

Definitions

A **Thermodynamic Property** of a substance is a characteristic or attribute that can be used to describe the substance.

An **Intensive Property** does not depend on the size or extent of the system (e.g., T and P).

An **Extensive Property** does depend on the extent of the system (e.g., m and V).

U - internal energy - related to T

H - enthalpy ($H = U + PV$) - variable of convenience

S - thermo property that defines the direction of processes

A - Helmholtz Free energy ($A = U - TS$) - variable of convenience

G - Gibbs Free energy ($G = H - TS$) - variable of convenience

Convert between intensive and extensive properties by mass or moles

$$h = H/m$$

Gibbs Phase Rule - determines the number of intensive variables needed to specify the thermodynamic state.

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

HINTS: Steam defined by only 1 variable (T or P) is almost always a two phase system. Steam defined by two variables (T and P) is always superheated.

Quality refers to the mass fraction of vapor in a process stream. A **saturated liquid** has a quality of 0 while a **saturated vapor** has a quality of 1. The saturated liquid and vapor lines mark the transition between the two phase region and the liquid and vapor regions of the phase diagram.

Lever Rule:

$$\theta = x\theta_g + (1-x)\theta_f \quad \text{where } g - \text{gas} \quad f - \text{liquid}$$

e.g.

$$h = xh_g + (1-x)h_f$$

HINTS: If in doubt, assume a quality between 0 and 1 and math will work out to show if incorrect.

Path-dependent Properties are those that are not defined by the beginning and end states but by the path used to get there.

Q - heat
W - work

NOTE: The signs associated with Q and W can be defined differently in some disciplines or books (especially CHE). FE exam appears to define:

Q (+) when heat flows into system

W (+) when system does work on surroundings

Therefore, equations may differ slightly from your past courses.

Heat capacity - defined as

$$C = \frac{dQ}{dT} \text{ which yields } C_p \neq C_v$$

$$C_p \equiv \left(\frac{\partial h}{\partial T} \right)_p$$

or $dh = c_p dT$

$$C_v \equiv \left(\frac{\partial u}{\partial T} \right)_v$$

or $du = c_v dT$

(Ideal Gas) $C_p - C_v = R$

FE exam nomenclature, \bar{R} is confusing

- it is trying to account for molar values rather than mass
- just use R but check units and use Mw as needed

Balance Equations

FE equations are confusing! This is because they define multiple specialized systems rather than 1 equation

Mass Balance

$$\frac{dm_s}{dt} = \sum \dot{m}_i - \sum \dot{m}_e \quad \text{where } \dot{m}_i \text{ and } \dot{m}_e \text{ are inlet and exit}$$

m_s - is system mass

Energy Balance

$$\frac{d}{dt} \left\{ U_s + \frac{V_s^2}{2} + gz_s \right\} = \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) + \dot{Q}_{in} - \dot{W}_{out}$$

Note: $\frac{dm_s U_s}{dt} = \frac{dU_s}{dt}$; Q & W signs

This balance equation can get you every other equation listed

Entropy Balance

Not specifically used other than to derive another useful equation which is the combination of the 1st and 2nd Laws of Thermo

$$du = Tds - pdv \text{ becomes}$$

$$ds = \frac{c_v}{T} dT + \frac{R}{v} dv$$

which yields (for an ideal gas)

$$\Delta s = c_v \ln T_2/T_1 + R \ln v_2/v_1$$

or $\Delta s = c_p \ln T_2/T_1 - R \ln P_2/P_1$

At constant entropy ($\Delta s = 0$), we can get

$$P_2/P_1 = \left(\frac{v_1}{v_2} \right)^k ; \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} ; \frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1}$$

