



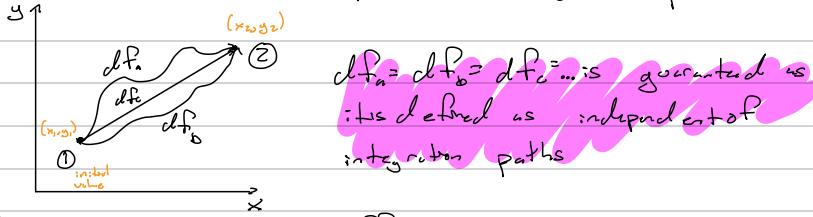
# Midterm Exam 1

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# 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

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

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

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

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

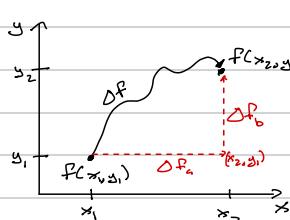
**Summary - Common points of confusion!**

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!

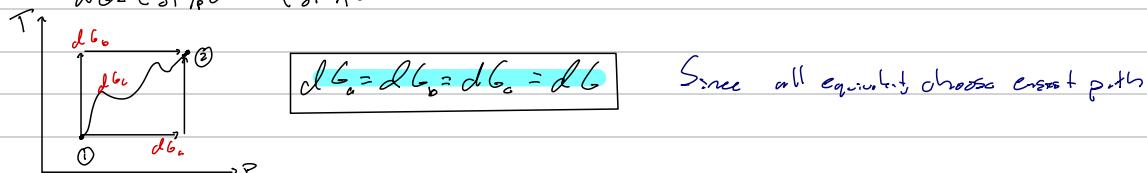
$\times \Rightarrow \int \frac{df}{dx}$  cannot be evaluated! Missing the differential!

$\hookrightarrow$  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  $\delta Q$  and  $\delta W$  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.

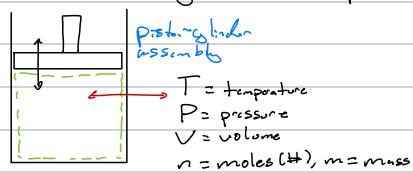
① System and Surroundings



• 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  $P, T, n, V, \rho$ )

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

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

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

$P$	$V$	$T$	$n$
↑ intensive ( $C_{\text{int}}$ )	↑ extensive ( $C_{\text{ext}}$ )	↑ 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:

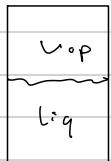
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑  
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  $\text{H}_2\text{O}$



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

↓  
molar of  $\text{H}_2\text{O}$

↓  
molar of  $\text{H}_2\text{O}$

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

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

↑  
average molar volume

↑  
 $x \equiv \text{"quality"}$

$$\text{Also: } \beta = (1-x) \beta_L + x \beta_V$$

We can't for example specify  $V_m$  for each phase

→ constrains all other intensive properties

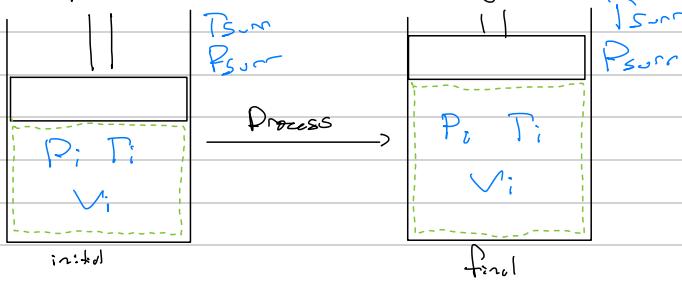
Also need to specify total amount in each phase

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

$Q_{\text{liq}} = \text{mole or mass fraction of } \text{H}_2\text{O}$   
for saturated (vapor) mixture

## 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  $\rightarrow P_{\text{sys}} = P_{\text{sum}}$

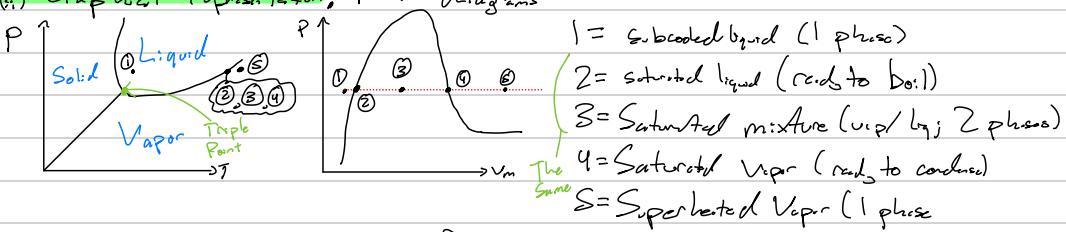
(iii) Phase Equilibrium  $\rightarrow$  Composition of phases is constant

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

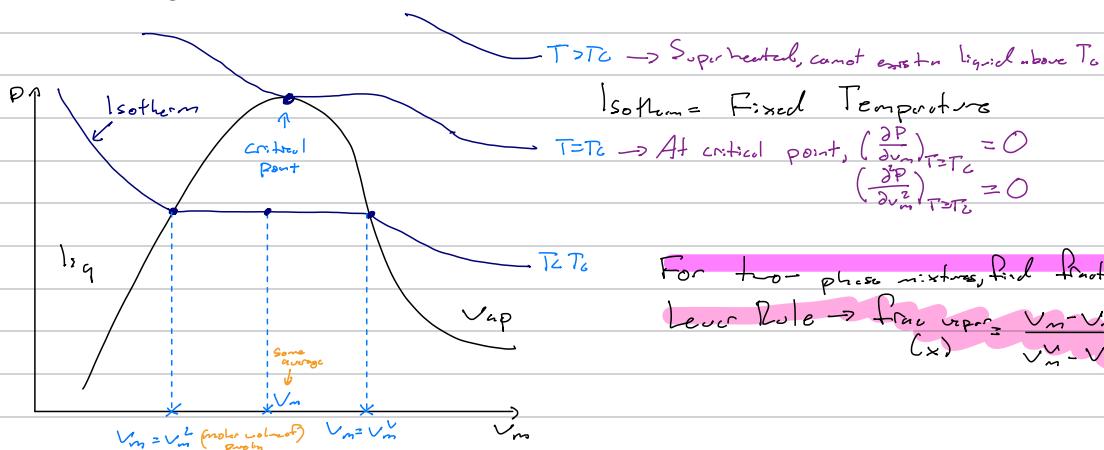
## Thermodynamic Property Sources

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

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



$T > T_c \rightarrow$  Superheated, cannot exist in liquid above  $T_c$

Isotherm = Fixed Temperature

$$T = T_c \rightarrow \text{At critical point, } \left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

For two-phase mixtures, find fraction of vapor using mass balance

$$\text{Lever Rule} \rightarrow \text{frac vapor} = \frac{V_m - V_m^L}{V_m - V_m^V} \quad (x) \quad (\text{Dowden's Camera})$$

(iii) Thermodynamic Tables (ex. steam tables  $\rightarrow$  Appendix B of Kotzschky)

• 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:  $U_m, U_m, h_m, \dots$

**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)

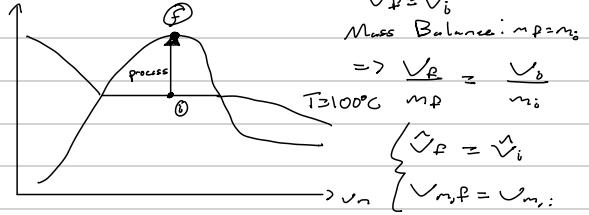
$$V_f = 100L = V_i$$

$$T_f = T_c$$

$$P_f = P_c$$

process

→ critical point



b) Find the mass and initial quality.

(outlines)

→ 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 →  $V_{i,g} = 0$

$$M = \frac{V}{V} = \frac{100 L}{0.0033155 \frac{m^3}{kg}} \times \frac{1 m^3}{1000 L} = 31.6 \text{ kg}$$

(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  $E_{\text{univ}}$ ?

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

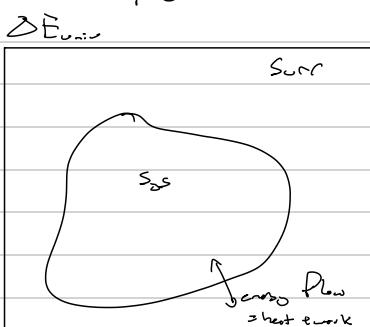
- phase changes

- 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

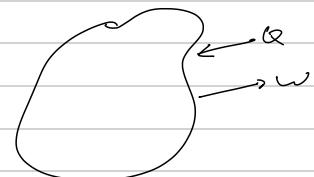
Q: Heat and work are flowing across the system boundary. What can we say about  $Q$  and  $W$ ?

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.)

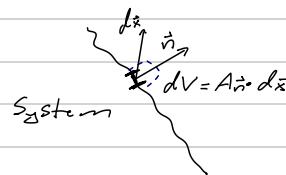
② Work ( $W$ ): this class!

a) System boundary moves against an external force

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

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

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



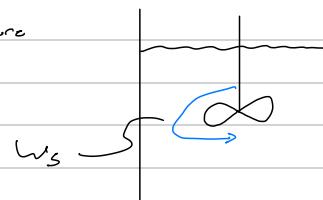
→ Calculating PV work requires us to know external pressure

\*  $P_E$  does not always equal  $P_{\text{ext}}$

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

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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

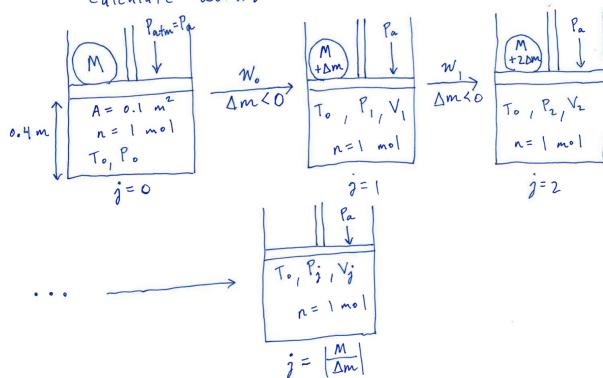
$$\frac{W}{n} = w_m = - RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

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

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

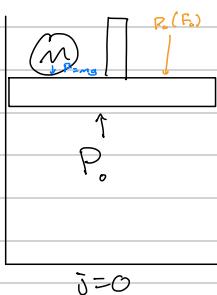
• PV work def'n →  $W = - \int P_E dV$  external pressure

↳ what is  $P_E$ ?

