Process and State Variables

Describing and analyzing processes requires that you can understand, calculate, and manipulate both process data as well as state variables.

How would you calculate process variable *values* from *measurements* ?

- Manipulate process flow data
  # Interconvert mass, volume, and moles(and their flows)
  # Calculate mass(mole) fractions from mole(mass) fractions for a mixture
- Calculate pressures using a manometer(and explain the concept of gauge pressure)
- Interconvert between different temperature scales
- Explain the difference between intensive and extensive variables

Certain calculations require you to know quite a bit about the "state" of a material(i.e., its state of aggregation(phase), temperature, pressure, chemical composition, etc.).How can we quantify properties about a material 's state?

- Calculate State Variables $\hat{U}$ and $\hat{H}$
  # Define "state variable"
  # Explain why one must choose a reference point when calculating state variables
  # Generate "fictitious paths" from your reference state to your desired state
  # Use heat capacities and phase data to calculate $\hat{H}$ and $\hat{U}$ from fictitious paths
- Use tabular data to determine $\hat{U}$ and $\hat{H}$

Mass and Flow Variables

In ChE processes there are a number of variables that typically play an important role. Let's review what some of them are.

DEFINITION:

> ***Density*** *is the mass of a material per unit volume (**specific volume** is inverse - i.e., volume per unit mass).*

DEFINITION:

> ***Specific Gravity*** *is the ratio of one material's density to that of a reference material (typically water at 4C).*

S.G. is dimensionless -> density A/density Ref.

Material moves in/out of process units -> flow rate!

DEFINITION:

> *The **flow rate** represents the amount of material that moves into (or out of) a process unit per unit time.*

(TRICK)
EXERCISE:

> *What are the units (dimensions) of a flow rate? [cheat]*

NOTE:

> We can interconvert a mass or volume (and therefore a mass or volumetric **flow rate**) by using the density (or the specific volume) as a "conversion factor" (1 mL glass = 2.5 g glass)!
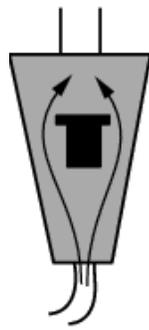
OUTCOME:

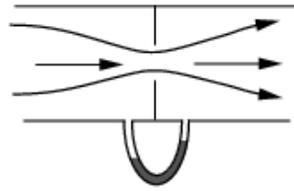> Interconvert mass, volume, and moles (and their flows)

TEST YOURSELF!

> *Convert the flow rate 10 g water per hour to L/h. How about mole/h?(if you can't we'll review that next lecture!)*

Measuring flow rates

rotameter   orifice meter

Typically one **measures** volumetric flowrates even though we are more often interested in mass flowrates.

Compositions and Mixtures

Since we are **chemical** engineers, every now and then we actually deal with chemicals!

In this lecture we will remind you of a bunch of things that you should have learned in chemistry about compositions and chemical "amounts".

DEFINITION:

> *Atomic weight is a measure of the mass of an atom (C^{12} -> 12 units)*

DEFINITION:

> *Molecular weight is the sum of the atomic weights of the atoms that make up a compound.*

DEFINITION:

> *A mole (or gram-mol) is the amount of a species (atom or molecule) whose mass is numerically equivalent to its molecular weight. (For example 12 grams of C^{12} = 1 gram-mol of C^{12})*

NOTE:

> Molecular (atomic) weight can be used as a conversion factor between the number of X-moles and the mass in X units!

EXERCISE:

> *How do you convert 1 lb-mol of H_2O to gram-moles of H_2O?*

Compositions as fractions:

$$\left. \begin{array}{l} \text{mass fraction} = \dfrac{\text{mass A}}{\text{total mass}} \\[2em] \text{mole fraction} = \dfrac{\text{moles A}}{\text{total moles}} \end{array} \right\} \text{x100 for percent}$$

NOTE:

> Percent = parts per hundred. We may also use parts per million (ppm) or parts per billion (ppb). (Purely for simplicity in describing dilute solutions, so that we need not say 0.0001% or $1.0e^{-7}$%)

OUTCOME:

> Calculate mass (mole) fractions from mole (mass) fractions for a mixture

TEST YOURSELF!

> *On a humid day, air may have a composition like this: O_2: 19%, N_2: 72%, and H_2O: 9.0% (all percents are by MASS). What is the composition in mole fractions?*

O₂ N₂ H₂O

O_2 N_2 H_2O

Compositions as concentrations:

DEFINITION:

> ***Concentration*** *refers to the "amount" (measured in mass or moles) of a material per unit volume (much like the density: in fact, mass concentration <-> density!).*

NOTE:

> The word **molarity** typically refers to the molar concentration in **solution**

Pressure

Pressure and temperature are two of the most important of chemical engineering process variables.

