


CHAP. 2 - FIRST LAW


MANY TYPES OF ENERGY

- KINETIC, POTENTIAL
- HEAT
- WORK

ENERGY INHERENT IN MOLECULES -

= INTERNAL ENERGY


TRANSLATION


ROTATION


INTERNAL
VIBRATION

} TYPES
OF
KINETIC
ENERGY

(HOW MUCH INTERNAL ENERGY CORRESPONDS
TO THE RATE OF THE MOTIONS)

⇒ CHANGES BECAUSE OF

→ HEAT ADDITION (ΔT)

→ WORK (ΔV on GAS PHASE)

INTERMOLECULAR FORCES

BOND ENERGIES HOLDING MOLECULES
TOGETHER

} TYPES
OF
POTENTIAL
ENERGY

KINETIC + POTENTIAL ENERGY CONTRIBUTIONS
TO INTERNAL ENERGY $\neq E_K, E_P$

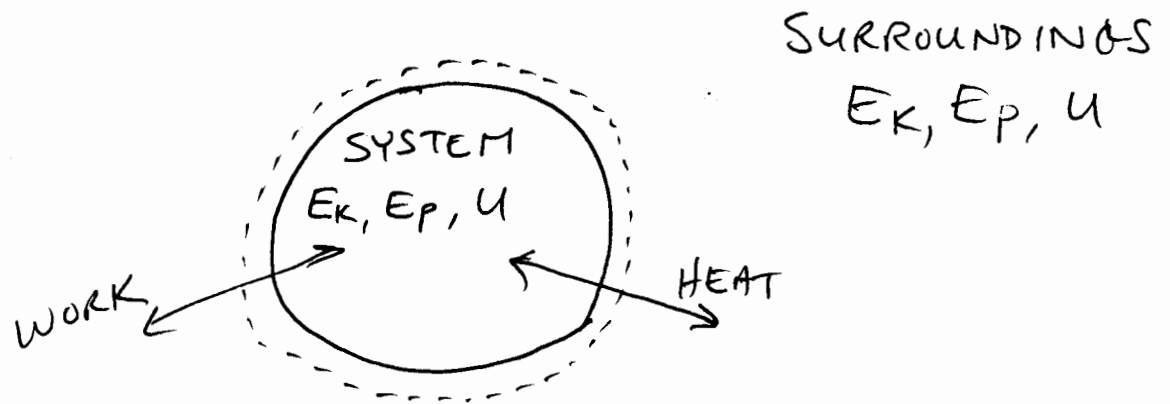
E_K } MACROSCOPIC POSITION + MOTION
 E_P } \Rightarrow EXTERNAL ENERGY

2.3 FIRST LAW OF THERMODYNAMICS
(AKA CONSERVATION OF ENERGY)

FROM SMITH + VAN NESS, p. 22:

"ALTHOUGH ENERGY ASSUMES MANY FORMS,
THE TOTAL QUANTITY OF ENERGY IS CONSTANT,
AND WHEN ENERGY DISAPPEARS IN ONE FORM
IT APPEARS SIMULTANEOUSLY IN OTHER FORMS."

PLURAL \nearrow



NOTES:

- WORK & HEAT CROSS THE BOUNDARY BETWEEN SYSTEM & SURROUNDINGS (AND VICE VERSA)
- ENERGY IN THE SYSTEM IS STORED AS $(E_k)_{\text{system}}, (E_p)_{\text{system}}, (U)_{\text{system}}$
- ENERGY IN THE SURROUNDINGS IS STORED AS $(E_k)_{\text{SURROUNDINGS}}, (E_p)_{\text{SURROUNDINGS}}, (U)_{\text{SURROUNDINGS}}$

$$(\Delta E)_{\text{system}} + (\Delta E)_{\text{SURROUNDINGS}} = 0$$

- FINITE CHANGES
- BEWARE THE SIGNS

REMEMBER :

- HEAT ADDED TO THE SYSTEM IS (+)
- WORK DONE ON THE SYSTEM IS (+)

- HEAT ADDED TO THE SURROUNDING IS (-)
- WORK DONE ON THE SURROUNDINGS IS (-)

2.4 ENERGY BALANCE FOR CLOSED SYSTEMS

"CLOSED" \Rightarrow NO MASS TRANSPORT

ENERGY TRANSPORT BY HEAT + WORK ONLY.

$$(\Delta E)_{\text{SURROUNDINGS}} = -Q - W$$

$$(\Delta E)_{\text{SYSTEM}} = Q + W$$

SPECIAL CASE: NO MOTION, CLOSED SYSTEM

HEAT + WORK ALL GO TOWARDS U^t
 \uparrow
 total in system

$\Rightarrow \boxed{\Delta U^t = Q + W}$ NO MOTION, CLOSED SYSTEM

DIFFERENTIAL CHANGES

$\boxed{dU^t = dQ + dW}$

ALL UNITS OF ENERGY (J, ft·lbf, Btu)

RECALL FROM CHE 254:

EXTENSIVE PROPERTIES
 (depend on amount of material)
 (e.g.: V^t , U^t)

INTENSIVE PROPERTIES
 (DO NOT Depend on Amount of material)

(e.g.: P, T)

6

⇒ Intensive versions of V^t & U^t :

$$V^t = m V \quad \text{or} \quad n V$$

$(\text{mass}) \left(\frac{\text{Volume}}{\text{mass}} \right)$ $(\text{moles}) \left(\frac{\text{Volume}}{\text{moles}} \right)$

$\frac{m}{\rho} \leftarrow \text{mass density}$ $\frac{m}{\rho} \leftarrow \text{molar density}$

$$U^t = m U \quad \text{or} \quad n U$$

$(\text{mass}) \left(\frac{\text{J}}{\text{mass}} \right)$ $(\text{moles}) \left(\frac{\text{J}}{\text{moles}} \right)$

$\underbrace{\hspace{10em}}_{\text{Specific Internal Energy}}$ $\underbrace{\hspace{10em}}_{\text{molar Internal Energy}}$

Effect on Energy Balance:

MASS: $\Delta(mU) = Q + W$

Closed System: $m = \text{constant}$

$$m \Delta U = Q + W$$

Differential Changes:

$$d(mu) = dQ + dW$$

$$m du = dQ + dW$$

If $m=1$, then

$$\Delta U = Q + W$$

and

$$du = dQ + dW$$

Likewise for moles:

$$n \Delta U = Q + W \Rightarrow \Delta U = Q + W$$

$$d(nu) = dQ + dW \Rightarrow du = dQ + dW$$

for $n=1$.

NOTE:

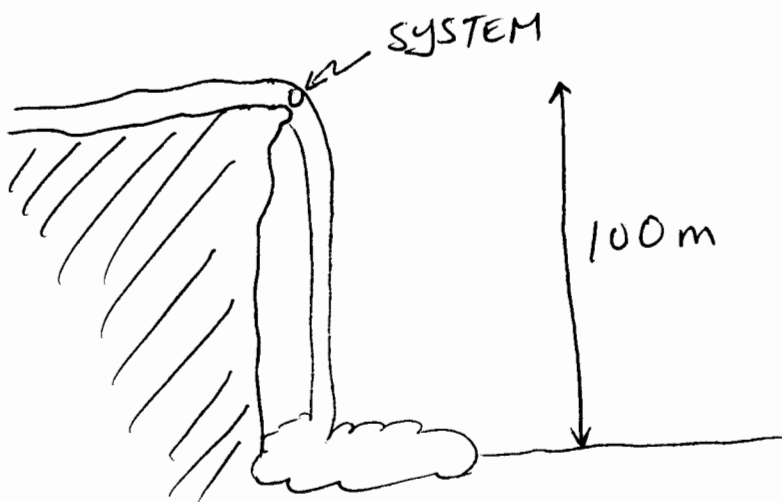
THERE IS NO ABSOLUTE VALUE FOR U .

REALLY JUST A CATCH-ALL TO MAINTAIN
THE FIRST LAW. (HENCE, ΔU)

EXAMPLE: (2.1)

WATER FLOWS OVER A WATERFALL 100 m IN
HEIGHT. TAKE 1 kg OF THE WATER AS THE
SYSTEM, AND ASSUME THAT IT DOES NOT
EXCHANGE ENERGY WITH ITS SURROUNDINGS.

(a) What is its potential energy at the top
of the falls w/ respect to the base of
the falls?



Closed System
(no ^{AND} energy exchanged
w/ surroundings)

$$\Rightarrow Q = 0$$

$$W = 0$$

$$(\Delta E)_{\text{sur.}} = 0$$

(9)

$$(\Delta E)_{\text{system}} = \Delta U + E_K + E_P = 0$$

$$E_P = m z g \quad (\text{Recall Eqn. 1.7})$$

$$m = 1 \text{ kg}$$

$$z = 100 \text{ m}$$

Plug + Chug

$$g = 9.8066 \text{ m/s}^2$$

$$E_P = \frac{1 \text{ kg} \mid 100 \text{ m} \mid 9.8066 \frac{\text{m}^2}{\text{s}^2}}{1 \text{ kg m}} = 980.66 \text{ Nm} = \boxed{980.66 \text{ J}}$$

(b) What is the kinetic energy of the water just before it strikes bottom?

Has not stricked bottom, so potential energy all going to kinetic energy...

$$\Delta U = 0$$

$$\Delta E_K + \Delta E_P = E_{K_2} - E_{K_1} + E_{P_2} - E_{P_1} = 0$$

$$\text{Estimate! } E_{K_1} = E_{P_2} = 0$$

$$\Rightarrow E_{K_2} - E_{P_1} = 0$$

$$\Rightarrow E_{K_2} = E_{P_1} = \boxed{980.66 \text{ J}}$$

(c) After the 1 kg of water enters the stream below the falls, what change has occurred in its state?

$$U \rightarrow 0 \quad (E_K \rightarrow 0)$$

$$Z = 0 \quad (E_P \rightarrow 0)$$

So where does the energy go?

$$\underline{\underline{\Delta U}} = 980.66 \text{ J}$$

And, since no heat transferred to surroundings,

$$\Delta U = \cancel{c_p \Delta T} m C_p \Delta T$$

$$C_p(\text{water}) = 4,184 \frac{\text{J}}{\text{kg} \cdot ^\circ\text{C}}$$

$$\Delta T = \frac{\Delta U}{m C_p} \quad \text{Plug + Chug}$$

$$\Delta T = \frac{980.66 \text{ J} \cdot \text{kg} \cdot ^\circ\text{C}}{4,184 \text{ J} \cdot \text{kg}}$$

$$\Delta T = 0.234 ^\circ\text{C}$$

IN ALL CASES, ENERGY IS CONSERVED.

2.5 THERMODYNAMIC STATE + STATE FUNCTIONS.

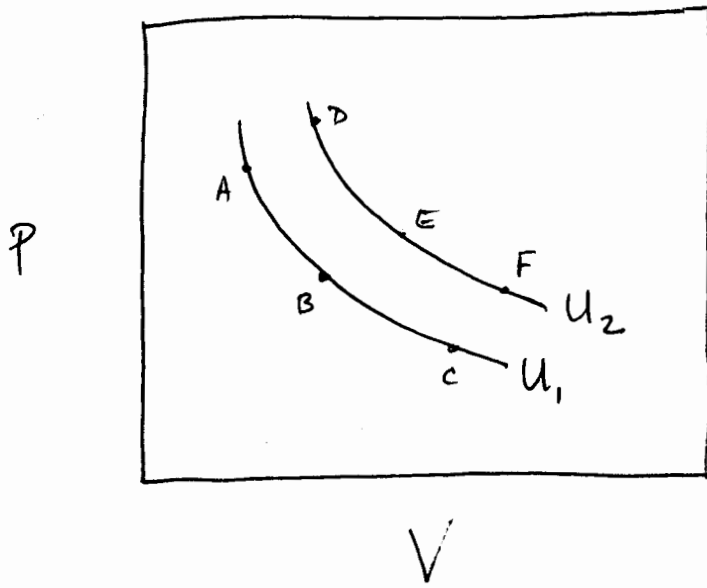
THE THERMODYNAMIC STATE OF A SYSTEM IS THE COMPLETE SET OF INTENSIVE VARIABLES AT A PARTICULAR CONDITION OF THE SYSTEM.