• At eq.  $P_E$  should equal  $P_{\text{ext}}$

• pressure / force balance:

### Pressure / Force Balance



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

cross-section area of piston

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

$\Delta m < 0$  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. law

$P_1 V_1 = P_0 V_0$

$$\text{Now, sub } P's \text{ from force balance} = -V_0 \left[ (P_1 + \frac{Mg}{A}) - (P_0 + \frac{Mg + \Delta mg}{A}) \right] = +V_0 \cdot \frac{\Delta mg}{A} < 0$$

negative indicates S<sub>o</sub> class work

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

$(\text{from } j=1 \text{ to } j=2)$

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

$P_0$

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

Expansion → S<sub>o</sub> class work

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)

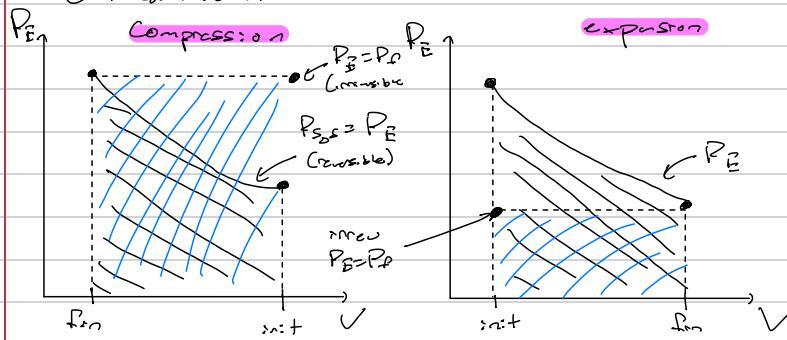
This is a reason why assuming a reversible process can be convenient.  $W_{\text{re}} = -5545 \text{ J}$

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  $\Delta U$  ( $dU$ )?

→ 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)

1<sup>st</sup> Law:  $dU_m = \delta q_m - Pdv_m$  ( $P_E = P$ )

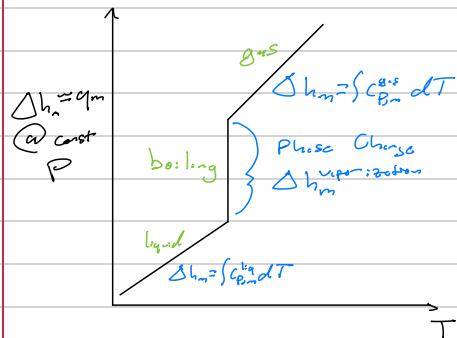
$dU_m = \delta q_m - d(PV_m)$  can make this more only bc Pressure P is constant

$$dU_m + d(PV_m) = \delta q_m$$

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

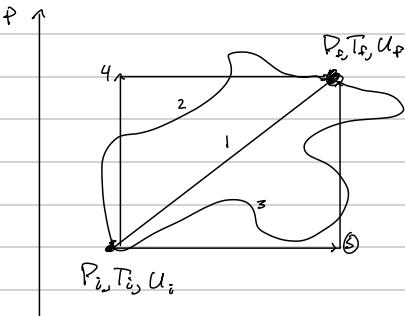
$\leftarrow$  measure T to determine  $h_m$  &  $C_{p,m}$

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



## Calculation Paths

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

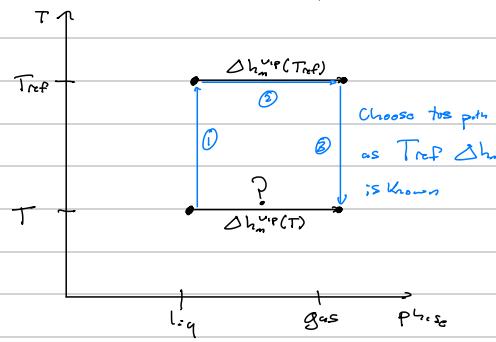


$$\Delta U = U_f - U_i$$

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

True for any process!

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



\*  $T_{ref}$  is usually 298K

Solution:

$$\Delta h_m^{vp}(T) = \Delta h_{m1} + \Delta h_{m2} + \Delta h_{m3}$$

$$\textcircled{1} \text{ Single phase heating/cooling} \quad \Delta h_{m1} = \int_{T_{ref}}^T C_{P,m}^{lq} dT$$

$$\textcircled{2} \text{ Phase change @ } T_{ref}; \Delta h_{m2} = \Delta h_m^{vp}(T_{ref})$$

$$\textcircled{3} \text{ Single phase cooling/heating} \quad \Delta h_{m3} = \int_{T_{ref}}^T C_{P,m}^{ss}(T) dT$$

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

## 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

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

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

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

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

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

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

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

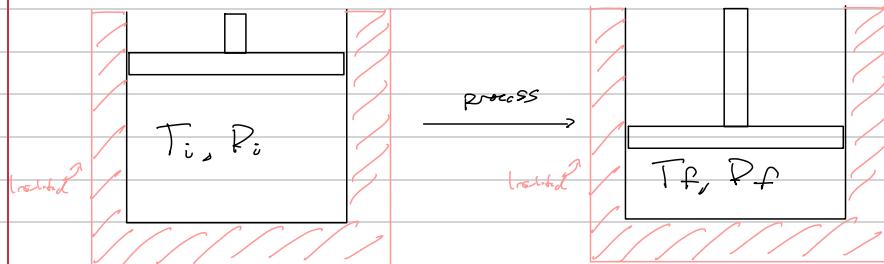
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

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

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

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

**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  $P_{\text{bulk}}$ )
- Reversible  $P_B = P$

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

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

$$\cancel{n} C_{v,m} dT = -\cancel{\frac{nRT}{V}} dV$$

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

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

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

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

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

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

### Final Notes on Ideal Gas Heat Capacities

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

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

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



1.G.

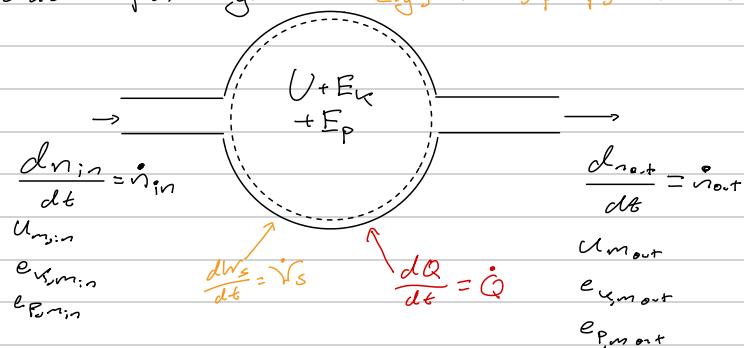
$$C_{p,m} = C_{v,m} + R$$

↑ from  $\partial T$   
only

(for ideal gas)

↑ from  $\partial T$   
only

## 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?

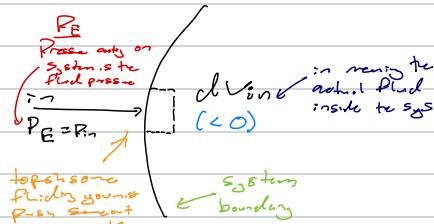
→ Flow Work

Rate of flow work:

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

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

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



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

$= \text{flow work per mol}$

→  $P > 0, V_m > 0$ , 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

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

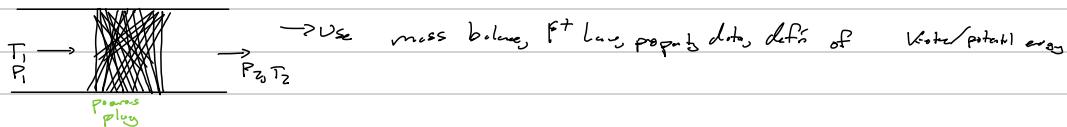
accumulation of moles

- Total mass/mole accumulation:

$$\Delta n = \dot{\nu}_{in} t - \dot{\nu}_{out} t = \int_{t_0}^{t_f} d\dot{m}$$

## 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)

$e_{kin} \approx 0$  (smaller than  $u^2$ ) ← 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

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

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

mole basis } independent of fluid  
mass basis } of fluid

a) Let's assume fluid is water:

$T_1 = 350^\circ\text{C}$

$P_1 = 10 \text{ MPa}$

→  $T_2 ?$   
 $P_2 = 1 \text{ bar}$

Find  $T_2$ !

$\stackrel{\text{Superheated}}{\rightarrow} h_1 = \hat{h}(350^\circ\text{C}, 10 \text{ MPa}) = 2923.4 \frac{\text{kJ}}{\text{kg}}$   
by law  $\hat{h}_2 = \hat{h}_1$  since  $\Delta h = 0$

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,  $\hat{h}(200^\circ\text{C}) = 2875.3 \quad \hat{h}(250^\circ\text{C}) = 2974.3$  } Superheated

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

→  $\boxed{T_2 = 224.293^\circ\text{C}}$

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  $\Rightarrow P$

Why?

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

$\Delta h_m = 0$

$\Delta h_m = \int_{T_1}^{T_2} dh_m = 0$  (Change in properties is constant of diffn.)

