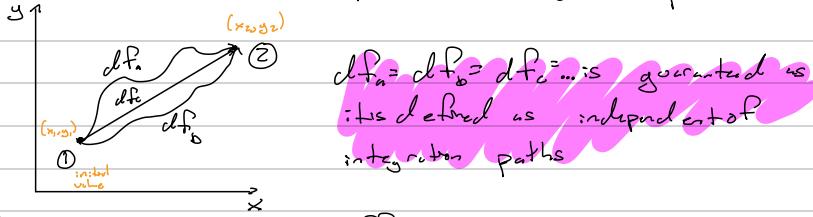




# Math Review

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)

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

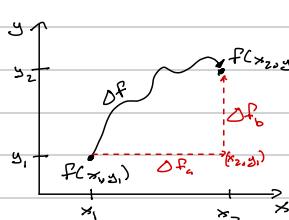
**Summary - Common points of confusion!**

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!

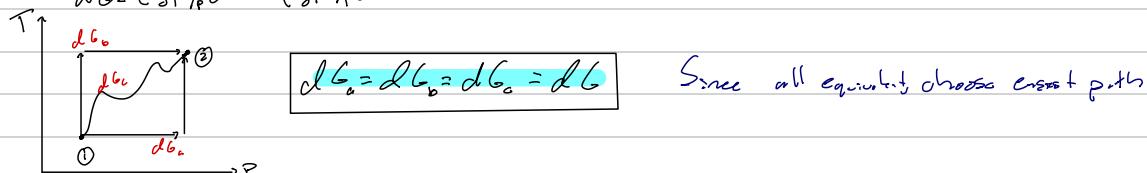
$\times \Rightarrow \int \frac{df}{dx}$  cannot be evaluated! Missing the differential!

$\hookrightarrow$  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

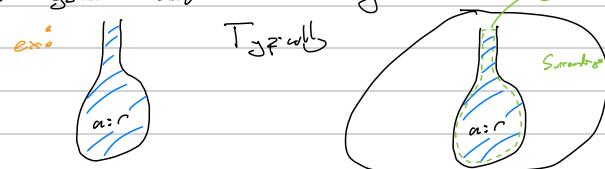
$\Delta S_{\text{univ}} \geq 0$  for any process

• 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.

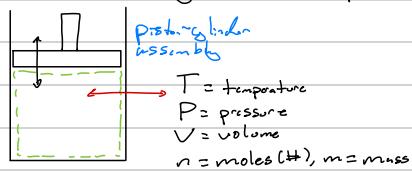
① System and Surroundings



• 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 ( $C_{\text{inf}}$ )	↑ extensive ( $C_{\text{ext}}$ )	↑ int	↑ ext

density

We can convert ext quantities to int ones:

extensive = "specific property" ↗ lowercase with or w/o mass  
mass

extensive = "molar property" ↗ lowercase w/ subscript  $m$   
moles

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

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

## ③ "State" of a System

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

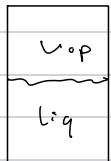
$$f = m - \pi + 2 \quad \text{for non-reactive systems}$$

↑  
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"

$$\text{Also: } \beta = (1-x) \beta_{\text{L}} + x \beta_{\text{V}}$$

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

→ constrains all other intensive properties

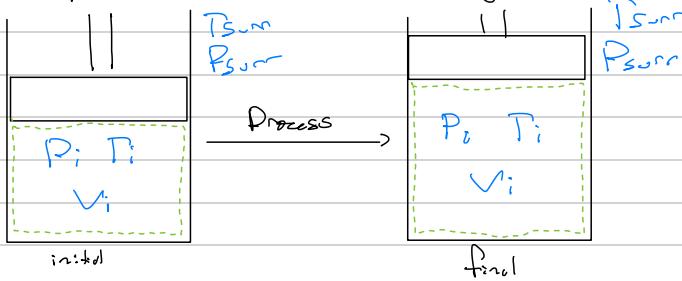
Also need to specify total amount in each phase

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

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

## ④ Processes

- A process is a change in the system



## 4 Special Types of Processes

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

## ⑤ Equilibrium

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

### → Examples:

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

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

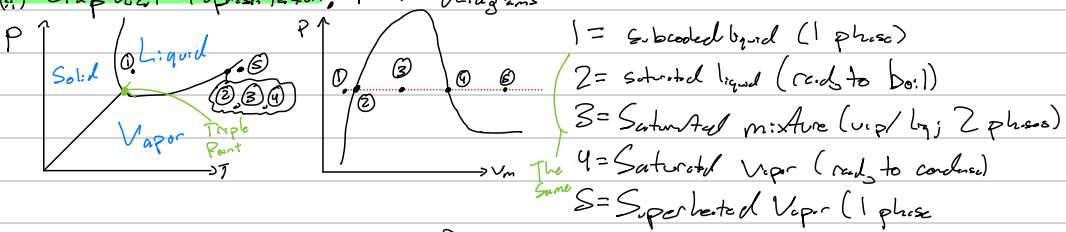
(iii) Phase Equilibrium  $\rightarrow$  Composition of phases is constant

