Intermediate Thermodynamics

Multiphase-Multicomponent Systems

Equilibrium

We want to develop expressions that will lead to criteria for equilibrium. A system that is not in equilibrium will undergo a process toward equilibrium, and it is of interest also to be able to understand how that process will develop.

If we have a closed system, consisting of different phases and components, that is not in equilibrium, processes of mass and heat transfer and chemical reactions will tend to bring the system to equilibrium. Let's consider such a closed system in an isothermal condition with uniform pressure, in thermal and mechanical equilibrium with the surroundings, in such a way that heat and work interactions with the surroundings are reversible.

In addition, the system and the surroundings form an isolated system, so the second law of thermodynamics requires:

$$dS_{isol} \geq 0 \tag{1}$$

and as the isolated system is formed by the closed system plus the surroundings we can write:

$$dS_{CS} + dS_{surr} \geq 0 \tag{2}$$

where S_{CS} is the total entropy of all the phases and components within the closed system. The entropy change on the surroundings is due to the heat transfer to or from the system:

$$dS_{surr} = \frac{\delta Q_{surr}}{T_{surr}} = -\frac{\delta Q}{T} \tag{3}$$

where $T = T_{surr}$ because the interaction is reversible, and $\delta Q = -\delta Q_{surr}$. Eqs. (2) and (3) imply that:

$$\delta Q \leq T \, dS_{CS} \tag{4}$$

Energy conservation for a simple compressible system with reversible work interactions on the boundary states that:

$$dU_{CS} = \delta Q - p \, dV_{CS} \tag{5}$$

so combining Eqs. (4) and (5) we obtain:

$$dU_{CS} + p\, dV_{CS} - T\, dS_{CS} \leq 0 \tag{6}$$

Notice that all variables in Eq. (6) are only functions of the state of the closed system, and therefore Eq. (6) can be applied to any changes within the system: the hypotheses of mechanical and thermal reversibility are not necessary to derive the expression as long as pressure and temperature are uniform. The directions of the processes that will lead the system to equilibrium are given by the inequality. Particular forms of Eq. (6) are of importance when analyzing equilibrium.

For a system held at constant total volume and entropy we obtain:

$$dU_{CS}\big|_{S,V} \leq 0 \tag{7}$$

thus the internal energy decreases as a system with constant total entropy and volume proceeds to equilibrium, and at equilibrium the internal energy will be minimum.

Example: a tank contains 50 % water at 10 °C and 50 % water at 30 °C, separated by an adiabatic wall. At t=0 the separation is raised and the system evolves toward equilibrium at constant volume and entropy. What was the initial internal energy? What will be the final temperature and internal energy? What will be the heat transfer?

Ans: $u_i = 83.89\ kJ/kg$, $T_f = 19.83\ ^oC$, $u_f = 83.24\ kJ/kg$, $\Delta Q = -0.712\ kJ/kg$

Similarly, in a constant internal energy and volume system the entropy changes will satisfy:

$$T\, dS_{CS} \geq 0 \tag{8}$$

that states an isolated system must always increase its entropy, which we already knew, since an isolated system is a constant volume and internal energy system.

If the system under consideration is constrained to a constant pressure and temperature process we can rewrite Eq. (6) as:

$$dU_{CS}\big|_{T,P} + d\left(PV_{CS}\right)_{T,P} - d\left(TS_{CS}\right)_{T,P} \leq 0 \tag{9}$$

and since the Gibbs function is $G_{CS} = H_{CS} - T\, S_{CS}$ we obtain:

$$dG_{CS}\big|_{T,P} \leq 0 \tag{10}$$

which means that in an isobaric and isothermal process the Gibbs function must always decrease until equilibrium is reached. At equilibrium, dG is zero. Eq. (10) is very important, since phase changes and many chemical reactions occur at constant pressure and temperature.

If the process develops at constant volume and temperature, Eq. (6) leads to:

$$dU_{CS}\big|_{T,V} - d(TS_{CS})_{T,V} \leq 0 \qquad (11)$$

and using the definition of the Helmholtz free energy $(A = U - TS)$ we obtain:

$$dA_{CS}\big|_{T,V} \leq 0 \qquad (12)$$

Phase equilibrium

Two or more phases not in equilibrium will experience mass transfer among them. As an example, subcooled vapor will condense transferring mass from the vapor phase to the liquid phase. Once equilibrium is attained, the mass transfer process stops.

Let's consider two phases α and β containing C component each. The system is under isothermal and isobaric conditions (constant P and T). The evolution process towards equilibrium will be such that inequality (10), $dG_{CS}\big|_{T,P} \leq 0$, is satisfied. Recall that the total differential of the Gibbs function for each phase of a multicomponent system is given by (Eq. 9 in Homogeneous Mixtures):

$$dG = V\,dP - S\,dT + \sum_i \mu_i\,dN_i \qquad (13)$$

where i covers all the components. Substituting into (10) we obtain:

$$\sum_i \mu_i^{\alpha}\,dN_i^{\alpha} + \sum_i \mu_i^{\beta}\,dN_i^{\beta} \leq 0 \qquad (14)$$