→ Ideal G.s.:  $h_m = h_m(T)$  only

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

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

$\rightarrow C_{pm}(T_2 - T_1) = 0 \Rightarrow T_2 = T_1 = 350^\circ\text{C}$  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

$$S_o \quad \hat{h}_m = \hat{h}_1 + T_2 - T_1$$

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

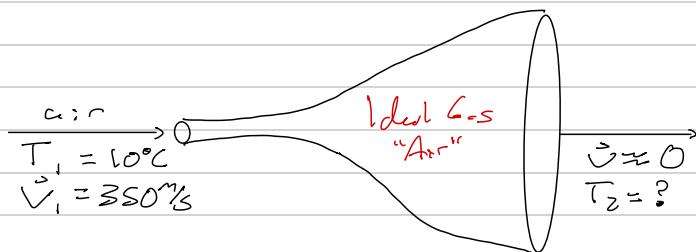
3) Flows in open systems have enthalpy  $\hat{h}_m$ , but not internal energy. Of course they have internal energy!

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  $\dot{Q} = 0$

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

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

$$\cdot \text{Simpl. 1st Law: } \hat{h}_2 = \hat{h}_1 + \hat{e}_{k,m} \quad (\text{Solving on a mass basis is bc of kinetic energy})$$

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

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

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

ideal g.s.

"Air": assuming ideal gas

$$\rightarrow \text{From Koretz } K_{20} \quad \hat{C}_{p,m} \approx 3.355 \text{ J}$$

$$\text{constant } C_p \quad \frac{K}{2 \text{ kg/mole}} \hat{C}_p = \frac{C_p}{M W_{air}} \leftarrow (-28 \times 10^{-3} \text{ kg/mol})$$

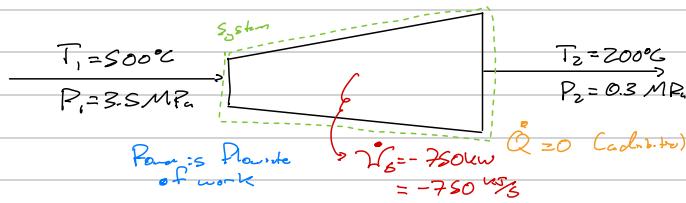
$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,m} \rightarrow T_2 = \frac{\hat{e}_{k,m}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ\text{C}$$

\*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  $750 \text{ kW}$  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  $h_{in}$ ,  $h_{out}$ )

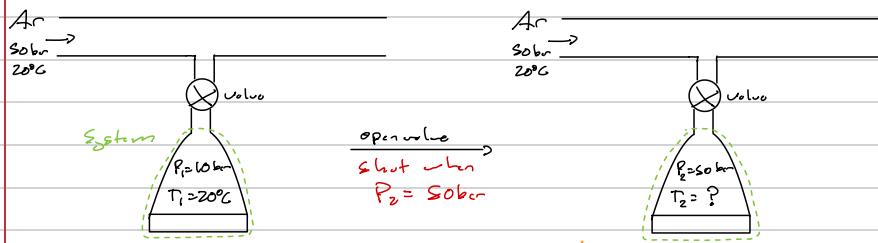
$$\dot{m} = \frac{-750 \text{ kW}}{2865.9 - 3451 \frac{\text{kJ}}{\text{kg}}} = 1.28 \frac{\text{kg}}{\text{s}}$$

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

$$\frac{dU}{dt} = \dot{m}_{in} h_{min} - \dot{m}_{out} h_{max} + \dot{W}_s$$

MB

$$\left( \frac{dU}{dt} = \dot{m}_{in} h_{min} \right) \downarrow \frac{dn}{dt} \neq 0 \text{ (not steady state)}$$

Gas flows into tank

$$\int_{U_1}^{U_2} dU = \int_{h_{min}}^{h_{max}} dn$$

Gas insulation

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

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

$$n_2 U_{m,2} - n_1 U_{m,1} = h_{m,in} (n_2 - n_1)$$

$$\rightarrow n_1 (h_{m,in} - U_{m,1}) = n_2 (h_{m,in} - U_{m,2})$$

$$\text{defn: } h_m = U_m + P_m \rightarrow h_{m,i} = U_{m,i} + P_{T_i}$$

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

$$\rightarrow n_1 [(h_{m,in} - U_{m,1}) + RT_1] = n_2 [(h_{m,in} - U_{m,2}) + RT_2]$$

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

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

$$\rightarrow \text{sub } n_2 \text{ in } \rightarrow T_2 = \frac{\frac{S_2}{P_2} T_1}{\frac{S_1}{P_1} + \frac{3}{2}} = 187.9^\circ\text{C}$$

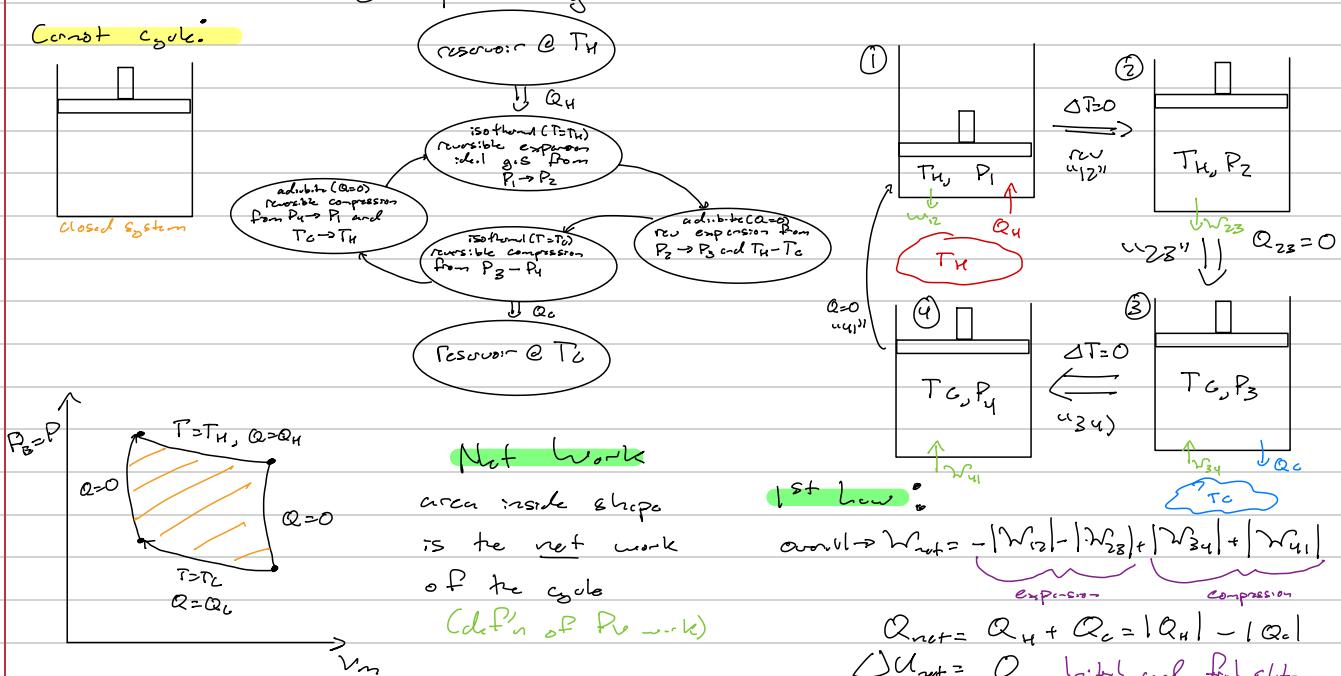
$$(C_{p,m} = \frac{5}{2} R)$$

# 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.  
 →  $\Delta S$  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 ( $T=T_H$ )

$$\rightarrow 1\text{st Law: } \Delta U_{12} = Q_{12} + W_{12} \quad W_{12} = -Q_{12}$$

$$\Delta U_{12} = n \int_{P_1}^{P_2} C_v dT \Rightarrow T_1 = T_2 = T_H \text{ so } \Delta U_{12} = 0$$

$$\Rightarrow \begin{cases} W_{12} = nRT_H \ln \left( \frac{P_2}{P_1} \right) < 0 & \text{expansion} \\ Q_{12} = Q_H = -W_{12} = -nRT_H \ln \left( \frac{P_2}{P_1} \right) \end{cases}$$

$$\begin{aligned} W_{12} &= - \int P_2 dV = -n \int P_2 dV \\ \text{reverse} &= -n \int P_2 dV \\ &= -n \int \frac{RT_H}{V} dV \\ &= -n \int_{V_{12}}^{V_{21}} \frac{RT_H}{V} dV \\ &\rightarrow W_{12} = -nRT_H \ln \left( \frac{V_{21}}{V_{12}} \right) \end{aligned}$$

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

adiabatic, reversible, constant  $C_p, m$

$$\rightarrow PV^k = \text{constant}$$

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

→ solve  $P_3$  and  $R_1$  in terms of  $P_1, P_2$  &  $P_3$

$$"23" \text{ is adiabatic} \rightarrow P_2 V_2^k = P_3 V_3^k$$

$$"41" \text{ is adiabatic} \rightarrow P_4 V_4^k = P_1 V_1^k$$

$$\begin{aligned} \frac{P_3}{P_2} &= \frac{P_4}{P_1} \\ \text{Substitute} \end{aligned}$$

$$\Delta U_{12} = nRT_H \ln \left( \frac{P_2}{P_1} \right)$$

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

\* 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

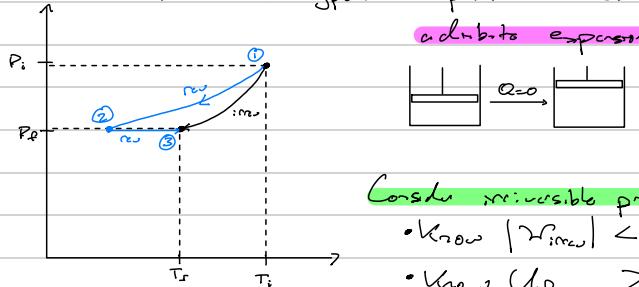
Q: Which process has the most positive change of the fluid P  $\Delta S_m$ ?

