QF.DQB
Química-Física
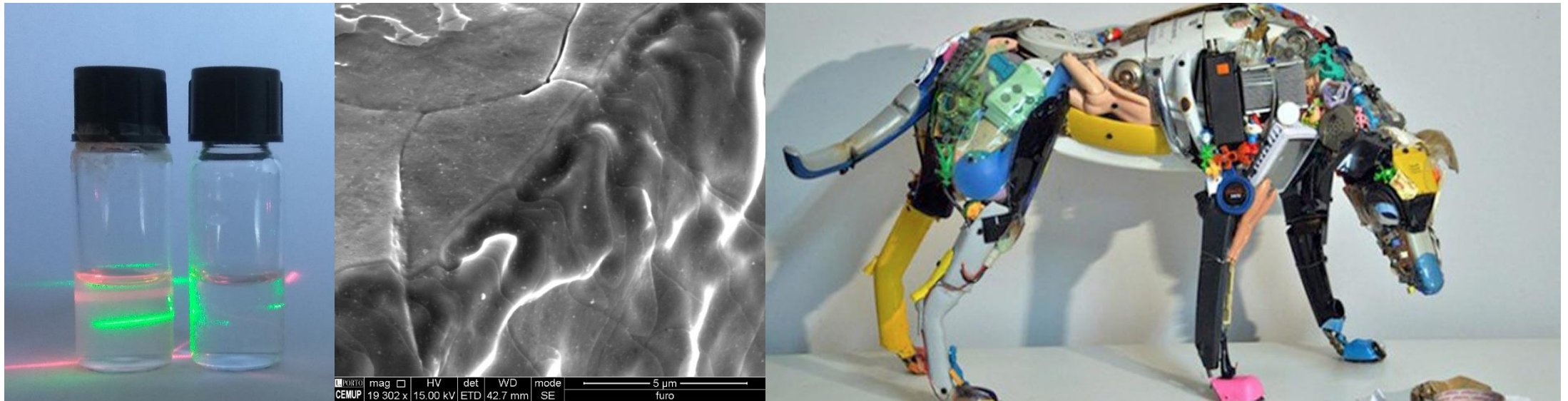Faculdade de Ciências da Universidade do Porto

Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.

The solvent activity

The quantity a_A is the **activity** of A, a kind **of 'effective' mole fraction,**

$$a_A \rightarrow x_A \quad \text{as} \quad x_A \rightarrow 1$$

$$\mu_A = \mu_A^\star + RT \ln x_A + RT \ln \gamma_A$$

Activity coefficient

Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^\star$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a = \gamma b/b^\ominus$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

In each case, $\mu = \mu^\ominus + RT \ln a$.

Activities of ions in solution

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

$$\mu_+ = \mu_+^{ideal} + RT \ln \gamma_\pm \qquad \mu_- = \mu_-^{ideal} + RT \ln \gamma_\pm$$

