Introduction to Chemical Engineering: Thermodynamics of Separation Processes

Notes for the class Separation Process Technology

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Welcome

Welcome to the class Separation Process Technology. What is Chemical Engineering about? According to the AIChE (the biggest association of chemical engineers) it is the profession in which a knowledge of mathematics, chemistry, and other natural sciences gained by study, experience, and practice is applied with judgment to develop economic ways of using materials and energy for the benefit of mankind. As this is a rather broad definition, quite a few fields do belong to chemical engineering such as chemical reactions, separation processes, biological reactions, research on thermodynamics, energy conversion, solids processing, fluid dynamics, and construction and design of equipment. Many industrial fields apply chemical engineering knowledge such as the chemical-, food-, pharmaceutical-, energy-, or automotive industries. This class aims at giving you a first impression and an overview over these fields by studying the following specific topics: phase equilibrium thermodynamics, liquid-vapor and liquid-solid equilibria, flash evaporation and nucleation of particles and crystals, kinetic gas theory with applications, chemical reaction engineering (including ideal reactor design).

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Preprint submitted to Script *February 20, 2020*

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1.1. Introduction

In this section we provide the basis for the study of thermodynamic equilibrium for systems involving multiple chemical species and multiple phases. This requires extending the thermodynamics presented in previous classes (namely Thermodynamics I given by Prof. Poulikakos in the HS 2012; chapters 2, 6 and 8 of the corresponding script are particularly useful), which was more focused on single component systems.

1.2. An axiomatic approach to thermodynamics

Thermodynamics addresses macroscopic systems and processes related to heat, energy, and work consisting of a gargantuan number of elementary objects, either atoms or molecules, i.e. of the order of the Avogadro number, $N_A = 6 \times 10^{23}$. While classical thermodynamics is based on the first and the second law, which were first established through experimental observations and then plugged into a theoretical framework, our approach is axiomatic. We start from four postulates that establish a mathematical framework consistent with the physical reality, in which all thermodynamics can be developed rigorously. The justification of this approach is that chemical engineers need dealing with multicomponent multiphase systems, involving quantities that are much more difficult to observe and measure than those involved in for instance simple heat transfer problems.

1.2.1. Four Postulates

1^{st} *postulate. Simple systems* at equilibrium are completely characterized by the following *extensive* properties: internal energy U, volume V, and number of moles $n_1, n_2, \ldots, n_C$ of each of the C components i, with index $i = 1, 2, \ldots, C$.

Simple systems are characterized as such by being macroscopically homogeneous, isotropic, electrically neutral, chemically inert, under no external field influence, and large enough to neglect surface effects.
For an *extensive* property its value U for a system consisting of the combination of a number of subsystems is equal to the sum of the values $U^{(j)}$ of the same property for each subsystem j, i.e.: $U = \Sigma_j U^{(j)}$, etc.

2^{nd} *postulate.* At equilibrium, there exists a function S defined in terms of the extensive quantities above, i.e. $S = S(U, V, n_1, n_2, \ldots, n_C)$, which is called entropy. This is the so-called *entropy representation.*
At equilibrium the quantities U, V, n_1, …, n_C attain values, which must at the same time be compatible with the external constraints and maximize the entropy S. Therefore at equilibrium, S is maximum, $dS = 0$ and $d^2S < 0$.

3^{rd} *postulate.* The entropy S is also an extensive property, i.e. $S = \Sigma_j S^{(j)}$. If this is applied to λ identical subsystems, the Euler formula is derived:

$$S(\lambda U, \lambda V, \lambda n_1, \lambda n_2, \ldots, \lambda n_C) = \lambda S(U, V, n_1, n_2, \ldots, n_C). \tag{1}$$

Moreover, S is a continuous, differentiable, and monotonically increasing function of U, i.e. $(\partial S/\partial U)_{V,n_i} > 0$. As a consequence S can be inverted, and the internal energy U can be expressed as a function of S, V, n_1, …, n_C, i.e. $U = U(S, V, n_1, n_2, \ldots, n_C)$. This is the so-called *internal energy representation.*

4^{th} *postulate.* The entropy is zero when:

$$S = 0 \leftrightarrow \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = 0 \tag{2}$$

This condition applies at a temperature T =0 K, i.e. at the absolute zero temperature.

Four postulates

1. Simple systems at equilibrium are defined by their U,V,$n_1, n_2, ..., n_C$.

2. $S = S(U, V, n_1, n_2, ..., n_C)$; U,V,$n_1, n_2, ..., n_C$ attain values compatible with the external constraints that maximize $S \rightarrow dS = 0$;$d^2S < 0$

3. S is extensive, i.e. $S = \sum_j S_j$; S is continuous, differentiable, monotonically increasing function of $U \rightarrow U$ representation: $U = U(S, V, n_1, n_2, ..., n_C)$

4. $S = 0 \leftrightarrow (\partial U/\partial S)_{V,n_1,n_2,...,n_C} = 0 \rightarrow S = 0$ at $T = 0$ K

1.2.2. Entropy Representation

According to the 2^{nd} postulate:

$$S = S(U, V, n_1, n_2, \ldots, n_C); \tag{3}$$

therefore its differential is given as:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n_i} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n_i} dV + \sum_{i=1}^{C} \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} dn_i \tag{4}$$

All partial derivatives in the equation above are *intensive* properties. If the system under consideration is split into a number of subsystems, all subsystems exhibit the same *intensive* properties of the original system, whereas their *extensive* properties, such as V or U or n_i, are equal to that of the original system multiplied by the ratio between the size of the subsystem and that of the original system. We will see when introducing the conditions for thermodynamical equilibrium that among the *intensive* properties there are system temperature T and system pressure P, which are obviously the same for all parts of the original homogeneous system.

1.2.3. Internal Energy Representation

Let us consider the function defining the internal energy U (see the 3^{rd} postulate):

$$U = U(S, V, n_1, n_2, \ldots, n_C); \tag{5}$$

its differential is:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{C} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \tag{6}$$

1.3. Thermodynamic Equilibrium

The fundamental problem of thermodynamics can be described as follows. Given a composite system, isolated from the external world, what is its final equilibrium state after some of the internal constraints are removed? For example, if in a closed system consisting of two subsytems A and B, a rigid, adiabatic, impermeable wall is suddenly replaced by a rigid, impermeable, but heat conducting wall, what will be the final temperature of the two subsystems? Or alternatively, what happens if the same wall is replaced by a rigid but permeable wall (a membrane) instead?

We will analyze thermodynamic equilibrium using the entropy and internal energy representations introduced above, and we will see that the partial derivatives of the entropy function play a crucial role. For the sake of simplicity, we will recast the differential form of the entropy function as follows:

$$dS = \underbrace{\alpha}_{\left(\frac{\partial S}{\partial U}\right)_{V,n_i}} dU + \underbrace{\beta}_{\left(\frac{\partial S}{\partial V}\right)_{U,n_i}} dV + \sum_{i=1}^{C} \underbrace{\gamma_i}_{\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}}} dn_i \tag{7}$$

We will investigate three different cases to derive conditions for thermal, mechanical, and equilibrium with respect to mass transfer.

1.3.1. Thermal Equilibrium

We consider an isolated system which consists of two subsystems A and B. These subsystems are separated by a rigid, impermeable, but heat conducting wall, as shown schematically in figure 1. In other words, only heat can be transported from one subsystem to the other. The following constraints apply to this system:

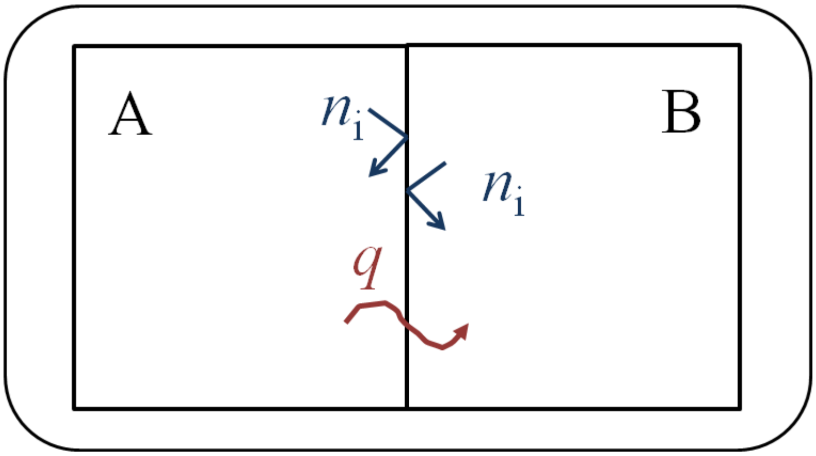

Figure 1: System consisting of subsystems A and B which are separated by a rigid, impermeable, heat conducting wall.

$$\text{isolated system:} \quad dU = dV = dn_i = 0 \ \ (i = 1, \ldots, C) \tag{8}$$

$$\text{rigid wall:} \quad dV^A = dV^B = 0 \tag{9}$$

$$\text{impermeable wall:} \quad dn_i^A = dn_i^B = 0 \ \ (i = 1, \ldots, C) \tag{10}$$

$$\text{diathermal wall:} \quad dU^A, dU^B \neq 0; dU = dU^A + dU^B; dU^B = -dU^A \tag{11}$$

At equilibrium $dS = 0$ (see the 2^{nd} postulate); substituting the relationships above that enforce the physical constraints specified for the system under examination yields:

$$0 = dS = dS^A + dS^B = \alpha^A dU^A + \alpha^B dU^B = (\alpha^A - \alpha^B) dU^A \tag{12}$$

As a consequence, the condition for thermal equilibrium is:

$$\alpha^A = \alpha^B \tag{13}$$

From physical experience we know that heat flux between two bodies (or phases) occurs only if the two temperatures are different, and accordingly there is equilibrium, i.e. no heat flux, only if the two temperatures are the same. This implies that $\alpha = \alpha(T)$. The following thought experiment can elucidate the relationship between α and T. If the system were initially slightly out of equilibrium (e.g. $\alpha^A > \alpha^B$, with the difference small enough to allow using the differentials to express the changes of the thermodynamic variables occurring when the system evolves towards equilibrium), it would exhibit the following entropy and internal energy changes as it reaches equilibrium (this is the finite difference form of the right hand side of Equation 12):

$$\Delta S = (\alpha^A - \alpha^B) \Delta U^A \tag{14}$$

The entropy evolves towards the maximum that it attains at equilibrium, hence $\Delta S > 0$, whereas the term $(\alpha_A - \alpha_B) > 0$ by definition. Therefore from the last equations $\Delta U^A > 0$, and the heat flows from system B to system A. the simplest relationship between α and T that fulfills this criterion as well as that that the heat flows from a hot to a cold body is the following:

$$\alpha = \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, n_i} . \tag{15}$$

Accordingly $T^A = T^B$ at equilibrium and entropy has the units of an energy per unit temperature change, i.e. J/K.

1.3.2. Mechanical Equilibrium

We consider an isolated system which consists of two subsystems A and B, which are separated by a moveable, impermeable, heat conducting wall, e.g. a piston (see figure 2). The following constraints apply to this system:

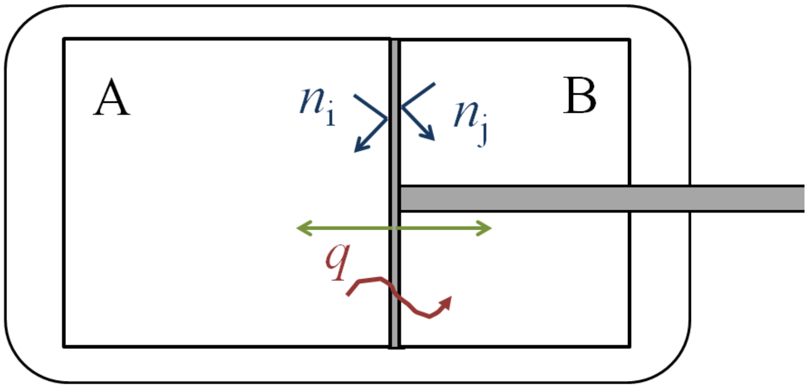

Figure 2: System consisting of subsystems A and B which are separated by a moveable piston which is impermeable but heat conducting.

$$\text{isolated system:} \quad dU = dV = dn_i = 0 \;\; (i = 1, \ldots, C) \tag{16}$$

$$\text{impermeable wall:} \quad dn_i^A = dn_i^B = 0 \;\; (i = 1, \ldots, C) \tag{17}$$

$$\text{diathermal wall:} \quad dU^A, dU^B \neq 0; dU = dU^A + dU^B; dU^B = -dU^A \tag{18}$$

$$\text{moving wall:} \quad dV^A, dV^B \neq 0; dV = dV^A + dV^B; dV^B = -dV^A \tag{19}$$

At equilibrium $dS = 0$ (see the 2^{nd} postulate); substituting the relationships above yields:

$$0 = dS = dS^A + dS^B = \left(\frac{1}{T^A} - \frac{1}{T^B}\right) dU^A + (\beta^A - \beta^B) dV^A \tag{20}$$

Since $T^A = T^B$, the condition for mechanical equilibrium is:

$$\beta^A = \beta^B. \tag{21}$$

Equilibrium in this case is of a mechanical nature, and is associated to an equilibrium of forces, which in this example implies that the pressures in the two chambers (subsystems) are the same; therefore β depends on pressure. Since $\beta = (\partial S/\partial V)_{U,n_i}$, it has the units of energy per unit temperature change and unit volume, i.e. the units of a pressure per unit temperature change. The simplest definition of β that is consistent with these conditions is:

$$\beta = \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,n_i} \tag{22}$$

Since we already know that at equilibrium $T^A = T^B$, therefore mechanical equilibrium requires that $P^A = P^B$.

