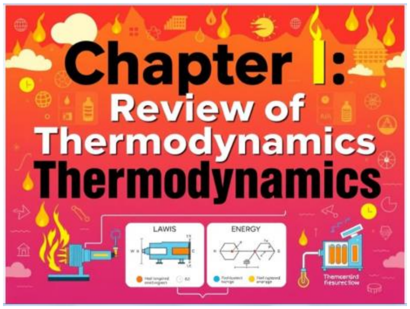


Chapter I:

Review of Thermodynamics

Chapter I: Pure Substances and the Phase Theorem

I.1 Definition of matter

Matter can exist in different **phases** under standard conditions of pressure and temperature. It can also change phase when these conditions are altered.

The most suitable formalism for describing these **phase transitions** is that of **thermodynamics** .

In this context, we will examine two simple cases:

- **Pure simple** substance.
- **Binary mixtures** of simple pure substances.

I.2 Definition of a pure substance:

A **pure substance** is a substance consisting of only one chemical species (element or compound), regardless of its physical state (solid, liquid or gas).

- **Examples:** H_2O, CO_2, NaCl, Fe.
- Warning: a homogeneous mixture (e.g., ethanol solution in water) is not **a** pure substance.

Characteristics of a pure substance:

- Defined by its invariable chemical composition.
- It possesses well-defined physical properties (molar mass, density, melting point, etc.).

- Can exist in several states of matter depending on the conditions of **P** (pressure) and **T** (temperature).

Therefore: Pure substance: A system consisting of only one chemical species

I.3 Phase : Part of a system in which the intensive parameters (pressure, temperature, composition, etc.) have the same value at every point. A phase is therefore homogeneous.

A pure substance can exist in several phases, which can coexist under certain conditions. Four phases are commonly distinguished:

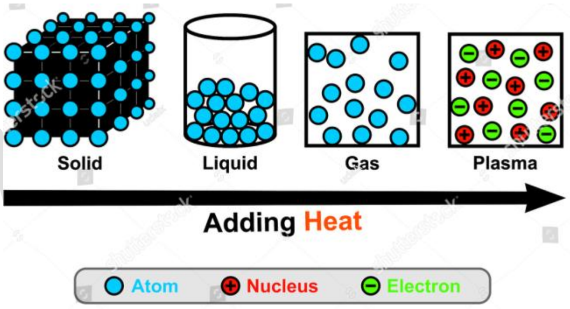


Fig.I.1 : states of mater

- **The solid phase** : characterized, at the microscopic scale, by an ordered and periodic structure (crystalline solid). There can be different solid phases, each corresponding to a particular crystalline symmetry.
- **The liquid phase** : a particular fluid state characterized by molecular disorder, but with a density comparable to that of solids. Molecular interactions play an essential role in this phase.
- **The gaseous phase** : a low-density fluid state in which the molecules are sufficiently far apart that the molecular interaction energy is negligible compared to their kinetic energy. In the limiting case where interactions are totally negligible, we speak of an *ideal gas* .

- **Plasma:** is considered the **fourth state of matter** , sometimes called *ionized gas* . It appears when enough energy (heat, radiation, electric field, etc.) is supplied to a gas to strip electrons from atoms or molecules, thus creating a mixture of ions, free electrons and neutral particles.

Examples:

- Air is a mixture of gases forming a single phase, because all gases are miscible with each other.
- A water-ethanol mixture also constitutes a single phase, as these two liquids are miscible.
- A **water/oil mixture** consists of two phases. Indeed, the volumetric density exhibits a discontinuity at the water/oil interface. It therefore comprises two liquid phases belonging to two different pure substances.
- Graphite and **diamond** represent two distinct solid phases of the same pure substance, carbon. They are referred to as **allotropic** *varieties* .

I.4 Phase transition :

Transition from one phase to another under the effect of a continuous variation of an intensive external parameter (pressure, temperature, electric field, etc.). Two main types of transitions are distinguished:

- **First-order transitions**: these are accompanied by the absorption or release of heat and allow the coexistence of phases in varying proportions.
- **Second-order transitions** : these are not accompanied by heat release and do not allow the coexistence of the two phases. Typical examples are the *normal conductor → superconductor* or *paramagnetic → ferromagnetic transitions* .

Changes **of state in a pure substance** constitute first-order phase transitions. They are accompanied by a change in enthalpy and entropy.

Depending on the nature of the initial and final phases, these transitions are given specific names.

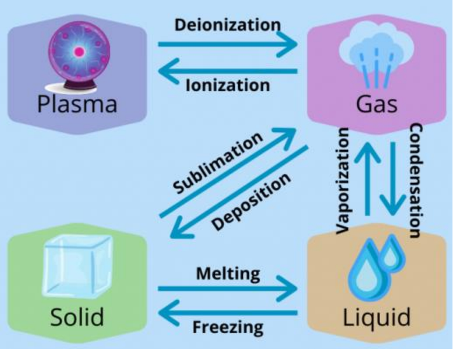


Fig.I.2 : Phase changes

- ✓ **Solid → Liquid e** : Melting
- ✓ **Liquid → Solid** : Solidification
- ✓ **Liquid → Gas** : Vaporization (Evaporation / Boiling)
- ✓ **Gas → Liquid** : Condensation
- ✓ **Solid → Gas** : Sublimation
- ✓ **Gas → Solid** : Solid condensation (deposition)
- ✓ **Gas → Plasma** : Ionization
- ✓ **Plasma → Gas** : Deionization

I.4 Gibbs Phase Theorem :

The phase theorem allows us to determine the **number of degrees of freedom (variance, F)** of a thermodynamic system.

$$F = C - P + 2$$

- ✓ **F** : number of degrees of freedom (independent intensive parameters needed to define the state of the system).
- ✓ **C** : number of constituents (independent chemical species).
- ✓ **P** : number of phases in equilibrium.

- For a **pure substance (C=1)** :

$$F=3-P$$

- If **P = 1** (a single phase, e.g., liquid alone) → F = 2 (T and P must be fixed).
- If **P = 2** (liquid-vapor equilibrium) → F = 1 (for example, at a given pressure, the boiling point is fixed).
- If **P = 3** (solid-liquid-vapor triple point) → F = 0 (T and P are fixed, no freedom).

Example: Water reaches its triple point at **0.01 °C and 611 Pa** .

II.5. Equilibrium Diagrams:

The stability domains of the different phases of a pure substance can be represented using diagrams such as **(P, T), (P, V)** or **(V, T).**

In the **(P, V, T) space** , single-phase regions are delimited by surfaces that meet along lines **of coexistence** . These lines intersect at specific points :

- the **triple point** , where three phases coexist in equilibrium,
- the **critical point** , which marks the boundary between the liquid and gaseous states.

The condition for **the coexistence of phases** is determined by the equality of the **thermodynamic potentials** (or chemical potentials) of the phases in equilibrium.

- **Critical point:** The **critical point** is a particular equilibrium condition that lies at the end of the liquid-vapor coexistence curve in a phase (P, T) diagram.

At this point, the properties of the **liquid** and the **gas** become indistinguishable:

- ✓ The **density of the liquid** decreases,
- ✓ The **density of the gas** increases,
- ✓ Until they become **equal.**

- Beyond the critical point, there is no longer a distinction between liquid and gas: we then speak of a **supercritical fluid.** This fluid possesses both certain properties of a liquid (strong solvent power) and of a gas (high diffusivity).

The critical point is defined by:

- A **critical temperature (Tc)** : the maximum temperature above which the liquid can no longer exist.
- a **critical pressure (Pc)** : the minimum pressure required to liquefy the gas at this temperature,
- a **critical volume (Vc)** .