What does this mean?

A STATE FUNCTION CAN BE REPRESENTED BY A SINGLE VALUE AT A GIVEN SET OF CONDITIONS.

(NOT PATH OR HISTORY DEPENDENT)

EXAMPLE:



CONSTANT SPECIFIC U ALONG U₁ & U₂.

FOR U₁:

U₁(A) , P_A , V_A , T_A , l_A , etc.

U₁(B) , P_B , V_B , T_B , l_B , etc.

U₁(C) , P_C , V_C , T_C , l_C , etc.

FOR U₂:

U₂(D) , P_D , V_D , T_D , l_D , etc.

U₂(E) , P_E , V_E , T_E , l_E , etc.

U₂(F) , P_F , V_F , T_F , l_F , etc.

NOTES:

- 1) COMPLETE SET OF INTENSIVE THERMODYNAMIC PROPERTIES FOR THE STATE PROPERTY.
- 2) THE STATE PROPERTY REPRESENTS A SINGLE POINT ON THE GRAPH.

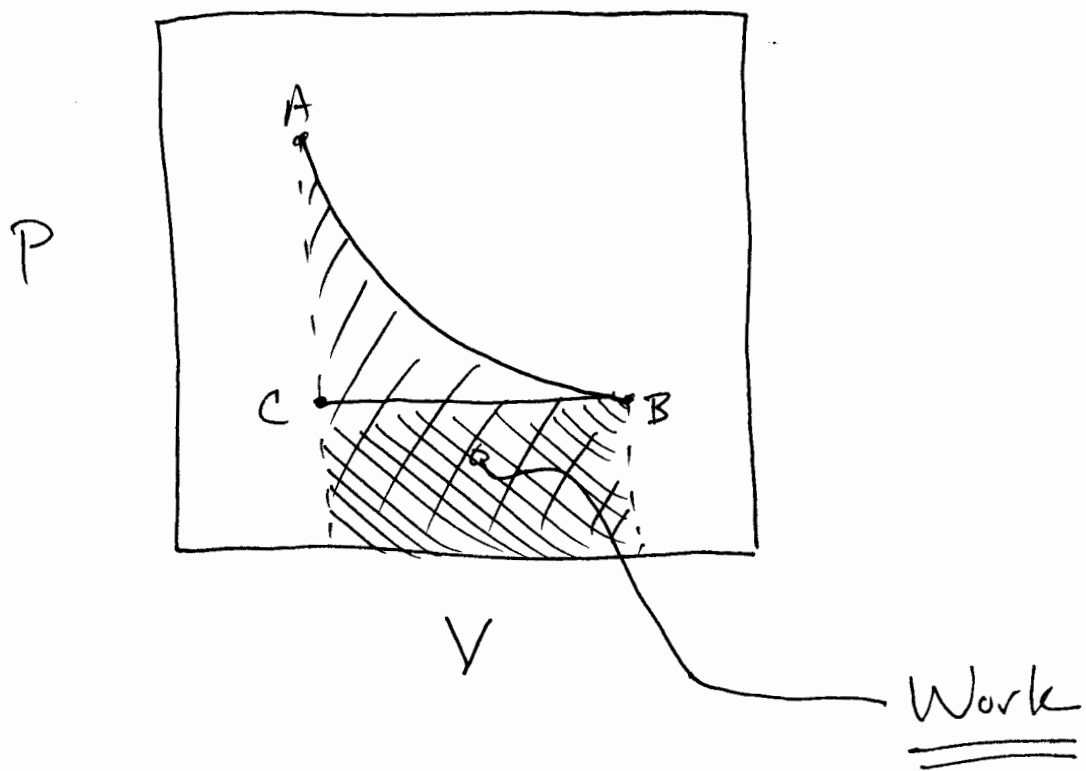
PATH FUNCTIONS

THEY DEPEND ON THE PATH TAKEN, AND THE HISTORY OF THE SYSTEM.

KEY EXAMPLES: HEAT + WORK

$\int dQ = Q$	}	SINGLE VALUES, BUT THESE REPRESENT THE AREA UNDER A CURVE.
$\int dW = W$		

EXAMPLE - WORK



$$W = - \int P dV$$

Two PATHS:

B → A

- SAME END POINTS
- DIFFERENT PATHS

B → C → A

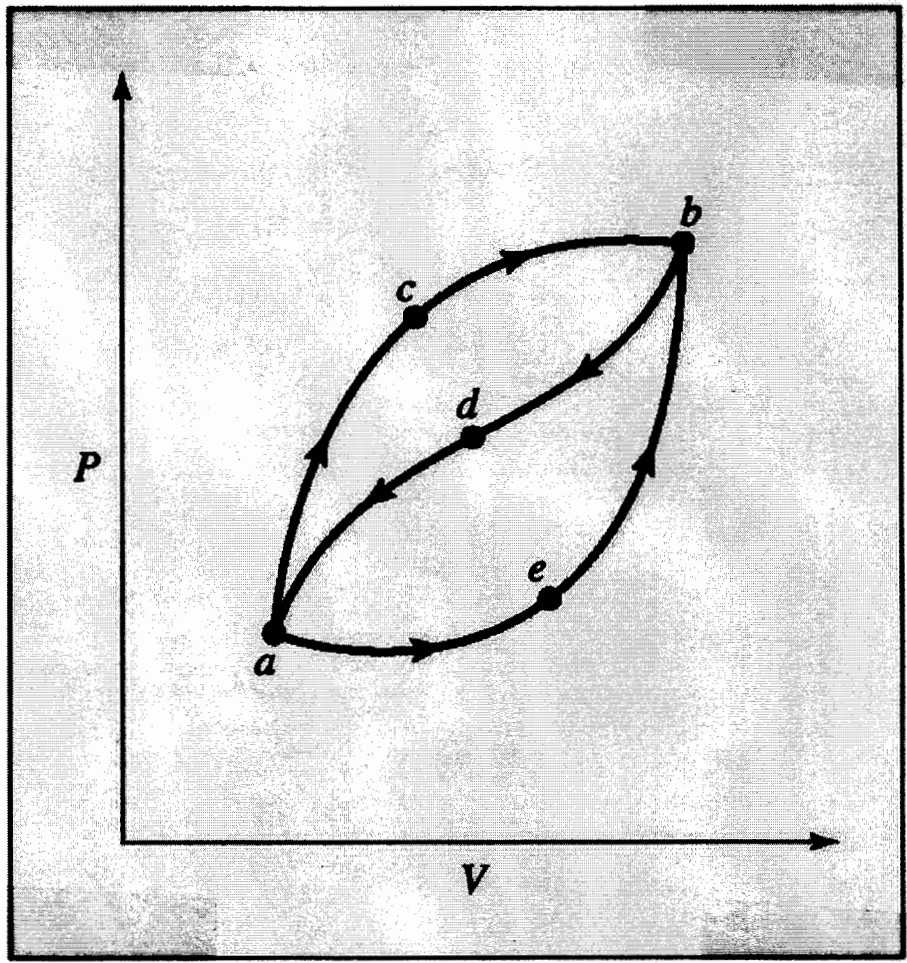
- WHICH HAS MORE WORK?

EXAMPLE 2.4

When a system is taken from state a to b in Figure 2.1 along path acb, 100 J of heat flows into the system and the system does 40 J of work.

- (a) How much heat flows into the system along path aeb if the work done by the system is 20 J?
- (b) The system returns from b to a along path bda. If the work done on the system is 30 J, does the system absorb or liberate heat? How much?

FIG. 2.1:



NO INFORMATION REGARDING MOTION IN SYSTEM

⇒ ASSUME ALL CHANGES IN U^t .

ENERGY BALANCES:

$$\Delta U_{ab}^t = Q_{acb} + W_{acb} = 100\text{ J} - 40\text{ J}$$

⏟
⏟

HEAT ADDED
WORK

TO THE
DONE

SYSTEM
BY

SYSTEM

(⇒ (-))

$$\Delta U_{ab}^t = 60\text{ J}$$

(a) FOR PATH AEB:

$$W_{acb} = -20\text{ J} \quad (\text{Work done } \underline{\text{by}} \text{ system}).$$

$$Q_{acb} = ?$$

$$\Delta U_{ab}^t = 60\text{ J}$$

Plug + Chug

$$60\text{ J} = Q_{acb} + (-20\text{ J})$$

$$\Rightarrow \boxed{Q_{acb} = 80\text{ J}}$$

(+) SO HEAT
ADDED TO SYSTEM.

(b) For PATH bda:

(17)

$$W_{bda} = 30\text{ J} \quad (\text{Work done } \underline{\text{on}} \text{ system})$$

$$Q_{bda} = ?$$

$$\Delta U_{ab}^t = 60\text{ J} \quad \Rightarrow \quad \Delta U_{ba}^t = -60\text{ J}$$

Plug + Chug

$$\Delta U_{ba}^t = Q_{bda} + W_{bda}$$

$$-60\text{ J} = Q_{bda} + (30\text{ J})$$

$$\Rightarrow \boxed{Q_{bda} = -90\text{ J}}$$

(-) \Rightarrow Heat goes
from system to
surroundings
(Heat liberated)

2.6 EQUILIBRIUM

In thermodynamics, this means:

A) ABSENCE OF CHANGE

B) ABSENCE OF TENDENCY FOR CHANGE
(NO DRIVING FORCES FOR CHANGE)

⇒ NO CHANGE IN STATE.

WHAT POTENTIAL DRIVING FORCES → ϕ ?

1) MECHANICAL (PRESSURE)

2) THERMAL (TEMPERATURE)

3) MASS TRANSFER (CHEMICAL POTENTIAL)
(like concentration)

4) CHEMICAL (REACTIONS)

→ OFTEN JUST NOT CATALYZED,
SO WE ASSUME NO REACTION.

2.7 The Phase Rule (AT EQUILIBRIUM)

How MANY UNKNOWNs MUST BE FIXED BEFORE ALL OTHER PROPERTIES ARE SET?

$$F = 2 - \pi + N$$

↑ DEGREES OF FREEDOM ↑ NUMBER OF PHASES ← NUMBER OF CHEMICAL SPECIES

WHAT VARIABLES ARE WE TALKING ABOUT?

T, P, composition of each phase.
 (ALL INTENSIVE PROPERTIES)

PHASES:

GAS PHASE

→ PURE OR MIXTURE

→ CAN BE ONLY ONE

Why? All gases are miscible.

LIQUID PHASES

→ PURE OR MIXTURES

→ MULTIPLE OK. (NOT MANDATORY)

SOLID PHASES

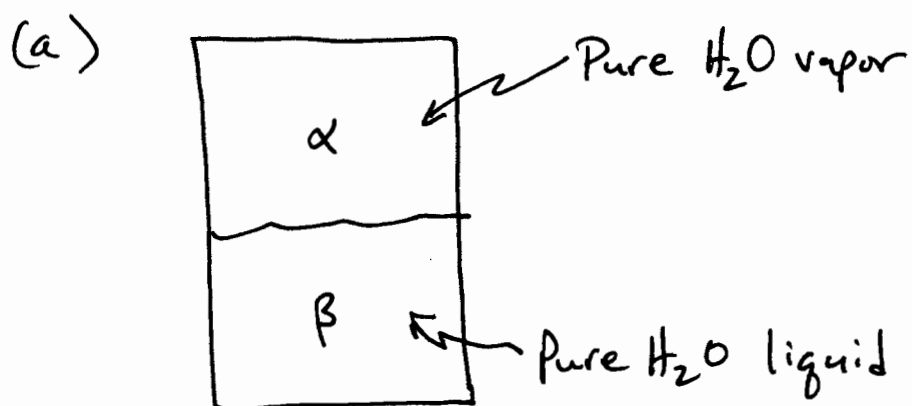
→ CRYSTALLINE (PURE)

→ SOLID SURFACES

(NOT OUR FOCUS) ← VERY COMPLEX

EXAMPLE 2.5 How many degrees of freedom has each of the following systems?

