❖ Thermodynamics of equilibrium

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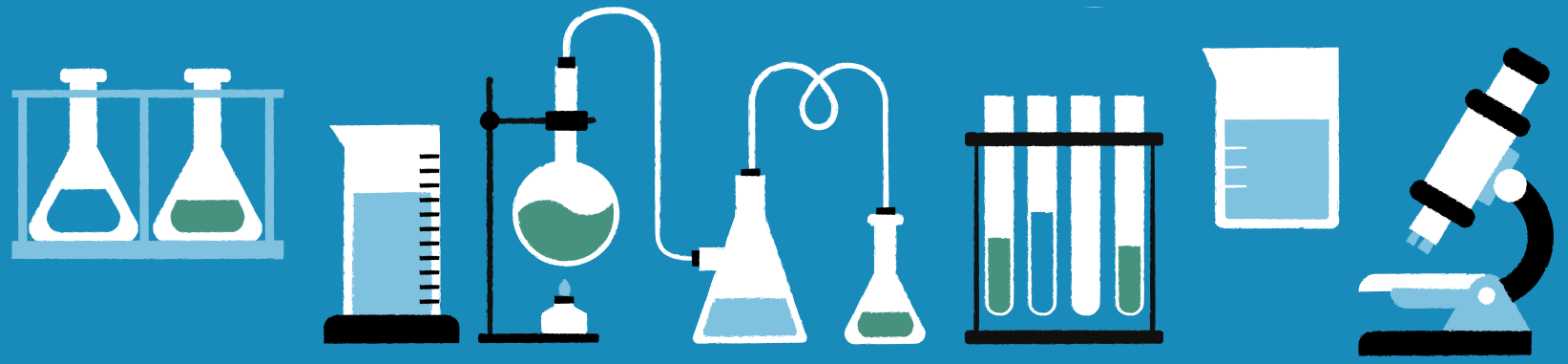


Chapter 1: Thermodynamics of solutions

I.1 Notions On Solutions And Mixtures

I.I.I Definitions Of A Solution And A Mixture

1) **A solution** is any **homogeneous** phase that can be **solid, liquid or gaseous** and that contains several constituents. **The majority** constituent is called a **solvent** (generally a pure compound). The **minority** compound(s) are called **solute(s).** The solvent disperses the molecules or ions of the solute.

The intensive properties of a solution do not depend on the quantity of matter available but are a function of its composition:

- **intensive ppts ≠ f (quantity of matter): pressure, temperature, molar volume,**
- **extensive ppts = f (quantity of matter): mass, volume, number of moles, …**

2)A mixture is a single-phase or multi-phase system (gas, liquid, or solid) containing simple (or pure) substances that do not react: All substances are considered in the same way. In other words, they are equivalent from the point of view of thermodynamic description (same thermodynamic status).

I.1.2 COMPOSITION PARAMETERS

The intensive quantities allowing us to characterize the proportions of the different constituents of a mixture or a homogeneous solution are:

- **Molar Fraction**

The molar fraction or molar titer xi of constituent i, in a single-phase mixture, is expressed by the ratio: $x_i = \frac{n_i}{\sum_i n_i}$ **with** $\sum_i x_i = 1$, ni: The number of moles of the constituent i (mol)

- **for binary solution: $X_1+X_2=1$**

The molar fraction xi is directly related to the molar percentage Xi: $\mathbf{X_i\% = 100x_i}$

- **Mass fraction :** The mass fraction wi of a constituent, in a single-phase mixture, is expressed according to the relation

$$\mathbf{w_i = \frac{n_i M_i}{\sum_i n_i M_i}} \qquad \textbf{with} \qquad \sum_i w_i = 1$$

Where Mi: The molar mass of the constituent i (kg/mol).
The mass fraction is directly related to the mass percentage Wi: $\mathbf{W_i\% = 100w_i}$

- **Mass concentration:** The mass concentration Cm,i of a constituent i is the mass of i per unit volume of solution:

$$C_{m,i} = \frac{masse(i)}{V} = \frac{m_i}{V}$$

$C_{m,i}$ is in g/L^{-1} if mass(i) is in g and V in L. V is the volume of solution.;

- **Molar concentration:** The molar concentration C_i of a constituent i is the quantity of matter of i per unit of volume of solution:

$$c_i = \frac{n_i}{V}$$

The concentration Ci is in $mol \cdot L^{-1}$

- **Molality:** The molality mi is a common composition variable in solution chemistry: it is the number of moles ni of a solute in aqueous solution for **1 Kg** of solvent:

$$\mathbf{m_i(mol.kg^{-1}) = \frac{n_i}{1kg\ du\ solvant}} \qquad m_i = \frac{n_i}{n_S M_S} = \frac{x_i}{x_S M_S} = \frac{x_i}{(1 - x_i) M_S}$$

Where n_s is the number of moles of the solvent s (mol), Ms its molar mass in (Kg/mol):

We can also give the molar fraction xi as a function of the molality mi: $n_i = n_s m_i M_s$

$$x_i = \frac{n_i}{n_S + n_i} = \frac{m_i n_S M_S}{n_S + m_i n_S M_S} = \frac{m_i M_S}{1 + m_i M_S}$$

Example of application

200 g of saturated water are prepared by dissolving a mass of sugar (sucrose (i)) in water.
Knowing that the mass of sugar is approximately 8.55 g.
The sugar is made up of sucrose C12H22O11 with a molar mass Mi=342 g/mol.
Calculate the mass fraction, molar fraction, and molality of the sucrose.

