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## Thermodynamics (Th)

### Thermodynamics

Thermodynamics can be used to make the number of necessary measurements smaller, or to make the *type* of measurement easier.

It turns out that *volumetric* flowrates are far easier to measure than mass or molar flows. How can we make use of this information ?

- Use single - phase thermodynamics to convert from volumetric flows to mass / molar flows
  - Determine the density of a mixture of liquids
  - Use the ideal gas law to determine P, V, or T of a single component
  - Determine the composition of a mixture of ideal gases from their partial pressures or volume fractions
  - Use one(or all) of the covered non - ideal equations(SRK, compressibility factor, van der Waals, virial equation) to determine P, V, or T
  - Use equations of state for mixtures of gases
- Use equations of state in material balances

When *multiple* phases are in equilibrium with each other, the problem becomes *constrained* . Can we use this information, along with Thermodynamics, to further reduce the number of necessary measurements ?

- Sketch a phase diagram and label relevant regions / points(solid, liquid, gas, critical point, etc.)
  - Use Gibbs phase rule to determine how much information is necessary to specify the thermodynamic state of a system
  - Explain the difference between the Gibbs phase rule and a Degrees - of - freedom analysis
  - Perform vapor - liquid equilibrium(VLE) calculations
    - Estimate the vapor pressure of liquid components
    - Use ideal solution expressions to determine the composition of liquids and their corresponding vapors
    - Define and use K values, Raoult 's law, and relative volatility
    - Distinguish between when Henry 's Law and Raoult' s Law would be applicable
    - Use Txy or Pxy diagrams for non - ideal(and ideal) solutions
    - Explain the relationship between y - x, Txy, and Hxy diagrams
  - Estimate the composition of liquids in equilibrium with solids
  - Estimate the composition of immiscible liquids in equilibrium with each other(using either partition ratios or ternary phase diagrams)
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Th: Determine the density of a mixture of liquids

## Single Phase Systems

In (almost) all of the problems that we have discussed, you were given all the information that you needed. Obviously, in real life, you will be required to get all the information you need by yourself.

This information can come from:

Measured Data from an existing process (experiments!)

Process Specifications/Design

Physical Properties/Laws

(Obviously, you are also limited by physical constraints and must not violate balances of mass or energy.)

Just like we were sometimes given process specifications to be used in our degree-of-freedom analysis, we will also use physical laws as additional relations to lower the number of degrees-of-freedom.

### NOTE

*We have already seen how to use measurements (calibration curves) to determine the composition and density of a process stream*

## Liquid and Solid Densities

Most Liquids and Solids → density decreases with heating, and density increases with pressure.

NOT VERY MUCH → "incompressible"!

### NOTE

*Because solids and liquids are essentially incompressible you can use the density at one T and P for almost any other T and P.*

Mixtures are difficult, but usually assume either:

### DEFINITION

*For mixtures of "similar" solid or liquid materials (e.g., ethanol and methanol) the density of a mixture may be approximated by averaging the specific volumes. This is termed assuming **volume additivity**.*

SIMILAR:  $\rho_{average} = \frac{1}{\hat{V}_{average}} = \frac{1}{\sum x_i \hat{V}_i}$

### DEFINITION

*Another method of approximating the density of a solid or liquid mixture is to average the densities.*

OTHERWISE:  $\rho_{average} = \sum x_i \rho_i$

### OUTCOME:

*Determine the density of a mixture of liquids.*

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Th: Use the ideal gas law to determine P, V, or T of a single component

## Gas Densities

For gases, the density is obtained by using an equation of state.

### DEFINITION

An **equation of state** relates the molar density (or specific molar volume) of a fluid (so they sometimes work for liquids, too!) to the temperature and pressure of the fluid.

simplest -> ideal gas law ( $PV=nRT$ )!

### NOTE

The ideal gas law may also be written as  $P\hat{V} = nRT$  for a flowing system or  $P\hat{V} = RT$ , where  $\hat{V}$  is the specific molar volume.

### IMPORTANT

The ideal gas law is an approximation (!) that has only limited applicability. It is usually used for diatomic gas when  $(RT/P) > 5$  L/mol and for other gases when  $(RT/P) > 30$  L/mol (i.e., at high specific volumes!).

## Standard Temperature and Pressure

A technique for dealing with ideal gases that is of dubious utility is to utilize the reference point of standard temperature and pressure.