- (a) Liquid water in equilibrium w/ water vapor.
- (b) Liquid water in equilibrium w/ a mixture of water vapor and nitrogen.
- (c) A liquid solution of alcohol in water in equilibrium with its vapor.



Two phases:
 α, β

One component:
 H_2O

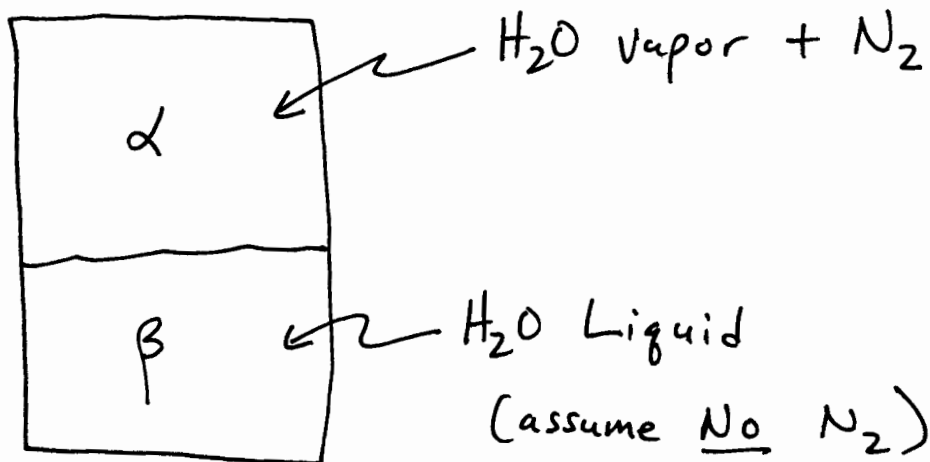
$$F = 2 - \underset{\substack{\uparrow \\ 2}}{\Pi} + \underset{\substack{\uparrow \\ 1}}{N} = 2 - 2 + 1 = 1$$

Need to fix one variable for a pure fluid (VLE).

Example: Pick $T \Rightarrow$ Calculate vapor pressure.
or

Pick $P \Rightarrow$ Calculate boiling point.

(b)



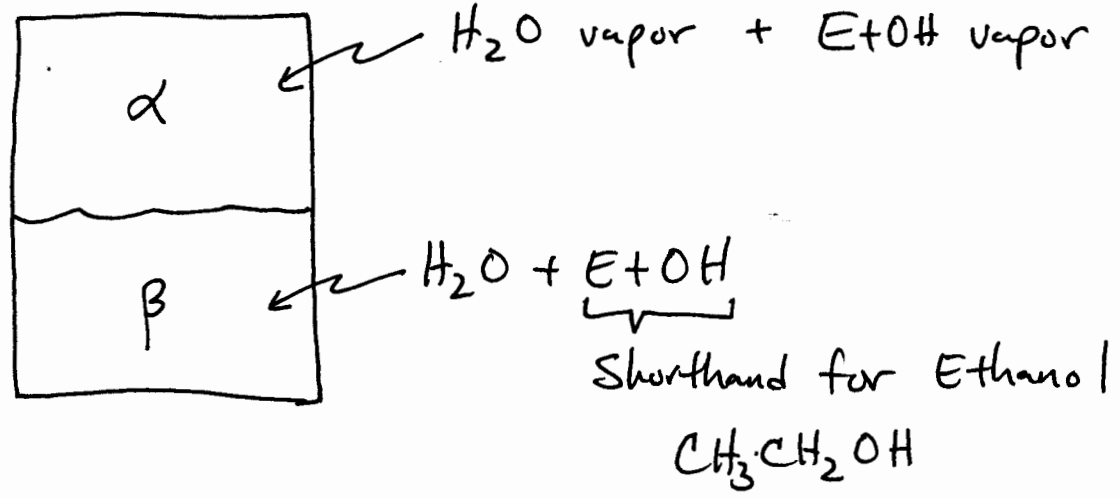
$$\Pi = 2 \quad (\alpha + \beta)$$

$$N = 2 \quad (\text{H}_2\text{O} + \text{N}_2)$$

$$F = 2 - 2 + 2 = 2$$

Need to fix 2 variables.

(c)



$$\pi = 2 \quad (\alpha + \beta)$$

$$N = 2 \quad (H_2O + Ethanol)$$

$$F = 2 - 2 + 2 = 2 \quad \text{Need to fix 2 Variables.}$$

FOR VAPOR/LIQUID EQUILIBRIUM (VLE)

$$T_\alpha = T_\beta = T$$

$$P_\alpha = P_\beta = P$$

LIQUIDS: (OUR β PHASE)

x_i (where $i = 1$ to N)

VAPOR: (OUR α PHASE)

y_i (where $i = 1$ to N)

2.8 THE REVERSIBLE PROCESS

ANOTHER "SPECIAL" CLOSED SYSTEM

from Smith + Van Ness (p. 31)

"A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions."

NOTES:

- ITS DIRECTION

⇒ Can't just be one direction

e.g.: Compression or Expansion

- REVERSED AT ANY POINT

⇒ Accelerations are a big problem
(inertia)

- INFINITESIMAL CHANGE

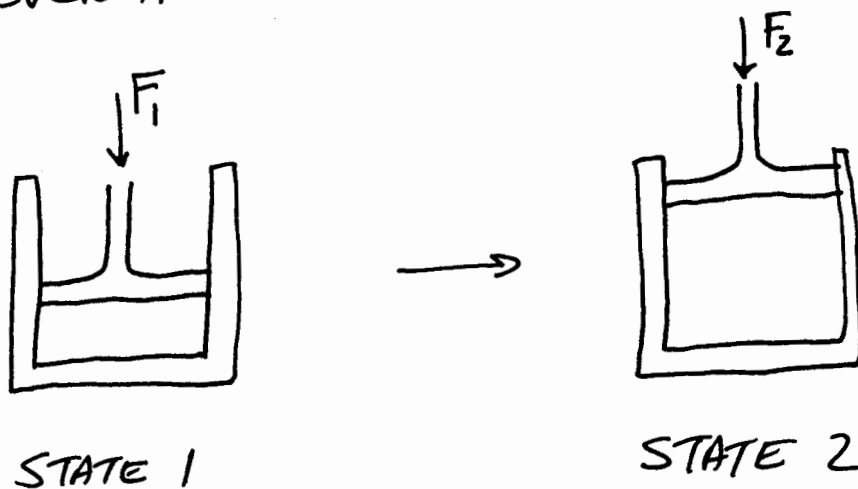
⇒ EVEN SMALL CHANGES HAVE DESIRED EFFECT (REVERSIBILITY)

EXTERNAL CONDITIONS

⇒ Changes in the surrounding affect the system.

EXAMPLE SYSTEM:

REVERSIBLE EXPANSION OF A GAS



in both cases, surroundings @ $P=0$ (vacuum).

Couple of ways to go from STATE 1 to STATE 2:

(a) Sudden changes
 +
 Step changes } IRREVERSIBLE

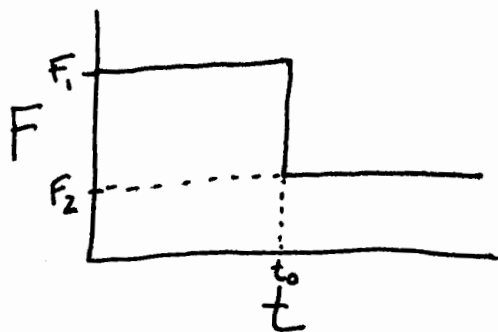
(b) Differential changes } REVERSIBLE

WHY?

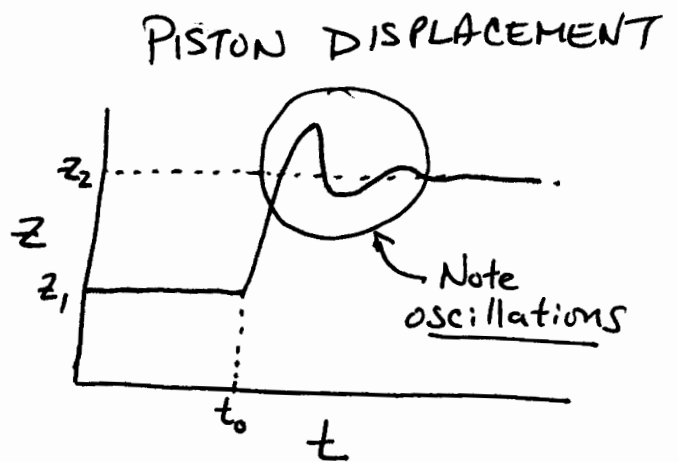
(a) SUDDEN CHANGE

(25)

$$F_1 \rightarrow F_2 \quad (\text{where } F_2 \ll F_1)$$



STEP CHANGE IN F.



Why the oscillation?

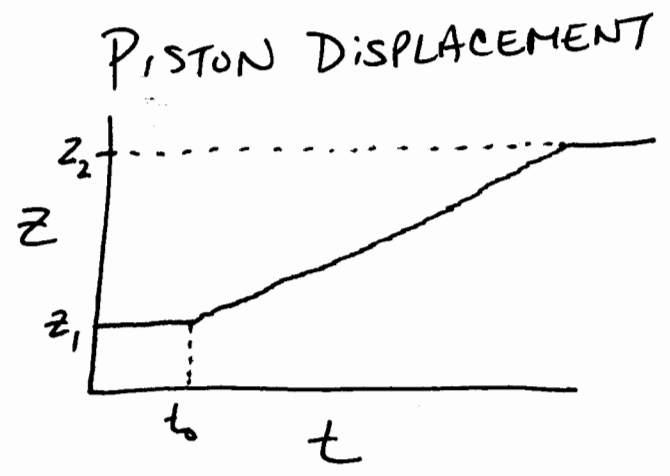
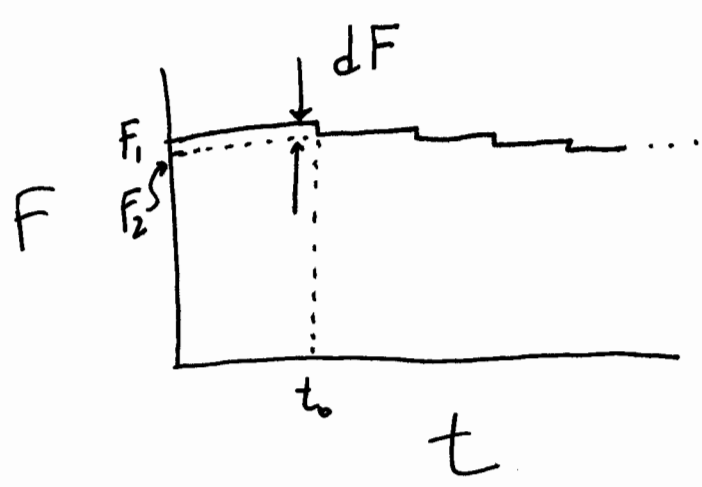
When $F_1 \rightarrow F_2$, there is a force misbalance. (P_1 is exerting F_1 on piston still).

Since $F_1 \gg F_2$, the piston accelerates up.

When the piston reaches z_2 , it still has a velocity (and momentum), so the piston will overshoot z_2 .

During this process, small changes in external properties cannot reverse the process.