Solution:

The mass fraction wi of sucrose (i) in water:
The molar fraction xi of sucrose (i) in water: xi= ni/(ni+ns) knowing that ni= mi/Mi so:
The molality of sucrose in aqueous solution:

$m_i \longrightarrow$ 1kg du solvant (eau) = 1000g

$n_i = \frac{\text{masse i}}{M_i} \longrightarrow$ 200g d'eau

$= \frac{8{,}55 \cdot 1000}{342 \cdot 200} = 0.125$ mol/kg

❖ I.2: Partial Molar Properties

In the case of a **multi-component system**, **extensive** properties are not obtained, in the vast majority of cases, by simply adding the quantities of the constituents taken in their pure state under the same temperature and pressure conditions. These properties are called **non-conservative** and, to describe these multi-component systems, it is necessary to use the concept of **partial molar properties**. Two phenomena, which are cumulative in most cases, are responsible for this situation:

- **Dissolving** most often leads to **a modification of molecular interactions**;
- **Dissolving** is a mixing operation, therefore **irreversible**, which always leads to a **production of entropy** and therefore always to a **reduction** in the **free enthalpy** for a system at constant temperature and pressure.

I.2.a: Non-conservative quantities

Let us imagine that we mix **n1** moles of a constituent **A1** and **n2** moles of a constituent **A2** in order to obtain a homogeneous system. We are **interested** here in the **extensive quantities** characterizing this system. Let us start with the simple case of **mass**. This is conserved during mixing. We can therefore consider **the mass of the system** as **the sum of the masses** of the two pure constituents, as they were before mixing. If **M1** and **M2** designate the two molar masses of the constituents, the mass **M** of the system can be written: $M = n_1.M_1 + n_2.M_2$

- The situation becomes more complicated for most of the other extensive quantities characterizing the system: in fact, it becomes more complicated each time that the mixture causes a variation of this extensive quantity.

Let's take the example of volume:

- ✓ A vial 1 containing: m1=**152,5g** of ethanol n**1**=**3,325mol** of pure ethanol of molar volume: v_1^*(molar)=**58,3016ml.mol^{-1}**

Note: The properties of the pure constituents are noted with a subscript *.

- The volume of alcohol in the flask is: $v_1 = n_1 v_1^*$ molar =**193,5ml**.
- ✓ A second vial 2 containing: m2=**120,5g** of water n2=**6,675mol** of pure water molar volume: v_2^* molar =**18,0524ml.mol^{-1}**
- The volume of water in the vial is: $v_2 = n_2 v_2^*$ molar molar=**120,0ml**
- The sum of the 2 volumes is: V_1+V**2**=**314,5**ml
- Let's **mix the 2 liquids** in a large graduated flask: The volume of the mixture is:

V(***réel***)=**305,98**ml ≠ V**1**+V**2**≠ $n_1 v_1^*$ molar+ $n_2 v_2^*$ molar=**314,35ml**

- ➢ The mixture results in a **decrease** in volume of approximately **2.7%**.

Another example: the mixture of two liquids is often exothermic or endothermic. Under these conditions,

- the internal energy and enthalpy are not the same before and after mixing. We can therefore write:

$$U \neq n_1.U_{1m} + n_2.U_{2m} \qquad H \neq n_1.H_{1m} + n_2.H_{2m}$$

- Similarly, mixing is an irreversible process that increases disorder at the molecular scale.

Mixing of the two constituents generally occurs with an increase in entropy and a decrease in free enthalpy:

$$S > n_1.S_{1m} + n_2.S_{2m} \qquad G < n_1.G_{1m} + n_2.G_{2m}$$

I.2.b:Definition of partial molar properties

I)Euler's theorem states that a function of several real variables, continuous, differentiable and verifying the relation f (x, y, z,...) = p f(x, y, z,...), is homogeneous of degree p. For such a function, we show that the following relation, between the function and its partial derivatives, is verified:

$$f(x, y, z, \ldots) = \frac{1}{p}\left(x\left(\frac{\partial f}{\partial x}\right)_{y,z,\ldots} + y\left(\frac{\partial f}{\partial y}\right)_{x,z,\ldots} + z\left(\frac{\partial f}{\partial z}\right)_{x,y,\ldots} + \quad \ldots \right)$$

Examples of mathematical applications:

I) Find the degree of homogeneity of the following function: $f(x, y) = x^3y^4$

$$f'_x = 3x^2y^4 \quad ; \quad f'_y = 4x^3y^3$$

$$f'_x + f'_y = (3x^2y^4)\,x + (4x^3y^3)\,y = 3x^3y^4 + 4x^3y^4 = 7\,x^3y^4 = 7\,f(x, y)$$

So f is homogeneous and of degree p = 7

2. $f(x, y, z) = x^2 + 2yz$

$$\frac{\partial f(x,y,z)}{\partial x} = 2x\,; \frac{\partial f(x,y,z)}{\partial y} = 2z\,; \quad \frac{\partial f(x,y,z)}{\partial z} = 2y$$

$$\frac{\partial f(x,y,z)}{\partial x}.x + \frac{\partial f(x,y,z)}{\partial y}.y + \frac{\partial f(x,y,z)}{\partial z}.z = 2x^2 + 2zy + 2yz = 2x^2 + 4yz = 2\left(x^2 + 2yz\right) = 2f(x,y,z)$$