- 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  $\Delta S$  for irreversible processes

- Construct a hypothetical path consisting of only reversible processes



Process '12'

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

Consider irreversible process (1  $\rightarrow$  3)

- Know  $|W_{12, \text{irr}}| < |W_{12, \text{rev}}|$  For expansion ( $\text{H}_2\text{O}$ )
- Know  $U_{3, \text{irr}} > U_{3, \text{rev}}$
- Since  $S$  is a state function,

$$\Delta S_{13} = \Delta S_{12} + \Delta S_{23} \quad \begin{matrix} \text{(defining this to} \\ \text{be a reversible} \\ \text{process)} \\ \text{at constant Pressure,} \\ \text{not adiabatic} \end{matrix}$$

How to get from  
S<sub>2</sub> to S<sub>3</sub>?

$$\Delta S_{23} = \int_{T_2}^{T_3} \frac{dQ_{23}}{T} \quad \begin{matrix} \text{"23"} \\ \text{(constant P)} \end{matrix}$$

$$\begin{aligned} 1^{\text{st Law: }} \quad dU &= dQ + PdV \\ dQ &= dU + PdV \end{aligned}$$

$$dQ = dU + PdV$$

$$\Delta Q = dU + PdV$$

$$\Delta Q = dH$$

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

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

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!

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

### $\Delta S$ for Surroundings

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

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

$$\delta Q_{\text{surv}} = -\delta Q \quad \begin{matrix} \text{real heat} \\ \text{transfer} \\ \text{not law} \end{matrix} \quad \rightarrow \text{From perspective of surroundings, my change in } S_{\text{surv}} \text{ is tiny} \\ \therefore \text{always seems like reversible } Q_{\text{surv}}$$

In our previous example...

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

$\Delta S_{\text{surv}}$  is also 0 for adiabatic processes.

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

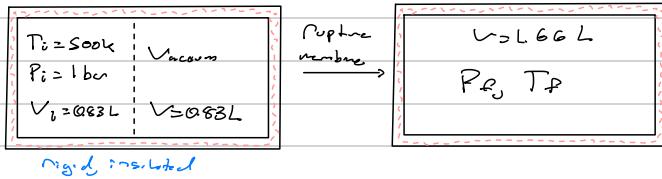
$$\Delta S_{12} = 0, \Delta S_{\text{surv}} = 0 \quad \text{reversible}$$

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  $\rightarrow$  not reversible due to sudden expansion

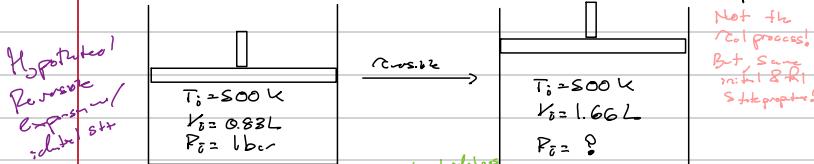
• 1st Law:  $\Delta U = Q + W \xrightarrow{\text{adiabatic}} \text{no } Q, \text{ no } W \rightarrow \Delta U = 0$  (constant volume system)

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

What about  $\Delta S$ ?

→ use a convenient reversible calculation path! ( $\Delta S$  is a state function / thermodynamic property)

→ must define a reversible calculation path,  $\delta S = \frac{\delta Q_{\text{rev}}}{T}$



$$\Rightarrow \Delta S_{\text{calc}} = \Delta S_{\text{real process}}$$

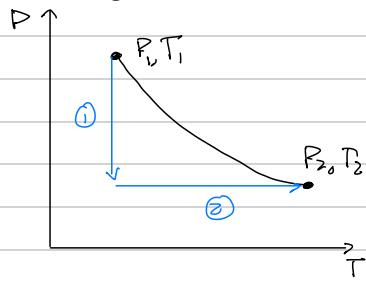
$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = \int \frac{dU_{\text{real}} - dU_{\text{hypoth}}}{T} = - \int \frac{\delta W_{\text{rev}}}{T} = - \int \frac{-P_{\text{ext}} dV}{T} = \int \frac{P_{\text{ext}} dV}{T} \xrightarrow{\text{isothermal}} = n \int_{V_i}^{V_f} \frac{P}{V} dV = n R \ln \left(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

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

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

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

## 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 ( $c_v + c_p$ )

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

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

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

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

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

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  $\Delta S_{univ}$  for any process?

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

Example: 1 mol liquid H<sub>2</sub>O @ P=1 bar. T increases from 28°C to 50°C. Calculate  $\Delta S$ ,  $\Delta S_{sum}$

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

• Develop an expression for  $\Delta S$

→ 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

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

•  $\Delta S_{sum}$ : use real heat transfer

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

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

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

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

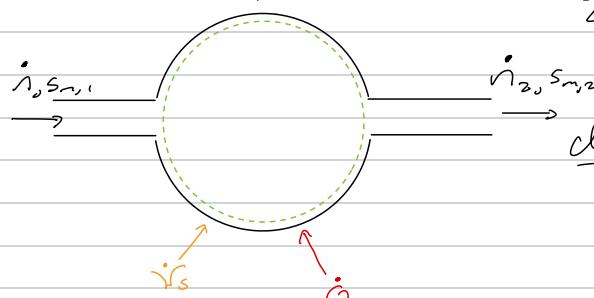
$$T_{sum} \mid \Delta S_{univ} = \Delta S + \Delta S_{sum}$$

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

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

Both  $\Delta S_{univ}$  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: fast steady state

(pol heat transfer)

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

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

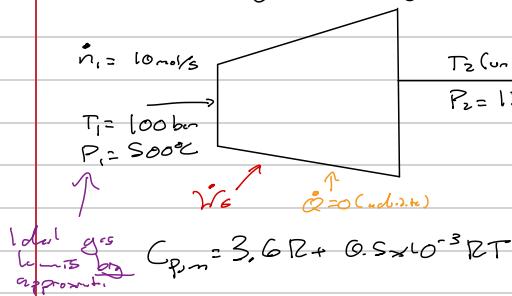
$\hookrightarrow$  steady  $\Rightarrow$  static  $\rightarrow \frac{dS_{\text{sys}}}{dt} = 0 \Rightarrow \frac{dS_{\text{univ}}}{dt} = \dot{n}_2 S_{m,2} - \dot{n}_1 S_{m,1} - \frac{\dot{Q}}{T_{\text{sum}}}$

## 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



- a) Maximum amount of power that can be generated?  
 $\hookrightarrow$  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:  $\Delta S_{\text{univ}} = 0$

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

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

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

$$\dot{W}_s = \dot{n} \int_{T_1}^{T_2} C_{P,m} dT \quad \text{temp. dependent}$$

$\hookrightarrow$  Be careful! don't skip steps

$\rightarrow$  1<sup>st</sup> L., 2 unknowns ( $\dot{W}_s, T_2$ )

Need more equations  $\rightarrow$  2<sup>nd</sup> L.

2<sup>nd</sup> Law to get  $T_2$ :

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

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

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

$$\text{prop. of } \dot{S}_m = \frac{C_{P,m}}{T} dT - \frac{R}{P} dP$$

ideal g.  
 (ideal gas assumption only)

$\rightarrow$  Back to 1<sup>st</sup> L.

$$\dot{W}_{\text{rev}} = \dot{n} \int_{T_1=273K}^{T_2=282K} (3.6 + 0.5 \times 10^{-3} T) dT = -173.2 \frac{kJ}{s} \xrightarrow{\text{max power}} \dot{W}_{\text{rev}} = -173.2 \text{ kW}$$

so work done  
 on surroundings

**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

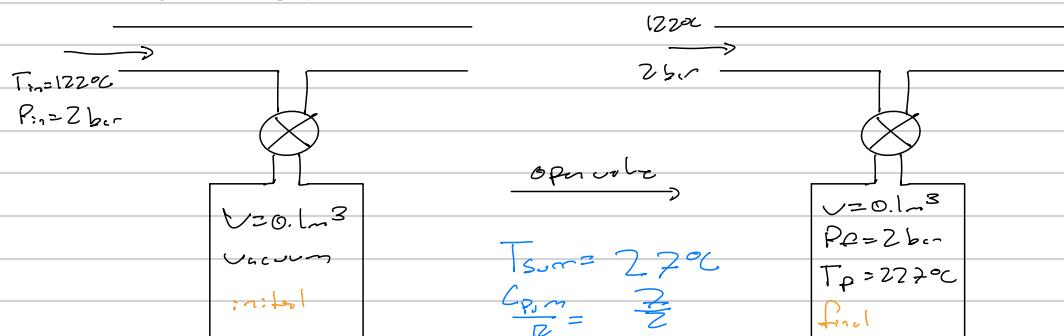
c) What is  $T_2$ ? (80% efficiency)

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

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  $dS_{\text{univ}}$



• Open system

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

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

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

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

$$\Rightarrow \frac{dS_{\text{univ}}}{dt} = \frac{ds}{dt} + \frac{dn_{\text{in}}}{dt} s_{\text{in}} - \frac{dQ}{dt}$$

**Differential Form**  $dS_{\text{univ}} = ds + \dot{n}_{\text{in}} s_{\text{in}} - T_{\text{sum}} \frac{dQ}{dt}$  entropy is state property  
and int. for prop. are  
constant T & P

$$\text{So, } \int dS_{\text{univ}} = \Delta S_{\text{univ}} = \int ds + \dot{n}_{\text{in}} s_{\text{in}} dt - \frac{1}{T_{\text{sum}}} \int dQ$$

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

→ What about  $(s_{\text{f}}, p - s_{\text{i}}, p)$

- For ideal gas: integrate  $ds_m$

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

"p" & gas mode  
gas exch. (input),  
not initial state  
of the tank

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

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

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

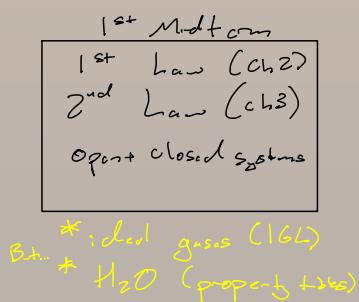
(compl. for remote answer)

✓ consistent w/  
Second law

# Midterm Exam 2



Previously...