$$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$$

mean activity coefficient
geometric mean of the individual coefficients

The solvent activity

The quantity a_A is the **activity** of A, a kind of 'effective' mole fraction,

$$a_A = \frac{p_A}{p_A^\star}$$

$$\mu_A = \mu_A^\star + RT \ln(p_A/p_A^\star)$$

$$\mu_A = \mu_A^\star + RT \ln a_A$$

activity coefficient < 1

activity coefficient > 1

Hipotetical a_A **activity**
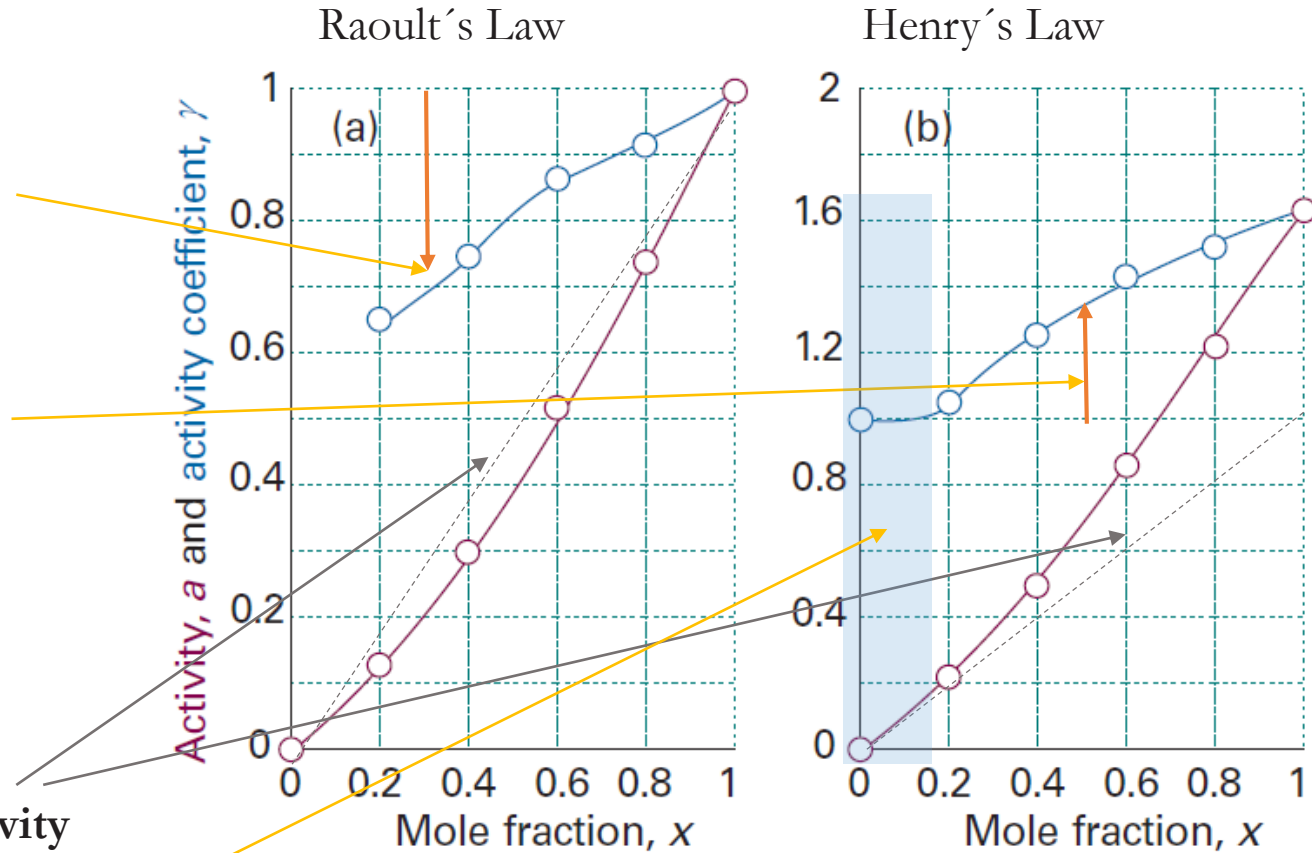**For activity coefficient = 1**

Fig. 5.31 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult's law, (b) Henry's law.

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Debye–Hückel theory of ionic solutions

Describes a **tendency for anions** to be found around cations, and of cations to be found around anions

The chemical potential, central ion is lowered as *a result of its electrostatic interaction* with its **ionic atmosphere**.
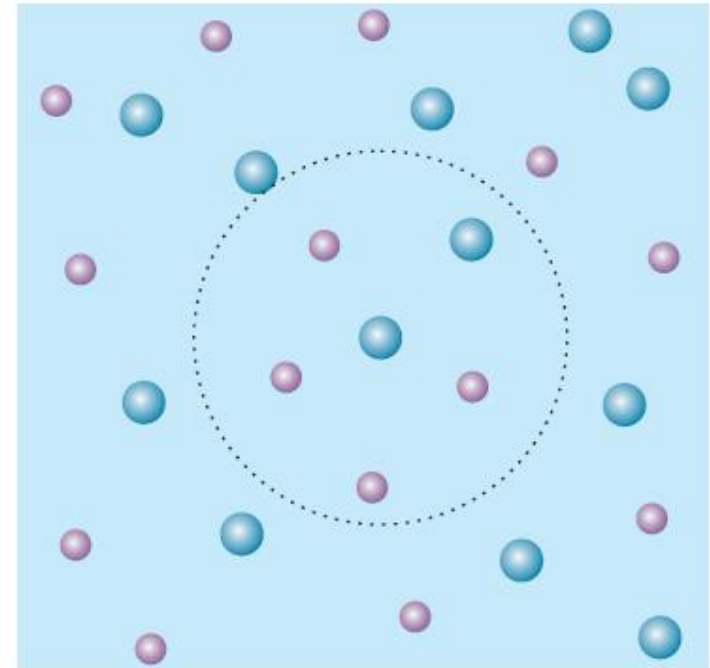
Debye–Hückel limiting law