1.3.3. Equilibrium with respect to mass transfer

By extending the concept used to derive conditions for thermal and mechanical equilibrium, we derive the conditions for equilibrium with respect to mass transfer. The closed system consists now of two subsystems A and B that are separated by a rigid and heat conducting wall that is permeable for species i but not for any other species $j \neq i$ (e.g. a membrane, see figure 3). The following

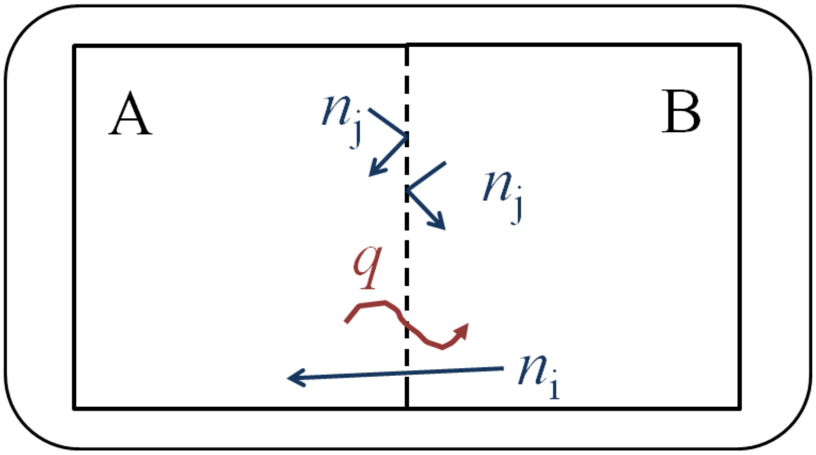

Figure 3: System consisting of subsystems A and B which are separated by a rigid, impermeable to species $i \neq j$ but permeable to species i, heat conducting wall.

constraints apply to this system:

$$\text{isolated system:} \quad dU = dV = dn_i = 0 \;\; (i = 1, \ldots, C) \tag{23}$$

$$\text{rigid wall:} \quad dV^A = dV^B = 0 \tag{24}$$

$$\text{diathermal wall:} \quad dU^A, dU^B \neq 0; dU = dU^A + dU^B; dU^B = -dU^A \tag{25}$$

$$\text{impermeable to } j\text{:} \quad dn_j^A = dn_j^B = 0 \;\; (j = 1, \ldots, C; j \neq i) \tag{26}$$

$$\text{permeable to } i\text{:} \quad dn_i^A, dn_i^B \neq 0; dn_i = dn_i^A + dn_i^B; dn_i^B = -dn_i^A \tag{27}$$

At equilibrium $dS = 0$ (see the 2^{nd} postulate); substituting the relationships above yields:

$$0 = dS = dS^A + dS^B = \left(\frac{1}{T^A} - \frac{1}{T^B}\right) dU^A + (\gamma_i^A - \gamma_i^B) dn_i^A \tag{28}$$

Since at equilibrium $T^A = T^B$, then $\gamma_i^A = \gamma_i^B$ as well, where:

$$\gamma_i = \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} \tag{29}$$

Neither intuition nor physical observation provide us with a measurable quantity associated to equilibrium with respect to mass transfer that can play the same role as temperature or pressure in the cases of thermal or mechanical equilibrium. It is in fact easy to see that the concentration of the species i in the two phases cannot be a criterion for equilibrium with respect to mass transfer. It follows that the quantity γ_i defined through the derivative in the last equation is indeed the decisive property in this context. For a number of reasons, including the fact that mass transfer cannot be decoupled from heat transfer, a new quantity, the chemical potential μ_i of species i has been introduced according to the following definition:

$$\gamma_i = \frac{-\mu_i}{T} = \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} . \tag{30}$$

According to this definition the chemical potential μ_i is a specific energy, i.e. it has units of energy per mole or J/mol. Since temperature has to be the same at equilibrium, also the chemical potential of the species that can be transferred from one subsystem to the other has to be the same in the two subsystems, i.e. $\mu_i^A = \mu_i^B$. Finally, the minus sign in the definition of μ_i stems from the requirement that mass flows from the subsystem with the larger μ_i value to that with the smaller μ_i value. This can be verified by a similar thought experiment like the one discussed in the context of thermal equilibrium. If we assume a slight initial unbalance with $\mu_i^A > \mu_i^B$ but $T^A = T^B$ (i.e. the two subsystems are already at thermal equilibrium) and we calculate the entropy change upon attainment of equilibrium, we obtain:

$$\Delta S = \left(\frac{-\mu_i^A}{T^B} - \frac{-\mu_i^B}{T^B} \right) \Delta n_i^A \tag{31}$$

Since ΔS must be positive and the term between brackets is negative by definition, then also $\Delta n_i^A < 0$ thus implying that molecules of species i are transported from subsystem A to subsystem B as required.

Three kinds of equilibrium can be distinguished:

Thermal equilibrium: $T^A = T^B$

Mechanical equilibrium: $P^A = P^B$

Equilibrium with respect to mass transfer: $\mu_i^A = \mu_i^B$

Using the results above, we can obtain a new expression for the total differential of the entropy function S:

$$dS = \underbrace{\frac{1}{T}}_{\left(\frac{\partial S}{\partial U}\right)_{V,n_i}=\alpha} dU + \underbrace{\frac{P}{T}}_{\left(\frac{\partial S}{\partial V}\right)_{U,n_i}=\beta} dV + \sum_{i=1}^{C} \underbrace{\left(\frac{-\mu_i}{T}\right)}_{\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}}=\gamma_i} dn_i \tag{32}$$

By multiplying the equation above by T and solving for the differential of the internal energy dU one obtains the following expression for the total derivative of the function $U = U(S, V, n_1, n_2, \ldots, n_C)$:

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i \tag{33}$$

Note that this implies:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} \tag{34}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,n_i} \tag{35}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} \tag{36}$$

1.4. Euler Equation

As a postulate we have taken that the entropy is a function of internal energy, volume, and composition:

$$S = S(U, V, n_1, n_2, ...) \tag{37}$$

Considering the three different types of equilibrium, we were able to identify the meaning of all terms in the total differential so that

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dn_i \tag{38}$$

or reformulated in the internal energy representation:

$$dU = TdS - PdV + \sum_i \mu_i dn_i \tag{39}$$

As S,U,V, and the composition n_i are extensive properties one can write for λ identical subsystems having entropy $S = S(U, V, n_1, n_2, ...)$ the following relationship:

$$S(\lambda U, \lambda V, \lambda n_1, \lambda n_2, ...) = \lambda S(U, V, n_1, n_2, ...) \tag{40}$$

Differentiating this equation by λ yields

$$\frac{\partial S}{\partial(\lambda U)}U + \frac{\partial S}{\partial(\lambda V)}V + \sum_i \frac{\partial S}{\partial(\lambda n_i)}n_i = S \tag{41}$$

This equation is true for all values of λ, hence for $\lambda = 1$ we find that

$$S = \frac{U}{T} + \frac{PV}{T} - \sum_i \frac{\mu_i n_i}{T} \tag{42}$$

or

$$U = TS - PV + \sum_i \mu_i n_i \tag{43}$$

Note that these are properties of functions fulfilling Euler equation:

$$\lambda f(x) = f(\lambda x) \tag{44}$$

For those functions one can always write by differentiating with respect to λ

$$f(x) = f'(\lambda x)x = \{\text{if}\lambda = 1\} = f'(x)x \tag{45}$$

Let us consider the special case with one component only ($C = 1 \Rightarrow n_1 = n$) in which we set $\lambda = 1/n$.

$$S\left(\frac{U}{n}, \frac{V}{n}, \frac{n}{n}\right) = \frac{1}{n}S(U, V, n) \tag{46}$$

The fractions do have a special meaing

- $\frac{U}{n}$: molar internal energy u
- $\frac{S}{n}$: molar entropy s
- $\frac{V}{n}$: molar volume v

So we can rewrite

$$s = S(u, v, 1) = s(u, v) \tag{47}$$

Accordingly

$$u = u(s, v) \tag{48}$$

u, v, s are intensive properties in contrast to the extensive properties U,V, and S. The fundamental equations in differential form can be written equivalently:

$$ds = \frac{1}{T}du + \frac{P}{T}dv \tag{49}$$

$$du = Tds - Pdv \tag{50}$$

The U-representation and S-representation provide all thermodynamic information on a system, but are not very convenient because they have only extensive variables as dependent variables. T and P are easier to handle as, for example, there exists no device to measure entropy directly. On the other side, there are many instruments to measure P and T.

Mathematics can be used to derive new potentials (instead of using U or S) to describe equilibrium that depend on T and P or other quantities instead. The method is called Legendre transformation which we will discover in the next section.

1.5. Legendre Transformations

As stated in the first postulate, a system is entirely characterized by the internal energy U, the volume V, and the composition n_i as $S(U, V, n_1, \ldots, n_C)$. The entropy function S can be inverted which yields the internal energy function $U(S, V, n_1, \ldots, n_C)$ which also fully characterizes the system. This function depends on the quantities S, V, n_i for $i = 1, 2, \ldots, C$. Some of these are not very practical if one wants to measure a system in reality (as for example, there is no method to measure the entropy directly). In this chapter we are investigating possibilities to change this dependence.

Helmholtz free energy. Let us consider the internal energy $U = U(S, V, n_1, \ldots, n_C)$ in the differential form:

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i \tag{51}$$

The partial derivative of U with respect to S is

$$\left(\frac{\partial U}{\partial S}\right)_{V,n_i} = T = T(S, V, n_1, \ldots, n_C) \tag{52}$$

By inverting the functional form for T we can find a new functional form for S which we call $\tilde{S}$.

$$T(S, V, n_1, \ldots, n_C) \to S = \tilde{S}(T, V, n_1, \ldots, n_C) \tag{53}$$

If one wants to switch $S \leftrightarrow T$, we have two options that are

(I) invert T and S to obtain a new function f:

$$U = U(\tilde{S}(T, V, n_1, \ldots, n_C), V, n_1, \ldots, n_C) = \tilde{U}(T, V, n_1, \ldots, n_C) \tag{54}$$

The old functional form U is thus transformed into a new function form $\tilde{U}$ which does now depend on T rather than S.

For a single component system where $C = 1$ one finds that $U = \tilde{U}(T, V, n)$. Using molar quantities one can write $u = \tilde{u}(T, v)$ This approach is of course valid, however it turns out to be less practical.

(II) The second option to find a functional form which does not depend on S but instead on T is a Legendre Transformation. Applying a Legendre Transformation to the internal energy and changing S with T yields a new quantity called Helmholtz Free Energy A which is defined as:

$$A = U - S\left(\frac{\partial U}{\partial S}\right)_{V, n_i} \tag{55}$$

Using the functions $\tilde{U}$ and $\tilde{S}$ that depend on T, V, and n_i allows expressing also A as a function of these variables:

$$A = \tilde{U} - T\tilde{S} = A(T, V, n_1, \ldots, n_C) \tag{56}$$

The corresponding differential form is

$$dA = dU - TdS - SdT = -SdT - PdV + \sum_{i=1}^{C} \mu_i dn_i \tag{57}$$

The following properties result:

$$\left(\frac{\partial A}{\partial T}\right)_{V,n_i} = -S; \qquad \left(\frac{\partial A}{\partial V}\right)_{T,n_i} = -P; \qquad \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \mu_i \tag{58}$$

In comparison to

$$U = ST - PV + \sum_{i=1}^{C} \mu_i n_i \tag{59}$$

for the Helmholtz free energy:

$$A = -PV + \sum_{i=1}^{C} \mu_i n_i \tag{60}$$

One should observe the symmetry of the partial derivatives $(\partial U/\partial S)_{V,n_i} = T$ and $(\partial A/\partial T)_{V,n_i} = -S$. This is a key feature of the Legendre Transformation and depends on the fact that the new thermodynamic potential A is defined as the difference between the old potential U and the product of the variables to be swapped, i.e. S and T. The same concept will now be used to swap V and P.

Enthalpy. Again considering the internal energy $U(S, V, n_i)$ but now looking for a function to replace V with $-P$ we convert the internal energy to a new state function called enthalpy $H(S, P, n_i)$. First, we consider the partial derivative of U with respect to V to obtain a new functional form:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = P(S, V, n_1, \ldots, n_C) \tag{61}$$

The enthalpy is then defined as:

$$H = U - V\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = U + PV = H(S, P, n_1, \ldots, n_C) \qquad (62)$$

The total differential (starting from $H = U + PV$) reads:

$$dH = dU + PdV + VdP = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i + PdV + VdP \qquad (63)$$

which yields

$$dH = TdS + VdP + \sum_{i=1}^{C} \mu_i dn_i \qquad (64)$$

As a comparison the following properties hold

$$\left(\frac{\partial H}{\partial S}\right)_{P,n_i} = T; \qquad \left(\frac{\partial H}{\partial P}\right)_{S,n_i} = V; \qquad \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_{j\neq i}} = \mu_i \qquad (65)$$

Note again the symmetry $(\partial U/\partial V)_{S,n_i} = -P$ and $(\partial H/\partial P)_{S,n_i} = V$. The enthalpy is then

$$H = TS + \sum_{i=1}^{C} \mu_i n_i \qquad (66)$$

Gibbs Free Energy. The enthalpy H depends on entropy S, pressure P, and the systems composition n_i. We are now looking for a quantity that does only depend on easy measurable independent variables instead that are P and T. In order to honor its discoverer this quantity is called Gibbs Free Energy G. We are seeking a quantity that depends on temperature, pressure and composition (expressed in number of moles): $G = G(T, P, n_1, \ldots, n_C)$. Applying a Legendre Transformation on H for exchanging S to T yields (using equations 43 and 62):

$$G = H - S\left(\frac{\partial H}{\partial S}\right)_{P,n_i} = H - TS = \sum_i \mu_i n_i = G(T, P, n_1, ..., n_C) \qquad (67)$$

The differential yields

$$dG = dH - TdS - SdT = -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i \tag{68}$$

Therefor the following relationships can be derived:

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S; \qquad \left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V; \qquad \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i \tag{69}$$

Note again the symmetry of the partial derivatives $(\partial H/\partial S)_{P,n_i} = T$ and $(\partial G/\partial T)_{P,n_i} = -S$.

The last equation in equation 69 is the most important defintion of μ_i, the chemical potential of species i. In fact it establishes that μ_i is the partial molar Gibbs free energy $\overline{G_i}$

$$\overline{G_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i(T, P, n_1, \ldots, n_C) \tag{70}$$

For any thermodynamic quantity M, its partial molar quantity is obtained in general as

$$\overline{M_i} = \left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{71}$$

i.e. as its derivative with respect to n_i as constant T,P and n_i with $j \neq i$. Please recall that it is the chemical potential which we identified to characterize thermodynamic equilibrium with respect to mass transfer.

For a single component system where $C = 1$ the equation above reduces to

$$G = n\mu \tag{72}$$

and

$$dG = -SdT + VdP + \mu dn \tag{73}$$

$$\overline{G} = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial (ng)}{\partial n}\right)_{T,P} = g\left(\frac{\partial n}{\partial n}\right)_{T,P} = g\left(T,P\right) = \mu\left(T,P\right) \tag{74}$$

where g is the molar Gibbs free energy $g = G/n$. At constant n one obtains

$$dg = d\mu = -sdT + vdP \tag{75}$$

For a multicomponent system taking into account that the sum of all substances i in a system is

$$n = \sum_{i=1}^{C} n_i \tag{76}$$

we can define the molar fraction z_i of component i as

$$z_i = \frac{n_i}{n} \tag{77}$$

with values of z_i between 0 and 1 and $\sum_{i=1}^{C} z_i = 1$. Please note that due to convention, a generic molar fraction is referred to using the symbol z; for liquid phases we use x_i and for gas phases y_i instead. These molar fractions z_i for all components $i = 1, \ldots, C$ can be written as vector $\underline{z} = (z_1, z_2, \ldots, z_C)^T$. Since μ_i is an intensive property, therefore

$$\mu_i(T, P, n_1, \ldots, n_C) = \mu_i(T, P, z_1, \ldots, z_C) = \mu_i(T, P, \underline{z}) \tag{78}$$

and we see that μ_i depends only on intensive properties.