Example: For water, the critical point is at **374 °C** and **221 bar**

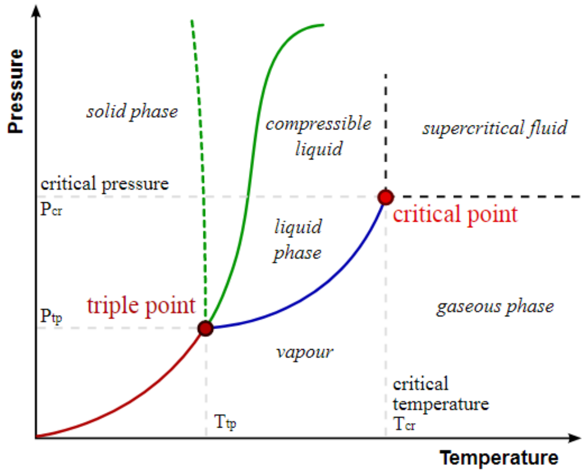


Fig. I. 3: Pressure-temperature diagram for a body

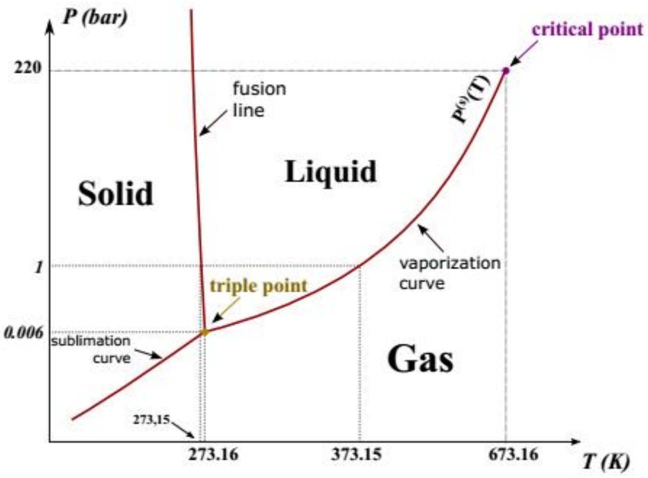


Fig.I. 4: Water phase diagram (P,T)

Example: of a binary system in liquid-vapor equilibrium (methanol/water)

Let us now consider the example of a **binary methanol/water system** (see Figure I.5). If the system exists in **a single phase** —that is, **above the bubble curve** or **below the dew point curve—** it possesses:

F=C−P+2=2−1+2=3 degrees of freedom.

The triplet (T,P, x) is generally chosen as the variable, where:

- T: Temperature,
- P: Pressure,
- X: the molar composition of the mixture.

If the system exists in **two phases** (in the **isothermal equilibrium zone,** ***called the "equilibrium lens»)***, it possesses:

F=C−P+2=2−2+2=2 degrees of freedom.

The variables generally used are the (T,P) pair, which is easily measurable. Indeed, knowing T and P then determines the **composition of each phase** (liquid and vapor) at equilibrium.

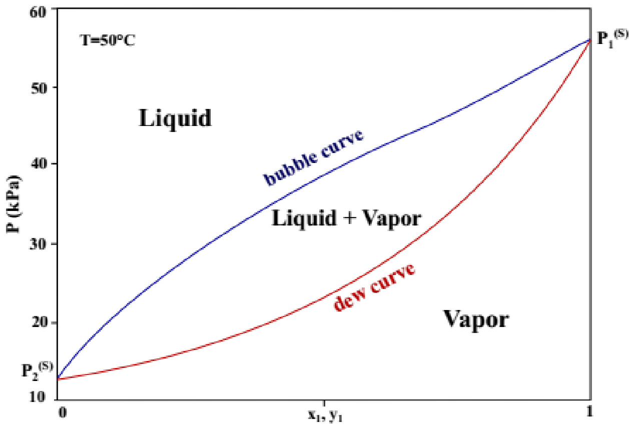


Fig.I. 5: Isothermal lens methanol (1)/ Water (2) at 50°C

I.5.1. Coexistence of liquid and vapor phases:

When **a pure substance is subjected to specific temperature (T)** and **pressure (P)** conditions, it can exist **simultaneously in two phases** : **liquid and vapor.** This situation corresponds to a **state of thermodynamic equilibrium** , which is called **phase coexistence.**

(a) Conditions for coexistence :

- The **coexistence** of liquid and vapor is only possible for **a single combination of T and** P.
- In the **phase diagram (P–T)** , these combinations form a **curve called the liquid–vapor equilibrium curve** .
- Any point on this curve corresponds to a **state of saturation** :
  - ✓ **Saturation temperature Ts** : temperature at which the liquid boils for a given pressure.
  - ✓ **Saturation pressure Ps** : pressure at which the liquid and vapor coexist for a given temperature.
  - ✓ Below the curve: the fluid is **liquid** ; Above: it is **vapor** . On the curve: **the two phases coexist** .

- **Definitions of. Saturation temperature ($T_{sat)}$:** The **saturation temperature** is the temperature at which a pure substance changes state (liquid ↔ vapor) for a given pressure.

Example: at **1 atm (101.3 kPa)** , the saturation temperature of water is **100 °C.**

- **Definitions of Saturation Pressure ($P_{sat)}$: Saturation pressure** is the pressure at which a pure substance changes state (liquid ↔ vapor) for a given temperature.

Example: at **100 °C,** the saturation pressure of water is **1 atm.**

*These two quantities are linked by the **liquid-vapor coexistence curve** (Clapeyron-Clausius equation).*

I.5.2. Raoult's Law (ideal mixtures, liquid solutions):

It gives the partial vapor pressure p_i of a volatile constituent iii in a liquid mixture:

$$p_i = x_i \cdot Pi_{sat}$$

Or :

- x_i : mole fraction of component iii in the liquid,
- Pi_{sat} : saturation pressure of component iii at temperature T.

Total pressure is the sum of partial pressures (***Dalton's law***):

$$P_T = \sum_i x_i P$$

I.5.3. Henry's Law (dilute solutions, solubility of a gas in a liquid):

It expresses the proportionality between the partial pressure of a gas above the liquid and its dissolved fraction:

$$Ci = k_H \cdot pi$$

Or :

- Ci: dissolved concentration of gas i in the liquid,
- k_H : Henry's constant (depends on the gas, solvent, and temperature) ,
- pi: partial pressure of gas i.

Note: This law is particularly useful for gases that are poorly soluble (O_2 , CO_2 , etc.).

I.5.4. Latent heat of phase change:

The **latent heat of phase change** is the amount of heat that must be supplied (or extracted) from a pure substance to change it from one physical state to another, reversibly, under constant pressure.

- When the pressure is kept constant, the heat exchanged corresponds directly to a **change in enthalpy** .
- This is why we also speak of the **enthalpy of phase change** . Thus, latent heat is nothing other than the enthalpy change associated with the phase transition.