So f is homogeneous and of degree p = 2

2.Definition

Let Z (U, H, S, G, F) =f (T, P, nI, n2, ..., ni, ...) be **an extensive quantity** of a **homogeneous system** with several constituents. It is a **homogeneous function** of degree **p = I** with respect to the quantities of matter; in other words, **Z** is proportional to the quantities of matter. The application of the Euler relation, at constant temperature T and pressure P, therefore leads to writing the relation:

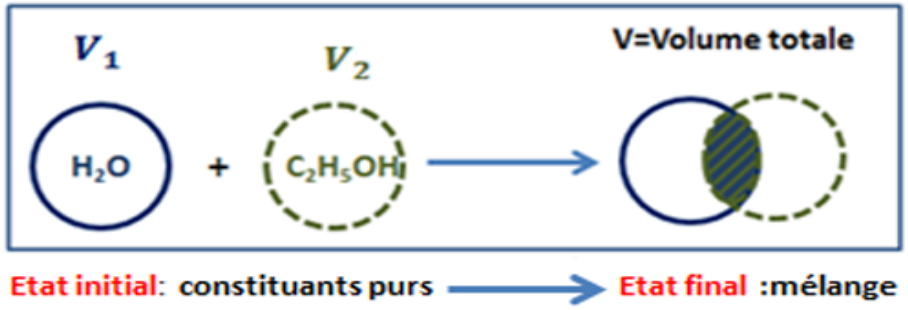
$$Z = \sum_{i=1}^{n} n_i \left(\frac{\partial Z}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \sum_{i=1}^{n} (n_i \overline{z_i})$$

- According to this relationship, we called **the partial molar property(quantity)** of constituent i in the **mixture the partial derivative of Z** with respect to the quantity of matter ni at T, P and quantities of matter n of constituents other than i constant.

$$\overline{z_i} = \left(\frac{\partial Z}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

Example: Applications to volumes ($Z = V, \overline{Z}_i = \overline{V}_i$)

Returning to the previous example. We determine **the volume** V of a solution obtained by mixing $\boldsymbol{V_1}$ of water (1) and $\boldsymbol{V_2}$ of ethanol (2) at 25 °C. In this case, we can have a contraction of **the total volume** V of the mixture:



With: $\begin{cases} V_1 = n_1 V_1^* \\ V_2 = n_2 V_2^* \end{cases}$ *The molar vulume of pure water* / *The molar culume of pure ethanol*

$$V \neq V_1 + V_2 = n_1 V_1^* + n_2 V_2^*$$

N.B.: The properties of pure constituents are noted with a higher index *.

In this example, additivity is not verified. The law of additivity is only possible if we assign to each constituent i the partial molar volume Vi (of i in the mixture) by definition by:

$$V = n_1 \overline{V_1} + n_2 \overline{V_2}$$

$$\overline{V_1} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} \qquad \overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1}$$

Where:

$$x_1 = \frac{n_1}{n_1 + n_1} \qquad x_2 = \frac{n_2}{n_1 + n_2} = 1 - x_1$$

- **Let us define the average molar volume of the mixture:**

$$V_m = \frac{V}{n_1 + n_2}$$

By dividing all the terms of the expression of Vm on n1+n2 boxed above, we easily obtain:

$$V_m = x_1 \cdot \overline{V_1} + x_2 \cdot \overline{V_2} = x_1 \cdot \overline{V_1} + (1 - x_1) \cdot \overline{V_2} = x_1 \cdot (\overline{V_1} - \overline{V_2}) + \overline{V_2}$$

❖ 3)Gibbs–Duhem Equation:

Let us return to the expression of any extensive property $\boldsymbol{Z}$ (V,G,S,M…) in a system at constant T and P: $Z = \sum_j n_j \bar{Z}_j$

where $$dZ = \sum_j n_j \, d\bar{Z}_j + \sum_j \bar{Z}_j dn_j$$

This differential of Z(T,P,ni) is also by definition: $$dZ = \sum_j \bar{Z}_j dn_j$$

Comparing with the 2 previous expressions →

$$\sum_j \bar{Z}_j dn_j = \sum_j n_j \, d\bar{Z}_j + \sum_j \bar{Z}_j dn_j$$

We therefore obtain the Gibbs-Duhem relation: →

$$\sum_j n_j \, d\bar{Z}_j = 0$$

A similar relationship is obtained in terms of mole fractions by dividing by the total number of moles: →

$$\sum_j x_j \, d\bar{Z}_j = 0$$

The Gibbs-Duhem equation $(\sum_j x_j \, d\bar{Z}_j = 0)$ is particularly useful in the case of the binary mixture of 2 compounds I and 2. The variation of one of the partial molar quantities is then directly linked to the evolution of the second.