Overview over Legendre Transformations:

$U(S,V,n_i) \overset{S\leftrightarrow T}{\rightarrow} A(T,V,n_i)$

$U(S,V,n_i) \overset{V\leftrightarrow P}{\rightarrow} H(S,P,n_i)$

$H(S,P,n_i) \overset{S\leftrightarrow T}{\rightarrow} G(T,P,n_i)$

$A(T,V,n_i) \overset{V\leftrightarrow P}{\rightarrow} G(T,P,n_i)$

1.6. Cross Derivatives

Let us recall the general properties of functions of more than one variable, e.g. $f(x,y)$. If f is continuous and differntiable in x and y, then the second order cross-derivatives are the same independent of the order of differentiation, i.e.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{79}$$

When this general property is applied to G, one obtains a very important relationship concerning the dependence of the chemical potential on pressure. From equation 69, particularly from the second and the third equation, one obtains

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \overline{V_i} \tag{80}$$

where the defintion of partial molar volume has been exploited.

In the case of a single component, the last equation reads:

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{T,P} = v \tag{81}$$

where v is the molar volume.

The Gibbs Free Energy depends only on measurable quantities $G = G(T, P, n_i)$

The derivative of G with respect to the number of moles of component i at constant temperature, pressure, and number of moles of species $j \neq i$ defines the chemical potential of component i,

i.e. this defines the condition for equilibrium with respect to mass transfer.

μ_i only depends on intensive properties $\mu_i(T, P, \underline{z})$

1.7. Gibbs Phase Rule

A phase is a region of a system in which the chemical composition and physical properties are constant from a macroscopic point of view. Think of a glass of water with ice in it. The fluid is one phase and the ice is a second phase. How many phases can coexist in equilibrium? This question can be answered using the properties that we have exploited within previous chapters. In a closed system with C components and φ phases $\alpha, \beta, \gamma, ...$ in equilibrium a number of constraints apply. The system is shown in figure 4.

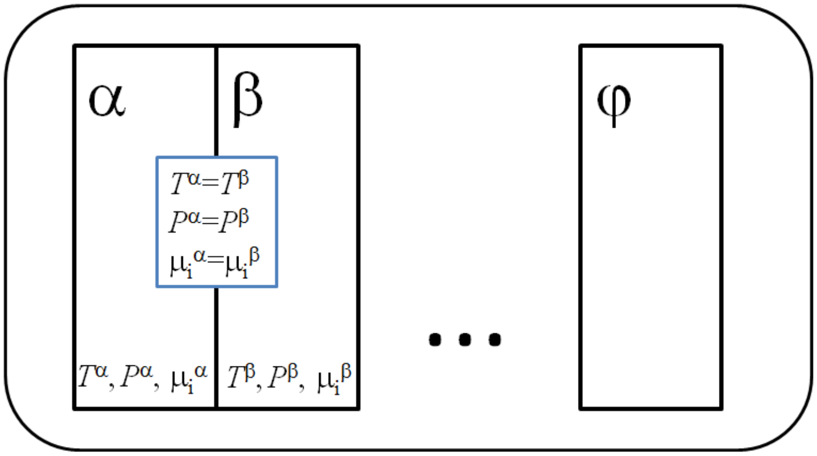

Figure 4: An isolated system consisting of $\alpha, \beta, \ldots, \varphi$ subsystems. Each subsystem has its own temperature T, pressure P, and consists of molecules of species $i = 1, 2, \ldots, C$. We require thermodynamic equilibrium between each subsystem. The equilibrium conditions for thermal (equal temperatures), mechanical (equal pressure) and equilibrium with respect to mass transfer (equal chemical potential for all species i) apply.

Thermal equilibrium requires that:

$$T^{\alpha} = T^{\beta} = ... = T^{\varphi} \Rightarrow \varphi - 1 \text{ equations} \tag{82}$$

Mechanical equilibrium means that:

$$P^{\alpha} = P^{\beta} = ... = P^{\varphi} \Rightarrow \varphi - 1 \text{ equations} \tag{83}$$

Equilibrium with respect to mass transfer requires that the chemical potential of each substance i is the same in each phase:

$$\mu_i^{\alpha} = \mu_i^{\beta} = ... = \mu_i^{\varphi} \qquad i = 1, \ldots, C \qquad \Rightarrow C(\varphi - 1) \text{ equations} \tag{84}$$

Summing up the number of equations yields $C\varphi + 2\varphi - C - 2$. We also have a number of unknown quantities, i.e. for every phase, T, P and the composition expressed as molar fraction (Note that $\sum_{i=1}^{C} z_i = 1$):

$$T^{\alpha}, T^{\beta}, ...T^{\varphi} \Rightarrow \varphi \text{ unknowns} \tag{85}$$

$$P^{\alpha}, P^{\beta}, ...P^{\varphi} \Rightarrow \varphi \text{ unknowns} \tag{86}$$

$$z_i^{\alpha}, z_i^{\beta}, ...z_i^{\varphi} \qquad i = 1, \ldots, C \qquad \Rightarrow \varphi(C - 1) \text{ unknowns} \tag{87}$$

The total number of unknowns is therefore $\varphi(1 + C)$. The degrees of freedom F for the system are therefore

$$F = \varphi(1 + C) - C\varphi - 2\varphi + C + 2 \tag{88}$$

$$F = C + 2 - \varphi \tag{89}$$

This equation is also known as Gibbs Phase Rule. It tells us how many instenive properties can be manipulated independently without changing the number of phases. For a single component system, the equation reads for example

$$F = 3 - \varphi \tag{90}$$

For (see Figure 5)

- $\varphi = 1$: F=2 $\Rightarrow$ in a $P-T$-diagram this is equivalent to an area, i.e. the solid, liquid, or vapor phase areas;
- $\varphi = 2$: F=1 $\Rightarrow$ in a $P-T$-diagram this is equivalent to a line, e.g. the boiling curve along the liquid to vapor areas of equilibrium;
- $\varphi = 3$: F=0 $\Rightarrow$ in a $P-T$-diagram this is equivalent to a point, e.g. the triple point where all three phases are at equilibrium.

Using this knowledge and combining it with a number of measurements one is able to construct a single component phase diagram. An example is given in the $P-T$ diagram in figure 5. Two single phase regions are separated from each other by a line: The boiling curve (vapor-liquid), the sublimation line (solid-vapor), and the melting line (solid-liquid).

The boiling curve (or vapor pressure curve) will be of central interest in this lecture. This curve is the pressure exerted by a vapor in thermodynamic equilibrium with its liquid phase at a given temperature in a closed system. The vapor pressure is a function of temperature:

$$P^V(T) \tag{91}$$

One common empirical expression to describe $P^V(T)$ is the Antoine equation which uses three substance specific constants A, B, and C to provide vapor pressure data for a certain temperature range. If you use this equation, keep an eye on the units that have been used to calculate A, B, and C.

$$\log P^V(T) = A - \frac{B}{C+T} \tag{92}$$

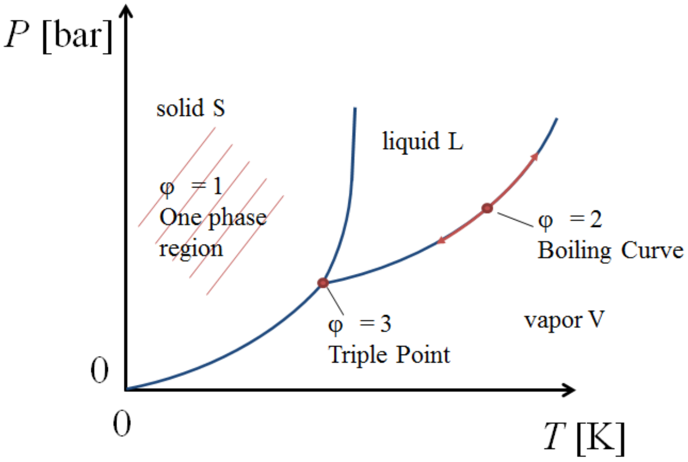

Figure 5: Single Component Diagram for illustrating the Gibbs Phase Rule.

The number of degrees of freedom of a system are:

$F = C + 2 - \varphi$

1.8. Pure Ideal Gases

Up to now, we have investigated thermodynamic conditions that define equilibrium between different phases. Next we will explore single phase regions and combine these findings with these equilibrium requirements to understand the behavior of multi-phase systems. We start by considering the gas phase. The most simple case is the ideal gas which behaves according to the ideal gas law (an equation of state: EOS). Equations of state define the state of matter in a certain range of physical conditions and connect state variables (such as temperature, pressure, volume, or internal energy). Such an EOS has the general form

$$f(P, T, V, n_1, n_2, .., n_C) \tag{93}$$

Where does an EOS come from? Taking the fundamental equation for the Gibbs Free Energy we already found that:

$$dG = -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i \tag{94}$$

Regarding the behavior of gases, one is particularly interested in the dependence of the volume on other state variables. The volume can be seen as the derivative of the Gibbs Free Energy with respect to pressure. The volume itself will depend on temperature, pressure, and the composition (given in number of moles):

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V(T, P, n_1, n_2, ..., n_C) \tag{95}$$

We are actually looking for a function which expresses this dependence. The ideal gas law itself is well known and was found empirically (law of Boyle-

Mariotte, laws of Gay-Lussac):

$$PV = nRT \tag{96}$$

by dividing the above equation by n we find that

$$Pv^* = RT \tag{97}$$

note that we are now considering the molar volume v instead of the volume V and that the * indicates that this equation is only true for ideal gases (ideal gas behavior, see script Prof. Poulikakos section 3.5). As we found out that the chemical potential is of central interest, we would like to use the EOS to calculate the value of the chemical potential and therefore to be able to write the condition that gives equilibrium with respect to mass transfer.

Recalling equation 75 for an ideal gas:

$$d\mu^* = v^* dP - s^* dT \tag{98}$$

At constant temperature ($dT = 0$):

$$d_T \mu^* = v^* dp \tag{99}$$

$$d_T \mu^* = \frac{RT}{P} dp = RT d_T \ln P \tag{100}$$

1.9. Pure Real Gases

The ideal gas law is a useful approximation for a number of gases (especially noble gases) and for a certain range of physical conditions (mostly low pressure). However, many applications require a more exact knowledge of the current state of a system. In order to match these demands, new EOS have been developed and are still subject to research. Among these EOS there are rather simple models that take into account interactions between gas molecules (such as the Van-der-Waals EOS), apply knowledge from statistical mechanics (such as the Virial EOS) or are even based on quantum chemical calculations. All of these EOS for gases aim at giving a function to express v.

1.9.1. Compressibility

One can define a term called compressibility Z:

$$Z(T, P, v) = \frac{Pv}{RT} \tag{101}$$

If one uses this defintion for the ideal gas law one easily finds that

$$Z(T, P, v) = \frac{Pv^*}{RT} = 1 \tag{102}$$

The less a constant a gas behaves like an ideal gas, the bigger the difference of Z from 1 will be:

$$\text{Ideal Gas: } Z(T, P, v) = 1 \leftrightarrow \text{ Real Gas: } Z(T, P, v) \neq 1 \tag{103}$$

1.9.2. Van-der-Waals EOS

The Van-der-Waals EOS is an extension of the ideal gas law an adds constants to cover two effects. a is a measure for the pairwise interaction between gas molecules (e.g. the Van-der-Waals force) and b is a constant to define the volume occupied by gas molecules themselves

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \tag{104}$$

which can be rewritten as

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{105}$$

or (*demonstration during the lecture*)

$$Pv = RT + \left(b - \frac{a}{RT}\right) P + ... \tag{106}$$

Figure 6 shows a schematic $P - v$ diagram of the Van-der-Waals EOS at a constant temperature.

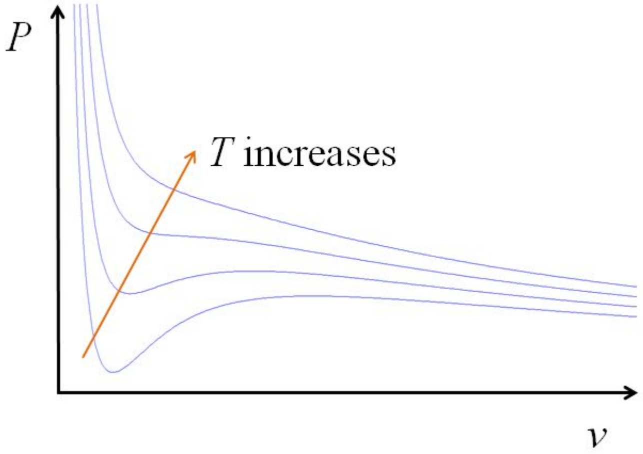

Figure 6: Schemativ $P - v$ diagram of the Van-der-Waals EOS at four differtent temperatures.

1.9.3. Virial EOS

The virial EOS is an another approach to describe v as a function. It is a Taylor series which comes from statistical mechanics. Two formulations are possible. The so called Leiden-Form is a series in the density ρ

$$Z(T, P, v) = 1 + B\rho + C\rho^2 + D\rho^3 + ... \tag{107}$$

The Berlin-Form uses pressure

$$Z(T, P, v) = 1 + B'P + C'P^2 + D'P^3 + ... \tag{108}$$

$B, C, D, ...$ and $B', C', D', ...$ respectively are functions of temperature. In many cases, stopping the development of the series after the second term yields a description that is sufficient which is

$$Z(T, P, v) = 1 + B'(T)P \tag{109}$$

The temperature for which B' is zero is called Boyle temperature, which indicates ideal gas behavior. Please note that one can either include R (the gas constant) into B or write it seperately leading to different expressions for B, which is usually given as an empirical equation, finally leading to many different formulations that can be found.

Gases can be characterized by the compressibility $Z(T, P, v) = \frac{Pv}{RT}$

Ideal gases: $Z(T, P, v) = 1$

Different EOS can be used to describe real gases.

1.10. Fugacity

In the scope of this class, the ideal gas law, the Van-der-Waals EOS, and the virial EOS will be the only EOS considered. Rather than recalculating all thermodynamic quantities for every EOS we will focus on the chemical potential μ (as this is the quantity that defines equilibrium with respect to mass transfer). We recall for an ideal gas (equation 100) for $T =$const.:

$$d_T\mu^* = \frac{RT}{P}dP \tag{110}$$

For a real gas one could insert an expression for v and try to come up with an expression for μ. A much more comfortable approach however is to replace the pressures P and P_r in equation 110 by a new quantity called fugacity:

$$d_T\mu = RTd_T \ln f \tag{111}$$

where the relationship between the fugacity f and pressure P is given as

$$\lim_{P\to 0} \frac{f(T,P)}{P} = 1 \tag{112}$$

This means that for very low pressures where one reaches ideal gas behavior, pressure and fugacity are the same. Hence, one can imagine the quantity fugacity to be something like a corrected pressure (for the gas phase) to reflect real gas properties.