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

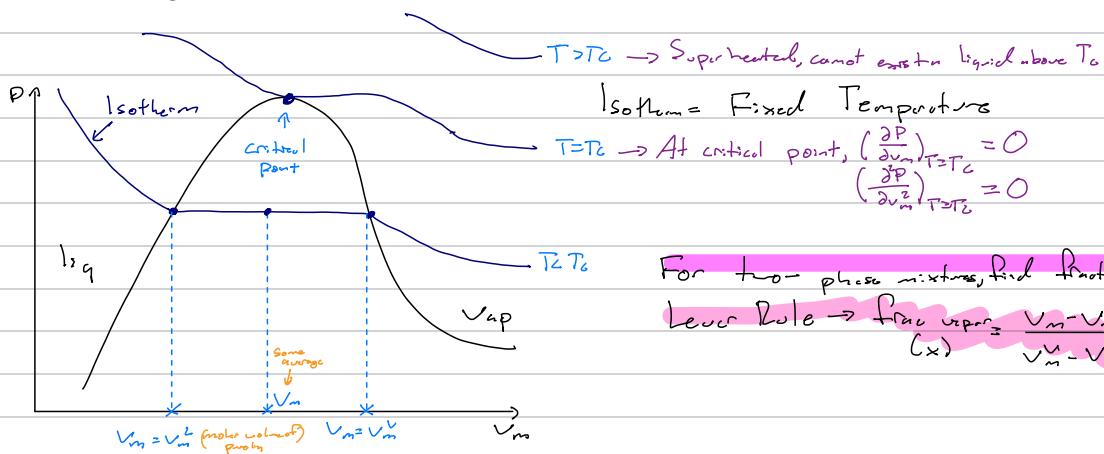
## Thermodynamic Property Sources

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

(ii) Graphical Representation: PVT diagrams



• PVT diagrams are very useful!



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

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

• Always use steam tables for water

• Linear interpolation required for conditions between values in the table

(iv) Equations of State

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

$\rightarrow$  van der Waals...

(v) Statistical Mechanics (molecular calculations)

$\hookrightarrow$  not focused on in this course

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

- If  $\dot{V}_i \geq \dot{V}_{i,sat}$  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)

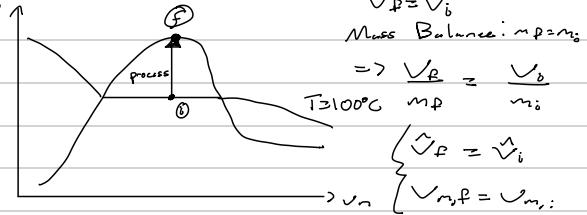
$$\begin{aligned} V_i &= 100L \\ T_i &= 100^\circ\text{C} \\ &\text{saturated} \end{aligned}$$

final (f)

$$\begin{aligned} V_f &= 100L = V_i \\ T_f &= T_c \\ P_f &= P_c \end{aligned}$$

process

→ critical point



b) Find the mass and initial quality.

(outcomes)

→ mass balance:  $m_f = m_i$

rigid:  $V_f = V_i = V$

$$\rightarrow V_f = V_i = V$$

Steam Tables

because  $P_c, T_c$  state is a crit point

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

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

bottom of tube  
↳ of temp →  $\dot{V}_{fg} = 0$

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

(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 C 100°C

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

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

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

# 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

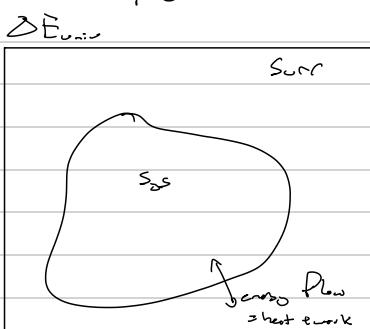
- phase changes

- 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

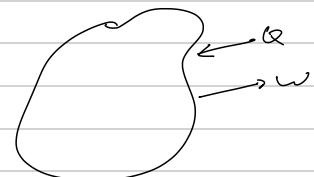
Q: Heat and work are flowing across the system boundary. What can we say about Q and W?