where $k = c_p/c_v$

Work - again, this is confusing because the FE handout book defines too many

W in Energy Balance equation contains **ALL** work terms

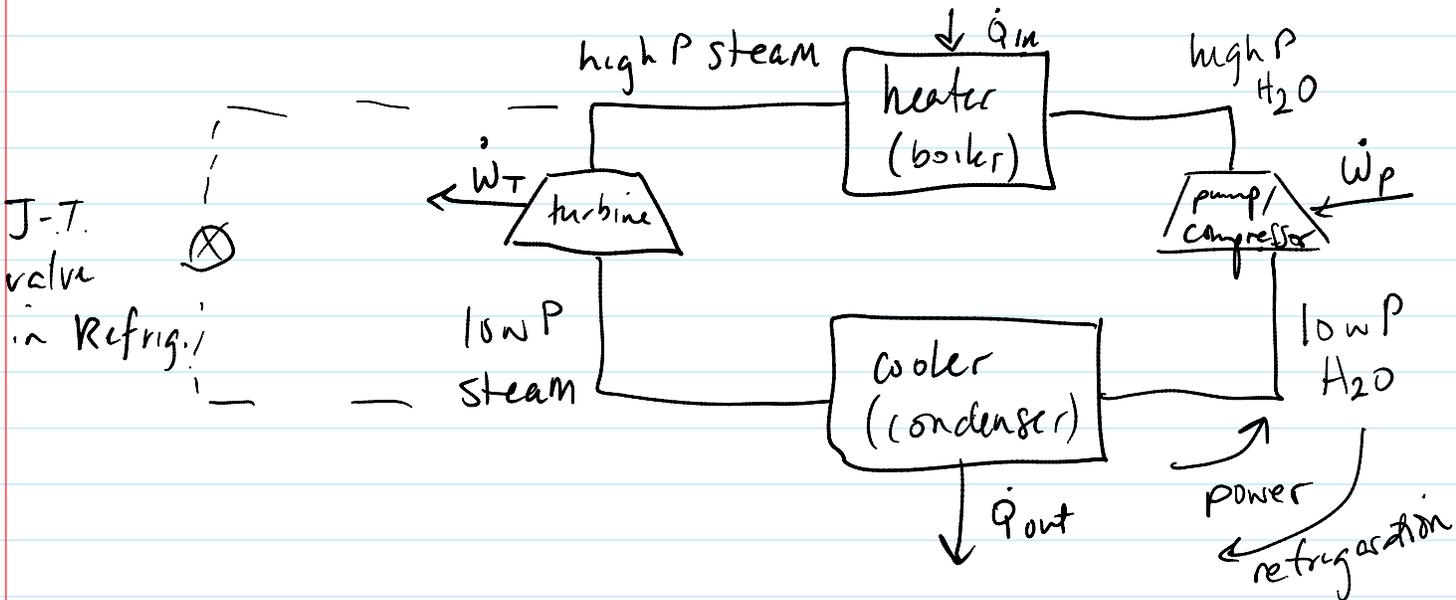
$$W = W_s + \int p dV \quad \text{where } W_s \text{ is shaft work and } \int p dV \text{ includes injection or boundary work}$$

$$\text{If } v = \text{const}, dv = 0 \text{ and } \int p dV = 0$$

$$\text{if } PV^n = \text{const}, \int p dV = \frac{P_2 V_2 - P_1 V_1}{1-n}$$

Cycles

Application of multiple balance equations around each component



$$\text{Power Cycles: } \eta = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{W_T + W_p}{Q_{\text{in}}}$$

$$\eta_{\text{max}} = \eta_{\text{carnot}} = 1 - \frac{T_L}{T_H}$$

$$\text{Refrigeration: } \text{COP} = \frac{Q_{\text{boiler}}}{W_p + W_T}$$

Note: liq pump $\Delta h \longrightarrow \Delta h = v(P_2 - P_1)$

Types:

Carnot Cycle - most efficient - isothermal expansion and compression

Rankine Cycle - isobaric expansion and compression

Stirling Cycle - vapor phase working liquid & isochoric heat exchanger

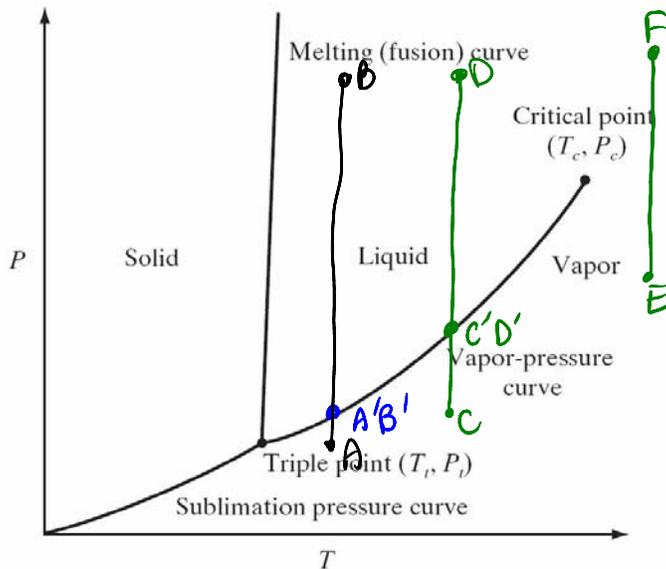
Otto Engine Cycle - car engine - compress and spark plug ignites

