m}_{in}$$

discrete ↑ differential ↑

Form of PV Work?

→ Flow Work

Rate of flow work:

$$\frac{dW_{flow}}{dt} = \dot{W}_{flow} = -P_E \frac{dV_{in}}{dt}$$

$$= -P_{in} \frac{d(V_{in} m_{in})}{dt} = -P_{in} \frac{d(m_{in} V_{in})}{dt}$$

$$= P_{in} \frac{d(m_{in} V_{in})}{dt} = P_{in} V_{in} \frac{d\dot{m}_{in}}{dt} = P_{in} V_{in} \dot{\nu}_{in} = \dot{W}_{flow} \therefore \text{molar rate} = \frac{d\dot{m}_{in}}{dt} = (P_{in} V_{in})_{in}$$

= flow work per mole

→ $P > 0, V_m > 0$, so flow work $\dot{W}_{flow} > 0$ always

⇒ Add flow work to energy balance

$$\frac{d}{dt} (U + E_k + E_p) = \dot{Q} + \dot{W}_s + \dot{\nu}_{in} (U_{in} + e_{kin,in} + e_{pot,in}) + \dot{\nu}_{in} (P_{in} V_{in})_{in}$$

accumulation

$$- \dot{\nu}_{out} (U_{out} + e_{kin,out} + e_{pot,out}) - \dot{\nu}_{out} (P_{out} V_{out})_{out}$$

$$\text{Result: } h_m \equiv U_m + P_m$$

$$\frac{d}{dt} (U + E_k + E_p) = \dot{Q} + \dot{W}_s + \dot{\nu}_{in} (h_m + e_{kin,in} + e_{pot,in}) - \dot{\nu}_{out} (h_m + e_{kin,out} + e_{pot,out})$$

First Law, Open Systems

Can also write on a mass basis:

IF open system is at steady-state

- no mass/moles accumulating in sys
- mass balance, $\frac{d\dot{m}}{dt} = 0 = \dot{\nu}_{in} - \dot{\nu}_{out} \Rightarrow \dot{\nu}_{in} = \dot{\nu}_{out} = \dot{\nu}$

- no change in energy of system

$$\frac{d}{dt} (U + E_k + E_p) = 0$$

- no change in properties with time

IF NOT steady-state

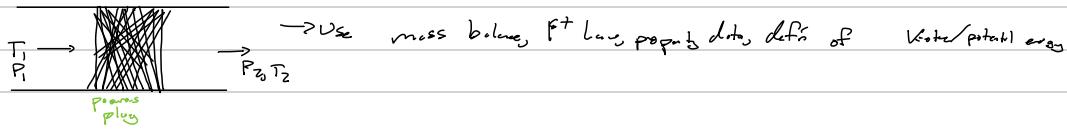
$$\rightarrow \text{mole balance: } \frac{d\dot{m}}{dt} = \dot{\nu}_{in} - \dot{\nu}_{out}$$

- Total mass/mole accumulation:

$$\Delta \dot{m} = \dot{m}_{in} - \dot{m}_{out} = \int_{t_0}^{t_1} d\dot{m}$$

Example 6: Throttling Process

- Simple obstruction to reduce pressure in a pipe (constant-insulated)



Steady state: $\frac{d}{dt}(u + E_k + E_p) = 0; \frac{du}{dt} = 0 \quad \dot{m}_{in} = \dot{m}_{out} = \dot{m}$

$\dot{m}_s = 0$ (no moving parts)

$\dot{Q} = 0$ (well-insulated)

$e_{v,m} \approx 0$ (smaller than c_s) ← good approximation if velocity is much lower than the speed of sound

$e_{p,m} = 0$ (no height difference)

does change but the change is negligible with respect to other quantities

→ Simplified F+ Law

$O = \dot{m}_{in} h_{m,in} - \dot{m}_{out} h_{m,out}$

so

$$\boxed{O = h_{m,in} - h_{m,out}}$$

$$\boxed{O = \hat{h}_{in} - \hat{h}_{out}}$$

Mole Balance ($\dot{m}_{in} = \dot{m}_{out}$)

mole basis } independent of T_2
mass basis }

a) Let's assume fluid is water:

$T_1 = 350^\circ C$

$P_1 = 10 \text{ MPa}$

→ $T_2 ?$
 $P_2 = 1 \text{ bar}$

Find T_2 !

$\hat{h}_1 = \hat{h}(350^\circ C, 10 \text{ MPa}) = 2923.4 \frac{\text{kJ}}{\text{kg}}$
by law $\hat{h}_2 = \hat{h}_1$ since $\Delta \hat{h} = 0$

Find T when $\hat{h}_2 = 2923.4 \frac{\text{kJ}}{\text{kg}}$ at $P_2 = 1 \text{ bar} = 0.1 \text{ MPa}$

→ At 1 bar, $\hat{h}(200^\circ C) = 2875.3 \frac{\text{kJ}}{\text{kg}}$
 $\hat{h}(250^\circ C) = 2974.3 \frac{\text{kJ}}{\text{kg}}$

$\frac{(2974.3 - 2875.3)}{250 - 200} (T_2 - 200) + 2875.3 = 2923.4$

→ $\boxed{T_2 = 224.293^\circ C}$

b) What will happen if fluid is ideal gas?

1) $T_2 < T_1$

3) $T_2 = T_1$

2) $T_2 > T_1$

4) real more $\Rightarrow T_2$

Why?

→ Still: $h_{m,2} - h_{m,1} = 0$ (same first law)

$\Delta h_m = 0$

$\Delta h_m = \int_{T_1}^{T_2} dh_m = 0$ (choose prop. is constant of diff. m.)

→ Ideal G.s.: $h_m = h_m(T)$ only

$dh_m = C_{pm} dT$ For ideal g.s.

$\Delta h_m = \int_{T_1}^{T_2} C_{pm} dT = 0$

$\rightarrow C_{pm}(T_2 - T_1) = 0 \Rightarrow T_2 = T_1 = 350^\circ C$ also true if $C_{pm} = C_{pm}(T)$ [i.e., not constant]

Note: Compare H_2O + ideal gas case of throttle

- ideal gas: $h_m = h_m(T)$ only

$$dh_m = C_p dT$$

- water (real fluid): $\hat{h}_m \neq h_m(T)$ only

$$\text{So } \hat{h}_m = \hat{h}_m + b + T_2 - T_1$$

Q: What is the significance of enthalpy \hat{h}_m , the first law for open systems?

1) A more fundamental molecular quantity for flow systems

2) Sum of internal energy + flow work between system & surroundings

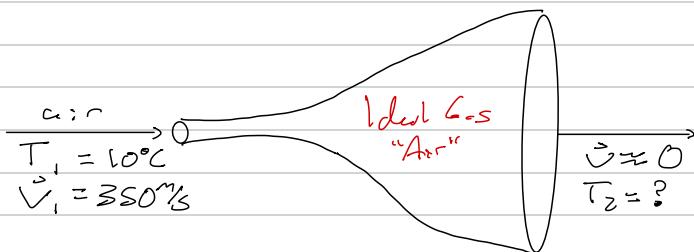
3) Flows in open systems have enthalpy \hat{h}_m , but not internal energy. Of course they have internal energy!

4) Amount of heat transferred at constant pressure

5) All of the above will do! closed systems

Ex: Nozzle or Diffuser

→ These relates to accelerate (or slow) flow streams



Process occurs @ constant pressure, $P_2 = P_1$

• Open system

• Steady state? yes!

$$\rightarrow \text{MB: } \frac{dm}{dt} = 0 = m_{in} - m_{out} \rightarrow m_{in} = m_{out}$$

• 1st Law, accumulations = 0:

$$\frac{d}{dt}(u + E_k + E_p) = 0$$

• $\dot{W}_s = 0$ no moving parts, assume adiabatic $\dot{Q} = 0$

$$\cdot e_{p,m,in} \approx e_{p,m,out} \approx 0$$

$$\cdot e_{k,m,out} = \frac{1}{2} m v_{out}^2 = \frac{1}{2} m (0)^2 = 0, e_{k,m,in} \approx 0$$

$$\cdot \text{Simpl. form 1st Law: } \hat{h}_2 = \hat{h}_1 + \hat{e}_{k,v_1} \quad \begin{matrix} \text{Solving on a mass basis is bc of} \\ \text{Variable energy} \end{matrix}$$

$$\rightarrow \hat{E}_{k,v_1} = \frac{1}{2} m |\vec{v}_1|^2$$

$$\hat{e}_{k,v_1} = \frac{1}{2} |\vec{v}_1|^2 = \frac{1}{2} (350 \frac{\text{m}}{\text{s}})^2 \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 61.25 \frac{\text{kJ}}{\text{kg}}$$

$$1^{\text{st}} \text{ Law} \rightarrow \hat{h}_2 - \hat{h}_1 = \hat{e}_{k,v_1}$$

$$\Delta \hat{h} = \int_{in}^{out} d\hat{h}_m = \int_{in}^{out} \hat{C}_p dT = \int_{T_1}^{T_2} \hat{C}_p dT$$

ideal g.s.

"Air": assuming ideal gas

$$\rightarrow \text{From Korets } K_{20} \hat{C}_{p,m} \approx 3.355 \text{ kJ/kgK}$$

$$\text{constant } C_p \quad \frac{K}{2.053} \hat{C}_p = \frac{C_p}{M w_{air}} \leftarrow (-28 \times 10^{-3} \text{ kJ/mol})$$

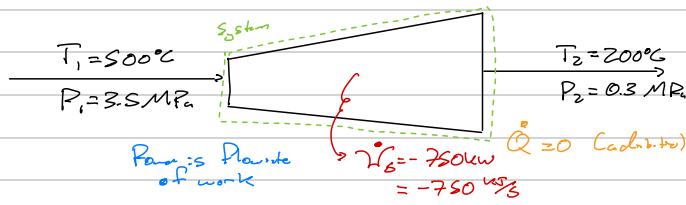
$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,v_1} \rightarrow T_2 = \frac{\hat{e}_{k,v_1}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ\text{C}$$

*Note: could be more accurate w/ T-dependent $\hat{C}_p(T)$

: (macroscopic) kinetic energy "contributes" to T (macroscopic)

Example: Turbo extracts work (power) from gas.

Adiabatic turbine: input steam @ $T_1 = 500^\circ\text{C}$, $P_1 = 3.5 \text{ MPa}$ expanded to $T_2 = 200^\circ\text{C}$ and $P_2 = 0.3 \text{ MPa}$. Turbine generates 750 kW of power. What is the required mass flow rate of steam?



- Open system
- Steady-state? Yes!
- Mass balance?

$$\frac{dm}{dt} = 0 = \dot{m}_{in} - \dot{m}_{out} \Leftrightarrow \dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

• 1st Law: $\frac{d}{dt} (U + E_k + E_p) = 0$ (steady-state)

$$\Delta \dot{E}_p \approx 0$$

$$\Delta \dot{E}_k \approx 0$$

1st Law $\rightarrow \dot{Q} = \dot{m}_{in} h_{in} - \dot{m}_{out} h_{out} + \dot{W}_s$

MB $\rightarrow \dot{Q} = \dot{m}(h_{in} - h_{out}) + \dot{W}_s$

$$\dot{m} = \frac{\dot{W}_s}{h_{out} - h_{in}}$$

steam tables

Superheated steam tables (guts h_{in} , h_{out})

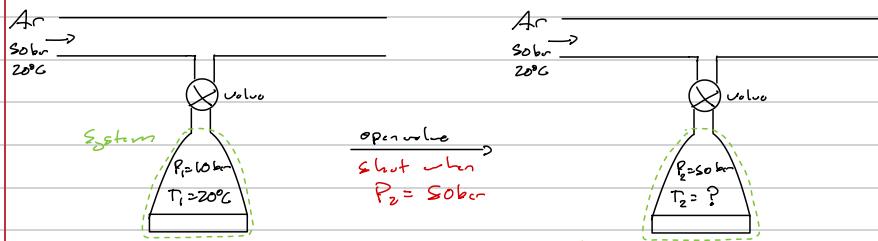
$$\dot{m} = \frac{-750 \text{ kW}}{2865.9 - 3451 \frac{\text{kJ}}{\text{kg}}} = 1.28 \frac{\text{kg}}{\text{s}}$$

How to find V ?

$V = \dot{m} V_{in}$ we like to control inlet conditions
so use V_{in} to convert!

Konstanty Problem 2.47

Argon gas, $C_{p,m} \approx \frac{5}{2}$ ($C_{p,m} = \frac{5}{2} R$). MW = 40 kg/kmol, treat as an ideal gas



a) T_2 right after valve is closed? ($\dot{Q} \approx 0$)

• Open system \rightarrow define system as tank

• Steady-state? No! transient

• Mass balance?

$$\frac{dn}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

gas only flows into tank

• 1st Law open system

$$\frac{dU}{dt} = \dot{m}_{in}(h_{in} + e_{kin} + e_{pot}) - \dot{m}_{out}(h_{out} + e_{kin} + e_{pot}) + \dot{W}_s$$

ignores PE

no mass出入

$$\frac{dU}{dt} = \dot{m}_{in} h_{min} - \dot{m}_{out} h_{max} \quad \text{MB}$$

assumption

$$\int_{U_1}^{U_2} dU = \int_{h_{min}}^{h_{max}} \dot{m}_{in} dh$$

Gas inside tank

$$h_{min} = h_m(\text{Ar}, 20^\circ\text{C})$$

$$\rightarrow U_2 - U_1 = h_{min}(n_2 - n_1) \quad \left. \begin{array}{l} \text{mols & } T \text{ change + same } \\ \text{extensive } \Delta U \text{ for sys(tank)} \end{array} \right\} \text{constant } T \text{ for Ar!}$$

$$n_2 U_{m2} - n_1 U_{m1} = h_{min}(n_2 - n_1)$$

$$\rightarrow n_1(h_{m1} - U_{m1}) = n_2(h_{m2} - U_{m2})$$

$$\text{defn: } h_m = U_m + P_m \rightarrow h_{m1} = U_{m1} + RT_1$$

$$h_m = U_m + RT \quad (\text{for ideal gas})$$

$$\rightarrow n_1[(h_{m1} - U_{m1}) + RT_1] = n_2[(h_{m2} - U_{m2}) + RT_2]$$

$$\text{Ideal g.s.: } \Delta h_m = \int_{T_1}^{T_2} C_{p,m} dT = 0 \quad \Delta h_m = \int_{T_1}^{T_2} C_{p,m} dT$$

bc $T_1 = T_2$

$$\begin{aligned} n_1 RT_1 &= n_2 RT_2 + n_2 C_{p,m} \int_{T_2}^{T_1} dT \\ n_1 RT_1 &= n_2 RT_2 + n_2 C_{p,m} (T_1 - T_2) \\ n_2 T_2 &\text{ unknown (1 eq, 2 unknowns)} \\ \text{but } V_2 &= V_1 \quad (\text{rigid tank}) \end{aligned}$$

$$\frac{n_2 RT_2}{P_2} = \frac{n_1 RT_1}{P_1} \rightarrow n_2^2 = \left(\frac{n_1 T_1}{P_1} \right) \left(\frac{P_2}{T_2} \right)$$

* not given n_1 , but it cancels out

$$\rightarrow \text{sub } n_2 \rightarrow \boxed{T_2 = \frac{\frac{S_2}{2} T_1}{\frac{P_2}{P_1} + \frac{3}{2}}} = 187.9^\circ\text{C}$$

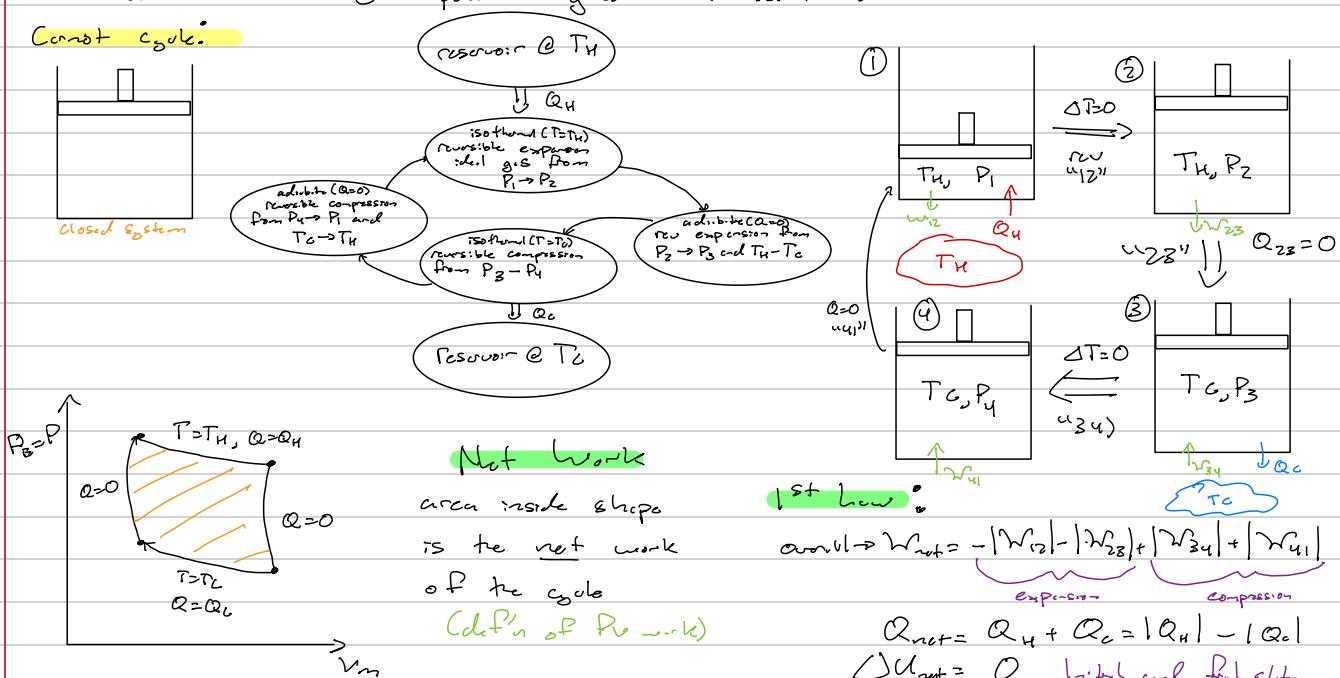
$$(C_{p,m} = \frac{5}{2} R)$$

Chapter 3 - Entropy and the Second Law

Recall: Any thermodynamic property (T, P, V, s, u, h, \dots) is independent of path
 → If we find a new property (S) that is also independent of path, it must also be a
 thermodynamic property.
 → ΔS for a cycle (same initial/ final state) is zero.