Also, as we don't have chemical reactions, the number of moles of each component must be conserved on phase change, thus:

$$dN_i^{\alpha} + dN_i^{\beta} = 0 \qquad (15)$$

thus, combining Eqs. (14) and (15) we obtain:

$$\sum_i \left(\mu_i^\alpha - \mu_i^\beta \right) dN_i^\alpha \leq 0 \tag{16}$$

where the equality applies under equilibrium conditions. Since the quantities dN_i^α are non-zero and independent of each other, then the condition for equilibrium is:

$$\mu_i^\alpha = \mu_i^\beta \tag{17}$$

independently for each of the C components. Generalizing for P phases we can write:

$$\mu_i^1 = \mu_i^2 = \cdots = \mu_i^P \tag{18}$$

for each of the C components. That means that the chemical potential must be the same for all the phases in equilibrium for the same component. The chemical potentials of each of the components can in principle be different.

In terms of the fugacities, the chemical potential is (see Eq. (47) in Fugacity):

$$d\mu_i = RTd \ln \bar{f}_i \tag{19}$$

where $\bar{f}_i$ is partial fugacity of each component. Integrating we obtain:

$$\mu_i = RT \ln \bar{f}_i + C_i \tag{20}$$

where the constant of integration can be defined using an arbitrary reference state. Using the same state for all the components we obtain an alternative expression for Eq. (18):

$$\bar{f}_i^1 = \bar{f}_i^2 = \cdots = \bar{f}_i^P \tag{21}$$

This criterion of identical fugacities for each phase is also useful.

Let's analyze the case of mass transfer between phases, that is when the system is not in equilibrium. In that case, the inequality applies in Eq. (16). If a differential amount of mass of component i is transferred from phase β to α, then dN_i^α is positive. Thus, Eq. (16) results in:

$$\left(\mu_i^\alpha - \mu_i^\beta \right) dN_i^\alpha \leq 0 \qquad \Rightarrow \qquad \mu_i^\beta > \mu_i^\alpha \tag{22}$$

which implies that mass transfer occurs from regions of higher to lower chemical potential. The chemical potential is the driving force for mass transfer, in the same way as temperature is the driving force for heat transfer. Diffusion of chemical species in a system is due to gradients in chemical potentials.

Gibbs Phase Rule

In single-component systems composed of simple compressible fluids at equilibrium, we know that any state can be fixed knowing any two intensive properties if one phase exists. If the system consists of two phases (for instance liquid and vapor), we have an additional constraint on the system (the saturation curve, or that at the state pressure and temperature are linked) and only one variable is necessary to fix the state.

In a general system we may have C components and P phases in equilibrium. The Gibbs rule (Gibbs, 1875) gives information on the number of independent properties necessary to fix the intensive state of a general system.

Consider a single-phase system with C components. The composition is specified with the molar fractions, such that $\sum_i x_i = 1$. This means that the composition can be defined with C - 1 molar fractions. Thus the state is fixed with $2 + C$ - 1 intensive variables, or $C + 1$. This works fine with $C = 1$ with the familiar result of 2 independent intensive variables.

In a system with more than one phase we will need the same number of intensive variables or each phase, that is $P\,(C + 1)$. However, we have an additional set of restrictions that provide equations that allow a reduction of the number of variables needed to fix the state. These are:

- If the phases are in thermal equilibrium, then the temperature is the same for all phases: $T^{\alpha} = T^{\beta} = \cdots = T^{P}$.
- If the phases are in mechanical equilibrium, then the pressure is uniform throughout the system, thus: $P^{\alpha} = P^{\beta} = \cdots = P^{P}$.
- Also, phase equilibrium requires the chemical potentials to be equal within each component, $\mu_i^{\alpha} = \mu_i^{\beta} = \cdots = \mu_i^{P}$.

These restrictions provide $(P$ - $1)(C + 2)$ equations that reduce the number of variables to fix the state. Thus the total number of intensive properties to fix the state of a general system consisting of C components with P phases is:

$$F = P(C+1) - (P-1)(C+2) = C - P + 2 \tag{23}$$

where F is the number of intensive properties necessary to fix the intensive state of the simple compressible system, usually called the *degrees of freedom* of the system.

In a three-phase system, single component, the state is fixed by the triple point. We don't have any degree of freedom, since if we vary any intensive variable we depart from the triple point and a three-phase system no longer exists. A three-phase, two-component

system has only one degree of freedom: the composition of the system. Other examples are straightforward.

Note that the derivation implied that all the components are present in all the phases. This is not a necessary conditions, since the absence of one component in one phase requires the removal of one phase of the conditions of chemical, mechanical and thermal equilibrium. Thus the phase rule has general validity.

Vapor-liquid equilibrium

The composition of the different phases are obviously all the same for a single-component system. However, in a multicomponent system the compositions are different for the different phases. This can be analyzed in an easier way if we restrict to a two-phase system.

The phase rule states that a two-phase system will have:

$$F = C - P + 2 = C \tag{24}$$

degrees of freedom. The unknowns are usually the pressure and temperature and the compositions of the vapor and gaseous phases, that we will represent with the liquid molar fractions x_i and gas molar fractions y_i. This results in $2\,C$ unknowns, since one of the molar fractions in both liquid and gas can be determined from $\sum_i x_i = 1$ and $\sum_i y_i = 1$.