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 = P  
V = nRT

Ex

Reversible work for ideal gas expansion under isothermal conditions.



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

reversible →  $P_E \approx P$

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

n is constant

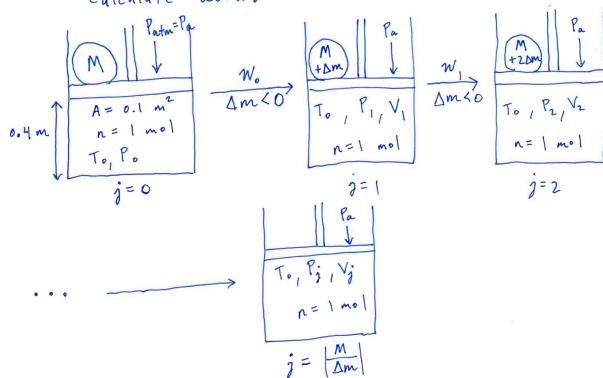
$$\frac{W}{n} = w_m = -RT_i \int_{V_{m,i}}^{V_{m,f}} \frac{dV_m}{V_m}$$

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

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 = const = 1 mol

• final mass = 0

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

• isothermal: T = const =  $T_0$

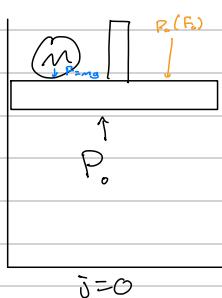
• PV work def'n →  $W = -\int P_E dV$  external pressure

↳ what is  $P_E$ ?

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

• pressure / force balance:

### Pressure / Force Balance



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

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

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

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

$$\text{Sub. ideal g. law} \\ P_1 V_1 = P_0 V_0$$

$$\text{Now, sub } P's \text{ from force balance} = -V_0 \left[ (P_0 + \frac{Mg}{A}) - (P_0 + \frac{Mg}{A} + \frac{\Delta mg}{A}) \right] = +V_0 \cdot \frac{\Delta mg}{A} \xrightarrow{\text{neglects } S_{\text{ext}}} \text{class work}$$

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

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

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

$$\downarrow P_1$$

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

Expansion →  $S_{\text{ext}}$  decreases

Example Continued

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

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

so, total work done is:

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

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

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

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

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

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

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

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

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

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

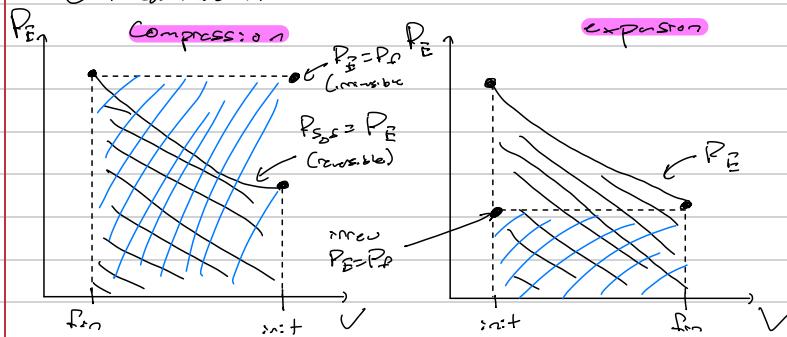
This is a reason why assuming a reversible process can be convenient.  $W_{\text{re}} = -5545 \text{ J}$

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

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

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

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



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

$$W = - \int P_E dV$$

## Internal Energy

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

→ Several Options:

(i) Property tables (NIST, steam tables)

(ii) Specific (molar) heat capacities

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

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

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

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

## Enthalpy ( $h_m$ )

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

→ For ideal gas,  $PV_m = RT$

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

Note that heat capacities are defined for a single phase.

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

→ closed system, calorimeter, system @ const P

const P →  $P_E = P$  (force balance)

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

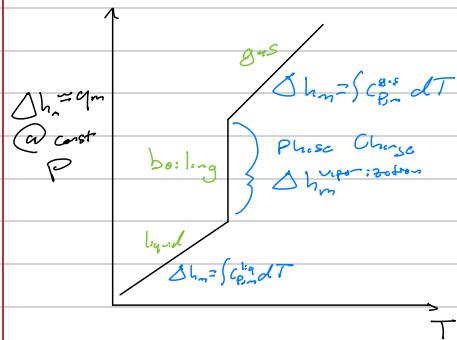
$dU_m = \delta q_m - d(PV_m)$  can make this more only bc Pressure P is constant