Example: the partial molar volume of constituent I is expressed as a function of that of constituent 2 according to the relation:

$$d\overline{V_2} = -\frac{n_1}{n_2} d\overline{V_1}$$

❖ Apparent molar properties

- For an infinitely dilute solution, the partial molar properties of the solvent $\bar{Z}_S$ tends towards Z_S^* (pure state of solvent) $\boxed{\overline{Z_S} \to Z_S^*}$
- and the partial molar property of the solute $\overline{Z_i}$ tends towards the apparent molar properties of the solute i (ϕi): $\boxed{\overline{Z_i} \to \phi_i}$

These remarks lead to the following expression of an extensive state properties: $\boxed{Z = n_S Z_S^* + \sum n_i \phi_i}$

- for the volume in a binary solution, we define the apparent molar volumes by $V = n_1 V_1^* + n_2 \Phi_2$

❑ Relationship between apparent molar properties ϕi and partial molar quantity $\bar{Z}_i$

Consider a binary solution containing only one solute: $\boxed{Z = n_S Z_S^* + n_i \phi_i}$

The derivation of Z with respect to the number of moles of solute ni allows access to the expression of the partial molar quantity of the solute $\bar{Z}_i$: $\boxed{\overline{Z_i} = \left(\frac{\partial Z}{\partial n_i}\right)_{T,P,n_S}}$

$$\boxed{\overline{Z_i} = \phi_i + n_i \left(\frac{\partial \phi_i}{\partial n_i}\right)_{T,P,n_S}}$$

❖ Mixture property Z^M

Let us consider a binary mixture formed of 2 constituents (1) and (2) whose numbers of moles are respectively $n1$ and $n2$. We have:

before mixture:

Z^*: property of pue constituent

$$Z^* = n_1 Z_1^* + n_2 Z_2^*$$

After mixture

Z is property of the mixture

$$Z = n_1 \bar{Z}_1 + n_2 \bar{Z}_2$$

the difference is called the mixture property : $Z^M = \mathbf{Z} - \Sigma n_i Z_i^*$

- Example: in the case of volume mixture : $V^M = \mathbf{V} - \Sigma n_i V_i^*$

❖ Molar property of mixture Zm

Let us consider a binary mixture formed of 2 constituents (1) and (2) whose numbers of moles are respectively $n1$ and $n2$.

a molar prperty of mixture, noted Z_M or $Z_{m'}$ corresponds to a mole of the mixture ($n1 + n2 = 1$ $mole$)

We know that $Z = n_1 \bar{Z}_1 + n_2 \bar{Z}_2$

So $Z \rightarrow (n_1 + n_2)$ Mole of mixture

And by difinition $Z_M \rightarrow 1$ Mole of mixture

Consequently, $Z_M = \dfrac{Z}{n_1 + n_2}$

Z_M can therefore be expressed as a function of $\bar{Z}_1$ and $\bar{Z}_2$:

$$Z_M = \frac{n_1}{n_1 + n_2}\bar{Z}_1 + \frac{n_2}{n_1 + n_2}\bar{Z}_2 \quad \Rightarrow \quad Z_M = x_1 \bar{Z}_1 + x_2 \bar{Z}_2$$

❖ Calculation of partial molar properties $\bar{z}_j$ from the molar property of the mixture Zm

We know that $Z = (n_1 + n_2)\, Z_M$

So we have: $\bar{Z}_2 = \left(\frac{\partial Z}{\partial n_2}\right)_{n_1} = Z_M + (n_1 + n_2)\left(\frac{\partial Z_M}{\partial n_2}\right)_{n_1}$

Or $\left(\frac{\partial Z_M}{\partial n_2}\right)_{n_1} = \left(\frac{\partial Z_M}{\partial x_1}\right)_{n_1}\left(\frac{\partial x_1}{\partial n_2}\right)_{n_1}$

like $\left(\frac{\partial x_1}{\partial n_2}\right)_{n_1} = \left(\frac{\partial}{\partial n_2}\left(\frac{n_1}{n_1 + n_2}\right)\right)_{n_1} = \frac{-n_1}{(n_1 + n_2)^2} = \frac{-x_1}{(n_1 + n_2)}$

finally $\bar{Z}_2 = Z_M + (n_1 + n_2)\left(\frac{\partial Z_M}{\partial x_1}\right)_{n_1}\frac{-x_1}{(n_1 + n_2)}$

the partial molar properties of $\bar{Z}_2$ → $\bar{Z}_2 = Z_M - x_1\left(\frac{\partial Z_M}{\partial x_1}\right)_{n_1} = Z_M + x_1\left(\frac{\partial Z_M}{\partial x_2}\right)_{n_1}$

the partial molar properties of $\bar{Z}_1$ → $\bar{Z}_1 = Z_M - x_2\left(\frac{\partial Z_M}{\partial x_2}\right)_{n_2} = Z_M + x_2\left(\frac{\partial Z_M}{\partial x_1}\right)_{n_1}$

I.3Excess properties and Activity

I.3.1:Excess properties **Excess functions** are correction terms that relate the properties of real solutions to those of ideal solutions. Excess functions are thermodynamic properties of solutions that are in excess of those of an ideal(or ideal dilute) solution at the same T, P and x.

