



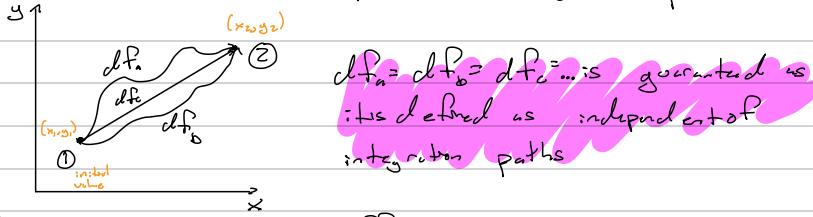
# Midterm Exam 1

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

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

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

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

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

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

$$\int f(x) dx$$

Integral  $\uparrow$  Differential

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

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

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

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

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

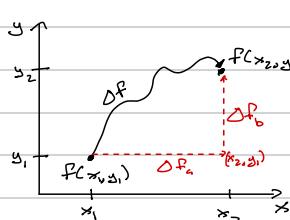
**Summary - Common points of confusion!**

① **Differential:** infinitesimal changes denoted  $df$

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

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

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



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

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

We can do this bc the differential is independent of path

\* Math no-no!

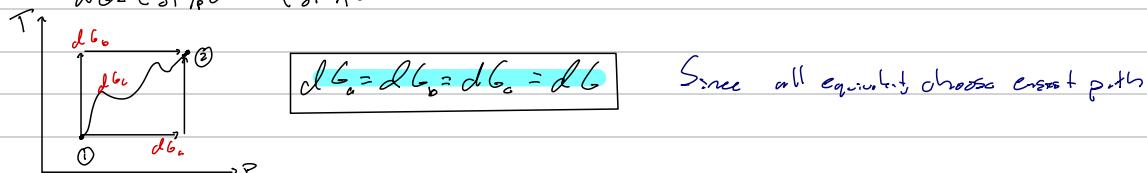
$\times \Rightarrow \int \frac{df}{dx} dx$  cannot be evaluated! Missing the differential!

$\hookrightarrow$  Must integrate over differential changes

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

# Chapter 1 - Thermodynamic Properties

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



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

ex: work ( $w$ ) and heat ( $Q$ )

→  $dW$  and  $dQ$  do depend on path

→ use notation  $\delta Q$  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.

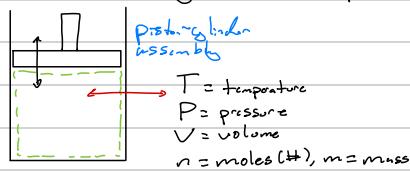
① System and Surroundings



• 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:

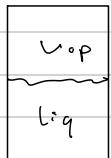
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑  
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  $\text{H}_2\text{O}$



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

mol/mol of  $\text{liq}$  mol/mol  $\text{vap}$

$$V_{\text{tot}} = V = V_{m,\text{L}} n_{\text{L}} + V_{m,\text{V}} n_{\text{V}} \quad \Rightarrow \text{divide by } V_{\text{tot}} = n = n_{\text{L}} + n_{\text{V}}$$

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

↑  
average molar volume  
x ≡ "quality"

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

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

→ constrains all other intensive properties

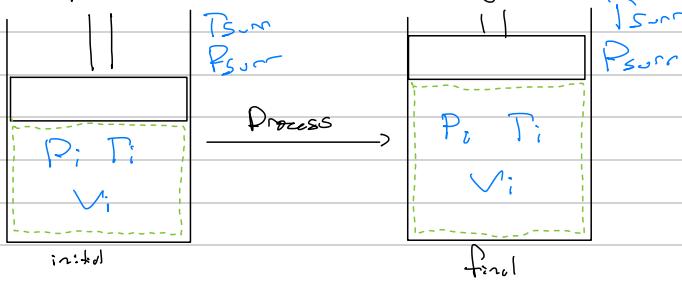
Also need to specify total amount in each phase

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

$Q_{\text{liq}} = \text{mole or mass fraction of } \text{P}_{\text{liq}}$   
 $Q_{\text{vap}} = \text{mole or mass fraction of } \text{P}_{\text{vap}}$

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

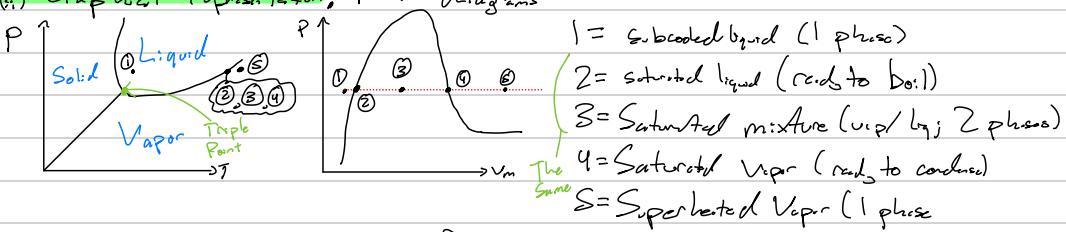
(iii) Phase Equilibrium  $\rightarrow$  Composition of phases is constant

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

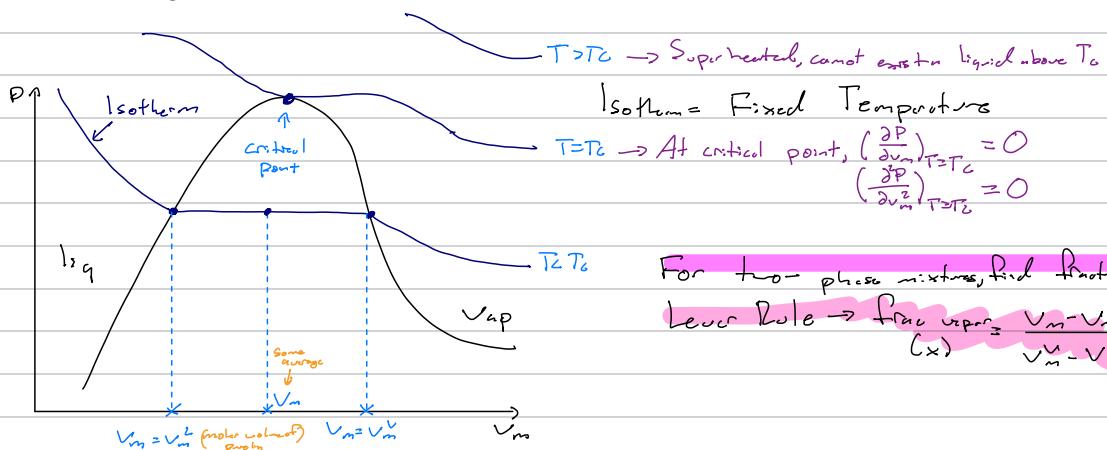
## Thermodynamic Property Sources

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

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



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

• Always use steam tables for water

• Linear interpolation required for conditions between values in the table

(iv) Equations of State

$\rightarrow$  ideal gas law,  $PV_m = RT$

$\rightarrow$  van der Waals...