The condition of two phases in equilibrium requires that the chemical potentials on the same components must be the same for each phase, and the temperatures and pressures must be the same also. In addition, the fugacities must be the same within each component, so:

$$\bar{f}_i^{\,V} = \bar{f}_i^{\,L} \tag{25}$$

From the definition of the fugacity coefficients for each component in a multicomponent mixture, we have that:

$$\overline{\phi}_i^{\,V} = \frac{\bar{f}_i^{\,V}}{y_i P} \qquad\qquad \overline{\phi}_i^{\,L} = \frac{\bar{f}_i^{\,L}}{x_i P} \tag{26}$$

and using Eq. (25) we have:

$$\overline{\phi}_i^{\,V} y_i = \overline{\phi}_i^{\,L} x_i \tag{27}$$

Eq. (27) relates the compositions and fugacities on each phase. In principle Eq. (27) is all we need to evaluate the compositions of the vapor and liquid phases. However, the

fugacity coefficients depend on the compositions as well as the temperature and pressure, and are therefore implicit and difficult to evaluate.

One approximation that allows to overcome these difficulties is to assume that the mixture behaves as an ideal solution. In this case we can use the Lewis-Randall rule that states that $\bar{f}_i = x_i f_{i,P}$, Eq. (81) in notes Fugacity, where P is the total pressure, used to evaluate the fugacities. Thus Eq. (25) for an ideal solution can be written as:

$$y_i f_{i,P}^V = x_i f_{i,P}^L \qquad (28)$$

which is explicit in the molar fractions since the fugacities are only a function of pressure and temperature. In addition, the liquid fugacity is approximately equal to the saturation liquid fugacity, which in turn is equal to the vapor saturation fugacity. Thus:

$$y_i f_{i,P}^V = x_i f_i^{V,sat} \qquad (29)$$

which requires the evaluation of the fugacity of each component at the saturation state at the temperature in consideration and at the pressure P and the temperature T. Therefore, the equilibrium composition can be evaluated.

An additional simplification is possible if the pressure is low enough such that the vapor phase behave as an ideal gas. In this case we have:

$$y_i P = x_i P_i^{sat} \qquad (30)$$

and since $p_i = y_i P$ in an ideal gas mixture, we have:

$$p_i = x_i P_i^{sat} \qquad (31)$$

Eqs. (30) and (31) are statements of the *Raoult's Law*, derived for ideal solutions in which the vapor phase behaves as an ideal gas. Eq. (29) is used when real-gas, ideal solutions are under consideration. Methods to evaluate real-solution, real substances are available and are not on the scope of this course.

Example: Five grams of sucrose ($C_{12}H_{22}O_{11}$) are added to 100 g of water at 50 °C. Estimate the vapor pressure of the solution.

From tables, the vapor pressure of pure water at 50 °C is 0.1235 bar. As the partial pressure of water vapor at saturation is small, the Raoult's law applies. The mole fraction of water on the mixture is ($M_{H_2O} = 18.02$, $M_{suc} = 342.3$):

$$x_{H_2O} = \frac{m_{H_2O}/M_{H_2O}}{m_{H_2O}/M_{H_2O} + m_{scr}/M_{scr}} = 0.99738$$

and neglecting the vapor pressure of the sucrose, the vapor pressure is:

$$P_{H_2O} = 0.99738 \, 0.1235 = 0.1232 \, bar$$

Ideal binary solutions

Let's consider an ideal solution composed by two-phases formed with components 1 and 2, and with pressure low enough so Raoult's Law holds. In this system we will have six unknowns: P, T, x_1, x_2, y_1, y_2. Liquid and vapor composition require:

$$x_1 + x_2 = 1 \tag{32}$$

$$y_1 + y_2 = 1 \tag{33}$$

and the Raoult law for each component states:

$$y_1 P = x_1 \, p_1^{sat} \tag{34}$$

$$y_2 P = x_2 \, p_2^{sat} \tag{35}$$

We have then 4 equations and 6 unknowns. According to the phase rule, with 2 phases and 2 components, we have $F = 2 - 2 + 2 = 2$ degrees of freedom. Usually the temperature or the pressure is one of the selected variables, and the concentration of one of the components in the liquid or gas phase is the other.

Pressure-concentration plot

Let's consider the case of a pressure-concentration plot. The total pressure can be found from:

$$P = p_1 + p_2 = x_1 \, p_1^{sat} + (1 - x_1) p_2^{sat} \tag{36}$$

which means that the total pressure varies linearly with the composition between the two vapor pressures. From Eq. (30) we can also write:

$$\frac{y_1}{x_1} = \frac{p_1^{sat}}{P} \tag{37}$$

Eq. (37) means that, if $p_1^{sat} > p_2^{sat}$, then $y_1 \geq x_1$, the equal will hold for $x_1 = 0$ or $x_1 = 1$. The physical explanation of this behavior is simple: since $p_1^{sat} > p_2^{sat}$, then

component 1 is more volatile than component 2. Thus component 1 will evaporate first and the vapor will have a larger composition of 1 than the liquid.

