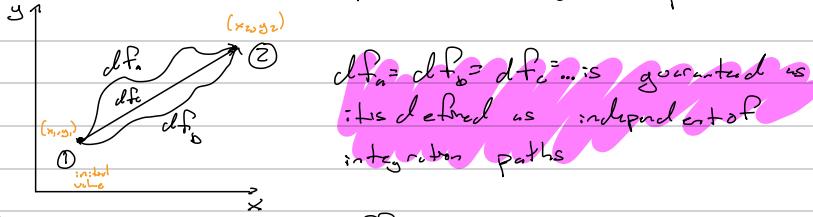




# Math Review

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



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

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

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

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

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

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

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

$$\int f(x) dx$$

Integral  $\uparrow$  Differential

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

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

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

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

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

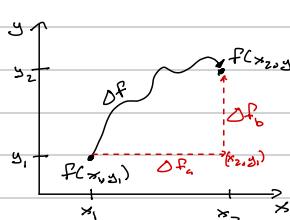
**Summary - Common points of confusion!**

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

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

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

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



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

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

We can do this bc the differential is independent of path

\* Math no-no!

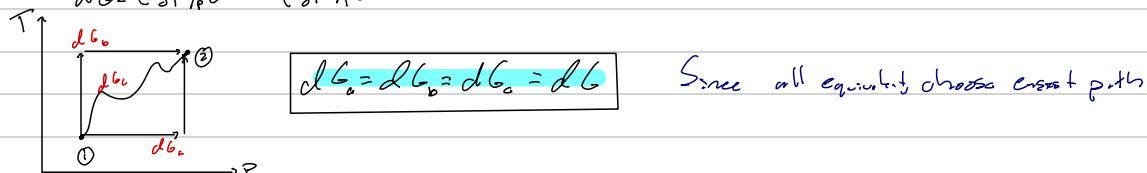
$\times \Rightarrow \int \frac{df}{dx}$  cannot be evaluated! Missing the differential!

$\hookrightarrow$  Must integrate over differential changes

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

# Chapter 1 - Thermodynamic Properties

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



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

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

→  $dW$  and  $dQ$  do depend on path

→ use notation  $\delta Q$  and  $\delta W$  to denote an inexact differential

What is Thermodynamics?

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

• First Law: Conservation of Energy

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

• Second Law: Entropy increases

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

• Two benefits of the 2nd Law

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

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

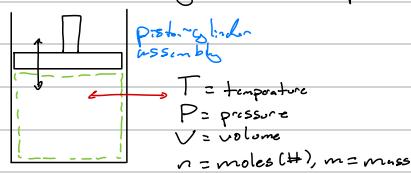
① System and Surroundings



• Three Types of Systems

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

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



### Types of Properties

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

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

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

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

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

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

density

We can convert ext quantities to int ones:

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

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

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

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

## ③ "State" of a System

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

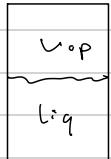
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑  
degrees of freedom  
↑  
# of chemical species  
↑  
# of phases

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

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

Example: Vapor-liquid mixture of  $\text{H}_2\text{O}$



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

↓  
molar of  $\text{H}_2\text{O}$

↓  
molar of  $\text{H}_2\text{O}$

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

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

↑  
average molar volume

x ≈ "quality"

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

→ constrains all other intensive properties

Also need to specify total amount in each phase

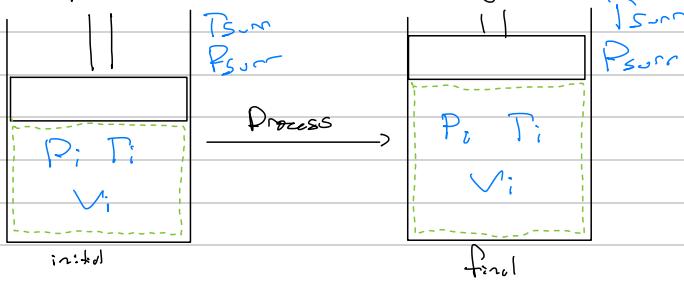
$$\rightarrow V_{\text{tot}} = V_{\text{liq}} + V_{\text{vap}}$$