Consider a Carnot cycle (Ch 2 § 2.9): ideal g.s. reversible process
 → Practical use: Converts temperature gradient to useful work

Carnot cycle:



Process 12: Isothermal ($T=T_H$)

$$\begin{aligned} \text{1st Law: } \Delta U_{12} &= Q_{12} + W_{12} & W_{12} &= -Q_{12} \\ \Delta U_{12} &= n \int_{P_1}^{P_2} C_v dT \Rightarrow T_1 = T_2 = T_H \text{ so } \Delta U_{12} = 0 \\ W_{12} &= nRT_H \ln \left(\frac{P_2}{P_1} \right) < 0 & \text{expansion} \\ Q_{12} &= Q_H = -W_{12} = -nRT_H \ln \left(\frac{P_2}{P_1} \right) \end{aligned}$$

$$\begin{aligned} W_{12} &= - \int P_2 dV = -n \int P_2 dV \\ \text{reverse} &= -n \int P_2 dV \\ &= -n \int \frac{RT_H}{V} dV \\ &= -n \int_{V_{12}}^{V_{23}} \frac{RT_H}{V} dV \\ \Rightarrow W_{12} &= -nRT_H \ln \left(\frac{V_{23}}{V_{12}} \right) \end{aligned}$$

Process 23: Adiabatic ($Q_{23}=0$)

$$\begin{aligned} \text{adiabatic, reversible, constant } C_p, m \\ \rightarrow PV^k &= \text{constant} \end{aligned}$$

$$W_{23} = - \int P dV = - \int \frac{P_2 V_2^k}{V^k} dV \quad \text{Too many unknowns:}$$

$$\begin{aligned} \rightarrow \text{solve } P_3 \text{ and } R \text{ in terms of } P_1, P_2 & \quad \text{Substitute} \\ "23" \text{ is adiabatic} & \rightarrow P_2 V_2^k = P_3 V_3^k \\ "41" \text{ is adiabatic} & \rightarrow P_4 V_4^k = P_1 V_1^k \end{aligned}$$

To Summary

$$W_{12} = nRT_H \ln \left(\frac{P_2}{P_1} \right), \quad Q_{12} = Q_H = -nRT_H \ln \left(\frac{P_2}{P_1} \right)$$

* Ideal g.s. constant C_p, m , reversible

$$W_{23} = \frac{nR}{k-1} (T_H - T_C), \quad Q_{23} = 0$$

$$W_{34} = -nRT_C \ln \left(\frac{P_2}{P_1} \right), \quad Q_{34} = Q_C = -nRT_C \ln \left(\frac{P_2}{P_1} \right)$$

$$W_{41} = \frac{nR}{k-1} (T_C - T_H), \quad Q_{41} = 0$$

Discuss Overall Cycle

$$\textcircled{1} \quad \eta = \text{Carnot efficiency} = \frac{W_{\text{out}}}{Q_H} = \frac{\cancel{W_{\text{out}}}}{\cancel{Q_H} \cancel{\text{heat added}}} = \frac{T_H - T_C}{T_H} \quad (\text{all rev})$$

$\rightarrow \eta$ is never 1. Heat is never converted entirely to work, so not all processes are reversible!

$$\textcircled{2} \quad \text{Consider: } \sum_{\text{cycle}} \frac{Q}{T} = \frac{Q_{12}}{T_H} + \frac{Q_{23}}{T} + \frac{Q_{34}}{T_C} + \frac{Q_{41}}{T}$$

$$= \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -nR \ln\left(\frac{P_2}{P_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right) \quad \text{Thus, } \sum_{\text{cycle}} \frac{Q}{T} = 0 \quad \text{for a full cycle}$$

idea: $\frac{Q}{T}$ is a thermodynamic property! Call this entropy (S).

$$\Delta S = \frac{Q_{\text{rev}}}{T} \quad \text{or} \quad dS = \frac{dQ_{\text{rev}}}{T}$$

Would calculate absolute function (S) from path function (Q).

Entropy

\rightarrow words associated with entropy?

- randomness
- disorder
- chaos
- number of states

Related to molecular probability and statistics

\rightarrow associated w/ # of molecular configurations a system can adopt

Q: Arrange the following : terms of the magnitude of their entropy, S_m .

- 1) solid \Rightarrow liquid \Rightarrow gas
- 2) $\text{gas} \Rightarrow \text{liquid} \Rightarrow \text{solid}$
- 3) solid \Rightarrow liquid \Rightarrow gas
- 4) need more info

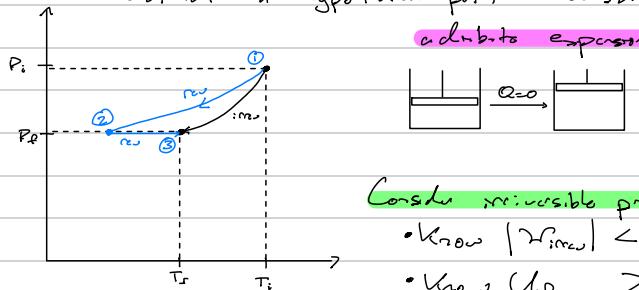
Q: Which process has the most positive change of the fluid P ΔS_m ?

- 1) evaporate $\text{H}_2\text{O(l)} \rightarrow \text{gas}$ $\Delta S_m > 0$
- 2) condense $\text{H}_2\text{O(g)} \rightarrow \text{liquid}$ $\Delta S_m < 0$
- 3) cool $\text{H}_2\text{O(g)}$ by 100°C $\Delta S_m < 0$
- 4) heat $\text{H}_2\text{O(l)}$ by 100°C $\Delta S_m > 0$

Carnot Cycle $\rightarrow \Delta S_{\text{cycle}} = 0$ for reversible processes

\rightarrow How about calculating ΔS for irreversible processes

- Construct a hypothetical path consisting of only reversible processes



Process '12'

$$\begin{aligned} &\text{reversible adiabatic expansion} \\ &1^{\text{st Law: }} \Delta U_{12} = Q_{12, \text{rev}} + W_{12, \text{rev}} \\ &\Delta S_{12} = \int \frac{dQ_{\text{rev}}}{T} = 0 \end{aligned}$$

Consider irreversible process (1 \rightarrow 3)

- Know $|W_{12, \text{rev}}| < |W_{12, \text{irr}}|$ For expansion (H_2O)
- Know $U_{12, \text{rev}} > U_{12, \text{irr}}$
- Since S is a state function,

$$\Delta S_{13} = \Delta S_{12} + \Delta S_{23} \quad \begin{matrix} \text{(defining this to} \\ \text{be a reversible} \\ \text{process at constant Pressure)} \end{matrix}$$

(not adiabatic)

$$\Delta S_{23} = \int_{T_2}^{T_3} \frac{dQ_{\text{rev}}}{T}$$

$$1^{\text{st Law: }} dU = dQ + PdV$$

$$dQ = dU - PdV$$

$$dQ = dU + PdV$$

$$dQ = dU + d(PV)$$

$$dQ = d(U + PV)$$

$$dQ = dH$$

Specific to adiabatic expansion: Increase in entropy S for system for irreversible processes.

$$\Delta S_{13} > 0$$

II
reversible & irreversible processes have very different entropy changes!

How to get from
SR to others
but!
SR to others

$$\Rightarrow \Delta S_{23} = \int_{T_2}^{T_3} \frac{dU_{\text{irr}}}{T} = \int_{T_2}^{T_3} \frac{C_{p,m}}{T} dT > 0$$

($T_3 > T_2$)
($U_3 > U_2$)

$$\Delta S_{13} = \Delta S_{12} + \Delta S_{23} > 0 \quad \text{increase in system } S \text{ for irreversible processes}$$

ΔS for Surroundings

$$\delta S_{\text{surroundings}} = \frac{\delta Q_{\text{surv}}}{T_{\text{sur}}} \quad \text{real heat transfer to the surroundings}$$

To calculate δS_{surv} , we can use the real heat transfer to the surroundings (does not have to be reversible) why? Surroundings are large \rightarrow constant T_{sur}

$$\delta Q_{\text{surv}} = -\delta Q \quad \begin{matrix} \text{real heat} \\ \text{transfer} \\ \text{to surv} \end{matrix}$$

From perspective of surroundings, my change in S_{surv} is tiny
∴ always seems like reversible δQ_{surv}

In our previous example...

$$\delta S_{\text{surv}} = \frac{\delta Q_{\text{surv}}}{T_{\text{sur}}} = -\frac{\delta Q}{T_{\text{sur}}} = 0 \quad \text{because process is adiabatic}$$

ΔS_{surv} is also 0 for adiabatic processes.

$$\Delta S_{13} > 0, \Delta S_{\text{surv}} = 0 \quad ; \text{missed}$$

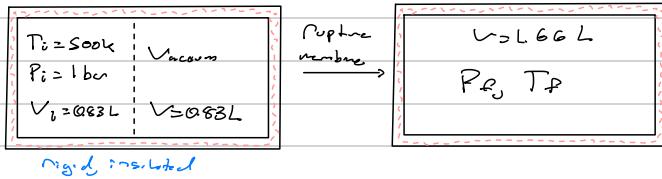
$$\Delta S_{12} = 0, \Delta S_{\text{surv}} = 0 \quad \text{reversible}$$

Conclusion: $\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surv}}$

$$\rightarrow \boxed{\Delta S_{\text{univ}} > 0 : \text{missed}} \quad \text{True for } \xrightarrow{\text{process}}$$

↑ Second Law of Thermodynamics

Example: Ideal gas Closed Sys



Final T_f

closed system: $n_i = n_f = n$

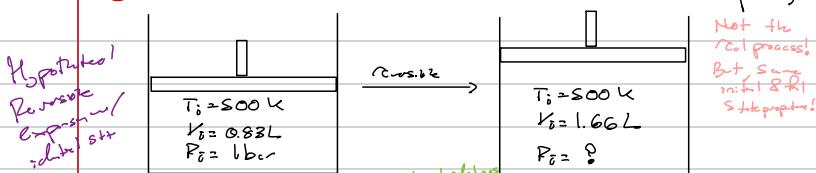
• rupture → not reversible due to sudden expansion

• 1st Law: $\Delta U = Q + W \xrightarrow{\text{adiabatic}} \text{no } Q, \text{ no } W \rightarrow \Delta U = 0$ (constant volume system)

$$\Delta U_{\text{int}} = 0 = \int_{T_i}^{T_f} C_v \, dT \rightarrow T_i = T_f = 500 \text{ K}$$

What about ΔS ?

→ use a convenient reversible calculation path! (ΔS is a state function / thermodynamic property)
must define a reversible calculation path, $\delta S = \frac{\delta Q_{\text{rev}}}{T}$



$$\Rightarrow \Delta S_{\text{calc}} = \Delta S_{\text{actual}}$$

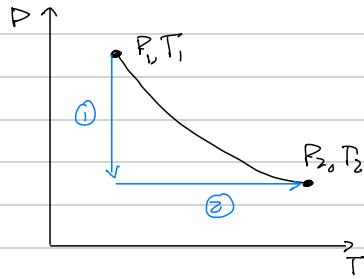
$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = \int \frac{dU_{\text{rev}} - dW_{\text{rev}}}{T} = - \int \frac{dW_{\text{rev}}}{T} = - \int \frac{-P_{\text{ext}} dV}{T} = \int \frac{P_{\text{ext}} dV}{T} \xrightarrow{\text{reversible}} n \int_{V_i}^{V_f} \frac{P}{V} dV = n R \ln \left(\frac{V_f}{V_i} \right)$$

$$\rightarrow \Delta S_m = \frac{\Delta S}{n} = R \ln \left(\frac{V_f}{V_i} \right) = +5.76 \text{ J/K mol}$$

$$\text{Surroundings: } \delta S_{\text{surv}} = \frac{\delta Q_{\text{surv}}}{T_{\text{sur}}} = -\frac{\delta Q_{\text{rev}}}{T_{\text{sur}}} = 0 \quad \text{adiabatic}$$

$$\therefore \Delta S_{\text{univ}} = \Delta S_m + \Delta S_{\text{surv}} = +5.76 \text{ J/K} > 0 \quad \checkmark \text{ consistent w/ second law}$$

Entropy changes for ideal G.S.



"T cycle": hypothetical, reversible paths to get $\Delta S_{m,sys}$

Process ①: reversible, isothermal (ideal g.s.)

$$\Delta S_1 = \int \frac{S Q_{rev}}{T} = \int_{\text{const } P} \frac{dU_{rev} - SW_{rev}}{T} = \int \frac{P}{T} dV \quad (\text{lost } c_v)$$

$$\therefore \Delta S_1 = nR \ln\left(\frac{V_2}{V_1}\right) = -nR \ln\left(\frac{P_2}{P_1}\right)$$

Process ②: reversible, const P ($c_v + c_p$)

$$S Q_{rev} = dU_{rev} + P dV = d(C_u + PV) = dH$$

$$\Delta S_2 = \int \frac{S Q_{rev}}{T} = \int \frac{dH}{T} = n \int \frac{C_p dT}{T}$$

$$\text{If } C_{p,m} \text{ is const: } \Delta S_2 = n C_{p,m} \ln\left(\frac{T_2}{T_1}\right)$$

$$\Rightarrow \Delta S = n C_{p,m} \ln\left(\frac{T_2}{T_1}\right) - n R \ln\left(\frac{P_2}{P_1}\right) \quad \text{if } C_{p,m} \text{ is constant}$$

$$\text{general: } dS_m = \frac{C_{p,m}}{T} dT - \frac{R}{P} dP$$

ideal gas
entropy change

Q: For which quantities is it possible to calculate changes using an arbitrary hypothetical calculation path?

- 1) Q ← path function, property
- 2) U } Thermodynamic property
- 3) S }
- 4) W ← path function

Q: How do we calculate ΔS_{univ} for any process?

- ① ΔS_m from reversible, hypothetical path; $\Delta S_{m,sum}$ from real heat → See previous example
- ② ΔS_m from real heat; $\Delta S_{m,sum}$ from real heat
- ③ ΔS_m from reversible path; $\Delta S_{m,sum}$ from real heat
- ④ ΔS_m from real heat; $\Delta S_{m,sum}$ from real heat

Example: 1 mol liquid H₂O @ P=1 bar. T increases from 28°C to 50°C. Calculate ΔS , ΔS_{sum}

ΔS_{univ} at $T_{sum} = 700^\circ\text{C}$ and 100°C.

• Develop an expression for ΔS

→ system: rev calc path (constant P)

$$\Delta S = \int dS = n \int \frac{S Q_{rev}}{T} = n \int \frac{dH}{T} = n \int_{T_i}^{T_f} \frac{C_{p,m}}{T} dT$$

(lost)
const P

$$C_{p,m} = 25.4 \frac{\text{J}}{\text{molK}} \approx \text{constant} \rightarrow \Delta S = n C_{p,m} \ln\left(\frac{T_f}{T_i}\right) = 6.07 \frac{\text{J}}{\text{K}}$$

• ΔS_{sum} : use real heat transfer

$$\Delta S_{sum} = \int \frac{S Q_{real,sum}}{T_{sum}} = \frac{Q_{real,sum}}{T_{sum}} = -\frac{Q}{T_{sum}}$$

$$\rightarrow Q = \int S Q = \int dH = n \int_{T_i}^{T_f} C_{p,m} dT = (1\text{ mol})(25.4 \frac{\text{J}}{\text{molK}})(25\text{ K}) \quad [=] \text{ J}$$

$$\therefore T_{sum} = 700^\circ\text{C} \therefore \Delta S_{sum} = -\frac{25.4 \times 25}{700 + 273} = -1.44 \frac{\text{J}}{\text{K}}$$

$$T_{sum} = 100^\circ\text{C} \therefore \Delta S_{sum} = -\frac{25.4 \times 25}{100 + 273} = -5.05 \frac{\text{J}}{\text{K}}$$

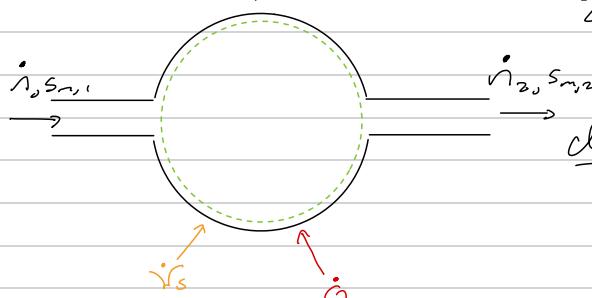
$$T_{sum} \mid \Delta S_{univ} = \Delta S + \Delta S_{sum}$$

$$700^\circ\text{C} \quad 3.87 \frac{\text{J}}{\text{K}}$$

$$100^\circ\text{C} \quad 1.02 \frac{\text{J}}{\text{K}}$$

Both ΔS_{univ} are positive, so it is thermodynamically allowed!