Equations of  
State (Ch 4)

Next!

1<sup>st</sup> & 2<sup>nd</sup> 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
 
$$\hookrightarrow P = f(T, V_m) \quad \text{2 intensive properties}$$

• Compressibility Factor ( $Z$ ):

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

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

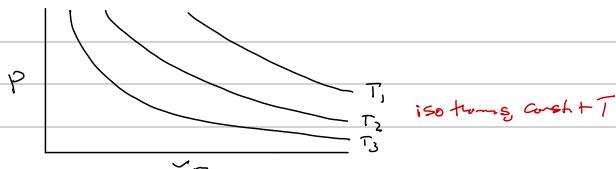
Examples of EOS's

(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

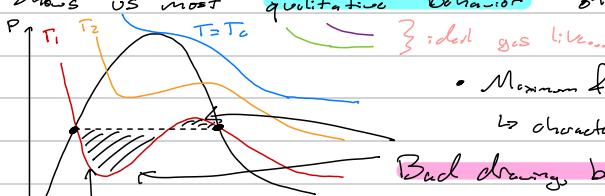
$b$  is a const vol for a fluid, independent of the fluid's  $T$  &  $P$ .

(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 region

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

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

$\alpha$  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 " $\alpha$ "
- **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

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

$$- \text{Total dF}_P \text{contd: } \frac{\partial V_m}{V_m} = \left( \frac{\partial V_m}{\partial T} \right)_P dT + \left( \frac{\partial V_m}{\partial P} \right)_T dP$$

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

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:

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

↑ 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, 1<sup>st</sup> 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

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

8 fundamental

groups closed

From fe 4

variants of  
the FE

Always holds for

single phase single  
component !!

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

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

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*

### Collected 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  
the dependent variables  
into correspondingly 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  $\Delta S$   
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.:  $PV_m = RT \rightarrow V_m = \frac{RT}{P}$

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

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

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

b) Apply to a First Law Problem

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



(i) Use ideal gas law

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

1<sup>st</sup> Law:  $\dot{Q} = v_1 h_{m1} - v_2 h_{m2} + \dot{Q}_{\text{heat}} + \dot{W}_{\text{work}}$  adiabatic no moving parts

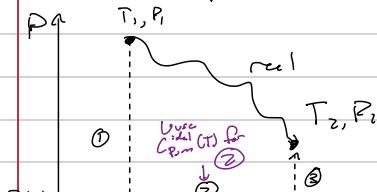
$$\rightarrow h_{m1} - h_{m2} = \dot{Q} \Rightarrow \Delta h_m = \int_{v1}^{v2} dh_m = \dot{Q} \quad T_1 = T_2 \quad \text{bc } dh_m = C_p dT \text{ for ideal gas}$$

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

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

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

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

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

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

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

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

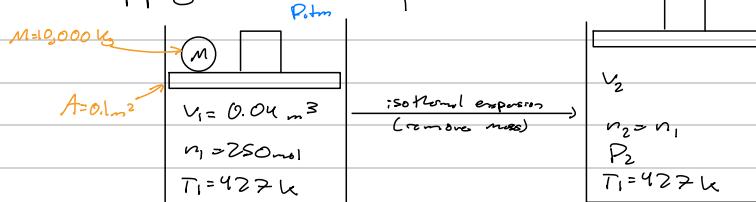
$$\frac{du_m}{dV_m} = T \frac{dS_m}{dV_m} - P \frac{dV_m}{dV_m} \Rightarrow \left( \frac{\partial u_m}{\partial V_m} \right)_T = T \left( \frac{\partial S_m}{\partial V_m} \right)_T - P$$

$$(iii) \text{ Use Maxwell equations for } dS_m$$

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

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

Lots apply this to a problem



Find  $\Delta U_m$  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

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

$$\text{given: } C_{P,m}^{ideal} = 28 \frac{J}{mol \cdot K}$$

$$\begin{cases} a = 0.8 \\ b = 4 \times 10^{-5} \end{cases} \quad \left\{ \begin{array}{l} \text{SI} \\ \text{units} \end{array} \right\}$$

Final  $\Delta U_m$

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

Need: enthalpy  $\left( \frac{\partial P}{\partial T} \right)_{V_m}$   
need  $V_{m,1}$  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 $\Delta P$ ?

(✗) 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  
 $\rightarrow$   
 $dU_m \text{ FE}$

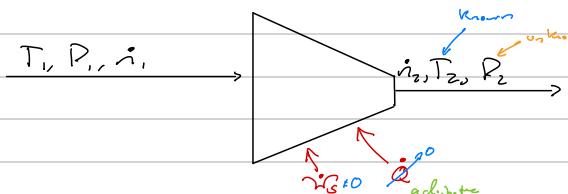
$$dS_m = \frac{C_{Pm}}{T} dT - \left(\frac{\partial U_m}{\partial T}\right)_P dP$$

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.



$$\text{• } \dot{Q}_m = 0 \text{ 2nd Law: } \frac{dS_m}{dt} = 0 = \frac{ds}{dt} + i_2 s_{m,2} - i_1 s_{m,1} - \frac{\dot{Q}_m}{T_{\text{corr}}} \xrightarrow[\text{Steady}]{\text{adibatic}} \Rightarrow S_{m,2} - S_{m,1} = 0 \text{ isentropic process}$$

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

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

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

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

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

$$\textcircled{2} \quad T \rightarrow T_2 \text{ under 1st law, deal w/ mass, last 3 eqn problem? } h(0) \text{ is undefined!}$$

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

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

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

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

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

Derived from ideal behavior

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

Note: If  $B=0$ : ideal gas ( $B=0$ )

\* Need numerical solution for  $P_2$  (only unknown)

\* Numbers: for CH<sub>4</sub> (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  $P$

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

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

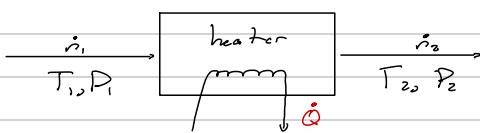
$$\left( \frac{\partial T}{\partial P} \right)_{S_m} = \frac{T}{C_{P,m}} \left( \frac{\partial v_m}{\partial T} \right)_P \quad \checkmark$$

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

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



Mole Balance:  $\frac{dot{m}}{dt} = 0 = dot{m}_1 - dot{m}_2 \rightarrow dot{m}_1 = dot{m}_2 = dot{m}$

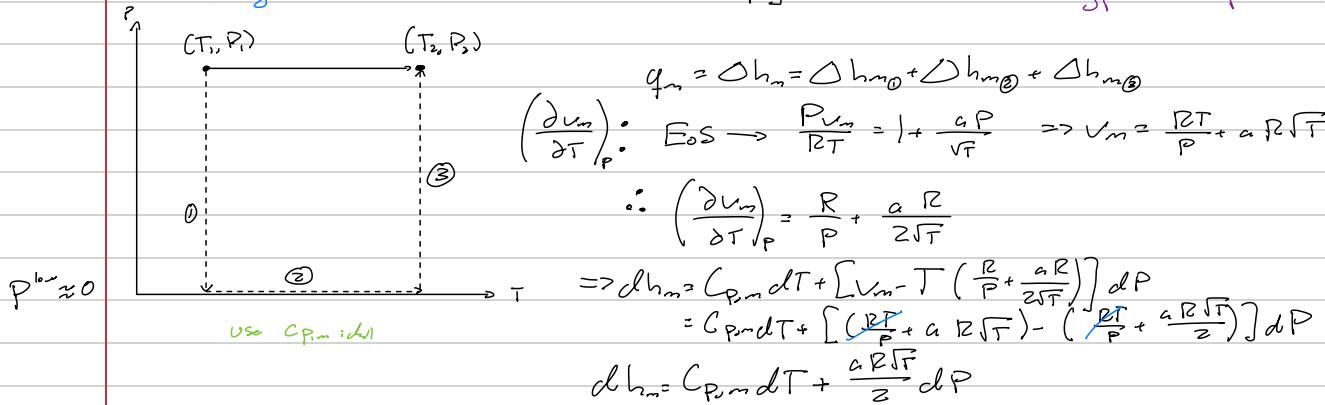
1st Law:  $\frac{d}{dt}(U + E_k + E_p) = 0 = dot{m}_1 h_{m,1} - dot{m}_2 h_{m,2} + dot{Q} + \cancel{W_s} \text{ no shaft work}$   
 $dot{Q} = dot{m}(h_{m,2} - h_{m,1})$

Plants not account  $\frac{dot{Q}}{dot{m}} = \frac{\left(\frac{dQ}{dt}\right)}{\left(\frac{dm}{dt}\right)} = q_m = h_{m,2} - h_{m,1} = \Delta h_m = \int_{T_1}^{T_2} dh_m \quad \text{need expressions for } dh_m$

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

real g.s  $dh_m = C_{Vm} dT + \left[ V_m - T \left( \frac{\partial V_m}{\partial T} \right)_P \right] dP \quad \text{constant P}$