(b) Differential Change
(very small changes)

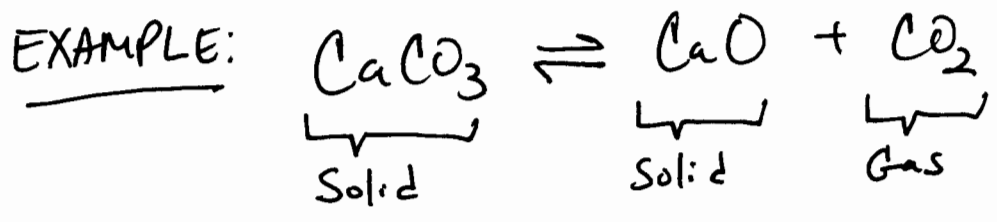


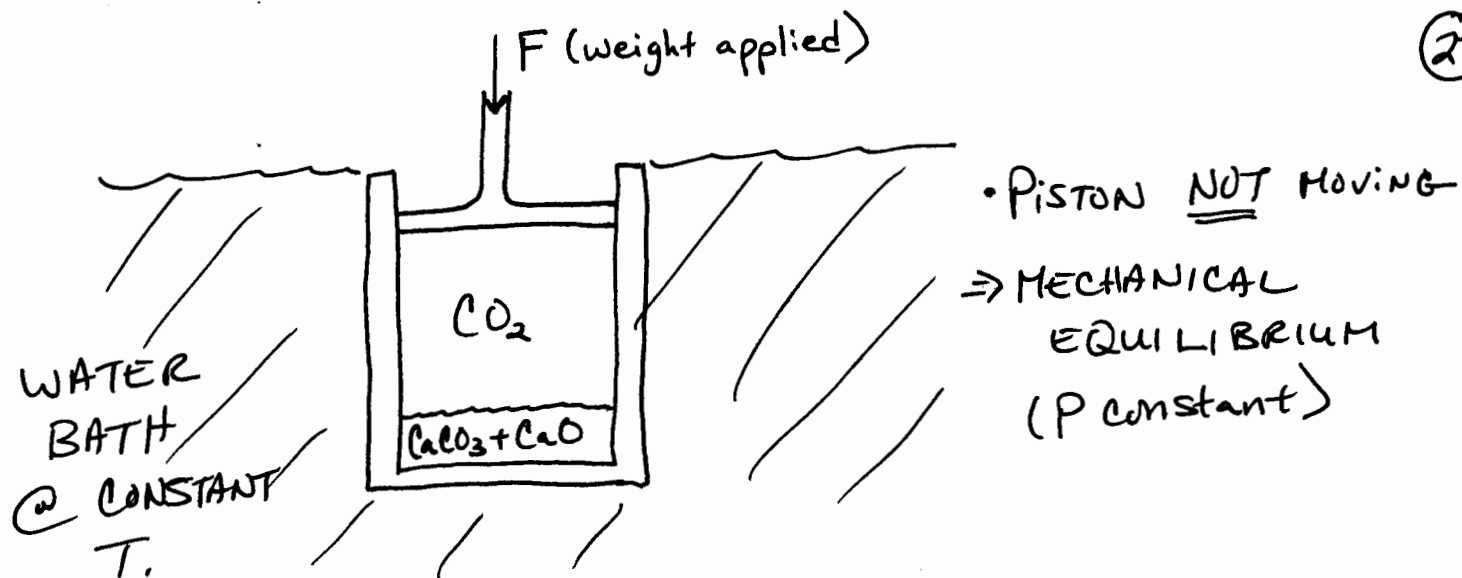
$dF \Rightarrow$ No chance to build momentum, so
no oscillation.

Because small changes, a small change in external
properties can reverse the process.

REVERSIBLE CHEMICAL CHANGE:

\rightarrow START WITH A REVERSIBLE REACTION





System at equilibrium based on pressure of CO_2 .

AGAIN, SMALL CHANGES (DIFFERENTIAL)

\Rightarrow REVERSIBLE.

TO BE REVERSIBLE:

- 1) NO FRICTION (HEAT LOSS)
- 2) DIFFERENTIAL CHANGES FROM EQUILIBRIUM
- 3) $d(\text{Property}) \Rightarrow$ New EQUILIBRIUM, then REPEAT.
- 4) $d(\text{Forces})$
- 5) Can be reversed at any point by differential change in external conditions.
- 6) When reversed, it retraces the path.

WHEN NOT REVERSIBLE, NEED EFFICIENCY
(η)

WHERE DOES THE REST GO?

⇒ USUALLY HEAT.

IS IT ALWAYS LOST TO SURROUNDINGS?

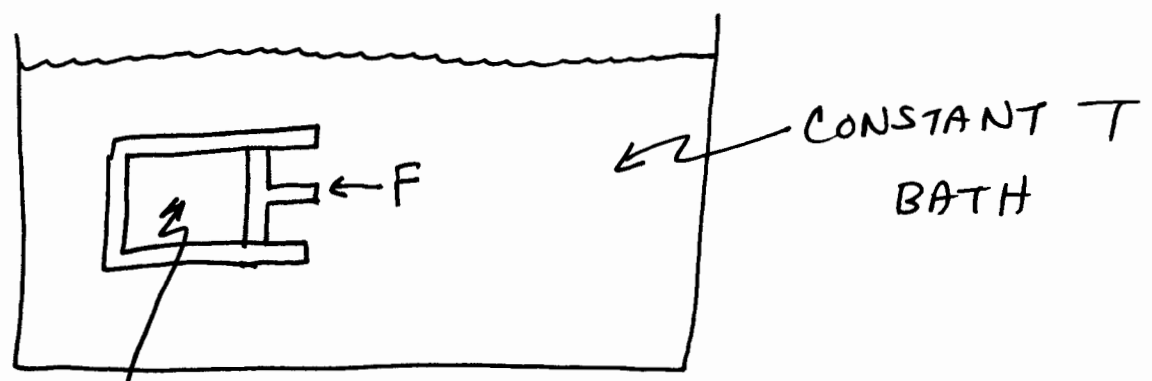
NO! (FORTUNATELY)

EXAMPLE → STEAM DRIVEN TURBINE
FOR ENERGY RECOVERY.

EXAMPLE 2.6 A HORIZONTAL PISTON/CYLINDER ARRANGEMENT IS PLACED IN A CONSTANT-TEMPERATURE BATH. THE PISTON SLIDES IN THE CYLINDER WITH NEGLIGIBLE FRICTION, AND AN EXTERNAL FORCE HOLDS IT IN PLACE AGAINST AN INITIAL GAS PRESSURE OF 14 bar. THE INITIAL GAS VOLUME IS 0.03 m^3 . THE EXTERNAL FORCE ON THE PISTON IS REDUCED GRADUALLY, AND THE GAS EXPANDS ISOTHERMALLY AS ITS VOLUME DOUBLES.

IF THE VOLUME OF THE GAS IS RELATED TO ITS PRESSURE SO THAT THE PRODUCT PV^t IS CONSTANT, WHAT IS THE WORK DONE BY THE GAS IN MOVING THE EXTERNAL FORCE?

HOW MUCH WORK WOULD BE DONE IF THE EXTERNAL FORCE WERE SUDDENLY REDUCED TO HALF ITS INITIAL VALUE INSTEAD OF BEING GRADUALLY REDUCED?



$P_0 = 14 \text{ bar}$
 $V_0 = 0.03 \text{ m}^3$

FRICTIONLESS PISTON
EXPANDED ISOTHERMALLY
($\Delta U = 0$)

⇒ All energy is work.

Also told $PV^t = \text{constant}$

How much work by gas if $V_2 = 2V_0$?

Recall,

$$W = - \int_{V_1^t}^{V_2^t} P dV^t$$

Note: We did not take P outside of the integral because it is changing.

We can substitute for P in terms of V^t .

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

$$P = \frac{k}{V^t}$$

Substitute...

$$W = - \int_{V_1^t}^{V_2^t} k \frac{dV^t}{V^t} = -k \int_{V_1^t}^{V_2^t} \frac{dV^t}{V^t}$$

$$W = -k \ln V^t \Big|_{V_1^t}^{V_2^t} = -k \ln \left(\frac{V_2^t}{V_1^t} \right)$$

$$k = PV^t = (14 \text{ bar})(0.03 \text{ m}^3) \left| \frac{10^5 \text{ N}}{1 \text{ bar} \cdot \text{m}^2} \right| \frac{1 \text{ J}}{1 \text{ Nm}}$$

$$\Rightarrow k = 42,000 \text{ J}$$

Plug + Chug...

$$W = (-42,000 \text{ J}) \ln\left(\frac{0.06 \text{ m}^3}{0.03 \text{ m}^3}\right)$$

$$W = -29,112 \text{ J} \leftarrow \text{REVERSIBLE}$$

WHAT IF SUDDEN CHANGE?

$$P_2 = 7 \text{ bar}$$

$$W = -P \Delta V^t$$

$$= (-7 \text{ bar})(0.06 - 0.03) \text{ m}^3 \left| \frac{10^5 \text{ N}}{1 \text{ bar} \cdot \text{m}^2} \right| \left| \frac{1 \text{ J}}{1 \text{ Nm}} \right|$$

$$W = -21,000 \text{ J} \leftarrow \text{IRREVERSIBLE}$$

Efficiency?

$$\eta = \frac{W}{W_{\text{rev}}} \times 100\% = \frac{-21,000}{-29,112} \times 100\% \Rightarrow \eta = 72.1\%$$

2.9 CONSTANT V + CONSTANT P PROCESSES

RECALL $d(nu) = dQ + dW$

- CLOSED SYSTEM
- n MOLES OF FLUID

RECALL $dW = -P d(nV)$

Substitute for dW...

$d(nu) = dQ - P d(nV)$

REVERSIBLE

Why? DIFFERENTIAL CHANGES

CASE #1: CONSTANT V

$\Rightarrow d(nV) = 0$

$\Rightarrow d(nu) = dQ$

Integrate:

$n \Delta u = Q$

NOTE: W=0
CONSTANT V

CASE #2: CONSTANT P

$$d(nu) = dQ - Pd(nv)$$

Solve for dQ:

$$dQ = d(nu) + Pd(nv)$$

$$= d(nu) + d(nPV)$$

$$= d(nu + nPV)$$

$$dQ = d[n(u + PV)]$$

NEW TERM:

$ENTHALPY \equiv H \equiv U + PV$ ← DEFINITION

NOTE: ALL INTENSIVE PROPERTIES
(molar or specific values)

SUBSTITUTE:

$$dQ = d[nH]$$

INTEGRATE:

$Q = n\Delta H$

CONSTANT P

← NOTE: W IS PART OF ENTHALPY

2.10 ENTHALPY

NOTES:

- 1) THIS TERM WILL SHOW UP ALL OVER THE PLACE FOR CALCULATING Q+W.
- 2) INTENSIVE PROPERTIES, SO IF WE SET T+P, THEY WILL BE FIXED, (RECALL PHASE RULE)
- 3) WE CAN TABULATE ENTHALPIES

EXAMPLE: Appendix F (Steam Tables)

→ U, P, V ALL STATE FUNCTIONS

→ SINCE $H = f(U, P, V)$, THEN IT IS ALSO A STATE FUNCTION.

FINALLY, FOR $n = 1$ mole

$$H = U + PV$$

$$\boxed{dH = dU + d(PV)}$$

INTEGRATE:

$$\boxed{\Delta H = \Delta U + \Delta(PV)}$$

EXAMPLE 2.8 Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100°C and the constant pressure of 101.33 kPa . The specific volumes of liquid and vapor water at these conditions are 0.00104 and $1.673 \text{ m}^3 \text{ kg}^{-1}$. For this change, heat in the amount of $2,256.9 \text{ kJ}$ is added to the water.

What do we know?