- **Excess properties** are denoted by the superscript "E" (e.g., $\mathbf{G^E}$, $\boldsymbol{H^E}$, $\mathbf{S^E}$, $\mu^{\boldsymbol{E}}$)
- are **extensive :** → depend on the **amount of the mixture**
- Excess properties are **zero** for **ideal solutions** and **non-zero** for **non-ideal solution**

✓ Relations between the excess functions are the same as those between the total functions. →

$$H^E = U^E + PV^E$$

$$G^E = H^E - TS^E$$

✓ Partial derivative of excess functions are the same as those between the total functions. →

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E$$

$$\left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2}$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E$$

Excess Gibbs Free Energy ($\mathbf{G^E}$) →

$$G^E = G_{\text{real}} - G_{\text{ideal}}$$

I.3.2: Activity and Activity Coefficients

The vapour pressures of relatively non-volatile solids and liquids may be extremely low, so, an experimental determination of their fugacity is impractical. When dealing with such substances, it would be convenient to work with another function called activity rather than with fugacity itself. 'Activity' is, **in fact, relative fugacity and is defined as the ratio of fugacity to fugacity in the standard state. It finds wide application in the study of homogeneous chemical reaction equilibria involving solids and liquids.** Activity **is denoted by the letter a, where**

$$a = \frac{f}{f^0}$$

- The activity **of a component in a solution** can be defined in a similar way. It is the ratio of fugacity of a component in the solution in a given condition to the fugacity of that component in the standard state. It is denoted by ai

$$a_i = \frac{\bar{f}_i}{f_i^0}$$

Two standard states are common: I. The pure component gas in its ideal state at I bar. At this state, the fugacity is unity if expressed in bar. The activity becomes

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{1} = \bar{f}_i$$

- The pure component gas at the pressure of the system. With this choice the activity of each component in ideal gas solution becomes equal to its mole fraction

For ideal solutions as $\bar{f}_i = x_i f_i$, the activity $a_i = x_i$

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{f_i} = \frac{x_i f_i}{f_i} = x_i$$

ACTIVITY COEFFICIENTS: Activity coefficients measure the extent to which the real solution departs from ideality

$$\bar{f}_i = \gamma_i x_i f_i$$

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{a_i}{x_i}$$

$$a_i = \gamma_i x_i$$

where:

- a_i = activity of component i
- γ_i = **activity coefficient** (measures deviation from ideality)
- X_i = mole fraction

- If $\gamma = 1$ → ideal solution (Raoult's Law holds).
- If $\gamma > 1$ → positive deviation (higher vapor pressure).
- If $\gamma < 1$ → negative deviation (lower vapor pressure).

I.4:Models of non-electrolytic liquid solutions

Models of non-electrolytic liquid solutions describe how different components interact in solutions where the solutes do not dissociate into ions (i.e., non-electrolytes). These models help predict properties such as vapor pressure, boiling point, freezing point, and mixing behavior. Some of the key models include:

❑ Ideal Solution Model (Raoult's Law)

Assumes that intermolecular forces between different components are similar to those within each component and **Obeys to Raoult's Law**

- **No enthalpy** change on mixing: $\Delta H\text{mix}=0$
- **No volume** change on mixing: $\Delta V\text{mix}=0$
  Intermolecular forces between A-A, B-B, and A-B are **similar.**

$$P_A = X_A P_A^0, \quad P_B = X_B P_B^0$$

where P_A and P_B are the partial vapor pressures, X_A and X_B are mole fractions, and P_A^0 and P_B^0 are the vapor pressures of pure components.

- No enthalpy or volume change upon mixing.

❖ CHEMICAL POTENTIAL

- The chemical potential **μi** of species i is therefore its partial molar free enthalpy $\overline{G_i}$. By analogous reasoning, we obtain similar expressions for the differentials of the other state functions, namely H, U and F:

$$\mu i = \left(\frac{\partial u}{\partial nj}\right)_{V,S,n_{j\#i}} = \left(\frac{\partial H}{\partial nj}\right)_{S,P,nj\#i} = \left(\frac{\partial G}{\partial nj}\right)_{T,P,nj\#i} = \left(\frac{\partial F}{\partial nj}\right)_{T,Vnj}$$

$$\mu i = \left(\frac{\partial G}{\partial ni}\right)_{T,p,ni} dnj$$

→ most important because chemical reactions are studied at T and P constant

❖ **Chemical Potential For an ideal solution(liquid or solid)**, the chemical potential of component i is given by:

$$\mu_i = \mu_i^0 + RT \ln X_i$$

where: μ_i^0 standard chemical potential (pure component at the same temperature and pressure), R = universal gas constant, T = absolute temperature (Kelvin), X i = mole fraction of component ii in the solution.

- The chemical potential decreases as the component is diluted (Xi decreases). The solution follows Raoult's Law: $P_i = X_i P_i^0$

Example:

For an ideal benzene-toluene solution, if $X_{\text{benzene}} = 0.5$, the chemical potential of benzene is:

$$\mu_{\text{benzene}} = \mu_{\text{benzene}}^0 + RT \ln(0.5)$$

❖ Chemical Potential in a Non-Ideal Solution

A non-ideal solution shows deviations from Raoult's Law due to differences in intermolecular interactions (e.g., hydrogen bonding, dipole-dipole interactions). To account for these deviations, we introduce the activity ai instead of mole fraction: $\mu_i = \mu_i^0 + RT \ln a_i$ Where $a_i = \gamma_i X_i$

If $\gamma i=1 \Rightarrow ai=Xi=1 \Rightarrow$ (follows Raoult's Law).
For non-ideal solutions: $\gamma i \neq 1$,

Example:

For a non-ideal ethanol-water solution, if $X_{\text{ethanol}} = 0.4$ and $\gamma_{\text{ethanol}} = 1.2$:

$$a_{\text{ethanol}} = (1.2)(0.4) = 0.48$$

$$\mu_{\text{ethanol}} = \mu^0_{\text{ethanol}} + RT\ln(0.48)$$

❖ Chemical potential of a pure liquid or a pure solid $\mu^*(T, P) = \mu^\circ(T) + RT\ln(a(T, P))$

We will admit that for a pure solid or liquid, the activity is practically equal to 1. That is,

$$\mu^*(T, P) = \mu^\circ(T).$$

❖ Chemical potential of an ideal pur gaz $\mu^*(T,P) = \mu^{*0}(T) + RT\left(\frac{p}{p_0}\right)$ Or $\mu = \mu^0 + RT\ln\left(\frac{f}{p0}\right)$ *if gz re*

$\mu^*(T,P)$ is the chemical potential of an ideal pur gas P is the presseure of the ideal gas

μ^{*0} is the standard chemical potential: the standard molar free energy of the pure gas (at $p_0 = 1$ bar and a given T).

I.5:Real gas mixtures and pseudocritical properties

I.5.1:Real gas mixtures

I.5.1.1Mixture of Ideal Gases

When dealing with **a mixture of ideal gases**, each gas behaves independently as if the other gases were not present. This follows **Dalton's Law of Partial Pressures** and the **ideal gas law.**

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots \longrightarrow P = \sum P_i$$

- where Pi is the partial pressure of gas i, which is calculated using: $\longrightarrow p_i = Py_i$
- yi id the molar fraction of gas i

❖ **Chemical potential of a pure ideal gas mixture:**

If pi be the partial pressure of the 'i' thconstituent in the gas mixture at total pressure P, then pi=xiP, where yi=mole fraction of the 'i' thconstituent: **Ln pi=lnp+lnyi**

Since for a given composition,yi remains constant $d\ln p_i = d\ln P$

So from equation (e) we have,

$$d\mu_{i,T} = RTd\ln p_i$$

$$\int_{\mu_{i(p_i=1\,atm)}}^{\mu_{i(p_i\,atm)}} d\mu_i = RT\int_{1\,atm}^{p_i\,atm} d\ln p_i$$

$$\mu i(T,P) = \mu i^0(T) + RT\left(\frac{pi}{p_0}\right)$$

- In this expression, the chemical potential of the'i' constituent is expressed in terms of its partial pressure instead of the total pressure of the mixture. However, at constant temperature and composition, $\mu i(T,P) = \mu i^0(T)$

❖ Relation between chemical potential and free gibbs energy G:

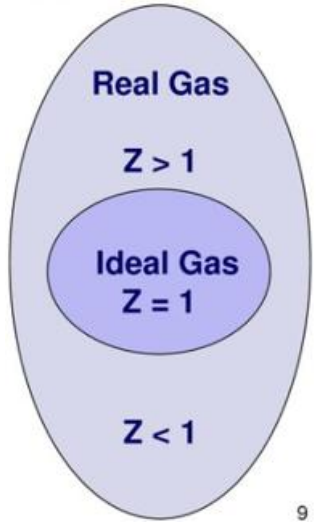
$\boldsymbol{G = \sum ni\mu_i}$ and the variation of gibbs energy of a mixture is given by : **Δ**G=Gf-Gi
Where; Gf is the gibbs energy after mixing ang Gi befor mixing

I.5.1.2: real gas mixtures do not obey the **ideal gas law** perfectly due to intermolecular interactions and molecular volumes. Instead, **equations of state** (EoS) such as **van der Waals, Redlich-Kwong, or Peng-Robinson** are used to describe their behavior.

- **Equations of State for Real Gas Mixtures** → $Z = \frac{PV}{nRT}$

where Z is the **compressibility factor**, which measures the deviation from ideal behavior:

- $Z = 1$ → Ideal gas behavior
- $Z > 1$ → Gas experiences repulsion (dominant molecular volume effects)
- $Z < 1$ → Gas experiences attraction (dominant intermolecular forces)



❖ Chemical Potential with Activity and Fugacity (Non-Ideal Gas Mixture):

In **non-ideal gases**, interactions between molecules cause deviations from ideal behavior. To account for this, we introduce **fugacity** (fi) and **activity coefficient** (γi\gamma_;γi=ai/yi).

$$\mu_i = \mu_i^0 + RT \ln f_i$$

where **fugacity** (fi) replaces partial pressure and is related by the **fugacity coefficient** (ϕi): $f_i = \phi_i P_i$

So, the equation becomes: $\mu_i = \mu_i^0 + RT \ln(\phi_i \text{ yi } P_{\text{total}})$ (For ideal fi=pi)

For **real gases**, ϕi≠ I, and we need experimental or equation-of-state data to determine fugacity coefficients.

- **What are Pseudo-Critical Properties?**

The **pseudo-critical properties** of a gas mixture are **averaged critical temperature and pressure** based on the composition of the mixture. These are used to determine **pseudo-reduced properties**, which help in applying real gas equations of state (e.g., Peng-Robinson, Van der Waals).

- **Pseudo-Critical Temperature (Tc′)** → Represents the mixture's effective critical temperature.
- **Pseudo-Critical Pressure (Pc′)** → Represents the mixture's effective critical pressure.