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



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

$\Delta h_{m,0} = \int_{P_1}^{P_{id}^*} dh_m = \int_{P_1}^{P_{id}^*} \frac{\alpha R \sqrt{T_1}}{2} dP = \left( \frac{\alpha R \sqrt{T_1}}{2} \right) (P_{id}^* - P_1) \approx - \frac{\alpha R \sqrt{T_1}}{2} P_1$

②  $P_{id}^* \rightarrow P_2 \quad (\bar{T} = T_2)$

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

③  $T_1 = T_2 \quad (@P_{id}^* \rightarrow \text{real conditions})$

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

$q_m = \Delta h_m = \Delta h_{m,0} + \Delta h_{m,2} + \Delta h_{m,3}$

$P_1 = P_2 \rightarrow \Delta h_{m,2} = 0$   
 $= \frac{\alpha R P_1}{2} (T_2 - T_1) + R \left[ 3.58(T_2 - T_1) + \frac{3.02 \times 10^{-3}}{2} (T_2^2 - T_1^2) \right]$

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

## 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

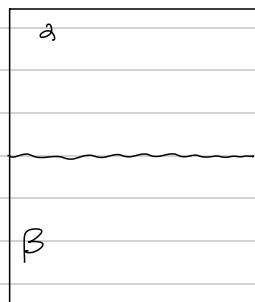
- we can be order of dP dT whatever does not matter for mixed 2nd derivatives

- 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,
- $\Delta S$  is minimized
- $\Delta G$  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

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

In special cases (single component systems)

Phase Equl 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 enthalpy:  $dh_m^A = dh_m^B$

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

No. of P = P<sup>A</sup> = P<sup>B</sup> = P, T<sup>A</sup> = T<sup>B</sup> = 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 equl

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.  $\text{H}_2\text{O}$  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.  $\frac{dP}{dT} = \frac{h_m^{\text{gas}} - h_m^{\text{liq}}}{T(V_m^{\text{gas}} - V_m^{\text{liq}})}$  : ideal gas assumption

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

(i) Recondo (Separato)

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

(i): Solve! 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 are an empirical form of the CCB

Answers: Key equations for single-component phase equilibria

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

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

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

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  $V_m^{\alpha}$  or  $V_m^{\beta}$  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  $\Delta h_m^{\text{vap}}$  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 Clapeyron 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,  $V_m^V \gg V_m^L$ )

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

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

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

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

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

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

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

**Example** Is  $\text{CO}_2$  a liquid at  $-40^\circ\text{C}$  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  $\text{CO}_2$

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

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

**Solution:** Construct a PT diagram for  $\text{CO}_2$ .

→ need to determine P-T relationships:

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

- Don't have info about  $\Delta h_{\text{m}}$ , we are forced to assume  $\Delta h_{\text{m}}$ '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

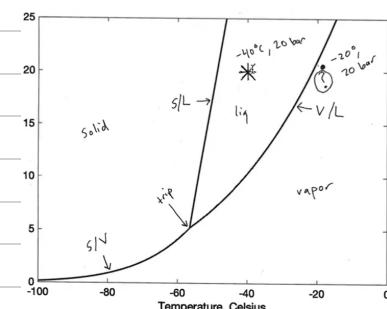
$$\Rightarrow P_{\text{S,V}} = (5.2 \text{ bar}) \times \exp\left[-3139\left(\frac{1}{T} - \frac{1}{216.6}\right)\right]$$

→ Now? 3 eqns ready P-T

- Plot these lines to determine phase @  $-40^\circ\text{C}$ , 20 bar

Code on Canva  
(Method)

$\text{CO}_2$  is a liquid!



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

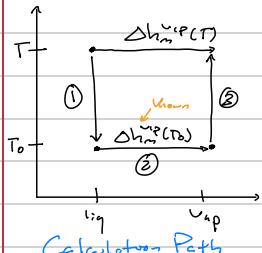
In vapor, but close  
constant assumptions!

- X1) Improve  $\Delta h_m^{\text{sub}}$  analysis? → solid- $\mu$ , not needed
- X2) Real phase of  $P_f$  about
- Better  $\Delta h_m^{\text{vap}}$
- Good  $\Delta h_m^{\text{vap}}$  → Improve estimate of  $v_m^L$  → Assume 16L initially, better EoS for
- $\Delta h_m^{\text{vap}}$  → 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

$$\begin{aligned}dG &= -SdT + VdP + \sum_i M_i dn_i \\ dU &= TdS - PdV + \sum_i M_i dn_i \\ dH &= TdS + VdP + \sum_i M_i dn_i \\ dA &= -SdT - PdV + \sum_i M_i dn_i\end{aligned}$$

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

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

What is  $\bar{G}_i P$

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

In general,

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

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 Trick: Euler integration

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

$$\int \text{differential of interior} = 0$$

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

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

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

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

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

Applies to  $dU$ .

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

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

$\downarrow$  use  $\bar{K}_i$  from mixture  
 $\bar{K}_i = \sum_i \bar{K}_i n_i$  PCT P, n<sub>tot</sub>  
contribution of "i" to  
total  $U$  of mixture  
(per mole "i")

Multicomponent systems have different properties

① Total solution properties

• exterior:  $G, U, S, \dots, K$

• interior:  $\rightarrow$  dials by  $n_i^{tot}$   
 $K_m = \sum_i n_i^{tot}, g_m = \frac{n_i^{tot}}{n_{tot}, \dots}$

② Pure species "i" properties

• exterior:  $G_i, U_i, \dots$  at  $T, P$  of mixture

• interior:  $u_i, g_i, \dots$  at  $T, P$  of mixture

③ Partial Molar properties

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

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

Comments: In a mixture with "i" and  $\rightarrow$  (mole fracs.)  $\rightarrow$  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  $T, P$ ,

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

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

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

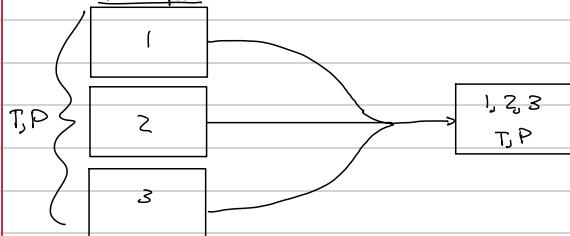
Q: What is the physical meaning of  $\bar{K}_i$  in a mixture?

- (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:

$$\Delta K_{mix} = K - \sum_i n_i K_{m,i}$$

argued ext. property  
at same T, P, f, g, s, h

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

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

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

Intensive

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

$$\rightarrow P_{tot} = RT + P^2 [A(y_1 - y_2) + B]$$

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 same  $T, P$ )

~~mole fractions ( $y_1, y_2, y_3$ )~~

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

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

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

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

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

$$V = V_m n_{tot} = \frac{n_{tot} RT}{P} + P[A(n_1 - n_2) + B(n_1 + n_2 + n_3)]$$

$$\text{Mix. func: } \bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, n_3} = \frac{\partial}{\partial n_i} \left( \frac{(n_1 + n_2 + n_3) RT}{P} + P[A(n_1 - n_2) + B(n_1 + n_2 + n_3)] \right)_{T, P, n_1, n_2, n_3}$$

$$\Rightarrow \bar{V}_1 = \frac{RT}{P} + P(A + B)$$

$$\bar{V}_2 = \frac{RT}{P} + P(B - A)$$

$$\bar{V}_3 = \frac{RT}{P} + P B$$

$$\left( \frac{\partial V}{\partial n_1} \right)_{T, P, n_2, n_3}$$

$$\left( \frac{\partial V}{\partial n_2} \right)_{T, P, n_1, n_3}$$

$$\left( \frac{\partial V}{\partial n_3} \right)_{T, P, n_1, n_2}$$

$$\Delta V_{mix} = \sum_i n_i (\bar{V}_i - V_{m,i})$$

$$= n_1 (\bar{V}_1 - V_{m1}) + n_2 (\bar{V}_2 - V_{m2}) + n_3 (\bar{V}_3 - V_{m3}) = 0$$

$$\therefore \Delta V_{mix} = 0$$

not guaranteed for this EoS  
specifically!

## Applying to first & second law problems

**Example:** Consider steady-state mixing of water (W) and ethanol (E).

→ From a handbook,

$$\text{at } 298\text{ K: } \frac{\Delta h_{m,\text{mix}}}{R} = x_W x_E \left[ -190 + 214.7(x_E - x_W) - 4.194(x_E - x_W)^2 + 383.3(x_E - x_W)^3 - 2.354(x_E - x_W)^4 \right]$$

### Process

(1)  $\dot{n}_1 = 1 \text{ mol/s}$

$x_W = 1$   
1 bar, 298 K

(2)  $x_W = 0.5$   
 $x_E = 0.5$   
 $\dot{n}_2 = 1 \text{ mol/s}$   
1 bar, 298 K

⇒ Find  $T_{\text{out}}$ !