(v) Statistical Mechanics (molecular calculations)

$\hookrightarrow$  not focused on in this course

## Final Notes about (Potentially) 2-phase systems

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

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

**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

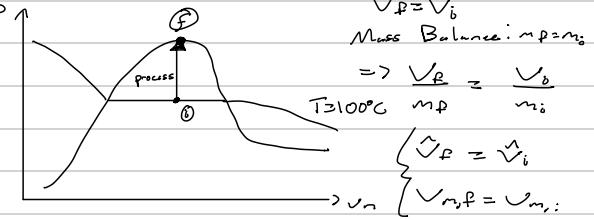
final (f)

$$V_f = 100L = V_i$$

$$T_f = T_c$$

$$P_f = P_c$$

process reaches  
at critical point



b) Find the mass and initial quality.

(outmass)

→ 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

$\Rightarrow$  of temp  $\rightarrow V_{i,g} = 0$

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

(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

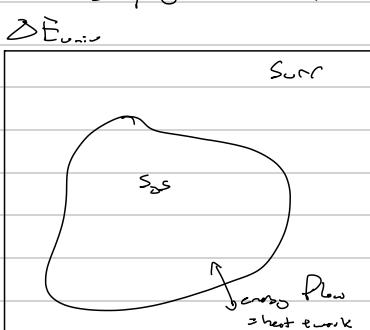
- phase changes

- 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

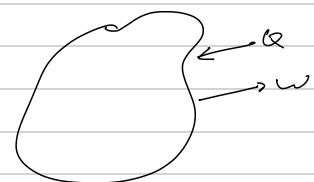
Q: Heat and work are flowing across the system boundary. What can we say about Q and W?

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.)

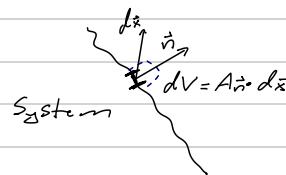
② Work ( $W$ ): this class!

a) System boundary moves against an external force

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

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

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



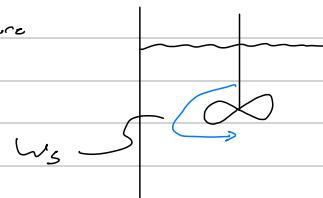
→ Calculating PV work requires us to know external pressure

\*  $P_E$  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 →  $P_E \approx P$

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

extensive/intensive

$n$  is constant

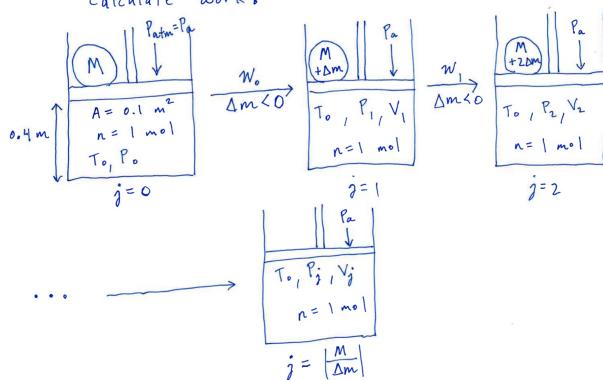
$$\frac{W}{n} = w_m = -RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

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

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

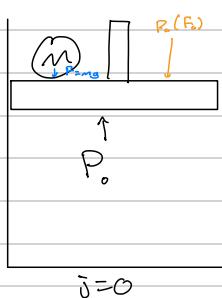
• PV work def'n →  $W = - \int P_E dV$  external pressure

↳ what is  $P_E$ ?

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

• pressure / force balance:

• Pressure / Force Balance



$$\text{initial } (j=0): A P_0 = A P_{E,0} \Rightarrow P_0 = P_{E,0} = \left( \frac{M_0}{A} + P_a \right)$$

cross-section  
area of piston

$$\rightarrow P_0 = P_a + \frac{M_0}{A}$$

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

$$\text{Similarly } (j=1): P_1 = P_{E,1} = \left( \frac{(M+Dm)_0}{A} + P_a \right)$$

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

$P_{E,1} = P_1$

Substitution law  
 $P_1 V_1 = P_0 V_0$

$$\text{Now, sub } P's \text{ from force balance} = -V_0 \left[ (P_0 + \frac{M_0}{A}) - (P_1 + \frac{M_0 + \Delta m_0}{A}) \right] = +V_0 \cdot \frac{\Delta m_0}{A} < 0$$

negative indicates  $S_o$  class work

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

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

$$\rightarrow \text{use force balance} = -V_0 \left( P_a + \frac{M_0}{A} \right) \left( \frac{(-\Delta m_0)}{P_0 + \frac{M_0}{A} + \frac{\Delta m_0}{A}} \right)$$

$\downarrow P_1$

$$\Rightarrow W_1 = \frac{V_0 \Delta m_0}{A} \cdot \frac{P_a + \frac{M_0}{A}}{P_0 + \frac{M_0}{A} + \frac{\Delta m_0}{A}} < 0$$

Expansion  $\rightarrow S_o$  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:

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

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)

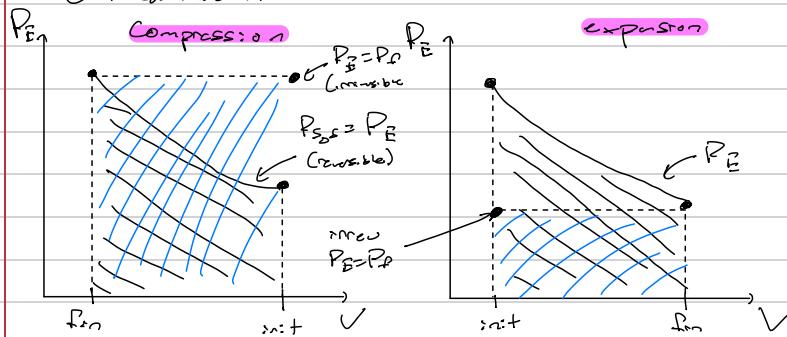
This is a reason why assuming a reversible process can be convenient.  $W_{\text{re}} = -5545 \text{ J}$

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 (Combination 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

$$\text{Reminder: } C_{v,m} = \left( \frac{\partial U_m}{\partial T} \right)_{V_m} = \frac{dU_m(T)}{dT}$$