Instead of looking at the integrated equations for the chemical potential we can also look at the differential. For the ideal gas this was derived as (note that the subscript $_T$ indicates constant temperature):

$$d_T\mu^* = RTd\ln P \tag{113}$$

which is for non-ideal gases by replacing P with f

$$d_T\mu = RTd\ln f \tag{114}$$

Integrating from any state (or phase) α to state β yields

$$\mu^\alpha - \mu^\beta = RT\ln\frac{f^\alpha}{f^\beta} \tag{115}$$

If one wants to calculate either μ^α or μ^β we start using the reference state $_\mathrm{r}$:

$$\mu^\alpha = \mu^\alpha_\mathrm{r} + RT \ln \frac{f^\alpha}{f^\alpha_\mathrm{r}} \tag{116}$$

$$\mu^\beta = \mu^\beta_\mathrm{r} + RT \ln \frac{f^\beta}{f^\beta_\mathrm{r}} \tag{117}$$

If we define a common reference state for the chemical potential such that

$$\mu^\alpha_\mathrm{r} = \mu^\beta_\mathrm{r} \text{ and } f^\alpha_\mathrm{r} = f^\beta_\mathrm{r} \tag{118}$$

the requirement for equilibrium with respect to mass transfer ($\mu^\alpha = \mu^\beta$) is only fullfilled when

$$f^\alpha(T,P) = f^\beta(T,P) \tag{119}$$

This is called isofugacity condition which has to be fulfilled if two phases are in equilibrium with each other. Exploiting the fugacity for a real gas we can write by integrating in the variabloe p from a reference gas pressure P_r to the actual pressure P

$$\frac{1}{RT} d_T\mu = d_T \ln f = \frac{v}{RT} d_T P \tag{120}$$

$$\ln \frac{f(T,P)}{f(T,P_\mathrm{r})} = \int_{P_\mathrm{r}}^{P} \frac{v}{RT} dp \tag{121}$$

In general

$$\ln \frac{P}{P_\mathrm{r}} = \int_{P_\mathrm{r}}^{P} \frac{1}{p} dp \tag{122}$$

Substracting the two equations yields

$$\ln \frac{f(T,P)}{f(T,P_\mathrm{r})} \frac{P_\mathrm{r}}{P} = \int_{P_\mathrm{r}}^{P} \left(\frac{v}{RT} - \frac{1}{p} \right) dp \tag{123}$$

If P^* is chosen so small the the gas at P^* behaves like an ideal gas, then $f(T, P^*) = P^*$ and the equation above simplifies to (where we now take that $P^* = 0$ for the sake of simplicity):

$$\ln \frac{f(T,P)}{P} = \int_0^P \frac{(Z-1)}{P} dP \tag{124}$$

Reconsidering all three EOS that we know so far:

- Ideal Gas Law: $Z = 1 \Rightarrow (Z(T,P,v) - 1) = 0 \Rightarrow f(T,P) = P$
- Virial EOS: $Z(T,P,v) = 1 + \frac{BP}{RT}$
- Van-der-Waals EOS: $Z(T,P,v) = 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT} \cdots$

The fugacity f can either have values bigger or smaller than P. Three example curves in a $P - f$ diagram are shown in figure 7. Note that in a closed box the pressure that you can measure directly (via a manometer) will still be P. However, the gas inside the box will behave in terms of equilibrium with respect to mass transfer like there was only the corrected pressure f.

The fugacity, the quantity that defines equilibrium with respect to mass transfer, can be calculated using an EOS and the compressibility Z.
The fugacity is defined by the differential equation $d_T\mu = RTd_T \ln f$ subject to the boundary condition $\lim_{P\to 0} \frac{f(T,P)}{P} = 1$.
For ideal gases $f(T,P) = P$. In general: $f(T,P) = P \exp\left(\int_0^P \frac{(Z(T,p,v)-1)}{p} dp\right)$
This shows that f is a corrected (or effective) pressure.

1.11. *Fugacity in the Liquid Phase - Single Component Vapor Liquid Equilibrium (VLE)*

Now that we know how to calculate the fugacity in the gas phase for ideal and non-ideal gases, we have to find out how to calculate the fugacity in the

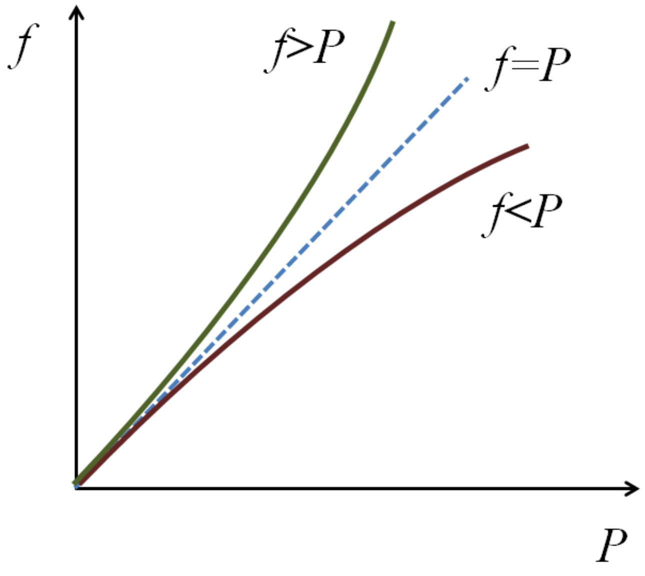

Figure 7: Schematic $P - f$ diagram.

liquid phase. If we recall the single component $P - T$ diagram in figure 5 and take into account our recent discoveries, we find that we know already a lot about the fugacity. First, at a pressure $P = 0$ we know that $f(T, 0) = P = 0$ (by defintion). Second, we are able to calculate the value of f in the entire vapor phase region using an EOS. And finally due to the condition for equilibrium with respect to mass transfer we require that $f^L(T, P^V(T)) = f^V(T, P^V(T))$ where $P^V(T)$ is the vapor pressure. A reasonable choice for that reference state is $P = 0$:

$$\ln \frac{f^V(T, P^V(T))}{P^V(T)} = \int_0^{P^V} \frac{(Z(T, p, v) - 1)}{p} dp \tag{125}$$

For a fixed temperature T, from the vapor pressure onwards to higher pressures in the liquid phase region we have to integrate from the vapor pressure $P^V(T)$ to the pressure of interest (indicated as the end of the red arrow in the figure below).

$$d_T \mu^L = v^L dP = RT d_T \ln f^L \tag{126}$$

At the vapor pressure line, the iso fugacity has to apply:

$$f^L(T, P^V(T)) = f^V(T, P^V(T)) \tag{127}$$

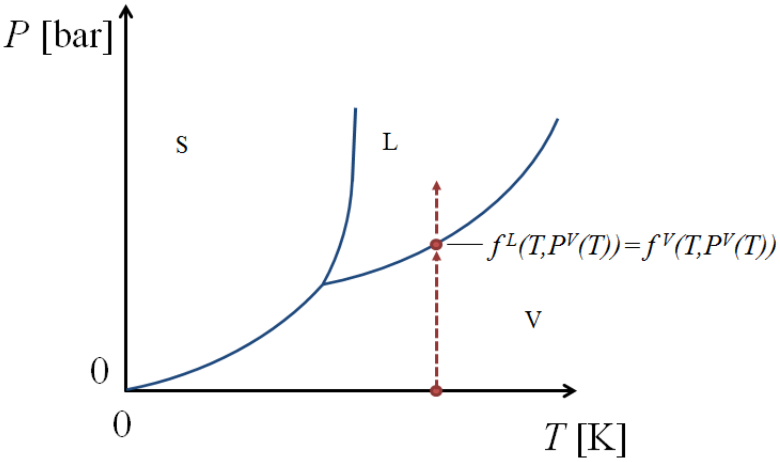

Figure 8: Schematic $P-T$ diagram.

$$\ln\frac{f^L(T,P)}{f^V(T,P^V(T))} = \int_{P^V}^{P} \frac{v^L}{RT}dp \tag{128}$$

As the molar volume of a liquid v^L is usually considered to be incompressible (for low pressures below 10 bar v^L is basically a constant), we can solve the integral by treating v^L as a constant:

$$\ln\frac{f^L(T,P)}{f^V(T,P^V(T))} = \frac{v^L(P-P^V(T))}{RT} \tag{129}$$

or

$$f^L(T,P) = f^V(T,P^V(T))\exp\left(\frac{v^L(P-P^V(T))}{RT}\right) = \tag{130}$$
$$= P^V(T)\exp\left(\int_0^{P^V(T)}(Z(T,p,v)-1)\frac{dp}{p}\right)\exp\left(\frac{v^L(P-P^V(T))}{RT}\right)$$

which is schematically drawn as blue dashed curve in figure 9. If the gas is ideal, this is

$$f^L(T,P) = P^V(T)\exp\left(\frac{v^L(P-P^V(T))}{RT}\right) \tag{131}$$

and if v^L and/or $\Delta P = P - P^V(T)$ are small

$$f^L(T,P) = P^V(T) \tag{132}$$

which is shown as blue solid curves in figure 9.

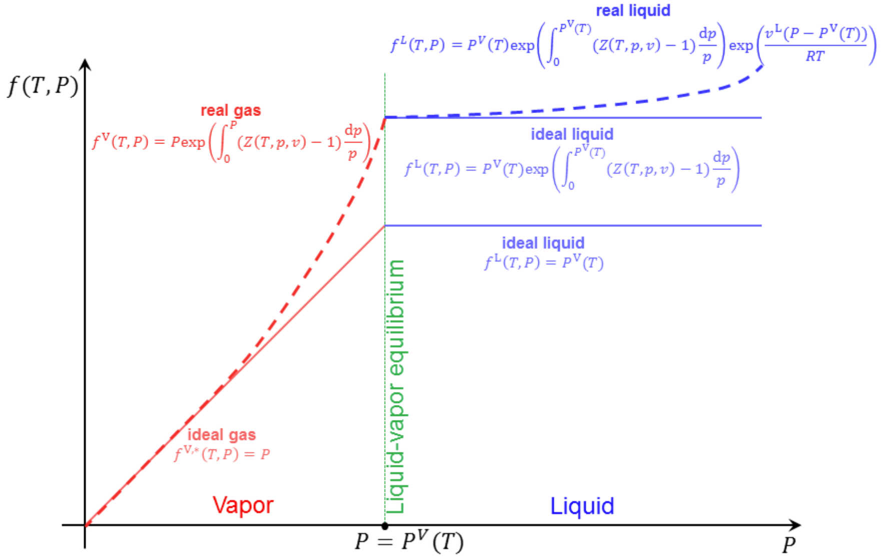

Figure 9: Schematic $P - f$ diagram illustrating the consequences of correction terms.

Ideal gas $(P \leq P^V(T))$

$f^{V*} = P$

real gas $(P \leq P^V(T))$

$f^V = P \exp\left(\int_0^P (Z(T,p,v) - 1) \frac{dp}{p}\right)$

liquid $(P \geq P^V(T))$

$f^L(T,P) = P^V(T) \exp\left(\int_0^{P^V(T)} (Z(T,p,v) - 1) \frac{dp}{p}\right) \exp\left(\frac{v^L(P - P^V(T))}{RT}\right)$

1.12. Mixtures

Until now, we have considered single component systems. We found ways to define the fugacity of ideal gases, of real gases, and of liquids. We will now extend these concepts to multi-component mixtures for the vapor and gas phase as well as to vapor-liquid equilibria. Let us start with recalling the differential definition forms for single component systems of the relation between fugacity and chemical potential.

$$d_T\mu^V = RTd_T \ln f^V \text{ with the boundary condition } \lim_{P\to 0} \frac{f}{P} = 1 \tag{133}$$

$$d_T\mu^L = RTd_T \ln f^L \text{ with the boundary condition } f^L(T, P^V(T)) = f^V(T, P^V(T)) \tag{134}$$

The key property to extend these definitions to mixtures is the Gibbs free enery and its partial derivative as:

$$\mu_i = \overline{G_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} \tag{135}$$

We will follow the same logic as for pure component systems but first considering mixtures of ideal gases, than of real gases, ideal liquids, and non-ideal liquids.

Ideal gas mixtures. Ideal gas mixtures are, very similiar to pure ideal gases, characterized by the fact that gas molecules do not interact with each other (one might say, they are not aware of the presence of other molecules and in the case of mixtures, even of molecules of another species). So using the defintion of the partial pressure $P_i = Py_i$ we find that the chemical potential of an ideal gas in a mixture is equal to the chemical potential of the same substance if it were a pure component at the pressure equal to the partial pressure of that species in the mixture:

$$\underbrace{\mu_i^{V*}(T,P,\underline{y})}_{\text{mixture}} = \underbrace{\mu_i^{V*}(T,P_i)}_{\text{pure}} \tag{136}$$

The equation above can also be considered as a defintion of an ideal gas mixture. If we consider a reference pressure P_r we can calculate the chemical potential of the ideal gas in the mixture

$$\begin{aligned} \mu_i^{V*}(T,P,\underline{y}) = \mu_i^{V*}(T,P_\mathrm{r}) + RT\ln\frac{P_i}{P_\mathrm{r}} = \\ = \mu_i^{V*}(T,P_\mathrm{r}) + RT\ln\frac{P}{P_\mathrm{r}} + RT\ln y_i = \\ = \mu_i^{V*}(T,P) + RT\ln y_i \end{aligned} \tag{137}$$

In differential form at constant T this is:

$$d_T\mu_i^{V*}(T,P,\underline{y}) = RT d_T \ln P_i \tag{138}$$

Real gas mixtures. When we compare the above equation to equation 133 we can recall that for a single component system we replaced the pressure with the fugacity which acted like a corrected pressure. The same approach is now used for mixtures of real gases:

$$d_T\mu_i^{V}(T,P,\underline{y}) = RT d_T \ln f_i(T,P,\underline{y}) \tag{139}$$

The boundary condition changes accordingly to

$$\lim_{P\to 0} \frac{f_i(T,P,\underline{y})}{P_i} = 1 \tag{140}$$

Using this defintion, we see that for an ideal gas $f_i^*(T,P,\underline{y}) = Py_i$. For a real gas, an equation of state that takes into account interactions between molecules of different gas species would be needed. One can obtain such EOS and different approaches exist in literature. However in the scope of our lecture, we will limit ourselves to ideal gas mixtures as there is no academic benefit from extending our findings in such a way. Instead, we want to determine the chemical potential in liquid mixtures.

Ideal liquid mixtures. First we need to define an ideal liquid mixture (note that we use ^{0} to indicate ideal behavior). An ideal mixture is characterized by $\Delta V_{\text{mix}} = 0$. We will investigate the meaning of this property in the next but one chapter. In ideal mixtures, molecules in this mixture do not interact with each other (one might formulate that molecules of different species are not aware of the presence of another species). So similar to equation 137:

$$\underbrace{\mu_i^0(T,P,\underline{x})}_{\text{mixture}} = \underbrace{\mu_i(T,P)}_{\text{pure}} + RT\ln x_i \tag{141}$$

Expressing this equation via the fugacity in the same manner as demonstrated for the gas phase yields

$$\underbrace{f_i^{L0}(T,P,\underline{x})}_{\text{mixture}} = \underbrace{f_i^L(T,P)}_{\text{pure}}\, x_i \tag{142}$$

Non-ideal liquid mixtures. Many real liquid mixtures however do not behave ideal. For non-ideal liquid mixtures of multiple components, we introduce a new correction term which we call activity coefficient $\gamma_i = \gamma_i(T,P,\underline{x})$, such that

$$f_i^L(T,P,\underline{x}) = f_i^{L0}(T,P,\underline{x})\gamma_i(T,P,\underline{x}) = f_i^L(T,P)x_i\gamma_i(T,P,\underline{x}) \tag{143}$$

In this way, the fugacity of a component $i = 1, 2, ..., C$ in a mixture is equal to the product of the fugacity of the pure component at T and P multiplied with the molar fraction x_i and the activity coefficient (which itself is a function of temperature T, pressure P, and composition $\underline{x}$). The activity coefficient for an ideal liquid is 1, which reduces equation 143 to equation 142.