- Constant T (100°C)
- Constant P (101.33 kPa)

$$V_{\text{lig}} = 0.00104 \text{ m}^3/\text{kg}$$

$$V_{\text{vap}} = 1.673 \text{ m}^3/\text{kg}$$

$$Q = 2,256.9 \text{ kJ}$$

Calculate ΔH : Constant P , so $Q = \Delta H$

$$\Rightarrow \boxed{\Delta H = 2,256.9 \text{ kJ}}$$

Next, Solve for ΔU ...

$$\Delta H = \Delta U + \Delta(PV)$$

Constant P, solve for ΔU ...

$$\Delta U = \Delta H - P \Delta V \Big|_{0.00104}^{1.673}$$

(water is vaporized)

Plug + Chug (+ units conversion)

$$\Delta U = 2,256.9 \text{ kJ} - (101.33 \text{ kPa}) (1.673 - 0.00104) \frac{\text{m}^3}{\text{kg}}$$

$$\left| \frac{1 \text{ kg}}{1} \right| \left| \frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^3} \right| \left| \frac{\text{kJ}}{1 \text{ kJ} \cdot \text{m}} \right| = \boxed{2,087.5 \text{ kJ} = \Delta U}$$

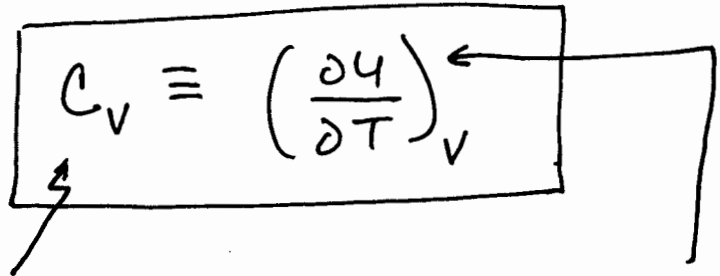
2.11 HEAT CAPACITY

→ Related to how much heat must be transferred to a unit mass/mole of fluid to change its temperature 1 degree.

$$C \equiv \frac{dQ}{dT} \equiv \text{HEAT CAPACITY (EXTENSIVE)}$$

NOTE! LOOK FOR DIFFERENT SUBSTITUTIONS FOR Q BASED ON THE PROCESS.

CASE #1: CONSTANT VOLUME



HEAT CAPACITY
AT CONSTANT
VOLUME
(INTENSIVE)

RECALL:
 $dQ = d(nU)$
@ CONSTANT VOLUME.

So, what happened to n?

C WAS EXTENSIVE

C_V IS INTENSIVE BECAUSE IT CONTAINS n

So, starting from:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$dU = C_V dT$$

INTEGRATE:

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

LOOKING FOR Q, SO MULTIPLY BOTH SIDES BY n

$$Q = \underbrace{n \Delta U}_{\text{STATE FUNCTION}} = n \int_{T_1}^{T_2} C_V dT$$

STATE
FUNCTION
(Independent of Path)

⇒ IN THIS CASE, Q IS INDEPENDENT OF PATH.

CASE #2: CONSTANT PRESSURE

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P$$

HEAT CAPACITY
AT CONSTANT
PRESSURE
(INTENSIVE)

RECALL:

$$dQ = d(nH)$$

@ CONSTANT PRESSURE

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$dH = C_p dT$$

INTEGRATE:

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

LOOKING FOR Q, SO MULTIPLY BOTH SIDES BY n

$$Q = n \Delta H = n \int_{T_1}^{T_2} C_p dT \quad \text{CONSTANT PRESSURE}$$

EXAMPLE 2.9 Air at 1 bar + 298.15K (25°C) is compressed to 5 bar and 298.15 K by two different mechanically reversible processes:

- (a) Cooling at constant pressure followed by heating at constant volume.
- (b) Heating at constant volume followed by cooling at constant pressure.

CALCULATE HEAT AND WORK REQUIREMENTS AND $\Delta U + \Delta H$ OF THE AIR FOR EACH PATH.

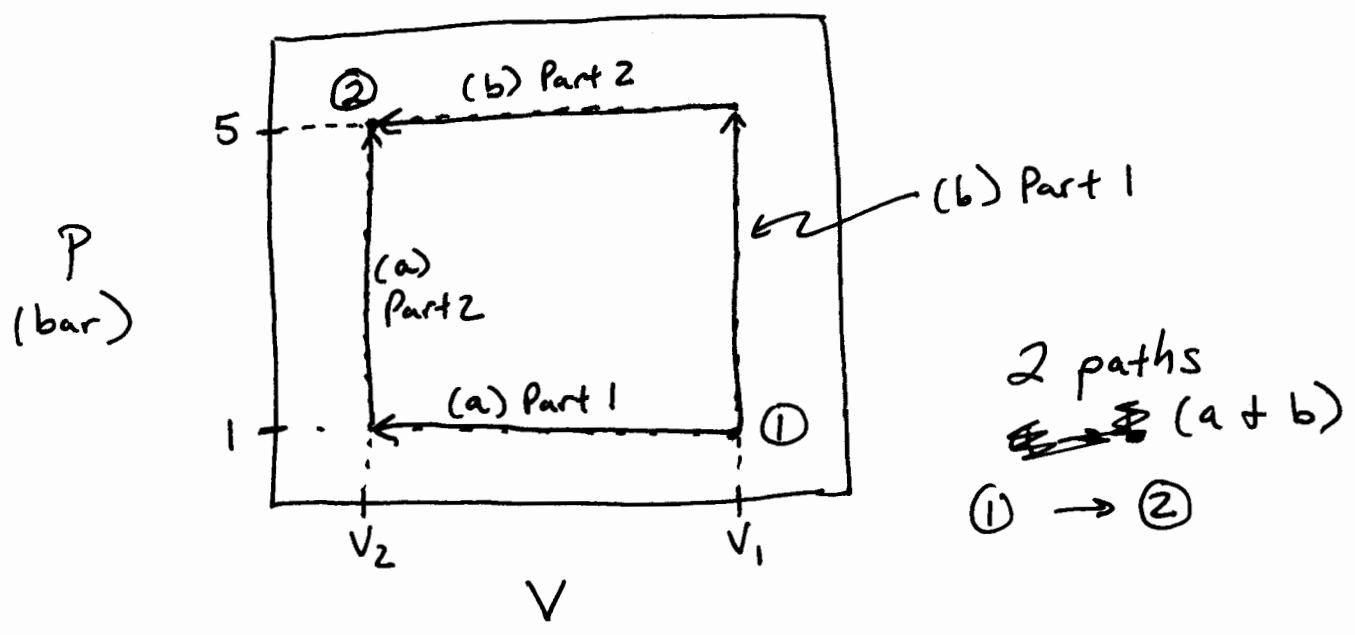
GIVEN: $C_v = 20.78 \frac{J}{mol \cdot K}$

$C_p = 29.10 \frac{J}{mol \cdot K}$

$\frac{P}{RT} = \text{constant}$

$V_1 = 0.02479 \frac{m^3}{mol}$ (@ 298.15K, 1 bar)

$\Rightarrow V_2 = \frac{V_1 P_1}{P_2} = \frac{0.02479 m^3}{mol} \left| \frac{1 \text{ bar}}{5 \text{ bar}} \right. = 0.004958 \frac{m^3}{mol}$



PATH (a)

Part 1: Cooling at constant pressure

Intermediate $T = ?$

$$\frac{P_1 V_1}{T_1} = \boxed{\frac{P V}{T}}$$

↑ Intermediate conditions.

$P = P_1$
 $V = V_2$ } SOLVE FOR T

$$T = \frac{V T_1}{V_1} = \frac{0.004958 \text{ m}^3}{\text{mol}} \left| \frac{\text{mol}}{0.02479 \text{ m}^3} \right| \frac{298.15 \text{ K}}{1}$$

$\Rightarrow \boxed{T = 59.63 \text{ K}}$ (Very cold!)

Constant Pressure $\Rightarrow Q = n \Delta H = n C_p \Delta T$

$$Q = \underbrace{(1 \text{ mol})}_{\text{unit mole}} \left| \frac{29.10 \text{ J}}{\text{mol} \cdot \text{K}} \right| \frac{(59.63 - 298.15) \text{ K}}{1}$$

$$Q = n \Delta H = -6,941 \text{ J} = Q \quad \text{path a-1}$$

$$\Delta H = -6,941 \frac{\text{J}}{\text{mol}} \quad \text{path a-1}$$

Recall: $n \Delta H = n \Delta U + n \Delta(PV)$

$$\Rightarrow n \Delta U = n \Delta H - n \Delta(PV)$$

And P constant.

$$\Delta U = \Delta H - P \Delta V \Big|_{V_1}^V$$

$$= \frac{-6,941 \text{ J}}{\text{mol}} - 1 \text{ bar} \Big| \frac{(0.004958 - 0.02479) \text{ m}^3}{\text{mol}} \Big| \frac{10^5 \text{ N}}{\text{bar} \cdot \text{m}^2} \Big| \frac{\text{J}}{\text{Nm}}$$

$$\Delta U = -4,958 \frac{\text{J}}{\text{mol}} \quad \text{path a-1}$$

CALCULATE WORK LATER.

Part 2: Heating at constant volume

$$\text{Constant Volume} \Rightarrow Q = n \Delta U = n C_V \Delta T \Big|_T^{T_2}$$

$$= \underbrace{(1 \text{ mol})}_{\text{unit mole}} \left| \frac{20.78 \text{ J}}{\text{mol} \cdot \cancel{\text{K}}} \right| \frac{(298.15 - 59.63) \cancel{\text{K}}}{1}$$

$$Q = n \Delta U = \boxed{4,958 \text{ J} = Q} \text{ path a-2}$$

$$\boxed{\Delta U = 4,958 \frac{\text{J}}{\text{mol}}} \text{ path a-2}$$

So, OVERALL:

$$Q = -6,941 \text{ J} + 4,958 \text{ J} = \boxed{-1,983 \text{ J} = Q} \text{ OVERALL}$$

$$\Delta U = -4,958 \frac{\text{J}}{\text{mol}} + 4,958 \frac{\text{J}}{\text{mol}} = \boxed{0 \frac{\text{J}}{\text{mol}} = \Delta U} \text{ OVERALL}$$

$$n \Delta U = Q + W = 0$$

$$\Rightarrow W = -Q = \boxed{1,983 \text{ J} = W} \leftarrow \text{OVERALL}$$

$$n \Delta H = n \Delta U + n \Delta(PV)$$

$$\text{BUT, } P_1 V_1 = P_2 V_2 \quad (T_1 = T_2)$$

$$\Rightarrow \Delta(PV) = 0$$

$$\cancel{P} \Delta H = \cancel{P} \Delta U$$

$$\Rightarrow \boxed{\Delta H = 0 \frac{\text{J}}{\text{mol}}} \leftarrow \text{OVERALL}$$

PATH (b)

Part 1: Heating at constant volume.

Intermediate $T = ?$

$$\frac{P_1}{T_1} = \boxed{\frac{P}{T}}$$

↑ Intermediate conditions

$$T = \left(\frac{P}{P_1}\right) T_1 = \left(\frac{5 \text{ bar}}{1 \text{ bar}}\right) (298.15 \text{ K}) = \boxed{1490.75 \text{ K}}$$

HOT!

Constant volume, so:

$$Q = n \Delta U = n C_v \Delta T$$

$$= \underbrace{(1 \text{ mol})}_{\text{unit mole}} \left| \frac{20.78 \text{ J}}{\text{mol} \cdot \text{K}} \right| \frac{(1490.75 - 298.15) \text{ K}}{1}$$

$$\Rightarrow \boxed{Q = 24,782 \text{ J}} \text{ path b-1}$$

$$\Delta U = 24,782 \frac{\text{J}}{\text{mol}} \text{ path b-1}$$

Calculate work later.

Part 2: Cooling at constant pressure.