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$A = 0.509$ for an aqueous solution at 25°C

IONIC STRENGTH
$$I = \tfrac{1}{2} \sum_i z_i^2 (b_i / b^{\ominus})$$

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Debye–Hückel limiting law

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

ionic strength

$$I = \tfrac{1}{2} \sum_i z_i^2 (b_i/b^{\ominus})$$

$A = 0.509$ for an aqueous solution at 25°C

Table 5.4 Ionic strength and molality, $I = kb/b^{\ominus}$

k	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

For example, the ionic strength of an M_2X_3 solution of molality b, which is understood to give M^{3+} and X^{2-} ions in solution is $15b/b^{\ominus}$.

Synoptic Table 5.5* Mean activity coefficients in water at 298 K

$b/b^{\ominus}$	KCl	$CaCl_2$
0.001	0.966	0.888
0.01	0.902	0.732
0.1	0.770	0.524
1.0	0.607	0.725

* More values are given in the *Data section*.

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Debye–Hückel limiting law

$$I = \tfrac{1}{2} \sum_i z_i^2 (b_i/b^\ominus)$$

ionic strength

$$\log \gamma_\pm = -|z_+ z_-| A I^{1/2}$$

$A = 0.509$ for an aqueous solution at 25°C

Illustration 5.4 *Using the Debye–Hückel limiting law*

The mean activity coefficient of 5.0×10^{-3} mol kg^{-1} KCl(aq) at 25°C is calculated by writing

$$I = \tfrac{1}{2}(b_+ + b_-)/b^\ominus = b/b^\ominus$$

where b is the molality of the solution (and $b_+ = b_- = b$). Then, from eqn 5.69,

$$\log \gamma_\pm = -0.509 \times (5.0 \times 10^{-3})^{1/2} = -0.036$$

Hence, $\gamma_\pm = 0.92$. The experimental value is 0.927.

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Debye–Hückel limiting law

ionic strength $\quad I = \frac{1}{2} \sum_i z_i^2 (b_i / b^\ominus)$

$$\log \gamma_\pm = -|z_+ z_-| A I^{1/2}$$

$A = 0.509$ for an aqueous solution at 25°C

The extended Debye–Hückel law

$$\log \gamma_\pm = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}} + CI$$

B and **C** are dimensionless constants

B Related with the closest approach of the ions,
C is best regarded as an adjustable empirical parameter.