Let $\beta = \dfrac{p_1^{sat}}{p_2^{sat}}$, thus β is only a function of temperature. Replacing Eq. (34) into Eq. (36) we obtain:

$$\frac{x_1 \, p_1^{sat}}{y_1} = x_1 \, p_1^{sat} + (1 - x_1)p_2^{sat} \qquad \Rightarrow \qquad y_1 = \frac{x_1 \beta}{1 + x_1(\beta - 1)} \tag{38}$$

or, rearranging,

$$x_1 = \frac{y_1 \beta}{\beta - y_1(\beta - 1)} \tag{39}$$

Eqs. (38) and (39) show that the compositions of the vapor and liquid phases will only be the same if the vapor pressures of both components are the same. Combining Eqs. (34) and (39) we obtain for the total pressure:

$$P = \frac{p_1^{sat}}{\beta - y_1(\beta - 1)} \tag{40}$$

The curves $P - x_1$ and $P - y_1$, as expressed by Eqs. (36) and (40) are shown in Fig. 1. Notice that Eq. (40) results in a nonlinear relation for the total pressure as a function of the composition of vapor. The curve $P - x_1$ shows the composition of liquid at the given total pressure. Therefore it marks the lower limit for liquid composition and is the saturated liquid line; above that pressure we have compressed liquid with composition x_1. Similarly, the curve $P - y_1$ describes the composition as a function of pressure of pure vapor, and therefore defines the upper pressure at which we will have vapor. Below that pressure, we have superheated vapor at the composition y_1.

Decreasing the pressure from a compressed liquid state

Let's evaluate qualitatively the behavior of a binary mixture as we decrease the pressure from point *a* in Fig. 1 (b). Point *a* is in compressed liquid with a composition x_1, thus the solution will remain liquid with the same composition until we reach point *b*, which marks the minimum pressure at which composition we will have liquid with composition x_1. A further decrease in pressure will result in the formation of gas bubbles, and thus point *b* marks the *bubble point* for composition x_1. The composition of the bubble vapor will be y_1 found in *c*. Further decrease of the pressure will cause larger vapor formation with compositions between *c* and *g*, while the liquid will change the composition

along the $P - x_1$ line (the bubble point line). At point g all the liquid has turned into vapor, and the composition is again the original of the compressed liquid.
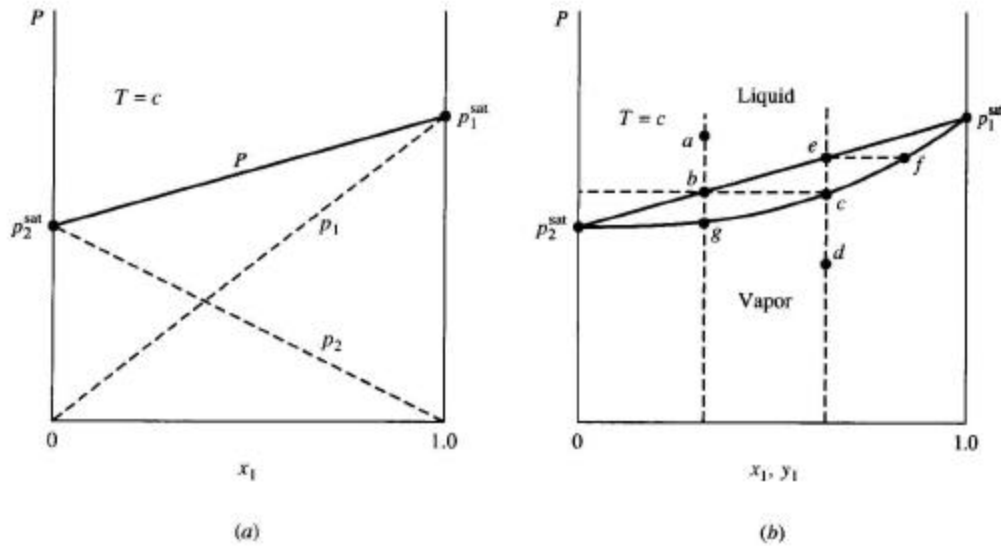
Figure 1: constant-temperature pressure-composition diagrams following Raoult's Law (from Wark)

Increasing the pressure from a superheated vapor state

In this case we start the pressure rise from point d in Fig. 1. The first drop of liquid will appear at point c, and therefore is called the *dew point*. Higher pressures, but below point e, will result in vapor compositions between points c and f, and liquid compositions between b and e. Once the pressure reaches the corresponding value with point e, we are in 100 % liquid with the same composition as the original vapor.

Example: A liquid-vapor mixture contains n-hexane and n-heptane at 27 °C. Assuming ideal solutions, estimate the composition of the liquid and vapor phases as a function of the total pressure. Take 1 for hexane and 2 for heptane, and use the following vapor pressure correlations (T in Kelvin, P in millibars):

$$\ln P_1 = 18.057 - \frac{3837.4}{T}, \qquad\qquad \ln P_2 = 18.217 - \frac{4231.0}{T}$$