Constant Pressure, so:

$$Q = n \Delta H = n C_p \Delta T$$

$$= \underbrace{(1 \text{ mol})}_{\text{unit mole}} \left| \frac{29.10 \text{ J}}{\text{mol} \cdot \text{K}} \right| \frac{(298.15 - 1490.75) \text{ K}}{1}$$

$$\Rightarrow Q = -34,705 \text{ J} \text{ path b-2}$$

$$\Delta H = -34,705 \frac{\text{J}}{\text{mol}} \text{ path b-2}$$

$$n \Delta H = n \Delta U + n \Delta(PV)$$

$$n \Delta U = n \Delta H - n \Delta(PV)$$

and constant pressure

$$\Delta U = \Delta H - P \Delta V \Big|_V^{V_2}$$

(46)

$$\Delta U = -34,705 \frac{\text{J}}{\text{mol}} - (5 \text{ bar})(0.004958 - 0.02479) \frac{\text{m}^3}{\text{mol}}$$

$$\left| \frac{10^5 \text{ N}}{1 \text{ bar} \cdot \text{m}^2} \right| \left| \frac{1 \text{ J}}{1 \text{ N} \cdot \text{m}} \right| = -34,705 + 9,916$$

$$\boxed{\Delta U = -24,789 \frac{\text{J}}{\text{mol}}} \text{ path b-z}$$

So, OVERALL:

$$\Delta U = 24,782 - 24,789 = -7 \text{ J}$$

$$\approx 0 \text{ J}$$

$$Q = 24,782 - 34,705 = \boxed{-9,923 \text{ J} = Q}$$

$$W = \Delta U - Q = -7 - (-9,923) = \boxed{9,916 \text{ J} = W}$$

Within Rounding Error

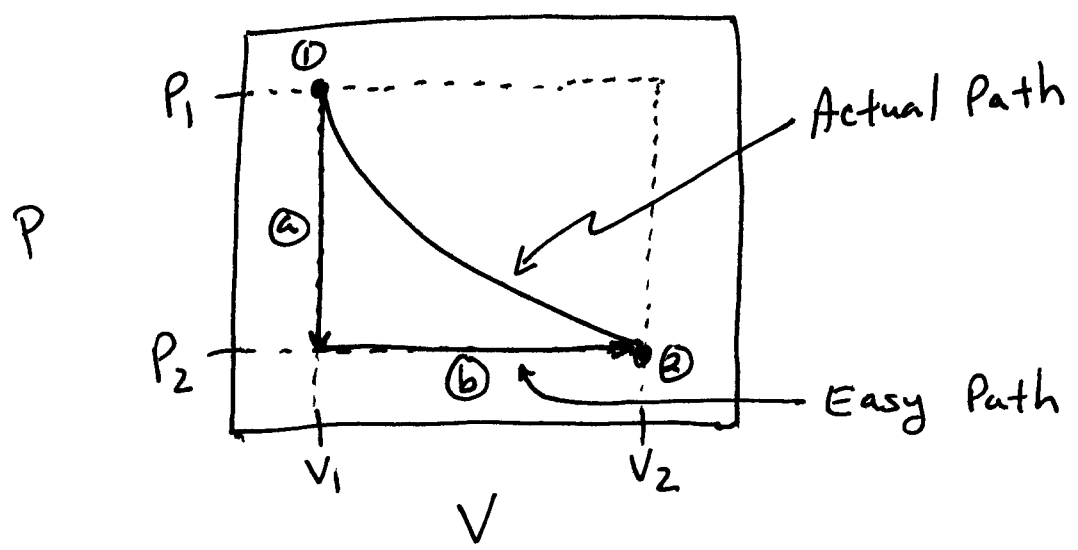
$$\boxed{\Delta U = \Delta H = 0} \leftarrow \text{SAME REASON AS BEFORE}$$

EXAMPLE 2.10 CALCULATE THE INTERNAL ENERGY AND ENTHALPY CHANGES THAT OCCUR WHEN AIR IS CHANGED FROM AN INITIAL STATE OF 40°F AND 10 atm, WHERE ITS MOLAR VOLUME IS 36.49 ft³/lbmol, TO A FINAL STATE OF 140°F AND 1 atm. ASSUME FOR AIR THAT PV/T IS CONSTANT AND THAT C_v = 5 AND C_p = 7 Btu/lbmol·°F.

FIRST THINGS FIRST... V₂ = ?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$= \frac{10 \text{ atm}}{1 \text{ atm}} \left| \frac{(140 + 459.67) \text{ R}}{(40 + 459.67) \text{ R}} \right| \left| \frac{36.49 \text{ ft}^3}{\text{lbmol}} \right| = 437.93 \frac{\text{ft}^3}{\text{lbmol}}$$



CALCULATING $\Delta U + \Delta H$ (STATE FUNCTIONS)
 SO WE CAN CHOOSE A PATH TO SIMPLIFY
 THE CALCULATION.

⇒ Two-STEP PROCESS

(a) Cooling at constant volume

Constant Volume, so;

$$Q = n C_V \Delta T \Big|_{T_i}^T$$

⇒ Need the intermediate temperature

$$\frac{P_i}{T_i} = \boxed{\frac{P}{T}}$$

↑ Intermediate conditions

$$T = \left(\frac{P}{P_i}\right) T_i = \left(\frac{1 \text{ atm}}{10 \text{ atm}}\right) (40 + 459.67) \text{ R}$$

$$\boxed{T = 49.967 \text{ R}} \quad (\text{Expect } Q < 0)$$

↑
Very cold! (= -409.703 °F)

$$Q = n C_v \Delta T$$

$$= \underbrace{(1 \text{ lbmol})}_{\text{unit mole}} \left| \frac{5 \text{ Btu}}{\text{lbmol} \cdot ^\circ\text{F}} \right| \frac{(-409.703 - 40)^\circ\text{F}}{1}$$

$$Q = -2,248.5 \text{ Btu} \text{ path (a)}$$

(b) Heating at constant pressure (expect Q > 0)

Constant pressure, so:

$$Q = n \Delta H = n C_p \Delta T \Big|_T^{T_2}$$

$$= \underbrace{(1 \text{ lbmol})}_{\text{unit mole}} \left| \frac{7 \text{ Btu}}{\text{lbmol} \cdot ^\circ\text{F}} \right| \frac{(140^\circ\text{F} - (-409.703^\circ\text{F}))}{1}$$

$$Q = n \Delta H = 3,847.9 \text{ Btu} = Q \text{ path (b)}$$

$$\Delta H = 3,847.9 \frac{\text{Btu}}{\text{lbmol}} \text{ path (b)}$$

$$\Delta U = \Delta H - \Delta(PV)$$

But, constant pressure, so...

$$\Delta U = \Delta H - P \Delta V \quad \left| \begin{array}{l} 437.93 \\ 36.49 \end{array} \right.$$

$$= 3,847.9 \frac{\text{Btu}}{\text{lbmol}} - \frac{1 \text{ atm}}{1 \text{ lbmol}} (437.93 - 36.49) \text{ ft}^3$$

$$\left| \frac{14.5038 \text{ lbf}}{0.986923 \text{ atm} \cdot \text{in}^2} \right| \left| \frac{144 \text{ in}^2}{1 \text{ ft}^2} \right| \left| \frac{9.47831 \times 10^4 \text{ Btu}}{0.737562 \text{ ft} \cdot \text{lbf}} \right|$$

$$= 3,847.9 \frac{\text{Btu}}{\text{lbmol}} - 1,091.7 \frac{\text{Btu}}{\text{lbmol}}$$

$\Delta U = 2,756.2 \frac{\text{Btu}}{\text{lbmol}}$

path (b)

Overall



From part (a)

$$n \Delta U = n C_v \Delta T = Q$$

$\Delta U = -2,248.5 \frac{\text{Btu}}{\text{lbmol}}$

part (a)

$$\Delta H = \Delta U + \Delta(PV)$$

But constant volume (part (a))

$$\Delta H = \Delta U + V \Delta P \Big|_{10 \text{ atm}}^{1 \text{ atm}}$$

$$= -2,248.5 \frac{\text{Btu}}{\text{lbmol}} + \frac{36.49 \text{ ft}^3}{\text{lbmol}} \Big| \frac{(1-10) \text{ atm}}{1}$$

$$\left| \frac{14.5038 \text{ lbf}}{0.986923 \text{ atm} \cdot \text{in}^2} \right| \left| \frac{144 \text{ in}^2}{1 \text{ ft}^2} \right| \frac{9.47831 \times 10^{-4} \text{ Btu}}{0.737562 \text{ ft} \cdot \text{lbf}}$$

$$= -2,248.5 \frac{\text{Btu}}{\text{lbmol}} - 893.1 \frac{\text{Btu}}{\text{lbmol}}$$

$$\Delta H = -3,141.6 \frac{\text{Btu}}{\text{lbmol}} \quad \text{part (a)}$$

So, overall:

$$\Delta U = -2,248.5 \frac{\text{Btu}}{\text{lbmol}} + 2,756.2 \frac{\text{Btu}}{\text{lbmol}} = 507.7 \frac{\text{Btu}}{\text{lbmol}}$$

$$\Delta H = -3,141.6 + 3,847.9 = 706.3 \frac{\text{Btu}}{\text{lbmol}}$$

2.12 MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

⇒ ADD MORE COMPLEXITY

→ FLOW IN + OUT OF SYSTEM

⇒ OPEN SYSTEMS

MASS + ENERGY CONSERVATION APPLY

HOW DO WE MEASURE FLOW?

\dot{m} mass flow rate $[=] \frac{\text{kg}}{\text{s}}$

\dot{n} mole flow rate $[=] \frac{\text{mol}}{\text{s}}$

\dot{V} volumetric flow rate $[=] \frac{\text{m}^3}{\text{s}}$

u velocity $[=] \text{m/s}$

(2)

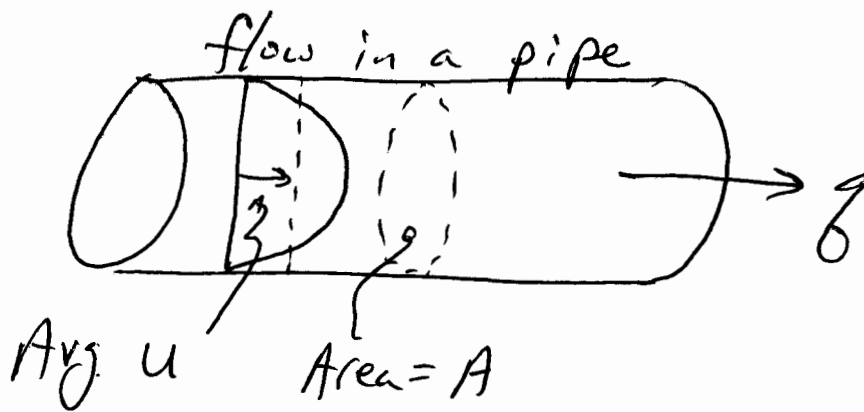
Flow terms are related

$$\dot{m} = M \dot{n}$$

↑
molecular weight

$$\dot{Q} = u A$$

↑
cross sectional area for flow.



$$\dot{m} = u A \rho$$

↑
Specific density

$$\dot{n} = u A \rho$$

↑
molar density

Example: Liquid n-hexane flows at a rate of $\dot{m} = 0.75 \text{ kg/s}$ in a pipe w/ inside diameter $D = 5 \text{ cm}$. What are \dot{Q} , \dot{n} , and u ? What would these quantities be for the same \dot{m} if $D = 2 \text{ cm}$? Assume for liquid n-hexane that $\rho = 659 \text{ kg/m}^3$.

$$\dot{m} = u A \rho \qquad \dot{q} = u A \Rightarrow \dot{q} = \frac{\dot{m}}{\rho}$$

$$\Rightarrow \dot{q} = \frac{0.75 \text{ kg}}{\text{s}} \Big| \frac{\text{m}^3}{659 \text{ kg}} = \boxed{1.14 \times 10^{-3} \frac{\text{m}^3}{\text{s}} = \dot{q}}$$

$$\dot{n} = \frac{\dot{m}}{M} = \frac{0.75 \text{ kg}}{\text{s}} \Big| \frac{\text{kmol}}{86 \text{ kg}} \Big| \frac{10^3 \text{ mol}}{1 \text{ kmol}} = 8.72 \frac{\text{mol}}{\text{s}}$$