↑ constant volume  
heat capacity

↑ generally true  
definition

↑ ideal gas only

$$\text{Similarly, } C_{p,m} = \left( \frac{\partial h_m}{\partial T} \right)_P = \frac{dh_m(T)}{dT}$$

↑ constant pressure  
specific heat (gas  
heat capacity)

↑ generally true  
definition

↑ ideal gas only

## Enthalpy ( $h_m$ )

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

$\rightarrow$  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 $C_{p,m}$

$\rightarrow$  Closed system, Calorimeter, system @ const  $P$

const  $P \rightarrow P_E = P$  (force balance)

$$1^{\text{st}} \text{ Law: } dU_m = \delta q_m - PdV_m \quad (P_E = P)$$

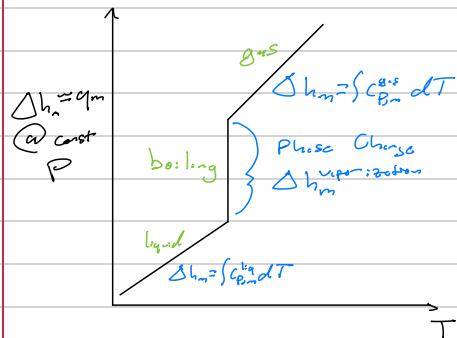
$dU_m = \delta q_m - d(PV_m)$  can make this more only bc Pressure  $P$  is constant

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

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

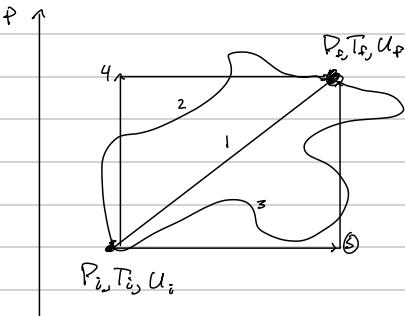
$\leftarrow$  measure  $T$  to determine  $h_m$  &  $C_{p,m}$

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 ( $T, P, V_m, U_m, h_m, \dots$ )

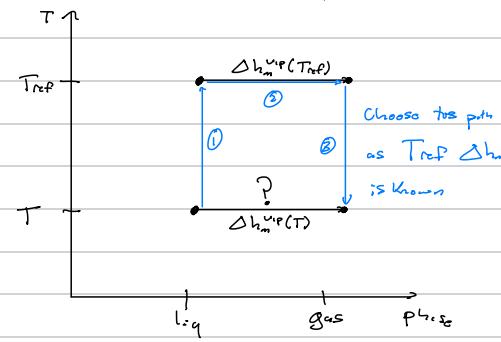


$$\Delta U = U_f - U_i$$

$$= \Delta U_1 = \Delta U_2 = \Delta U_3 = \Delta U_{\text{av}}$$

True for any process!

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



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

Solution:

$$\Delta h_m^{\text{ref}}(T) = \Delta h_{m,1} + \Delta h_{m,2} + \Delta h_{m,3}$$

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

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

$$\textcircled{3} \text{ Single phase cooling/heating} \quad \Delta h_{m,3} = \int_{T_{\text{ref}}}^{T_f} C_{P,m}^{\text{gas}} dT$$

$$\therefore \Delta h_m^{\text{ref}}(T) = \Delta h_m^{\text{ref}}(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T_f} [C_{P,m}^{\text{gas}}(T) - C_{P,m}^{\text{liq}}(T)] dT$$

## 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
$\text{Sat'd } H_2O$ $x = 0.42$ $P = 2 \text{ bar}$ $V_i$	$T_f = 540^\circ C$ $V_f = V_i (\text{rigid})$

Process:  
closed system  
constant volume

- initial state is sat'd water,  $x = 0.42$
- rigid  $\rightarrow V_f = V_i$ , and  $\dot{m}_f = \dot{m}_i = \dot{m}$  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

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

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

Table B.2	$\hat{u}_i = 504.47 \frac{\text{kJ}}{\text{kg}}$	$\hat{u}_f = 2529.5 \frac{\text{kJ}}{\text{kg}}$
	$\dot{m}_i = 0.001061 \frac{\text{kg}}{\text{s}}$	$\dot{m}_f = 0.8857 \frac{\text{kg}}{\text{s}}$

$$\Rightarrow \dot{m}_i = \dot{m}_f = 0.373 \frac{\text{kg}}{\text{s}}$$

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

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

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

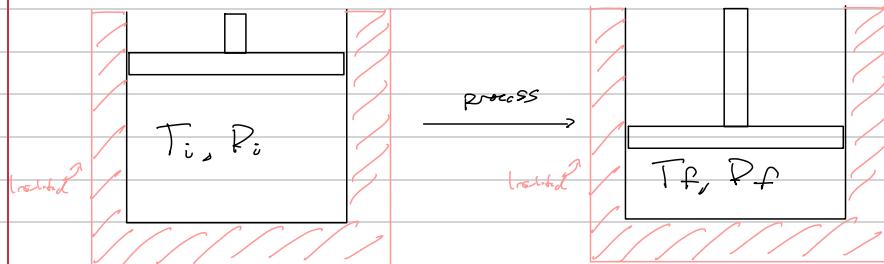
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

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

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

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

**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  $P_B = P$

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

$$nC_{v,m}dT = -P dV$$

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

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

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

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

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

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

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.

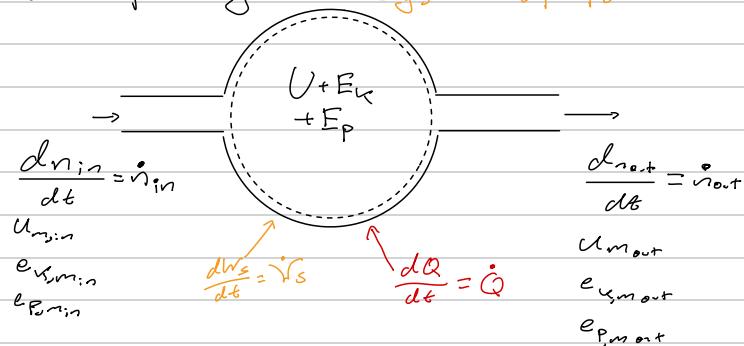
$$C_{p,m} = C_{v,m} + R$$

↑ 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:

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

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

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

= flow work on sys

→  $P > 0, V_m > 0$ , 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

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

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

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

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,  $\frac{d\dot{m}}{dt} = 0 = \dot{m}_{in} - \dot{m}_{out} \Rightarrow \dot{m}_{in} = \dot{m}_{out} = \dot{m}$