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

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

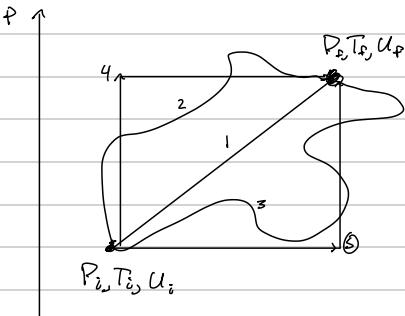
$\leftarrow$  measure T to determine  $h_m$  &  $C_{p,m}$

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



## Calculation Paths

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

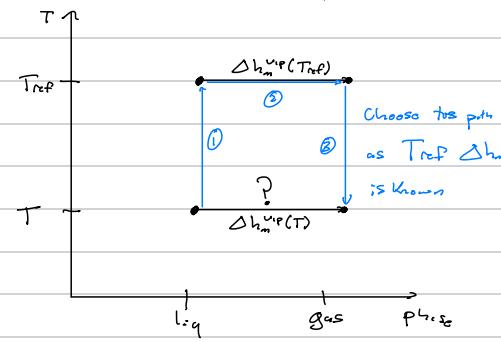


$$\Delta U = U_f - U_i$$

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

True for any process!

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



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

Solution:

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

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

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

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

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

## Example 1st Law w/ Property Tables

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

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

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

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

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

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

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

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

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

$\uparrow$   
orange

$$\hat{u}_f = x \hat{u}_w + (1-x) \hat{u}_l$$

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

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

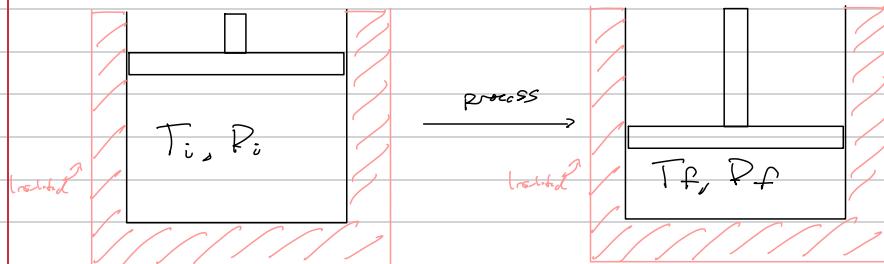
$$\hat{u}_f = 3194 \frac{\text{kJ}}{\text{kg}}$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

### Final Notes on Ideal Gas Heat Capacities

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

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

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



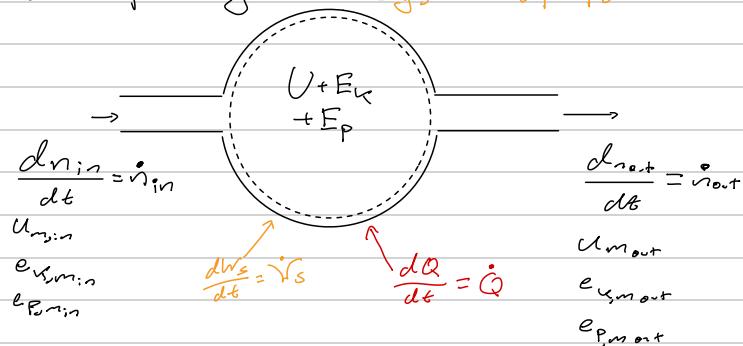
1.G.

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

↑ from  $\partial T$   
only      ↑ from  $\partial T$  only

(for ideal gas)

Sk. 9 2.8-2.9 |<sup>st</sup> Law Open Systems e.g. turbines, pumps, reactors...



## \* Important Calculus Note:

$$\dot{v}_{in} = \frac{d v_{in}}{dt} \neq v_{in}$$

$\downarrow$   
differential

## Form of PV Work?

→ Flow Work

### Rate of flow works

$$\frac{d \bar{W}_{\text{flow}}}{dt} = \dot{\bar{W}_{\text{flow}}} = -P_E \frac{d V_m}{dt}$$

$$\text{Extracting air and injecting air} \quad = -P_{in} \frac{dV_{in}}{dt}$$

$$= P_{in} \frac{d(V_{min} V_{max})}{dt} = P_{in} V_{min} \frac{dV_{max}}{dt} = P_{in} V_{min} \dot{V}_{max} = \dot{V}_{flow} \text{ mol/s} \quad r_{act} = \frac{\dot{n}_{act}}{\dot{V}_{max}} = (P_{V_{max}})_{in}$$

$\rightarrow P > \sigma$ ,  $V_m > 0$ , so flow works  $w_{flow} > 0$  always.