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

$$I = \tfrac{1}{2} \sum_i z_i^2 (b_i / b^{\ominus})$$

Ionic strength

Debye–Hückel limiting law
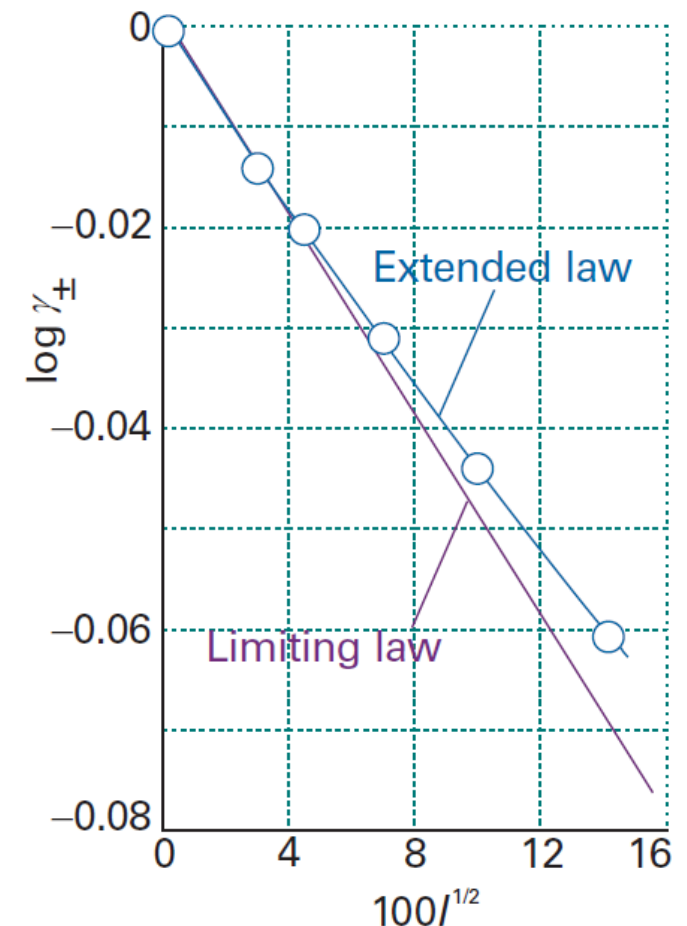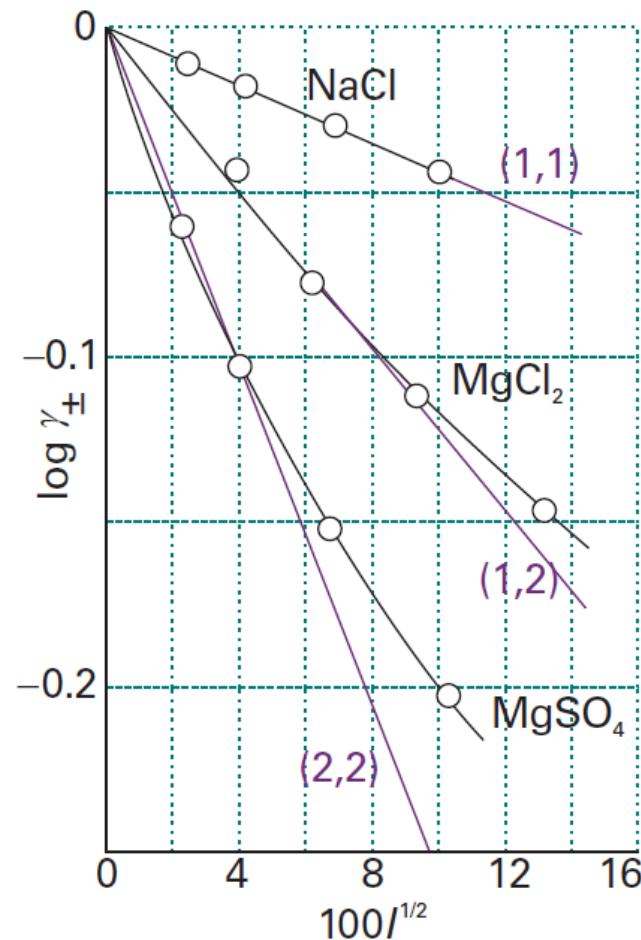
$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

The extended Debye–Hückel law

$$\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}} + CI$$

Gibbs–Duhem equation can also be used to estimate the activity coefficient of the solute

$$\mathrm{d}\mu_B = -\frac{n_A}{n_B} \mathrm{d}\mu_A$$

An experimental test of the Debye–Hückel limiting law.

Phase

state of matter that is uniform throughout

- chemical composition
- physical state
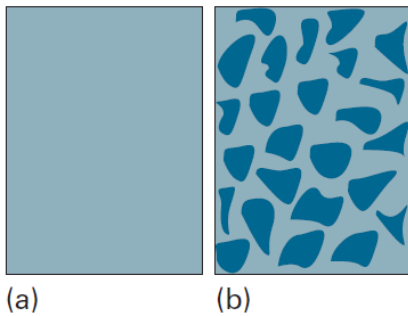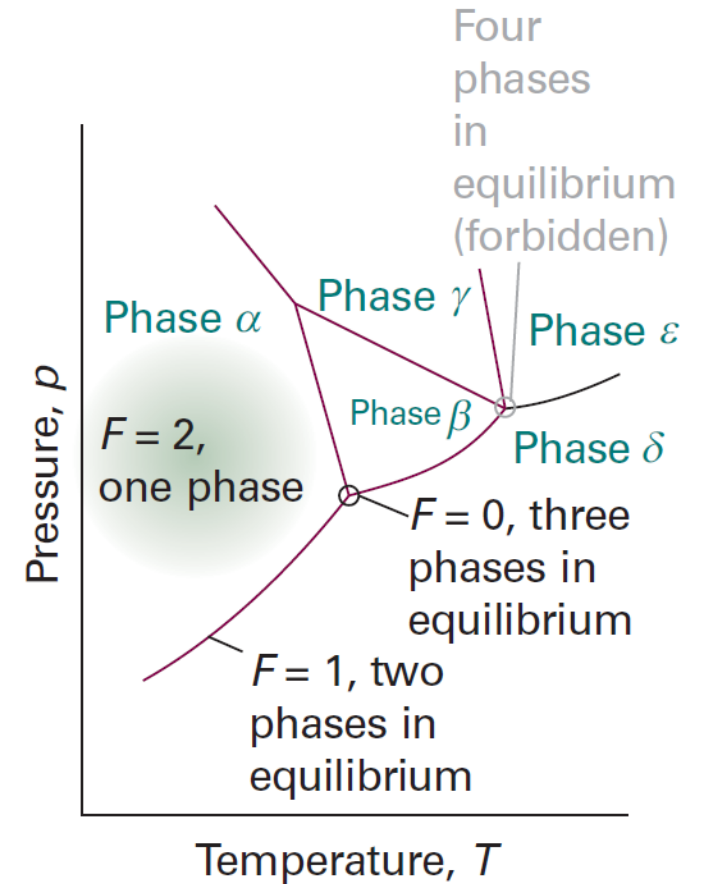