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

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

## ④ Processes

- A process is a change in the system



## 4 Special Types of Processes

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

## ⑤ Equilibrium

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

### → Examples:

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

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

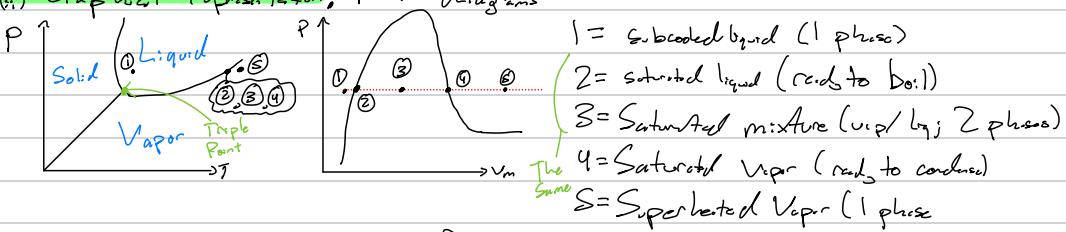
(iii) Phase Equilibrium  $\rightarrow$  Composition of phases is constant

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

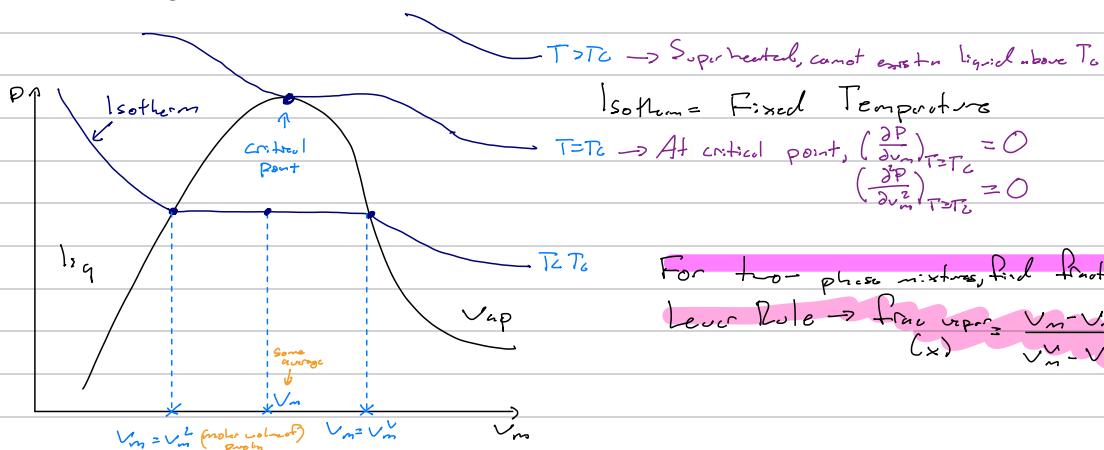
## Thermodynamic Property Sources

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

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



(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  $\dot{V}_i \geq \dot{V}_{i,sat}$  you have pure vapor
- If  $\dot{V}_{i,sat} > \dot{V} > \dot{V}_{i,l}$  you have a mixed phase
- If  $\dot{V}_{i,l} \geq \dot{V}$  you have pure liquid

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

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

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

initial (i)

$$V_i = 100L$$

$$T_i = 100^\circ C$$

saturated

final (f)

$$V_f = 100L = V_i$$

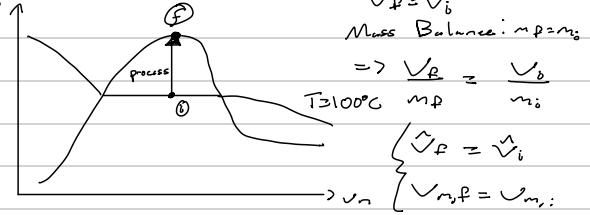
$$T_f = T_c$$

$$P_f = P_c$$

process

→ ends

at critical point



b) Find the mass and initial quality.

(outcomes)

→ mass balance:  $m_f = m_i$

rigid:  $V_f = V_i = V$

$\rightarrow \dot{V}_f = \dot{V}_i = \dot{V}$

Steam Tables

because  $P_c, T_c$  state is a crit point

$$\dot{V}_f = \dot{V}_i = \dot{V}_c = 0.0033155 \frac{m^3}{kg}$$

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

bottom of tube

↳ of temp →  $\dot{V}_{c,g} = 0$

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

(continued)

$$\dot{V}_i = \dot{V}_{i,L}^{sat} (1-x) + \dot{V}_{i,V}^{sat} x$$

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

S + Steam @ 100°C

$$\dot{V}_{i,L}^{sat} = 0.001047 \frac{m^3}{kg}$$

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

$$\rightarrow \dot{V}_{i,L}^{sat} < \dot{V} < \dot{V}_{i,V}^{sat} \Rightarrow L/V \text{ mixture}$$