- **Main state changes :**

✓ **Solid → Liquid** : **melting**

✓ **Liquid → Solid** : **solidification**

✓ **Liquid → Gas** : **vaporization**

✓ **Gas → Liquid** : **liquefaction**

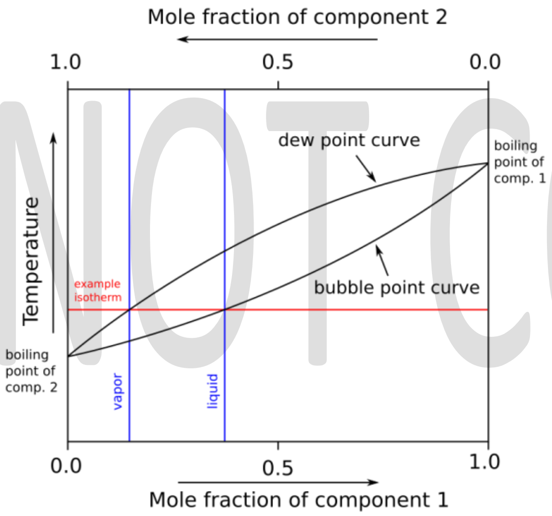
✓ **Solid → Gas** : **sublimation**

- **Gas → Solid:** sometimes called **solid condensation** (the term "condensation" being used generally).

- **Condensation (in the broad sense):** Generally speaking, **condensation is** the change from a gaseous state to a condensed state, i.e., **liquid** or **solid.**
- Liquefaction is therefore just a special case of condensation.

Key points during the liquid-gas transition

- ✓ **Dew point:** temperature (or state) at which the **first drop of liquid appears** while the rest is still gaseous.
- ✓ **Boiling point: temperature (or state) at which the first bubble of gas** appears while the rest is still liquid.



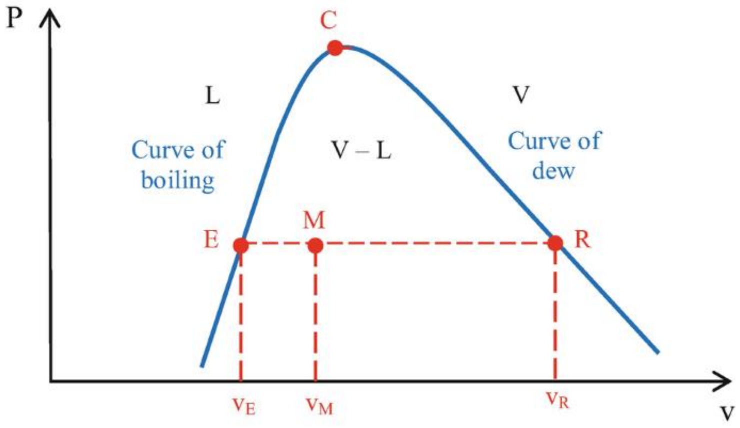


Fig.I.6: PV diagram

I.6. Liquid-vapor balance:

I.6.1. Andrews' Experiment:

Place **1 g of gas** in a bulb maintained at a **constant temperature T.** The **volume of the gas** can be changed using a **mercury column** , which is moved by means of a **piston** . A **manometer allows the pressure P of the gas** to be continuously measured .

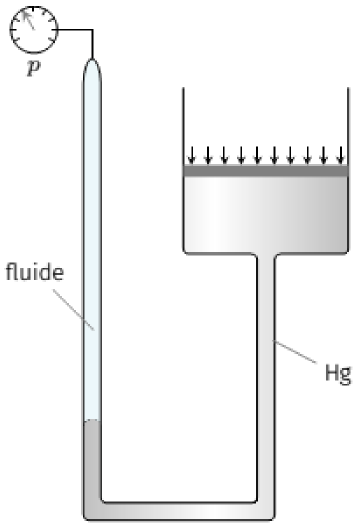


Fig. I.7: Andrews' Experiment Setup

By plotting the variation of pressure as a function of volume during compression, we obtain an **isotherm,** called **the Andrews isotherm.**

Depending on the temperature, two cases can be distinguished:

- **If T < Tc (critical temperature):** The pressure increases until it reaches a **plateau** , corresponding to the **coexistence of two phases** , vapor and liquid. As compression progresses, the proportion of liquid increases. Once the gas has **completely** liquefied, any further decrease in volume causes a **sudden increase in pressure** .

- **If T > Tc (critical temperature):** The pressure **increases continuously** without any plateau or phase change. The fluid then remains in a **supercritical (or hypercritical) state** .

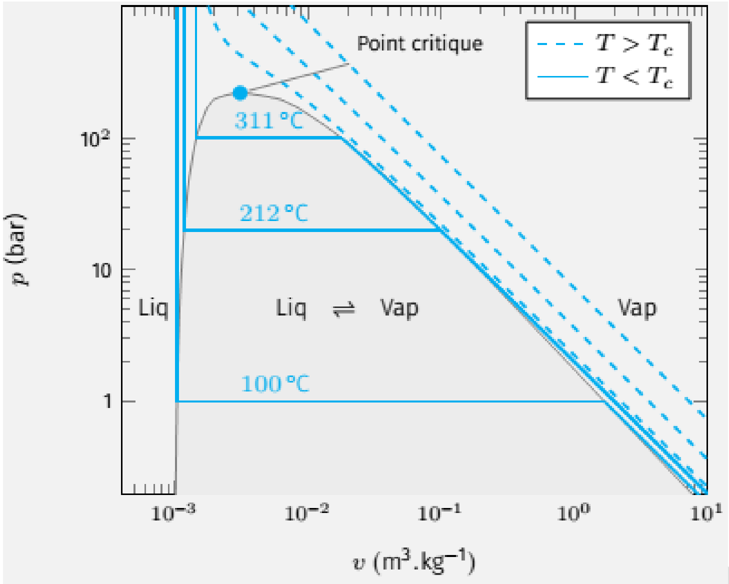


Fig. I.8: Andrew's isotherms of water on a logarithmic scale

I.6.2. Rule of Moments:

Consider a two-phase liquid-vapor **system in thermodynamic equilibrium.** Let :

- **Liquid** phase,
- mg: the mass of the **vapor phase.**

mass fraction of the vapor, x_g (and that of the liquid, x_ℓ), is defined as the mass fraction of each phase in the mixture.

By definition:

$$x_g = \frac{v_g}{v_g + v_l}$$

$$x_g + x_l = 1$$

Let (v_m) be the **average specific volume** of the two-phase mixture. The system then occupies a **total volume:**

$$V_m = (m_g + m_l).v_m$$

Likewise :

- The **liquid phase** occupies a volume Vℓ=mℓ ×vℓ where vℓ is the **specific volume of the liquid phase;**
- The **vapor phase** occupies a volume Vg=mg ×vg where vg is the **specific volume of the vapor phase** .

Thus, the **specific volume of the mixture** can be written as:

$$v_m = x_g.v_g + x_l.v_l$$

This relationship reflects the **rule of moments** , used to describe the properties of a two-phase mixture at equilibrium. It allows us to determine, for a given temperature and pressure, the proportion of liquid and vapor in a mixture.

$$x_g = \frac{v_M - v_l}{v_g - v_l} = \frac{AM}{AB}$$

If we denote **M** as the point representing the **two-phase mixture, A** as the point corresponding to the **saturated liquid,** and **B** as the point corresponding to the **saturated vapor,** then the ratio of the lengths **AM/BM** expresses the **mass fraction of the vapor.** This graphical relationship is known as the **rule of moments** (or **lever rule**).