(i) Assume  $C_{p,m}$  of all streams is constant,  $C_{p,m} = 9.02 R$

(ii) Assume mixing happens adiabatically,  $\dot{Q} = 0$

(iii) Shaft work not specified, assume that there is no shaft work  $\Rightarrow m_{\text{mix}} = \frac{1}{2} m_1 + m_2$

$$\text{Mole Balance: } \frac{dn}{dt} = 0 = \dot{n}_1 + \dot{n}_2 - \dot{n}_{\text{out}}$$

$$\dot{n}_{\text{out}} = \dot{n}_1 + \dot{n}_2 = 2 \text{ mol/s}$$

$$1^{\text{st}} \text{ Law: } \frac{d}{dt} (C_{p,m} (E_p + E_{\text{p}})) = \dot{n}_1 h_{m,1} + \dot{n}_2 h_{m,2} - \dot{n}_{\text{out}} h_{m,\text{out}} + 2 \dot{S} + \dot{Q} \xrightarrow{\text{assume adiabatic}}$$

$$0 = \dot{n}_1 h_{m,1} + \dot{n}_2 h_{m,2} - 2 \dot{n}_{\text{out}} h_{m,\text{out}} \quad \text{use mass balance } (\dot{n}_1 + \dot{n}_2 = 2 \dot{n}_{\text{out}})$$

$$(h_{m,\text{out}} - h_{m,1}) + (h_{m,\text{out}} - h_{m,2}) = 0 \quad (\text{move to 1 Lg. supports h}_{m,\text{out}} \text{ to get two } \Delta h \text{ expressions})$$

$$\text{Property data: } \Delta h_{m,\text{mix}} \quad C_{p,m} \\ \text{Analog outlet: } x_{W,\text{out}} = \frac{x_{W,1} \dot{n}_1 + x_{W,2} \dot{n}_2}{\dot{n}_{\text{out}}} = \frac{(1)(1) + (0.5)(1)}{2} = 0.75$$

For mixing streams (1) and (2) → (out):

$$\Delta h_{m,\text{mix}}(x_{W,\text{out}}, T_{\text{out}}) = h_{m,\text{out}} - x_{W,\text{out}} h_{m,W}(T_{\text{out}}) - x_{E,\text{out}} h_{m,E}(T_{\text{out}})$$

↑  
augmenting  
of mixture  
pure component @  $T=T_{\text{out}}$

important! not necessarily  $T_{\text{out}}$   
inlet streams!

↙ reason: as largest : sin 1st law expr.

$$h_{m,\text{out}}(T_{\text{out}}) = \Delta h_{m,\text{mix}}(T_{\text{out}}, x_{W,\text{out}}) + x_{W,\text{out}} h_{m,W}(T_{\text{out}}) + x_{E,\text{out}} h_{m,E}(T_{\text{out}})$$

What about  $h_{m,1}$  &  $h_{m,2}$ ?

$$h_{m,1}(T_1) = h_{m,W}(T_1) \rightarrow \text{pure water}$$

$\rightarrow$  Using similar logic as above,  $\xrightarrow{T_1=T_2}$

$$\Rightarrow h_{m,2}(T_2) = h_{m,E}(T_2) = \Delta h_{m,\text{mix}}(T_1, x_{W,2}) + x_{W,2} h_{m,W}(T_1) + x_{E,2} h_{m,E}(T_1)$$

Back to first law...

$$0 = (h_{m,\text{out}} - h_{m,1}) + (h_{m,\text{out}} - h_{m,2})$$

↑ ↑ ↑ ↑  
 $T=T_{\text{out}}$   $T>T_1$   $T<T_{\text{out}}$   $T>T_2>T_1$

notation means  $h_{m,E} = h_{m,E}(T=T_{\text{out}})$

$$0 = 2 \Delta h_{m,\text{mix}} + 2 x_{W,\text{out}} h_{m,W}(T_{\text{out}}) + 2(1-x_{W,\text{out}}) h_{m,E}(T_{\text{out}})$$

$$-h_{m,W}(T_1) - \Delta h_{m,\text{mix}}^{\text{Stream 2}} - x_{W,2} h_{m,W}(T_1) - (1-x_{W,2}) h_{m,E}(T_1)$$

↑  
Stream 1  
@  $T_1, x_{W,2}$

↑  
 $2 h_{m,\text{out}}$

↑  
 $h_{m,E}$

Plug-in expressions!

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 = 4.07 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  $\Delta T$ )

# **Final Exam**

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# Chapter 7 - Phase Equilibria, Part 2: Fugacity

Review: Partial molar properties = molar properties of species "i" in a mixture

Most Important + Partial Molar Property:

$$\mu_i \equiv \left( \frac{\partial \mu}{\partial n_i} \right)_{T, P, n_{\neq i}} = \bar{\mu}_i \text{ (chemical potential / partial molar gibbs free energy)}$$

-  $\mu$  is a central condition for equilibrium

$$\mu_i^A = \mu_i^B \text{ for phase equilibrium}$$

→ also a useful relationship for describing chemical equilibrium!

may or may not cover  
in this course, depends  
on time

Q: How do we calculate  $\mu$ ?

→ Start with simplest case: pure component, ideal gas

• In this case,

$$\mu \equiv \left( \frac{\partial \mu}{\partial n} \right)_{T, P} = \left( \frac{\partial (\nu_m g_m)}{\partial n} \right)_{T, P} = n \left( \frac{\partial g_m}{\partial n} \right)_{T, P} + g_m \left( \frac{\partial n}{\partial n} \right)_{T, P}$$

internal properties are constant  
for second gas added

•  $\mu = g_m$  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~~

⇒ ~~Ans: f<sub>1</sub>, f<sub>2</sub>~~ f<sub>1</sub>(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<sub>1</sub> can only depend on T!

$$\text{Integrate: } \mu = \int \frac{RT}{P} dP + f_1(T) \quad P_0 = \text{reference pressure}$$

$$\mu = RT \ln P + f_1(T)$$

To find f<sub>1</sub>(T), write:  $\mu_1(T, P_0) = RT \ln P_0 + f_1(T)$

$$\text{Solve: } \mu(T, P) - \underline{\mu(T, P_0)} = RT \ln \left( \frac{P}{P_0} \right)$$

denoted  $\mu^\circ(T)$  often ← but how do you get  $\mu^\circ$ ?

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  $\rightarrow dM_i = RT d \ln \hat{f}_i$

$$\xrightarrow[\text{const } T]{\text{Partial integral}} M_i(T, P, n_1, \dots, n_m) - M_i^o(T, P_o, n_1, \dots, n_m) = RT \ln \left( \frac{\hat{f}_i}{f_i^o} \right)$$

Definition is like an "effective pressure" for a real gas

→ For real gas, ①  $\lim_{P \rightarrow 0} f = P$  at  $\infty T$

$$\text{② } \lim_{P_i \rightarrow 0} \hat{f}_i = P_i \text{ at } \infty T, y_i$$

These give convenient boundary conditions that make calculating  $f$ 's and  $\hat{f}$ 's more straightforward

Fugacities at Phase Equil (multi-component)

Recall:  $M_i^o = M_i^B @ \infty T$

$\rightarrow dP_{\text{fugacity}} = dm_i^B$

def'n  $\hat{f}_i \rightarrow RT d \ln \hat{f}_i^A = RT d \ln f_i^B$

→ Integrate:  $\int_{P_{ref}}^{P_i} d \ln \hat{f}_i^A = \int_{P_{ref}}^{P_i} d \ln f_i^B$

$$\Rightarrow \ln \left( \frac{\hat{f}_i^A}{f_i^B} \right) = \ln \left( \frac{P_i}{P_{ref}} \right) \rightarrow \boxed{\hat{f}_i^A = f_i^B} @ \text{phase equil.}$$

Calculating  $f$  for pure real g.s.

$$P_{\text{ext}} + \int \nu_m dP \ln f \rightarrow RT d \ln f = \nu_m dP$$

(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 confusing 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  $\nu_m$

$$\rightarrow \text{If not, } RT d \ln f = -\left(\frac{\partial P}{\partial \nu_m}\right)_{T, \nu_m} dV \text{ For e.g. pure component fugacities}$$

↳ this is equivalent to the former, but is more useful if one can't directly solve for  $\nu_m$  (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

$$dP/f = dT \ln f = v_m dP = -\left(\frac{\partial P}{\partial T}\right)_{T_0} dP$$

$$\int dP = RT \int d \ln f \quad \text{no EoS!} \quad \text{no Eq. to ill!!}$$

$$u(T, P) - u(T_0, P_0) = RT \ln\left(\frac{f}{f_0}\right)$$

$$\rightarrow u(T, P) = g_m(T, P) \quad \text{for a pure component}$$

$$= h_m(T, P) - TS_m(T, P) \quad \text{3 look up } h, s \text{ in steam tables}$$

$\rightarrow$  what is  $P_0$ ?

use  $P_0 = P_{low} = 10 \text{ kPa}$  (lowest  $P$  in superheated steam tables)

$$\text{look up: } \begin{cases} h^0 = 322.9 \text{ kJ/kg} \\ s^0 = 0.826 \text{ kJ/kg K} \end{cases}$$

$\rightarrow$  look up  $\phi$ : 647K, 114 atm (interpolate):

$$\begin{cases} h = 2479 \text{ kJ/kg K} \\ s = 6 \text{ kJ/kg K} \end{cases}$$

$$\therefore M_w(M - M^0) = (2031 \text{ kJ/kg}) = M_w \times RT \ln\left(\frac{f}{P_0}\right) = (M_w) \times RT \ln\left(\frac{f}{P_0}\right)$$

$$\Rightarrow f = 899 \text{ Pa}$$

$$f = 88.8 \text{ atm}, \phi = \frac{f}{P} = 0.88 \quad \text{H bonding attractions win}$$

↪ best results if use prop. data

c) Vdw EoS

$$a = \frac{27}{64} \frac{(RT_0)^2}{P_0} = 0.854 \quad b = 3.05 \times 10^{-5} \quad (\text{SI units})$$

$$RT d \ln f = v_m dP = -\left(\frac{\partial P}{\partial T}\right)_{T_0, P_0} dV \quad \text{Skip part don't... (See Ex 2.2 in Vorotely)}$$

$$\Rightarrow \ln(\phi) = -\ln\left(\frac{(v_m + b)P}{RT}\right) + \frac{b}{v_m + b} - \frac{2a}{RTv_m}$$

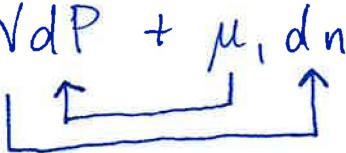
Solve numerically for  $v_m$

$$\text{Find } \boxed{P = 96 \text{ atm}, \phi = 0.84}$$

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 :  $\hat{\phi}_1 = \frac{\hat{f}_1}{\hat{p}_1}$