Diesel Engine Cycle - compress and auto-ignite

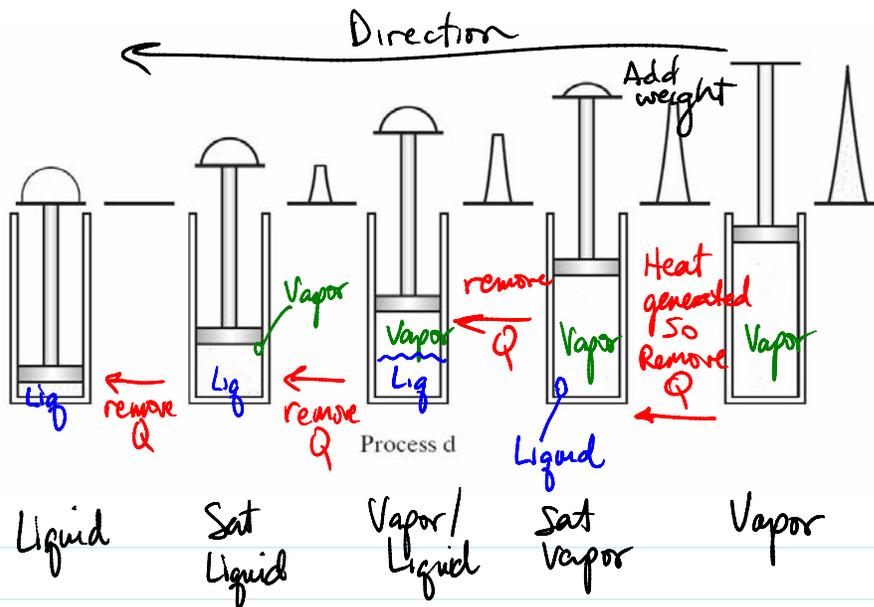
Brayton Cycle - air planes - combines the advantages of combustion and compression cycles

State Diagrams

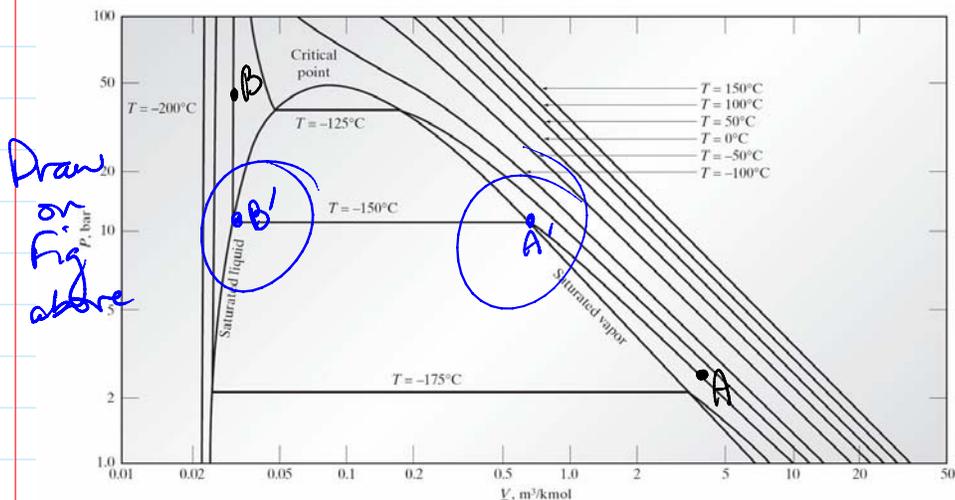
We have all seen the following state diagram that shows the vapor, liquid, and solid regions - obtained experimentally



If we envision a path from $A \rightarrow B$ that occurs by the following process (along isotherm)



From these experiments, we can prepare PV diagram



Note that during the phase transition, we see that the lines in PT diagram are the coexistence lines & that the pressure is constant

if we repeat for other isotherms (draw above), we see that pressure where we have coexistence region changes. we also see that above T_c there is no coexistence region.