$\Rightarrow$  Add flow work to energy balance

$$\frac{d}{dt} (U + E_k + E_p) = \dot{Q} + \dot{W}_s + \dot{m}_{in} (U_m + e_{k,m} + e_{p,m})_{in} + \dot{m}_{in} (P_{Um})_{in} - m_{out} (U_m + e_{k,m} + e_{p,m})_{out} - \dot{m}_{out} (P_{Um})_{out}$$

*accumulation*

$$\text{Reac1: } h_m \equiv M_m + P_m$$

$$\frac{d}{dt} (U + E_{\text{kin}} + E_p) = \dot{Q} + \dot{V}_S + \dot{V}_{in}(h_m + e_{usm} + e_{Bn})_{in} - \dot{V}_{out}(h_m + e_{usm} + e_{Bn})_{out}$$

Can also write on  
a mess basis!

If open system is at steady-state

- no mass/moles accumulating in sys  
 $\rightarrow$  mass balance,  $\frac{dm}{dt} = 0 = \dot{m}_{in} - \dot{m}_{out} \Rightarrow \dot{m}_{in} = \dot{m}_{out} = \dot{m}$
  - no change in energy of system:

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

- no change in properties with time

IF NOT ~~std::-std~~

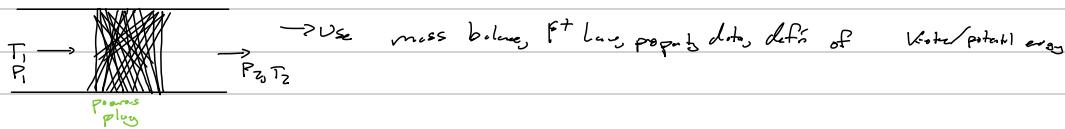
$$\rightarrow \text{mole balance: } \frac{dn}{dt} = r_{in} - r_{out}$$

- Total mass/mole accumulation:

$$\Delta n = n_{\text{fin}} - n_{\text{ref}} = \int_{z=2}^{z_{\text{fin}}} dm$$

## Example 6: Throttling Process

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



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

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

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

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

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

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

→ Simplified F<sup>+</sup> Law

$0 = \dot{m}_{in} h_{m,in} - \dot{m}_{out} h_{m,out}$

so

$0 = h_{m,in} - h_{m,out}$

$0 = \hat{h}_{in} - \hat{h}_{out}$

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

mole basis } independent of  $T_2$   
mass basis }

a) Let's assume fluid is water:

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

$P_1 = 10 \text{ MPa}$

→  $T_2 ?$

$P_2 = 1 \text{ bar}$

Find  $T_2$ !

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

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

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

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

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

b) What will happen if fluid is ideal gas?

1)  $T_2 < T_1$

3)  $T_2 = T_1$

2)  $T_2 > T_1$

4) real more  $\Rightarrow T_2$

Why?

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

$\Delta h_m = 0$

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

→ Ideal G.s.:  $h_m = h_m(T)$  only

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

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

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

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

- ideal gas:  $h_m = h_m(T)$  only  
 $dh_m = C_p dT$

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

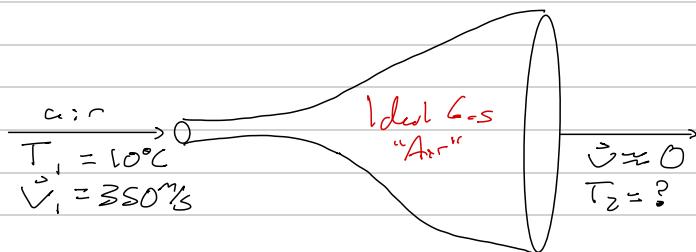
3) Flows in open systems have enthalpy  $\hat{h}$ , but not internal energy. Of course  $\hat{h}$  has internal energy!