# 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

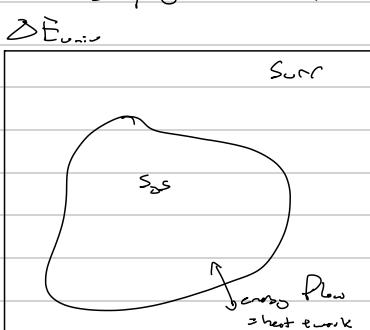
- phase changes

- 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

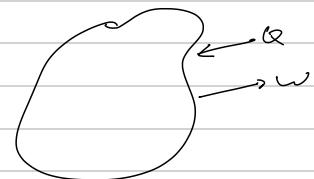
Q: Heat and work are flowing across the system boundary. What can we say about  $Q$  and  $W$ ?

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.)

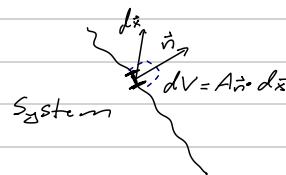
② Work ( $W$ ): this class!

a) System boundary moves against an external force

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

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

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



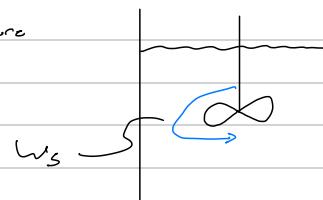
→ Calculating PV work requires us to know external pressure

\*  $P_E$  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

New  
Rec'd  
T<sub>ip</sub> Brovo  
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7

Ex

Reversible work for ideal gas expansion under isothermal conditions.



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

• reversible →  $P_E \approx P$

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

$n$  is constant

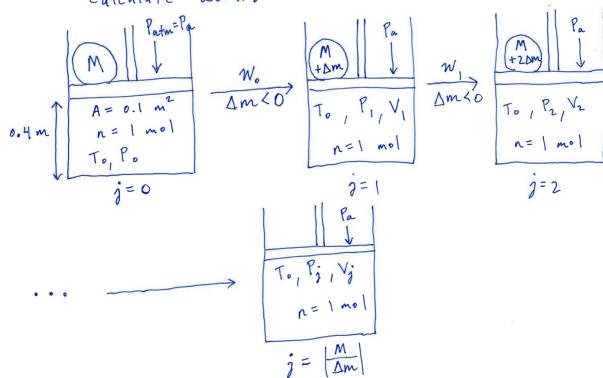
$$\frac{W}{n} = w_m = - RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

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

reversible work,  
isothermal,  
ideal gas

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

calculate work.



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

• final mass = 0

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

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

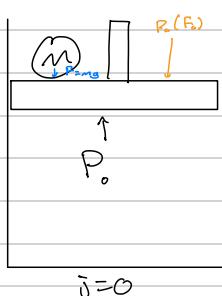
• PV work def'n →  $W = - \int P_E dV$  external pressure

↳ what is  $P_E$ ?

• At eq.  $P_E$  should equal  $P_{eq}$

• pressure / force balance:

### Pressure / Force Balance



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

cross-section area of piston

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

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

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

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

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

$P_{E,1} = P_1$

Subd. g.s.law

$P_1 V_1 = P_0 V_0$

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

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

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

$(V_1 \text{ to } V_2)$

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

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

$P_0$

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

Expansion → S<sub>down</sub> class work

Example Continued

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

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

so, total work done is:

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

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

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

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

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

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

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

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

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

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

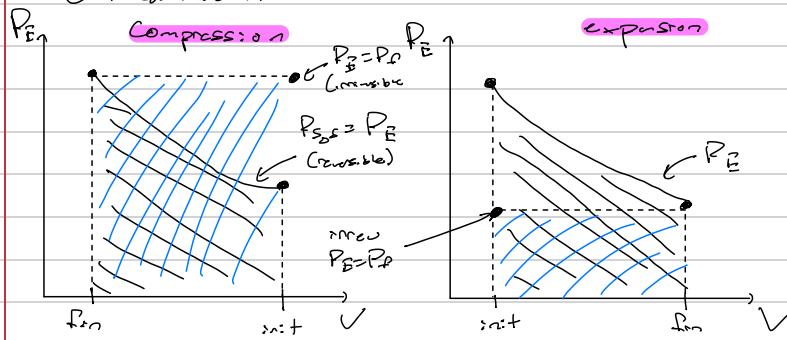
This is a reason why assuming a reversible process can be convenient.  $W_{\text{re}} = -5545 \text{ J}$

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

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

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

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



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

$$W = - \int P_E dV$$

## Internal Energy

• How do we calculate  $\Delta U$  ( $dU$ )?