Hexane: $(6 \times 12) + 14(1) = 72 + 14 = 86 \frac{\text{g}}{\text{mol}}$

$$A = \frac{\pi (5 \text{ cm})^2}{4} = 19.63 \text{ cm}^2$$

$$u = \frac{\dot{m}}{A \rho} = \frac{0.75 \text{ kg}}{\text{s}} \Big| \frac{1}{19.63 \text{ cm}^2} \Big| \frac{\text{m}^3}{659 \text{ kg}} \Big| \frac{10^4 \text{ cm}^2}{1 \text{ m}^2}$$

$$\boxed{u = 0.58 \text{ m/s}}$$

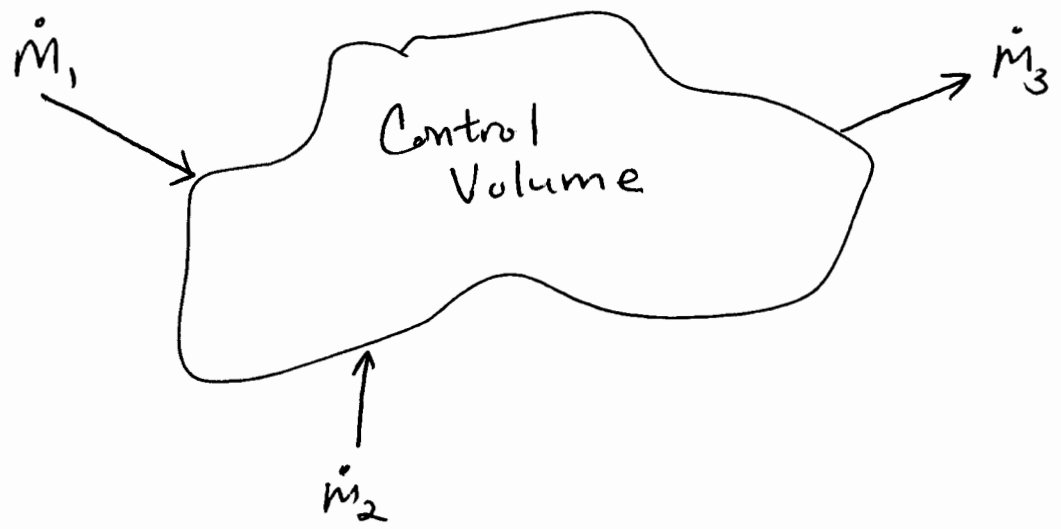
For D = 2cm: $\dot{q} = 1.14 \times 10^{-3} \frac{\text{m}^3}{\text{s}}$ (No change)

$\dot{n} = 8.72 \frac{\text{mol}}{\text{s}}$ (No change)

$$A = \frac{\pi (2\text{cm})^2}{4} = 3.14 \text{ cm}^2$$

$$\Rightarrow U = 0.58 \frac{\text{m}}{\text{s}} \left| \frac{19.63 \text{ cm}^2}{3.14 \text{ cm}^2} \right. = \boxed{3.63 \frac{\text{m}}{\text{s}} = U}$$

MASS BALANCE FOR OPEN SYSTEMS:



$$\underbrace{\frac{dm_{cv}}{dt}}_{\text{CHANGE IN CONTROL VOLUME MASS}} = \underbrace{\dot{m}_1 + \dot{m}_2}_{\text{IN}} - \underbrace{\dot{m}_3}_{\text{OUT}}$$

(5)

$$\frac{dm_{cv}}{dt} + \underbrace{\Delta (\dot{m})}_{fs} = 0$$

EXIT - ENTERING
FLOW STREAMS

But, $\dot{m} = u A \rho$

$$\boxed{\frac{dm_{cv}}{dt} + \Delta (u A \rho)_{fs} = 0}$$

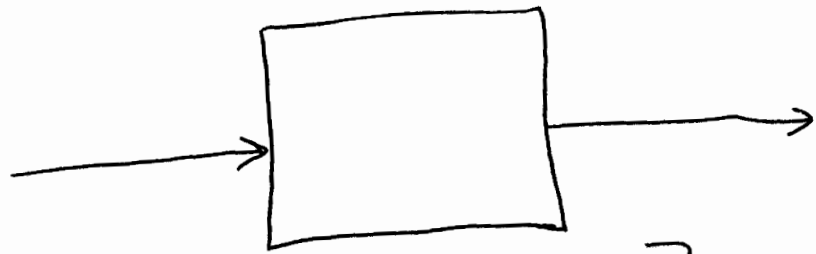
CONTINUITY
EQUATION.

If System @ Steady State:

$$\Delta (u A \rho)_{fs} = 0$$

$$\frac{dm_{cv}}{dt} = 0 \quad (\text{No change in System mass w/ time})$$

NOTE ! STILL FLOW IN & OUT OF SYSTEM,



one inlet } @ Steady
 one outlet } State

$$\Delta(uA\rho)_{fs} = u_2 A_2 \rho_2 - u_1 A_1 \rho_1 = 0$$

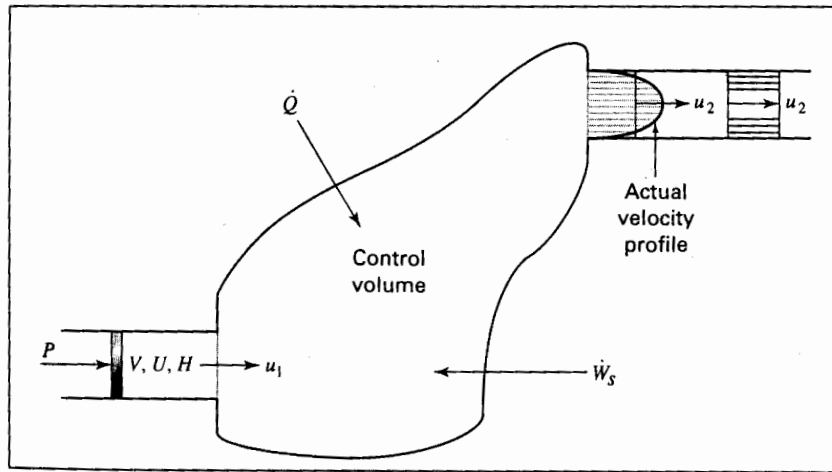
$\Rightarrow \dot{m}$ constant.

$$\Rightarrow \dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{u A}{V}$$

where V is specific volume $[=] \frac{m^3}{kg}$
 $(\frac{1}{\rho} = V)$

GENERAL ENERGY BALANCE:

FIGURE 2.4



Energy Balance:

$$\frac{d(mU)_{cv}}{dt} = - \Delta \left[\begin{array}{l} \text{internal} \\ \text{energy} \end{array} (U + \begin{array}{l} \text{kinetic} \\ \text{energy} \end{array} \frac{1}{2} u^2 + \begin{array}{l} \text{Potential} \\ \text{Energy} \end{array} zg) \dot{m} \right]_{fs} + \dot{Q} + \text{Work Rate}$$

$\frac{\text{kg}}{\text{kg} \cdot \text{s}} \left \frac{\text{J}}{\text{kg} \cdot \text{s}} \right.$	$\left(\frac{\text{J}}{\text{kg}} + \frac{\text{m}^2}{\text{s}^2} + \text{m} \left \frac{\text{m}}{\text{s}^2} \right. \right) \frac{\text{kg}}{\text{s}}$	$\frac{\text{J}}{\text{s}}$	$\frac{\text{J}}{\text{s}}$
┌──────────┐	┌──────────────────────────┐	┌──┐	┌──┐

Accumulation

NOTE:

$$\Delta = \text{OUT} - \text{IN}$$

$$-\Delta = \text{IN} - \text{OUT}$$

UNITS ALL CHECK OUT.

WORK RATE:

Types

- PV Work
 - Moving fluid through entrance + exit
- Shaft Work
 - Pumping
- Control volume expansion/compression
- Stirring

Work Rate = $-\Delta[(PV)\dot{m}]_{fs} + \dot{W}$

$\frac{N}{m^2} \left| \frac{m^3}{kg} \right| \frac{kg}{s}$

Recall how we justified the sign.

$\underbrace{\hspace{10em}}_{\text{All other work}}$

So,

$$\frac{d(mu)_{cv}}{dt} = -\Delta \left[\left(u + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} + \dot{Q} - \Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

COMBINE $H=U+PV$

Looking to get H into equation

(9)

$$\frac{d(mU)_{cv}}{dt} = -\Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} + \dot{Q} + \dot{W}$$

or ENERGY BALANCE OPEN SYSTEM.

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

Still no motion in the control volume.

(So our equation has limitations.)

EXAMPLE 2.12

Show that Eq. 2.29 reduces to Eq. 2.3 for the case of a closed system.

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

Closed System: $\dot{m} = 0$

$$\frac{d(mU)_{cv}}{dt} = \dot{Q} + \dot{W}$$

$$\int d(mU)_{cv} = \int_{t_1}^{t_2} \dot{Q} dt + \int_{t_1}^{t_2} \dot{W} dt$$

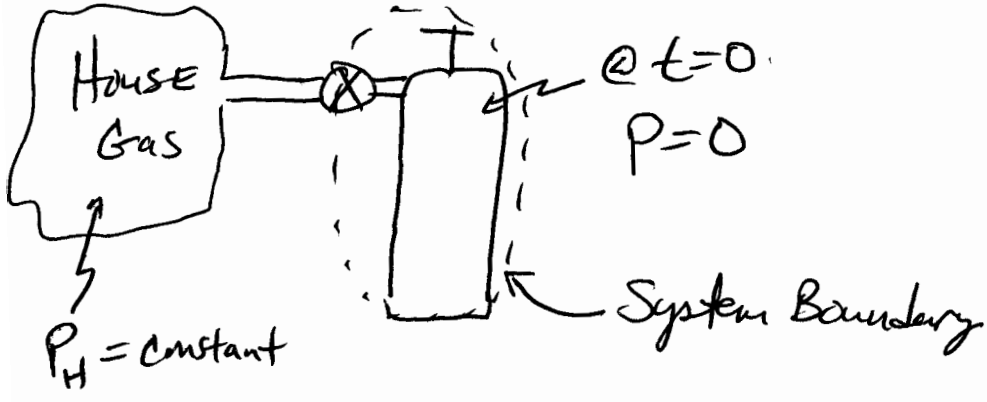
$$\Delta (mU)_{cv} = Q + W$$

$$\Delta U^t = Q + W$$

QED.

Example 2.13

An evacuated tank is filled w/ gas from a constant pressure line. What is the relation between the enthalpy of the gas in the entrance line and the internal energy of the gas in the tank? Neglect heat transfer between the gas and the tank.

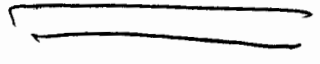


RIGID TANK

⇒ No expansion work

No stirring

No shaft work



$$\dot{w} = 0$$

Energy Balance:

$$\frac{d(mU)_{cv}}{dt} + \Delta (H_{in})_{fs} = \dot{Q} + \dot{W}$$

\downarrow neglect heat transfer \downarrow $\dot{W} = 0$

$$\frac{d(mu)_{cv}}{dt} + (H_{\dot{m}_{out}} - H_{\dot{m}_{in}}) = 0$$

No outlet

$$\frac{d(mu)_{cv}}{dt} - H_{\dot{m}_{in}} = 0$$

But $\dot{m}_{in} = \frac{dm_{Tank}}{dt}$

$$\int \frac{d(mu)_{cv}}{dt} - H_{HOUSE} \int \frac{dm_{Tank}}{dt} = 0$$

CV is tank

$$m_2 u_2 - m_1 u_1 - H_{HOUSE} (m_2 - m_1) = 0$$

Tank evacuated @ t=0 ⇒ u₁ = 0

@ t=0 m₁ = 0

$$m/2 u_2 - H_{HOUSE} m/2 = 0$$

$$u_2 = H_{HOUSE}$$

Why? No heat transfer,

Example 2.14

An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 60°C when a power outage occurs. If water is withdrawn from the tank at a steady rate of $\dot{m} = 0.2 \text{ kg/s}$, how long will it take for the temperature of the water in the tank to drop from 60 to 35°C?

Assume cold water enters the tank at 10°C, and negligible heat losses from the tank. For liquid water let $C_v = C_p = C$, independent of $T + P$.