- 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

✓ mole accumulation

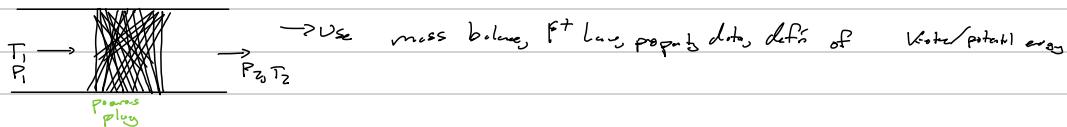
→ mole balance:  $\frac{d\dot{m}}{dt} = \dot{m}_{in} - \dot{m}_{out}$

- Total mass/mole accumulation:

$$\Delta n = n_{fin} - n_{ini} = \int_{n_{ini}}^{n_{fin}} dn$$

## Example: Throttling Process

- Script about rubber to reduce pressure in pipe (well-insulated)



Steady State:  $\frac{d}{dt}(U+E_k+E_p) = 0$ ;  $\frac{du}{dt} = 0$        $i_{in} = i_{out} = \dot{i}$

$\dot{m}_s = 0$  (no moving parts)       $e_{ext} \approx 0$  (assume much smaller than  $U$ ) & good approximation if velocity is much lower than the speed of sound

$\dot{Q} = 0$  (well insulated)       $e_{pm} = 0$  (no height difference)

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

$\rightarrow S$  : simple fact law

$$\text{so } \begin{aligned} O &= v_{in} h_{min} - v_{out} h_{max} \\ O &= h_{min} - h_{max} \\ O &= \hat{h}_{in} - \hat{h}_{out} \end{aligned}$$

Mole Balancing (in = out)  
 mole basis                      } independent or free  
 wsc basis                      of fluid

a) Let's assume fluid is water:

$$\begin{aligned} T_1 &= 350^\circ\text{C} & \rightarrow & T_2 ? \\ P_1 &= 10 \text{ MPa} & P_2 &= 1 \text{ bar} \\ && \text{Specified} \\ \rightarrow h_1 &= \hat{h}(350^\circ\text{C}, 10 \text{ MPa}) = 2923.4 \frac{\text{kJ}}{\text{kg}} \\ \stackrel{\text{1st Law}}{=} h_2 &= h_1 \quad \text{since } \Delta h = 0 \end{aligned}$$

$$\text{Find } T \text{ where } h_2 = 2923.4 \frac{\text{kJ}}{\text{kg}} \text{ at } P_2 = 1 \text{ bar} = 0.1 \text{ MPa}$$

$$\rightarrow A + 1 \text{ bar}, h(200^\circ\text{C}) = 2875.3$$

$$h(250^\circ\text{C}) = 2974.3 \quad \text{3 superheated}$$

$$\frac{(2974.3 - 2875.8)}{250-200} \left( T_2 - 200 \right) + 2875.8 = 2923.4$$

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

b) Welche Art von Lipp- oder Phlegmatischität geht es um?

- 1)  $T_2 < T_1$       3)  $T_2 = T_1$   
 2)  $T_2 > T_1$       4) real more : P-

Why?

$$\rightarrow \text{Stab} : h_{m_2} - h_{m_1} = 0 \quad (\text{Same first line})$$

$$\Delta h = 0$$

$$\oint dh_m = \sum_{m=1}^M dh_m = 0 \quad (\text{Chase's property is transnational of diff. m})$$

$\rightarrow$  def. col. G.s.:  $b_m = b_m(T)$  only

$$d\ln_{T_1} = C_p dT \quad \text{For adiabatic gases}$$

$$\Delta h_m = \int_{T_1}^{T_2} C_p m \, dT = 0$$

$$\rightarrow C_{pm}(T_2 - T_1) = 0 \Rightarrow T_2 = T_1 = 250^\circ C \quad \text{also to if } C_{pm} = C_{pm}(T) \quad [\text{i.e., not constant}]$$

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):  $\hat{h} \neq \hat{h}(T)$  only

$$S_o \quad \hat{h}_2 = \hat{h}_1 \quad \text{but} \quad T_2 \neq T_1$$

Q: What is the significance of enthalpy  $\hat{h}$ , 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

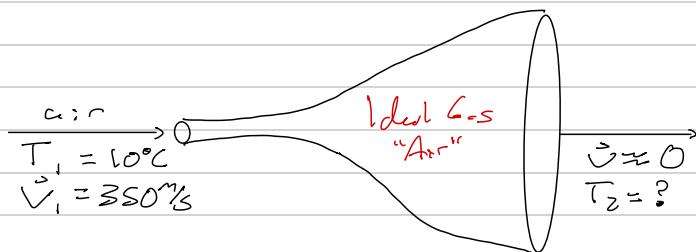
3) Flows in open systems have enthalpy  $\hat{h}$ , but not internal energy. Of course  $\hat{h}$  has internal energy!

4) Amount of heat transferred at constant pressure

5) All of the above will do! closed systems

E: 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  $\dot{Q} = 0$

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

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

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

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

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

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

ideal g.s.

"Air": assuming ideal gas

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

$$\text{constant } C_p \quad \frac{K_{20}}{2.053} \hat{C}_p = \frac{C_p}{M W_{air}} \leftarrow (-28 \times 10^{-3} \text{ kg/mol})$$

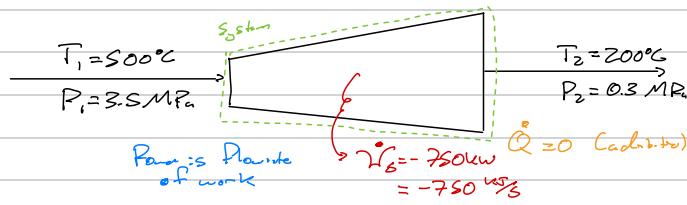
$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,1} \rightarrow T_2 = \frac{\hat{e}_{k,1}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ\text{C}$$

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

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

**Example:** Turbo extracts work (power) from gas.

Adiabatic turbine: input steam @  $T_1 = 500^\circ\text{C}$ ,  $P_1 = 3.5 \text{ MPa}$  expanded to  $T_2 = 200^\circ\text{C}$  and  $P_2 = 0.3 \text{ MPa}$ . Turbine generates  $750 \text{ kW}$  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  $h_{in}$ ,  $h_{out}$ )