At 300 K, the pure vapor pressures of hexane and heptane are 193.6 and 61.2 millibars. As these values are well below atmospheric pressure, we can expect that the Raoult's law will be valid if the solution behaves as ideal. Thus the total pressure as a function of liquid composition will be:

$$P = p_1 + p_2 = x_1 \, 193.6 + (1 - x_1) \, 61.2$$

To obtain the variation of composition against the vapor composition, we use Raoult's law, which implies:

$$y_1 = x_1 \frac{193.6}{P}$$

The results are plotted in the *P-x-y* diagram in Fig. 2.
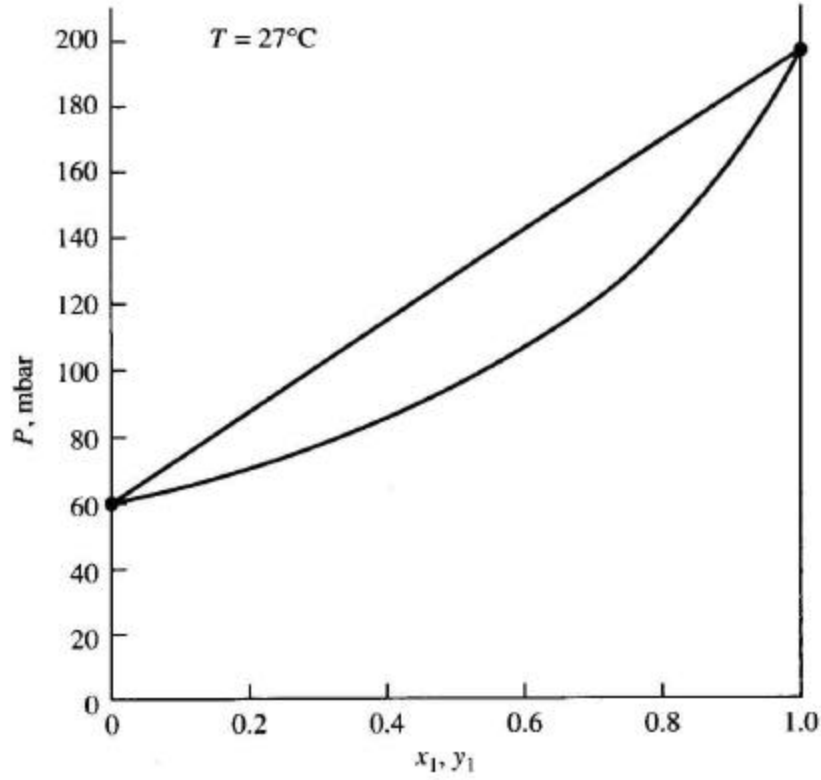


Figure 2: *P-x-y* diagram for the example (from Wark).

Temperature-concentration plot

Eq. (36) can be rewritten in terms of the total pressure (known and fixed) and composition as:

$$x_1 = \frac{P - p_2^{sat}}{p_1^{sat} - p_2^{sat}} \tag{41}$$

where the temperature appears implicitly in the saturation pressures of the pure components. At a given temperature, the saturation pressure of component 2 may equal the total pressure. In this case $x_1 = 0$ and we have pure component 2, and the corresponding temperature is T_1^{sat}. Similarly, if $p_1^{sat} = P$ then $x_1 = 1$ and the mixture is 100 % component 1 and the temperature is T_2^{sat}. So the temperature-composition plot will go from T_1^{sat} to T_2^{sat}. The values of y_1 can then be calculated using Raoult's law, Eq. (34).

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Fig. 3 shows a *T-x-y* plot in which the component 1 is more volatile than component 2 (because T_1^{sat} is smaller than T_2^{sat}, 1 will tend to evaporate more than 2). Notice that the none of the curves is linear, since the vapor pressure is a nonlinear function of the temperature.
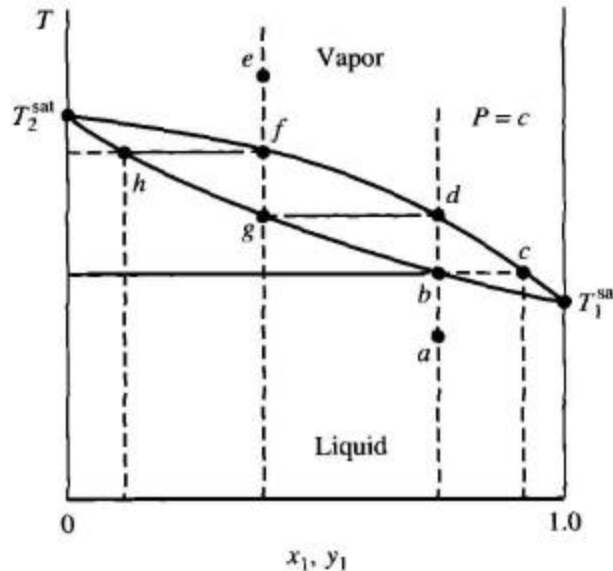
Figure 3: constant-pressure temperature-composition diagram following Raoult's Law (from Wark)

Increasing the temperature from a subcooled liquid state

Rising the temperature from point *a* to point *b*, the mixture will reach the liquid saturation temperature at the given composition and pressure. The corresponding curve is the liquid saturation curve or bubble curve. At this point *b* the vapor has a composition *c*, richer in component 1 since 1 is more volatile that 2. Further increase of the temperature will lead to point *d* on the diagram, where the saturated vapor curve is met. Immediately below that point, the liquid drops have composition *g* and the vapor composition *d*, coincident with composition *a* and *b*. Higher temperatures will result in 100 % vapor with composition *d*.