In order to calculate the fugacity of the non-ideal liquid phase, an expression for this correction term is needed. We consider the difference between an ideal and a non-ideal liquid mixture. In general, this can be done by splitting a thermodynamic quantity into one term that accounts for the ideal mixing behavior and one term for the excess of that quantity (indicated by ^{E}). For the Gibbs free energy this is:

$$G(T,P,\underline{n}) = G^0(T,P,\underline{n}) + G^E(T,P,\underline{n}) \tag{144}$$

Excess of the Gibbs free energy. It seems that information on the non-ideal behavior of a mixture can be obtained from investigation the excess Gibbs free energy. We recall equation 114

$$d_T\mu_i = RTd_T \ln f_i \tag{145}$$

The difference between the ideal liquid to the real liquid yields:

$$\begin{aligned} \mu_i^L(T,P,\underline{x}) - \mu_i^{L0}(T,P,\underline{x}) = RT\ln\frac{f_i^L(T,P,\underline{x})}{f_i^{L0}(T,P,\underline{x})} = \\ = RT\ln\gamma_i(T,P,\underline{x}) = \overline{G}_i - \overline{G}_i^0 = \\ = \left(\frac{\partial(G-G^0)}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial(ng^E)}{\partial n_i}\right)_{T,P,n_{j\neq i}} \end{aligned} \tag{146}$$

g^E (the molar excess gibbs free energy) is a quantity that describes how well two liquids mix. If it were 0, there would be no interaction between molecules of different species and the liquid would behave ideal. If it is bigger than 0, repulsive forces are present. If it is smaller than 0, attractive forces are present. Many models exist to describe g^E and hence γ_i as a function of temperature, pressure, and composition. For a binary mixture with $C = 2$, g^E can be described for example by an empirical equation that uses a constant A where x_1 and x_2 are the mole fractions of the two components of the binary mixture:

$$\frac{g^E}{RT} = Ax_1x_2 \tag{147}$$

Different values of A result in different values for g^E in the range between attractive and repulsive forces in the liquid mixture. Figure 10 shows possible behaviors. On the x-axis you find the composition so that at the left $x_1 = 0$ and $x_2 = 1$ and at the right $x_1 = 1$ and $x_2 = 0$ respectively. The y-axis is g^E. Inserting equation 147 into equation 146 yields

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial n g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{148}$$

$$\frac{ng^E}{RT} = \frac{An^2x_1x_2}{n} = A\frac{n_1n_2}{n_1+n_2} \tag{149}$$

$$\Rightarrow \ln \gamma_i = A(1-x_i)^2 \tag{150}$$

which is called Porter equation.

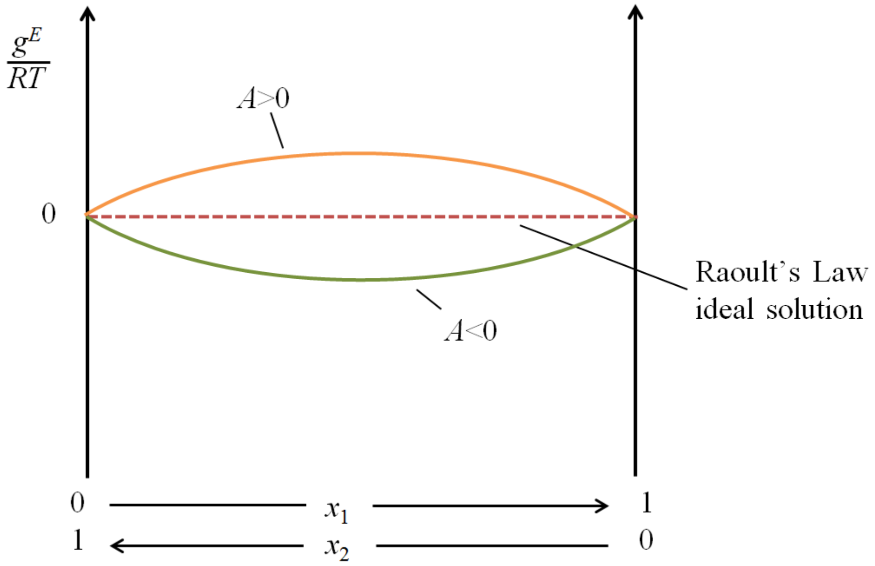

Figure 10: g^E diagram.

The non-ideal behavior of the liquid phase may be characterized by the activity coefficient γ_i which is is a function of T,P, and $\underline{x}$.

A common empirical equation for γ_i is the Porter eq. $\ln \gamma_i = A(1 - x_i)^2$.

1.12.1. Vapor Liquid Equilibrium for mixtures

The condition for phase equilibrium (iso-fugacity condition) for single component systens (equation 119) is extended for mixtures to:

$$\mu_i^\alpha = \mu_i^\beta \Leftrightarrow f_i^\alpha = f_i^\beta \tag{151}$$

So the iso-fugacity condition has to be fulfilled for every species i. For a vapor liquid equilibrium this reads as:

$$f_i^V(T, P, \underline{y}) = f_i^L(T, P, \underline{x}) \tag{152}$$

In the scope of this lecture, we will only use the two iso-fugacity conditions as shown in table 1.12.1, i.e. we will focus on an ideal gas phase (as mentioned above).

Table 1: Iso-fugacity conditions for mixtures.

vapor phase			liquid phase	
ideal	Py_i	$=$	$P_i^V(T)x_i$	ideal
ideal	Py_i	$=$	$P_i^V(T)x_i\gamma_i(T, P, \underline{x})$	non-ideal

In the case of an ideal gas and an ideal solution, the equation iso-fugacity condition can be written as

$$Py_i = P_i^V(T)x_i \tag{153}$$

which is also known as Raoult's Law and is the simplest expression for vapor-liquid equilibrium.

VLE for a mixture is defined by the isofugacity condition: $f_i^V(T, P, \underline{y}) = f_i^L(T, P, \underline{x})$. (Table 1)

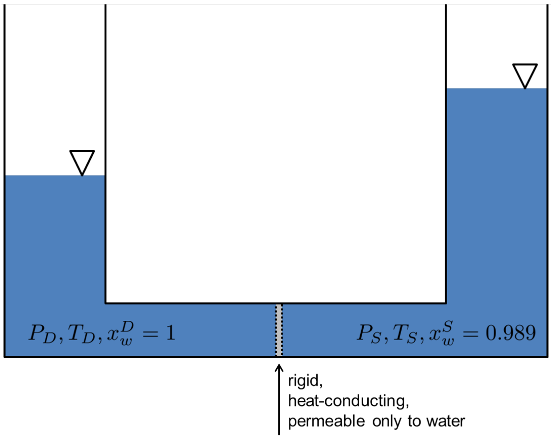

Figure 11: two compartments separated by a semipermeable membrane.

1.12.2. Fugacity in solutions: Osmotic pressure and reverse osmosis

Consider a system with two chambers, one filled with distilled water and one filled with seawater, connected by a membrane as shown in Figure 11. Let us assume that seawater is a solution with a concentration of 35 g/L of NaCl in water. The membrane is rigid, heat-conducting, and permeable to water molecules, but not to ions. As a result, at equilibrium the chambers need not be at the same pressure, but at the same temperature. Moreover, the isofugacity condition has to be fulfilled for water:

$$T_D = T_S = T \tag{154}$$

$$f_w^D\left(T, P_D, x_w^D\right) = f_w^S\left(T, P_S, x_w^S\right) \tag{155}$$

where D and S refer to the chamber with the distilled and the seawater, respectively; and w denotes water. The last equation can be written as

$$f_w^D\left(T, P_D\right) x_w^D \gamma_w\left(T, P_D, x_w^D\right) = f_w^S\left(T, P_S\right) x_w^S \gamma_w\left(T, P_S, x_w^S\right) \tag{156}$$

Assuming that the solution behaves ideally (so $\gamma_w = 1$), and keeping in mind that for distilled water $x_w^D = 1$, this becomes

$$f_w^D\left(T, P_D\right) = f_w^S\left(T, P_S\right) x_w^S \tag{157}$$

Using the expressions from Section 1.11 to describe the pure liquid fugacity, this is rewritten as

$$\begin{aligned} P_w^V(T) \exp\left(\int_0^{P^V(T)} (Z(T,p,v)-1)\frac{dp}{p}\right) \exp\left(\int_{P^V(T)}^{P_D} \frac{v_w^L}{RT} dp\right) = \\ = P_w^V(T) \exp\left(\int_0^{P^V(T)} (Z(T,p,v)-1)\frac{dp}{p}\right) \exp\left(\int_{P^V(T)}^{P_S} \frac{v_w^L}{RT} dp\right) x_w^S \end{aligned} \tag{158}$$

As the first two terms are the same on both sides of the equation, this simplifies to

$$\exp\left(\int_{P_D}^{P_S} \frac{v_w^L}{RT} dp\right) = \frac{1}{x_w^S} \tag{159}$$

For incompressible liquids (which water is typically taken for), v^L is constant, and the above expression becomes

$$\frac{v_w^L\left(P_S - P_D\right)}{RT} = \ln\frac{1}{x_w^S} \tag{160}$$

The difference between the pressures in the expression above is known as the osmotic pressure, $\Delta\pi = P_S - P_D$. It is given by

$$\Delta\pi = \frac{RT}{v_w^L} \ln\frac{1}{x_w^S} \tag{161}$$

For dilute systems (i.e. $x_w^S \approx 1$), a linear approximation can be used for the logarithm, resulting in

$$\Delta\pi = \frac{RT}{v_w^L}\left(1 - x_w^S\right) = RTc \tag{162}$$

where c is the concentration of ions in solution. The seawater considered in this example has a NaCl concentration of 35 g/L, and after dissolution an ion concentration of 1198 mol/m^3 (Na$^+$ + Cl$^-$ ions). Using the expression above one obtains $\Delta\pi = 2.9\,\mathrm{MPa}$ for a temperature of 20 °C. This is the pressure to be applied to a solution to prevent its dilution with pure water flowing into the solution through a semi-permeable membrane. If on the other hand, additional pressure is applied to the solution such that

$$P_S > P_D + \Delta\pi \tag{163}$$

then $f_w^S > f_w^D$, and pure water flows from the seawater compartment to the pure water compartment; a technique commonly used in seawater desalination.

1.12.3. Volume of a mixture

You might remember a high school experiment where one pours together 50 mL water and 50 mL ethanol. The total volume of that mixture is 97 mL instead of 100 mL as one might expect. This property of mixing is closely related to what we derived in the previous chapter.

Imagine C barrels that are filled with n_i number of moles of species i each as shown in figure 12 so that each barrel only contains molecules of one pure species i each. The initial total volume of all liquids in all small barrels is the sum of the products of the molar volumes and the number of moles in all barrels. The molar volume is the derivative of the chemical potential with respect to pressure of the pure species i.

$$V_{\text{initial}} = \sum_{i=1}^{C} n_i \nu_i^L = \sum_{i=1}^{C} n_i \left(\frac{\partial \mu_i}{\partial P}\right)_T = \sum_{i=1}^{C} n_i RT \left(\frac{\partial \ln f_i^L(T,P)}{\partial P}\right)_T \tag{164}$$

The final volume after mixing is the sum of the product of the number of moles of species i and the corresponding molar volume in the mixture $\overline{V_i}$.

$$\begin{aligned} V_{\text{final}} = \sum_{i=1}^{C} n_i \overline{V}_i = \sum_{i=1}^{C} n_i \left(\frac{\partial \mu_i^L}{\partial P}\right)_{T,\underline{n}} = RT \sum_{i=1}^{C} n_i \left(\frac{\partial \ln f_i^L(T,P,\underline{x})}{\partial P}\right)_{T,\underline{n}} \\ = RT \sum_{i=1}^{C} n_i \frac{\partial}{\partial P} \left(\ln f_i^L(T,P) + \ln x_i + \ln \gamma_i(T,P,\underline{x})\right)_{T,\underline{n}} = \\ = \sum_{i=1}^{C} n_i \nu_i^L + RT \sum_{i=1}^{C} \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\underline{n}} \end{aligned} \tag{165}$$

The difference between the total volume before and after mixing is ΔV_{mix}:

$$\Delta V_{\text{mix}} = V_{\text{final}} - V_{\text{initial}} = RT \sum_{i=1}^{C} n_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\underline{x}} \tag{166}$$

For an ideal solution, the activity coefficient is $\gamma = 1$ and hence $\Delta V_{\text{mix}} = 0$.

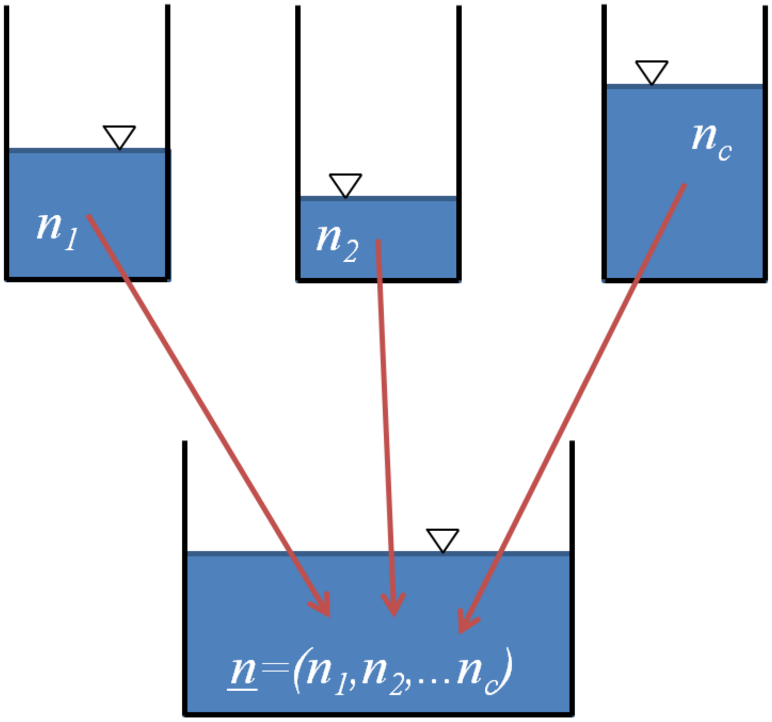

Figure 12: C barrels filled with n_i moles of pure species i are mixed into one big barrel.

1.12.4. Chemical equilibrium

Until now, we did not consider chemical reactions. However, also systems that undergo chemical reactions are subject to the conditions for thermodynamic equilibrium. We recall that thermodynamic equilibrium between two subsystems A and B requires equal temperature $T^A = T^B$, pressure $P^A = P^B$, and chemical potentials $\mu_i^A = \mu_i^B$ for all species $i = 1, 2, \ldots, C$. Imagine a reactor that is encased with a heating/cooling jacket and closed with a moving piston so that T =constant and P =constant ($dT = dP = 0$). These features allow us to use the Gibbs free energy, which is a function of temperature, pressure, and composition to describe the chemical equilibrium in the reactor.