### DEFINITION

**STP** is an arbitrary reference point chosen to be  $T = 273K$  (0C) and  $P = 1$  atm.

### OUTCOME:

Use the ideal gas law to determine P, V, or T of a single component

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Th: Determine the composition of a mixture of ideal gases

## Ideal Gas Mixtures

If you have  $n_i$  moles of each species (for example  $n_A$  moles of A), you can try to calculate the pressure or volume that that gas alone (i.e., ignoring the other gases that are around) exerts/occupies.

### DEFINITION

*Partial pressure* refers to the pressure that would be exerted by a species (in a mixture) if there were no other species present.

### DEFINITION

*The pure component volume,  $v_A$ , refers to the volume that would be occupied by a species (in a mixture) if there were no other species present.*

So, in an ideal gas mixture EACH COMPONENT satisfies the ideal gas law provided the partial pressure or pure component volumes are used!

$$P_A V = n_A RT$$

or

$$P v_A = n_A RT$$

In this way, the sum of the component pressures (partial pressures) or volumes (pure component volumes) should sum to the total pressure or volume:

$$P_A + P_B + \dots = P$$

$$V_A + V_B + \dots = V$$

This is easy to see if you divide either the partial pressure equation or the pure component volume equation by the ideal gas law for the total mixture:

$$\frac{P_A V = n_A RT}{P V = n RT}$$

$$\frac{P v_A = n_A RT}{P V = n RT}$$

Note that RT cancels in both equations and that V cancels in the first and P cancels in the second, also that  $n_A/n = y_a$ . We can then rearrange the result to get:

$$P_A = y_A P$$

$$v_A = y_A V$$

So The volume fraction (or pressure fraction) of an ideal gas is equal to the mol fraction!

$$(v_A/V = n_A/n)$$

### OUTCOME:

*Determine the composition of a mixture of ideal gases from their partial pressures or volume fractions*

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Th: Sketch a phase diagram and label relevant regions/points

## Critical temperature and pressure

The errors in ideal gas predictions become most striking as you approach the gases critical conditions.

### DEFINITION

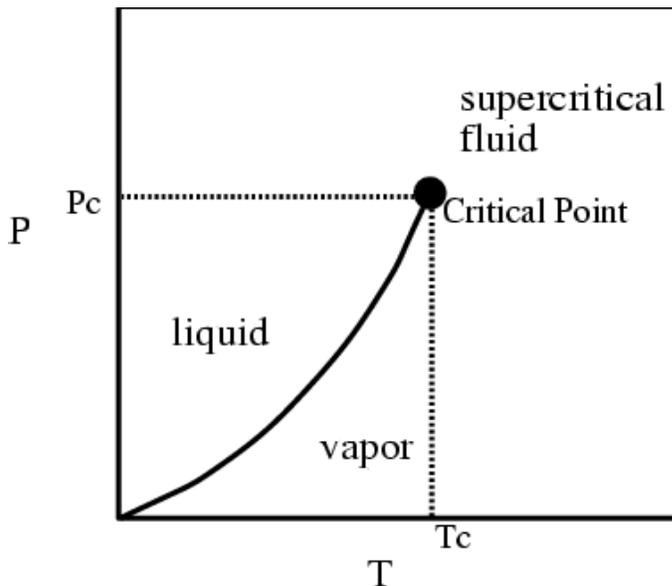
*At higher temperatures and/or higher pressures the difference between a gas and a liquid eventually disappears(!) and a supercritical fluid is formed. The point at which this happens is called the **critical point***

### DEFINITION

*The highest temperature at which a species can coexist as a liquid and a vapor is termed its **critical temperature,  $T_c$** .*

### DEFINITION

*The highest pressure at which a species can coexist as a liquid and a vapor is termed its **critical pressure,  $P_c$** .*