Second Law Open Systems



$$2^{\text{nd}} \text{ Law: } \frac{dS_{\text{univ}}}{dt} = \frac{dS_{\text{sys}}}{dt} + \frac{dS_{\text{env}}}{dt} \geq 0$$

accumulation = 0 : f at steady state

(pol heat transfer)

$$\frac{dS_{\text{univ}}}{dt} = \dot{\bar{n}}_2 s_{m,2} - \dot{\bar{n}}_1 s_{m,1} + \frac{\dot{Q}_{\text{univ}}}{T_{\text{univ}}} \quad \text{Also, } \dot{Q}_{\text{univ}} = -\dot{Q}$$

$$2^{\text{nd}} \text{ Law: } \frac{dS_{\text{univ}}}{dt} = \frac{dS_{\text{sys}}}{dt} + \dot{\bar{n}}_2 s_{m,2} - \dot{\bar{n}}_1 s_{m,1} - \frac{\dot{Q}}{T_{\text{univ}}} \geq 0$$

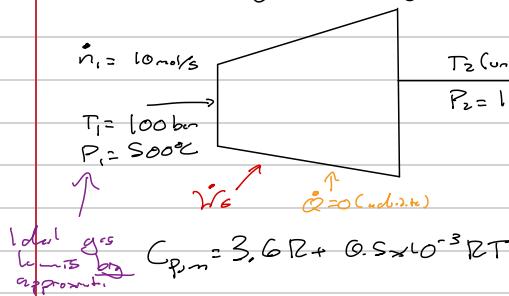
\hookrightarrow steady \Rightarrow static $\rightarrow \frac{dS_{\text{sys}}}{dt} = 0 \Rightarrow \frac{dS_{\text{univ}}}{dt} = \dot{\bar{n}}_2 s_{m,2} - \dot{\bar{n}}_1 s_{m,1} - \frac{\dot{Q}}{T_{\text{univ}}}$

What is Second Law useful?

- ① Another state function, and equation/inequality
- ② Consistency check for calculations, $\Delta S_{\text{univ}} = 0$
- ③ Limiting cases for evaluating maximum/minimum amount of work (reversibility)
- ④ Can be used for equilibrium analysis (will be done later)

Next example

Example: Ideal gas entering adiabatic turbine



ideal gas law approximation: $C_{p,m} = 3.6R + 0.5 \times 10^{-3}RT$

Want to know:

a) Maximum amount of power that can be generated?
→ This is for a reversible process

recall: $P = P_2$ for closed system

- infinitesimal changes
- max work for expansion,
- min work for compression

For open systems: $\Delta S_{\text{univ}} = 0$

mole balance: $\frac{dn}{dt} = 0 = \dot{\bar{n}}_{in} - \dot{\bar{n}}_{out}$ (steady-state)

no accumulation $\rightarrow \dot{\bar{n}}_1 = \dot{\bar{n}}_2 = \dot{\bar{n}}$

1st Law: $0 = \dot{\bar{n}}_1 h_{m,1} - \dot{\bar{n}}_2 h_{m,2} + \dot{W}_t + \dot{Q}$ $\xrightarrow{\text{adiabatic}} \dot{W}_t = \dot{\bar{n}} (h_{m,1} - h_{m,2})$

$\dot{W}_t = \dot{\bar{n}} \int_{T_1}^{T_2} C_{p,m} dT$ $\xrightarrow[\text{Lat.}]{} \text{temperature dependent}$ Be careful! don't skip steps

\rightarrow 1st Law, 2 unknowns (\dot{W}_t, T_2)

Need more equations! \rightarrow 2nd Law !!

2nd Law to get T_2 :

$$\frac{dS_{\text{univ}}}{dt} = 0 = \frac{dS_{\text{sys}}}{dt} + \dot{\bar{n}} (S_{m,2} - S_{m,1}) - \frac{\dot{Q}}{T_{\text{univ}}} \rightarrow S_{m,2} - S_{m,1} = 0 \quad (\text{isentropic process})$$

(conserv.) (steady state) (not-sh) (adiabatic)

$$\Delta S_{\text{univ}} = \int_{T_1}^{T_2} dS_m = \int_{T_1}^{T_2} \frac{C_{p,m}}{T} dT - \int_{P_1}^{P_2} \frac{R}{P} dP \rightarrow 0 = \int_{T_1}^{T_2} \left(\frac{3.6}{T} + 0.5 \times 10^{-3} \right) dT - R \ln \frac{P_2}{P_1}$$

prop. of $\int dS_m = \frac{C_{p,m}}{T} dT - \frac{R}{P} dP$

ideal gas \rightarrow (ideal gas assumption only)

\rightarrow Back to 1st Law

$$\dot{W}_{t,\text{rev}} = \dot{\bar{n}}_2 \left(3.6 + 0.5 \times 10^{-3} T \right) dT = -173.2 \frac{\text{kJ}}{\text{s}} \xrightarrow{\text{max power}} \dot{W}_{t,\text{rev}} = -173.2 \text{ kW}$$

so work done on surroundings

$$T_1, P_1, P_2 \text{ or known} \Rightarrow T_2 = 232 \text{ K}$$

Example Continued

b) The efficiency is *80%, what is $\dot{W}_{s,\text{real}}$?

$$\dot{W}_{s,\text{real}} = 0.8 \cdot \dot{W}_{s,\text{rev}} = -138.6 \frac{\text{kJ}}{\text{s}}$$

denote \dot{W}_s

EPP

$$\eta = \begin{cases} \dot{W}_{s,\text{rev}} / \dot{W}_{s,\text{real}} & \text{for expansion} \\ \dot{W}_{s,\text{rev}} / \dot{W}_{s,\text{real}} & \text{for compression} \end{cases}$$

* This efficiency is the isentropic efficiency, not actual efficiency

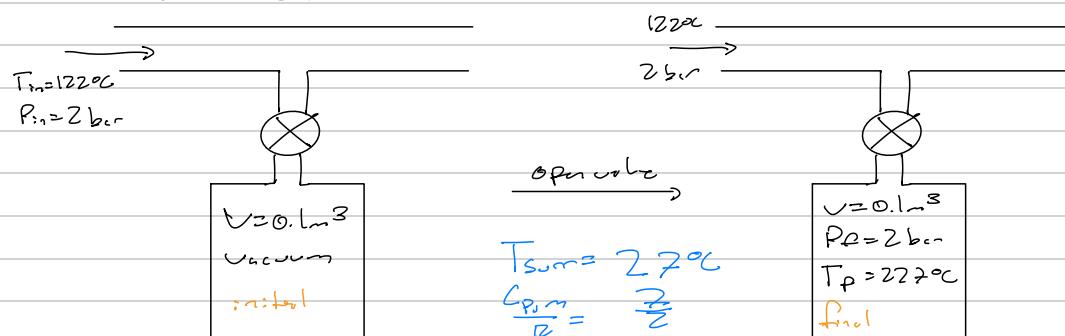
c) What is T_2 ? (80% efficiency)

$$\text{1st Law: } \dot{W}_s = 10 \int_{T_1}^{T_2} C_p dT$$

Know \dot{W}_s , $T_1 \rightarrow$ Solve to find $T_2 = 343 \text{ K}$

Example: Filling a tank w/ ideal gas, 6000J of heat are lost from system.

Find dS_{univ}



• Open system

$$\text{• mole balance: } \frac{dn}{dt} = \dot{n}_{in} - \dot{n}_{out} \Rightarrow \frac{dn}{dt} = \dot{n}_{in} = \frac{dn_{in}}{dt} \quad (\text{unsteady state})$$

$$\Rightarrow dn = dn_{in} \Rightarrow \int dn = \int dn_{in} \Rightarrow n_f = n_i$$

• 1st Law: skip (do not do this :)) \dot{Q} is not needed here given \dot{Q} & T_f

$$\text{• 2nd Law: } \frac{dS_{\text{univ}}}{dt} = \frac{ds}{dt} + \dot{n}_{out} s_{out} - \dot{n}_{in} s_{in} - \frac{\dot{Q}}{T_{\text{sum}}} = \frac{ds}{dt} - \dot{n}_{in} s_{in} - \frac{\dot{Q}}{T_{\text{sum}}} \leftarrow \frac{dQ}{dt}$$

$$\Rightarrow \frac{dS_{\text{univ}}}{dt} = \frac{ds}{dt} + \frac{dn}{dt} s_{in} - \frac{\dot{Q}}{T_{\text{sum}}}$$

$$\text{different form: } dS_{\text{univ}} = ds + d_{n,i} s_{in} - T_{\text{sum}} \text{ constant} \quad \begin{array}{l} \text{entropy is state property} \\ \text{and int for prop are} \\ \text{constant T & P} \end{array}$$

$$\text{so, } \int dS_{\text{univ}} = \Delta S_{\text{univ}} = \int ds + s_{in} d_{n,i} - \frac{1}{T_{\text{sum}}} \int \dot{Q}$$

$$\Delta S_{\text{univ}} = n_f s_{f,p} - n_i s_{i,p} - \frac{\dot{Q}}{T_{\text{sum}}} \\ = n_f (s_{f,p} - s_{i,p}) - \frac{\dot{Q}}{T_{\text{sum}}}$$

→ What about $(s_{m,p} - s_{m,i})$

- For ideal gas: integrate ds_m

$$\Delta S_m = s_{m,p} - s_{m,i} = \int ds_m = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{P_i}^{P_f} \frac{P}{P} dP$$

$$\Rightarrow \Delta S_m = \int_{T_i}^{T_f} \frac{C_p}{T} dT = \frac{3}{2} R \ln \left(\frac{T_f}{T_i} \right)$$

$$\Delta S_{\text{univ}} = n_f \Delta S_m - \frac{\dot{Q}}{T_{\text{sum}}}$$

$$\Delta S_{\text{univ}} = \frac{7}{2} R \ln \left(\frac{T_f}{T_i} \right) \left(\frac{P_f V}{R T_f} \right) - \frac{-6000 \text{ J}}{223 + 27} > 0$$

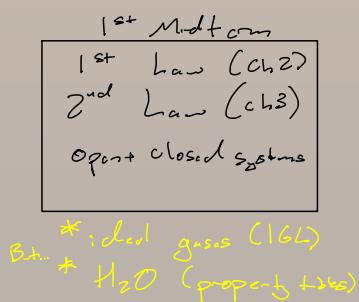
(complaining for remote answer)

✓ consistent w/
Second law

Midterm Exam 2



Previously...



Equations of
State (Ch 4)

Next!

1st & 2nd Law Problems
w/ Real Fluids

Need a mathematical framework to
describe properties of real fluids

Chapter 4 - Equations of State

Equations of state for pure fluids (1 phase)

- Gibbs phase rule: For a pure fluid, need 2 intensive properties to specify all intensive properties

$$\hookrightarrow P = f(T, V_m) \quad 2 \text{ intensive properties}$$

• Compressibility Factor (Z):

$$Z = \frac{P_{\text{m}}}{RT} = g(T, P) \quad \left. \begin{array}{l} \\ \text{2 intensive props} \end{array} \right\} Z=1 \text{ for ideal gas}$$

\hookrightarrow Tells us how "real" or "non-ideal" a gas is

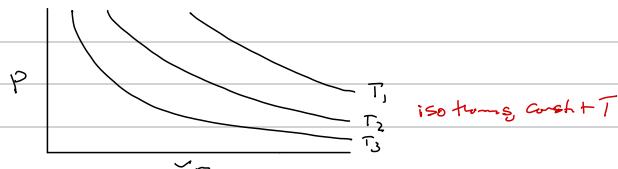
Examples of EOS's

(i) Ideal Gas Law:

$$\rightarrow PV = nRT$$

$$\rightarrow P V_m = RT$$

$$\rightarrow Z = \frac{PV_m}{RT} = 1$$



Assumptions: (a) Molecules do not interact with each other (No potential energy)

\hookrightarrow (b) No volume of molecules

\hookrightarrow We can improve our description of real gases by relaxing these assumptions

(ii) Clausius EOS

$$\rightarrow P = \frac{RT}{V_m - b}$$

where b : parameter for molecular volume ($b > 0$)

Consequence: less volume for the other gas molecules!

\hookrightarrow No intermolecular forces just molecular volume

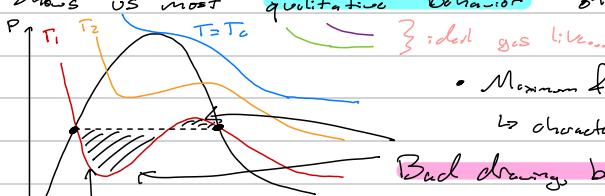
b is a const vol for a fluid, independent of the fluid's T & P .

(iii) Van der Waals EOS

$$\rightarrow P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{where } a: \text{Attractions between molecules: } \text{Forces} \sim r^{-6} \sim V_m^{-2}$$

improving our description of intermolecular forces

• Shows us most qualitative behavior of real fluids



\hookrightarrow Maximum & inflection point @ $T = T_c$

\hookrightarrow characteristic of real fluids

Bad drawing, but these two regions should have equal areas

\hookrightarrow Points that gives "equal area" shows us VL regions

Isotherms do not give accurate pressure inside the VL dome

Observation: $\left(\frac{\partial P}{\partial V_m} \right)_{T=T_c} = 0$ at critical point

Universal Truths: $\left(\frac{\partial^2 P}{\partial V_m^2} \right)_{T=T_c} = 0$ at critical point (inflection point)

For VDW EOS

$$\left(\frac{\partial P}{\partial V_m} \right)_{T=T_c} = \frac{\partial}{\partial V_m} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right]_{T=T_c} = -\frac{RT_c}{(V_{m,c}-b)^2} + \frac{2a}{V_{m,c}^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial V_m^2} \right)_{T=T_c} = \dots = 0 \quad \text{not expected here}$$

Set equal and solve to get these as a, b

2 eqns,

2 unknowns (a, b)

\Rightarrow Solve for a, b in terms of $T_c, V_{m,c}, P_c$!!

$$a = \frac{27}{64} \cdot \frac{(RT_c)^2}{R_c} \quad \text{and} \quad b = \frac{V_{m,c}}{3} \cdot \frac{RT_c}{8P_c}$$

If we know $T_c, V_{m,c}, P_c$ we can calculate $a + b$ for VDW EOS

expressions valid only for VDW EOS

$$Z_c = \frac{P_c V_{m,c}}{R T_c} = \frac{3}{8} \quad @ \text{critical point, for any fluid, for VDW EOS}$$

$\hookrightarrow Z_c$ does not depend on $a+b$

∴ All fluids that follow VDW EOS have same deviation from ideality at critical point
True for more complex EOS's too!

Principle of Corresponding States (Hypothesis)

- all fluids have similar behavior (deviation from ideality) at critical point
- \Rightarrow all fluids have similar behavior for the same "reduced conditions"

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_{m,r} = \frac{V_m}{V_{m,c}}$$

• VDW EOS predicts $Z_c = \frac{3}{8} = 0.375$

• Experimentally, $Z_c \approx 0.29 \rightarrow$ need better EOS for real applications

Back to 'Examples of EOS'

(i) Redlich-Kwong EOS

$$\rightarrow P = \frac{RT}{Vm - b} - \frac{a}{\sqrt{Vm(Vm+b)}} \quad \begin{matrix} a & \leftarrow \text{attraction terms} \\ \text{less attrac. @ low } T \end{matrix}$$

$$\begin{cases} a = \frac{0.42748 P_c^{5/2} T_c}{R} \\ b = \frac{0.08664 R T_c}{P_c} \end{cases} \quad \begin{matrix} \text{Not the same as} \\ a \text{ and } b \text{ in VDW} \\ \text{EOS} \end{matrix}$$

$$\Rightarrow Z_c = \frac{1}{3} \approx 0.33 \quad \text{But for the VDW!}$$

(ii) Peng-Robinson EOS

$$\rightarrow P = \frac{RT}{Vm - b} - \frac{a \alpha(T)}{Vm(Vm+b) - b(Vm-b)}$$

Common in industry

$$\rightarrow Z_c = 0.307 \text{ pretty good!}$$

α is a factor (\propto shape of molecules)

(::)- (✓) acc. w/ cubic EOS's

Q: What is the about corresponding states

(✓) All fluids have same T_c, P_c

(::) Z_c is about the same for all fluids

(::) Properties not the same reduced variables are the same

(✓) None of these

(i) "2" and "3"

Compressibility Charts

$$Z = Z^{(0)} + \omega Z^{(1)} = f(T, P) \quad \begin{matrix} \text{kind of boring & only not really total} \\ \text{in this case} \end{matrix}$$

\uparrow Simple molecules Correction for "non-sphericity"

Liquids and Solids

- Most EoS's are not very accurate for liquids
- Very strong intermolecular interactions; cannot be described by 1 parameter " α "
- **Defn:** $B = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_P$ coefficient of thermal expansion
 $K = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T$ coefficient of isothermal compressibility
- In liquids (not solids), B and K are often approximately constant
- Gibbs phase rule: Solid phase plus fluid, $f=2$ independent interior variables

$$\rightarrow V_m = V_m(T, P)$$

$$- \text{Total d.P}_{\text{total}}: \frac{\partial V_m}{V_m} = \left(\frac{\partial V_m}{\partial T} \right)_P dT + \left(\frac{\partial V_m}{\partial P} \right)_T dP$$

$$\Rightarrow \frac{\partial V_m}{V_m} = B dT - K dP$$

useful eqn: P, B and K
are approximately constant

Example: Calculate volume occupied by 10 kg of benzene at 50 bar and 60°C using VdW EoS

→ How do we solve w/o given $a+b$?