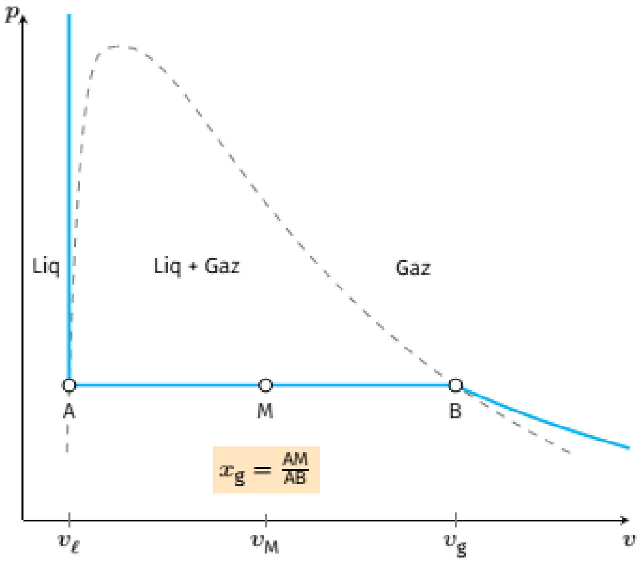


Fig. I. 9: Determination of vapor quality in a Clapeyron diagram.

On the **diagram:**

- Segment **AB** represents the constant temperature phase change plateau.
- **A:** saturated liquid (volume v_ℓ),
- **B:** saturated vapor (volume v_g),
- **M:** state of the mixture (volume v_m).
- The surface area under the plateau corresponds to the **total latent heat absorbed** during vaporization.

I.6.3. Latent heat:

(a) General definition:

During a **change of state** (melting, vaporization, condensation, etc.), the system exchanges a quantity of heat **without a change in temperature.** This quantity is called **latent heat** L. It is defined by:

$$L = Q/m$$

Or :

- Q: is the total amount of heat exchanged (J),

- (m): is the mass of the substance (kg),
- L: is the specific latent heat ($J\cdot kg^{-1}$).

isobaric and isothermal change of state, the heat exchanged is therefore:

$$Q=m\times L$$

- **Case of liquid ⇌ vapor transition**

Consider a mass mmm of liquid brought to its boiling point T_{sat} under a pressure P_{sat}. If the liquid evaporates completely, the heat received is:

$$Q_{vap}=m\times L_v$$

Conversely, during condensation :

$$Q_{cond}=m\times L_v$$

Where: **Lv** is the latent heat of vaporization.

- **Microscopic interpretation:** During vaporization, molecules absorb energy to **break the cohesive forces** of the liquid. Thus, L_v corresponds to the energy required to **remove molecules** from the liquid and bring them to a gaseous state, at a constant temperature.

I.6.4. Relationship with the first law of thermodynamics:

For a reversible, isothermal, and isobaric phase transformation:

$$\delta Q=dU+P\,dV$$

During a **change of state,** the internal energy changes abruptly from U_l(liquid) to U_g (vapor). Integrating between the two states, we obtain:

$$Lv=(Ug-U_{\ell})+P(v_g-v_{\ell})$$

Or :

- (vg): is the specific volume of the vapor ($m^3\cdot kg^{-1}$) ,

- (vℓ): is the specific volume of the liquid (m³·kg ⁻ ¹).

In general, vg ≫ vℓ therefore: Lv≈Pvg

(a) Differential expression: Clapeyron equation:

(Phase transition and Clapeyron equation)

At a given temperature, the **change of state** of a pure substance — passing from one phase α to another phase β — takes place at **constant pressure** Psat, as can be represented on a **phase diagram** P–TP.

During a **first-order phase transition,** according to the **Ehrenfest classification,** there is a discontinuity in the first derivative of the thermodynamic potential (enthalpy, volume, entropy). In other words, the transformation is accompanied by a **latent heat exchange** and a **change in volume** between the two phases.

The **pressure at which a phase change occurs** depends on the **temperature** according to the **Clapeyron equation** , which is written:

$$\left(\frac{dP_{\alpha\to\beta}}{dT}\right)=\frac{\Delta_{\alpha\to\beta}H}{T\,\Delta_{\alpha\to\beta}V}$$

Or: $$\left(\frac{dP_{\alpha\to\beta}}{dT}\right)=\frac{\Delta_{\alpha\to\beta}S}{\Delta_{\alpha\to\beta}V}$$

Or: $$\left(\frac{d\ln P_{\alpha\to\beta}}{d\frac{1}{T}}\right)=\frac{\Delta_{\alpha\to\beta}H}{R\,\Delta_{\alpha\to\beta}Z}$$

- **Characteristic quantities of the change of state**

During a **change of state** of a pure substance between two phases 〈 and ® , several thermodynamic quantities are involved:

✓ T: **temperature of change of state** (in kelvins, K).

- ✓ $P_{\alpha\to\beta}$: **pressure of change of state** at temperature T (in pascals, Pa).
- ✓ $\Delta_{\alpha\to\beta}H$: **molar enthalpy of change of state** from phase (in joules per mole, $J\cdot mol^{-1}$).
- ✓ $\Delta_{\alpha\to\beta}S$: **molar entropy of change of state** from phase 〈 to phase ® at temperature T (in $J\cdot K^{-1}\cdot mol^{-1}$).

These two quantities are linked by the fundamental thermodynamic relationship:

$$\Delta_{\alpha\to\beta}H = T\,\Delta_{\alpha\to\beta}S$$

- $\Delta_{\alpha\to\beta}V$: **variation of molar volume** during the change of state at temperature T and under pressure $P_{\alpha\to\beta}$ (in $m^3\cdot mol^{-1}$).
- V: **molar volumes** of the pure substance in the 〈 and ® πηασεσ , respectively.
- $\Delta_{\alpha\to\beta}Z$ Difference in compressibility factors of the pure substance in the α and β phases, dimensionless quantities:

Special case:

The variation of saturated vapor pressure with temperature is given by the **Clapeyron equation:**

$$\left(\frac{dP_s}{dT}\right)=\frac{L_V}{T\left(v_g - v_l\right)}$$

I.7. Thermodynamic Potential and Chemical Potential:

I.7.1. Definition of chemical potential:

The **chemical potential** (μ_i) of a constituent i is a thermodynamic quantity that represents the change in free energy (or chosen thermodynamic potential) when the amount of that constituent varies, with other parameters held constant.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,nj\neq i}$$

Consider a mixture of N constituents. The chemical potential of each constituent is defined for each of the four thermodynamic potentials: internal energy (it was through this relationship that Gibbs introduced the chemical potential):

- Internal energy (it was through this relationship that Gibbs introduced the chemical potential):

$$dU = -PdV + TdS + \sum_{i=1}^{N} \mu_i \, dn_i$$

- Free Energy: F = U - TS

$$dF = -PdV + SdT + \sum_{i=1}^{N} \mu_i \, dn_i$$

- Entalpy: H = U + PV

$$dH = PdV + TdS + \sum_{i=1}^{N} \mu_i \, dn_i$$

- energy : G = H – TS

$$dG = VdP - SdT + \sum_{i=1}^{N} \mu_i \, dn_i$$

Chemical potential, as a partial derivative of thermodynamic potential, can therefore be defined in various ways, all equivalent.

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,nj\neq i} = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,nj\neq i} = \left(\frac{\partial GH}{\partial n_i}\right)_{T,P,nj\neq i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,nj\neq i}$$

Chemical potential is expressed in: J/mol

Or :

- G: is Gibbs free energy,
- (n_i): is the number of moles of component i.

- It is a measure of the **tendency of a chemical species to participate in a transformation** (reaction or transfer of matter).

The relationship between chemical potential and free energy is particularly important in calorimetry, where chemical reactions are studied at constant volume and temperature. It also plays a central role in statistical physics.

However, it is the last of these definitions, the one that links chemical potential to free enthalpy , that is the most important, because chemical reactions are generally studied at constant pressure and temperature (see the article *Chemical equilibrium*).