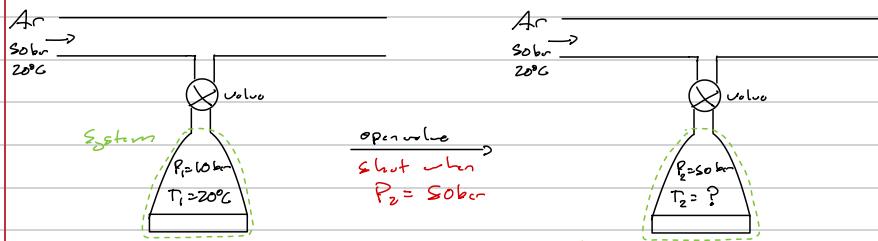
$$\dot{m} = \frac{-750 \text{ kW}}{2865.9 - 3451 \frac{\text{kJ}}{\text{kg}}} = 1.28 \frac{\text{kg}}{\text{s}}$$

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

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

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

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

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

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

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

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

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

$$\Delta h_m = \int_{T_1}^{T_2} C_{p,m} dT$$

bc  $T_1 = T_2$

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

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

\* not given  $n_1$ , but it cancels out

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

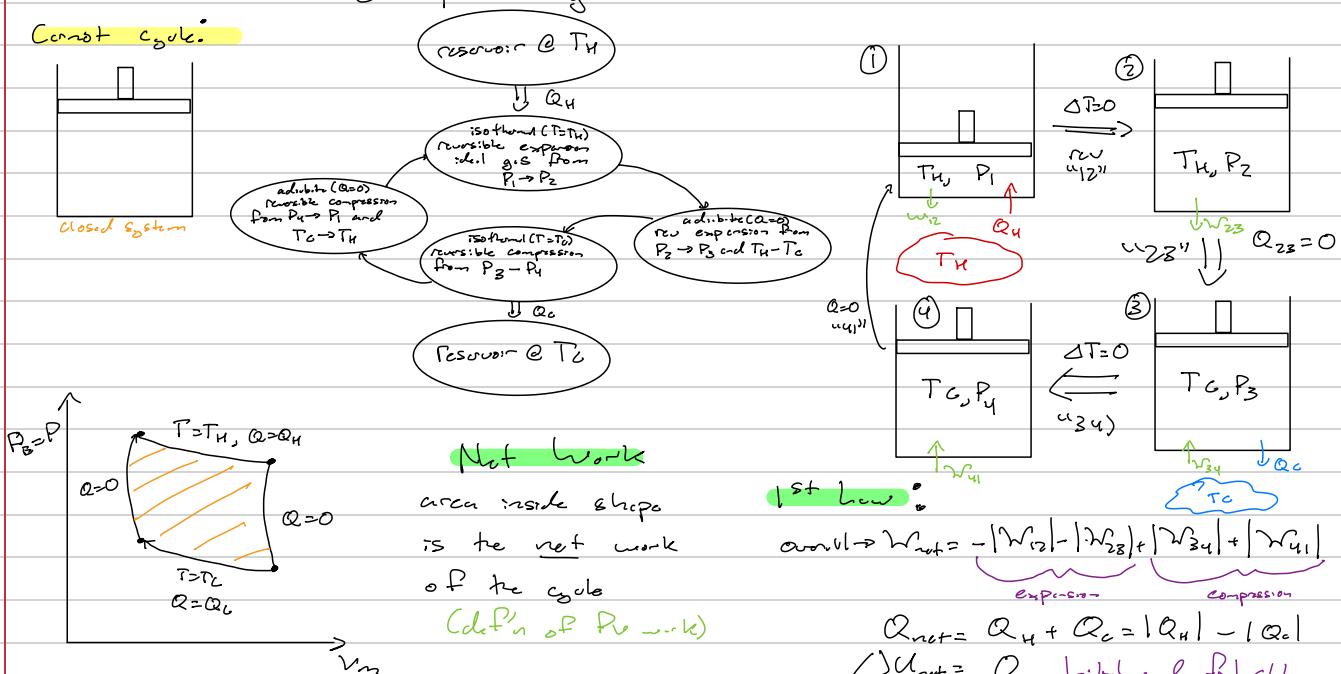
$$(C_{p,m} = \frac{5}{2} R)$$

# 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 ( $T=T_H$ )

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

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

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

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

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" is adiabatic  $\rightarrow P_2 V_2^k = P_3 V_3^k$

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

Substitute

$$\frac{P_3}{P_2} = \frac{P_4}{P_1}$$

To Summary

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

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

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

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

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

## Discuss Overall Cycle

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

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

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

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

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

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

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

## Entropy

$\rightarrow$  words associated with entropy?

- randomness
- disorder
- chaos
- number of states

Related to molecular probability and statistics

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

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

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

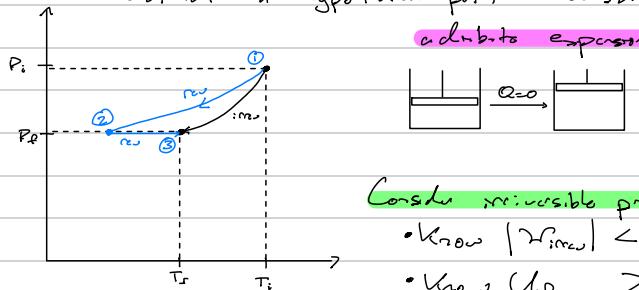
Q: Which process has the most positive change of the fluid P  $\Delta S_m$ ?

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

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

(not adiabatic)

$$\Delta S_{23} = \int_{T_2}^{T_3} \frac{dQ_{23, \text{irr}}}{T} \quad \begin{matrix} \text{"2" } \\ \text{const P} \end{matrix}$$

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

$$dQ = dU + PdV$$

$$dQ = dU + PdV$$

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

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

$$dQ = dH$$

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

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

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

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

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

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.

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

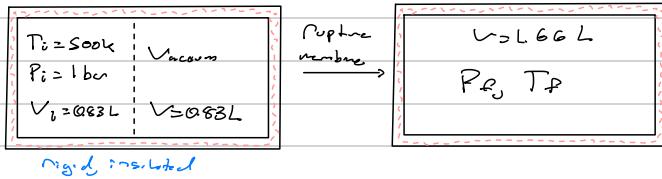
$$\Delta S_{12} = 0, \Delta S_{\text{surv}} = 0 \quad \text{reversible}$$

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

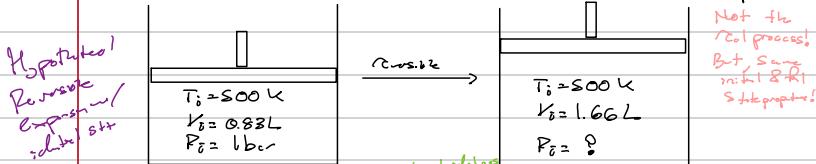
• 1st Law:  $\Delta U = Q + W \stackrel{\text{adiabatic}}{=} 0 \quad \text{no } Q, \text{ no } W \quad (\text{constant volume system})$

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

What about  $\Delta S$ ?