⇒ can we solve if we have property data: T_c, P_c

algebra

↑ given or look up

Calculate T_r, P_r :

$$\left\{ P_r = \frac{P}{P_c} = \frac{50 \text{ bar}}{329 \text{ bar}} = 1.52 \right.$$

$$\left\{ T_r = \frac{T}{T_c} = \frac{333 \text{ K}}{425 \text{ K}} = 0.78 \right.$$

D. difficult to tabulate

From $a+b$ expressions, rewrite VdW EoS as:

$$P_r = \frac{8 T_r}{3 V_{m,r} - 1} - \frac{3}{V_{m,r}^2}$$

want to know
↓ solve numerically

$$V_{m,r} = 0.476$$

$$V_{m,r} = \sqrt{\frac{V_m}{V_{m,c}}} \rightarrow V_m = V_{m,r} \cdot V_{m,c}$$

$$Z_L = \frac{3}{8} = \frac{P_c V_{m,c}}{R T_c} \longrightarrow V_{m,c} = 0.000208 \frac{\text{m}^3}{\text{mol}}$$

$$S_o, V_m = 4.9 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

Convert V_m to V :

$$V = \text{mol} \cdot V_m$$

$$\text{mol} = 10 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{60 \text{ g}} = 0.01666 \text{ mol}$$

$$\checkmark = 0.017 \text{ m}^3$$

Compare w/ ideal gas:

$$V_{\text{ideal}} = 0.017 \text{ m}^3 \quad 5 \text{ times larger volume w/ 1.6L}$$

↑ because we are not account for attractive forces

Chapter 5 - Thermodynamic Web, and Calculus of Thermo

Goal: Make property predictions for real gases. Apply these predictions to first & second law problems.

→ Calculate U_m, h_m, s_m in terms of P, T, V_m, C_{pm}, C_u for real gases
(P: given or EoS)

In introduce new Thermodynamic Relationships

First: Fundamental equation of thermodynamics (FE)

- Recall for closed system, 1st Law:

$$dU_m = \delta q_m + \delta w_m$$

- For reversible processes,

$$\rightarrow \delta w_m = -P dV_m \quad (P = P_B : \text{P reversible})$$

$$\rightarrow \delta q_m, \text{rev} = T dS_m$$

$$\therefore dU_m = T dS_m - P dV_m \quad \text{Fundamental Equation of Thermo}$$

- Recall: $h_m \equiv U_m + P V_m$

$$\rightarrow dh_m = d(U_m + P V_m) \stackrel{\text{chain rule}}{=} dU_m + P dV_m + V_m dP$$

$$(FE) dh_m = T dS_m - P dV_m + P dV_m + V_m dP$$

$$dh_m = T dS_m + V_m dP \quad \text{Fundamental Equation of Thermo (equivalent, just different form)}$$

Also define:

(just definitions)

$$\rightarrow \text{Gibbs Free energy: } G = H - TS$$

$$g_m = h_m - TS_m$$

$$\rightarrow \text{Helmholtz Free energy: } A = U - TS$$

$$a_m = u_m - TS_m$$

$$\Rightarrow dg_m = d(h_m - TS_m) = dh_m - T dS_m - S_m dT$$

$$dg_m = T dS_m + V_m dP - T dS_m - S_m dT$$

$$dg_m = -S_m dT + V_m dP \quad \text{Fundamental Equation (Gibbs) of Thermo}$$

$$\text{Similarly } da_m = -S_m dT - P dV_m \quad \text{Fundamental Equation (Helmholtz) of Thermo}$$

∴ Summary, Forms of FB:

Intensive

$$dU_m = T dS_m - P dV_m$$

$$dh_m = T dS_m + V_m dP$$

$$dg_m = -S_m dT + V_m dP$$

$$da_m = -S_m dT - P dV_m$$

Extensive

$$dU = T dS - P dV$$

$$dH = T dS + V dP$$

$$dG = -S dT + V dP$$

$$dA = -S dT - P dV$$

Q: The Fundamental Equations (Any form) is valid for:

- ✓ 1) reversible processes
- ✓ 2) irreversible processes
- ✓ 3) Open Systems
- ✗ 4) non
- ✓ 5) all

It pertains to changes in thermodynamic properties!

State of system is only factor!

\Rightarrow FE is derived for closed system, reversible process

BUT: FE describes changes in state functions \leftrightarrow Changes in state functions cannot depend on path or process!

\therefore FE can be used for calculations of state functions for \hookrightarrow process!!
See also: entropy calculations on systems

Math Fundamental Review Again (To exploit FE)

Total differential of a function, $z = z(x, y)$

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

also: $\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_y$ for some unspecified variable

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial y}\right)_x} \leftarrow \text{reciprocal}$$

$$-1 = \left(\frac{\partial z}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial y}\right)_x \leftarrow \text{Triple product rule (Göte rule)}$$

All of these properties
can be used to effectively
use the FE

Derive additional relations

① FE for dU_m : $dU_m = TdS_m - PdV_m$
 $U_m = U_m(S_m, V_m)$

For a pure phase,
 $f = C - P + 2 = 1 - 1 + 2 = 2$ intensive variables

Total diff. function:

$$dU_m = \left(\frac{\partial U_m}{\partial S_m}\right)_{V_m} dS_m + \left(\frac{\partial U_m}{\partial V_m}\right)_{S_m} dV_m$$

$$\therefore T = \left(\frac{\partial U_m}{\partial S_m}\right)_{V_m} \text{ and } -P = \left(\frac{\partial U_m}{\partial V_m}\right)_{S_m} \text{ Fundamental Groups}$$

Similar relations from dH_m , dG_m , dA_m

Forms of FE

| | |
|---|---|
| $T = \left(\frac{\partial U_m}{\partial S_m}\right)_{V_m}$ | $-P = \left(\frac{\partial U_m}{\partial V_m}\right)_{S_m}$ |
| $T = \left(\frac{\partial H_m}{\partial S_m}\right)_P$ | $V_m = \left(\frac{\partial H_m}{\partial P}\right)_{S_m}$ |
| $-S_m = \left(\frac{\partial A_m}{\partial T}\right)_{V_m}$ | $-P = \left(\frac{\partial A_m}{\partial V_m}\right)_T$ |
| $-S_m = \left(\frac{\partial G_m}{\partial T}\right)_P$ | $V_m = \left(\frac{\partial G_m}{\partial P}\right)_T$ |

8 fundamental

groups closed
From fe 4

variants of
the FE

Always holds for
single phase single
component !!

② Useful relationships for: $F = f(x, y)$

$$\frac{\partial}{\partial y} \left[\left(\frac{\partial F}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial x} \left[\left(\frac{\partial F}{\partial y} \right)_x \right]_y$$

order of differentiation
does not matter!

• Use this w/ PB:

$$dU_m = TdS_m - PdV_m$$

$$\text{Fund Groups} \rightarrow T = \left(\frac{\partial U_m}{\partial S_m} \right)_{V_m} \text{ and } -P = \left(\frac{\partial U_m}{\partial V_m} \right)_{S_m}$$

$$\left(\frac{\partial T}{\partial V_m} \right)_{S_m} = \frac{\partial}{\partial V_m} \left[\left(\frac{\partial U_m}{\partial S_m} \right)_{V_m} \right]_{S_m}$$

and

$$-\left(\frac{\partial P}{\partial S_m} \right)_{V_m} = \frac{\partial}{\partial S_m} \left[\left(\frac{\partial U_m}{\partial V_m} \right)_{S_m} \right]_{V_m}$$

is Also the case *Must be the same*

Called Maxwell Relations

$$\text{Thus, } \left(\frac{\partial T}{\partial V_m} \right)_{S_m} = - \left(\frac{\partial P}{\partial S_m} \right)_{V_m} \text{ from } dU_m$$

$$\left(\frac{\partial T}{\partial P} \right)_{S_m} = \left(\frac{\partial U_m}{\partial S_m} \right)_P \text{ from } dU_m$$

$$\left(\frac{\partial S_m}{\partial V_m} \right)_T = \left(\frac{\partial P}{\partial T} \right)_{V_m} \text{ from } dU_m$$

$$-\left(\frac{\partial S_m}{\partial P} \right)_T = \left(\frac{\partial U_m}{\partial T} \right)_P \text{ from } dU_m$$

Maxwell

Relations

→ Come from mixed

Second derivative

of the PB

Bottom variables
(in PB & etc
total constant) are
to dependent variables
into corresponding PB.

Always holds for
single phase single
component !!

Working with Total Differentials

$$\text{ex: } dU_m = TdS_m - PdV_m \text{ (PB)}$$

$$\text{what is } \left(\frac{\partial U_m}{\partial P} \right)_T? \quad (\text{Note: } = 0 \text{ for ideal g.s.)}$$

→ Approach:

(i) "Divide" the differentials in PB by dP

$$\frac{dU_m}{dP} = \frac{TdS_m}{dP} - \frac{PdV_m}{dP} \text{ ← total derivative}$$

(ii) Impose constant T conditions to yield partial derivatives

$$\left(\frac{\partial U_m}{\partial P} \right)_T = T \left(\frac{\partial S_m}{\partial P} \right)_T - P \left(\frac{\partial V_m}{\partial P} \right)_T \quad \text{evaluate using EoS}$$

$$\left(\frac{\partial S_m}{\partial P} \right)_T ? \quad \xleftarrow[\text{relations}]{\text{Maxwell}} \quad \left(\frac{\partial S_m}{\partial P} \right)_T = - \left(\frac{\partial V_m}{\partial T} \right)_P$$

$$\therefore \left(\frac{\partial U_m}{\partial P} \right)_T = -T \left(\frac{\partial V_m}{\partial T} \right)_P - P \left(\frac{\partial V_m}{\partial P} \right)_T$$

Can be evaluated if F (should be C for 1 GL)
given an EoS

ex: Express h_m as a function of T & P for a pure, single phase fluid
 ↳ goal: $h_m = h_m(T, P)$ or $dh_m = dh_m(T, P)$

→ **Approach:**

(i) Want total diffential?

$$dh_m = \left(\frac{\partial h_m}{\partial T}\right)_P dT + \left(\frac{\partial h_m}{\partial P}\right)_T dP \quad C_p(T, P) \text{ by definition}$$

(ii) To find $\left(\frac{\partial h_m}{\partial P}\right)_T$

look at PE for dh_m : $dh_m = T dS_m + V_m dP$

(iii) "Divide" differential by dP

$$\frac{dh_m}{dP} = T \frac{dS_m}{dP} + V_m \frac{dP}{dP}$$

(iv) Enforcing constant T

$$\left(\frac{\partial h_m}{\partial P}\right)_T = T \left(\frac{\partial S_m}{\partial P}\right)_T + V_m$$

$$\text{Maxwell Relations} \quad \left(\frac{\partial S_m}{\partial P}\right)_T = -\left(\frac{\partial V_m}{\partial T}\right)_P$$

$$\therefore dh_m = C_p dT + \left[V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P\right] dP$$

Does not imply no ΔS
purely a mathematical relationship

form associates w/ h_m change - it changes in pressure

Left's app's first relations / strategies

a) Ideal G.S.: $PV_m = RT \rightarrow V_m = \frac{RT}{P}$

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{R}{P} \quad \text{"dP per +" of } dh_m$$

$$\rightarrow \left[V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P\right] dP = \left[V_m - \frac{RT}{P}\right] dP = \left[\frac{RT}{P} - \frac{RT}{P}\right] dP = 0$$

$\therefore dh_m = C_p dT$ for an ideal gas

b) Apply to a First Law Problem

-Throttling process for a gas. Adiabatic throttle w/ ∞ and inlet conditions (T_1, P_1) .
 Final T_2 .



(i) Use ideal gas law

MB: $v_1 = v_2 = v$ (stagny)

1st Law: $\dot{Q} = v_1 h_{m1} - v_2 h_{m2} + \dot{Q}_{ext} + \dot{W}_{ext}$ adiabatic no moving parts

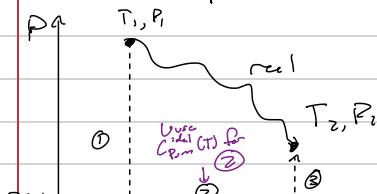
$$\rightarrow h_{m1} - h_{m2} = \dot{Q} \Rightarrow \Delta h_m = \int_{v1}^{v2} dh_m = \dot{Q} \quad T_1 = T_2 \quad \text{bc } dh_m = C_p dT \text{ for ideal gas}$$

(i) Real Gas - Virial EoS: $Z = \frac{P_{Vm}}{RT} = 1 + B'(T)P + \dots$ (ignores higher order terms e.g., $B''(T)P^2, \dots$)

1st Law: $\Delta h_m = \int_{T_1, P_1}^{T_2, P_2} dh_m = 0$

$\int_{T_1, P_1}^{T_2, P_2} [C_{P,m} dT + \sum V_m - T \left(\frac{\partial V_m}{\partial T} \right)_P dP] = 0$

Need to find hypothetical path value \rightarrow use $C_{P,m}^{ideal}$ for "dT path" & $d h_m$



$$\therefore dh_m = \left(\frac{\partial h_m}{\partial T} \right)_P dT + \left(\frac{\partial h_m}{\partial P} \right)_T dP$$

$$dh_m = C_{P,m} dT - RT^2 \frac{dB'}{dT} dP$$

What else do we know?

$\rightarrow C_{P,m}^{ideal}(T)$ tabulated for most fluids
(e.g., low P) (See $B'_m \leq 3$)
* note: $C_{P,m}^{ideal} \neq C_{P,m}^{real}$ (for solubility)

$$\rightarrow V_m = \frac{RT}{P} + B'(T)RT \quad (\text{ideal EoS})$$

Evaluate dh_m :

$$V_m = \frac{RT}{P} + B'(T)RT$$

$$\left(\frac{\partial V_m}{\partial T} \right)_P = \frac{R}{P} + B''(T)R + RT \frac{dB'}{dT}$$

$$\left(\frac{\partial V_m}{\partial P} \right)_T = \left(\frac{RT}{P} + B'(T)RT \right)_T - \left(\frac{RT}{P} + B'(T)RT + RT^2 \frac{dB'}{dT} \right)_T$$

\rightarrow Use dh_m to get $\Delta h_{m,1}, \Delta h_{m,2}, \Delta h_{m,3}$

$$\Delta h_m = \Delta h_{m,1} + \Delta h_{m,2} + \Delta h_{m,3}$$

① Isothermal, $T = T_1$ ($dT = 0$); $P_i \rightarrow P_{ion}$

$$dh_{m,1} = -RT^2 \frac{dB'}{dT} dP = -RT_1^2 \frac{dB'}{dT} \Big|_{T=T_1} dP$$

$$\Delta h_{m,1} = \int_{P_i}^{P_{ion}} dh_{m,1} = -RT_1^2 \frac{dB'}{dT} \Big|_{T=T_1} \int_{P_i}^{P_{ion}} dP = -RT_1^2 \frac{dB'}{dT} \Big|_{T=T_1} (P_{ion} - P_i)$$

$$\therefore \Delta h_{m,1} = RT_1^2 \frac{dB'}{dT} \Big|_{T=T_1} P_i$$

② Iso baric ($P = P_{ion} \approx 0, dP = 0$); $T_1 \rightarrow T_2$

$$dh_{m,2} = C_{P,m} dT = C_{P,m}^{ideal}(T) dT \quad \text{because } P \approx 0$$

$$\therefore dh_{m,2} = \int_{T_1}^{T_2} C_{P,m}^{ideal}(T) dT$$

③ Isoenthalpic, $T = T_2$ ($dT = 0$); $P_{ion} \rightarrow P_2$

$$\Delta h_{m,3} = -RT_2^2 \frac{dB'}{dT} \Big|_{T=T_2} \int_{P_{ion}}^{P_2} dP = -RT_2^2 R_2 \frac{dB'}{dT} \Big|_{T=T_2} dP$$

$$\therefore \Delta h_{m,3} = -RT_2^2 R_2 \frac{dB'}{dT} \Big|_{T=T_2} dP$$

$$\Rightarrow \text{Find } \Delta h_m = \Delta h_{m,1} + \Delta h_{m,2} + \Delta h_{m,3} = 0 \quad (1^{\text{st}} \text{ Law})$$

$$\Delta h_m = 0 = RT_1^2 P_i \frac{dB'}{dT} \Big|_{T=T_1} - RT_2^2 P_2 \frac{dB'}{dT} \Big|_{T=T_2} + \int_{T_1}^{T_2} C_{P,m}^{ideal}(T) dT$$

Real gas behavior

Ideal gas

* Provided $C_{P,m}^{ideal}$
 B'_m, T_2 is only unknown
and can be solved first

Consider $C_{P,m}$ as for gas in the problem.

$$T_1 = 500K$$

$$T_2 = ?$$

$$P_1 = 50 \text{ bar}$$

$$P_2 = ? \text{ bar}$$

$$\text{Look up } C_{P,m}^{ideal} = R(1.702 + 9.1 \times 10^{-3} T - 2.16 \times 10^{-6} T^2)$$

$$\text{Given } B'(T) = \frac{3.44 \times 10^{-6}}{T} - \frac{0.7778}{T^{2.6}} \text{ (SI units)}$$

$$\text{Derivative } \frac{dB'}{dT} = -\frac{3.44 \times 10^{-6}}{T^2} + \frac{0.2022}{T^{3.6}}$$

$$\text{Solve numerically} \rightarrow T_2 \approx 486K$$

$$(\text{If ideal} \rightarrow T_2 = T_1 = 500K)$$

Ex: Express Internal Energy as a function of T, V_m for a pure fluid (single phase)

$$\text{Goal is: } u_m = u_m(T, V_m) \Leftrightarrow du_m = du_m(T, V_m)$$

(i) Total Differential:

$$du_m = \left(\frac{\partial u_m}{\partial T} \right)_{V_m} dT + \left(\frac{\partial u_m}{\partial V_m} \right)_T dV_m \stackrel{?}{=} C_{U,m}(T, V_m) \text{ for a real gas}$$

$$\begin{aligned} & \text{From FE for dam} \\ & \left(\frac{\partial S_m}{\partial V_m} \right) = \left(\frac{\partial P}{\partial T} \right)_{V_m} \\ & \text{Combining w/ EoS} \end{aligned}$$