→ Several Options:

(i) Property tables (NIST, steam tables)

(ii) Specific (molar) heat capacities

a) Ideal Gas:  $U_m = U_m(T)$  only (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

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

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

## Enthalpy ( $h_m$ )

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

→ For ideal gas,  $PV_m = RT$

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

Note that heat capacities are defined for a single phase.

## How to Measure $C_{p,m}$

→ closed system, calorimeter, system @ const P

const P →  $P_E = P$  (force balance)

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

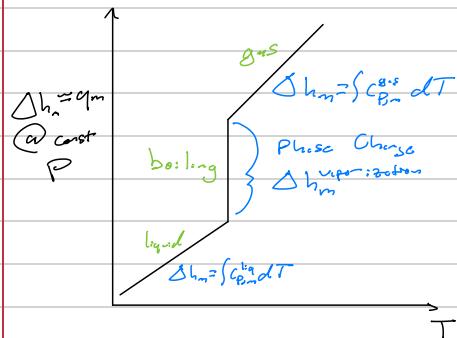
$dU_m = dq_m - d(PV_m)$  can make this more only bc Pressure P is constant

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

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

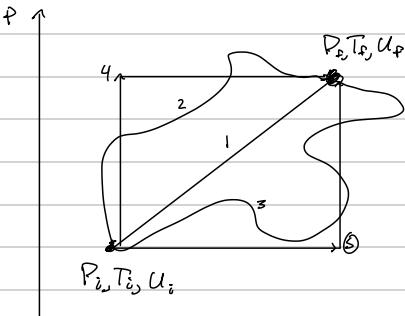
$\leftarrow$  measure T to determine  $h_m$  &  $C_{p,m}$

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



## Calculation Paths

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

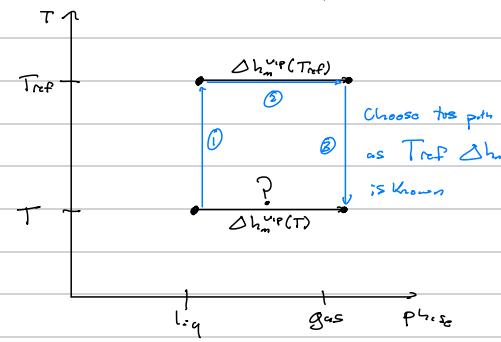


$$\Delta U = U_f - U_i$$

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

True for any process!

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



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

Solution:

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

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

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

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

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

## Example 1st Law w/ Property Tables

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

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

Process:  
closed system  
constant volume

- initial state is sat'd water,  $x = 0.42$
- rigid  $\rightarrow V_f = V_i$ , and  $\dot{V}_f = \dot{V}_i = 0$
- closed system  $\rightarrow m_i = m_f$  From mass balance
- water is heated  $\rightarrow q \neq 0$
- $\dot{W}_s = 0$  no moving parts or mixing
- $\dot{W} = - \int_{V_i}^{V_f} P_E dV = 0$  (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	$\hat{u}_i = 504.47 \frac{\text{kJ}}{\text{kg}}$	$\hat{u}_f = 2529.5 \frac{\text{kJ}}{\text{kg}}$
$B.2$	$\dot{V}_i = 0.001061 \frac{\text{m}^3}{\text{kg}}$	$C_v = 0.8857 \frac{\text{m}^2}{\text{kg}}$

$$\Rightarrow \dot{V}_i = \dot{V}_f = 0.373 \frac{\text{m}^3}{\text{kg}}$$

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

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

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

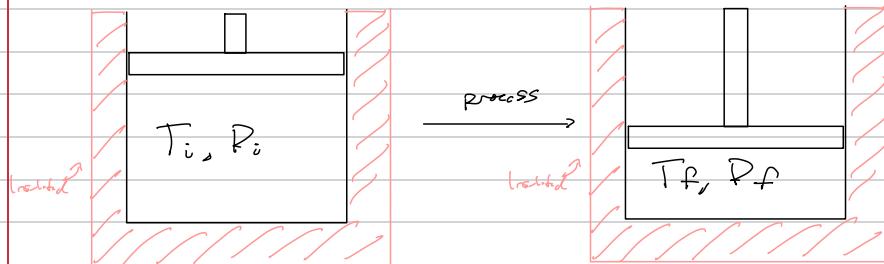
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