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

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



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

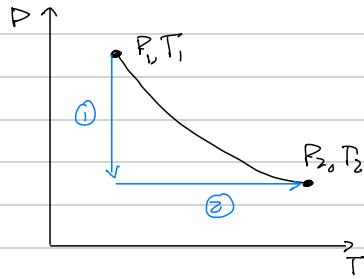
$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = \int \frac{dU_{\text{real}} - dW_{\text{real}}}{T} = - \int \frac{dW_{\text{real}}}{T} = - \int \frac{-P_{\text{real}} dV}{T} = \int \frac{P_{\text{real}} dV}{T} \stackrel{\text{isothermal}}{=} n \int_{V_i}^{V_f} \frac{R}{V} dV = n R \ln \left( \frac{V_f}{V_i}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

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

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

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

## Entropy changes for ideal G.S.



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

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

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

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

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

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

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

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

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

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

ideal gas  
entropy change

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

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

Q: How do we calculate  $\Delta S_{univ}$  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

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

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

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

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

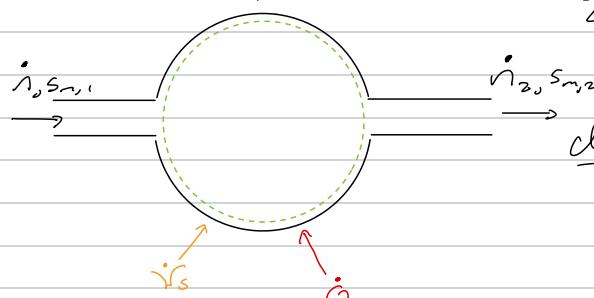
$$T_{sum} \mid \Delta S_{univ} = \Delta S + \Delta S_{sum}$$

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

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

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)

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

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

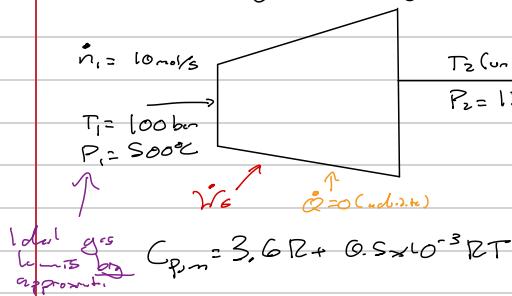
$\hookrightarrow$  steady  $\Rightarrow$  static  $\rightarrow \frac{dS_{\text{sys}}}{dt} = 0 \Rightarrow \frac{dS_{\text{univ}}}{dt} = \dot{n}_2 S_{m,2} - \dot{n}_1 S_{m,1} - \frac{\dot{Q}}{T_{\text{sum}}}$

## 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:  $\Delta S_{\text{univ}} = 0$

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

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

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

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

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)

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

$$\text{prop. of } \cdot \quad dS_m = \frac{C_{P,m}}{T} dT - \frac{R}{P} dP$$

ideal g.<sup>s</sup>  $\rightarrow$  (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

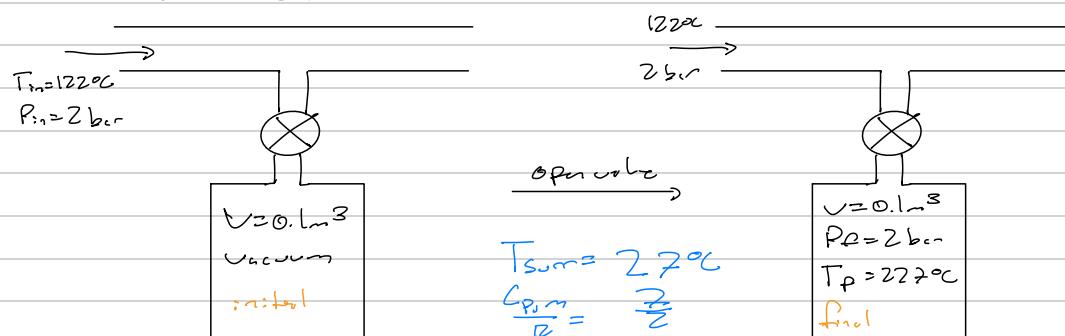
c) What is  $T_2$ ? (80% efficiency)

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

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

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

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

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

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

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

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

→ What about  $(s_{m,p} - s_{m,i,p})$

- For ideal gas: integrate  $ds_m$

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

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

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

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

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

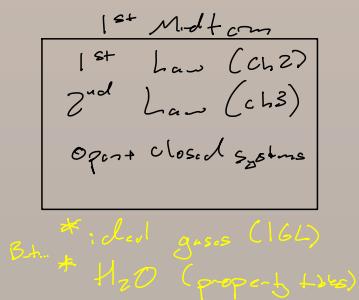
(Comparing to remote answer)

✓ 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

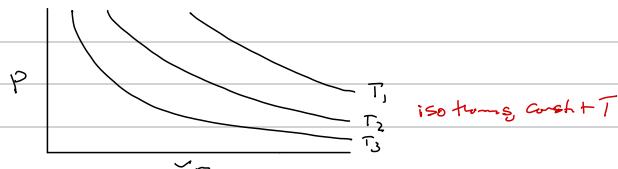
Examples of EOS's

(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

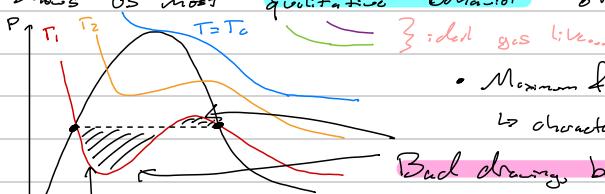
$b$  is a const vol for a fluid, independent of the fluid's  $T$  &  $P$ .