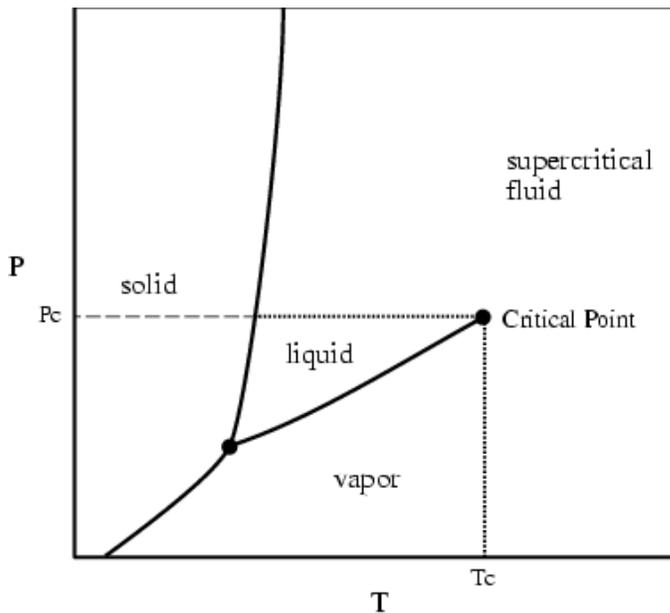


### DEFINITION

*A **supercritical fluid** is a substance which is above its critical temperature,  $T_c$  or pressure,  $P_c$ .*

### Phase Diagrams (single component)

One way to envision the behavior of a material is to use a phase diagram. It is often the case that we plot P vs. T in order to show the phase behavior of the material:



### DEFINITION:

A **phase diagram** is a plot of one system variable versus another which shows the conditions at which the substance is a solid, liquid, gas, or s.c. fluid.

### NOTE:

*If vapor and liquid are coexisting then setting either T OR P determines the conditions...we will look at this further in a minute.*

On the vapor-liquid line the temperature is called the **boiling point** and the pressure is the **vapor pressure**.

On the vapor-solid line the temperature is called the **sublimation point**.

On the liquid-solid line the temperature is called the **freezing/melting point**.

### OUTCOME:

*Sketch a phase diagram and label relevant regions/points (solid, liquid, gas, critical point, etc.)*

Th: Use one (or all) of the covered non-ideal equations

## Non-ideal Gases

As mentioned, the ideal gas law is only applicable at high specific volumes and becomes essentially useless at lower specific volumes. (Sometimes too high, sometimes too low ... )

For gases under non-ideal conditions, something else needs to be done.

### Non-Ideal Equations of State

#### DEFINITION (REMINDER)

*An **equation of state** relates the molar density (or specific molar volume) of a fluid to the temperature and pressure of that fluid. (Note that I am using the term fluid rather than gas!)*

Ideal gas law works very well when fluids are very "gassy" (high specific volume). Need others when we are closer to "liquidy" conditions.

In general, as fluids become less "gassy" the assumptions of the ideal equation of state become incorrect (we assume that individual gases molecules take up NO VOLUME and that they do NOT INTERACT WITH EACH OTHER when we derive the ideal gas law).

Since the non-ideal equations that we will be talking about here relax these assumptions, you should always "see" a way to reduce them to the ideal gas law by making these assumptions again!

As we will discuss, these more complex equations of state are sometimes motivated by mathematics and sometimes by theory. (Just in case you might wonder, "where on earth did they get that?!", we will mention it if I know (or maybe I will just make something up!))

### Virial Equations of State

A primarily mathematics motivated (theory is from statistical mechanics) equations of state, the virial equation uses a power series in the form:

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \dots$$

where B, C, and D (etc.) are material dependent constants.

These constants are sometimes difficult to determine (theoretically) so the expression is typically truncated after the B (so there is only one "fitting" parameter! (i.e.,

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}}$$

#### NOTE

*This expression is good for non-polar gases.*

The constant, B, can be obtained from the following relation:

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

where  $T_c$  and  $P_c$  are the critical temperature and pressure, and  $B_0$  and  $B_1$  are given by the following expressions:

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

### DEFINITION

The **reduced temperature (pressure)** is a dimensionless temperature (pressure) given as the ratio of the actual temperature (pressure) to the critical temperature (pressure) and is denoted by  $T_r$  ( $P_r$ ).

### DEFINITION

The **Pitzer acentric factor** ( $\omega$ ) is a material parameter that reflects the polarity and "shape" of the molecule (i.e., it is different for every molecule and therefore must be looked up!)

There are other expressions similar to this that are ALSO called virial equations of state. We will ignore them entirely.

### Cubic Equations of State

Another important class of equations of state are the cubic ones. They are called this because, mathematically, the equations are third order polynomials (cubic equations) in  $\hat{V}$

(Note that the truncated virial equation is quadratic!)

Why are cubic equations "good" as equations of state?! Look at the shape of the phase envelope!

The two most important cubic equations of state are the van der Waals equation and the Soave-Redlich-Kwong (SRK) equation. We will use only the van der Waals equation. (They are very similar to use and SRK just makes our life more tedious at this point.)