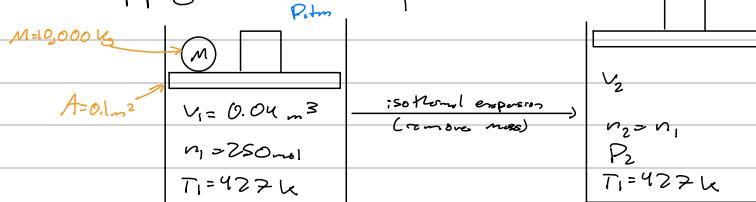
(ii) PE: $du_m = T dS_m - P dV_m$, "Deduct" by dV_m , enthalpy const + T

$$\frac{du_m}{dV_m} = T \frac{dS_m}{dV_m} - P \frac{dV_m}{dV_m} \Rightarrow \left(\frac{\partial u_m}{\partial V_m} \right)_T = T \left(\frac{\partial S_m}{\partial V_m} \right)_T - P$$

$$\left(\frac{\partial u_m}{\partial V_m} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_{V_m} - P$$

$$\therefore du_m = C_{U,m}^{real} dT + \left[T \left(\frac{\partial P}{\partial T} \right)_{V_m} - P \right] dV_m$$

Lots apply this to a problem



Find ΔU_m for this process

(i) Ideal gas

$$\Delta U_m = \int_{T_1}^{T_2} C_{U,m}^{ideal} dT = \int_{427}^{427} C_{U,m}^{ideal} dT = 0 \quad (\text{isothermal})$$

(ii) Real gas: Van der Waals EoS

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

$$\text{given: } C_{P,m}^{ideal} = 28 \frac{J}{mol \cdot K} \quad \left\{ \begin{array}{l} a = 0.8 \\ b = 4 \times 10^{-5} \end{array} \right. \quad \left\{ \begin{array}{l} \text{SI} \\ \text{units} \end{array} \right\}$$

$$\Delta U_m = \int_{V_1}^{V_2} dU_m \rightarrow dU_m = C_{U,m}^{real} dT + \left[T \left(\frac{\partial P}{\partial T} \right)_{V_m} - P \right] dV_m$$

Need: calculate $\left(\frac{\partial P}{\partial T} \right)_{V_m}$
need V_m and $V_{m,2}$

① Calculating $V_{m,1}$ and $V_{m,2}$

$$V_{m,1} = \frac{V_1}{n} = \frac{0.04 \text{ m}^3}{250 \text{ mol}} = 0.00016 \frac{\text{m}^3}{\text{mol}}$$

$V_{m,2}$? use EoS! (need P_2 and T_2)

Free b/w
isotherm

$$\Rightarrow \begin{cases} V_{m,1} = 0.00016 \frac{\text{m}^3}{\text{mol}} \\ V_{m,2} = 0.0534 \frac{\text{m}^3}{\text{mol}} \end{cases}$$

→ Force balance

$$P_1 = P_{atm} = 1.01 \times 10^5 \text{ Pa}$$

$$P_1 = 1.01 \times 10^5 \text{ Pa} \quad (\text{Free b/w})$$

EOS $V_{m,2} = 0.0534 \frac{\text{m}^3}{\text{mol}}$

→ Summary of information

init (1)

$$P_1 = 1.01 \times 10^5 \text{ Pa}$$

$$V_{m,1} = 0.00016 \frac{\text{m}^3}{\text{mol}}$$

$$T_1 = 427 \text{ K}$$

f. (2)

$$P_2 = 1.01 \times 10^5 \text{ Pa}$$

$$V_{m,2} = 0.0534 \frac{\text{m}^3}{\text{mol}}$$

$$T_2 = 422 \text{ K}$$

② Solving for dU_m

$$dU_m = \left[T \left(\frac{\partial P}{\partial T} \right)_{Vm} - P \right] dVm \quad \text{don't need a calculation just to use } C_v^{\text{ideal}} \text{ as } T_1 = T_2$$

$$\left(\frac{\partial P}{\partial T} \right)_{Vm} = \frac{\partial}{\partial T} \left[\frac{RT}{Vm-b} - \frac{a}{Vm^2} \right]_{Vm} = \frac{R}{Vm-b}$$

P for $V \frac{dW}{dV}$

$$\Rightarrow dU_m = \left[T \left(\frac{R}{Vm-b} \right) - P \right] dVm = \left[\frac{RT}{Vm-b} - \left(\frac{RT}{Vm-b} - \frac{a}{Vm^2} \right) \right] dVm$$

$$dU_m = \frac{a}{Vm^2} dVm \quad (\text{isothermal, VdW EoS})$$

$$\therefore \Delta U = n \Delta U_m = n \int_{Vm,1}^{Vm,2} \frac{a}{Vm^2} dVm = n \int_{Vm,1}^{Vm,2} \frac{a}{Vm^2} dVm = -na \left[\frac{1}{Vm,2} - \frac{1}{Vm,1} \right] = 728 \text{ kJ}$$

Q: Why does the internal energy (U_m) increase a little for small ΔP ?

(✗) There is more molecular KE

(✗) There is less molecular KE because molecules are farther apart

(✗) There is less PE because molecules are closer

(✗) All of the above

(v) None of the above

In this example, same mol. KE (same T)

↳ eliminates (i), (ii), and (iv)

→ VdW has more PE!

Temp is same:

$$KE_{dr,1} = KE_{dr,2}$$

$$U = KE_{mole} + PE_{mole} \quad \leftarrow : P \text{ KE is const, } PE \text{ not const}$$

$$PE = 0 \text{ for ideal gas}$$

Ex: Express $U_m = U_m(T, P)$

(\therefore) Total Differential

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

↑ not C_{Vm} or C_{Pm} !

Use definition: $h_m \equiv U_m + P_m$

$$C_{Pm}! \quad \left(\frac{\partial h_m}{\partial T}\right)_P = \left(\frac{\partial U_m}{\partial T}\right)_P + P \left(\frac{\partial U_m}{\partial P}\right)_P$$

$$\text{1st Part} \Rightarrow \left(\frac{\partial U_m}{\partial T}\right)_P = C_{Pm} - P \left(\frac{\partial V_m}{\partial T}\right)_P$$

(\therefore) Differentiate $\left(\frac{\partial U_m}{\partial P}\right)_T$: FE $\rightarrow dU_m = T dS_m - P dV_m$

"Divide" by $dP \neq \text{const} + T$

$$\left(\frac{\partial U_m}{\partial P}\right)_T = T \left(\frac{\partial S_m}{\partial P}\right)_T - P \left(\frac{\partial V_m}{\partial P}\right)_T$$

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

Maxwell relation from
FE for dU_m

$$\therefore dU_m = [C_{Pm} - P \left(\frac{\partial V_m}{\partial T}\right)_P] dT - [T \left(\frac{\partial U_m}{\partial T}\right)_P + P \left(\frac{\partial U_m}{\partial P}\right)_T] dP$$

Ex: Express $S_m = S_m(T, V_m)$

FE: $dU_m = T dS_m - P dV_m$

$$\text{Recall: } dU_m = C_{Vm} dT + [T \left(\frac{\partial P}{\partial T}\right)_{Vm} - P] dV_m$$

Sub & divide
 \rightarrow
 $m \neq B$

$$dS_m = \frac{C_{Vm}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{Vm} dV_m$$

Ex: Express $S_m = S_m(T, P)$

FE: $dU_m = T dS_m + V_m dP$

$$\text{Recall: } dU_m = C_{Pm} dT + [V_m - T \left(\frac{\partial U_m}{\partial T}\right)_P] dP$$

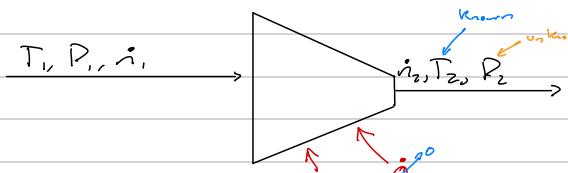
Sub & divide
 \rightarrow
 $dU_m \text{ FE}$

$$dS_m = \frac{C_{Pm}}{T} dT - \left(\frac{\partial U_m}{\partial T}\right)_P dP$$

Note: for ideal gas, $\left(\frac{\partial U_m}{\partial T}\right)_P = \frac{\partial}{\partial T} \left[\frac{RT}{P} \right]_P = \frac{R}{P}$
and recall that $dS_m = \frac{C_{Pm}}{T} dT - \frac{R}{P} dP$ for an IG



Example A reversible compressor compresses a fluid from (T_1, P_1) to T_2 . What is P_2 ? Assume compressor is adiabatic.



$\text{1st Law: } \frac{dS_m}{dt} = 0$

$$\frac{dS_m}{dt} = 0 = \frac{ds}{dt} + i_2 s_{m,2} - i_1 s_{m,1} - \frac{\dot{Q}}{T_{\text{corr}}} \xrightarrow{\text{adibatic}}$$

$$\Rightarrow S_{m,2} - S_{m,1} = 0 \text{ isentropic process}$$

$$\Delta S_m = \int_{i_1}^{i_2} dS_m = 0$$

We need a calc. path that goes through real gas conditions

$$\Delta S_m = \int_{i_1}^{i_2} dS_m = 0 = \Delta S_{m,0} + \Delta S_{m,0} + \Delta S_{m,0}$$

$$\textcircled{1} \quad P_1 \rightarrow P_{\text{ideal}}, \text{ constant } T = T_1$$

$$\Delta S_{m,0} = - \int_{P_1}^{P_{\text{ideal}}} \left[\frac{12}{P} + B' R + RT_1 \frac{dB'}{dT} \right] dP = -R \ln \left(\frac{P_{\text{ideal}}}{P_1} \right) - \left[B'(T_1) R + RT_1 \frac{dB'}{dT} \right] \Big|_{P=P_1} (P_{\text{ideal}})$$

$$\textcircled{2} \quad T \rightarrow T_2 \text{ under 1st law, deal w/ mass lost? Problem? } h(0) \text{ is undefined!}$$

$$\Delta S_{m,0} = \int_{T_1}^{T_2} \frac{C_{P,m}^{\text{real}}}{T} dT = \int_{T_1}^{T_2} \frac{C_{P,m}^{\text{ideal}}(T)}{T} dT$$

because $P^{\text{ideal}} = 0$

$$\textcircled{3} \quad P^{\text{ideal}} \rightarrow P_2, \text{ const } T = T_2$$

$$\Delta S_{m,0} = -R \ln \left(\frac{P_2}{P_{\text{ideal}}} \right) - \left[B'(T_2) R + RT_2 \frac{dB'}{dT} \Big|_{T=T_2} \right] (P_2 - P^{\text{ideal}})$$

$$\therefore \Delta S_m = 0 = \Delta S_{m,0} + \Delta S_{m,0} + \Delta S_{m,0} \quad (\text{P.ideal's cancel!})$$

Derv'd from ideal b/w

$$\text{ideal g.s. } \frac{dS_m}{dT} = \int_{T_1}^{T_2} \frac{C_{P,m}^{\text{ideal}}}{T} dT - R \ln \left(\frac{P_2}{P_1} \right) + R \left[B'(T_1) P_1 - B'(T_2) P_2 \right] + R \left[T_1 P_1 \frac{dB'}{dT} \Big|_{T_1} - T_2 P_2 \frac{dB'}{dT} \Big|_{T_2} \right]$$

Note: If $B=0$: ideal g.s. ($B=0$)

* Need numerical solution for P_2 (only unknown)

* Numbers: for CH₄ (parameters in previous example)

$$\& T_1 = 300 \text{ K}, T_2 = 600 \text{ K}, P_1 = 1 \text{ bar}$$

Compared to
 $P_2^{\text{ideal}} = 3 \text{ bar}$

$$Q: \text{ If } \frac{dS_m}{dT} = \frac{C_{P,m}}{T} - \left(\frac{\partial v_m}{\partial T} \right)_P dP = 0 \text{ and we solve: } \left(\frac{\partial T}{\partial P} \right)_X = \frac{T C_{P,m} \frac{\partial v_m}{\partial T}}{C_{P,m}}$$

(i) $S_m = dS_m = 0$ given, thus S_m is held constant

x (ii) T

x (iii) P

(iv) v_m

x (v) T and P

$$dS_m = \frac{C_{P,m}}{T} dT - \left(\frac{\partial v_m}{\partial T} \right)_P dP$$

$$dT = \frac{T}{C_{P,m}} dS_m + \frac{T}{C_{P,m}} \left(\frac{\partial v_m}{\partial T} \right)_P dP \quad \% \text{ by dP is const } S_m (dS_m = 0)$$

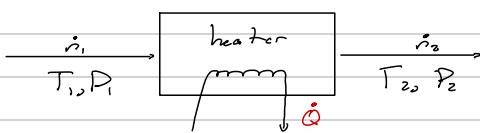
$$\left(\frac{\partial T}{\partial P} \right)_{S_m} = \frac{T}{C_{P,m}} \left(\frac{\partial v_m}{\partial T} \right)_P \quad \checkmark$$

Solve for dT

Examp 3 S.38) You need to design a heater to preheat a g.s going into a reactor. The inlet is at 27°C and 50 bar, and you desire to heat the g.s to 227°C and 50 bar.

Given $\left\{ \begin{array}{l} \text{EoS: } z = \frac{P_{Vm}}{RT} = 1 + \frac{aP}{RT} \text{ where } a = -0.70 \text{ K}^{1/2}/\text{bar} \\ C_{Vm} = \frac{C}{R} = 3.58 + 3.02 \times 10^{-3}T \end{array} \right.$

Determine the heat required for this process in J/mol.



Mole Balance: $\frac{dn}{dt} = 0 = \dot{n}_1 - \dot{n}_2 \rightarrow \dot{n}_1 = \dot{n}_2 = \dot{n}$
Steady-state

$$\text{1st Law: } \frac{d}{dt} (U + E_k + E_p) = 0 = \dot{n}_1 h_{m,1} - \dot{n}_2 h_{m,2} + \dot{Q} + \cancel{W_s} \text{ no shaft work}$$

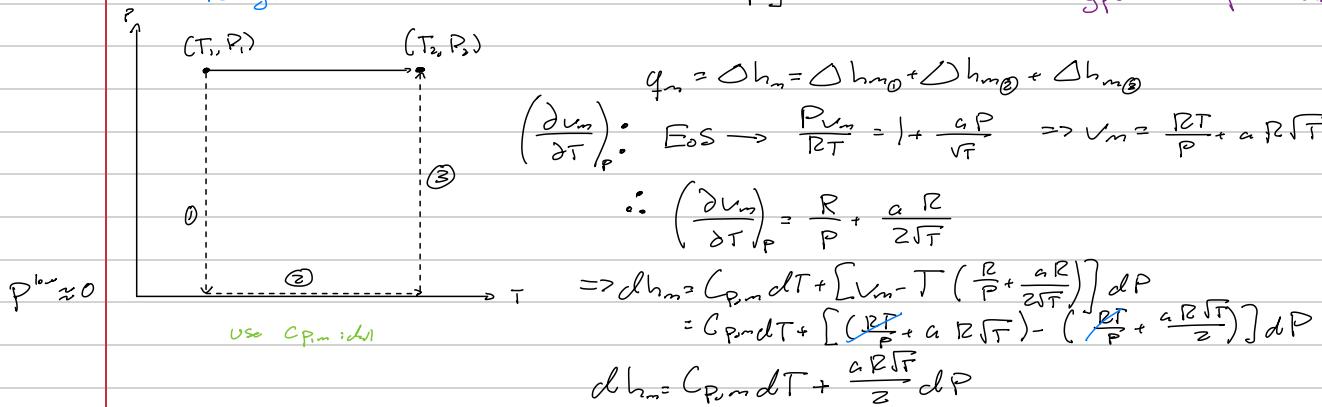
$$\dot{Q} = \dot{n} (h_{m,2} - h_{m,1})$$

$$\frac{\dot{Q}}{\dot{n}} = \frac{\left(\frac{dQ}{dt} \right)}{\left(\frac{dn}{dt} \right)} = q_m = h_{m,2} - h_{m,1} = \Delta h_m = \int_{1,1}^{2,2} dh_m \quad \begin{matrix} \text{need} \\ \text{expressions} \\ \text{for } dh_m \end{matrix}$$

$$\Rightarrow \text{use } dh_m = dh_m(T, P)$$

$$dh_m = C_{Vm} dT + \left[V_m - T \left(\frac{\partial V_m}{\partial T} \right)_P \right] dP \quad \begin{matrix} \text{constant } P \\ \text{pressure} \end{matrix}$$

do not cross out dP , as we used a hypothetical path through real conditions



$$① P_1 \rightarrow P^{id} \quad (\bar{T} = T_1, \text{ isothermal})$$

$$\Delta h_{m,1} = \int_{P_1}^{P^{id}} dh_m = \int_{P_1}^{P^{id}} \left(\frac{aR\sqrt{T}}{2} \right) dP = \left(\frac{aR\sqrt{T}}{2} \right) (P^{id} - P_1) \approx - \frac{aR\sqrt{T_1}}{2} P_1$$

$$③ P^{id} \rightarrow P_2 \quad (\bar{T} = T_2)$$

$$\Delta h_{m,3} \approx \frac{aR\sqrt{T_2}}{2} P_2 \quad \text{note: } P_2 = P_1, \text{ but } T_1 \neq T_2 \quad \text{Good that } \rightarrow \text{didn't ignore } dP$$

$$② T_1 = T_2 \quad (@P^{id} \rightarrow \text{real conditions})$$

$$\begin{aligned} \Delta h_{m,2} &= \int_{T_1}^{T_2} dh_m = \int_{T_1}^{T_2} C_{Vm} dT = R \int_{T_1}^{T_2} \left(3.58 + 3.02 \times 10^{-3}T \right) dT \\ &= R \left[3.58(T_2 - T_1) + \frac{3.02 \times 10^{-3}}{2} (T_2^2 - T_1^2) \right] \end{aligned}$$

$$q_m = \Delta h_m = \Delta h_{m,1} + \Delta h_{m,2} + \Delta h_{m,3}$$

$$\begin{aligned} P_1 = P_2 \rightarrow & aR P_1 (\sqrt{T_2} - \sqrt{T_1}) + R \left[3.58(T_2 - T_1) + \frac{3.02 \times 10^{-3}}{2} (T_2^2 - T_1^2) \right] \end{aligned}$$

$$\therefore q_m = 2888 \text{ J/mol}$$

Other Chapter 5 Information

- Did not cover:

- Ch 5.4 - derivative functions

- Ch 5.5 - Joule-Thomson Expansions

- Equations for Ch 5 on Canvas

- Summary of Techniques

- ① Manipulate the FB (4 forms!)