I.7.2. Partial molar free enthalpy:

Chemical potential is particularly related to free enthalpy, as it is the only thermodynamic potential for which chemical potential is the partial molar quantity:

$$\mu_i = g_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,nj\neq i}$$

According to Euler's theorem on first-order homogeneous functions, we can write, for any extensive quantity, the relation between this quantity and the partial molar quantities:

$$X = \sum_{i=1}^{N} n_i x_i$$

In the specific case of free enthalpy, this implies, given the identity of chemical potentials and partial molar free enthalpies:

$$G=\sum_{i=1}^{N} n_i\, g_i$$

$$\mu_i = g_i$$

$$G=\sum_{i=1}^{N} n_i\, \mu_i$$

By dividing by: $n=\sum_{i=1}^{N} n_i$

The molar free enthalpy of the mixture is obtained: $g=\sum_{i=1}^{N} x_i\, \mu_i$

I.7.3. Gibbs-Duhem relation:

The **Gibbs-Duhem relation** expresses the **link between variations in the chemical potentials** of the constituents of a system and variations in the temperature and pressure of the system. It reflects the fact that the **chemical potentials µi** of a mixture **are not independent** of each other.

$$G=\sum_{i=1}^{N} n_i\, \mu_i \Rightarrow dG=\sum_{i=1}^{N} n_i\, d\mu_i + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = VdP - SdT + \sum_{i=1}^{N} \mu_i\, d\, n_i$$

Hence the relationship between Gibbs and Duhem: $VdP - SdT = \sum_{i=1}^{N} n_i d\mu_i$

For constant P and T: $\sum_{i=1}^{N} n_i d\mu_i = 0$

This relationship can be written in the form:

$$\sum_{i=1}^{N} x_i d\mu_i = 0$$

For a mixture of two components:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \Rightarrow \frac{d\mu_1}{d\mu_2} = -\frac{x_2}{x_1}$$

I.7.4.. Formulation of chemical potential:

$dG = -S \cdot dT + V \cdot dP$

$V = \left(\frac{\partial G}{\partial P}\right)_{P,T,n\,j\neq i} \Rightarrow v = \left(\frac{\partial \mu_i}{\partial P}\right)_{P,T,n\,j\neq i}$: the partial molar volume

Case 1: For the case of a pure gas and constant temperature, we have:

$PV = nRT$

Case of a perfect gas in an ideal mixture: $PV = \sum_{I} n_i RT$

Hence: $\mu_i = \mu^0(T,P) + RT\ln\left(\frac{P_i}{P_0}\right)$

$$\mu_i = \mu^0(T,P) + RT\ln\left(\frac{y_i P}{P_0}\right)$$

Where: P_0 is the pressure in the standard state

For a pure body in balance: $\mu_i = \mu^0(T,P) + RT\ln(a_i)$

Or :

- $\mu°$: standard chemical potential ,
- R: universal gas constant,
- T: absolute temperature

- a: chemical activity of the species (which can be replaced by concentration, partial pressure or mole fraction as appropriate).

An ideal mixture is a mixture in which the activities of the compounds are equal to their partial pressures for gases, their mole fractions for liquids, and their concentrations for solutes. An ideal mixture for gases corresponds to a mixture of perfect gases. This assumption of ideality presupposes that there are no interactions between the components of the mixture. This is rarely the case in practice; in such cases, we speak of a real mixture.

Case: real gases

In the case of a real gas, we introduce the notion of fugacity ***f*** , which measures the deviation from the ideality of the real gas.

Hence: $\mu_i = \mu^0(T,P) + RT\ln\left(\frac{f_i}{P_0}\right)$

The fugacity factor or coefficient: $\phi = \frac{f_i}{P_i}$

Case : condensed phase

$$\mu_i = \mu^0(T,P) + RT\ln(x_i)$$

In the case of a less-than-ideal mixture:

$$\mu_i = \mu^0(T,P) + RT\ln(a_i)$$

$$\mu_i = \mu^0(T,P) + RT\ln(\gamma_i x_i)$$

Where: $\gamma_i = \frac{a_i}{x_i}$ is the activity coefficient?

Note: every real gas tends towards an ideal gas as its pressure tends towards 0:

$$\lim_{P\to 0} \frac{f}{p} = 1$$

I.7.5. Thermodynamic properties of condensed phases:

A condensed phase refers to matter in a solid or liquid state. Two physical quantities are important :

- **Compressibility,** which indicates how much the system deforms when subjected to a change in pressure (with the temperature kept constant) **.**
- **Expansiveness,** which indicates how much the system **deforms** when subjected to a change in temperature (with the pressure kept constant).

To get an idea of the limits of the incompressible hypothesis, we can experimentally measure the change in volume dV caused by an increase in pressure dP. We keep the temperature constant during this experiment.

We can then obtain **the isothermal compressibility coefficient,** which is defined as follows:

$$\chi_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_{T,n} \quad \text{, in } (\text{atm}^{-1})$$

The minus sign is used to have a positive coefficient, because we can clearly see that if we increase the pressure ($dp > 0$), then the volume decreases ($dV \le 0$), and therefore $-\frac{dV}{dP} \ge 0$.

To test the validity of the non-dilatable hypothesis, we can experimentally measure the change in volume dV caused by a temperature increase of dT. We keep the pressure constant during this experiment. We then define the isobaric expansion coefficient :

$$\alpha_P = \frac{1}{V}\left(\frac{dV}{dT}\right)_{P,n} \quad \text{, in } (\text{K}^{-1})$$

- These coefficients α_P are called thermoelastic coefficients . χ_T

- **Other coefficients:**

- **Isochoric compression coefficients:** $\beta = \frac{1}{P}\left(\frac{dP}{dT}\right)_V$

The three **thermoelastic coefficients** are used to express the variation in volume or pressure of a pure substance or a mixture of constant composition during a reversible transformation:

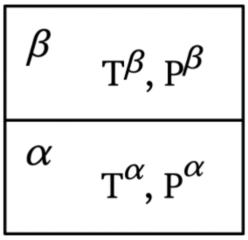
- $\frac{dV}{V} = -\chi_T dP + \alpha dT$
- $\frac{dP}{P} = -\frac{1}{P\chi_T}\frac{dV}{V} + \beta dT$

Table 1: Summary table of the different expressions of the chemical potential

Phase	Expression of μ i
Pure perfect gas	$a_i = \frac{P}{P^0}$
Mixture of perfect gases	$a_i = \frac{P_i}{P^0}$
Mixture of real gases	$a_i = \frac{f_i}{P^0}$
Pure substance	$a_i = 1$
Ideal mixture	$a_i = x_i$
Real mixture	$a_i = \gamma_i x_i$
Ideal solution	$a_i = \frac{c_i}{c^0}$
Real solution	$a_i = \frac{c_i}{c^0}$

I.7.6. Phase balance:

Phase equilibrium refers to the state of a system in which several phases coexist without macroscopic change over time. In this state, intensive properties such as temperature, pressure, and chemical potential are identical in each phase. For example, in a liquid-vapor system, equilibrium is reached when the rate of evaporation of the liquid equals the rate of condensation of the vapor. This equilibrium reflects a stable distribution of constituents among the different phases, resulting from an energy compromise that minimizes the total free energy of the system. Thus, any variation in pressure or temperature conditions can disrupt this equilibrium and lead to a phase transition. The study of phase equilibrium is essential for understanding changes of state in matter and for designing physicochemical processes such as distillation, crystallization, or extraction.