Decreasing the temperature from a superheated vapor state

Starting from point *e*, a reduction in temperature at constant pressure will take us to point *f*, where incipient condensation occurs. The first drops will have a composition *h*, richer in component 2. At point *g* the mixture reaches the saturated liquid point, in which the composition is the same as in *e* but 100 % liquid. Lower temperatures will lead to a compressed liquid state with the same composition. A temperature immediately above point *g* will have bubbles of vapor with composition *d*.

Example: A mixture of hexane and heptane is at 2 bar. Plot a *T-x-y* diagram using the information on the previous example.

Using the saturation pressure curves of the previous example, the saturation temperatures at 2 bar (2000 millibar) are 367 and 399 K for hexane and heptane. Combining Eq. (41) with the vapor pressure relations given on the previous example we obtain:

$$x_1 = \frac{2000 - e^{18.217 - \frac{4231.0}{T}}}{e^{18.057 - \frac{3837.4}{T}} - e^{18.217 - \frac{4231.0}{T}}}$$

that evaluated on the range $367\ K \leq T \leq 399\ K$ leads to the $T\text{-}x_1$ curve. Then applying Eq. (34) we get the $T\text{-}y_1$ curve:

$$y_1 = \frac{x_1}{2000} e^{18.057 - \frac{3837.4}{T}}$$

The results are shown in Fig. 4.
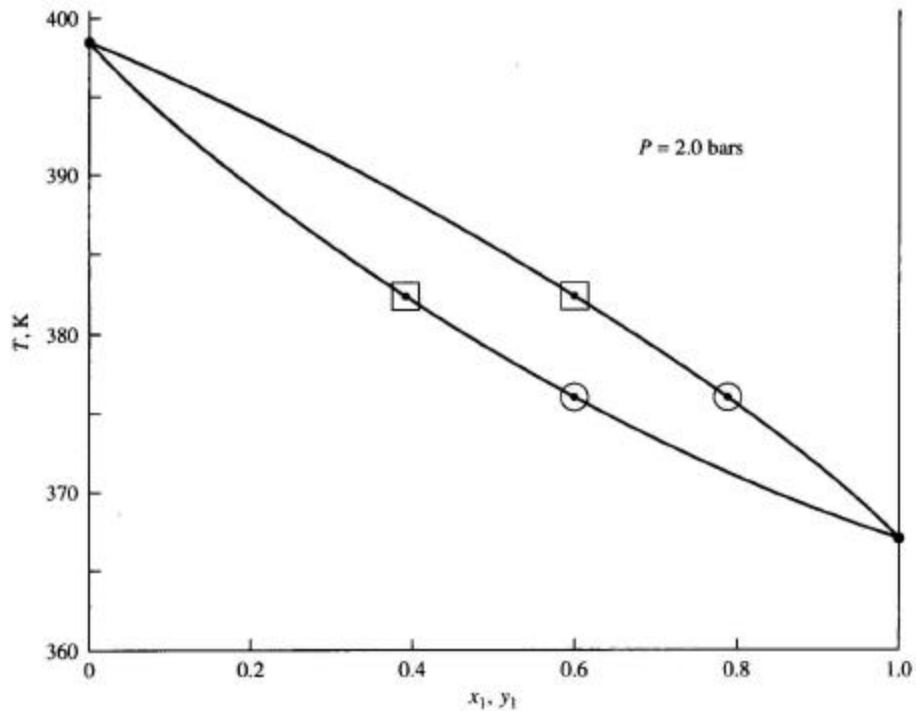
Figure 4: *T-x-y* diagram for the example (from Wark).

Notice that the determination of the bubble or dew points is going to be implicit in temperature at constant pressure. To obtain the bubble point Eq. (36) applies:

$$P = x_1\, p_1^{sat}(T) + (1 - x_1)\, p_2^{sat}(T) \tag{42}$$

which is implicit in T and can be solved with any method to solve implicit equations. The dew point is calculated from Eq. (42) and the Raoult law, namely:

$$P = x_1\, p_1^{sat}(T) + (1 - x_1)\, p_2^{sat}(T), \qquad y_1 = \frac{x_1}{P}\, p_1^{sat} \quad \Rightarrow$$

$$ \tag{43}$$

$$P = \frac{p_1^{sat}(T)\, p_2^{sat}(T)}{y_1\, p_2^{sat}(T) + (1 - y_1)\, p_1^{sat}(T)}$$

which again is an implicit equation.

Example: a mixture of 60 % hexane and 40 % heptane is at 2 bar. Find the bubble point temperature and vapor composition if the initial temperature is 350 K. Find the dew point temperature and the liquid composition if the initial temperature is 420 K.

We can find the bubble point temperature by solving for T the following equation:

$$0.6 = \frac{2000 - e^{18.217 - \frac{4231.0}{T}}}{e^{18.057 - \frac{3837.4}{T}} - e^{18.217 - \frac{4231.0}{T}}}$$

which results in a bubble point temperature of 376.6 K.