- "Dimension Tricks"

- ② Total differential expressions

- ③ Maxwell Relations

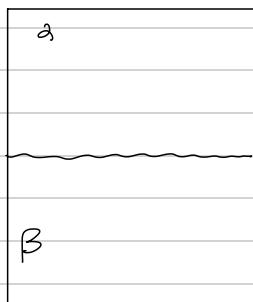
- worse be order of d.P. Partial derivatives does not matter for mixed 2nd derivatives

- ④ Definitions: h_{ij} ; a_{ij} ; g_{ij} ; C_{ijm} ; C_{imj}

- ⑤ Chain rule, reciprocal rule, triple product/cyclic rule

Chapter 6 - Phase Equilibria

- Little Pictures
- At equil,
- ΔS is minimized
- ΔG is minimized
- A and B are in thermal & mechanical equilibrium
- $T^A = P^A$
- $P^A = P^B$
- $M^A = M^B$ (2nd Law)
- Cohesive potential
- env: Vapor-Liquid Equil (VLE)



* Criteria of equilibrium:

$$\textcircled{1} \Delta S_{\text{uni}} \geq 0 \quad (\text{2nd Law})$$

$$\textcircled{2} \Delta S + \Delta S_{\text{sur}} \geq 0$$

→ Eventually @ equil, $\Delta S + \Delta S_{\text{sur}}$ is minimized

② For a system at known T, P :

$$\textcircled{3} \Delta G \leq 0 \quad (\text{recall } G = H - TS)$$

→ G is minimized @ equilibrium

Q: What does M represent?

(i) Free energy

(ii) Free energy per mole

(iii) Enthalpy per mole

(iv) Enthalpy per mole for a reversible process

Chemical Potential (M): $M \equiv \left(\frac{\partial G}{\partial n} \right)_{T, P} = \frac{G}{n} = g_m$

In special cases (single component systems)

Phase Equil Requirements:

$$T^A = T^B$$

$$P^A = P^B$$

$$M^A = M^B$$

So what! Can we make this practical

$$M^A = M^B$$

pure component: $g_m^A = g_m^B$

$$h_m^A - T^A s_m^A = h_m^B - T^B s_m^B$$

d.PF eqn: $dh_m^A = dh_m^B$

$$\text{FE: } v_m^A dP^A - s_m^A dT^A = v_m^B dP^B - s_m^B dT^B$$

No. of P = P^A = P^B = P, T^A = T^B = T

$$\Rightarrow (v_m^A - v_m^B) dP = (s_m^A - s_m^B) dT$$

$$s_m^A - s_m^B = \frac{h_m^A - h_m^B}{T} \quad (\text{easier to measure})$$

$$\frac{dP}{dT} = \frac{h_m^A - h_m^B}{T(v_m^A - v_m^B)}$$

Clapeyron Equation:
relates T & P for systems in phase eq.

Q: How many unknown independent intensive variables are there in the Clapeyron eqn?

(i) 0

(ii) 1

(iii) 2

(iv) 3

(v) > 3

$$h_m^A = h_m^B (T, P)$$

$$h_m^B = h_m^A (T, P)$$

$$v_m^A (T, P), v_m^B (T, P) \text{ EoS}$$

$$\text{Thus, } \frac{dP}{dT} = f(T, P)$$

• At phase eq, pure single component,
↳ 1 equation (Clapeyron), 2 unknowns (T, P) → 1 DoF "

• Compare to Gibbs phase rule:

$$f = C - P + 2 = 1 - 2 + 2 = 1$$

→ Clapeyron equation quantifies the Gibbs phase rule

Consider Vapor-liquid equilibrium (eg. H_2O in a pressure cooker)

↳ Let $a = \text{gas}$, $B = \text{liquid}$

- assumption: $h_m^{\text{gas}} - h_m^{\text{liq}} = \Delta h_m^{\text{vap}}$ is a constant (can be a good assumption)
- assumption: $V_m^{\text{gas}} \gg V_m^{\text{liq}}$ (a really good assumption, allows $V_m^{\text{liq}} \rightarrow 0$)
- assumption: Vapor is ideal (not until @ low P)
 $\rightarrow V_m^{\text{gas}} = \frac{RT}{P}$

⇒ Apply Assumptions to Clapeyron Eqn:

$$\frac{dP}{dT} = \frac{h_m^{\text{gas}} - h_m^{\text{liq}}}{T(V_m^{\text{gas}} - V_m^{\text{liq}})} \stackrel{\text{Assume}}{=} \frac{\Delta h_m^{\text{vap}}}{T V_m^{\text{gas}}} = \frac{\Delta h_m^{\text{vap}}}{T(\frac{RT}{P})} = \frac{\Delta h_m^{\text{vap}}}{RT^2/P}$$

(i) Recondo (Separato)

$$\frac{dP}{P} = \frac{\Delta h_m^{\text{vap}}}{R} \frac{dT}{T^2}$$

(i): Solve! \checkmark assumed constant

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta h_m^{\text{vap}}}{R} \int_{T_0}^T \frac{dT}{T^2}$$

(ii) Integrate

$$\int_{P_0}^P \frac{dP}{P} = \frac{\Delta h_m^{\text{vap}}}{R} \int_{T_0}^T \frac{dT}{T^2}$$

Choose reference conditions / stato

$$\therefore \ln\left(\frac{P}{P_0}\right) = -\frac{\Delta h_m^{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

- valid: $P \rightarrow \text{VLE}$

$\rightarrow \Delta h_m^{\text{vap}}$ is constant

\rightarrow ideal gas $V_m^{\text{gas}} \gg V_m^{\text{liq}}$

Clausius-Clapeyron Eqn (CCB)

Antoine Eqn: $\ln P^{\text{(sat)}} = A - \frac{C}{B+T}$ where A, B, C are constants of the fluid
 ↳ Antoine eqns is an empirical form of the CCB

Answers: Key equations for Single-Component phase equilibria

$$M^{\alpha} = M^{\beta}$$

$$h_m^{\alpha} - TS_m^{\alpha} = h_m^{\beta} - TS_m^{\beta}$$

$$\text{FE: } d_g m = V_m^{\alpha} dP - S_m^{\alpha} dT = V_m^{\beta} dP - S_m^{\beta} dT \quad \left\{ \begin{array}{l} \cancel{dP} \\ \frac{dP}{dT} = \frac{h_m^{\alpha} - h_m^{\beta}}{T(V_m^{\alpha} - V_m^{\beta})} \end{array} \right. \quad \hookrightarrow \text{Clapeyron Eqn}$$

Key Questions to ask for single component phase analysis: (Trick to Success!)

① Can $h_m^{\alpha} - h_m^{\beta}$ be treated as a constant?

② Are either V_m^{α} or V_m^{β} negligible?

③ Can vapor be treated as an ideal gas?

If all the above holds, the Clausius-Clapeyron Eqn (CCB) is valid for VLE

Example: The vapor pressure of liquid silver has been measured (at 61384 K and 2985 K):

$$\ln P = -\frac{14260}{T} - 0.458 \ln T + 12.23 \quad P = 3 \text{ torr} \quad T = 298 \text{ K} \Rightarrow \text{Estimate } \Delta h_m^{\text{vap}} @ 1500 \text{ K}$$

Recall: $\frac{dP}{dT} = \frac{V_m^L - h_m^L}{T(V_m^V - V_m^L)}$

1st Q: Is the vapor ideal at 1500 K? Vapor is very likely ideal
 $P = \exp\left(-\frac{14260}{1500} - 0.458 \ln 1500 + 12.23\right) \approx 0.53 \text{ torr} \ll 1 \text{ atm} \leftarrow \text{Very low pressure!}$

2nd Q: Is $V_m^L \ll V_m^V$? Yes, usually a very good assumption

3rd Q: Is Δh_m^{vap} a constant? No!

\rightarrow CCF assumes this to be true, but the CCF does not have an $\ln(T)$ term!

$\Rightarrow \Delta h_m^{\text{vap}}$ of silver is not constant

• Use Raoult's law equation (not CCF, $\Delta h_m^{\text{vap}} \neq \text{constant}$)

$$\rightarrow \frac{dP}{dT} = \frac{\Delta h_m^{\text{vap}}}{T(V_m^V - V_m^L)} = \frac{\Delta h_m^{\text{vap}}}{RT^2/P}$$

Constant treated as constant $\approx V_m^V \approx \frac{RT}{P}$ (ideal gas, $V_m^V \gg V_m^L$)

$$\frac{dP}{P} = \frac{\Delta h_m^{\text{vap}}(T)}{RT^2} dT$$

$$\text{Integrate} \rightarrow \ln P = \int \frac{\Delta h_m^{\text{vap}}(T)}{RT^2} dT + \text{Constant}$$

$$\text{Compare to Expt} \rightarrow \ln P = -\frac{14260}{T} - 0.458 \ln T + 12.23$$

$$\therefore \int \frac{\Delta h_m^{\text{vap}}(T)}{RT^2} dT = -\frac{14260}{T} - 0.458 \ln T$$

$$\text{Take Derivative} \rightarrow \frac{d}{dT} \left[\int \frac{\Delta h_m^{\text{vap}}(T)}{RT^2} dT \right] = -\frac{14260}{T} - 0.458 \ln T \quad (\text{PTG})$$

$$\text{Gen Expr.} \rightarrow \frac{\Delta h_m^{\text{vap}}(T)}{RT^2} = \frac{14260}{T^2} - \frac{0.458}{T} \Rightarrow \Delta h_m^{\text{vap}}(T) = RT^2 \left(\frac{14260}{T^2} - \frac{0.458}{T} \right)$$

$$\text{Solve for } \Delta h_m^{\text{vap}}, \text{ plug in } T = 1500 \text{ K} \rightarrow \Delta h_m^{\text{vap}}(1500 \text{ K}) = 113 \text{ kJ/mol}$$

Example: Is CO_2 a liquid at -40°C and 20 bar?

Given: $\Delta h_{\text{m}}^{\text{fus}} = \Delta h_m^L - \Delta h_m^S = 8.65 \frac{\text{kJ}}{\text{mol}}$ } at triple point
 $\Delta h_{\text{m}}^{\text{sub}} = \Delta h_m^V - \Delta h_m^S = 26.1 \frac{\text{kJ}}{\text{mol}}$

triple point: 216.6 K, 5.2 bar for CO_2

$P_{\text{trip}} = 1.18 \frac{\text{mol}}{\text{cm}^2}$ @ triple point

$P_{\text{S,L}} = 1.56 \frac{\text{mol}}{\text{cm}^2}$ @ 1 bar, -78°C

Solution: Construct a PT diagram for CO_2 .

→ need to determine P-T relationships:

(i) Liquid-vapor equilibrium (ii) Solid-liquid equil. (iii) Solid-vapor equil.

- Don't have info about Δh_{m} , we are forced to assume Δh_{m} 's are constant and that our vapor is ideal
- need: $\Delta h_{\text{m}}^{\text{vap}} = \Delta h_m^V - \Delta h_m^L = \Delta h_m^V - h_m^S + h_m^S - \Delta h_m^L$
 $\Rightarrow \Delta h_{\text{m}}^{\text{vap}} \approx 17.5 \frac{\text{kJ}}{\text{mol}}$

1) Vap-Liq Equil.

$$\frac{dP}{dT} = \frac{h_m^V - h_m^L}{T(V_m^V - V_m^L)} = \frac{\Delta h_{\text{m}}^{\text{vap}}}{T(V_m^V - V_m^L)}$$

- assume

$\Delta h_{\text{m}}^{\text{vap}}$ is const. } → forced

$\rightarrow V_m^V \gg V_m^L$ → usually very good assumption } Use Clausius-Clapeyron Eqn

$\rightarrow V_m^V \approx \frac{RT}{P}$ } → forced

$$\Rightarrow \ln\left(\frac{P}{P_0}\right) = -\frac{\Delta h_{\text{m}}^{\text{vap}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

How to find P_0, T_0 ? → Refine Pt. on vap-liq equal line.

let $P_0 = P_{\text{trip}}$, $T_0 = T_{\text{trip}}$

2) Solid-Liq Equil.

- Starting w/ Clapeyron eqn, assume:

$\rightarrow \Delta h_{\text{m}}$ is const. } → already discussed

$\rightarrow V_m^L \gg V_m^S$ → miserably awful, stinky assumption

\rightarrow however, $(V_m^L - V_m^S) \approx$ constant → for condensed phases

$$\text{Clapeyron } \frac{dP}{dT} = \frac{h_m^L - h_m^S}{T(V_m^L - V_m^S)} = \frac{1}{T} \cdot \frac{\Delta h_{\text{m}}}{V_m^L - V_m^S}$$

constit

$$\int \frac{dP}{P_{\text{trip}}} = \frac{\Delta h_{\text{m}}^{\text{fus}}}{\Delta V_m^{\text{fus}}} \int_{T_{\text{trip}}}^T dT \Rightarrow P_{\text{S,L}} - (5.2 \text{ bar}) = \left(\frac{\Delta h_{\text{m}}^{\text{fus}}}{\Delta V_m^{\text{fus}}} \right) \ln\left(\frac{T}{216.6}\right)$$

Temp

3) Solid-Vapor Equil.

- assume: $\rightarrow \Delta h_{\text{m}}^{\text{sub}}$ is const. } → already discussed

$\rightarrow V_m^V \gg V_m^S$? } → amazing assumption between VLE

$\rightarrow V_m^V = \frac{RT}{P}$ } → already discussed

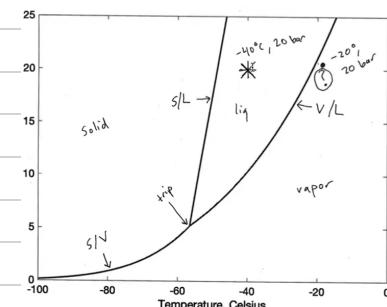
$$\Rightarrow P_{\text{S,V}} = (5.2 \text{ bar}) \times \exp\left[-3139\left(\frac{1}{T} - \frac{1}{216.6}\right)\right]$$

→ Now? 3 eqns ready P-T

- Plot these lines to determine phase @ -40°C , 20 bar

Code on Canva
(Method)

CO_2 is a liquid!



Q: How could we improve our predictions at 20 bar - 20°C?

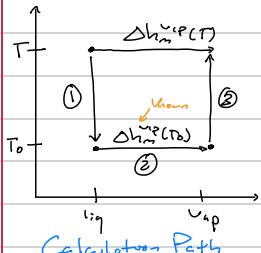
In vapor, but close
constant assumptions!

- X1) Improve Δh_m^{sub} analysis? → solid- μ , not needed
- X2) Real phase of P_f about
- Better Δh_m^{vap}
- Good Δh_m^{vap} → Improve estimate of v_m^L → Assume 16L initially, better EoS for
- Δh_m^{vap} → more confidence

Derive an Eqn for $\Delta h_m^{\text{vap}}(T)$ ($C_{p,m}$ is not constant)

$\rightarrow C_{p,m}^L \& C_{p,m}^V$ are constant and given $\Delta h_m^{\text{vap}}(T_0)$

\rightarrow Assume vapor is ideal g.s and $h_m^L = h_m^V(T)$



$$\begin{aligned}\Delta h_m^{\text{vap}}(T) &= \Delta h_m^{\text{m0}} + \Delta h_m^{\text{m1}} + \Delta h_m^{\text{m2}} \\ &= C_{p,m}^L(T_0 - T) + \Delta h_m^{\text{vap}}(T_0) + C_{p,m}^V(T - T_0) \\ \Rightarrow \Delta h_m^{\text{vap}} &= \Delta h_m^{\text{vap}}(T_0) + (C_{p,m}^V - C_{p,m}^L)(T - T_0)\end{aligned}$$

\hookrightarrow would plug into Clapeyron equation

Describe Single Phases w/ > 1 Component

① Consider a total differential of $G(T, P, n_1, n_2, \dots, n_m)$ for an m -component mixture

Zeroth-order (CPD)
needed for multi-component

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_m} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots, n_m} dn_1 + \dots + \left(\frac{\partial G}{\partial n_m}\right)_{T, P, n_1, \dots, n_{m-1}} dn_m$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_m} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_m} dn_i$$

Recall:

$$\circ \text{Sole component} \rightarrow \left(\frac{\partial G}{\partial n_i}\right)_{P, \dots} \equiv n_i$$

$$\circ \text{Multi-comp} \rightarrow \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_m} \equiv M_i \quad \text{each component has its own chem potential}$$

$$\therefore dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_m} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \sum_i M_i dn_i$$

Recall: Sole comp

$$FB \Rightarrow dG = -SdT + VdP + \sum_i M_i dn_i$$

To summarize

$$dG = -SdT + VdP + \sum_i M_i dn_i$$

$$dU = TdS - PdV + \sum_i M_i dn_i$$

$$dH = TdS + VdP + \sum_i M_i dn_i$$

$$dA = -SdT - PdV + \sum_i M_i dn_i$$

FE for

multi-comp
(extn)

② Generate Extensive Property V

$$V = V(T, P, n_1, \dots, n_m) \quad \text{where } V = U, S, G, H, \dots \text{etc}$$

Total diffent.:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P, n_1, \dots, n_m} dT + \left(\frac{\partial V}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \sum_i \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_m} dn_i$$

most all species except i hold const

$\star \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_m} = V_i \leftarrow p^{-1}$ molar propert.