The Volumetric EOS should be able to describe the PVT behavior of a real fluid

Can think of this as $P(T, V)$ — i.e. P is dependent variable & T, V are independent

Ideal gas $Pv = RT$

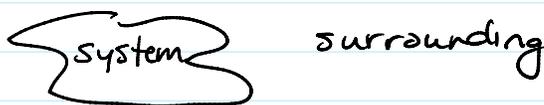
van der Waals $\left(P + \frac{a}{v^2}\right)(v-b) = RT$

TIPS

- Always use K or degree R!!
- $P(\text{abs}) = P(\text{atm}) + P(\text{gauge})$
- Reference States (need to make sure that all data is taken at same reference state)

Step 1: Choose a System

Application of thermodynamics to any real problem, therefore, starts w/ identification of a particular body of matter as the focus of attention, known as the **system**. Everything outside the system is the **surroundings**.



*point out that the boundary may be real, imaginary or a combination of both

Isolated systems are those that do not change w/changes in the surroundings

Adiabatic systems are those that are thermally isolated from the surroundings

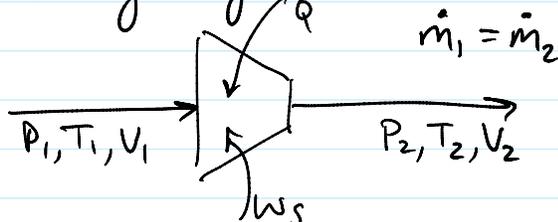
Closed systems are those that have no mass transfer to/from the surroundings (open systems are the opposite)

Consider a compressor in a continuous steady-state process

Analyze as both open & closed system

Closed system : unit mass of gas moving through the compressor

Choosing a system



Step 2: Write Overall Balance Equation

$$\frac{d(m_s u_s)}{dt} = \sum \dot{m}_i \left[h_i + \frac{v_i^2}{2} + g z_i \right] - \sum \dot{m}_e \left[h_e + \frac{v_e^2}{2} + g z_e \right] + \dot{Q} - \dot{W}$$

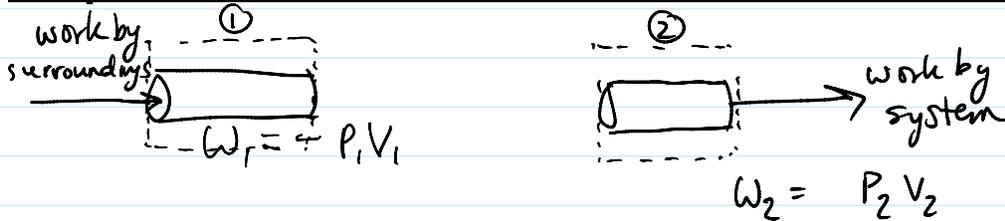
Step 3: Cancel Out Irrelevant Terms

For closed system,

$$\frac{d(m_s u_s)}{dt} = \sum \dot{m}_i \left[h_i + \frac{v_i^2}{2} + g z_i \right] - \sum \dot{m}_e \left[h_e + \frac{v_e^2}{2} + g z_e \right] + \dot{Q} - \dot{W}$$

$\hookrightarrow \Delta U = Q - W$

Step 4: Determine Relevant Work Terms and Solve



$$W = -P_1 V_1 + W_S + P_2 V_2$$

$$\Delta U = Q + P_1 V_1 - W_S - P_2 V_2$$

$$\Delta U + \Delta(PV) = Q - W_S$$

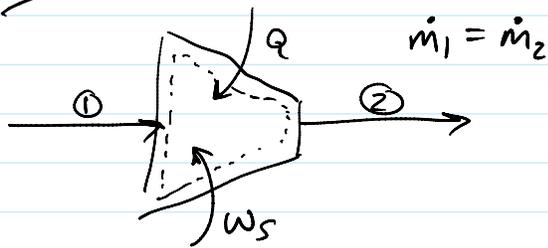
Recall

$$h = u + Pv$$

$$\Delta h = \Delta u + \Delta(Pv)$$

$$\therefore \Delta h = Q - W_S$$

Open System = contents of compressor at any time



$$\frac{d(m_s u_s)}{dt} = \sum \dot{m}_i \left[h_i + \frac{V_i^2}{2} + g z_i \right] - \sum \dot{m}_e \left[h_e + \frac{V_e^2}{2} + g z_e \right] + \dot{Q} - \dot{W}$$

(ss)

$$\dot{W} = \dot{W}_s + \int p dV \quad \text{No added work}$$

Recall that streams have energy associated with them
 $\dot{m}_1 h_1 - \dot{m}_2 h_2 + \dot{Q} - \dot{W}_s = 0$

divide by \dot{m} & rearrange $\Delta h = Q - W_s$