In addition to reminding you a bit about them, it is importnat to discus how one might find out what they are in a given process!
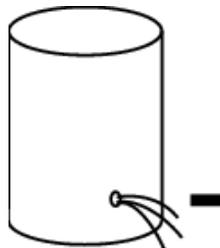
DEFINITION:

> ***Pressure*** *is the ratio of force to the area over which that force acts (or the area over which that force is transmitted).*

What ar the units of pressure then?

Pressure on a solid surface is easy to follow.

The pressure in a fluid is tougher. One way to think of it:

DEFINITION:

> ***Hydrostatic Pressure*** *is the pressure in a fluid due solely to the fluid's weight. [ρgh].*
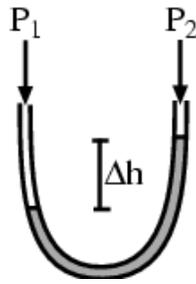
EXERCISE:

> *Check the dimensions on ρgh.*

NOTE:

> For this reason, pressure is sometimes given in terms of fluid height instead of regular pressure units. (e.g., "mmHg" or "ft of water")

Pressure measurements:

$$\left.\begin{array}{l}\text{Absolute Pressure}\\\text{Atmospheric Pressure}\\\text{Gauge Pressure}\end{array}\right\} \qquad P_{abs} = P_{atm} + P_{gauge}$$
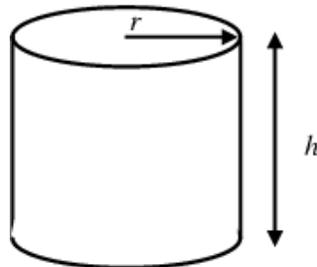
Manometers

Calculate pressures using a manometer (and explain the concept of gauge pressure)

TEST YOURSELF!

If we know P_2 and the difference in fluid heights, how do we calculate P_1?

Hydrostatic Pressure

Consider a cylindrical tank filler with water:

We want to measure the hydrostatic pressure on the bottom of the tank.

Volume of cylinder (fluid): $\pi r^2 h$
Weight of fluid: $\rho g V$
Area of base: πr^2

Pressure on Base: F/A -> $\frac{\rho g (\pi r^2 h)}{\pi r^2}$ -> $\rho g h$

So, hydrostatic pressure is independent of radius of cylinder!

Temperature

DEFINITION:

Temperature is a measure of the average kinetic energy of the molecules in a substance.

Measure temperature using physical properties of substance that **change** as a function of temperature:

- volume of a fluid (thermometer)
- resistance of a metal (resistance thermometer)
- voltage at the junction of two dissimilar metals (thermocouple)
- spectra of emitted radiation (pyrometer)

Temperature scales are defined in terms of these (and other) phenomena:

- freezing/boiling point of water
- resistance of a copper is X

Common temperature scales:

- Fahrenheit: Freezing point of water is 32 and boiling point is 212.
- Celcius: Freezing point of water is 0 and boiling point is 100.
- Rankine: Absolute zero (when all kinetic energy vanishes) is 0, increments = Fahrenheit. (459.67 R = 0 F)
- Kelvin: Absolute zero (when all kinetic energy vanishes) is 0, increments = Celcius. (273.15K = 0 C)

Converting temperatures:

- T(K) = T(C) + 273.15
- T(R) = T(F) + 459.67
- T(R) = 1.8*T(K)
- T(F) = 1.8*T(C) + 32

NOTE:

Converting temperature **differences** is slightly different (the additive corrections calcel out!).

OUTCOME:

Interconvert between different temperature scales

TEST YOURSELF!

Convert 20C to F. How about R? Convert -40C to F :)

Intensive versus Extensive Variables

Thus far we have discussed a number of "process variables" (variables that may be measured and used to characterize the operation of a process). It is helpful, prior to discussing state variables to group these variables into two categories:

DEFINITION:

> *An **extensive variable** is one which depends on system size (like mass or volume).*

While extensive variables are useful for characterizing the *specific* system being analyzed, they are not general and (as we will see later in the course) do not help us to determine the "state" of the system.

DEFINITION:

> *An **intensive variable** is one which does not depend on system size (like temperature, pressure, or density).*

While it may not be immediately obvious, intensive variables tell us *much more* about the system than extensive variables. In particular, the temperature and pressure are two of the most critical intensive variables.

OUTCOME:

> Explain the difference between intensive and extensive variables.

NOTE:

> A **ratio** of extensive variables will yield an intensive variable! (For example, mass/volume -- two extensive variables -- gives density, an intensive variable) This is one way to understand why intensive variables "tell you more".