(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



• Maximum & inflection point @  $T=T_c$

$\hookrightarrow$  characteristic of real fluids

Bad drawing, but these two regions should have equal areas

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

Isotherms do not give accurate pressure inside the VL dome

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

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

For VDW EOS

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

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

Set equal and solve to get these as  $a, b$

2 eqns,

2 unknowns ( $a, b$ )

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

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

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

expressions valid only for VDW EOS

$$Z_c = \frac{P_c V_{m,c}}{R T_c} = \frac{3}{8}$$

@ 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"

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

• 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

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

loss attrn @ low T

more accurate intermolecular term

$$\left. \begin{array}{l} a = \frac{0.42748 P_c^{5/2} T_c}{R} \\ b = \frac{0.08664 R T_c}{P_c} \end{array} \right\} \begin{array}{l} \text{Not the same as} \\ a \text{ and } b \text{ in VDW} \\ \text{EOS} \end{array}$$

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

#### (ii) Peng-Robinson EOS

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

where  $\alpha$  is a function of  $T$  and  $K$  is a factor of  $\omega$

← common in industry

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

← acentric factor ( $\omega$ : shape of molecules)

(::)- (✓)  $\sim$  all 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

✓ "2" and "3"

### Compressibility Charts

$$Z = Z^{(0)} + \omega Z^{(1)} = f(T, P)$$

Kind of boring & only not really total  
in this case

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.:  $PV_m = RT \rightarrow V_m = \frac{RT}{P}$

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

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

∴  $dh_m = C_p dT$  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:  $\dot{m}_1 = \dot{m}_2 = \dot{m}$  (steady)

1st Law:  $\dot{Q} = \dot{m}_1 h_{m1} - \dot{m}_2 h_{m2} + \dot{W}_s$  adiabatic no moving parts

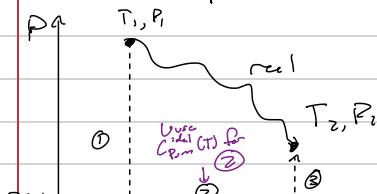
$$\rightarrow h_{m1} - h_{m2} = \dot{Q} \Rightarrow \Delta h_m = \int_{T_1}^{T_2} dh_m = \dot{Q} \quad T_1 = T_2 \quad \text{bc } dh_m = C_p dT \text{ for ideal gas}$$

(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  $dh_m$ :

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

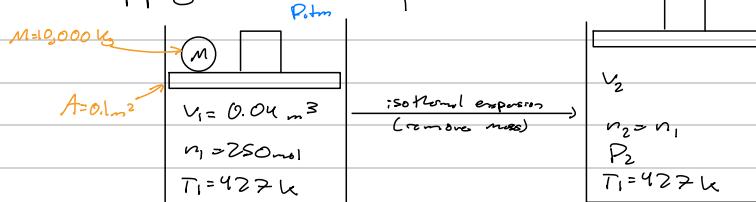
$$\frac{du_m}{dV_m} = T \frac{dS_m}{dV_m} - P \frac{dV_m}{dV_m} \Rightarrow \left( \frac{\partial u_m}{\partial V_m} \right)_T = T \left( \frac{\partial S_m}{\partial V_m} \right)_T - P$$

(iii) 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  $\Delta U$  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

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

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

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

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: enthalp.  $\left( \frac{\partial P}{\partial T} \right)_{V_m}$   
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  
isothermal

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

### → 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:

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

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

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

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

( $\therefore$ ) Total Differential

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

↑ not  $C_{Vm}$  or  $C_{Pm}$ !

Use definition:  $h_m \equiv U_m + P_m$

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

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

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

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

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

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

Maxwell relation from  
FE for  $dU_m$

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

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

FE:  $dU_m = T dS_m - P dV_m$

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

Sub & divide  
 $\rightarrow$   
 $m \neq B$

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

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

FE:  $dU_m = T dS_m + V_m dP$

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

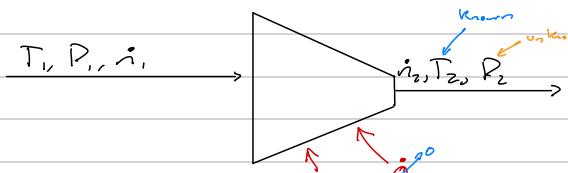
Sub & divide  
 $\rightarrow$   
 $dU_m \text{ FE}$

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

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



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



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

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

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

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

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

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

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

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

②  $T \rightarrow T_2$  under 1st law, deal w/ ~~last 3~~ ~~last 3~~ Problem?  $L(0)$  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  $P^{\text{ideal}} = 0$

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

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

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

Derv'd from ideal behavior

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

Note: If  $B=0$ : ideal 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: If  $dS_m = \frac{C_{P,m}}{T} dT - \left( \frac{\partial v_m}{\partial T} \right)_P dP = 0$  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  $P$

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

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

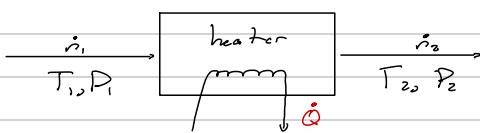
$$\left( \frac{\partial T}{\partial P} \right)_{S_m} = \frac{T}{C_{P,m}} \left( \frac{\partial v_m}{\partial T} \right)_P \quad \checkmark$$

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

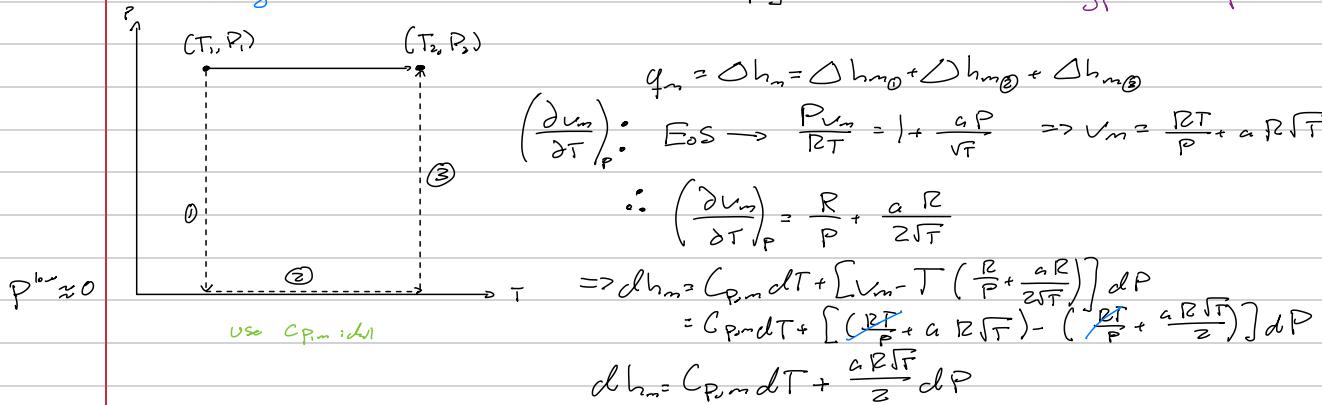
1st Law:  $\frac{d}{dt}(U + E_k + E_p) = 0 = dot{m}_1 h_{m,1} - dot{m}_2 h_{m,2} + dot{Q} + dot{W}_s$  no shaft work  
 $dot{Q} = dot{m}(h_{m,2} - h_{m,1})$

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

$\Rightarrow$  use  $dh_m = dh_m(T, P)$

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

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



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

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

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

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

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

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

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

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

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

## Other Chapter 5 Information

- Did not cover:

- Ch 5.4 - derivative functions

- Ch 5.5 - Joule-Thomson Expansions

- Equations for Ch 5 on Canvas

- Summary of Techniques

- ① Manipulate the FB (4 forms!)