(a)   (b)

Fig. 6.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.


Four phases in equilibrium (forbidden)

Phase α Phase γ Phase ε

$F = 2$, one phase   Phase β Phase δ

$F = 0$, three phases in equilibrium

$F = 1$, two phases in equilibrium

Pressure, p

Temperature, T

Constituent of a system
chemical species (an ion or a molecule) that is present

Mixture of **ethanol** and **water** has 2 **constituents**

A solution of **sodium chloride** has **3 constituents**:
water, Na^+ ions, and Cl^- ions
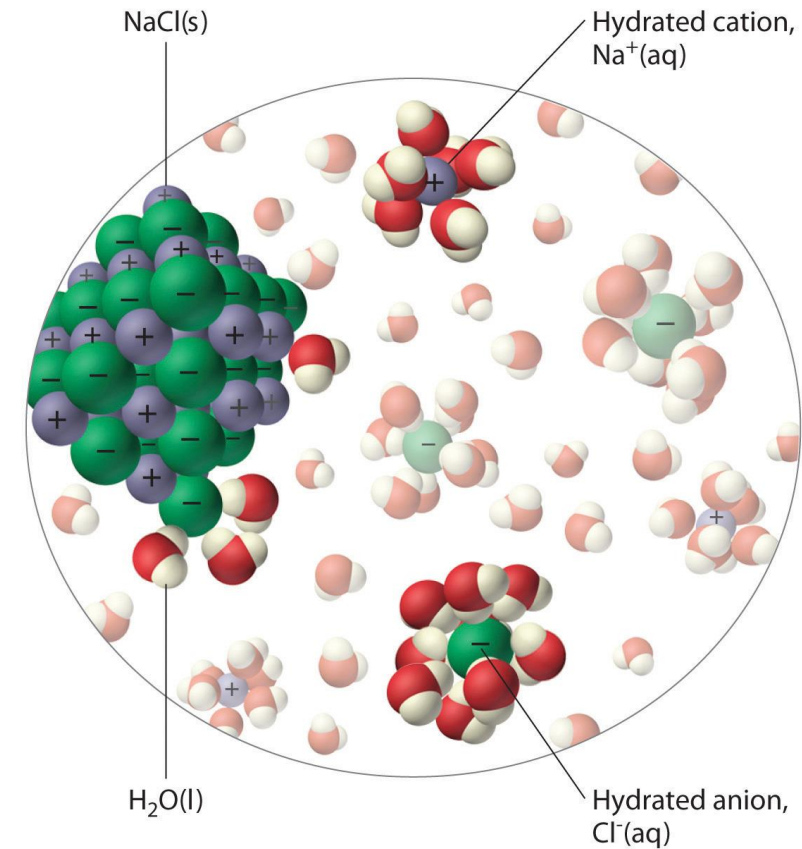
Component is a *chemically independent* constituent of a system. C

Minimum number of independent species necessary to define the **composition** of all the **phases** present in the system.
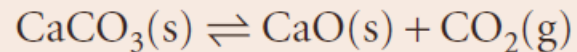
 # component = # Constituents − # constraints system

e.g. mixture of **ethanol** and **water**

2 Constituents -   **2** component system (C = 2 - 0 = **2**)

Aqueous NaCl

C = 2 = **3** (Constituents) − 1 (**constraints**) = **2**

Constraints= Charge balance, $|Na^+| = |Cl^-|$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Phase 1   Phase 2   Phase 3

C = 2 = **3** (Constituents) − 1 (**constraints**) = **2**

Constraints= Massa balance…chemical reaction