Use  $dV$  form of integral  $\rightarrow \left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} dV$

$$V_m = \frac{V}{n_{tot}} = \frac{V}{n_1 + n_2}$$

$$P = \frac{RT}{V_m - b} = \frac{RT}{\frac{V}{n_1 + n_2} - y_1 b_1 - y_2 b_2} = \frac{(n_1 + n_2) RT}{V - n_1 b_1 - n_2 b_2}$$

$y_1 = \frac{n_1}{n_1 + n_2}$

$$\left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} = \frac{RT(V - n_1 b_1 - n_2 b_2) - RT(n_1 + n_2)(-b_1)}{(V - n_1 b_1 - n_2 b_2)^2}$$

$$= \frac{RT}{V - n_1 b_1 - n_2 b_2} + \frac{RT b_1 (n_1 + n_2)}{(V - n_1 b_1 - n_2 b_2)^2}$$

$$\begin{aligned}
 RT \ln\left(\frac{\hat{f}_i}{y_i P_{low}}\right) &= - \int_{V^{id}}^V \left(\frac{\partial P}{\partial n_1}\right)_{T, V, n_2} dV \\
 &= -RT \ln\left(\frac{V - n_1 b_1 - n_2 b_2}{V^{id} - n_1 b_1 - n_2 b_2}\right) \\
 &\quad + RT b_1 (n_1 + n_2) \left[ \frac{1}{V - n_1 b_1 - n_2 b_2} - \frac{1}{V^{id} - n_1 b_1 - n_2 b_2} \right]
 \end{aligned}$$

$$V^{id} \gg n_1 b_1 + n_2 b_2$$

$$RT \ln\left(\frac{\hat{f}_1}{y_1 P_{low}}\right) = -RT \ln\left(\frac{V - n_1 b_1 - n_2 b_2}{V^{id}}\right) + RT b_1(n_1 + n_2) \left[ \frac{1}{V - n_1 b_1 - n_2 b_2} - \frac{1}{V^{id}} \right] \approx 0$$

$\stackrel{R = nRT/P_{low}}{\cancel{RT}}$

$$\ln\left(\frac{\hat{f}_1}{y_1 P_{low}}\right) = -\ln\left(\frac{V - n_1 b_1 - n_2 b_2}{nRT/P_{low}}\right) + b_1(n_1 + n_2) \left[ \frac{1}{V - n_1 b_1 - n_2 b_2} \right]$$

$$\ln\left(\frac{\hat{f}_1}{y_1}\right) = -\ln\left[\frac{V - n_1 b_1 - n_2 b_2}{(n_1 + n_2)RT}\right] + \frac{b_1(n_1 + n_2)}{V - n_1 b_1 - n_2 b_2}$$

$$\hat{\phi}_1 = \frac{\hat{f}_1}{y_1 P} \rightarrow \text{subtract } \ln P \text{ from both sides}$$

$$\ln \hat{\phi}_1 = \ln\left(\frac{\hat{f}_1}{y_1 P}\right) = -\underbrace{\ln\left[\frac{P(V - n_1 b_1 - n_2 b_2)}{(n_1 + n_2)RT}\right]}_{\frac{P}{RT}(V_m - b)} + \frac{b_1(n_1 + n_2)}{V - n_1 b_1 - n_2 b_2}$$

$$\frac{P}{RT}(V_m - b) = 1! \rightarrow \ln(1) = 0!$$

$$\therefore \boxed{\ln \hat{\phi}_1 = \frac{b_1}{v_m - b}}$$

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  $\phi_i$  is deviation of "i" from ideality  
( $\phi$  is 1 for an ideal gas)

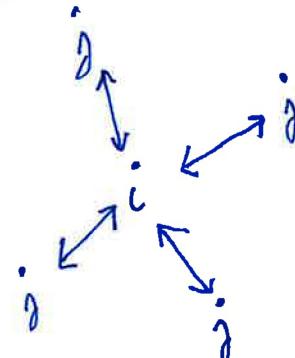
∴ LFR says, under certain circumstances, "i" has the same non-ideality in mixture and in pure form

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  $P_{\text{total}}$  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

# Chapter 7 - Liquid Phase Fugacities

## Pure Components

$$\text{Result} \rightarrow dM = dg_m = V_m dP - \bar{s}_m dT \quad (\text{FE})$$

$$\text{Partial } f \text{ (constant } T \text{)}: \rightarrow dM = V_m dP$$

$$RT \ln \left( \frac{f}{P_{\text{low}}} \right) = \int_{P_{\text{low}}}^P V_m dP \quad (\text{Same definition for liquids!})$$

Integrate w/ Boundary Conditions:  $f(P_{\text{low}}) \approx P_{\text{low}}$

$$RT \ln \left( \frac{f}{P_{\text{low}}} \right) = \int_{P_{\text{low}}}^P V_m dP$$

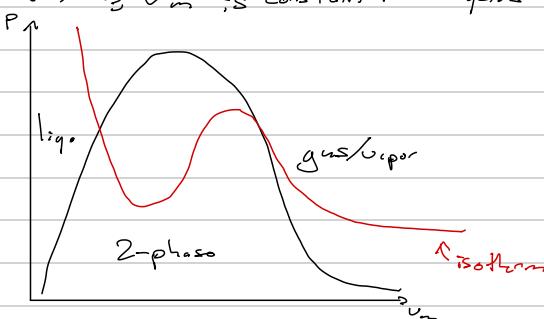
Q: Can we calculate liquid fugacities using our partial integral:  $\int_{P_{\text{low}}}^P V_m dP$ ?

X(i) No, this eqn is only valid for gases - Integrating eqn derived from FB

(ii) No, the integral cannot pass through 2-phase regions

(iii) Yes, but only with an EoS that describes both liquids & gases Theoretically possible, but not common!

(iv) Yes,  $V_m$  is constant for liquids



Most EoS's (Vdw, even R-K, P-R) do a very poor job of describing liquids  
→ calculated  $f$ 's are not accurate!

To overcome this problem take advantage of VLE.

Result, at eqi.:  $M^V = M^L$  (eqi. criteria for phase equil: pure component)

$$P = P_i^{\text{sat}} \quad f_i^V = f_i^L \quad (\text{note: no "1's" } \rightarrow \text{pure component})$$

$$\text{ Vapor: } \frac{f_i^V}{P} = \phi_i \frac{P = P_i^{\text{sat}}}{\text{at VLE}} \Rightarrow f_i^V = P_i^{\text{sat}} \phi_i(T, P_i^{\text{sat}}) = f_i^L(T, P_i^{\text{sat}})$$

But we want  $f_i^L(T, P)$ , not just  $f_i^L(T, P_i^{\text{sat}})$

For the liquid phase only, we can integrate

$$\int_{P_i^{\text{sat}}}^P RT d\ln f_i^L = \int_{P_i^{\text{sat}}}^P V_m^L dP \Rightarrow RT \ln \left( \frac{f_i^L}{f_i^{\text{sat}}} \right) = \int_{P_i^{\text{sat}}}^P V_m^L dP$$

$f_i^L(T, P_i^{\text{sat}}) \rightarrow f_i^L(\text{at eqi) (VLE)}$

$$\therefore f_i^L(T, P) = f_i^L(T, P_i^{\text{sat}}) \exp \left[ \frac{1}{RT} \int_{P_i^{\text{sat}}}^P V_m^L dP \right]$$

→ For most conditions  $V_m^L \approx \text{constant}$ , so we can simplify

$$\Rightarrow f_i^L(T, P) = f_i^L(T, P_i^{\text{sat}}) \exp \left[ \frac{V_m^L}{RT} (P - P_i^{\text{sat}}) \right]$$

Thus

$$f_i^L = P_i^{\text{sat}} \phi_i^V(T, P_i^{\text{sat}}) \exp \left[ \frac{V_m^L}{RT} (P - P_i^{\text{sat}}) \right]$$

assuming constant  $V_m^L$

Clapeyron EoS (gasphase)

data table (pure liquid densities)

$$\rightarrow \text{If } P \approx P_i^{\text{sat}} \text{ as low temp} \quad \therefore P \approx P$$

$$\phi_i^L(T, P_i^{\text{sat}}) \rightarrow 1 \quad (\phi = \frac{P}{P_i^{\text{sat}}}; P \text{ is low, } \phi \text{ is near 1})$$

and

$$\exp \left[ \frac{V_m^L}{RT} (P - P_i^{\text{sat}}) \right] \approx 1 \quad \Rightarrow \quad f_i^L(T, P) \approx P_i^{\text{sat}}(T)$$

If  $P_i^{\text{sat}}$  is small

Example: Find  $f_i^L$  of pure liquid acetone @ 100 bar, 382 K.

$$V_m^L, \text{acetone} = 73.4 \text{ cm}^3/\text{mol}$$

Procedure:

1) Calculate  $P_i^{\text{sat}}$  @ T = 382 K

$\rightarrow$  Use Antoine eqn:  $P_i^{\text{sat}} = 41.691 \text{ bar}$  (Appendix: 1 - Antoine eq)

2)  $\phi_i^L(T, P_i^{\text{sat}}) = \phi_i^L(T, P)$

- need EoS,  $P_i^{\text{sat}}$  is kind of small-ish

$\rightarrow$  so,  $\phi_i^L(T, P_i^{\text{sat}}) \approx 1$

$\Rightarrow$  could do a lot better w/ a good EoS

3)  $\exp \left[ \frac{1}{RT} \int_{P_i^{\text{sat}}}^P V_m^L dP \right] = \exp \left[ \frac{V_m^L}{RT} (P - P_i^{\text{sat}}) \right] \approx 1.25$

assume  $V_m^L$  is const

Thus,  $f_i^L(T, P) = P_i^{\text{sat}} \phi_i^L(T, P) \exp \left[ \frac{V_m^L}{RT} (P - P_i^{\text{sat}}) \right] \approx 5.8 \text{ bar}$