Consider a system composed of two phases α and β in a state of equilibrium. The two phases are in equilibrium if the following conditions are met:

$(T_{\alpha} = T_{\beta} = T;\ P_{\alpha} = P_{\beta} = P;\ G_{m\alpha} = G_{m\beta})$.

Where T_{α} (T_{β}); P_{α} (P_{β});and G_{α} (G_{β}) denote, respectively, the temperature, pressure, and molar Gibbs free energy of the pure α(β) phase. The first two equalities represent the thermal and dynamic equilibria, respectively. The third expresses the chemical equilibrium. Since each phase is characterized by a molar Gibbs free energy that depends on the variables P and T, at equilibrium we have:

$$\Delta G = G_{m\beta} - G_{m\alpha} = 0.$$

- In a **heterogeneous system** (several phases in contact), the equilibrium condition imposes:

$$\mu_i^{(\text{phase 1})} = \mu_i^{(\text{phase 2})} = \mu_i^{(\text{phase 3})} = \ldots$$

(a) Liquid-gas transition: Clausius-Clapeyron equation:

During a **liquid → vapor change of state,** the two phases are in **thermodynamic equilibrium** at a temperature T and a pressure P.

Balance between phases

In balance:

$$\mu_{\text{liquid}} = \mu_{\text{vapor}}$$

where μ: is the **molar chemical potential.**

By deriving this condition:

$$d\mu_{\text{liquid}} = d\mu_{\text{vapor}}$$

Now, for a given phase:

$$d\mu = V_m\, dP - S_m\, dT$$

Or :

- Vm: molar volume,
- Sm: molar entropy.

Hence: $V_m^{(v)}\,dP - S_m^{(v)}\,dT = V_m^{(l)}\,dP - S_m^{(l)}\,dT$

This gives: $\left(V_m^{(v)} - V_m^{(l)}\right)dP = \left(S_m^{(v)} - S_m^{(l)}\right)dT$

Hence the Clapeyron equation

$$\frac{dP}{dT} = \frac{\left(S_m^{(v)} - S_m^{(l)}\right)}{\left(V_m^{(v)} - V_m^{(l)}\right)}$$

$$\left(S_m^{(v)} - S_m^{(l)}\right) = \frac{\Delta H_{vap}}{T}$$

So :

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T.\left(V_m^{(v)} - V_m^{(l)}\right)}$$ This is the Clapeyron equation

Simplified form (Clausius – Clapeyron):

(For the liquid-to-gas transition)

$$V_m^{(v)} \triangleright\triangleright V_m^{(l)}$$

- Steam is considered to be an ideal gas: $V_m^{(v)} = \frac{RT}{P}$

We obtain:

$$\frac{dP}{dT} = \frac{P\Delta H_{vap}}{R.T^2}$$ *Clausius–Clapeyron* equation

I.7.7. Amagat's equation:

Amagat's equation is a **real gas law** that concerns **gas mixtures** . It expresses how the **total volume** of a gas mixture is the **sum of the partial volumes** that each gas would occupy **if it were alone** at the same **temperature (T)** and **pressure (P).**

$$V = \sum_{i=1}^{N} V_i$$

The **Amagat diagram** is a thermodynamic diagram representing, for a given fluid at constant temperature, the variation of the product of pressure and volume as a function of the pressure applied to that fluid. It can also represent the evolution of the compressibility factor as a function of pressure.

This diagram is named after the French physicist Émile Amagat (1841-1915) who worked in particular on high-pressure gases.

The Amagat diagram is useful for graphically representing the deviation in behavior of a real gas compared to an ideal gas .

Normalized Amagat diagram

- **Amagat diagram:**

The **Amagat diagram** (or PV diagram as a function of P at constant temperature) represents, for a given fluid and at a fixed temperature, the variation of the PV product as a function of the applied pressure.

Boyle-Mariotte Point

On the isotherm of a real gas, the point where the slope $(\partial(PV)/\partial P)T=0$ (that is, where the curve reaches a minimum) is called **the Boyle-Mariotte point** for that isotherm. The locus of all these minima points, for different isotherms, forms the **Boyle-Mariotte curve** .

Reduced pressure, temperature, and volume

Reduced variables allow us to compare the behavior of different substances by reducing them to normalized dimensionless values.

- **Reduced temperature** :

  $Tr=T/Tc$

  where Tc: is the critical temperature.

- **Reduced pressure** :

  $Pr=P/Pc$

  where Pc is the critical pressure.

- **Reduced volume (or reduced molar volume)** :

  $Vr=V/Vc$

  Where: Vc is the molar critical volume.

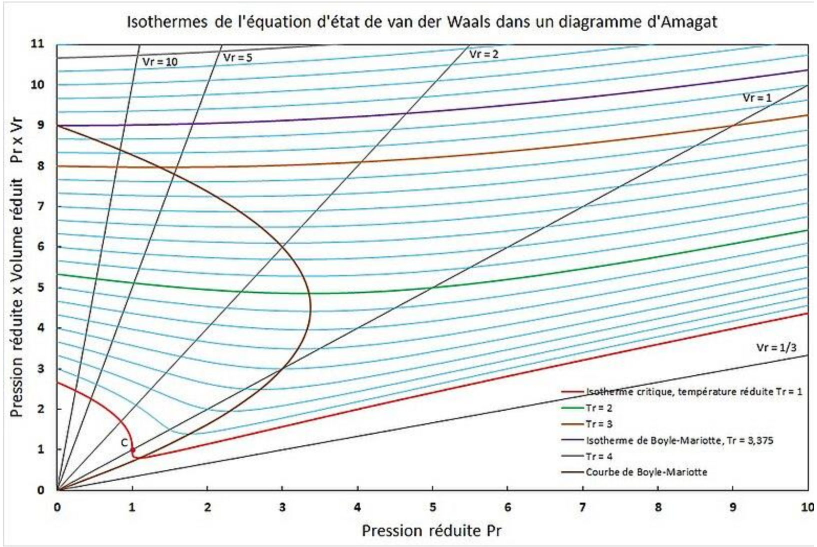


Fig.I.9: Isotherms of the van der Waals equation of state in an Amagat diagram. In brown: Boyle-Mariotte curve; in purple: Boyle-Mariotte isotherm; in red: critical isotherm. The reduced pressure is the ratio of the pressure to the critical pressure .

I.8. Mixture quantities and excess quantities:

I.8.1. Introduction:

When several pure substances are mixed, certain thermodynamic properties of the resulting system differ from those of the individual components.
The study of these variations leads to two important concepts:

- **mixing quantities,** which reflect the overall change in a property during mixing,
- **excess quantities,** which measure the deviation of the actual behavior from that of an ideal mixture.

I.8.2. Mixture quantities:

(a) Definition:

the **size of the mixture** X ^{mix} represents the difference between the real extensive thermodynamic quantity X of a solution and the sum of the extensive quantities ni. xi of the pure constituents i , taken at their reference concentrations xi , under the same conditions of quantity, pressure, temperature and phase as those of the real solution.