The vapor composition can be found from Raoult's law. The hexane saturation pressure at the bubble point is $p_1^{sat} = 2614\ millibar$, thus the vapor composition at the bubble point is:

$$y_1 = \frac{2614}{2000} 0.6 = 0.784$$

The dew point temperature can be calculated from Eq. (43), which in this case is:

$$2000 = \frac{e^{18.057 - \frac{3837.4}{T}}\, e^{18.217 - \frac{4231.0}{T}}}{0.6\, e^{18.217 - \frac{4231.0}{T}} + 0.4\, e^{18.057 - \frac{3837.4}{T}}}$$

whose solution is 383.12 K. The hexane saturation pressure is at this temperature 3104.9 $millibar$. Thus, the liquid composition at the dew point will be:

$$x_1 = \frac{2000}{3104.9} 0.6 = 0.386$$

These results are marked on Fig. 4.

Elevation of the boiling point and depression of the freezing point

If we add a non-volatile solute to a pure solvent, the vapor pressure of the solvent will decrease, as indicated by Raoult's law. Therefore, the boiling temperature of the mixture will increase at the same pressure as compared to the solvent boiling point.

Figure 5 shows the *P-T* diagram for the pure solvent and for the solution on the boiling curve. A the total pressure *P*, the pure solvent has a boiling saturation temperature T_{b0} found by the intersection of the constant *P* line and the boiling saturation curve, point W. As the addition of a solute will decrease the vapor pressure, the new intersection will lie at a temperature T_b.
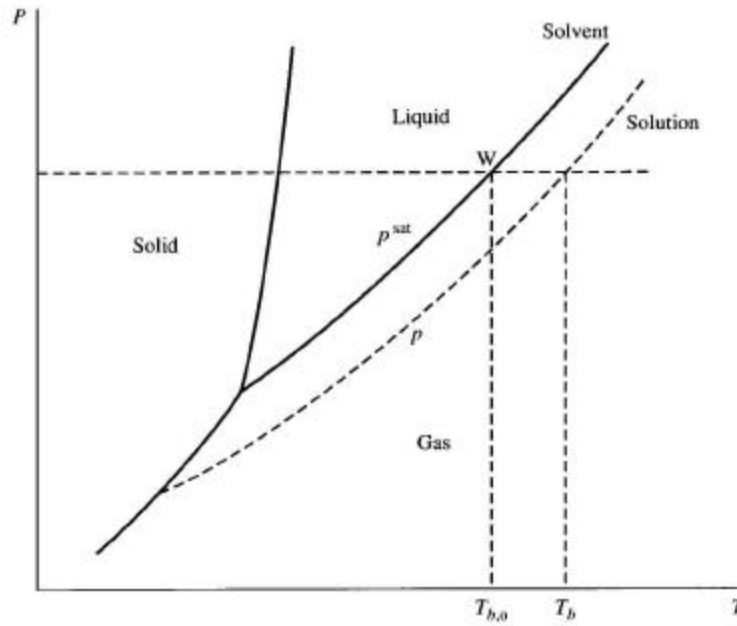
Figure 5: Change of the boiling point due to the addition of a non-volatile solute in a solvent (from Wark).

Let's analyze the elevation of the boiling point using the ideal solution model. In general this model will not be adequate for this type of problem. However, for very dilute concentrations the solution will behave as ideal.

In this case, as the solute is non-volatile, the total pressure will be:

$$P = x \, p^{sat} \tag{44}$$

where x and p^{sat} are the molar fraction and the saturation pressure of the solvent. The equilibrium condition between the liquid and the vapor on the solvent is the equality of the chemical potentials. As the temperature is constant during a phase change, we can write:

$$\frac{\mu_i^{liq}}{T} = \frac{\mu_i^{vap}}{T} \tag{45}$$

If we add a small amount of solute to the solvent, both the chemical potential and the temperature will change. However, on the new state, Eq. (45) will still be valid, therefore:

$$d\left(\frac{\mu_i^{liq}}{T}\right) = d\left(\frac{\mu_i^{vap}}{T}\right) \tag{46}$$

We consider a process at constant pressure. In this case, the differential on the liquid phase is a function of the composition and temperature. On the vapor phase is a function of the temperature only, since only the solvent is present on the vapor phase. Then the differential is:

$$\frac{\partial\left(\mu_i^{liq}/T\right)}{\partial T}dT + \frac{1}{T}\frac{\partial \mu_i^{liq}}{\partial x_i}dx_i = \frac{\partial\left(\mu_i^{vap}/T\right)}{\partial T}dT \tag{47}$$

The different terms in Eq. (47) are evaluated as follows. Assuming ideal solution we have that $\mu_i^{liq} = \mu_i^* + RT \ln x_i$, and thus:

$$\frac{1}{T}\frac{\partial \mu_i^{liq}}{\partial x_i} = \frac{R}{x_i} \tag{48}$$

The other differential is evaluated using the relation introduced in "Homogeneous Mixtures", $\dfrac{\partial\left(\mu_i^{liq}/T\right)}{\partial T} = -\dfrac{\overline{h}_i^{liq}}{T^2}$. Also, in an ideal solution $\overline{h}_i = h_i$ Then Eq. (47) can be rewritten as:

$$-\frac{h_i^{liq}}{T^2}dT + \frac{R}{x_i}dx_i = -\frac{h_i^{vap}}{T^2}dT \tag{49}$$

that rearranging results in:

$$\frac{dx_i}{x_i} = -\frac{\left(h_i^{vap} - h_i^{liq}\right)}{RT^2}dT = -\frac{h_{fg,i}}{RT^2}dT \tag{50}$$