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

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

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

**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.

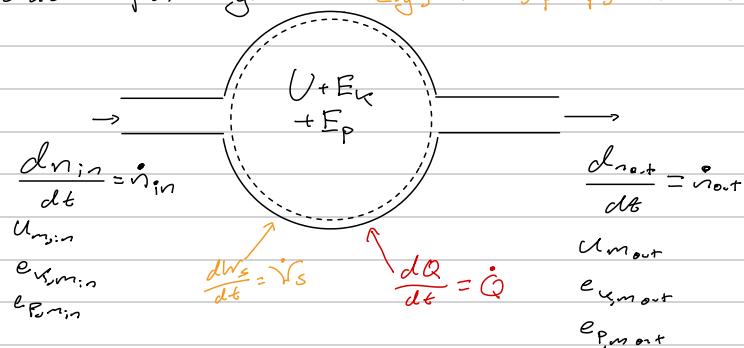
$$C_{p,m} = C_{v,m} + R$$

↑ 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:

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

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

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

= flow work per kg

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

⇒ Add flow work to energy balance

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

accumulation

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

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

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

First Law, Open Systems

Can also write on a mass basis:

IF open system is at steady-state

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

- no change in energy of system

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

- no change in properties with time

IF NOT steady-state

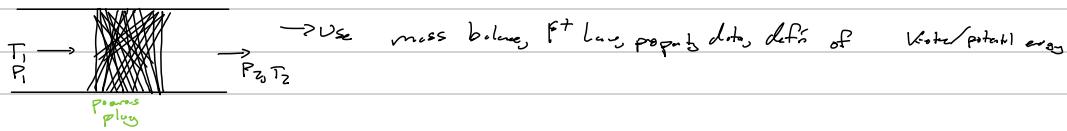
$$\rightarrow \text{mole balance: } \frac{d\dot{m}}{dt} = \dot{\nu}_{in} - \dot{\nu}_{out}$$

- Total mass/mole accumulation:

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

## Example 6: Throttling Process

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



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

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

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

$e_{kin} \approx 0$  (smaller than  $u^2$ ) ← good approximation if velocity is much lower than the speed of sound

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

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

→ Simplified F+ Law

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

so

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

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

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

mole basis } independent of fluid  
mass basis }

a) Let's assume fluid is water:

$T_1 = 350^\circ C$

$P_1 = 10 \text{ MPa}$

$\rightarrow T_2 ?$

$P_2 = 1 \text{ bar}$

Find  $T_2$ !

$\hat{h}_1 = \hat{h}(350^\circ C, 10 \text{ MPa}) = 2923.4 \frac{\text{kJ}}{\text{kg}}$

1st law  $\hat{h}_2 = \hat{h}_1$  since  $\Delta h = 0$

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

$\rightarrow$  At 1 bar,  $\hat{h}(200^\circ C) = 2875.3 \quad \hat{h}(250^\circ C) = 2974.3$  } Superheated

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

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

b) What will happen if fluid is ideal gas?

1)  $T_2 < T_1$

3)  $T_2 = T_1$

2)  $T_2 > T_1$

4) real more  $\Rightarrow T_2$

Why?

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

$\Delta h_m = 0$

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

$\rightarrow$  1st law L.s.:  $h_m = h_m(T)$  only

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

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

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

Note: Compare  $H_2O$  + ideal gas case of throttle

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

$$dh_m = C_p dT$$

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

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

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

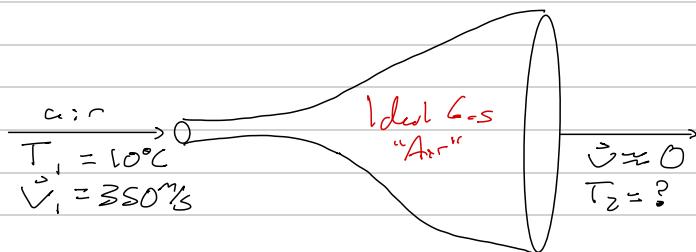
3) Flows in open systems have enthalpy  $\hat{h}$ , but not internal energy. Of course  $\hat{h}$  has internal energy!

4) Amount of heat transferred at constant pressure

5) All of the above will do! closed systems

E: Nozzle or Diffuser

↳ These devices 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  $\dot{Q} = 0$

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

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

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

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

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

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

ideal g.s.