➢ These values are obtained using **Kay's Rule**, which assumes **ideal mixing of critical properties**.

$$T_c' = \sum y_i T_{c,i}$$
$$P_c' = \sum y_i P_{c,i}$$

→ **Kay's Rule**

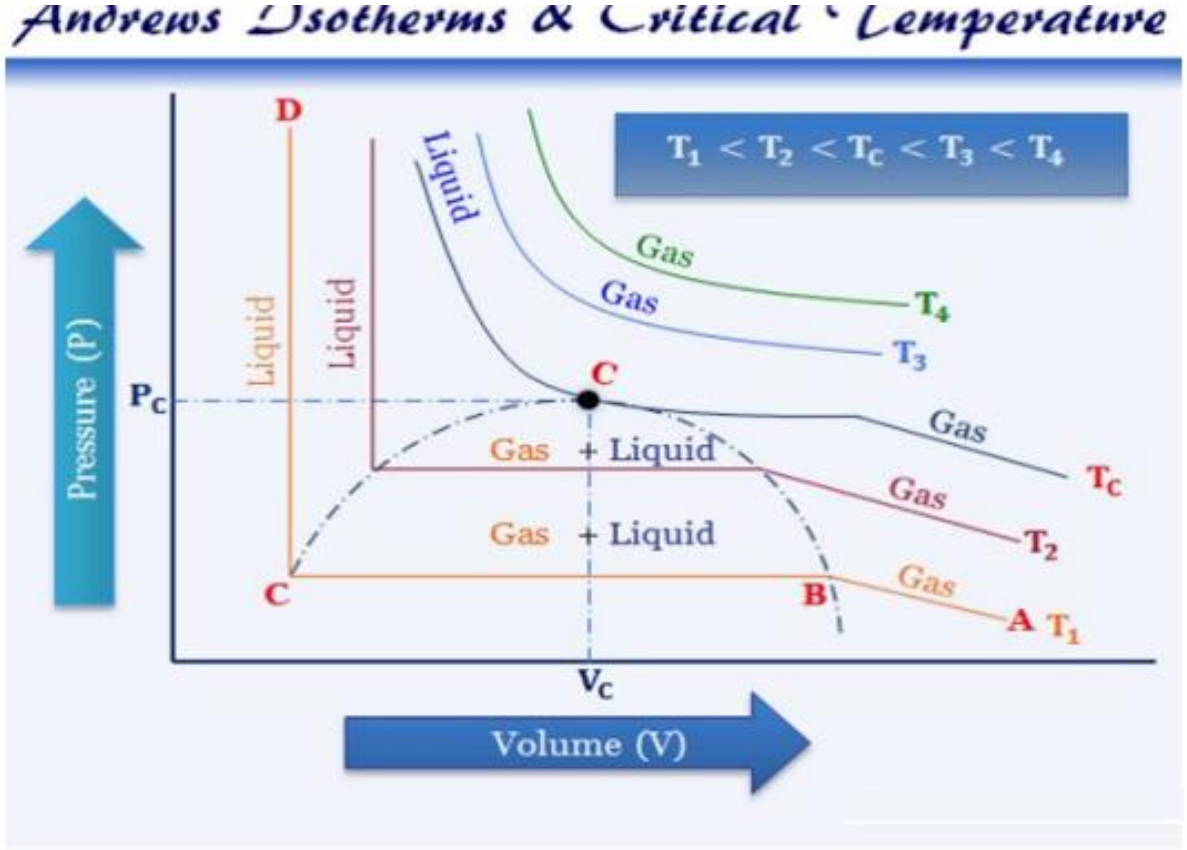
where

- ***yi*** = mole fraction of component ***i***,
- ***Tc*** = critical temperature of component ***i*** (K),
- ***Pc*** = critical pressure of component i (bar or atm).

I.5.2: pseudocritical properties Pseudo-Critical Properties for Real Gas Mixtures

- **the critical temperature (Tc) :** The Critical temperature (Tc) is the maximum temperature at which the gas can be liquefied and the temperature above which the liquid cannot exist.
- **Acritical pressure (Pc) :** Critical pressure (Pc) is the maximum pressure required for the liquefaction of gases at the critical temperature.

- At high temperatures or above the critical temperature the isotherms for liquefaction of carbon dioxide follow ideal gas law.



Carbon dioxide isotherms of p against V

- At low temperatures **or below Tc**, the nature of the curves has altogether different appearances. As **the pressures increase**, the volume of the gas **decreases** in curves A to B. At this point, B **liquefaction** commences and the volume **decreases** rapidly as the gas is converted into a liquid with a much higher density.
- **Point C**, liquefaction of carbon dioxide is complete. The **CD** of the curve is evidence of this fact.
- **AB** represents the gaseous state, **BC** represents liquid or vapor in equilibrium, and **CD** shows the liquid state only.
- Still higher temperatures at T2, we get a similar type of curve to **ABCD**.
- A temperatures **Tc**, the horizontal portion is reduced to a mere point, called the critical point or state of the gases. Every gas can have a limit temperature above which it cannot be liquefied

❖ Pseudo-Reduced Properties

Once we have Tc′ and Pc′ or we define **pseudo-reduced properties:**

$$T_r' = \frac{T}{T_c'}$$

$$P_r' = \frac{P}{P_c'}$$

where:

- Tr′ (Tr)= pseudo-reduced temperature,
- Pr′(Pr)= pseudo-reduced pressure,
- T= actual temperature of the mixture,

Problem:

A gas mixture contains:

- **40% Methane** (CH_4) ($T_c = 190.6K$, $P_c = 46.0$ bar)
- **60% Ethane** (C_2H_6) ($T_c = 305.4K$, $P_c = 48.2$ bar)

Find the **pseudo-critical properties** and **pseudo-reduced temperature** at $T = 400K$.