State functions extensive properties that characterize the solution (volume , entropy , internal energy , enthalpy) Free energy and free enthalpy may differ from those of a mechanical mixture made up of the same number of moles of the same constituents :

$$X \neq \sum_{i=1}^{N} n_i x_i^*$$

x_i^* : Designates the molar scale of component i in the form of a pure substance in the same physical state (gas, liquid, solid) and at the same temperature T and pressure P as the solution

For example:

$$V \neq \sum_{i=1}^{N} n_i v_i^*$$

- v_i^* volume of component i in pure form

The mixing quantity (mixing function) is called the difference characterizing the inequality:

$$X^{mix} = X - \sum_{i=1}^{N} n_i x_i^*$$

Case of free enthalpy:

$$G^{mix} = G - \sum_{i=1}^{N} n_i g_i^* = \sum_{i=1}^{N} n_i \left(g_i - g_i^*\right)$$

$$G^{mix} = \sum_{i=1}^{N} n_i \left(\mu_i - \mu_i^*\right) = \sum_{i=1}^{N} n_i \, RT \ln(a_i)$$

$$g^{mix} = \sum_{i=1}^{N} x_i \, RT \ln(x_i.\gamma) = \sum_{i=1}^{N} x_i \, RT \ln(x_i) + \sum_{i=1}^{N} x_i \, RT \ln(\gamma)$$

$$\mu_i = \mu^0(T,P) + RT \ln(a_i)$$

I.8.3. Magnitudes of excess:

(a) Definition:

The **excess quantities** reflect the difference between the actual behavior and that of the ideal mixture. They are defined by :

$X^{ex} = X - X^*$

Or :

- X : Magnitude of the actual mixture,
- X^* : Magnitude of the ideal mixture under the same conditions (T, P, x_i).

I.8.4. Deviations from the ideal:

(a) Definition:

To account for the non-ideality of liquid mixtures, the expression for the fugacity of a constituent of a mixture is corrected with respect to the ideal case (proportionality equation of fugacity's and compositions), by introducing an activity coefficient :

(b) Chemical potential and fugacity :

The chemical potential μ_i can be written as a function of the fugacity f_i (reference: P^0, often 1 bar):

$\mu_i(T,P) = \mu_i^0(T,P) + RT \ln \frac{f_i}{P^0}$

We can also write the chemical potential of substance i in the liquid phase using a **standard liquid reference** (standard state denoted 0):

$$\mu_i^L(T,P)=\mu_i^{0,L}(T,P)+RT\ln a_i$$

$\mu_i^{0,L}$: is the chemical potential of the **reference** (for example, the standard pure liquid at the same T, P).

Let's replace $a_i=\gamma_i x_i$ and express it μ_i^0 in terms of the reference fugacity f_i^0 :

$$\mu_i^{0,L}(T,P)=\mu_i^0(T,P)+RT\ln\frac{f_i^0}{P^0}$$

So:

$$\mu_i^L(T,P)=\mu_i^{0,L}(T,P)+RT\ln a_i=\mu_i^0(T,P)+RT\ln\frac{f_i^0}{P^0}+RT\ln a_i=\mu_i^0(T,P)+RT\ln\frac{a_i f_i^0}{P^0}$$

But also, by general definition,

$$\mu_i^L(T,P)=\mu_i^0(T,P)+RT\ln\frac{f_i^L}{P^0}$$

We obtain: $f_i^L=a_i f_i^0=\gamma_i\, x_i\, f_i^0$

(c) What does it represent f_i^0 ?

f_i^0 is the **reference fugacity** associated with the chosen standard state for the liquid phase. Two common choices:

- **Reference = pure liquid (same T, P):** f_i^0 is the fugacity of the pure liquid i at T, P.
- **Common practice (for VL:** VLE = **Vapor-Liquid Equilibrium):** we take $f_i^0\approx f_i^{sat}$ the fugacity of the saturated pure liquid (or an approximation f_i^{sat} if ideal vapor). Thus, we find the form used in ***VLE:***

$f_i^L\approx\gamma_i\, x_i\, f_i^{sat}$ if ($\phi_i^{sat}=1$)

- **Useful borderline cases**

- ✓ If the solution **is ideal** (γi=1), then $f_i^0 = f_i^{sat}$ we recover **Raoult's law** :

  $f_i^L = x_i f_i^{sat}$

- ✓ **Henry's law** is used : $f_i^L \approx x_i H(T)$

The activity coefficient γ_i depends on temperature, composition, and, - to a lesser extent - pressure.

Expressing the chemical potential of constituent i based on the definition of fugacity , we obtain :

$$\begin{aligned}\mu_i^L(T,P) &= \mu_i^{std}(T,P) + RT\ln\frac{\gamma_i x_i f_i^{L,pur}}{P^{std}}\\ &= \mu_i^{L,pur}(T,P) + RT\ln\gamma_i x_i\\ &= \mu_i^{L,id}(T,P) + RT\ln\gamma_i\end{aligned}$$

$\mu_i^{(L,id)}$ Representing the chemical potential that component i would have in the same mixture, if that mixture were ideal. We see the product called activity appear in the expression for the chemical potential of a component of a non-ideal mixture. $x_i\gamma_i$ a_i of component i of the mixture.

By calculating the molar free enthalpy $g = \sum x_i\mu_i$, we see that it is expressed as the sum of the molar free enthalpy of the assumed ideal solution, and an excess free enthalpy , which represents the deviations from ideality:

$$g = \sum x_i\mu_i$$

$$g = \sum x_i\mu_i^{L,id}(T,P) + RT\sum x_i\ln\gamma_i = g^{L,id} + g^E$$

$$\mu_i^L(T,P) = \mu_i^{L,id}(T,P) + RT\ln\gamma_i = g^{L,id} + g^E = \left(\frac{n\partial g^L}{\partial n_i}\right)_{T,P,nj\neq j} + \left(\frac{n\partial g^E}{\partial n_i}\right)_{T,P,nj\neq j}$$

By identifying the two sides of this equation term by term, we finally find:

$$RT\ln\gamma_i=\left(\frac{n\partial gE}{\partial n_i}\right)_{T,P,nj\neq j}$$

This relationship shows that the activity coefficients of the constituents of the mixture are all obtained by derivation of a single excess free enthalpy function : they are therefore not independent functions of each other.

Using the usual set of relationships between thermodynamic functions, we can define an excess volume and an excess enthalpy by:

$$v^L=\sum x_i v_i^{L,id}(T,P)+v^E \quad \text{where}: v^E=\left(\frac{\partial g^E}{\partial P}\right)_T$$

$$h^L=\sum x_i h_i^{L,id}(T,P)+h^E \quad \text{where}: v^E=-T^2\left(\frac{\partial\left(g^E/T\right)}{\partial T}\right)_P$$

- The excess volume represents the difference between the volume of the mixture and the volume of the assumed ideal solution, which is in fact equal to the sum of the volumes of the separate pure substances. The excess volume is almost always negligible compared to the volume of the mixture. For the sake of simplicity, we will therefore neglect it hereafter, which amounts to assuming the **excess Gibbs free energy is independent of pressure** .

- The excess enthalpy is the difference between the enthalpy of the mixture and the enthalpy of the assumed ideal solution, which is in fact equal to the sum of the enthalpies of the pure substances. It corresponds to the heat absorbed during the mixing process at constant pressure to maintain a constant temperature. Some mixing processes are exothermic ($h^E < 0$), while others are endothermic ($h^E > 0$).

I.8.5. Some general properties :

Consider a non-ideal binary mixture. The reference state for each component is the symmetrical state (pure liquid at the considered temperature and pressure).