Negligible heat losses, Insulated

$$\Rightarrow \dot{Q} = 0$$

No real info on work:

\Rightarrow No stirring (even though we assume perfectly mixed)

\Rightarrow Incompressible, so no compression/expansion

\Rightarrow No pumping (\dot{W}_s) because power outage

\Rightarrow PV in H.

$$\Rightarrow \dot{W} = 0$$

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = 0$$

If $\dot{m}_{in} = \dot{m}_{out}$, the $m_{cv} = \text{constant}$.

$$m \frac{du_{ev}}{dt} + \left(\underset{\substack{\uparrow \\ \text{tank}}}{H} - \underset{\substack{\uparrow \\ \text{cold water} \\ \text{in.}}}{H_1} \right) \dot{m} = 0$$

But $\Delta H = C \Delta T = C (T - T_1)$
 \uparrow
 heat capacity

AND,

$$m \frac{du}{dt} = m c \frac{dT}{dt}$$

So

$$m c \frac{dT}{dt} + c (T - T_1) \dot{m} = 0$$

Separate Variables.

$$\frac{m dT}{T - T_1} = - \dot{m} dt$$

$$\Rightarrow \int_0^t dt = - \frac{m}{\dot{m}} \int_{T_0}^T \frac{dT}{(T - T_1)}$$

\uparrow initial tank temperature

$$t = -\frac{m}{\dot{m}} \ln\left(\frac{T-T_1}{T_0-T_1}\right)$$

Now start
substituting real
numbers...

$$m = 190 \text{ kg}$$

$$T_1 = 10^\circ\text{C}$$

$$\dot{m} = \frac{0.2 \text{ kg}}{\text{s}}$$

$$T_0 = 60^\circ\text{C}$$

$$T = 35^\circ\text{C}$$

Plug + Chug

$$t = -\frac{190 \text{ kg} \cdot \text{s}}{0.2 \text{ kg}} \ln\left(\frac{35 - 10}{60 - 10}\right)$$

$$= -950 \text{ s} (-0.6931) \Rightarrow t = 658 \text{ s}$$

$$\sim 11 \text{ min}$$

Next, Steady Flow Processes ...

Energy Balances for Steady-State Flow Processes (15)

$$\Rightarrow \frac{d(mU)_{cv}}{dt} = 0$$

\Rightarrow No expansion/compression work

So,

$$\Delta \left[(H + \frac{1}{2}u^2 + zg) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s$$

If one entrance & one exit...

$$\Delta (H + \frac{1}{2}u^2 + zg) \dot{m} = \dot{Q} + \dot{W}_s$$

$$\Delta (H + \frac{1}{2}u^2 + zg) = \frac{\dot{Q}}{\dot{m}} + \frac{\dot{W}_s}{\dot{m}} = Q + W_s$$

NOT
RATES

or

$$\Delta H + \frac{1}{2} \Delta(u^2) + g \Delta z = Q + W_s$$

FIRST LAW FOR STEADY STATE, STEADY FLOW PROCESS
w/ ONE ENTRANCE

Check units:

$\frac{\Delta H}{\text{kg}}$	$\frac{\Delta(u^2)}{\text{s}^2}$	$g\Delta z$	$\frac{Q}{\text{kg}}$	$\frac{W_s}{\text{kg}}$
		$\frac{\text{m}}{\text{s}^2} \cdot \frac{\text{m}}{1}$		
for unit mass	$\left(\frac{\text{kg} \cdot \text{m}}{\text{s}^2}\right) \cdot \frac{\text{m}}{\text{kg}}$		for unit mass	
	for unit mass			

Often, kinetic & potential energies are negligible. Therefore!

$$\Delta H = Q + W_s$$

FIRST LAW FOR STEADY STATE, STEADY FLOW

SIMILAR TO

$$\Delta u = Q + W$$

FIRST LAW FOR NON-FLOW PROCESS,

A Flow Calorimeter for Enthalpy Measurements

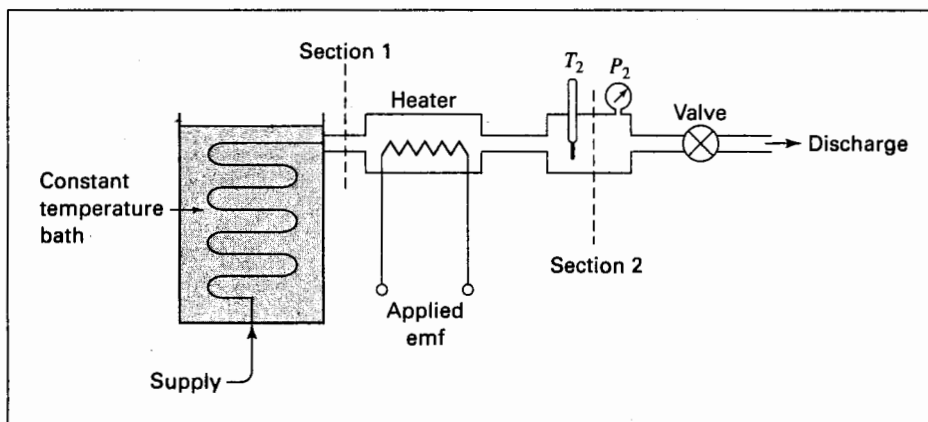
(17)

- Very low velocity $\Rightarrow \frac{1}{2} u^2 \approx 0$
- No elevation change $\Rightarrow \Delta z \approx 0$
- No shaft work

$$\Rightarrow \Delta H = Q = H_2 - H_1$$

Q is determined from resistance heater, so Q is known.

FIGURE 2.7

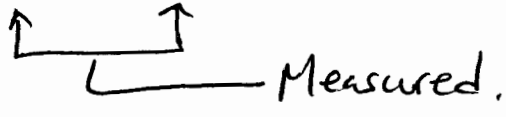


H_1 set arbitrarily = 0 @ $T=0^\circ\text{C}$ (Water)

$$\Rightarrow H_2 = H_1 + Q = Q$$

We can add specific quantity Q , and therefore

We know H_2 @ P_2 & T_2 .



\Rightarrow Tabular Data. (See Appendix F.)

Once H is set, calculate U from

$$U = H - PV.$$

Example 2.15

Flow rate: $4.15 \frac{\text{g}}{\text{s}}$

$$t_1 = 0^\circ\text{C}$$

$$t_2 = 300^\circ\text{C}$$

$$P_2 = 3 \text{ bar}$$

$$Q = 12,740 \text{ W}$$

Water completely vaporized.

$$H_2 = ? \text{ if } H_1 = 0 \text{ @ } 0^\circ\text{C}.$$

$$H_2 = \frac{Q}{\dot{m}} = \frac{12,740 \text{ J}}{\text{s}} \bigg/ \frac{\text{s}}{4.15 \text{ g}} = 3,070 \frac{\text{J}}{\text{g}}$$

Example 2.16 Air at 1 bar and 25°C enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m/s at the initial conditions of pressure + temperature. If the work of compression is 240 kJ/kg air, how much heat must be removed during compression?

$$F = 2 - 1 + 1 = 2 \quad (\text{and } T \& P \text{ set})$$

$\begin{array}{cc} \uparrow & \uparrow \\ \text{phases} & \text{components} \\ \text{(gas)} & \text{(air)} \end{array}$

Also, enthalpy is state property. Start + end at same point, so $\Delta H = 0$

No elevation change in nozzle, so $\Delta z = 0$.

$$\underbrace{\frac{1}{2} \Delta(u^2)} = Q + \underbrace{W_s}_{\text{Work of compression}}$$

$$\frac{1}{2} \left[\left(600 \frac{\text{m}}{\text{s}} \right)^2 - \left(0 \frac{\text{m}}{\text{s}} \right)^2 \right] = Q + 240 \frac{\text{kJ}}{\text{kg}}$$

(+) because work done on system.
(compression)

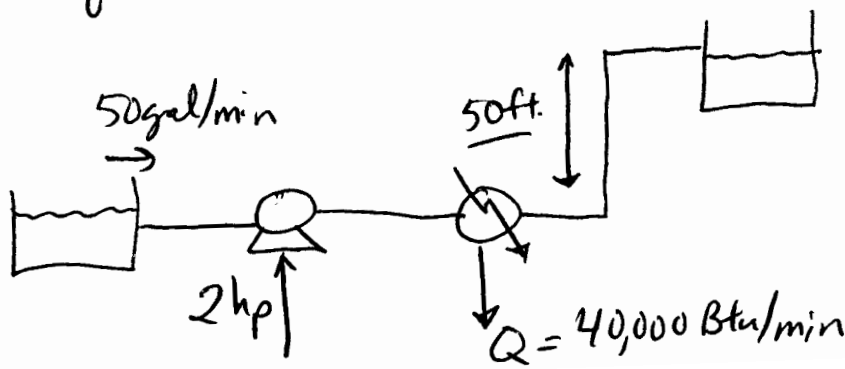
$$\frac{180,000 \text{ m}^2}{\text{s}^2} \cdot \frac{\text{kg}}{\text{kg}} \left| \frac{1 \text{ kJ}}{10^3 \text{ J}} \right. = Q + 240 \frac{\text{kJ}}{\text{kg}}$$

$$180 \frac{\text{kJ}}{\text{kg}} - 240 \frac{\text{kJ}}{\text{kg}} = Q = -60 \frac{\text{kJ}}{\text{kg}}$$

Heat Removed from System.

Example 2.17

Water at 200°F is pumped from a storage tank at the rate of 50 gal/min. The motor for the pump supplies work at the rate of 2 hp. The water goes through a heat exchanger, giving up heat at the rate of 40,000 Btu/min, and is delivered to a second storage tank at an elevation of 50 ft above the first tank. What is the temperature of the water delivered to the second tank?



Steady State, Steady Flow Process

$$\Delta H + \frac{\Delta(u^2)}{2gc} + \frac{g}{gc} \Delta z = Q + W_s$$

Storage tank
velocities ≈ 0

$$\dot{V} = \frac{50 \text{ gal}}{\text{min}}$$

$$\dot{m} = \rho \dot{V}$$

@ 200°F

$$\left(\rho = \frac{60.1 \text{ lb}_m}{\text{ft}^3} \right)$$

$$\dot{m} = \frac{50 \text{ gal}}{\text{min}} \left| \frac{60.1 \text{ lb}_m}{7.48 \text{ gal}} \right| = 402 \frac{\text{lb}_m}{\text{min}}$$

$$Q = \frac{-40,000 \text{ Btu}}{\text{min}} \left| \frac{\text{min}}{402 \text{ lb}_m} \right| = -99.50 \frac{\text{Btu}}{\text{lb}_m}$$

(-) because heat transferred to the surroundings

$$W_s = 2 \text{ hp} \left| \frac{0.947831 \text{ Btu}}{1.34102 \text{ hp} \cdot \text{s}} \right| \left| \frac{60 \text{ s}}{1 \text{ min}} \right| \left| \frac{\text{min}}{402 \text{ lb}_m} \right| = 0.21 \frac{\text{Btu}}{\text{lb}_m}$$

(+) because added to system

$$\frac{g}{g_c} \Delta z = \frac{32.174 \text{ ft}}{\cancel{\text{ft}^2}} \left| \frac{\cancel{\text{lb}_f \cdot \text{ft}^2}}{32.174 \text{ lb}_m \cdot \cancel{\text{ft}}} \right| \frac{50 \cancel{\text{ft}}}{1}$$

$$\left| \frac{9.47831 \times 10^{-4} \text{ Btu}}{0.737562 \cancel{\text{ft}} \cdot \cancel{\text{lb}_f}} \right| = 0.064 \frac{\text{Btu}}{\text{lb}_m}$$

$$\Rightarrow \Delta H = -99.5 \frac{\text{Btu}}{\text{lb}_m} + 0.21 \frac{\text{Btu}}{\text{lb}_m} - 0.064 \frac{\text{Btu}}{\text{lb}_m}$$

$$\Delta H = -99.35 \frac{\text{Btu}}{\text{lb}_m}$$

Go to steam tables for water property at
200°F (p. 756)

$$H_{\text{sat, liq}} = 168.09 \frac{\text{Btu}}{\text{lb}_m}$$

$$H_2 - 168.09 = -99.35 \Rightarrow H_2 = 68.74 \frac{\text{Btu}}{\text{lb}_m}$$

from Steam Table $T_{\text{sat}} = 100.74^\circ \text{F}$ p. 755