### van der Waals Equation

The van der Waals equation is interesting to examine because it is easy to qualitatively discuss the origin of its deviation from ideality.

$$P = \frac{RT}{\hat{V}-b} - \frac{a}{\hat{V}^2}$$

The symbols,  $b$  and  $a$  are material dependent constants (however, you can calculate them from a set of material *independent*. equations!). They represent (roughly) the volume of the gas molecules ( $b$ ) and the "interaction" of the gas molecules ( $a$ ).

As usual, the constants are correlated to the critical constants of the materials:

$$a = \frac{27R^2T_c^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

## Compressibility Factor and Corresponding States

A simpler (mathematically) way of representing non-ideality is the compressibility factor.

$$PV = znRT$$

$$\text{or } P\hat{V} = zRT$$

### DEFINITION

The **compressibility factor**,  $z$ , is a dimensionless number that represents a material's deviation from ideal gas behavior.

While this equation (being linear) is very simple to use, obtaining values of  $z$  is not! Like our previous examples, it would be nice to generate material-independent correlations for this parameter.

### DEFINITION

The "**law**" at **corresponding states** suggests that gases behave similarly depending on how far from their critical point they are. (In other words, if we use the reduced temperature and pressure instead of the actual  $T$  and  $P$ , all gases behave similarly.)

### NOTE

For Hydrogen and Helium it is necessary to add 8K and 8atm to the critical temperature and pressure respectively in order for them to behave like a "corresponding states" material.

Charts are available for the (generalized) compressibility factor,  $z$ , as a function of the reduced temperature and pressure.

What happens if we don't know the  $T$  or  $P$ ? (but are given  $\hat{V}$  instead)? Use the (ideal) "reduced volume":

$$\hat{V}_r^{ideal} = \frac{\hat{V}}{RT_c P_c}$$

### OUTCOME:

Use one (or all) of the covered non-ideal equations (SRK, compressibility factor, van der Waals, virial equation) to determine  $P$ ,  $V$ , or  $T$

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Th: Use equations of state for mixtures of non-ideal gases

## Non-Ideal Gas Mixtures

It is unclear how you would use any of the above expressions for mixtures (since we have material-dependent quantities like  $\omega$ , B, a, b, etc. how do we know which one to use?). Empirical (experience-based) rules have been developed. We will only discuss the one for the compressibility factor: Kay's Rule.

### DEFINITION

*Kay's Rule uses pseudo-critical properties to calculate pseudo-reduced quantities that are then used in the generalized compressibility charts.*

$$T'_c = Y_A T_{cA} + Y_B T_{cB} + \dots$$

$$P'_c = Y_A P_{cA} + Y_B P_{cB} + \dots$$

$$\hat{V}'_{r,ideal} = \frac{\hat{V}}{RT'_c P'_c}$$

Using the same procedure as with single-component systems, you can then get the pseudo-reduced quantities and obtain the (generalized) compressibility factor off of a chart.

### OUTCOME:

*Use equations of state for mixtures of non-ideal gases.*

### TEST YOURSELF

*A gas mixture contains 20.0 mole % CH<sub>4</sub>, 30.0% C<sub>2</sub>H<sub>6</sub>, and the balance C<sub>2</sub>H<sub>4</sub>. Ten kilograms of this gas is compressed to 200 bar at 90C. What is the volume?*

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Th: Use Gibbs phase rule

## Gibbs Phase Rule

Previously, we used "degrees of freedom" to denote the number of things we needed to know in order for our material balance problem to be completely specified.

The Gibbs phase rule tells you how many intensive variables must be known in order to completely specify a system! (It tells you the total number of degrees of freedom.)

Recall the definition of an intensive variable:

### DEFINITION:

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

### DEFINITION:

*The **Gibbs Phase Rule** states that the number of degrees of freedom is 2 plus the number of components minus the number of phase, i.e.,  $DF = 2 + C - \pi$*

Prove to yourself that the number of degrees of freedom of boiling water is 1.

### OUTCOME:

*Use Gibbs phase rule to determine how much information is necessary to specify the thermodynamic state of a system*

### TEST YOURSELF

*How many degrees of freedom are there at the triple point?!*

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Th: Estimate the vapor pressure of liquid components

## Vapor Pressure

Please see the <http://www.chemguide.co.uk/physical/phaseeqia/raoultnonvol.html> for an informative description of vapor pressure.

Vapor-liquid processes are quite common, so estimating vapor pressure is vital.

Essentially three ways to do so:

- Clapeyron equation
- Antoine equation
- Cox charts

Clapeyron Equation:

$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\hat{V}_g - \hat{V}_l)}$$

which may be reduced (by assuming that  $\hat{V}_l$  is negligible for the liquid phase,  $\hat{H}_v$  (the latent heat of vaporization : the amount of energy needed to make a substance change phase) is temperature independent, and the gas to be ideal)

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$

where  $B$  is a material-specific constant. **This equation is useful at low pressures.**

Antoine Equation:

$$\log_{10} p^* = A - \frac{B}{T+C}$$

where  $A$ ,  $B$ , and  $C$  are material-specific constants. (NOTE:  $B$  is different in each equation! and different from the virial coefficient for that matter!) This empirical relation is useful for a wide range of conditions.

### OUTCOME:

*Estimate the vapor pressure of liquid components.*

### TEST YOURSELF

*Prove that the vapor pressure of water at 100C is 1 atm (using both the Clapeyron and Antoine equations).*

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Th: Use ideal solution expressions to determine the composition of liquids and vapors

## Gas-Liquid Systems

Like the simple example of boiling a pot of water, there are many processes which may contain a substance capable of being both a liquid and a vapor at the operating conditions:

- evaporation
- drying
- (de)humidification
- condensation

In this course, we will not deal with mass transfer operations (you will learn that in a year or two), so we will not discuss how a system actually *gets* to equilibrium or how *fast* it gets there, but we will simply accept the fact that it is or is not at equilibrium. There are a number of important definitions that will help us clearly discuss vapor-liquid systems in equilibrium.

### DEFINITION

*A vapor in equilibrium with a liquid is said to be **saturated**.*

### DEFINITION

*A vapor which has a partial pressure less than the saturation value is **superheated**.*

### DEFINITION

*The **dew point** is the temperature at which saturation will occur in the gas phase (for a given pressure).*

### DEFINITION

*The **bubble point** is the temperature at which saturation will occur in the liquid phase (for a given pressure).*

### DEFINITION

***Degrees of superheat** refers to the difference in temperature between the actual temperature and the dew point.*

### DEFINITION

*If we have a two component mixture which has one of its components in both the liquid and vapor phase (let's consider air and water):*

*Gibbs:  $DF = 2+2-2=2$*

Therefore fixing two intrinsic variables will fix the thermodynamic state of the system! (i.e., tell me the temperature and the pressure, or the pressure and the composition, etc.)

## Raoult's Law

If we continue with our water/air mixture, we could calculate the composition if we fixed the temperature and pressure (since we only had two degrees of freedom).

At equilibrium, this system would obey Raoult's Law (for a single condensable species):

$$y_i P = p_i^* = p_i$$

### NOTE

*Raoult's Law looks very much like our ideal gas expression for partial pressures, except that the partial pressure is **equal** to the vapor pressure (since we are at equilibrium).*

### Will the real Raoult's Law please stand up....

The above example was a simple one: air and water. Why?

In real multi-phase, multi-component processes it is often the case that we have multiple components in **both** the liquid and gas phases. This makes the problem of using physical laws to determine these compositions more difficult. (But the Gibbs Phase Rule still applies for determining just *how much* we can theoretically calculate)

### NOTE

*Just like in the last chapter with the gas phase, multi-component, multi-phase systems **also** may behave as ideal and non-ideal; however, you will take a course (the Thermodynamics Pillar) that will help you to determine the non-ideal ones, so for the most part (see Txy and relative volatility), in this class, we will assume that the solution is ideal.*

With ideal solutions in gas-liquid equilibrium, we have two options:

- Raoult's Law:  $y_i P = x_i p_i^*(T)$   
(Useful when  $x_i \sim 1$  ... see our example above)
- Henry's Law:  $y_i P = x_i H_i(T)$   
(Useful when  $x_i \sim 0$ )

NOTE: The (T)'s are simply a reminder that the vapor pressure (and Henry's constant) are functions of T only.

### OUTCOME:

*Use ideal solution expressions to determine the composition of liquids and their corresponding vapors (Distinguish between when Henry's Law and Raoult's Law would be applicable)*

### TEST YOURSELF

*Let's look at an example:*

*Using Raoult's or Henry's Law for each substance, calculate the pressure and gas-phase composition in a system containing a liquid that is 0.3 mole %  $N_2$  and 99.7% water in equilibrium with water vapor and  $N_2$  gas at 80C. (Note that the  $N_2$  is considered a condensable component for this problem.)*

### NOTE

***Bubble** (composition of the liquid is given) and **Dew** (composition of the gas is given) point temperature calculations are obtained by iteratively solving for the temperatures, using one of our partial pressure equations and either  $x_i$  must sum up to one (for dew-point calculations) or that the partial pressures must sum to the total pressure (bubble-point calculation).*

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Th: Define and use K values, relative volatility, and x-y diagrams

## K Values, Relative Volatility, and x-y Diagrams

A convenient way to rearrange vapor-liquid equilibrium equations is through the use of K values.

### DEFINITION

*K values, also known as equilibrium ratios or distribution coefficients are ratios of the mole fraction in one phase to that in a different phase, and are functions of temperature and pressure (and composition as well in non-ideal systems). For vapor-liquid systems it is the ratio in the vapor phase to that in the liquid phase.*

We can use K values in several ways:

(1) to re-write the Raoult's Law expression as:

$$K = y_i/x_i = p_i^*(T)/P$$

and Henry's Law expression as:

$$K = y_i/x_i = H_i(T)/P$$

(2) We can use K-values directly, by looking values up (DePriester Charts) or using correlations.

(3) For a binary mixture, we will often take a ratio of K-values in order to try to eliminate (most of) the temperature dependence:

### DEFINITION

*The relative volatility is a ratio of the K value for one component to that of another. This is useful because it will often be only a weak function of temperature, and thus depends almost exclusively on pressure.*

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A(1-x_A)}{(1-y_A)x_A}$$

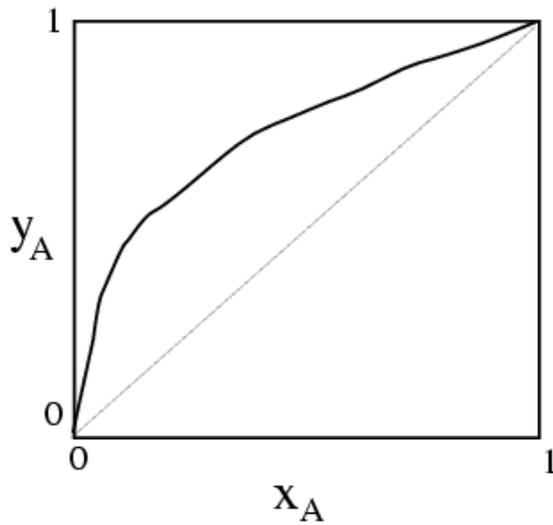
### NOTE

*The relative volatility is harder to use in non-binary systems, as the last version of this equation is no longer true (can you prove this to yourself?)*

This last equation can be rearranged to yield:

$$y_A = \frac{\alpha_{AB}x_A}{1+(\alpha_{AB}-1)x_A}$$

which is useful for plotting x-y diagrams like the following:



**OUTCOME:**

*Define and use  $K$  values, relative volatility, and  $x$ - $y$  diagrams*

**TEST YOURSELF**

*An **azeotropic** mixture is one where the vapor and liquid phases have the same composition. What would an  $x$ - $y$  diagram for such a mixture look like?*

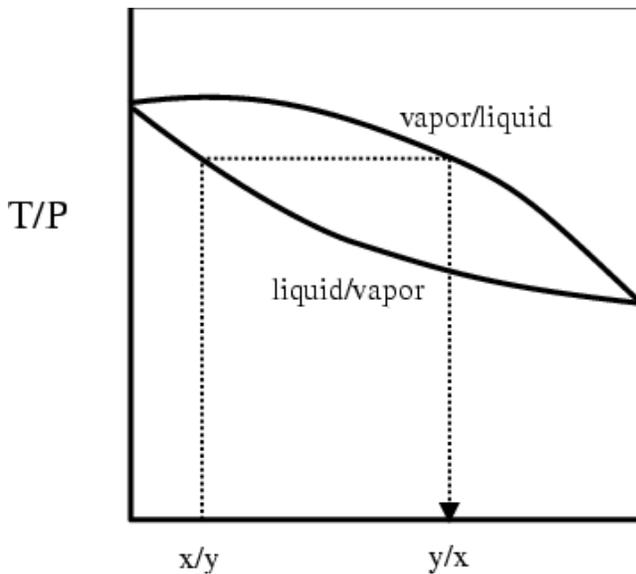
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Th: Use Txy or Pxy diagrams for non-ideal (and ideal) solutions

## Txy or Pxy: Representing Equilibrium

We already noted that if a liquid and vapor are in equilibrium for a PURE substance that there is only one degree of freedom (fix T and you know P and vice versa).

If we have a mixture of two components (in two phases):  $2 + 2 - 2 = 2$ . So the Gibbs Phase Rule tells us that we have *two* degrees of freedom. Typically what is done is that either T **or** P is fixed (measured) and then the composition of either the liquid or gas phase is fixed (or measured). (This, of course, specifies the thermodynamic state of the system)



### NOTE

*These diagrams are an easy way to handle non-ideal solutions!*

### OUTCOME:

*Use Txy or Pxy diagrams for non-ideal solutions.*

### TEST YOURSELF

*We are examining a distillation column designed to separate Benzene and Toluene. We are interested in "simulation" each stage in a small closed boiling apparatus, where we can closely control both the temperature and the pressure in an attempt to optimize the separation at each stage.*

*One of the stages that we are examining is kept at atmospheric pressure and the vapor phase is analyzed by an optical technique and yields a 30 mole % Benzene reading.*

- First prove that you have enough information to specify the Thermodynamic state of the system.
- Calculate the liquid phase composition and the temperature within the vessel.  
*You determine that the last reading was only slightly too hot for the particular stage that you are interested in, so you lower the temperature to 100C keeping the vapor phase composition fixed. How low did you need to lower the pressure? Do you still get the same liquid compositions?*



Th: Estimate the composition of liquids in equilibrium with solids

## Solid-Liquid Systems

There are two things about solid-liquid systems that we will consider important in this class: the amount of solid material that can be dissolved in a liquid solvent, and the effect of this solute on the phase characteristics of the solvent.

This section is somewhat easy to understand because we have simple every-day experiences to draw on for these two phenomena:

- You can't dissolve an arbitrary amount of sugar in your iced tea  
(we will ignore for this class the *length of time* that the sugar might take to dissolve)
- Dropping salt on ice melts the ice!

### Solubility

#### DEFINITION:

*The **solubility** refers to the maximum amount of solute that you can dissolve in a solvent at a given temperature. (In other words, the solubility depends on BOTH the solute-solvent pair AND the temperature.)*

As with vapor-liquid equilibrium, the solution (gas phase) is said to be **saturated** with the solute (vapor) at equilibrium.

FYI, if we somehow added **more** than the equilibrium amount the solution is called supersaturated (this must be done *very carefully* because the solid will precipitate out at the earliest chance) and if we add **less** it is subsaturated.

#### NOTE:

*Solubilities are typically reported in (mass solute)/(mass solvent) units.*

#### OUTCOME:

*Estimate the composition of liquids in equilibrium with solids*

#### TEST YOURSELF

*You want to make "sweet tea", but you are not sure how much sugar can dissolve in the water at serving temperatures (~5C). Determine how much sugar to use for the sweetest possible tea if you have 2 liters of tea. (The solubility of glucose in water at 5C is 0.1 g glucose/g water.)*

### Colligative Properties

We all know that adding salt to ice makes the ice melt, but do we know WHY?

#### DEFINITION:

***Colligative solution properties** refer to the changes in the value of certain solvent properties when a solute is added to them (vapor pressure, boiling point, freezing point, and osmotic pressure).*

It is fairly easy to see why this is true (that solvent properties change) if we consider the effect of dissolving a solute in a liquid on that liquid's vapor pressure (we won't actually talk about the ice problem, but it is very similar to this discussion).

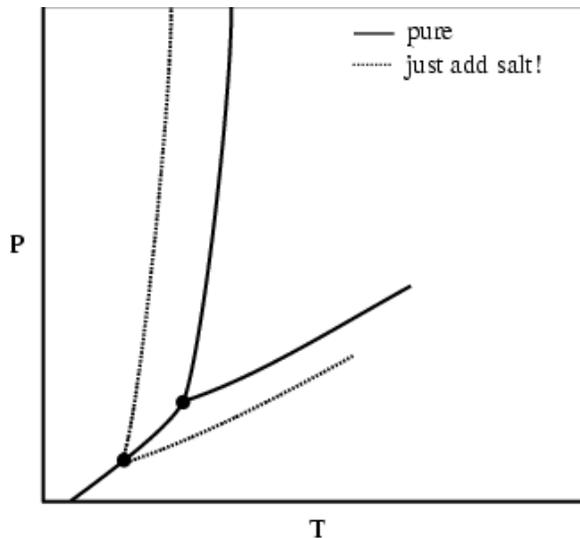
If we ignore for a second where the "foreign material" came from, but assume that it is only a small amount of material, we can recall that Raoult's Law says that the partial pressure of the solvent will be given by

$$p_i = (1-x) p_i^*$$

where  $x$  is the mole fraction of solute.