State Variables

If I asked you to tell me the specific enthalpy or internal energy (that is, a measure of the energy available in the material per unit mass or moles) of the *final* material in each of the two examples below, would they differ? would you need more information?

- 100.0 kg of methane gas initially at 100C is cooled to room temperature and atmospheric pressure
- 1.0 g of liquid methane at -10C is vaporized rapidly to form a gas at room temperature and pressure

While the answer to this question may notbe immediately obvious, hopefully the answer to an analogous question is: what is the corresponding *final* height (above sea level) of each of the following students?

- Student A takes the bus from Shadyside, arrives at Benedum Hall and takes the elevator to the 12th floor
- Student B gets on a helicopter on Mt. Washington, lands on the room of Benedum Hall and climbs down the stairs to the 12th floor

Much like the student whose *final* height is unaffected by *how* (s)he got to the 12th floor, the amount of energy in each of the samples of methane (per unit mass or moles) is unaffected by its history. The specific energy and enthalpy are both **state functions/variables** whose value depends only on the (thermodynamic) **state** of the system, not on the path of how you got there. This is important for anumber of reasons, as we will see...

DEFINITION

> *State Functions/Variables* depend only on the thermodynamic state of the system (T, P, phase, chemical composition).

OUTCOME

> Define "state variable".

State Variables and Reference States

So, now we know that as long as we know "where we are" in the state of the material, we know that the energy and enthalpy are fixed values, but what are those values?!

This is a trick question. It is, in fact, impossible to measure the energy or enthalpy exactly, but it is easy to measure *changes* in the energy or enthalpy (as you can see from the energy balance equation: hold kinetic and potential energy fixed, apply no work, and add a known amount of heat).

OUTCOME:

> Explain why one must choose a reference point

So if we don't know the actual value, but only differences, what do we do?!

Since we are doing balances, we are really only interested in differences of differences! Just like in the case of changing a temperature difference from Celsius to Kelvin, where the offset (reference state!) was canceled out, here we can choose things such that the reference state chosen is immaterial! To get the change in enthalpy in a **balance**, we define *both* enethalpies relative to the same reference state and then that reference state *cancels out*!

$$(H_1 - H_{ref}) - (H_2 - H_{ref}) = H_1 - H_2$$

In all of our dealings with these state variables (energy and enthalpy), we will use a reference state (set equal to zero) in order to do the calculation).

NOTE

> As we will see in our next lecture, when we choose a reference state, we can set the enthalpy (energy) of that reference to any arbitrary value. For simplicity, we will set these arbitrary values to zero.

Calculating Energy and Enthalpy

We have already discussed the fact that we must use reference states in order to get numerical values for the energy and enthalpy (since we can not know the *actual* numbers!). This didn't bother us since we are only interested in *differences* in these quantities (so that the reference state that we choose cancels out!).

We will assume that we have "ideal mixtures" in all cases! (That means that the *total* energy or enthalpy of a mixture will be equal to the sum of all of the component's energy/enthalpy.)

NOTE

> This is not strictly true! In fact, it is only a good approximation for gas mixtures or mixtures of similar liquids. We will not get a chance to talk about energy/enthalpy of mixing, but it is a simple way to alleviate our assumption.

Fictitious Paths

Since we know that the Energy depends on:

- Temperature
- State of Aggregation (phase)
- Chemical Composition

and we know that H = U + PV, then H depends on all of these as well as P.

So, there are four things (ΔT, ΔP, phase change, rxn) that may cause a change in energy or enthalpy.
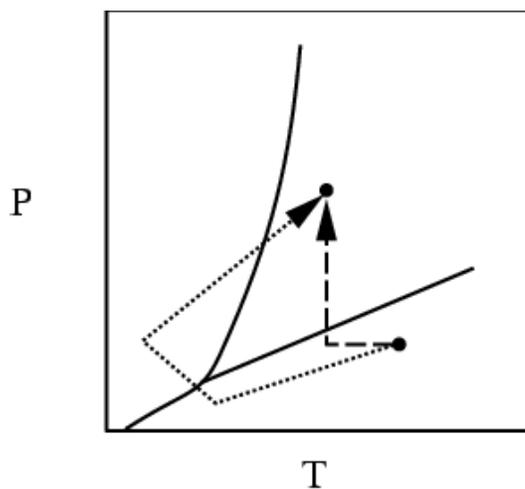
NOTE

> You are already familiar with the "heat" (change in enthalpy) involved in changing the state of aggregation (Latent Heat of vaporization, for example)
>
> We will talk ahout changes in chemical composition in a few lectures.
>
> We need to deal with changes in T and P

So in order to calculate enthalpies or energies, we need to determine the *changes* that occur as we move fromour (required!) reference state to our actual state.