What is \bar{G}_i ?

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, \text{rest}} = \mu_i$$

In general,

$$dU = \left(\frac{\partial U}{\partial T} \right)_{P, \text{rest}} dT + \left(\frac{\partial U}{\partial P} \right)_{T, \text{rest}} dP + \sum_i \bar{K}_i dn_i$$

What is the physical meaning of \bar{K}_i in a mixture?

→ Contributions per mole of component "i" to the total U of mixture

Meth Track: Euler integration

- G_{ext} = total differential for an exterior prop., Euler integral gives

$$\int \text{differential of } P \text{ intence} = 0$$

$$\int \text{differential of extence} = \text{the quality : ts. v}$$

ex: $dG = -SdT + VdP + \sum_i \mu_i dn_i$

$$\rightarrow \text{Euler } \int \rightarrow G = 0 + 0 + \sum_i \mu_i n_i \quad G = \sum_i \mu_i n_i$$

ex: $dU = TdS - PdV + \sum_i \mu_i dn_i$

$$\rightarrow \text{Euler } \int \rightarrow U = TS - PV + \sum_i \mu_i n_i$$

Applies to dU .

$$dU = \left(\frac{\partial U}{\partial T} \right)_{P, \text{rest}} dT + \left(\frac{\partial U}{\partial P} \right)_{T, \text{rest}} dP + \sum_i \bar{K}_i dn_i$$

$$\rightarrow \text{Euler } \int \rightarrow U = 0 + 0 + \sum_i \bar{K}_i n_i$$

\downarrow use \bar{K}_i from mixture
 $\bar{K}_i = \sum_j \bar{K}_i n_j$ contribution of "i" to total K of mixture (per mole i)

Mult. Comp. systems have different properties

① Total solution properties

• extence: G, U, S, \dots, K

• intence: \rightarrow density ρ $\frac{n_{\text{tot}}}{V_{\text{tot}}}$
 $K_m = \sum_i \frac{n_i}{n_{\text{tot}}} \quad g_m = \frac{m}{m_{\text{tot}}}$

② Pure species "i" properties

• extence: G_i, U_i, \dots, K_i at T, P of mixture

• intence: μ_i, g_i, \dots at T, P of mixture

③ Partial Molar properties

~~extence~~: $\underline{\mu_i} \rightarrow \bar{K}_i = \left(\frac{\partial U}{\partial n_i} \right)_{T, P, \text{rest}}$ intice

intence: $\bar{U}_i, \bar{G}_i, \dots, \bar{K}_i$

Comments: In a mixture with "i" and \rightarrow (mole fr.) \rightarrow 1

$$\bar{K}_i \approx K_{n,i} \approx K_m$$

Gibbs-Duhem Eqn (G-D)

Recall: $d\kappa = \left(\frac{\partial \kappa}{\partial T}\right)_{P, n_1, \dots, n_m} dT + \left(\frac{\partial \kappa}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \sum_i \bar{\kappa}_i d\eta_i$

$$\text{Euler } \int \rightarrow \kappa = \sum_i \bar{\kappa}_i \eta_i$$

" $T \propto \kappa$ " \rightarrow diff. prob.

$$\cancel{d\kappa = \sum_i \bar{\kappa}_i d\eta_i + \sum_i d\bar{\kappa}_i}$$

\rightarrow Eq w.r.t. $d\bar{\kappa}_i$

$$0 = -\left(\frac{\partial \kappa}{\partial T}\right)_{P, n_1, \dots, n_m} dT - \left(\frac{\partial \kappa}{\partial P}\right)_{T, n_1, \dots, n_m} dP + \sum_i \eta_i d\bar{\kappa}_i \quad \leftarrow \text{G-D} \quad \begin{matrix} \text{Handy} \\ \text{part.} \end{matrix} \leftarrow \text{to relate} \\ \text{molar prop.}$$

Ex: A binary (2-component) mixture is described by a "mixture EoS"

$$V_m = 100y_a + 80y_b + 2.5y_a y_b \quad (\text{measured } Q(T, P))$$

$$y_a = \frac{n_a}{n_a + n_b} \quad \leftarrow \text{total}$$

\Rightarrow Find \bar{V}_a, \bar{V}_b .

Recall: $\bar{V}_a = \left(\frac{\partial V}{\partial n_a}\right)_{T, P, n_b} \quad \leftarrow \text{must convert } V \text{ and its molar values of } P, n_a, \text{ & } n_b \quad \leftarrow \text{common notations!}$

To get \bar{V} :

$$V = V_m \leftarrow = (n_a + n_b) \left[\frac{100n_a}{n_a + n_b} + \frac{80n_b}{n_a + n_b} + \frac{2.5n_a n_b}{(n_a + n_b)^2} \right]$$

$$V = 100n_a + 80n_b + \frac{2.5n_a n_b}{n_a + n_b}$$

$$\bar{V}_a = \left(\frac{\partial V}{\partial n_a}\right)_{T, P, n_b} = 100 + 0 + 2.5 \left[\frac{(n_a + n_b)n_b - n_a n_b}{(n_a + n_b)^2} \right]$$

$$\text{Some approx.} \Rightarrow \bar{V}_a = 100 + 2.5(y_b - y_a y_b)$$

$$\text{and} \Rightarrow \bar{V}_b = 80 + 2.5(y_a - y_a y_b)$$

Using \Rightarrow G-D @ const T, P ,

$$0 = n_a d\bar{V}_a + n_b d\bar{V}_b$$

$$0 = n_a (2.5)(dy_b - y_a dy_b - y_b dy_a) + n_b (2.5)(dy_a - y_a dy_b - y_b dy_a)$$

$$\begin{aligned} \text{Binary mixture } y_a + y_b &= 1 \\ \Rightarrow dy_a + dy_b &= 0 \quad \left\{ \begin{array}{l} dy_a = -dy_b \\ \text{Sub. into G-D} \end{array} \right. \\ \therefore 0 &= 0 \quad \checkmark \end{aligned}$$

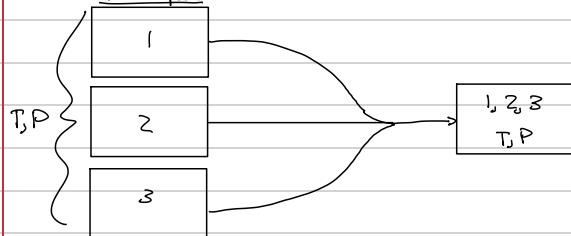
Q: What is the physical meaning of \bar{K}_i in a mixture?

- (i) Molar value of K for pure component "i"
- (ii) Excess of "i" present in mixture
- (iii) Difference b/t contribution of "i" to K in mixture vs. value of K_m
- (iv) Contribution per mole of component "i" to total K of mixture
- (v) Molar value K_m of "i" in mixture

Partial molar property

Property Changes of Mixing

Pure Species



Extensive Property change of mixing:

$$\Delta K_{mix} = K - \sum_i n_i K_{m,i} \quad \text{molar } K_m \text{ of pure}$$

$$\text{Recall: } K = \sum_i n_i \bar{K}_i$$

$$\Rightarrow \Delta K_{mix} = \sum_i x_i (\bar{K}_i - K_{m,i})$$

$$\text{and } \Delta V_{mix} = \sum_i x_i (\bar{V}_i - V_{m,i}) \quad \text{Intensive}$$

Example: Mixture of species 1, 2, 3 is described by a multicomponent EoS.

$$\rightarrow P_{mix} = RT + P^2 [A(y_1 - y_2) + B] \quad \text{A and B are for the mixture, assume known}$$

~~Find $V, V_m, V_{m1}, V_{m2}, V_{m3}, \bar{V}_1, \bar{V}_2, \bar{V}_3, \Delta V_{mix}$~~ (at some T, P)

~~Mole fractions (y_1, y_2, y_3)~~

$$\text{Defn: } y_1 = \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{n_{tot}}, y_2 = \frac{n_2}{n_{tot}}, y_3 = \frac{n_3}{n_{tot}}$$

$$\text{Ratio: } V_m = \frac{RT}{P} + P[A(y_1 - y_2 + B)]$$

$$V_{m1} = V_m (y_1 = 1, y_2 = y_3 = 0) = \frac{RT}{P} + P(A + B)$$

$$V_{m2} = V_m (y_2 = 1, y_1 = y_3 = 0) = \frac{RT}{P} + P(B - A)$$

$$V_{m3} = V_m (y_3 = 1, y_1 = y_2 = 0) = \frac{RT}{P} + P B$$

$$V = V_m n_{tot} = \frac{n_{tot} RT}{P} + P[A(n_1 - n_2) + B(n_1 + n_2 + n_3)]$$

$$\text{Mixture: } \bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, n_3} = \frac{\partial}{\partial n_i} \left(\frac{(n_1 + n_2 + n_3) RT}{P} + P[A(n_1 - n_2) + B(n_1 + n_2 + n_3)] \right)_{T, P, n_1, n_2, n_3}$$

$$\Rightarrow \bar{V}_1 = \frac{RT}{P} + P(A + B)$$

$$\bar{V}_2 = \frac{RT}{P} + P(B - A)$$

$$\bar{V}_3 = \frac{RT}{P} + P B$$

$$\Delta V_{mix} = \sum_i n_i (\bar{V}_i - V_{m,i})$$

$$= n_1 (\bar{V}_1 - V_{m1}) + n_2 (\bar{V}_2 - V_{m2}) + n_3 (\bar{V}_3 - V_{m3}) = 0$$

$$\therefore \Delta V_{mix} = 0 \quad \text{not guaranteed for this EoS}$$

specifically!

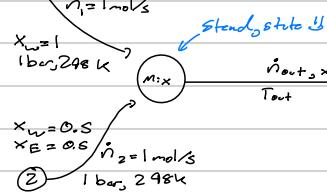
Applying to first second law problems

Example: Consider steady-state mixing of water (W) and ethanol (E).

$$\text{④ } \frac{\Delta h_{m, \text{mix}}}{R} = x_w x_E \left[-190 + 214.7(x_E - x_w) - 4.194(x_E - x_w)^2 + 383.3(x_E - x_w)^3 - 2.354(x_E - x_w)^4 \right]$$

Process

- ① $\dot{m}_1 = \dot{m}_2$ $\Rightarrow F_{\text{end}} T_{\text{out}}$!



- (i) Assume $C_{P,m}$ of all streams is constant, $C_{P,m} = 9.02 \text{ kJ/kg}$
 (ii) Assume mixing happens adiabatically, $\dot{Q} = 0$

- (1) Assume missing inputs additively, i.e.,

- (i) If shaft work is not specified, assume that there is no shaft work \Rightarrow mass守恒

$$\text{Mole Balance: } \frac{d\gamma}{dt} = 0 = \dot{n}_1 + \dot{n}_2 - \dot{n}_{\text{out}}$$

$$n_{\text{out}} = n_1 + n_2 = 2 \text{ mol/s}$$

$$1^{\text{st}} \text{ Law: } \frac{d}{dt} (C_{\text{st}} + E_{\text{in}} + E_p) = \dot{m}_1 h_m + \dot{m}_2 h_m - \dot{m}_{\text{out}} h_{m_{\text{out}}} + \dot{Q}_{\text{additive}} + \dot{Q}_{\text{loss}}$$

$$O = \dot{m}_{h_1} + \dot{m}_{h_2} - 2\dot{m}_{\text{water}} \quad \text{use mass balance} (\dot{m}_1 + \dot{m}_2 = 2\dot{m})$$

$(h_{\text{out}} - h_1) + (h_{\text{out}} - h_2) = 0$ (now to 1st supports h_{out} to get two Oh expressions)

$$\text{Property data: } \Delta h_{\text{mix,max}}, C_{p,m} \\ \text{Analog outlet ratio } x_{\text{out}} = \frac{x_{w_1}v_1 + x_{w_2}v_2}{n_{\text{out}}} = \frac{(1)(1) + (0.5)(1)}{2} = 0.75$$

For mixing streams ① and ② → ③:

$$\Delta h_{m,n;x} (x_{w,out}, T_{out}) = h_{m,out} - x_{w,out} h_{m,w} - x_{E,out} h_{m,E}$$

↑
 avg. enthalpy
 of mixture

pure component @ $T=T_{out}$

important! not
 necessarily Top
 inlet streams!

↗ occurs as latent in first law expr.

$$h_{m_{out}}(T_{out}) = \Delta h_{m_{mix}}(T_{out}, x_{w,out}) + x_{w,out} h_{mw}(T_{out}) + x_{B,out} h_{m_B}(T_{out})$$

What about b_{m_1} & b_{m_2} ?

$h_{m,i}(T_1) = h_{m,w}(T_1) \rightarrow$ pure water mixing
 \rightarrow Using similar logic as above,

$$\Rightarrow h_{m_2}(T_2) \geq h_{m_2}(T_1) = \underbrace{h_{m,m:x}(T_1, x_{w_2})}_{P_1 = P_2} + x_{w_2} h_{m,w}(T_1) + x_{E_2} h_{m_B}(T_1)$$

Book to first law--

$$\textcircled{O} = (h_{m_{out}} - h_{m_1}) + (h_{m_{out}} - h_{m_2})$$

$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$
 $T=T_{out} \quad T>T_i \quad T=T_{out} \quad T=T_2=T_i$

$$\text{infinitesimal means } h_{m,E} = h_{m,E} (\bar{T} = T_{\text{out}})$$

$$O = 2\Delta h_{m,\text{mix}}^{\text{out}} + 2x_{w,\text{out}} h_{m,w}(T_{\text{out}}) + 2(|-\chi_{w,\text{out}}|) h_{m,E}(T_{\text{out}})$$

$$-\dot{h}_{\text{nw}}(T_1) - \Delta h_{\text{nw},\text{mix}}^{\text{steam2}} - x_{w,2} h_{\text{nw}}(T_i) - (1-x_{w,2}) h_{\text{nwB}}(T_i)$$

steam 1 @ $T_{1,\text{nw}}$ \uparrow h_{nw2}

Almost true... but we have 2 temperatures $\leftarrow T_1 \& T_2$

→ use C_{pm} to express h_m 's in terms of T_{out}

→ note: C_{pm} assumed constant = 9.07 R

→ Assumed $h_m \approx h_m(T, x_i)$ only no pressure dependence, only data with liquid

$$h_{m,i}(T_i) = h_{m,i}(T_{out}) + C_{pm} (T_i - T_{out})$$

$$h_{m,E}(T_i) = h_{m,E}(T_{out}) + C_{pm} (T_i - T_{out})$$

No info given on
 $\Delta h_{m,\text{mix}}$ \Rightarrow assume
no temp.-dependence

\Rightarrow Substitute, cancel h_m 's (T_{out})

$$\therefore 2\Delta h_{m,\text{mix}}^{\text{out}} - \Delta h_{m,\text{mix}} = 2C_{pm} (T_i - T_{out})$$

$$\boxed{T_{out} = 305 \text{ K}}$$

easy to solve, T_{out} is only unknown. What about our many assumptions?

So assumption of no T-dependence of $\Delta h_{m,\text{mix}}$ is probably OK! (small ΔT)

Final Exam



Chapter 7 - Phase Equilibria, Part 2: Fugacity

Review: Partial molar properties = molar properties of species "i" in a mixture

Most Important + Partial Molar Property:

$$\bar{m}_i \equiv \left(\frac{\partial \mu}{\partial n_i} \right)_{T, P, \text{ngg}} = \bar{g}_i \quad (\text{chemical potential / partial molar gibbs free energy})$$

- μ is a control condition for equilibrium

$$M_i^A = M_i^B \text{ for phase equilibrium}$$

→ also a useful relationship for describing chemical equilibrium!

may or may not cover
in this course, depends
on time

Q: How do we calculate μ ?

→ Start with simplest case: pure component, ideal gas

• In this case,

$$m \equiv \left(\frac{\partial \mu}{\partial n} \right)_{T, P} = \left(\frac{\partial (\nu_m)}{\partial n} \right)_{T, P} = n \left(\frac{\partial \nu_m}{\partial n} \right)_{T, P} + g_m \left(\frac{\partial n}{\partial n} \right)_{T, P}^1$$

internal properties are constant
for second gasses

• $m = g_m$ for pure component

$$\Rightarrow d\mu = dg_m$$

From PE for dg_m :

$$d\mu(T, P) = v_m dP - s_m dT$$

$$d\mu = dg_m = v_m dP - s_m dT \rightarrow \left(\frac{\partial \mu}{\partial P} \right)_T \quad \left(\frac{\partial \mu}{\partial T} \right)_P$$

$$v_m = \left(\frac{\partial \mu}{\partial P} \right)_T \quad ; \quad s_m = \left(\frac{\partial \mu}{\partial T} \right)_P \quad \begin{cases} \text{true for any pure} \\ \text{component systems} \end{cases}$$

$$\text{For an ideal gas, } v_m = \frac{RT}{P}$$

we can do partial integration:

$$\mu(T, P) = \int v_m dP + f_1 = \int \frac{RT}{P} dP + f_1 \quad ; \quad \mu(T, P) = - \int s_m dT + f_2$$

Q: What can we say, mathematically, about f_1 and f_2 ?