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

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

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

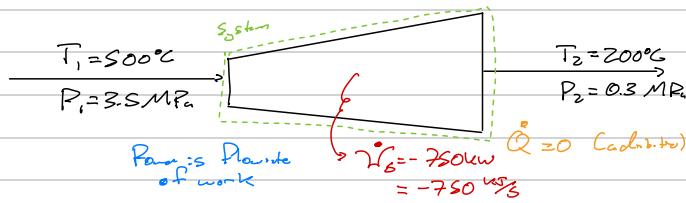
$$\Delta \hat{h} = \int_{T_1}^{T_2} \hat{C}_p dT \approx \hat{C}_p (T_2 - T_1) = \hat{e}_{k,1} \rightarrow T_2 = \frac{\hat{e}_{k,1}}{\hat{C}_p} + T_1 \quad \text{Solve: } T_2 = 73^\circ\text{C}$$

\*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)

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

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

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  $h_{in}$ ,  $h_{out}$ )

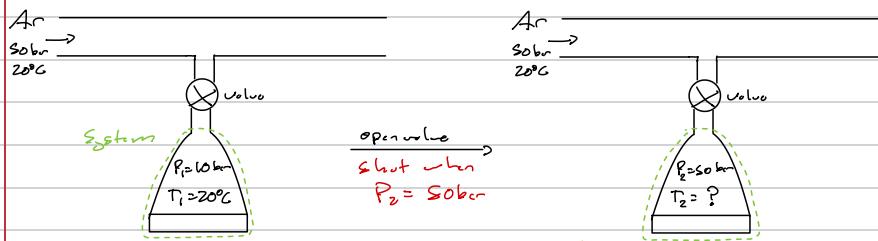
$$\dot{m} = \frac{-750 \text{ kW}}{2865.9 - 3451 \frac{\text{kJ}}{\text{kg}}} = 1.28 \frac{\text{kg}}{\text{s}}$$

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

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

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

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

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

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

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

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

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

bc  $T_1 = T_2$

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

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

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

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

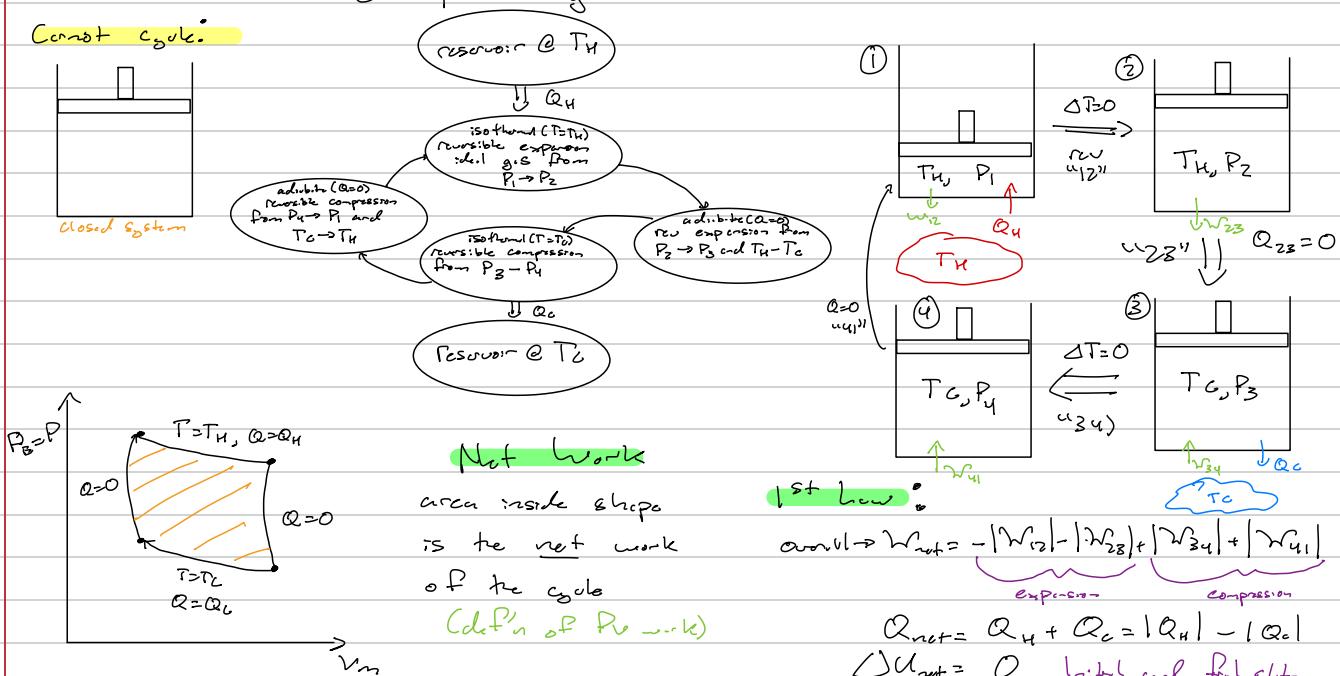
$$(C_{p,m} = \frac{5}{2} R)$$

# Chapter 3 - Entropy and the Second Law

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

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

Carnot cycle:



Process 12: Isothermal ( $T=T_H$ )

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

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

$$\text{adiabatic, reversible, constant } C_p, m$$

$$\rightarrow P V^{\kappa} = \text{constant}$$

$$W_{23} = - \int P dV = - \int \frac{P_2 V_2^{\kappa}}{V^{\kappa}} dV$$

Too many unknowns:

$$\begin{aligned} \rightarrow \text{solve } P_3 \text{ and } R_1 \text{ in terms of } P, P_1 \text{ & } P_2 \\ "23" \text{ is adiabatic } \rightarrow P_2 V_2^{\kappa} = P_3 V_3^{\kappa} \\ "41" \text{ is adiabatic } \rightarrow P_4 V_4^{\kappa} = P_1 V_1^{\kappa} \end{aligned}$$

To Summary

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

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

$$W_{23} = \frac{n R}{\kappa-1} (T_H - T_C), \quad Q_{23} = 0$$

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

$$W_{41} = \frac{n R}{\kappa-1} (T_C - T_H), \quad Q_{41} = 0$$

## Discuss Overall Cycle

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

$\rightarrow \eta$  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 a state 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

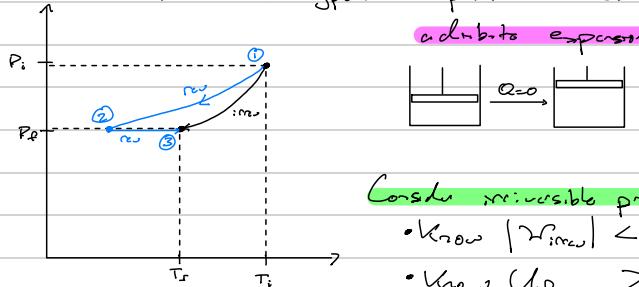
Q: Which process has the most positive change of the fluid P  $\Delta S_m$ ?

- 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'

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

Consider irreversible process (1  $\rightarrow$  3)

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

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

(not adiabatic)

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

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

$$dQ = dU + PdV$$

$$dQ = dU + PdV$$

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

$$dQ = dU + dH$$

$$dQ = dH$$

Specific to adiabatic expansion: Increase in entropy  $S$  for system for irreversible processes.  $\Delta S_{13} > 0$

How to get from  
SR to others

heat  $\rightarrow$  others

SR to others

heat  $\rightarrow$  others

heat  $\rightarrow$

### $\Delta S$ 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.

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

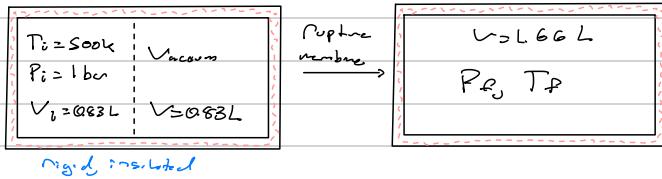
$$\Delta S_{12} = 0, \Delta S_{\text{surv}} = 0 \quad \text{reversible}$$

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

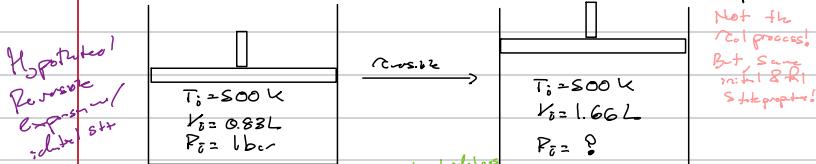
• 1st Law:  $\Delta U = Q + W \stackrel{\text{adiabatic}}{=} 0 \quad \text{no } Q, \text{ no } W \quad (\text{constant volume system})$

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

What about  $\Delta S$ ?

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

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



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

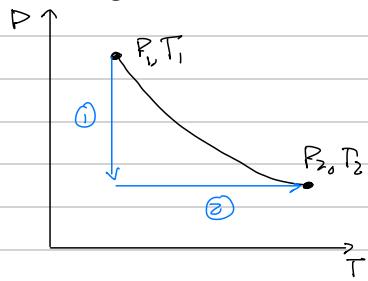
$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = \int \frac{dU_{\text{real}} - dU_{\text{hyp}}}{T} = - \int \frac{\delta W_{\text{rev}}}{T} = - \int \frac{-P_{\text{ext}} dV}{T} = \int \frac{P_{\text{ext}} dV}{T} \stackrel{\text{isothermal}}{=} n \int_{V_i}^{V_f} \frac{R}{V} dV = n R \ln \left( \frac{V_f}{V_i}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

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

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

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

## 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 ( $c_v + c_p$ )

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

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

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

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

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

ideal gas  
entropy change

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

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

Q: How do we calculate  $\Delta S_{univ}$  for any process?