"Air": assuming ideal gas

$$\rightarrow \text{From Kortets } K_{20} \hat{C}_{p,m} \approx 3.3552$$

$$\text{constant } C_p \quad \frac{KJ}{kg \cdot K} \hat{C}_p = \frac{C_p}{MW_{air}} \leftarrow (-28 \times 10^{-3} \text{ kg/mol})$$

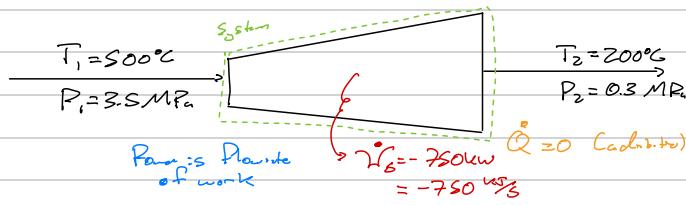
$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,1} \rightarrow T_2 = \frac{\hat{e}_{k,1}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ C$$

\*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:  $\frac{d}{dt} (U + E_k + E_p) = 0 \quad (\text{steady-state})$

$$\Delta \hat{e}_k \approx 0$$

$$\Delta \hat{e}_p \approx 0$$

1st Law:  $\dot{Q} = \dot{m}_{in} \hat{h}_{in} - \dot{m}_{out} \hat{h}_{out} + \dot{W}_s$

MB:  $0 = \dot{m} (\hat{h}_{in} - \hat{h}_{out}) + \dot{W}_s$

$$\dot{m} = \frac{\dot{W}_s}{\hat{h}_{out} - \hat{h}_{in}} \quad \begin{matrix} \text{steam tables} \\ \text{steam tables} \end{matrix}$$

Supersaturated steam tables (guts  $\hat{h}_{in}$ ,  $\hat{h}_{out}$ )

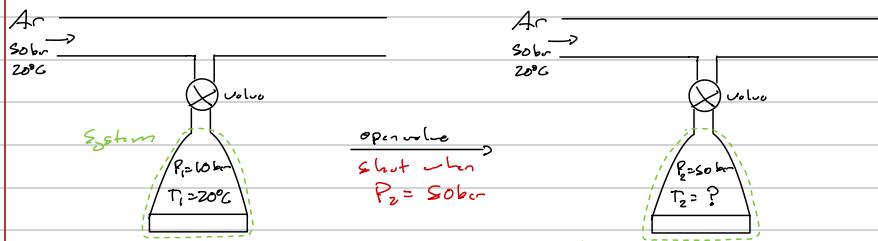
$$\dot{m} = \frac{-750 \text{ kW}}{2865.9 - 3451 \frac{\text{kJ}}{\text{kg}}} = 1.28 \frac{\text{kg}}{\text{s}}$$

How to find  $\dot{V}$ ?

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

### 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 → define system as tank

• Steady-state? No! transient

• mole balance?

$$\frac{dn}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad \text{gas only flows into tank}$$

• 1st Law open system

$$\frac{dU}{dt} = \dot{m}_{in} (h_{in} + e_{kin} + e_{pot}) - \dot{m}_{out} (h_{out} + e_{kin} + e_{pot})_{out} + \dot{W}_s \quad \begin{matrix} \text{no more} \\ \text{assumption} \end{matrix}$$

ignores PE

$\frac{dU}{dt} \neq 0 \quad \text{(not steady state)}$

$\frac{dU}{dt} = \dot{m}_{in} h_{min} - \dot{m}_{out} h_{max} \quad \text{Gas flows into tank}$

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

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

$$\rightarrow U_2 - U_1 = h_{min} (n_2 - n_1) \quad \begin{matrix} \text{mols & T change + same} \\ \text{extensive DE for sys(tank)} \end{matrix} \quad \begin{matrix} \text{constant} \\ \text{n constant} \end{matrix} \quad \text{find } U_2$$

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

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

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

$$h_m = U_m + RT \quad (\text{for all g.s.})$$

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

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

bc  $T_1 = T_2$

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

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

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

$$\rightarrow \text{sub } n_2 \rightarrow \begin{aligned} T_2 &= \frac{\frac{5}{2} T_1}{\frac{5}{2} + \frac{3}{2}} = 187.9^\circ\text{C} \\ \left( C_{p,m} = \frac{5}{2} R \right) \end{aligned}$$

# 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 gas, reversible process

→ Practical use: Converts temperature gradient to useful work

Carnot cycle:

