

**ME 370B**  
**Energy Systems II:**  
**Modeling and Advanced Concepts**

Chris Edwards  
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**More than you ever wanted to know about... Multicomponent Vapor-Liquid Equilibrium**

Calculation of vapor-liquid equilibrium (VLE) in multicomponent mixtures is central to performing chemical separations. Although this really amounts to nothing more than a generalization of the single-component phase equilibrium problem that you worked on last week, the difficulties of dealing with the properties for multicomponent mixtures of real fluids makes this a challenging problem in practice.

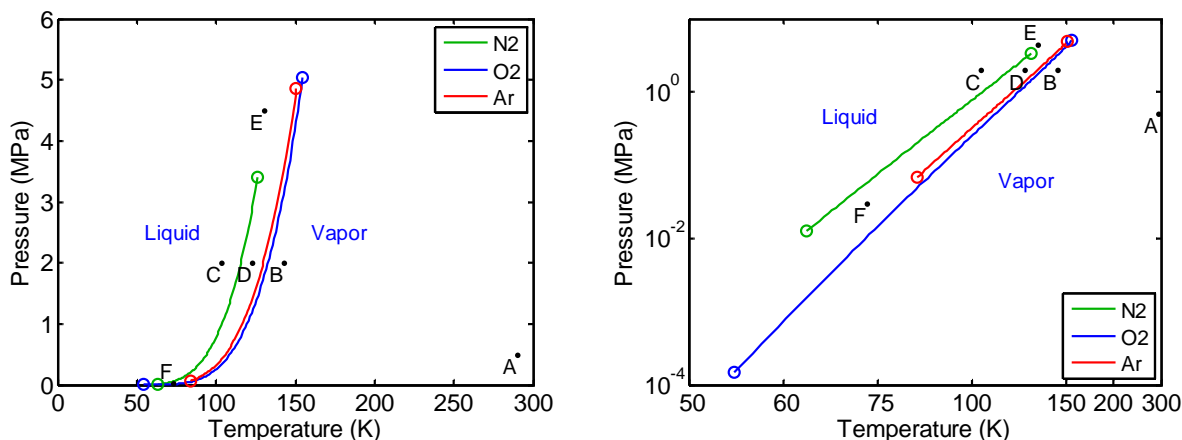
**Ideal Solutions and Saturation**

Think back to your discussion of ideal solutions in 370A. A multicomponent mixture behaves as though it were ideal if each component contributes to the solution's properties as though it were surrounded only by itself. Said another way, if the various components are similar in size and intermolecular interaction, then the main effect of mixing them together is to raise the entropy of the system due to the increased number of ways that the energy of the system can be rearranged—we have to add in the entropy of mixing. But as you already know, the basic assumption—unaltered intermolecular interaction—is inapplicable for many fluid mixtures. The other place where the ideal solution model gets into trouble is when you approach saturation conditions—exactly where we want to work for chemical separations.

The two figures below help to illustrate the situation. They should look familiar from last week's assignment: a  $P$ - $T$  plot and a Dühring plot of the saturation curves for pure oxygen, nitrogen, and argon. For the moment, consider just the problem of how to form an ideal solution of oxygen and nitrogen in order to represent engineering air. (We will return to argon later.) Thinking about the structure of the two molecules involved,  $N_2$  and  $O_2$ , you would probably conclude that use of an ideal solution to represent their mixture should be viable—and you would be correct. Bringing these two species together on a molecular scale does not involve chemical bonding or phobic/philic interactions, they are about the same size, and each experiences the other (and its own kind) only through long-range van der Waal interactions. Engineering air is a good candidate for treatment as an ideal solution.

Let's assume that you would like to know the properties of engineering air at the series of points labeled  $A$ - $B$ - $C$ - $D$  on the plots. Point  $A$  is at low pressure and high temperature *w.r.t.* the critical points of the components. Not surprisingly, this point is well represented by treating the mixture as an ideal gas. (Recall that an ideal gas mixture is the dilute-limit of the ideal solution model.) But what about point  $B$ ? How would we form an ideal solution at this point? Since we are approaching the saturation curve for at least one of the components, and the pressure is neither low, nor the temperature high *w.r.t.* the critical points, we can be pretty certain that use of the

ideal gas model is not justified—under these conditions each of the individual components must certainly be treated as a real fluid even if the mixture (solution) can be represented as ideal.



The way you go about doing this is just as you learned in 370A: Calculate the properties you need for each individual component as though it were a pure, real substance at the temperature and pressure of the solution (*i.e.*, at Point *B* on the diagram), sum them according to their proportions, and add in the entropy of mixing for those properties that are affected by it (entropy, Gibbs and Helmholtz functions, etc.). Use the Amagat model to find the volume: Sum the volumes of each of the pure components calculated at the temperature and pressure of the solution. The result is the ideal-solution-model representation of engineering air at Point *B*. In forming this solution, the properties you combine for each of the real fluids can be obtained from Cantera by making two real fluid objects—one for oxygen and one for nitrogen, both of which are in the liquid-vapor properties file—then setting each of these objects to the *T* and *P* corresponding to Point *B*, and asking for the properties required (*u*, *h*, *s*, ...) in the usual fashion. Note that in making a solution to represent air at Point *B*, Cantera will use properties from the vapor phase for both substances, as we expect that it should in order to represent a dense-but-not-saturated vapor mixture. Repeating this process for Point *C*, the essentials are unchanged; the only difference is that the properties for each of the real-fluid components will be drawn from their liquid phases.

What happens when we try to make an ideal solution at Point *D*? Now we have a problem. Since *D* lies between the saturation curves of the two components, the ideal solution formed would comprise contributions from the vapor phase of nitrogen and the liquid phase of oxygen. That doesn't sound right: If the premise of the model is that the environment around each molecule is as if the other species did not exist (or at least had no effect), then combining properties from two phases with vastly different densities seems, to say the least, unjustified. Even if you could somehow rationalize this, what would you conclude about the phase of the mixture so formed? Is it a liquid, a vapor, a saturated mixture? We really would have no idea.

What happens if we now switch from engineering (binary) air to a more realistic (ternary) model that includes argon? Considering Points *A-D*, there is no essential change in what we have already observed, *A-C* are tractable and easily interpreted, *D* is problematic in interpretation. Now consider Points *E* and *F*. Point *E* is interesting in that there is no new problem presented by

the inclusion of argon, but we now have the problem that the pressure exceeds the critical value for the single largest component, nitrogen. As a practical matter this is okay—nitrogen is supercritical at these conditions so there is only one phase to draw data from. But what does it mean for the mixture? Is the mixture supercritical due to its large proportion of nitrogen, or is it in the liquid phase due to its being well below critical conditions for its two low-volatility components, oxygen and argon?

Finally Point *F* provides another essential complication: What do you do if the point lies in a location where one of the components is below its triple point? Following the rules of the ideal solution we should now add the solid-vapor (sublimation) curve to diagram and add the argon to the solution as whatever phase it turns out to be at Point *F*, solid or vapor. But what does this mean for the phase of the mixture? We might suspect that since argon is not unlike oxygen in terms of volatility, and since it is present as only about one percent of the mixture (in air) that we may still be a fluid, but we really cannot know. For mixtures that have a higher proportion of argon than air, we must seriously consider the possibility of having solid-liquid or solid-vapor in addition to liquid-vapor equilibrium.

So while using the real-fluid properties in Cantera with the ideal-solution model can be an effective way to find mixture properties away from saturation, it is not a viable solution method near saturation conditions. We need another way.

## **Helmholtz Mixture Models**

The state-of-the-art method for dealing with multicomponent mixtures of real fluids is the Helmholtz mixture model. This model is built on the notion that since state-of-the-art fundamental relation (FR) surfaces already exist for many fluids (I have expressions for about 50 species), and since any mixture model should ultimately revert to a pure, single-component fluid if any component's mole fraction is set to unity, then the best way to model an arbitrary mixture is by using the fundamental relation surfaces for the pure components themselves. If the model uses FRs in the Helmholtz representation, it is then a Helmholtz mixture model.

We will discuss how this model is constructed in class, but for our present purpose there are just three essential elements we need to know. The first is that by having access to the FR surface for each pure component—including information inside of its vapor dome—it is possible to get data for each fluid in regions that overlap between liquid and vapor. This is really no surprise since we used this (data up to the spinodals) to find single-component saturation conditions last week. What this does is to allow a sort of “Helmholtz ideal solution” to be formed in the vicinity of Point *D* since the FRs themselves have no knowledge of saturation boundaries. Stated another way: Since the FRs are smooth and continuous well inside their own vapor domes, it is possible to make a smooth, continuous ideal solution from the pure components regardless of the location of the individual component saturation conditions. This also means that just as before, the conditions for saturation of the mixture will have to be drawn out from the model (using equality of chemical potentials) rather than being an a priori input to the model.

The second important element is that even though each component of the mixture has a well-defined critical point that is known a priori and used to normalize the FR surface for fitting, the location of the critical point for any mixture composition is not known a priori, nor does it have the same interpretation for a mixture as it does for a single-component fluid (more about this in class). So we will need a different approach to normalizing the solution surface for the mixture. In the parlance of property research, this is referred to as defining the “reducing properties” of the mixture. Fortunately this is handled as part of the formation of the mixture model, and it will remain transparent to us as users for the most part. The reason why you should know about it is to simply recognize that the reducing temperature and density are not the critical-point values for the mixture (those must now be found just like we had to find saturation last week), and even when the critical point values are known (found), they cannot be interpreted in the same way as for single-component fluids. Of particular importance is that the first and second derivatives of pressure *w.r.t.* density are not zero at the critical point of a mixture. Instead we refer to this point as the  $P$ - $\rho$  inflection point for the mixture surface. As you may already suspect, this point is important to us, not for thermodynamic reasons, but for numerics; it is the point at which the spinodals terminate and hence our ability to separate information between liquid and vapor phases connects through this point.

The last thing you need to know is that the basic approach is to use the “Helmholtz ideal solution” described above using the “reducing properties” of the specified composition to define what amounts to a “Helmholtz excess function” that represents how the real-fluid mixture differs from the ideal mixture. The reason for all the quotations in the above is that the term “ideal solution” is defined such that it is captive to the Gibbs representation  $(T,P)$  of the FR. In using it in the way we do above, we are really redefining the ideal solution such that it is constructed using a specified temperature and density, and as such is compatible with the Helmholtz representation  $(T,\rho)$  of the FR. To be very precise, the latter function should really be referred to as a *departure* function (not an *excess* function), and the solution we make by using the same physical assumptions as the ideal solution model but with the data chosen at specified  $(T,\rho)$  instead of  $(T,P)$  should not be referred to as an ideal solution. But since it has no agreed-upon name, I will simply refer to it as a Helmholtz ideal solution when talking about it.

What does all this mean for you practically? Fortunately, not too much. Almost everything you need to use these mixture models has already been programmed in a series of Matlab files. But since using these models requires understanding the physics involved, there are some key processes /procedures that are sufficiently important that you really need to write your own code to solve them, or at least write enough of the code to be able to understand what is happening. That is what we are after this week—the three key problems in multicomponent vapor-liquid equilibrium: bubble, dew, and flash.

### **Solving Bubble- and Dew-Point Problems**

Recall from 370A that when discussing saturation for multicomponent mixtures the problem is discussed in terms of the bubble and dew points of the mixture. While these terms are equally apt for description of single-component phase transformation (the formation of the first tiny bubble or droplet of dew), they are generally reserved for use with mixtures. One reason for this

convention is that it places emphasis on an essential difference between the single- and multi-component saturation problems: In the single-component problem, the composition of the first bubble or droplet of dew is fixed, and therefore known. In the multi-component problem, it varies with conditions, and determination of the joint composition and thermal state (typically either  $T$  or  $P$ , given the other) is the essential, difficult aspect of the problem.

The bubble point is that point at which the first element of gas can co-exist with a specified liquid composition at specified conditions. By specified conditions we usually mean temperature or pressure, but others are possible too. By specified composition we mean that the composition of the liquid phase is known and unaffected by the formation of the first, tiny bubble. Similarly the dew point is that point at which the first element of liquid can co-exist with a specified vapor composition at specified conditions.

Consider what I will refer to as the *bubble- $P$*  problem: heating of a liquid mixture at constant pressure until the first bubble appears. Envision this process as starting from well into the liquid region, and occurring in a piston-cylinder arrangement such that the pressure of the fluid always remains fixed. What we seek is the temperature at which the first bit (bubble) of gas is formed. As such, this *bubble- $P$*  problem returns as its answer the temperature  $T$  at which you can first form a bubble. Not surprisingly, the complementary problem—expanding a liquid held at constant temperature until it forms its first bubble—what I will call the *bubble- $T$*  problem—will return as its answer the pressure at which the first bit (bubble) of gas can be formed.

Returning to the *bubble- $P$*  problem, as we slowly heat the liquid, how do we know when the first bubble can be formed? We know that when the temperature is too low, the mixture can only exist as a liquid. But as we raise the temperature in tiny steps, what is it that determines when that first bit of gas can form? The answer is, as soon as there exists a condition at which a gas-phase mixture can be formed that has a matching set of chemical potentials for all components. This is a non-trivial statement. What it says is that below the bubble point, there is no possible composition that has gas-phase chemical potentials—for each and every component—that match the liquid phase. Conversely, when the bubble point has been reached, there now exists exactly one gas-phase composition that is capable of matching all the chemical potentials.

This description outlines the essential challenge and the key difference from the single-component saturation problem. For single-component saturation the only thing we need to find is the temperature (or pressure) at which the known-composition complementary phase (gas in this case) can first be formed. For multi-component saturation we must find the temperature (or pressure) at which an unknown and completely arbitrary mixture of any composition in the complementary phase can first be formed. This is a tremendously more complex problem. One obvious difficulty is that we are no longer matching just one chemical potential—the conditions for phase equilibrium now require that we match each individual chemical potential between the two phases. But the real problem is the arbitrary, unknown composition. In essence we must now search through the space of all possible compositions in order to see if a composition exists that can satisfy the chemical potential matching conditions. For systems with more than two components this could be a minor nightmare!

But maybe it isn't so bad. There are a few things we know. One is that there does exist a region in which we know we cannot make a match—the liquid region. So at least we know where to start from and the direction (in terms of increasing  $T$ , assuming fixed  $P$ ) from which we must approach. We also know, for a given candidate composition for the bubble, how to determine if it is compatible or not—calculate its chemical potentials (at the liquid  $T$  and  $P$ ) and compare them to those of the known liquid. We even know one more thing: If the chemical potential of a particular component in the candidate vapor mixture is too low, the direction in which the mixture must be adjusted is that which raises that component's chemical potential. Since we know that chemical potential must always rise with mole fraction (from our discussion of stability), the answer can only lie in the direction of higher mole fraction for that species. Repeating this for each species in turn, adjusting its mole fraction until the chemical potential matches that in the liquid phase while simultaneously readjusting all the previously matched mole fractions to maintain balance, then forms the basis for vectoring our way through composition space to find a composition that *might possibly* match our specified liquid.

What happens if you get to the last of the components and find that it cannot be adjusted to match? After all, the mole fractions must sum to unity, so after freely adjusting all but one, the last mole fraction is determined. This becomes our criterion for whether or not we have hit the bubble point: If the last mole fraction—after all others have been adjusted to match—does not yield a chemical potential that matches its value in the liquid phase, then it is not possible to form a compatible gas phase, and the bubble point has not been reached (yet). Whew! That's a lot of work only to get the answer: no, not yet. But never mind, this just means we need to raise the temperature a little and try again. Is this starting to sound like a numerical method we can hand over to a computer?

Actually, it almost is. The only difference between the thought experiment described above and what you will find in the *Bubble\_cT* function you have been given ( $c$  stands for composition), is that instead of creeping along in pressure bit by bit from the liquid side, we use Newton-Raphson to vector us from an initial guess rapidly toward the solution. We also use the error in the chemical potential for the last species (the closure component) to tell us which way we have to go in pressure (up for higher chemical potential, down for lower—think Gibbs-Duhem equation) so we know which way to proceed in the overall pressure-stepping process. A script for the vapor-side version of the problem—compression of a specified vapor composition at fixed  $T$  until the first tiny bit of liquid can be formed—can be found in the *Dew\_cT* file. Note that because we are using Helmholtz-based properties, it is most natural (and therefore fastest) to write the bubble and dew functions in terms of temperature rather than pressure. As such if you look at the *Bubble\_cP* and *Dew\_cP* files you will see that these are wrap-around functions that use the temperature-based  $cT$  functions to find a solution to the specified-pressure problem.

The answer to a *bubble-T* (or *bubble-P*) problem consists of finding both the pressure (or temperature) and the composition of the *complementary phase* that has matching chemical potentials. This complementary phase forms a phase-equilibrium pair with the specified liquid phase, and the two are referred to as being connected by a *tie-line* in thermodynamic state space. (This will become clearer when we begin depicting these using *plot3* in Matlab.) The reason for pointing this out is that you may have already heard this term: It was probably used to refer to the horizontal line across the vapor dome that connects saturated liquid and saturated vapor for

single-component fluids back when you first studied thermo. That horizontal line denotes that those two points are tied together as a phase-equilibrium pair.

### What is a *Flash*?

Let me answer by asking a question: What happens when you keep going past the bubble or dew points and proceed “under the dome” (officially called the *liquid-vapor coexistence region*)? The answer is: You have a flash. The term flash comes from throttling processes (isenthalpic expansion) where a single-phase liquid is allowed to *flash* into a liquid-vapor mixture by dropping under the vapor dome (a process sometimes referred to as *flash boiling*). This is the essential process of refrigeration (Joule-Thomson cooling) but the term refers more generically to any process that places the fluid at a specified thermal state under the dome. In this connection it is useful to think of flash processes in relation to bubble- and dew-point calculations: *Bubble* and *Dew* tell you where the edges of the vapor dome lie, and they tell you the complementary composition pairs that are found along the edges (the tie-lines). *Flash* calculations tell you what you find when you jump to a specified thermal state under the dome from a point outside with a specified composition.

This last point—that the process is thought of as coming from outside the dome with a specified composition—is important and helps to distinguish flash processes from bubble and dew calculations. The key idea is that when the flash occurs, the complementary phases that are formed, the liquid and vapor, are tied to each other in both amount (quality) and composition (mole fractions). The reason is that the sum of each component in each phase must equal the original amount of that component available in the single-phase fluid prior to the flash. What this means practically is that there are two key differences between bubble/dew and flash calculation procedures. The first is that in bubble and dew calculations, one of the two phases has known composition. So the only thing you need to seek during an iteration is a complementary phase composition that can satisfy equality of chemical potentials. This is not true for flash processes. Neither of the phase compositions is known a priori, only the overall (without regard to vapor or liquid) composition. The second difference is that in bubble and dew calculations, constraints on the amount of each species present in each phase play no role. This is because the problem is, by definition, formation of an *infinitesimal amount* of the complementary phase. As such, it does not deplete the parent phase in any way, and there is no overall species constraint to be satisfied. That is not true for flash processes. In fact it is this constraint—that the moles of any component which do not appear in the liquid *must* appear in the vapor—that makes the problem tractable. You can see how this is handled by taking a look at the *Flash\_zTP* script in the procedures folder (*z* stands for overall composition).

Although there are as many kinds of flash processes as there are ways to specify the thermal state point under the dome, we will only be concerned with two here: the *T-P* flash in which a fluid of known overall composition is taken under the dome to a point with specified temperature and pressure, and the *h-P* flash in which a fluid of known overall composition is taken under the dome (usually by throttling) to a point with specified enthalpy and pressure. While the utility of the *h-P* flash might be readily apparent in terms of Joule-Thomson processes, the utility of the *T-P* flash may be less obvious. As you will see, it has two special roles: The first is that it is the *natural* version of the flash problem since equality of temperature and pressure are required for

phase equilibrium to exist. (In fact  $h$ - $P$  flash routines are invariably built as wrap-around, implicit-solution functions using  $T$ - $P$  flash as the core solver.) The second is that for problems like isobaric cooling,  $T$ - $P$  flash usually provides the most direct (and efficient) method of solution since both the pressure and temperature are usually specified.

## Getting a Start on Bubble and Dew

Although you could certainly handle it, writing general bubble, dew, and flash routines is really too much to ask given time constraints. So I have given you various forms of these procedures as part of the set-up scripts for working with Helmholtz mixture properties. But as stated above, these are all Newton-Raphson-based procedures (for speed) so they require good initial guesses (i.e., an approximate solution) as a starting point. That is what you are going to provide. We will do this by forming an ideal solution for the unknown (complementary) phase in the bubble and dew problems and using it to find an approximate answer for the bubble and dew problems. Once we have your approximate solution to the problem, we will want to know over what range of conditions this approach can be used to provide a good starting point to the full-blown N-R solver for the real-mixture version of the problem. And as long as we have both solution methods, we should compare them—this might help us to understand why we cannot use this method in some part of the solution space.

The fact is that there will be places where we need to find bubble and dew points where we cannot form an ideal solution, or where our ideal solution procedure will not place us within the convergence radius of N-R for the real-mixture problem. This is a common problem, and one that exists even when working with single-component fluid properties (as in Cantera). The usual approach is then to “walk the solution” from where you can get an answer into the space where your initial guess fails so as to generate a complete solution path across the range of conditions of interest. Since the problem is one of the convergence radius of the N-R method, you know that if you take small enough steps (for example, moving up in  $T$  by 1 K at a time in a *bubble- $T$*  problem) then the answer that you found on the previous step should lie within the convergence radius of N-R for the next step of the solution process. This is what is usually done in solving single-component saturation problems—you solve at one point then step along to generate a vector of solution points. After you have done this, you curve fit the vector to form what is called an *ancillary function* or *auxiliary equation* which is close enough to the real answer that it can be used to launch the N-R solver.

Unfortunately that does not work well for multicomponent problems. The difficulty is dimensionality. For a single-component fluid there is only one composition, hence generation of an ancillary equation for, say, the saturated vapor density curve need only be done once. With multiple components, however, this would need to be done for each and every mixture composition—an infinite number of curves, or a fit with composition as a variable used to determine its coefficients—would be required.

You can probably see that a pre-computation approach to this is going to be difficult, and that the pain involved grows very rapidly with the number of components in the mixture (the dimensionality of the composition space). So our process of using an ideal solution



approximation to get started is looking like a pretty good choice. How about combining the two? Maybe we could get an answer using the ideal solution starting guess at some location that is not too far from where we want and then walk the solution to where we need it. The answer is yes, we could. The only problem will be that the process will be very slow since the closest viable starting point can be a long way away in terms of convergence steps.

There is another approach that could work: What if we generated a number of starting guesses using our ideal-solution approximation, fit these on the fly, and then used these to either interpolate or extrapolate to the conditions where we need to find a solution? That could work. In fact it does. Among the scripts you have been supplied you will find routines with names like *Bubble\_Start\_cT* and *Dew\_Start\_cT* that will use your ideal solution script (if configured correctly) and Matlab's interpolation functions to generate a spline fit to your data that can be used to extrapolate viable starting points from the bottom of the dome to near the top of the dome (or at least the  $P$ - $\rho$  inflection point, which is near the top of the dome).

Using this function (which, in turn, uses your function!) you will be able to exercise the *Bubble\_cT* and *Dew\_cT* functions from the bottom of the dome to very near the top. In doing so, you will be able to effectively sweep out the vapor dome for the real-fluid mixture we call air.

## Interpolation and the Vapor Dome

While we are now in a position to generate the vapor dome for air, we still have two problems. The first is that this will be slow. We really don't want to have to do this again and again if we can avoid it. The second is the problem of getting over the top of the dome. In the single-component problem you knew where the top of the dome was in  $T$  and  $P$ —the critical point. In the general, multicomponent problem the critical point is unknown, and as we will discuss in class, the critical point is still the place where phase distinction is lost, but it is neither the highest temperature nor pressure. (The highest temperature point on the dome is the *maxcondentherm*, and the highest pressure point is the *maxcondenbar*.) Fortunately, these three points are all known for the ternary air, so we can decide whether to include these in our procedure for getting the top of the dome or not. In the general case, however, these are not known and must be teased out of the mixture model in much the same way that you had to find saturation conditions last week and bubble/dew conditions this week.

It turns out that the key to finding these points is to have a starter function that you can use to guide N-R along the saturation surface near the top of the dome. That function is the same as the one we are asking you to develop, so you might consider this as a third reason for making such a function—being able to use it to find the real top-of-the-dome conditions. A final point: The  $P$ - $\rho$  inflection point will be found to be close to the top of the dome (near *maxcondentherm*, *maxcondenbar*, and critical) but still inside it. So while it is easy to find (you have a function for this), and it is useful for general guidance about where the top of the dome is located, you should not force your function to pass through this point—it is not located on the saturation surface.

One might argue that it is sufficient to be able to generate solutions up to the near-critical region—beyond this any solution obtained is inherently uncertain because the data on which the

mixture model is based are increasingly uncertain—so why put in the effort to spline across this region? The answer has two parts. The first is aesthetic—it really does not look good to just jump to the other side of the dome (or the  $P$ - $\rho$  inflection point) from your last solution. The second is practical: What are you going to do numerically when the problem you are trying to solve forces you to move through this region? Even if you are not ending up there, you need some systematic, internally consistent way to decide whether or not you are in the two-phase region.

The approach we will take to this problem is to spline across the top of the dome between the bubble and dew lines. When we speak of the vapor dome for a multicomponent problem what we are really talking about is the joint path formed by combining the dew-point curve from the vapor side (where the density is below critical) with the bubble-point curve from the liquid side (where the density is above critical) to form the complete locus of saturation conditions. After all, whether we are talking about a single-component fluid or a complex mixture, the meaning of the vapor dome remains unchanged: It is the place where we hit saturation and must begin to consider multiphase effects.

In addition to providing a nice graphical representation of the vapor dome for use in plots, note that the numerical arrays you generate form the basis for testing whether or not a particular point hits the dome. (Consider how you would determine where an isenthalp crosses the dome during a flash process...) And since a collection of these functions can be cross interpolated (see the *interp2* and *interp3* functions in Matlab) it is possible to make vapor domes that span a range of binary or ternary compositions such that you can work anywhere in the composition space with full, testable knowledge of the location of the saturation surface. Since the surface is defined in terms of  $T$  and  $\rho$ , it is testable for all properties— $h$ ,  $u$ ,  $s$ ,  $P$ —since all are calculable in terms of  $T$  and  $\rho$ .

One final note: If you were wondering how one finds the actual path across the top of the dome—including the numerical values of maxcondentherm, maxcondenbar, and critical point—this spline provides the starter function you need to guide Newton-Raphson. If you interpolate all of the starting variables needed by the bubble or dew functions, and tighten your numerical tolerances down to machine precision (1 ppm will not be sufficient for this), these splines will give you good enough initial guesses to be able to work your way (iteratively) across the top. But it will be very slow, so I really don't suggest that you try this.