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

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

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

• Develop an expression for  $\Delta S$

→ system: rev calc path (constant P)

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

(lost)  
const P

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

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

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

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

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

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

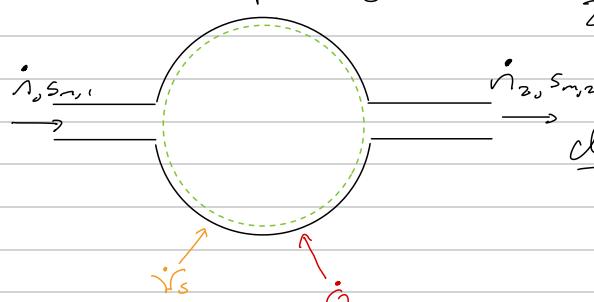
$$T_{sum} \mid \Delta S_{univ} = \Delta S + \Delta S_{sum}$$

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

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

Both  $\Delta S_{univ}$  are positive, so it is thermodynamically allowed!

## Second Law Open Systems



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

accumulation = 0 : f at steady state

(pol heat transfer)

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

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

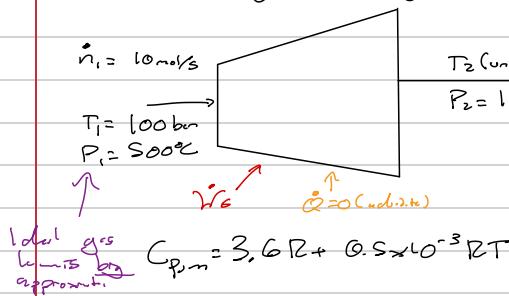
$\hookrightarrow$  steady  $\Rightarrow$  static  $\rightarrow \frac{dS_{\text{sys}}}{dt} = 0 \Rightarrow \frac{dS_{\text{univ}}}{dt} = \dot{n}_2 S_{m,2} - \dot{n}_1 S_{m,1} - \frac{\dot{Q}}{T_{\text{sum}}}$

## 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



Want to know:

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

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

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

$$1^{\text{st}} \text{ Law: } 0 = \dot{n}_1 h_{m,1} - \dot{n}_2 h_{m,2} + \dot{W}_t \xrightarrow{\text{adi. turbine}} \dot{W}_t = \dot{n} (h_{m,1} - h_{m,2})$$

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

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

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

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

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

(reversible)      (steady state)      note: not static      (adiabatic)

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

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

ideal g.  
 $\rightarrow$  (ideal gas assumption only)

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

$$\dot{W}_{\text{turb}} = \dot{n} \int_{T_1=773K}^{T_2=282K} (3.6 + 0.5 \times 10^{-3} T) dT = -173.2 \frac{kJ}{s} \xrightarrow{\text{max power}} \dot{W}_{\text{turb}} = -173.2 \text{ kW}$$

LO so work done on surroundings

$T_1, P_1, P_2$  or  $V$  known  $\Rightarrow T_2 = 232K$

**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

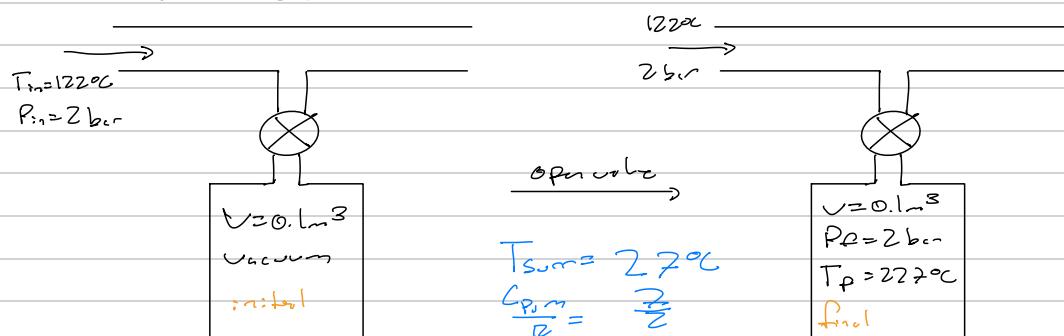
c) What is  $T_2$ ? (80% efficiency)

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

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

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

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

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

→ What about  $(s_{in,f} - s_{in,i})$

- For ideal gas: integrate  $ds_m$

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

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

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

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

(Comparing to remote answer)

✓ consistent w/  
Second law