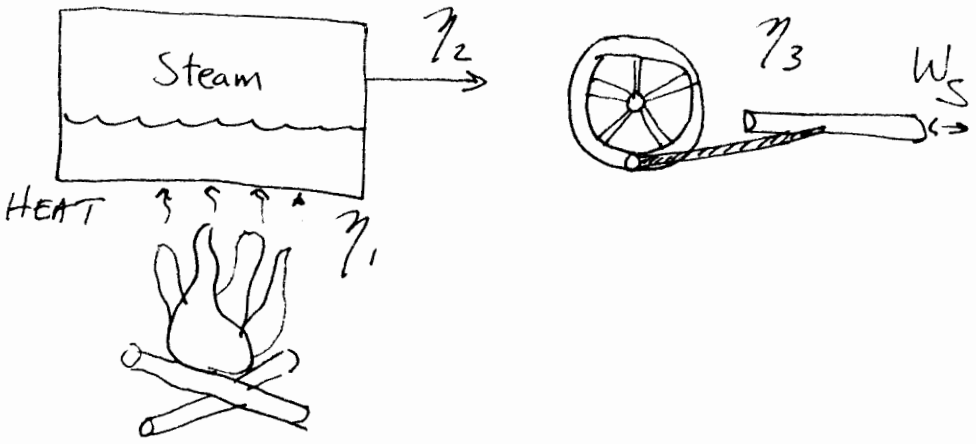
# CHE 255 - Chemical Engineering Thermodynamics

## CHAP. 1 — INTRODUCTION

THERMODYNAMICS ← WHAT DOES THIS MEAN?

HISTORICALLY:

STEAM ENGINE




How to get power from heat...

- DIFFERENT FORMS OF ENERGY
- CONVERSION BETWEEN DIFFERENT FORMS
- EFFICIENCY DURING CONVERSION

THINGS TO CONSIDER:

1) HOW DOES THE SYSTEM RELATE WITH ITS SURROUNDINGS?

2) EFFICIENCY OF ALTERNATIVE PROCESSES

3) WHAT IS THE EQUILIBRIUM STATE?

4) HOW TO GET THERMODYNAMIC PROPERTIES? (MEASUREMENT, ESTIMATION, CORRELATION)

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## BASIC RELATIONS

(1) FIRST LAW: (CONSERVATION OF ENERGY)

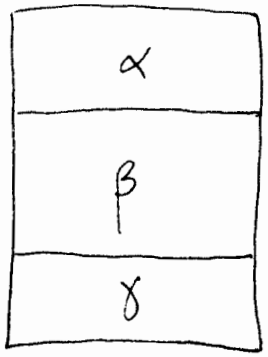
$$\Delta E^t = Q + W + E(flow) + E(gen)$$

- $Q$: HEAT
- $W$: WORK
- $E(flow)$: ENERGY RELATED TO FLOW
- $E(gen)$: ENERGY GENERATION

## (2) SECOND LAW: (CAN'T GO UPHILL - SOLELY)

$$\Delta S^t = \sum_i \frac{Q}{T} + S(\text{flow}) + S(\text{gen})$$

## (3) PHASE EQUILIBRIUM




$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \hat{f}_i^{\gamma} = \dots$$

Chemical potential of each component is the same in each phase. (EQUILIBRIUM)

## (4) CHEMICAL REACTION EQUILIBRIUM

$$-RT \ln K = \Delta G^{\circ}$$

$K$: EQUILIBRIUM CONSTANT

$\Delta G^{\circ}$: STANDARD GIBBS ENERGY CHANGE

where $K = \prod_i \left( \frac{\hat{f}_i}{f_i^{\circ}} \right)^{\nu_i}$

$\nu_i$: STOICHIOMETRY

product: $\prod_i$

$\frac{\hat{f}_i}{f_i^{\circ}}$: fugacities

FUNCTIONS OF MANY VARIABLES...

$\mu, f, T, P, U, E, w_s, Q$, etc.

HOW DO WE GET ALL OF THESE?
(AND WHAT UNITS?)

⇒ TRY TO PUT ABSTRACT VARIABLES IN TERMS OF THINGS YOU CAN MEASURE...

$T$, $P$, Composition, $\rho$ (↑ density), etc.