We will consider the formation of ammonia as an example reaction. Ammonia NH_3 is formed from hydrogen H_2 and nitrogen N_2 as

$$1N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{167}$$

or

$$0 = 2NH_3 - 1N_2 - 3H_2 \tag{168}$$

In general, a chemical reaction will be written as:

$$\sum_{i=1}^{C} \nu_i A_i = 0 \tag{169}$$

where A_i represents species i, and ν_i is its stoichiometric coefficient, i.e. positive for products and negative for reactants. Table 2 illustrates its meaning (compare to equation 167). Two remarks are worth noting. First, note that the last equation enforces fulfillment of atmoic balance, i.e. atoms are neither created nor destroyed in a chemical reaction. Second, the last equation is formulated in s slightly different manner than in the script of Thermo II, Prof. Boulouchos. In this lecture we use equation 169.

Table 2: Stoichiometric coefficients for the formulation of ammonia.

A_1 =NH_3	ν_1	=	2	$\nu > 0 \Rightarrow$ product
$A_2 = H_2$	ν_2	=	-3	$\nu < 0 \Rightarrow$ reactant
$A_3 = N_2$	ν_3	=	-1	$\nu < 0 \Rightarrow$ reactant

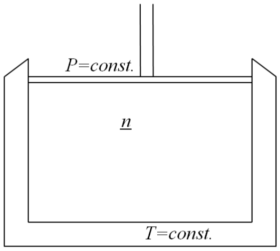

Figure 13: Reactor with T =const. and $P = const.$

In a closed reactor conservation of mass applies. Let us consider a mixture of products and reactants that are initially present in amounts n_i^0 $(i = 1, \ldots, C)$. Let us also assume that the reaction defined by equation 167 has proceeded, and let us call the extent of the reaction (number of moles reacted) as λ. Therefore, the number of moles of species i can be written as:

$$n_i = n_i^0 + \Delta n_i = n_i^0 + \nu_i \lambda \tag{170}$$

where Δn_i is the number of moles that have been formed or consumed during the reaction, which is equal to the product of the stoichiometric coefficient ν_i and λ. The differential form of the above equation is:

$$dn_i = \nu_i d\lambda \tag{171}$$

The differential of the Gibbs free energy is:

$$dG = -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i \tag{172}$$

At T, P constant $(dP = dT = 0)$ the equation above reduces to

$$dG = \sum_{i=1}^{C} \mu_i dn_i \tag{173}$$

Using equation 171 yields

$$dG = \left(\sum_{i=1}^{C} \mu_i \nu_i \right) d\lambda \tag{174}$$

in chemical equilibrium, G is minimal and $dG = 0$. Hence:

$$\sum_{i=1}^{C} \mu_i \nu_i = 0 \tag{175}$$

In the special case of an ideal gas phase, the chemical potential in the mixture is:

$$\mu_i^*(T, P, \underline{y}) = \mu_i^*(T, P_\mathrm{r}) + RT \ln \frac{P_i}{P_\mathrm{r}} \tag{176}$$

combining the last two equations we find

$$\frac{dG}{d\lambda} = \sum_{i=1}^{C} \nu_i \mu_i^*(T, P, \underline{y}) = \sum_{i=1}^{C} \nu_i \mu_i^*(T, P_\mathrm{r}) + RT \sum_{i=1}^{C} \nu_i \ln \frac{P_i}{P_\mathrm{r}} \tag{177}$$

One defines the Gibbs free energy of a reaction ΔG_r^0 as

$$\Delta G_\mathrm{r}^0(T, P_\mathrm{r}) = \sum_{i=1}^{C} \nu_i \mu_i^*(T, P_\mathrm{r}) \tag{178}$$

The sum of the logarithms can be expressed as a product so that

$$\begin{aligned} \frac{dG}{d\lambda} = \sum_{i=1}^{C} \nu_i \mu_i^*(T, P, \underline{y}) &= \Delta G_\mathrm{r}^0(T, P_\mathrm{r}) + RT \ln \prod_{i=1}^{C} \left(\frac{P y_i}{P_\mathrm{r}} \right)^{\nu_i} = \\ &= \Delta G_\mathrm{r}^0(T, P_\mathrm{r}) + RT \ln \left(\left(\frac{P}{P_\mathrm{r}} \right)^{\nu} \prod_{i=1}^{C} y_i^{\nu_i} \right) = \\ &= RT \left[\frac{\Delta G_\mathrm{r}^0(T, P_\mathrm{r})}{RT} + \ln \left(\left(\frac{P}{P_\mathrm{r}} \right)^{\nu} \prod_{i=1}^{C} y_i^{\nu_i} \right) \right] \end{aligned} \tag{179}$$

where $\nu = \sum_{i=1}^{C} \nu_i$. At equilibrium $dG = 0$, hence

$$\underbrace{\exp \frac{-\Delta G_R^0(T)}{RT}}_{K_\mathrm{eq}(T)} = \left(\frac{P}{P_\mathrm{r}} \right)^{\nu} \prod_{i=1}^{C} y_i^{\nu_i} \tag{180}$$

$K_\mathrm{eq}(T)$ is called equilibrium constant and is a function of temperature. Note that the right hand side of the equation is often called Q, which is a function of T,P,$\underline{y}$.

$$\frac{dG}{d\lambda} = -RT \ln K_\mathrm{eq}(T) + RT \ln Q(T, P, \underline{y}) \tag{181}$$

Two important calculations based on these findings can be performed. The first application is to calculate the equilibrium composition in a closed reactor by coupling equation 180 with equation 170. In this manner, the molar fraction of species i becomes a function of the extent of the reaction λ:

$$y_i = \frac{n_i}{\sum_{j=1}^{C} n_j} = \frac{n_i^0 + \nu_i \lambda}{\sum_{j=1}^{C} n_j^0 + \lambda \sum_{j=1}^{C} \nu_j} = y_i(\lambda) \tag{182}$$

For a given temperature T and pressure P, the extent of the reaction in equilibrium and hence the equilibrium composition can be obtained.

The second application is to find out about the direction of the evolution of a reaction if it is a spontaneous process

$$0 > dG = \left(\sum_{i=1}^{C} \nu_i \mu_i \right) d\lambda \tag{183}$$

that proceeds towards reaching equilibrium ($dG = 0$). Using equation 181 we may write:

$$\sum_{i=1}^{C} \nu_i \mu_i = \Delta G_{\mathrm{r}}^0 + RT \ln Q = -RT \ln K_{\mathrm{eq}} + RT \ln Q = RT \ln \frac{Q}{K_{\mathrm{eq}}} \lesseqgtr 0 \tag{184}$$

If $Q > K_{\mathrm{eq}} \Rightarrow d\lambda < 0$, the reaction proceeds backwards (products → reactants).
If $Q < K_{\mathrm{eq}} \Rightarrow d\lambda > 0$, the reaction proceeds forwards (reactants → products).
If $Q = K_{\mathrm{eq}} \Rightarrow d\lambda = 0$, the reaction is in equilibrium.

Returning to the ammonia formation example where $\nu = -2$ we find that equation 180 is:

$$K_{\mathrm{eq}}(T) = \left(\frac{P}{P_{\mathrm{r}}} \right)^{-2} \frac{y_{\mathrm{NH_3}}^2}{y_{\mathrm{N_2}} y_{\mathrm{H_2}}^3} \tag{185}$$

Note that a common procedure is to take $P_{\mathrm{r}} = 1$ bar.

1.13. Liquid vapor equilibrium in binary mixtures

While the iso-fugacity condition that we used in previous chapters is valid also for high numbers of components, in the scope of this chapter we will focus on binary systems ($C = 2 \Rightarrow i = 1, 2$) and we consider situations when there can be equilibrium between a liquid and a vapor phase. Equilibrium with respect to mass transfer for these systems (LVE) is characterized by the iso-fugacity condition

$$f_i^V(T, P, y_1, y_2) = f_i^L(T, P, x_1, x_2) \qquad i = 1, 2 \tag{186}$$

where we have implicitly enforced the condition for thermal and mechanical equilibrium, i.e. same T and P in the two phases. Note that for $C = 2$, $x_2 = 1 - x_1$ and $y_2 = 1 - y_1$. We assume that component 1 is more volatile than component 2.

1.13.1. LVE in single component systems

Each component has its own phase diagram (schematically drawn in Figure 14 for components 1 and 2). LVE is given by the boiling curve which can be calculated with the Antoine equation (equation 92). At temperature T we find $P_1^V(T)$ and $P_2^V(T)$, with $P_1^V(T) > P_2^V(T)$ because of our choice that component 1 is more volatile than component 2. At $P = 1$ bar, we have the boiling points T_1^b and T_2^b, with $T_1^b < T_2^b$ again because 1 is more volatile than 2. At a fixed pressure P a single component evaporates at constant temperature, i.e. the temperature on the LVE curve of the phase diagram corresponding to P. We want to investigate liquid vapor equilibrium in binary mixtures for which we will develop suitable diagrams.

1.13.2. P-xy diagrams

The first type of diagram that we want to consider is the $P - xy$ diagram where the temperature is kept constant. With reference to figure 14, at a fixed

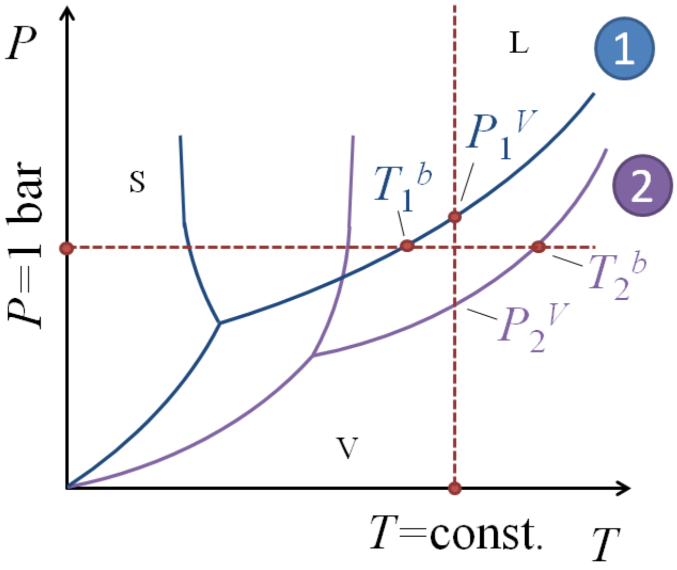

Figure 14: Schematic $P-T$ diagram for two components 1 and 2.

temperature T one finds that by increasing the pressure from $P=0$, we reach the vapor pressure of component 2 first. Below this pressure, component 2 is in the gas phase, above this pressure, the pure component 2 will be a liquid. By further increasing the pressure we arrive at $P_1^V(T)$. Above this point, also the pure component 1 will be in the liquid state. However for a mixture of components 1 and 2 we are not able to tell yet at which pressure we will find a liquid mixture, a vapor mixture, or a two phase (vapor liquid) mixture.

The iso-fugacity condition as given in equation 186 holds information on the composition of both phases and their relative amounts at equilibrium.

In a $P-xy$ diagram such as shown in figure 15 the ordinate is the pressure P and the abscissa is the composition of the vapor and liquid phase at mole fractions x_1 and y_1. At $x_1=y_1=0$ one finds the vapor pressure of the pure component 2, $P_2^V(T)$ (purple point), whereas at $x_1=y_1=1$ one finds the vapor pressure of the pure component 1, $P_1^V(T)$ (blue point). If we consider ideal gas and ideal liquid phase behavior the fugacities of species i are:

$$\begin{aligned} f_i^{V*} &= Py_i = P_i \\ f_i^{L0} &= P_i^V(T)x_i \end{aligned} \tag{187}$$

LVE is given by the iso-fugacity conditions

$$\begin{aligned} P_1 &= P_1^V(T)x_1 \\ P_2 &= P_2^V(T)x_2 \end{aligned} \tag{188}$$

Plotting the partial pressure of each of the two components, which is given by the fugacity in the liquid phase, yields the blue (component 1) and purple (component 2) lines in figure 15. The sum of the partial pressures is the total pressure of the system:

$$P = P_1 + P_2 = P_1^V(T)x_1 + P_2^V(T)x_2 \tag{189}$$

which is drawn in orange in figure 15. This curve is commonly called bubble point curve.

The vapor mole fraction y_1 that is in equilibrium with a given liquid mole fraction x_1 at the system pressure P is:

$$y_1 = \frac{P_1}{P} = \frac{f_1^L}{f_1^L + f_2^L} = \frac{P_1^V(T)x_1}{P_1^V(T)x_1 + P_2^V(T)x_2} \tag{190}$$

It is used to draw the dew point curve (green curve in figure 15), i.e. the curve that represents the vapor phase mole fraction in equilibrium with the liquid phase mole fraction at the pressure P. In other words the liquid and vapor phases at equilibrium correspond to the points on the orange and green curves, respectively.

For a non-ideal liquid mixture the construction is almost identical. The liquid phase fugacity in the non-ideal case is described by correcting the ideal liquid fugacity with the activity coefficient γ_i as

$$f_i^L = P_i^V(T)x_i\gamma_i(T,P,x_1,x_2) \tag{191}$$

Please recall that γ_i can either be bigger or smaller than 1 which leads to a bended curve as compared to the straight line of the ideal case ($\gamma_i = 1$, drawn as dashed blue line for component 1 into figure 16 and dashed purple line for component 2 into figure 16). If γ_i is bigger than 1, the resulting curve will be above the ideal case straight line (this is drawn as solid blue (component 1) and solid purple (component 2) curves into figure 16), if γ_i is smaller than 1 the resulting curve will be below the straight line of the ideal case. The total system pressure curve which is drawn in solid orange in figure 16 is given by

$$P = P_1 + P_2 = P_1^V(T)x_1\gamma_1(T,P,x_1,x_2) + P_2^V(T)x_2\gamma_2(T,P,x_1,x_2) \tag{192}$$

which is a bended curve that is above the straight line of the ideal case (ideal: dashed orange curve in figure 16) for $\gamma_i > 1$ and below the straight line of the ideal case if $\gamma_i < 1$.

The green curve in figure 16, i.e. the dew point curve, is obtained similar to the ideal liquid case and is indicating the vapor composition y_1 that is in equilibrium with a given liquid composition x_1 at pressure P:

$$y_1 = \frac{P_1}{P} = \frac{f_1^L}{f_1^L + f_2^L} = \frac{P_1^V(T)x_1\gamma_1(T,P,x_1,x_2)}{P_1^V(T)x_1\gamma_1(T,P,x_1,x_2) + P_2^V(T)x_2\gamma_2(T,P,x_1,x_2)} \tag{193}$$

You can use the code that you prepared for the home assignment 5.1 to visualize different values of γ_i by changing the value of A of the porter equation.