- "Dimension Tricks"

- ② Total differential expressions

- ③ Maxwell Relations

- 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

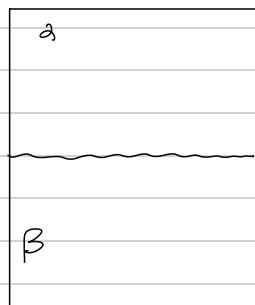
## Liquid Phases

At equil,

- $\Delta S$  is minimized
- $\Delta G$  is minimized
- A and B are in thermal & mechanical equilibrium

$$\left\{ \begin{array}{l} T^A = P^A \\ P^A = P^B \end{array} \right.$$

- Consistency of
- $M^A = M^B$  (2nd Law)  $\Rightarrow$  phase envelope: vapor-liquid Equil (VLE)



Criteria of equilibrium:

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

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

$\rightarrow$  Eventually @ equil,  $\Delta S + \Delta S_{\text{sum}}$  is minimized

For a system at known  $T, P$ :

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

$\rightarrow G$  is minimized @ equilibrium

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

In special cases (single component systems)

## Phase Equil Requirements

$$T^A = T^B$$

$$P^A = P^B$$

$$M^A = M^B$$

So what! Can we make this practical

$$M^A = M^B$$

$$\text{pure component: } g_m^A = g_m^B$$

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

↓  $dP/dT$

d.PF content:  $dh_m^A = dg_m^B$

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

↓  $P^A = P^B = P_j$

No. of:  $T^A = T^B = T$

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

↓

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

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

Clapeyron Equation:  
relates  $T, P, R$  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)  $> 3$

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

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

FE

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

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

• At phase eq, pure single component,  
 $\hookrightarrow$  1 equation (Clapeyron), 2 unknowns ( $T, P$ )  $\rightarrow$  1 DoF "

• Compare to Gibbs phase rule:

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

$\rightarrow$  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

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

(i) Recondo (Separato)

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

(ii) Solve! assumed constant

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

(iii) Integrate

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

Choose reference conditions / stato

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

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

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

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

Clausius-Clapeyron Eqn (CCB)

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

Answers: Key equations for single-component phase equilibria

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

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

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

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

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

② Are either  $V_m^{\alpha}$  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 Raoult's law equation (not CCF,  $\Delta h_m^{\text{vap}} \neq \text{constant}$ )

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

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

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

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

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

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

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

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

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

**Example:** Is  $\text{CO}_2$  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  $\text{CO}_2$

$P_{\text{trip}} = 1.18 \frac{\text{mol}}{\text{cm}^2 \cdot \text{K}}$  @ 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-liquid 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

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

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

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

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

2) Solid-Liq Equil.

- Starting w/ Clapeyron eqn, assume:

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

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

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

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

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta h_{\text{m}}^{\text{sub}}}{\Delta V_m^{\text{L-S}}} \left( \frac{1}{T} \right) \Rightarrow P_{\text{S,L}} - (5.2 \text{ bar}) = \frac{\Delta h_{\text{m}}^{\text{sub}}}{\Delta V_m^{\text{L-S}}} \ln\left(\frac{T}{216.6}\right)$$

3) Solid-Vapor Equil.

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

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

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

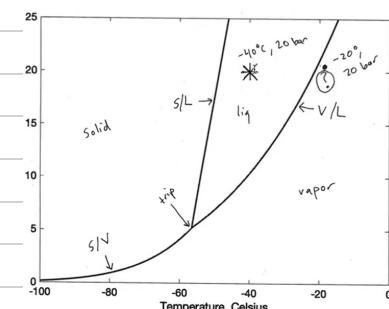
$$\Rightarrow P_{\text{S,V}} = (5.2 \text{ bar}) \times \exp\left[-3139\left(\frac{1}{T} - \frac{1}{216.6}\right)\right]$$

→ Now? 3 eqns relating 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?

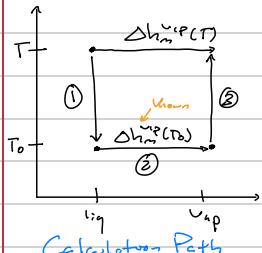
In vapor, but close  
constant assumptions!

- 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

$\frac{\partial V}{\partial n_i} \Big|_{T, P, n_1, \dots, n_{i-1}, n_{i+1}, \dots, n_m} = V_i \leftarrow p^{-1} \text{ molar prop.}$

What is  $\bar{G}_i$ ?

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

In general,

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

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

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

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

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

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

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

Applies to  $dU$ .

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

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

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

Multicomponent systems have different properties

① Total solution properties

• exterior:  $G, U, S, \dots, K$

• interior:  $\rightarrow$  dn<sub>i</sub>  $\rightarrow \frac{n_i}{n_{\text{tot}}} = f_i$   
 $K_m = \sum_i f_i = \frac{n_m}{n_{\text{tot}}} > \frac{n_m}{n_{\text{tot}}}$

② Pure species "i" properties

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

• interior:  $n_i, g_i, g_m, \dots$  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  $\bar{V}$   $\rightarrow$  G-D @ const  $T, P$ ,

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

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

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

$$\therefore 0 = 0$$

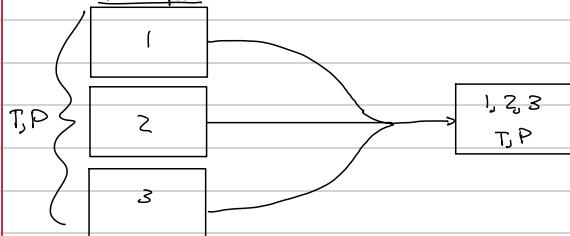
Q: What is the physical meaning of  $\bar{K}_i$  in a mixture?

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

Partial molar property

### Property Changes of Mixing

Pure Species



Extensive Property change of mixing:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\text{Mixture: } \bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{2B, n_1, n_2, n_3} = \frac{\partial}{\partial n_i} \left( \frac{(n_1 + n_2 + n_3) RT}{P} + P[A(n_1 - n_2) + B(n_1 + n_2 + n_3)] \right)_{2B, n_1, n_2, n_3}$$

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

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

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

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

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

$$\therefore \Delta V_{mix} = 0 \quad \text{not guaranteed for this EoS}$$

specifically!