(i) f_1 and f_2 are both constants ← not constants, these aren't total integrals!

(ii) f_1 and f_2 are both functions of T & P

(iii) $f_1(P)$ & $f_2(T)$

(iv) $f_1(T)$ & $f_2(P)$

~~Q: all of the above~~

⇒ $v_m: f_1, f_1(T)$

$$\mu = \int \frac{RT}{P} dP + f_1(T)$$

$$\left(\frac{\partial \mu}{\partial P} \right)_T = v_m = \frac{RT}{P} + \left(\frac{\partial f_1}{\partial P} \right)_T \rightarrow \left(\frac{\partial f_1}{\partial P} \right)_T = 0 \quad \text{for ideal gas as } v_m = \frac{RT}{P}$$

∴ f_1 can only depend on T !

Integrate: $\mu = \int \frac{RT}{P} dP + f_1(T)$ $P_0 = \text{reference pressure}$

$$\mu = RT \ln P + f_1(T)$$

To find $f_1(T)$, write: $\mu_1(T, P_0) = RT \ln P_0 + f_1(T)$

Solve: $\boxed{\mu(T, P) - \mu(T, P_0) = RT \ln \left(\frac{P}{P_0} \right)}$

denoted $\mu^\circ(T)$ often ← but how do you get μ° ?

Using 2nd Equat Eq : $M = - \int S_m dT + F_2(P)$
 \dots (full derivative or correct)
 $M^o(T) = [h_m(T_0, P_0) + c_{pm}(T-T_0)] - T[c_{pm} \ln(\frac{T}{T_0}) - s_m(T_0, P_0)]$
 ↳ only for ideal gas, const c_{pm} !

Common form: $M(T, P) = M^o(T) + RT \ln(\frac{P}{P_0})$

Physical interpretation of $M(T, P)$:

- M increases as P increases (for T held constant)
- relationship of $M(T, P)$ to T is more complex

For a pure ideal gas:

$$M(T, P) - M^o(T) = RT \ln(\frac{P}{P_0})$$

$\hookrightarrow M(T, P)$

→ For a multi-component mixture

$$\cdot \text{ideal gas: } M_i(T, P_i, n_1, \dots, n_m) - M_i^o(T, P_i^o, n_1, \dots, n_m) = RT \ln(\frac{P_i}{P_i^o}) \text{ where } P_i = y_i P$$

* What if G.s is not ideal?

→ Equations of state are useful!

Recall (pure component): $dM = v_m dP - s_m dT$

$$\xrightarrow[\text{const } T]{\text{Partial integral}} M(T, P) - M^o(T) = \int_{P_0}^P v_m dP$$

use v_m from EoS

$$\text{(multi-component): } dM_i = \bar{V}_i dP \quad (\text{for const } T)$$

\hookrightarrow use multi-component EoS

G.N. Lewis introduced more mathematically convenient version of M , which he called fugacities (f)

Fugacities

Definition: pure component $\rightarrow dM \equiv RT d \ln f$ (for const T)

$$M(T, P) - M^o(T) = RT \ln \left[\frac{f(T, P)}{f^o(T)} \right] \rightarrow \text{for non-ideal g.s, } f = P$$

Multi-component $\rightarrow dM_i \equiv RT d \ln \hat{f}_i$

$$\xrightarrow[\text{const } T]{\text{Partial integral}} M_i(T, P, n_1, \dots, n_m) - M_i^o(T, P_o, n_1, \dots, n_m) = RT \ln \left(\frac{\hat{f}_i}{f_i^o} \right)$$

Definition is like an "effective pressure" for a real gas

→ For real gas, ① $\lim_{P \rightarrow 0} f = P$ at ∞T

$$\text{② } \lim_{P_i \rightarrow 0} \hat{f}_i = P_i \text{ at } \infty T, y_i$$

These give convenient boundary conditions that make calculating f 's and \hat{f} 's more straightforward

Fugacities at Phase Equil (multi-component)

Recall: $M_i^a = M_i^B @ \text{equl}$

$\rightarrow dP_{\text{fugacity}} \equiv dm_i^a = dM_i^B$

def'n $\hat{f}_i \rightarrow RT d \ln \hat{f}_i^a = RT d \ln \hat{f}_i^B$

→ Integrate: $\int_{P_{ref}}^{P_a} d \ln \hat{f}_i^a = \int_{P_{ref}}^{P_B} d \ln \hat{f}_i^B$

$$\Rightarrow \ln \left(\frac{\hat{f}_i^a}{\hat{f}_i^B} \right) = \ln \left(\frac{P_a}{P_B} \right) \rightarrow \boxed{\hat{f}_i^a = \hat{f}_i^B} @ \text{phase equil.}$$

Calculating f for pure real g.s.

$$P_{\text{ext}} + \int \nu_m dP = RT d \ln f \rightarrow \frac{RT}{\nu_m} d \ln f = dP$$

(const T)

We can use EoS to get f
 (i) Clausius EoS $\rightarrow P = \frac{RT}{\nu_m - b}$ $b > 0$ molecular volume

$$\text{Solve for } \nu_m \rightarrow \nu_m = \frac{RT}{P} + b$$

$$\text{Sub} \rightarrow RT d \ln f = \left(\frac{RT}{P} + b \right) dP$$

$$\int_{P_{\text{low}}}^P d \ln f = \int_{P_{\text{low}}}^P \left(\frac{1}{P} + \frac{b}{RT} \right) dP \Rightarrow \ln \left(\frac{f}{P_{\text{low}}} \right) = \ln \left(\frac{P}{P_{\text{low}}} \right) + \frac{b}{RT} \left(P - P_{\text{low}} \right)$$

Use BC that $f(P_{\text{low}}) > P_{\text{low}}$

$$\therefore \ln f - \ln P_{\text{low}} = \ln P - \ln P_{\text{low}} + \frac{bP}{RT}$$

$$\ln \left(\frac{f}{P} \right) = \frac{bP}{RT} \quad \leftarrow \text{of tr., we use def'n: } \phi = \frac{f}{P}$$

$$\ln(\phi) = \frac{bP}{RT}; f = P_{\text{exp}} \left(\frac{bP}{RT} \right)$$

fugacity coefficient

Q: For the Clausius EoS $f = P_{\text{exp}} \left(\frac{bP}{RT} \right)$.

For a gas that obeys the Clausius EoS

$$(i) f > P \rightarrow b, P, R, RT > 0, \text{ so } f > P \text{ for } \ln \left(\frac{f}{P} \right) \text{ to be positive!}$$

$$(ii) f < P$$

$$(iii) f = P$$

(iv) It depends

Q: What does fugacity represent?

(i) An effective pressure the pressure a gas is feeling it has units of pressure!

(ii) A different form of chemical potential related logarithmically just a math tool used to handle

X (iii) A standard entropy

(iv) A confining variable

(v) A criterion of phase equilibrium yes!

We use it:

$$dM = RT d \ln f = \nu_m dP$$

P const. /
const T

This approach works well if we can solve for ν_m

$$\rightarrow \text{If not, } RT d \ln f = - \left(\frac{\partial P}{\partial \nu_m} \right)_{T, P} dV \text{ For e.g. pure component fugacities}$$

↳ this is equivalent to the former, but is more useful if one can't directly solve for ν_m (e.g. VDW)

Optional Exercise: Shows some result for $P = \frac{RT}{\nu_m - b}$

derivation on curves,
will be on Eq sheet

Q: For water at 114 atm, 647 K

possible reasons

(i) $f > P$ → molecules have volume

(ii) $f < P$ → molecules H-bonds (attractions)

(iii) $f = P$ → ideal gas? ... skeptical

This problem is answered on the next page

Example: Calculate properties of H_2O at 647K and 114 atm using:

- a) ideal gas b) Steam tables c) Vdw EoS

a) Ideal Gas: $f = P/114 \text{ atm}$ for 1.6.

b) Steam Tables

$$dP/f = dT \ln f = v_m dP = -\left(\frac{\partial P}{\partial T}\right)_{T_0} dP$$

$$\int dP = RT \int d \ln f \quad \text{no EoS!} \quad \text{no Eq. to ill!!}$$

$$u(T, P) - u(T_0, P_0) = RT \ln\left(\frac{f}{f_0}\right)$$

$$\rightarrow u(T, P) = g_m(T, P) \quad \text{for a pure component}$$

$$= h_m(T_0, P) + TS_m(T, P) \quad \text{3 look up } h, s \text{ in steam tables}$$

\rightarrow what is P_0 ?

use $P_0 = P_{low} = 10 \text{ kPa}$ (lowest P in superheated steam tables)

$$\text{look up: } \begin{cases} h^0 = 322.9 \text{ kJ/kg} \\ s^0 = 0.826 \text{ kJ/kg K} \end{cases}$$

$$\begin{cases} h = 247.9 \text{ kJ/kg K} \\ s = 0.6 \text{ kJ/kg K} \end{cases}$$

\rightarrow look up ϕ : 647K, 114 atm (interpolate):

$$\begin{cases} h = 247.9 \text{ kJ/kg K} \\ s = 0.6 \text{ kJ/kg K} \end{cases}$$

$$\therefore M_w(M - M^0) = (2031 \text{ kJ/kg}) = M_w \times RT \ln\left(\frac{f}{P_0}\right) = (M_w) \times RT \ln\left(\frac{f}{P_0}\right)$$

$$\Rightarrow f = 899 \text{ Pa}$$

$$f \neq P$$

$$f = 88.8 \text{ atm}, \phi = \frac{f}{P} = 0.88 \quad \text{H bonding attractions win}$$

↪ best results if use proper data

c) Vdw EoS

$$a = \frac{27}{64} \frac{(RT_0)^2}{P_0} = 0.854 \quad b = 3.05 \times 10^{-5} \quad (\text{SI units})$$

$$RT d \ln f = v_m dP = -\left(\frac{\partial P}{\partial T}\right)_{T_0, P_0} dV \quad \text{Skip part don't... (See Ex 2.2 in Vorotely)}$$

$$\Rightarrow \ln(\phi) = -\ln\left(\frac{(v_m - b)P}{RT}\right) + \frac{b}{v_m - b} - \frac{2a}{RTv_m}$$

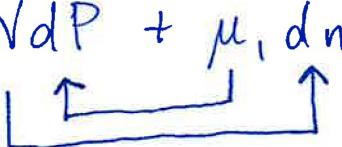
Solve numerically for v_m

$$\text{Find } \boxed{P = 96 \text{ atm}, \phi = 0.84}$$

understand other notes,
but still does fine → II

Fugacities (gas-phase) with multiple components

Recall: $dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \dots$



Maxwell relations (multicomponent):

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T, n_1, \dots} = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} = \bar{V}_1$$

In general,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \dots} = \bar{V}_i$$

Partial integral $\rightarrow d\mu_i = \bar{V}_i dP$

We have: $d\mu_i = \bar{V}_i dP = RT d\ln \hat{f}_i$ "i" in mixture

\bar{V}_i replaces
 V_m



Combine: $RT d\ln \hat{f}_i = \bar{V}_i dP$

BC's: $\hat{f}_i(P_{i,low}) = P_{i,low}$

$$\hat{f}_i(P_{i,low}) = y_i P_{low}$$

This works if we can solve an EOS for \bar{V}_i

→ multicomponent EOS

→ solvable for \bar{V}_i

If we can't solve for \bar{V}_i (e.g. VdW EOS for mixtures)

$$d\mu_i = RT d \ln \hat{f}_i = \bar{V}_i dP = - \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq i} dV$$

* derivation on canvas

Substitute and use BC's:

$$RT \ln \left(\frac{\hat{f}_i}{y_i P_{low}} \right) = - \int_{V_{ideal} = \frac{nRT}{P_{low}}}^V \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq i} dV$$

where $y_i P_{low} = P_{i, low}$

Ex : We have a 2-component gas mixture w/ EOS

$$P = \frac{RT}{v_m - b}$$

where b obeys a simple "mixing rule"

$$b = y_1 b_1 + y_2 b_2$$

↑ ↑
pure component 1 pure component 2

Calculate : $\hat{\phi}_1 = \frac{\hat{f}_1}{P_1}$

Use dV form of integral $\rightarrow \left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} dV$

$$V_m = \frac{V}{n_{tot}} = \frac{V}{n_1 + n_2}$$

$$P = \frac{RT}{V_m - b} = \frac{RT}{\frac{V}{n_1 + n_2} - y_1 b_1 - y_2 b_2} = \frac{(n_1 + n_2) RT}{V - n_1 b_1 - n_2 b_2}$$

$y_1 = \frac{n_1}{n_1 + n_2}$

$$\begin{aligned} \left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} &= \frac{RT(V - n_1 b_1 - n_2 b_2) - RT(n_1 + n_2)(-b_1)}{(V - n_1 b_1 - n_2 b_2)^2} \\ &= \frac{RT}{V - n_1 b_1 - n_2 b_2} + \frac{RT b_1 (n_1 + n_2)}{(V - n_1 b_1 - n_2 b_2)^2} \end{aligned}$$

$$\begin{aligned}
 RT \ln\left(\frac{\hat{f}_i}{y_i P_{low}}\right) &= - \int_{V^{id}}^V \left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} dV \\
 &= -RT \ln\left(\frac{V - n_1 b_1 - n_2 b_2}{V^{id} - n_1 b_1 - n_2 b_2}\right) \\
 &\quad + RT b_1 (n_1 + n_2) \left[\frac{1}{V - n_1 b_1 - n_2 b_2} - \frac{1}{V^{id} - n_1 b_1 - n_2 b_2} \right]
 \end{aligned}$$

$$V^{id} \gg n_1 b_1 + n_2 b_2$$

$$RT \ln\left(\frac{\hat{f}_1}{y_1 P_{low}}\right) = -RT \ln\left(\frac{V - n_1 b_1 - n_2 b_2}{V^{id}}\right) + RT b_1(n_1 + n_2) \left[\frac{1}{V - n_1 b_1 - n_2 b_2} - \frac{1}{V^{id}} \right] \approx 0$$

$\stackrel{R = nRT/P_{low}}{\cancel{RT}}$

$$\ln\left(\frac{\hat{f}_1}{y_1 P_{low}}\right) = -\ln\left(\frac{V - n_1 b_1 - n_2 b_2}{nRT/P_{low}}\right) + b_1(n_1 + n_2) \left[\frac{1}{V - n_1 b_1 - n_2 b_2} \right]$$

$$\ln\left(\frac{\hat{f}_1}{y_1}\right) = -\ln\left[\frac{V - n_1 b_1 - n_2 b_2}{(n_1 + n_2)RT}\right] + \frac{b_1(n_1 + n_2)}{V - n_1 b_1 - n_2 b_2}$$

$$\hat{\phi}_1 = \frac{\hat{f}_1}{y_1 P} \quad \rightarrow \text{subtract } \ln P \text{ from both sides}$$

$$\ln \hat{\phi}_1 = \ln\left(\frac{\hat{f}_1}{y_1 P}\right) = -\underbrace{\ln\left[\frac{P(V - n_1 b_1 - n_2 b_2)}{(n_1 + n_2)RT}\right]}_{\frac{P}{RT}(V_m - b)} + \frac{b_1(n_1 + n_2)}{V - n_1 b_1 - n_2 b_2}$$

$$\frac{P}{RT}(V_m - b) = 1! \rightarrow \ln(1) = 0!$$

$$\therefore \boxed{\ln \hat{\phi}_1 = \frac{b_1}{v_m - b}}$$

obeys mixing rule,
depends on composition ($y_1 + y_2$)

side note:

$$\begin{aligned}
 \frac{b_1 (n_1 + n_2)}{V - n_1 b_1 - n_2 b_2} &= \frac{b_1}{\frac{V - n_1 b_1 - n_2 b_2}{n_1 + n_2}} \\
 &= v_m - y_1 b_1 - y_2 b_2 = v_m - b
 \end{aligned}$$

In some cases, it's possible to simplify multicomponent \hat{f}_i 's using Lewis Fugacity Rule (LFR):

$$\text{Recall: } \hat{\phi}_i = \frac{\hat{f}_i}{y_i P} \longleftrightarrow \hat{f}_i = y_i \hat{\phi}_i P$$

Lewis Fugacity Rule:

$$\hat{\phi}_i(T, P_{\text{total}}, n_1, \dots, n_m) = \underbrace{\phi_i(T, P_{\text{total}})}_{\text{"i" in mixture}} \quad \underbrace{\phi_i(T, P_{\text{total}})}_{\text{pure "i"}}$$

$\hat{\phi}_i$ or ϕ_i is deviation of "i" from ideality
(ϕ is 1 for an ideal gas)

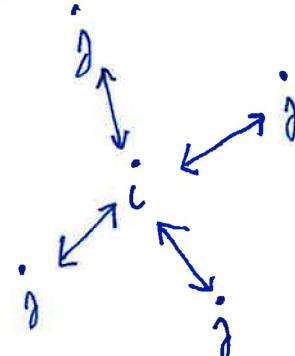
∴ LFR says, under certain circumstances, "i" has the same non-ideality in mixture and in pure form

When is LFR \approx true?

- 1) If "i" is chemically similar to all other components "j".

$$\text{if } i-i \approx i-j$$

ex: different alkanes
 $(\text{CH}_4 + \text{C}_2\text{H}_6)$
 $(\text{C}_6\text{H}_6 + \text{C}_2\text{H}_6)$



- 2) If P_{total} is small, all components behave ideally, and $\hat{\phi}_i = \phi_i = 1$

- 3) If $y_i \rightarrow 1$, then "i" will interact mostly with itself and follow LFR