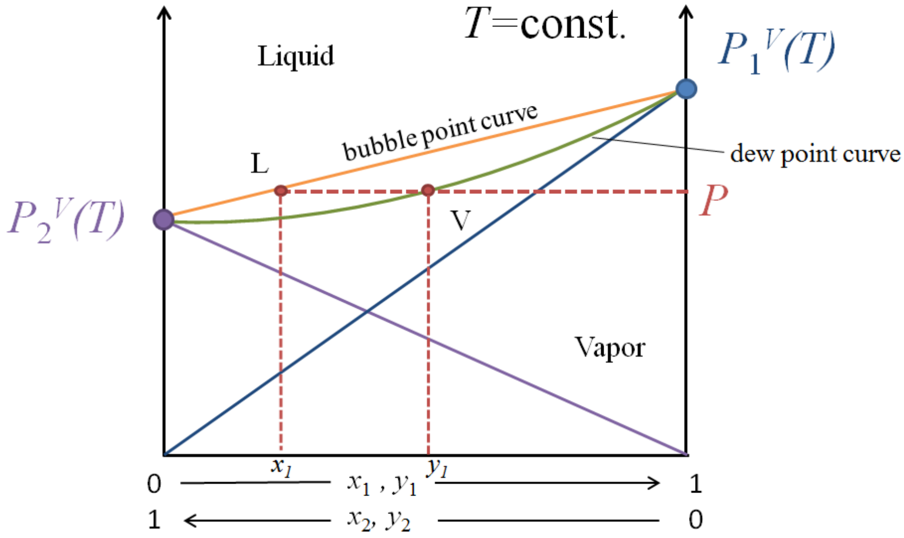

Figure 15: Binary $P - xy$ diagram characterizing LVE at T =const. for an ideal gas phase and an ideal liquid phase.

A number of information can be extracted from a binary $P - xy$ diagram. Consider a binary mixture with an overall composition $z_1 = n_1/(n_1 + n_2)$ which is shown in figure 17. At a given temperature T and given pressure P we can use the $P - xy$ diagram to determine if the system is in the vapor or liquid phase or if both phases are present. If the pressure P of interest is above the orange curve the whole system will be a liquid mixture. If P is below the green curve, the whole system is in the vapor phase. If P is between the orange and green curve, both phases are present. This case is indicated by the red dashed line. The composition of the liquid phase at P is given by x_1 and the composition of the vapor phase that is in equilibrium with the liquid phase of composition x_1 is given by y_1. The values of x_1 and y_1 represent the composition that fulfills the iso-fugacity condition at P and T.

If the overall composition in the system z_i, the total number of moles in the system n, and P are given and x_i and y_i are read from the curves (note that

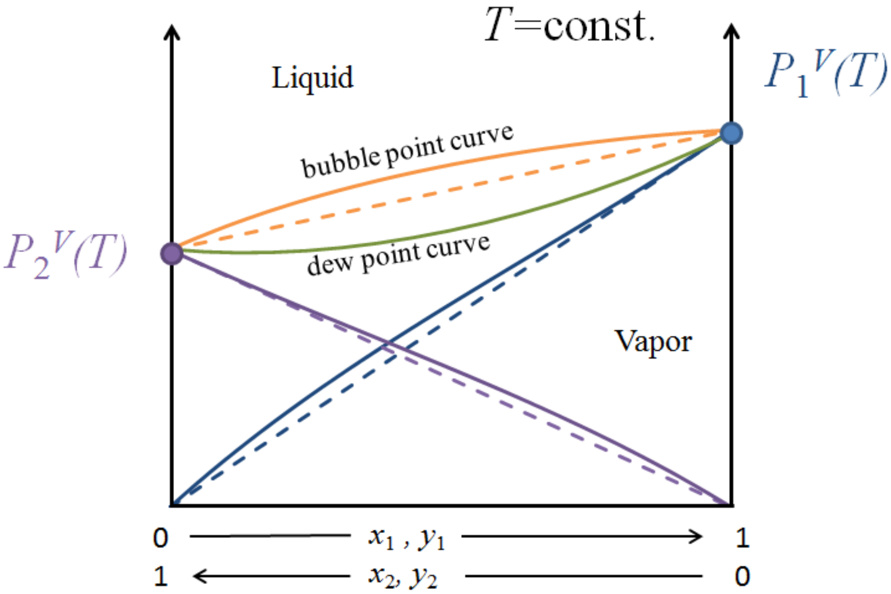

Figure 16: Binary $P - xy$ diagram characterizing LVE at T =const. for an ideal gas phase and a non-ideal liquid phase (solid lines). Dashed lines indicate the ideal liquid case and have been drawn as a comparison.

$x_1 < z_1 < y_1$ for the more volatile component in the case without azeotrops (see later)), a material balance can be used to calculate the molar amounts of vapor n^V and liquid n^L. The total number of moles in the system n is the sum of the moles in the vapor phase and the moles in the liquid phase:

$$n^V + n^L = n \tag{194}$$

Additionally, a component material balance can be written. The total number of moles of species 1 is the overall mole fraction of 1 z_1 times the total number of moles in the system n. This must be equal to the sum of the number of moles of species 1 in the liquid phase $x_1 n^L$ and the number of moles of 1 in the gas phase $y_1 n^V$:

$$y_1 n^V + x_1 n^L = z_1 n \tag{195}$$

Note that in a binary mixture $x_2 = 1 - x_1$ and $y_2 = 1 - y_1$ so that a third equation, the component material balance for 2 ($y_2 n^V + x_2 n^L = z_2 n$) does not contain additional information. Using the two equations 194 and 195 one can calculate for the two unkowns (n^L and n^V):

$$\frac{n^L}{n^L + n^V} = \frac{y_1 - z_1}{y_1 - x_1} = \frac{b}{a + b} \tag{196}$$

and

$$\frac{n^V}{n^L + n^V} = \frac{z_1 - x_1}{y_1 - x_1} = \frac{a}{a + b} \tag{197}$$

where a and b are the lengths of the lever arms as shown in figure 17. By reading out a and b, the relative amounts of moles of vapor and moles of liquid are easily obtained in a graphical manner.

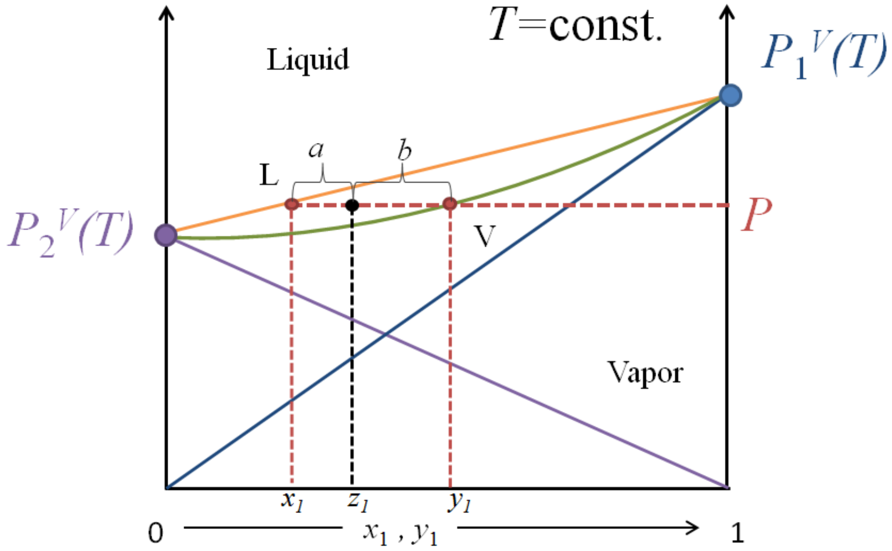

Figure 17: Binary $P-xy$ diagram characterizing LVE at T =const. for an ideal gas phase and an ideal liquid phase. Illustration of the lever arm rule when a mixture of overall compoistion ($z_1, z_2 = 1 - z_1$) splits at P into a liquid phase with mole fraction x_1 and a vapor phase with mole fraction y_1.

1.13.3. T-xy diagrams

In industrial processes one is often more interested in the phase and composition data at constant pressure rather than at constant temperature (because equipment used in practice in the chemical industry exhibits usually homogeneous pressure). Phase equilibrium of a binary mixture at constant pressure can be displayed in a $T-xy$ diagram as shown in figure 18. The ordinate is the temperature and the abscissa is the composition of the vapor and liquid phase as mole fractions x_1 and y_1. At $x_1 = y_1 = 0$ one finds the boiling temperature of the pure component 2, T_2^b whereas at $x_1 = y_1 = 1$ one finds the boiling temperature of the pure component 1, T_1^b.

The diagram is constructed by generating $P-xy$ diagrams at different temperatures (as shown in figure 20) and reading out the corresponding x_1 and y_1 values at the pressure P at which the $T-xy$ diagram is to be constructed. The molar fractions x_1,y_1 are then plotted at the corresponding temperature into the $T-xy$ diagram.

Note that unlike in a $P-xy$ diagram, the vapor phase is here above the two phase region (at high temperatures). So the dew point curve is above the bubble point curve. The interpretation of the diagram is similar to the $P-xy$ diagram. In figure 18 at temperature T the composition of the vapor phase and liquid phase that are in equilibrium with each other can be found according to the three red dashed lines. The lever arm rule applies in the same manner as for the $P-xy$ diagram.

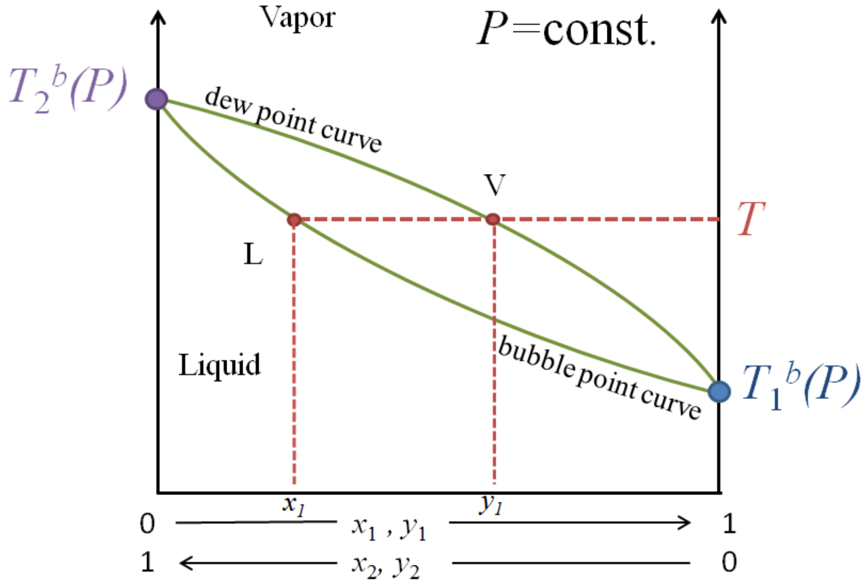

Figure 18: Binary $T - xy$ diagram characterizing LVE at P =const. for an ideal gas phase and an ideal liquid phase.

1.13.4. x-y diagrams

Another way of representing $T - xy$ data is by plotting the pairs of x_1 and y_1 which have already been used to construct the $T - xy$ diagram against each other directly so that x_1 is plotted on the abscissa and y_1 is plotted on the ordinate. The diagonal is $x_1 = y_1$ and is usually plotted as a visual guide. For a given liquid composition x_1 one immediately finds the composition y_1 that corresponds to the equilibrium composition of the vapor phase at the pressure of the diagram. Note that the temperature, according to the $T - xy$ data, changes along the green equilibrium curve, namely it increases in the direction of the arrow in figure 19.

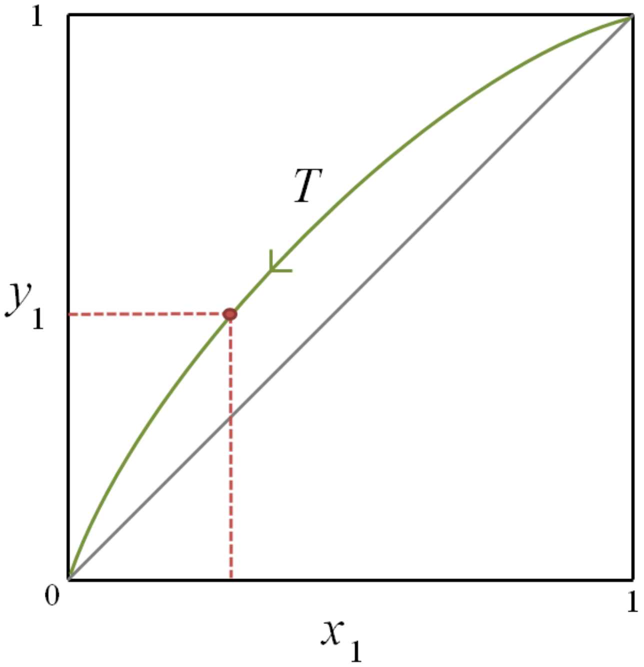

Figure 19: Binary $x - y$ diagram characterizing LVE at P =const. for an ideal gas phase and an ideal liquid phase.

Figure 20 shows an overview of the procedure to construct binary phase diagrams from single component $P-T$ diagrams and by applying the iso-fugacity condition. By using the pure component data from the $P-T$ diagram in the top right corner of figure 20 one is able to draw the pure component vapor pressures into a $P - xy$ diagram (top left corner). The next step is to draw the total pressure curve (orange lines) into the diagram. Using the iso-fugacity condition one may calculate and draw the equilibrium composition of the gas phase for a given pressure and liquid phase composition (green lines in the $P-xy$ diagram) at temperature T. If one repeats this exercise for different temperatures, one can read out the liquid and vapor composition for a fixed pressure (at different temperatures) and draw a $T - xy$ diagram or a $x - y$ diagram (as shown below the $P - xy$ plots).