The heat of vaporization of the volatile component i in the mixture is in principle different from the heat of vaporization of the pure component, h_{fg}. As an approximation, for very dilute solutions, we can take both values as coincident. In addition, the boiling

temperature change due to the addition of the solute will be small, so we can approximate h_{fg} as constant. This allows as to integrate Eq. (50) to obtain:

$$\int_1^{x_i} d \ln x_i = -\int_{T_{b0}}^{T_b} \frac{h_{fg,i}}{RT^2} dT \quad \Rightarrow$$

$$\ln x_i = -\frac{h_{fg}(T_b - T_{b0})}{RT_b T_{b0}} \tag{51}$$

Two further simplifications are possible under the hypotheses stated. As $T_b \approx T_{b0}$ in kelvins, thus $T_b T_{b0} \cong T_{b0}^2$. Also, $\ln x_i = \ln(1 - x_{solute}) \cong -x_{solute}$ for small concentrations of the solute, and then Eq. (51) reduces to:

$$T_b - T_{b0} \cong \frac{RT_{b0}^2 x_{solute}}{h_{fg}} \tag{52}$$

Eq. (52) states that the elevation of the boiling point in an ideal solution under the hypotheses stated in this section is only a function of the concentration of the solute and not of the solute itself, ie, the type of solute does not really matters as long as it is non volatile and the solution behaves as ideal. A property that varies with the quantity and not with the identity of a substance is called *colligative.*
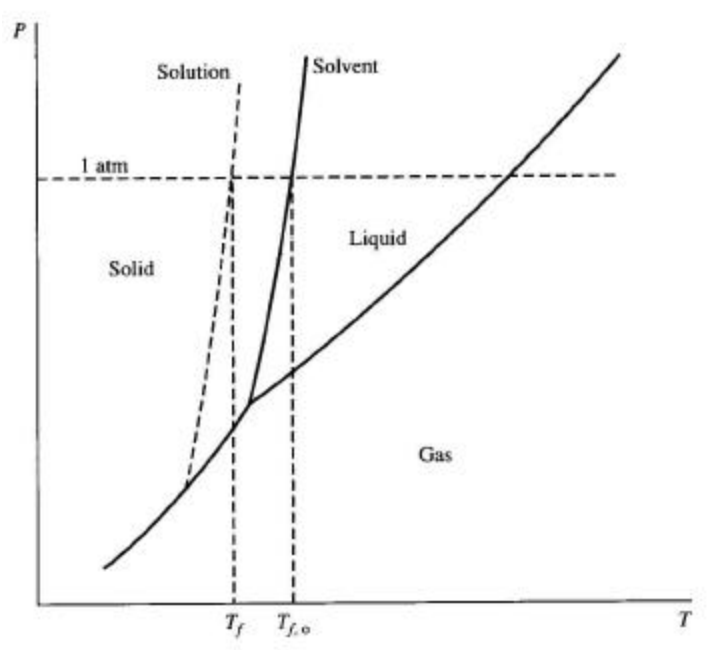
Figure 6: Change of the freezing point due to the addition of a non-volatile solute in a solvent (from Wark).

A similar effect on the freezing point is obtained if we add a nonvolatile substance to a volatile pure substance, see Fig. 6. In this case the freezing temperature decreases. For instance, we add ethylene glycol to the water on the radiator of a car to lower the freezing point below the lowest expected temperature.

It is quite obvious that the analysis will be the same to that already performed for a liquid-vapor system. In our present case, the solid phase can be only composed of the solvent, so we can write Eq. (50) as:

$$\frac{dx_i}{x_i} = -\frac{\left(h_i^{solid} - h_i^{liq}\right)}{RT^2} dT \tag{53}$$

In the case of solidification, the only approximations that we can make are that of molar enthalpy of solidification equal to the pure component enthalpy of solidification, and that this phase change enthalpy is constant over the temperature range of interest. Thus, Eq. (53) can be integrated to yield:
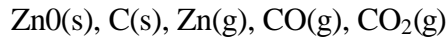
$$\ln x_i = -\frac{h_{if}\left(T_f - T_{f0}\right)}{RT_f T_{f0}} \tag{54}$$

and in terms of the final freezing temperature we can write:

$$T_f = \frac{h_{if} T_{f0}}{h_{if} + RT_{f0} \ln x_i} \tag{55}$$

Problems

1.- Solid zinc oxide is reduced by solid carbon at high temperature. The system is in equilibrium and found to contain the following species:

　　　Zn0(s), C(s), Zn(g), CO(g), CO$_2$(g)

Find the degrees of freedom of the system.

2.- Solid solutions consisting of GaAs and InAs can be produced by equilibrating a gas mixture composed of H$_2$, HCl, InCl, GaCl and As$_4$. The composition of the solid solution is determined by the thermodynamic conditions of the system. In order to produce GaAs-InAs solid solution with a particular composition, how many intensive thermodynamic variables need to be fixed?