Step 1: Calculate Pseudo-Critical Temperature

$$T_c' = (0.4 \times 190.6) + (0.6 \times 305.4)$$

$$T_c' = 76.24 + 183.24 = 259.48K$$

Step 2: Calculate Pseudo-Critical Pressure

$$P_c' = (0.4 \times 46.0) + (0.6 \times 48.2)$$

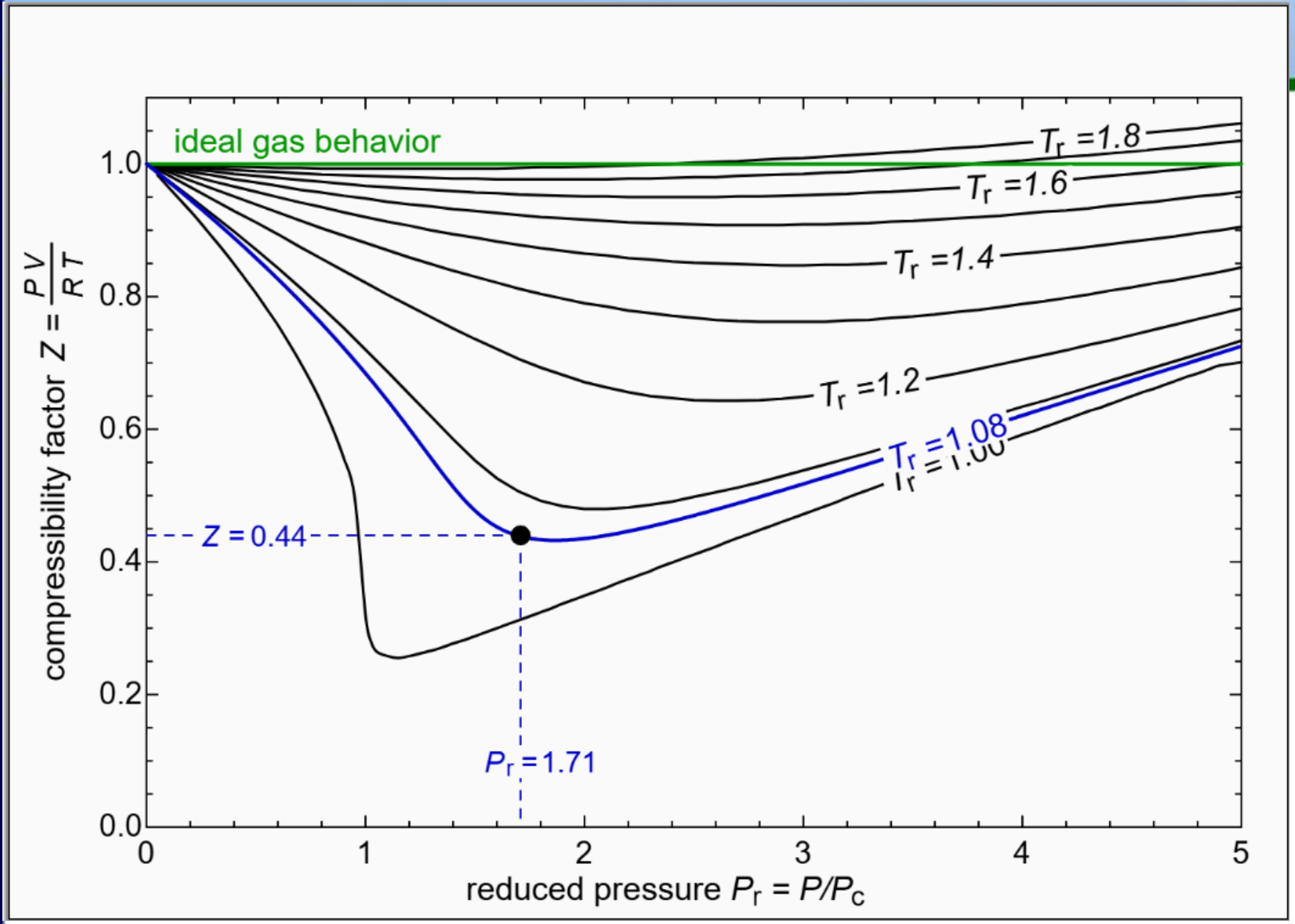
$$P_c' = 18.4 + 28.92 = 47.32 \text{ bar}$$

Step 3: Calculate Pseudo-Reduced Temperature

$$T_r' = \frac{T}{T_c'} = \frac{400}{259.48} = 1.54$$

Using compressibility charts, we estimate $Z \approx 0.95$ for $T_r' = 1.54$ at moderate pressure.

❖ Compressibility Factor Charts



Compressibility chart z for (Tr=1.08 and P=1.71) is 0.44