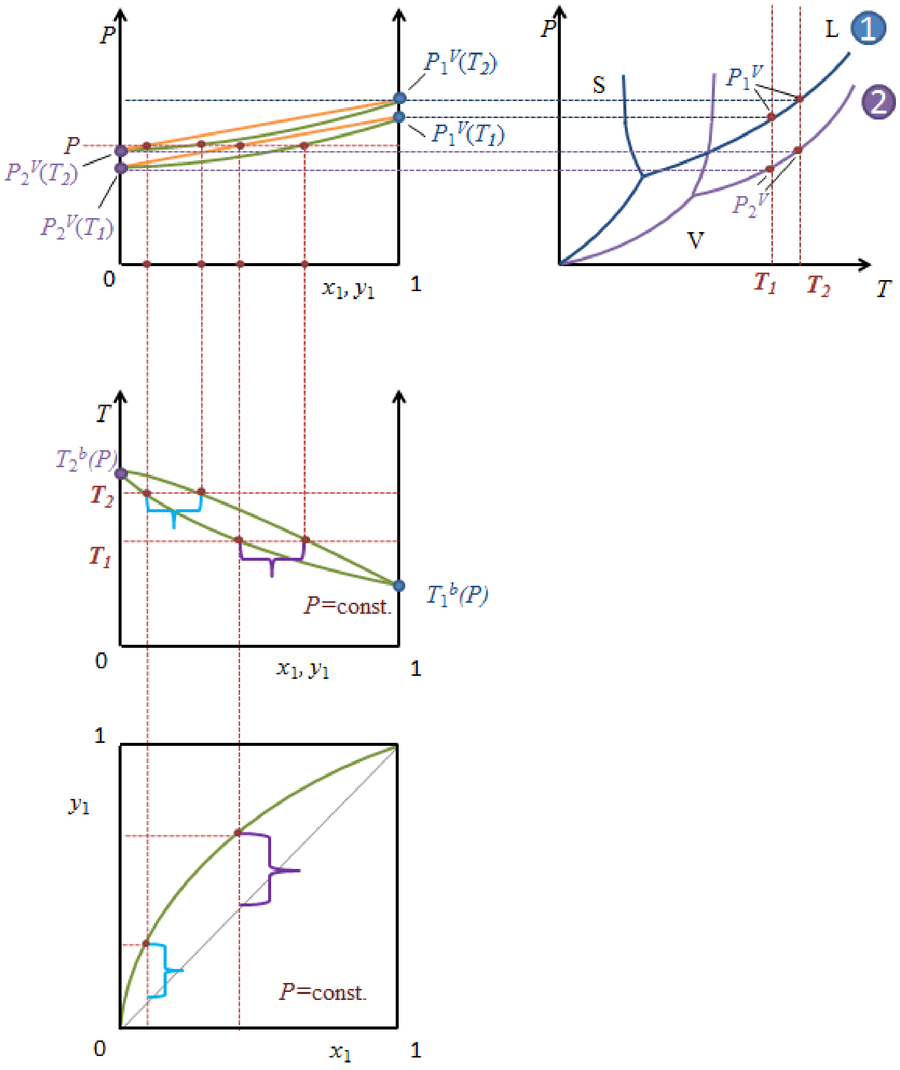

Figure 20: Summary: from single component phase data to xy diagrams.

1.13.5. H-xy diagrams

The last type of diagram that we want to discuss is the enthalpy-composition diagram which is very useful for the design of the separation unit in the next chapter. On the abscissa one finds again the composition plotted in the same manner as in the $T - xy$ and $P - xy$ diagrams. On the ordinate one plots the specific enthalpy h. The diagram is based on the $T - xy$ diagram from the previous chapter (so P =const.), i.e. one plots the specific enthalpy of a liquid mixture $h^L(T_{\mathrm{bp}}(x_1), P, x_1, x_2)$ at the same temperature $T_{\mathrm{bp}}(x_1)$ and composition x_1 as given by the bubble point curve (see figure 18) and the specific enthalpy of a vapor mixture $h^V(T_{\mathrm{dp}}, P, y_1, y_2)$ at the same temperature $T_{\mathrm{dp}}(y_1)$ and composition y_1 as given by the dew point curve (see figure 18). If one considers an ideal vapor phase, the enthalpy of species i is:

$$h_i^V(T, P) = h_i^*(T_{\mathrm{r}}) + \int_{T_{\mathrm{r}}}^{T} c_{p,i}^* dT \tag{198}$$

where $h_i^*(T_{\mathrm{r}})$ is the enthalpy of an ideal gas at a reference temperature T_{r} and $c_{p,i}^*$ is the heat capacity of an ideal gas (i.e. for a monatomic gas $c_{p,i}^* = \frac{5}{2}R$ or for a diatomic gas $c_{p,i}^* = \frac{7}{2}R$)). If one neglects the enthalpy of mixing and treats the vapor phase as ideal, the enthalpy of the vapor phase along the dew point curve at temperature $T_{\mathrm{dp}}(y_1)$ and at the corresponding vapor phase composition y_1 is:

$$h^V(T_{\mathrm{dp}}(y_1), P, y_1, y_2) = y_1 h_1^V(T_{\mathrm{dp}}(y_1), P) + y_2 h_2^V(T_{\mathrm{dp}}(y_1), P) \tag{199}$$

The specific liquid phase enthalpy of component i is:

$$h_i^L(T, P) = h_i^*(T_{\mathrm{r}}) + \int_{T_{\mathrm{r}}}^{T_i^b} c_{p,i}^* dT - \Delta h_i^{LV}(T_i^b) + \int_{T_i^b}^{T} c_{p,i}^L dT \tag{200}$$

where $\Delta h_i^{LV}(T_i^b)$ is the heat of vaporization at standard pressure and boiling temperature T_i^b, and $c_{p,i}^L$ is the liquid phase heat capacity. If one neglects the enthalpy of mixing we obtain an expression for the enthalpy of the liquid phase of a mixture along the bubble point curve at temperature $T_{\mathrm{bp}}(x_1)$ and at the corresponding liquid phase composition $x_1$is:

$$h^L(T_{\mathrm{bp}}(x_1), P, x_1, x_2) = x_1 h_1^L(T_{\mathrm{bp}}(x_1), P) + x_2 h_2^L(T_{\mathrm{bp}}(x_1), P) \tag{201}$$

A schematic diagram is drawn in figure 21. At the bottom we find the liquid phase area which is separated by the $h^L(T_{\mathrm{bp}}(x_1), P, x_1, x_2)$ curve from the two phase region. The vapor area on top of the diagram is separated from the two phase region by the $h^V(T_{\mathrm{dp}}(y_1), P, y_1, y_2)$ curve. Note that at $x_1 = y_1 = 0$ we find $T_{\mathrm{bp}} = T_{\mathrm{dp}} = T_2^b$ and at $x_1 = y_1 = 1$ we find $T_{\mathrm{bp}} = T_{\mathrm{dp}} = T_1^b$. The difference between the liquid and vapor phase enthalpies at $x_1 = y_1 = 0$ is $\Delta h_2^{LV}(T_2^b)$ and at $x_2 = y_2 = 1$ the difference is $\Delta h_1^{LV}(T_1^b)$.

Orange lines and the red dashed line in figure 21 are called tie lines. In an $H - xy$ diagram they connect the specific enthalpy of a liquid mixture of a composition x_1, x_2 at $T = T_{\mathrm{bp}}$ with the specific enthalpy of the vapor phase that is in equilibrium with that liquid phase and has the composition y_1, y_2 at the same temperature T. Please compare to the red dashed horizontal line in figure 18.

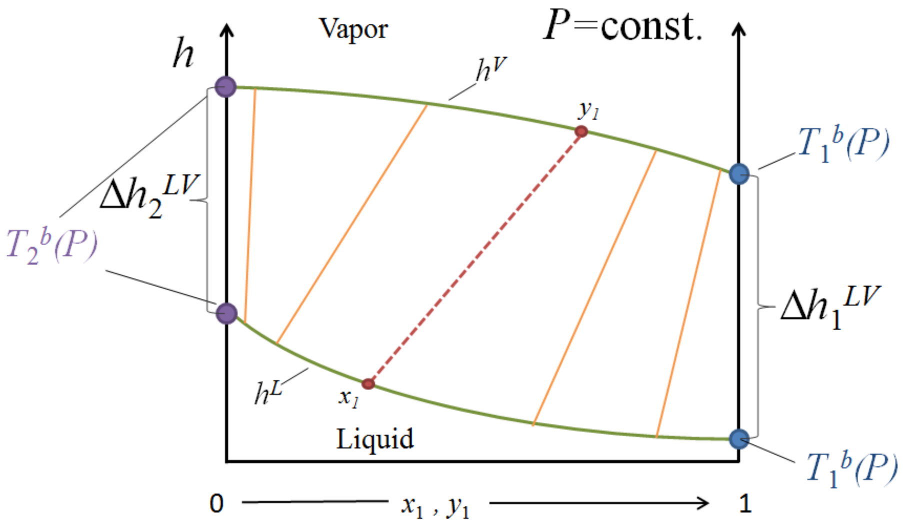

Figure 21: Binary $H - xy$ diagram characterizing the specific enthalpies of liquid and vapor mixtures in equilibrium as shown in figure 18 at P =const. for an ideal gas phase and an ideal liquid phase.

1.13.6. Azeotropes

Let us recall the binary liquid vapor equilibrium for an ideal vapor and a non-ideal liquid phase. In this case, the fugacity of the liquid phase was modified by multiplying with a correction term, the acitivity coefficient $\gamma_i(T, P, x_1, x_2)$. This led to bending of the bubble point curve (solid orange in figure 16) away from the straight line of the ideal case (dashed orange line in figure 16, i.e. Raoult's law). For certain values of γ_i, the bubble point curve will have a maximum or minimum. Systems that exhibit such a behavior are called azeotropic systems. One can distinguish between two cases, a positive deviation from the ideal liquid phase behavior which leads to a maximum of the bubble point curve in a $P - xy$ diagram and a minimum boiling temperature that is below the boiling temperatures of the pure components in the corresponding $T - xy$ diagram (→ minimum boiling azeotrop). This is shown in figure 22. The second case is a negative deviation from the ideal liquid phase behavior which leads to a minimum of the bubble point curve in a $P - xy$ diagram and results as a maxmimum boiling temperature of the azeotropic mixture which is higher than the boiling temperatures of the pure components as shown in figure 23 (→ maximum boiling azeotrop). At the maximum/minimum, bubble point curve and dew point curve meet. In a $x - y$ diagram, the azeotropic point is the intersection of the equilibrium curve with the diagonal.

Boiling of a liquid mixture with a composition corresponding to the azeotropic point leads to an equilibrium with a vapor phase with the same composition. Note that left and right of an azeotropic point, the composition of the gas phase y_1 that is in equilibrium with a given liquid phase composition x_1 is such that for a minimum boiling azeotrope for $x_1 < x_{1,\text{azeotrope}}$(→ left of the azeotropic point) there will be a higher concentration of 1 in the gas phase than in the liquid phase and for $x_1 > x_{1,\text{azeotrope}}$ (→ right of the azeotropic point) there will be a higher concentration of 2 (not 1!) in the gas phase as compared to the liquid phase. For a maximum boiling azeotrope, the situation is inverse.

Azeotropes have a special meaning for separation processes that we will investigate when discussing the separation unit in the next part of the lecture.

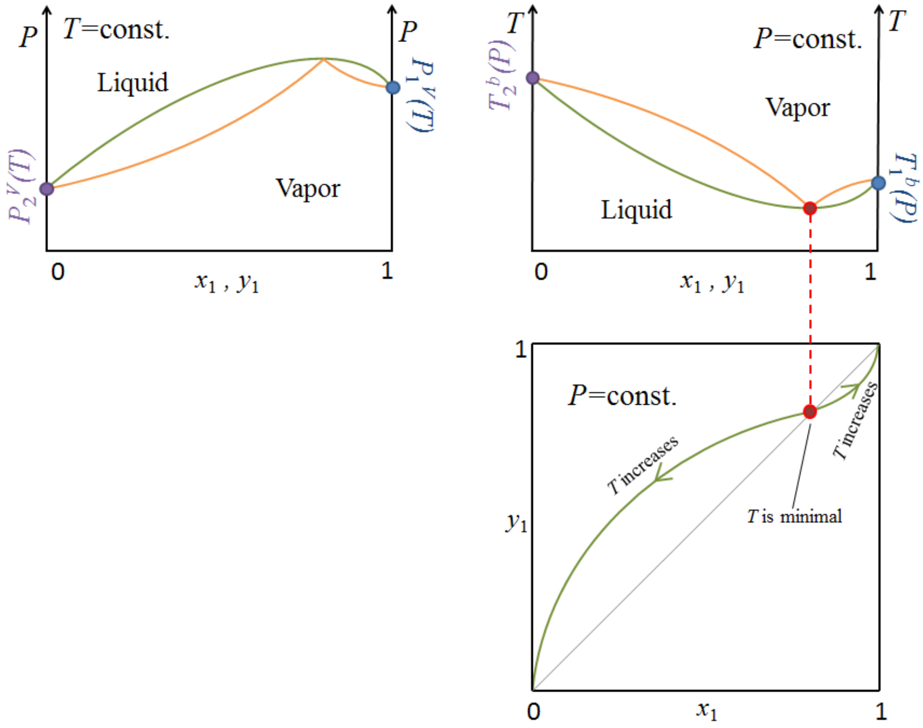

Figure 22: Positive deviation of the liquid phase fugacities from the ideal case (Raoults law) leading to a maximum pressure in the $P - xy$ diagram of the bubble point curve (upper left) and a minimum in boiling temperature in the $T - xy$ diagram (upper right) which is below the boiling temperatures of the pure components (→ minimum boiling azeotrop). In the $x - y$ diagram (lower right) the equilibrium curve intersects with the diagonal at the azeotropic point.

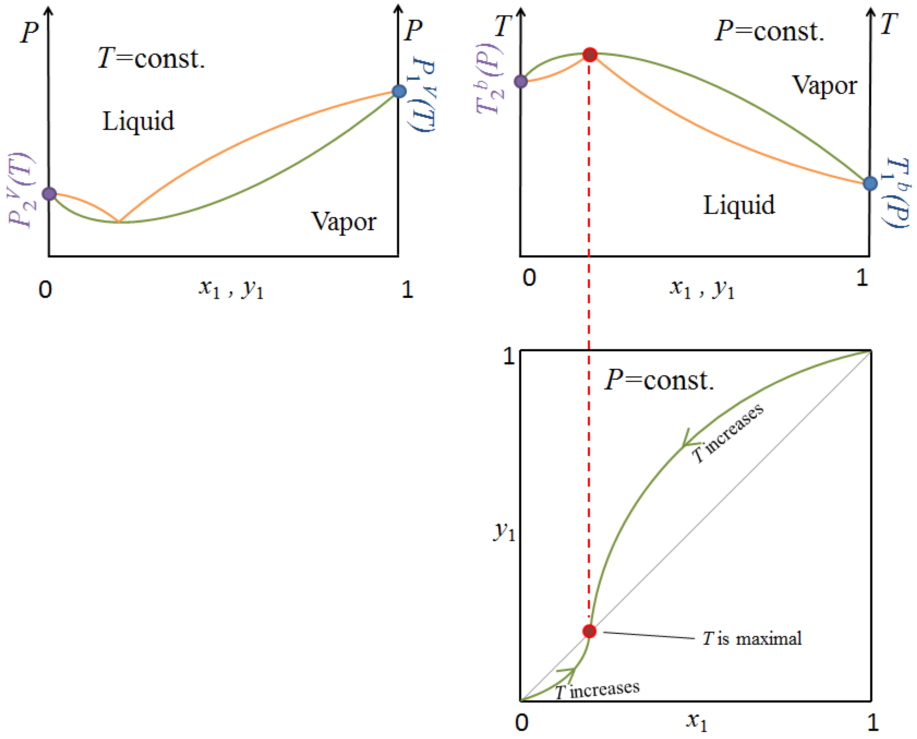

Figure 23: Negative deviation of the liquid phase fugacities from the ideal case (Raoults law) leading to a minimum pressure in the $P - xy$ diagram of the bubble point curve (upper left) and a maximum in boiling temperature in the $T - xy$ diagram (upper right) which is above the boiling temperatures of the pure components (→ maximum boiling azeotrop). In the $x - y$ diagram (lower right) the equilibrium curve intersects with the diagonal at the azeotropic point.