Let's consider a simple example:

Is there a reason we should choose one of these paths over the other?

Our ideal fictitious path can be decomposed into the smallest number of steps that are each of 1 of the following several types: a change in T (at constant P and constant phase), a change in P (at constant T and constant phase), and phase changes (again, we will consider reactions later).

OUTCOME:

> Generate "fictitious paths" from your reference state to your desired state

TEST YOURSELF

> *Develop a path for calculating the enthalpy of steam at 200C and 1.5atm relative to a reference state of ice at -10C and 1 atm. How about internal energy?*

Energy Calculations

If we consider a pure, single-phase substance (which we will do for all of our calculations), we can show (later) that 2 intensive variables fix the state of the system.

Since we know that internal energy is NOT a strong function of P, we might be tempted to say that $\hat{U} = F(T, \hat{V})$.

If we keep $\hat{V}$ constant, we can then find the dependence of $\hat{U}$ on T only.

We have no reason to suspect that this is a straight line (and in fact it isn't), but for a small enough ΔT, we can safely say that $\Delta \hat{U} = (\text{slope}) \, \Delta T$.

DEFINITION

> *This slope is called the **specific heat at constant volume** (or **heat capacity at constant volume**) and is denoted as c_v*

As you all recall from calculus, integration simply means adding up lots of little pieces. Since we know that $\Delta \hat{U} = (\text{slope}) \, \Delta T$ as long as ΔT is small enough, in the limit that $\Delta T \rightarrow dT$ (infintely small change), we can write an exact answer mathematically as:

"ALL" MATERIALS

$$\Delta \hat{U} = \int c_v dT \approx c_v \Delta T$$

NOTE

> This expression is equally valid for (ideal) gases, solids, and liquids!

Enthalpy

The difference between energy and enthalpy, of course, is the "flow work" term. If we take $\hat{H} = F(T, P)$ (since we can write it in terms of any two variables) and we think about getting to our final state first by keeping P constant (rather than $\hat{V}$, as we did last time), and then letting P change, the flow work term can be changed from $\Delta(P\hat{V})$ to $\hat{V} \Delta P$ (since the changes in $\hat{V}$ would have occured in the constant P part!).

By analogy to the section above, keeping P constant and letting T change, we can get the expression for the constant P part as:

$$\Delta H = \int c_P dT \approx c_P \Delta T \text{ (at constant P)}$$

DEFINITION

*c_p in the expression above is the **specific heat at constant pressure** (or **heat capacity at constant pressure**) and, as before, it represents the slope of the $\hat{H}$ vs. T curve.*

We, finally, then need to consider the flow work part.

For an ideal gas, there is no "friction" to the flow (since they are essentially infinitely dilute), so there is no flow work involved! This gives us that:

IDEAL GAS

$$\Delta \hat{H} = \int c_p dT \approx c_P \Delta T$$

Solids and liquids are incompressible. Therefore, the flow work term ignores changes in pressure (even if there is not change in temperature) so we get:

SOLIDS/LIQUIDS

$$\Delta \hat{H} = \int c_p dT + \hat{V} \Delta P \approx c_P \Delta T + \hat{V} \Delta P$$

NOTE

> So, we have now given ourselves expressions for each of the types of changes proposed for our fictitious paths: T changes at constant P (for gases, liquids, or solids), P changes at constant T (for gases, liquids, or solids), and we already know that we can simply "look up" the heat of phase changes!

OUTCOME:

> Use heat capacities and phase data to calculate H and U from fictitious paths

TEST YOURSELF

> *Actually perform the calculations from your previous test yourself: Get the enthalpy (and internal energy) of steam at 200C and 1.5atm relative to a reference state of ice at -10C and 1 atm.*

Steam Tables (and other tabulated data)

An even easier way to "calculate" these quantities is to look them up!

Since we only need to fix two variables, you will typically look these quantities up on a table which is grouped by T and P.

The most common -> Steam Tables (See Appendix B)

NOTE

> If you are using multiple **different** tables for the same component, make sure that the reference states are the same!

Charts

Again, the most common is related to water -> an air/water mixture. (This is the only non-ideal case we will consider!)

Since we now have two components (and still one phase) we need to fix three things (again, we will see why later).

DEFINITION

> ***Psychrometric Charts*** *fix the pressure and then let you look up the values of interest fixing any two of the other intrinsic variables (T, specific volume, humidity, enthalpy, etc.).*

OUTCOME:

> Use tabular data to determine U and H