⇒ CHARTS, TABLES, EQUATIONS

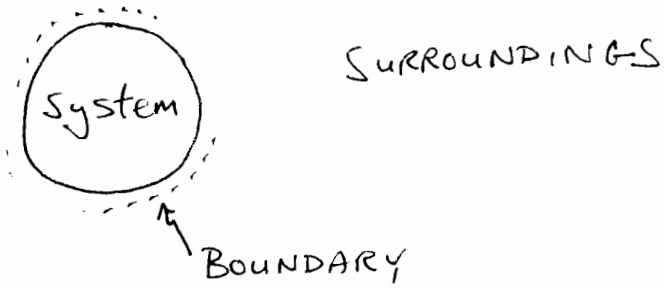
⇒ EVALUATE THE ACCURACY OF YOUR RESULTS.

DOES IT MAKE SENSE?

# BASIC TERMS IN THERMODYNAMICS:

1) SYSTEM

⇒ THIS IS WHAT THE ENERGY BALANCE IS ON.




2) SURROUNDINGS

⇒ EVERYTHING OUTSIDE THE SYSTEM.

3) BOUNDARY

⇒ You CHOOSE ... WHERE THE SYSTEM ENDS & THE SURROUNDINGS BEGIN.

4) TEMPERATURE

a) ABSOLUTE

1) Kelvin

2) Rankine

b) Relative

1) Celsius

2) Fahrenheit

NOTES ON TEMPERATURE

1) Absolute is default in equations unless otherwise specified.

2) $\Delta T \Rightarrow$ Absolute or Relative fine because a difference.

3) Watch units

4) $T_1 = T_2 = T_3 = \ldots$ at EQUILIBRIUM

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5) ~~MEAN~~ PRESSURE

$$P = \frac{\text{FORCE}}{\text{AREA}} = \frac{mg}{A} = \frac{Ah\rho g}{A} = h\rho g$$

$h$: fluid height; $\rho$: fluid density; $g$: acceleration of gravity

GAUGE VS. ABSOLUTE PRESSURE

$$P_{ABS} = P_{GAUGE} + P_{ATM}$$

$P_{ATM}$ ↳ ATMOSPHERIC PRESSURE

NOTE:

- ALWAYS USE $P_{ABS}$ IN EQUATIONS.
- GAUGE PRESSURE OK FOR $\Delta P$

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6) WORK

→ MOVING FLUIDS (KINETIC + POTENTIAL ENERGY)

→ COMPRESSION ($\Delta V \neq 0$)

→ SHAFT WORK (MIXING)

ADDED TO SYSTEM (+)

SYSTEM ON SURROUNDINGS (−)

# FOCUS ON COMPRESSION + EXPANSION

$$dW = F\,dl$$

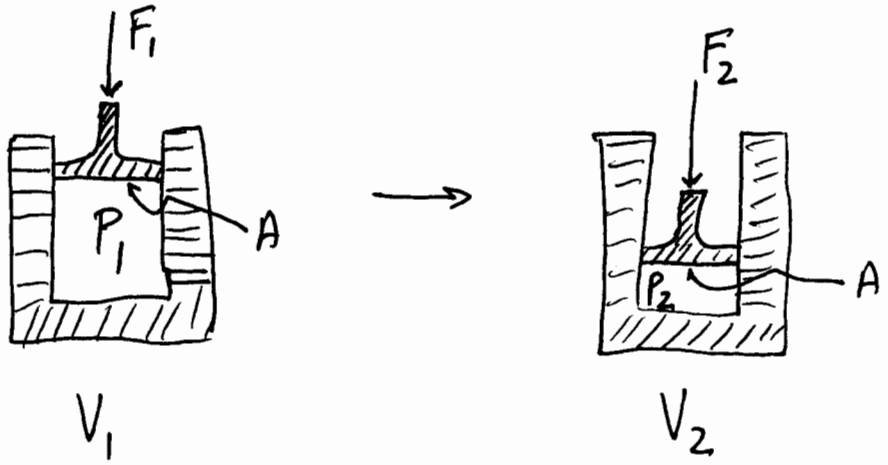
WORK = FORCE · DISTANCE

HOW TO APPLY TO COMPRESSION/EXPANSION?

$$dW = \bigcirc\, PA\; d\frac{V^t}{A}$$

SIGN force DISTANCE

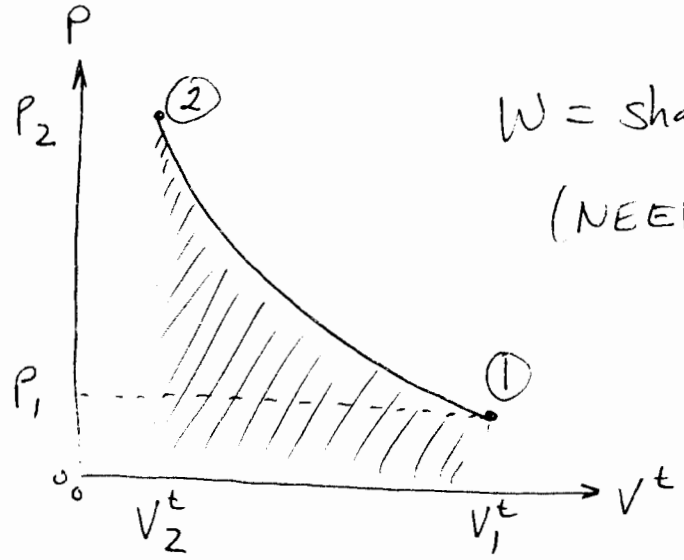
BUT WHAT SIGN???