If we now consider the partial pressure of the solvent to be the "vapor pressure" of the solution (i.e., that we have only one condensable component since the solute will not form a vapor), we now have a lower "vapor pressure" than we would if we had a pure solvent!

We can look at how this would effect the phase diagram of the solution:



With a "hand waving" argument, we can "prove" that if the difference in "boiling point" is dependent only on the mole fraction of the solute, then the difference in freezing point is **also** dependent only on the mole fraction of the solute (hence the ice really works!).

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Th: Estimate the composition of immiscible liquids in equilibrium with each other

## Liquid-Liquid Systems

If we have a system with more than one phase, it is often important for us to determine the *compositions* for each phase, when we know the total compositions present in the combination of both phases (like we just did for vapor and liquid phases).

Having said that, when dealing with liquid-liquid systems, if they mixed completely (were completely **miscible**) then we wouldn't need to learn anything else, since there would only be one phase and we already know its composition.

Similarly, if they didn't mix at all (were completely **immiscible**), we would have two phases, but we would know that both of the phases were pure components.

## Solubility and Distribution Coefficients

There are two interesting cases then:

- partial miscibility
- three component systems

### DEFINITION:

*A liquid is **partially miscible** in another liquid if, when mixed, the two liquids make two (liquid) phases that contain some fraction of each liquid in each phase.*

Systems of two partially miscible fluids are treated in the exact same fashion as a solid in a liquid. In other words, you look up a "solubility" (mass/mass) and then can determine what the compositions are. (see the solid-liquid example problem for how to use this type of data)

There are two ways to handle these problems: with a distribution coefficient (partition ratio); with a ternary phase diagram.

### DEFINITION:

*A **distribution coefficient (partition ratio)** is essentially the same as a *K* value (i.e., a number (with no units) that tells us the ratio of material in one phase relative to that in another) except that it is typically expressed as a ratio of mass fractions of a solute (in the two different (immiscible) phases).*

### NOTE:

*It is necessary that two of the liquids are **completely immiscible** in order for this technique to work!*

## Phase Diagrams

In reality, all liquid are partially miscible (to some small extent). If you are worried about the **actual** compositions (i.e., trace amounts are important; in drinking water, for example), one simple way to handle this is a ternary phase diagram (see page 274 for an example).

### DEFINITION:

***Tie lines** are the lines that connect two phases which are in equilibrium on a ternary phase diagram.*

## NOTE:

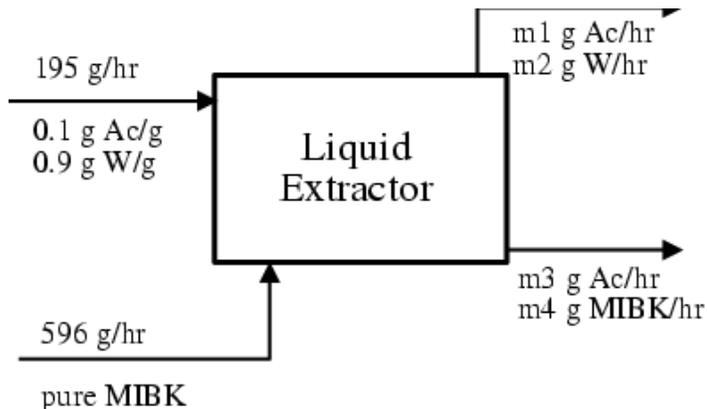
This technique will **always** work!

## OUTCOME:

Estimate the composition of immiscible liquids in equilibrium with each other (using either partition ratios or ternary phase diagrams)

## TEST YOURSELF

A liquid extractor is used to try to remove acetone from a water stream using MIBK (NOTE: Assume that MIBK and water are completely immiscible!). A flowchart of the process is shown below. If the partition ratio at the specified temperature is  $K = 1.72$  (this number is unitless, but you may think of it as g Ac in each g of MIBK mixture/g AC in each g of W mixture), determine the outlet streams.



Using the same liquid extractor as before to remove acetone from a water stream (using MIBK), let's now assume that the MIBK and water are **not** completely immiscible! A revised flowchart of the process is shown below. Determine the outlet streams.