We know that for a binary mixture:

$$G^{mix} = G - G^{*} = x_A RT\ln(x_A) + x_B RT\ln(x_B) + x_A RT\ln(\gamma_A) + x_B RT\ln(\gamma_B)$$

$$\Rightarrow\ G^E = x_A RT\ln(\gamma_A) + x_B RT\ln(\gamma_B) = RT\left[x_A\ln(\gamma_A) + x_B\ln(\gamma_B)\right]$$

$$\Rightarrow\ \frac{G^E}{RT} = \left[x_A\ln(\gamma_A) + x_B\ln(\gamma_B)\right]$$

Similarly, it can be shown that:

$$\Rightarrow\ S^E = -\frac{\partial\left(G^E\right)}{\partial T}$$

$$\Rightarrow\ S^E = -x_A R\ln(\gamma_A) - x_B R\ln(\gamma_B) - x_A RT\frac{\left[\partial\ln(\gamma_A)\right]}{\partial T} - x_B RT\frac{\left[\partial\ln(\gamma_B)\right]}{\partial T}$$

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

$$\Rightarrow\ V^E = -\frac{\partial\left(G^E\right)}{\partial P}$$

I.8.1 Margules equation with one parameter:

The **Margules equation is an empirical** model that allows us to represent the **deviation from Raoult's law** (i.e., non-idealism) of a **binary liquid mixture.** It expresses the **excess free energy** G^E or the **activity coefficients** γ_i as a function of the mixture's composition.

$$\frac{G^E}{RT} = A\,x_1x_2$$

Or :

- G^E: molar excess free energy
- R: ideal gas constant
- T: absolute temperature
- x_1,x_2: mole fractions of constituents 1 and 2
- A: **Margules parameter** (empirical constant, dependent on temperature and the nature of the mixture)

I.8.2 Derived activity coefficients:

The **activity coefficients** γ_1 and γ_2 are obtained by derivation of G^E:

$$\ln \gamma_1 = A\, x_2^2$$

$$\ln \gamma_2 = A\, x_1^2$$

I.8.3. Isobaric equilibrium diagram:

(a) Azeotrope:

*** Isobaric equilibrium diagram (or T–x–y diagram)**

*** Definition**

An **isobaric equilibrium diagram** represents the relationship between **temperature** and **composition** of a liquid-vapor mixture **at constant pressure** (often 1 atm). It shows how the composition of the liquid and that of the vapor change during the boiling or condensation of a binary mixture.

An **azeotrope** is a **binary (or multicomponent) mixture** that behaves **like a pure substance** when boiling. In other words, **the liquid and vapor have the same composition** at the boiling point.

$$xi=yi$$

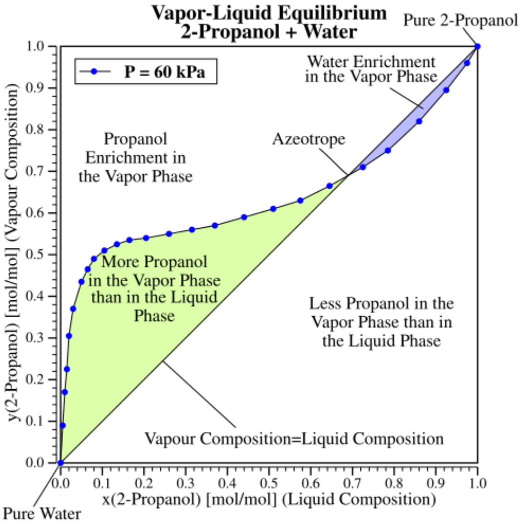


Fig. I.10: Vapor-liquid equilibrium of 2-propanol /water showing positive azeotropic behavior

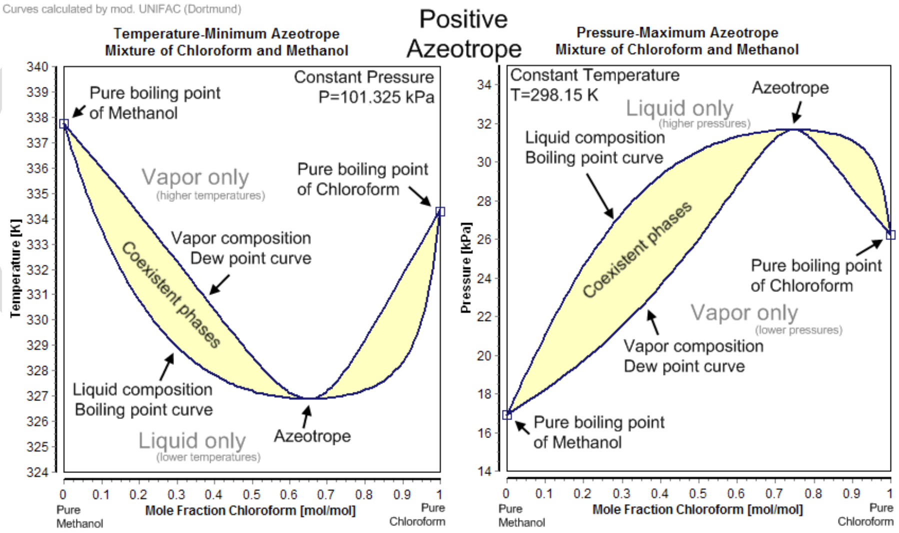


Fig. I.11: Positive azeotrope – mixture of chloroform and methanol

(b) Types of azeotropes :

- **Minimum boiling azeotrope**
  - It forms when the interactions between molecules **are weaker** than in ideal solutions.
  - The boiling point of the mixture is **lower** than that of each of the pure components.
  - Example: **ethanol–water** (~95% ethanol, T = 78.2 °C).

Maximum boiling azeotrope :

- It forms when the interactions between molecules **are stronger** than in ideal solutions.
- The boiling point of the mixture is **higher** than that of each pure component.
- Example: **hydrochloric acid–water** (~20% HCl, T = 110 °C).

Representation on the T–x–y diagram :

- The azeotrope point corresponds to the intersection of the **liquid** and **vapor curves** .
- At this point, xi=yi and the temperature is **extreme** (minimum or maximum).
- The mixture behaves **like a single pure substance** .

Difference between chemical potential and electrochemical potential

- **Chemical potential (μ_i)** : Measures the molar free energy of a species as a function of its nature, concentration and thermodynamic conditions.
- **Electrochemical potential (μ_i)** : Takes into account, in addition to the chemical potential, the effect of the electric field on charged species (ions).

$$\mu{\sim}i=\mu i+ziF\ \phi$$

Or :

- z_i charge of ion i ,
- F: Faraday constant,
- Φ: electrical potential of the medium.

SO :

- For **neutral molecules** , chemical potential = electrochemical potential.

- For **ions** , the electrochemical potential is more complete because it includes the energy due to the electric field.

3. Polymorphism of pure substances

A pure substance can exist in several different crystalline solid forms → **polymorphism** .

- Example: **Carbon**
    - Graphite (laminated structure, stable at ambient pressure).
    - Diamond (tetrahedral structure, stable at high pressure).
- Example : **Sulfur**
    - Rhombic sulfur (stable at room temperature).
    - Monoclinic sulfur (stable at T > 95 °C).

I.9. Enantiotropy and monotropy:

These terms describe the behavior of two polymorphic forms as a function of temperature and thermodynamic stability.

- **Enantiotropy** :
    - Two polymorphic forms can transform each other **reciprocally according to T and P.**
    - Example: rhombic sulfur ↔ monoclinic sulfur.
- **Monotropy** :
    - Only one form is stable under all conditions, the other is metastable.
    - Example: carbon: graphite (stable) ↔ diamond (metastable at ambient P).

I.9.1. High-pressure dimorphism :

- **(a) Dimorphism:** existence of two solid forms of a pure substance.
- Under the effect of **high pressures** , some substances change from one crystalline structure to another.
- **Example :**
    - **SiO $_2$** (α quartz → β quartz → tridymite → cristobalite according to P and T).
    - **Ice** : H_2O has more than 12 different crystalline forms depending on the pressure (ice I, II, III…).