$F_1 < F_2$ $\qquad V_1 > V_2$

$P_1 < P_2$ $\qquad A = A$

GRAPHICALLY:




$W$ = shaded area

(NEED TO INTEGRATE)

$$dW = \bigcirc P \cancel{A}\, d\left(\frac{V^t}{\cancel{A}}\right)$$ but $A$ constant

$$dW = \bigcirc P\, dV^t$$

Integrate ...

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

BUT WHAT ABOUT THE SIGN?!?

$W > 0$ (WORK DONE ON THE SYSTEM)

$P > 0$

$\Delta V < 0$ $\Rightarrow$ SIGN $\rightarrow$ (−)

WHY?

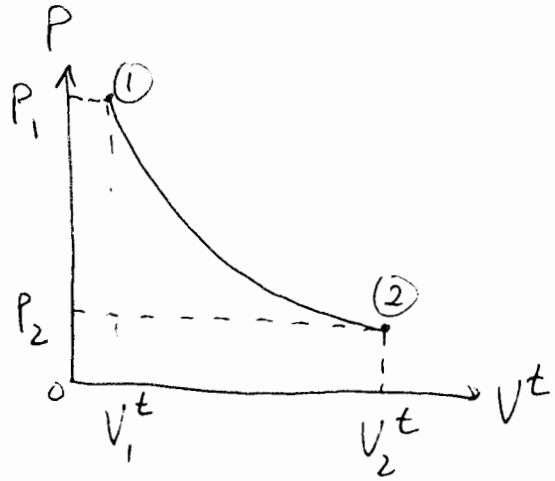
WE DEFINED WORK ON THE SYSTEM TO BE (+).

THEREFORE, WE NEED THE (−) SIGN BECAUSE $\Delta V^t < 0$.

$$\Rightarrow \boxed{dW = -\int_{V_1^t}^{V_2^t} P\,dV^t}$$

WHAT IF EXPANSION?

(SYSTEM DOES WORK ON SURROUNDINGS)




$P > 0$

$\Delta V > 0$

$\Rightarrow \underline{W < 0}$ ✓

(USING SAME SIGN CONVENTION)

# 7) ENERGY

LOTS OF DIFFERENT TYPES

FOCUS ON:

A) KINETIC ENERGY

B) POTENTIAL ENERGY

## KINETIC ENERGY

$$dW = F\,dl$$

$$= ma\,dl$$

$a = \frac{d}{dt}(u)$

↑ acceleration ↑ velocity

$$dw = m\frac{du}{dt}dl = mdu\underbrace{\frac{dl}{dt}}_{u}$$

$$\Rightarrow dw = m\,u\,du$$

$u_1$ velocity in

$u_2$ velocity out

Integrate:

$$W = m\int_{u_1}^{u_2} u\,du = \frac{mu^2}{2}\Big|_{u_1}^{u_2} = \frac{mu_2^2}{2} - \frac{mu_1^2}{2}$$

$$E_K \equiv \frac{1}{2} m u^2$$

KINETIC ENERGY

## POTENTIAL ENERGY

$$dW = F\,d\ell$$

$z_1$ Initial Height

$z_2$ FINAL Height

INTEGRATE

$$W = \underbrace{mg}_{\text{force}} \ell \Big|_{z_1}^{z_2} = mg(z_2 - z_1)$$

$$E_p \equiv mgz$$

POTENTIAL ENERGY

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8) HEAT (STILL ENERGY)

Q

- FROM HOT TO COLD
- $\Delta T$ DRIVING FORCE

# MASS & ENERGY BALANCES

→ RECALL CHE 254

→ OUR FOCUS MORE ON ENERGY

$$E^t = \frac{mu^2}{2} + mgz + U^t$$

Potential

Kinetic

Internal energy (the molecules have energy)

$$\Rightarrow \Delta E^t = Q + W + E(flow) + E(gen)$$

NEXT TIME:

FIRST LAW

(CONSERVATION OF ENERGY)