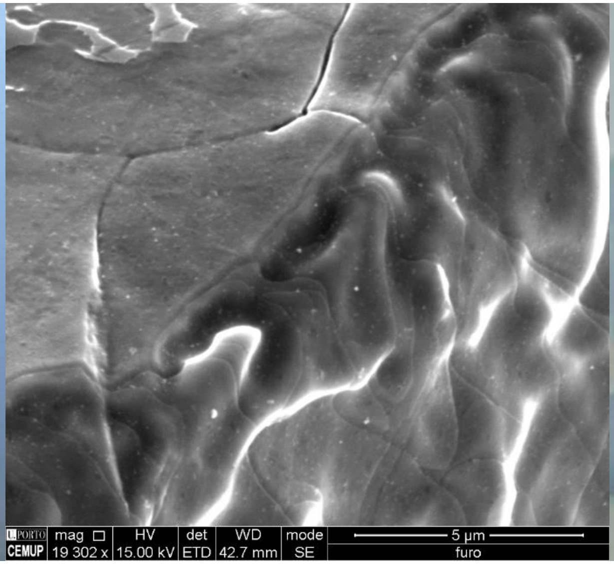
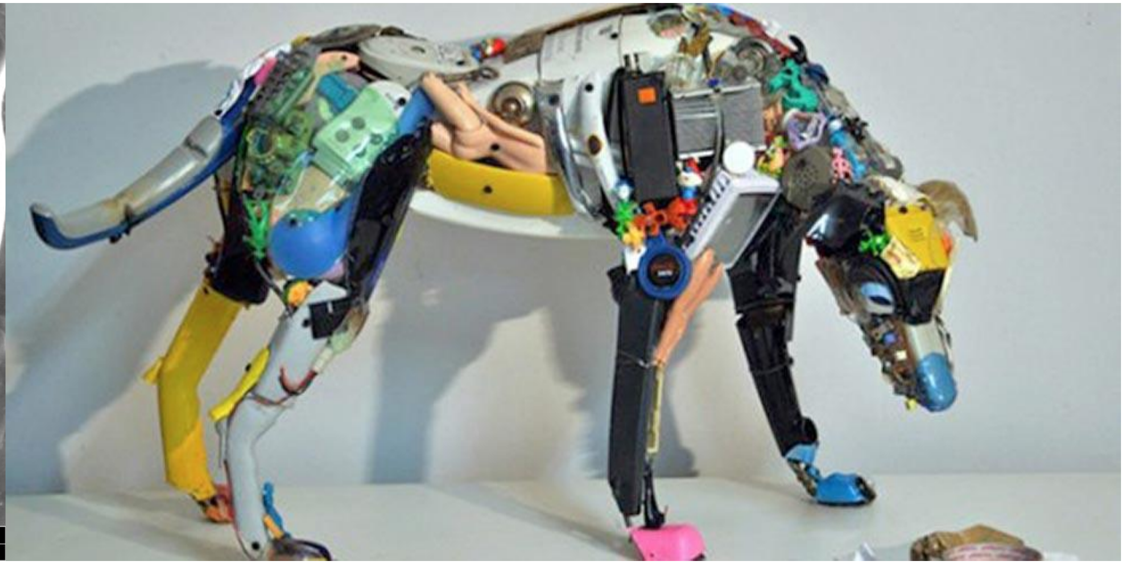
Physical Chemistry

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

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





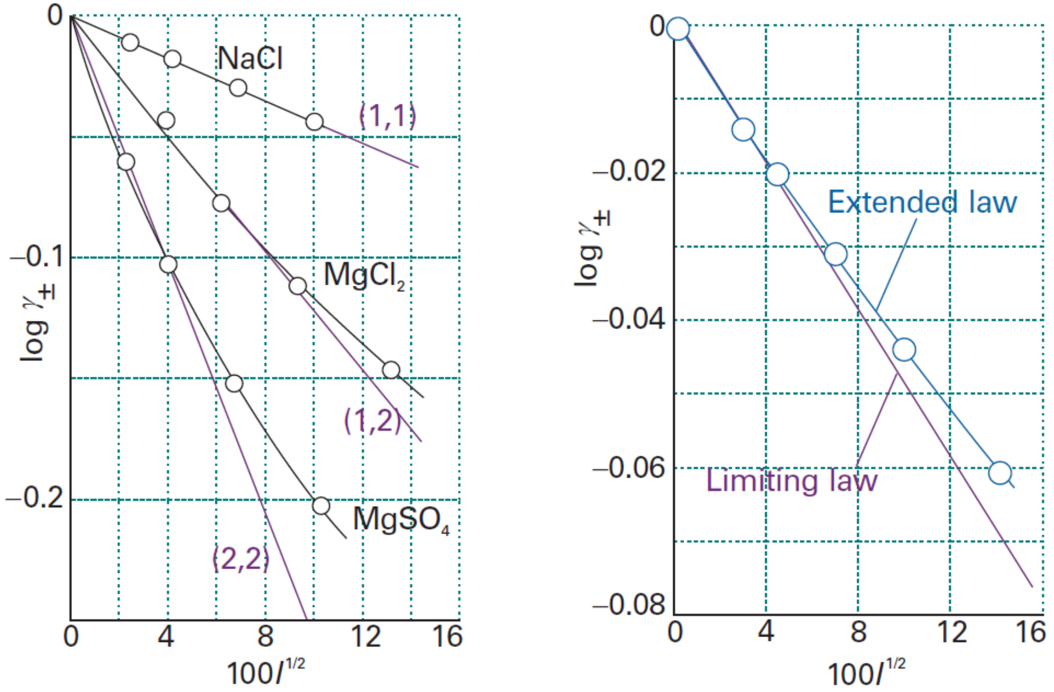
The activities of ions in solution

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

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

Ionic strength

An experimental test of the Debye–Hückel limiting law.



Debye–Hückel limiting law

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

The extended Debye–Hückel law

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

Phase diagrams

Phase

state of matter that is uniform throughout

- chemical composition
- physical state

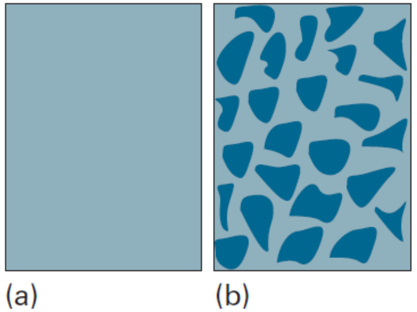


Fig. 6.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

Constituent of a system

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

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.

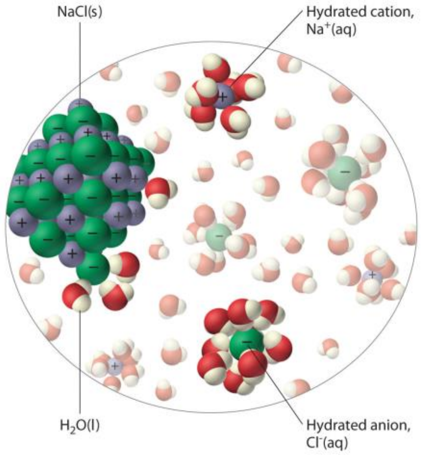
Phase diagrams

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

component = # Constituents – # **constraints** system

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

2 Constituents - **2** component system ($\boldsymbol{C} = 2 - 0 = \mathbf{2}$)



A solution of **sodium chloride** has **3 constituents**:
water, Na^+ ions, and Cl^- ions

$\boldsymbol{C} = 2 = \mathbf{3}$ (Constituents) – 1 (**constraints**) = **2**

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

Phase diagrams

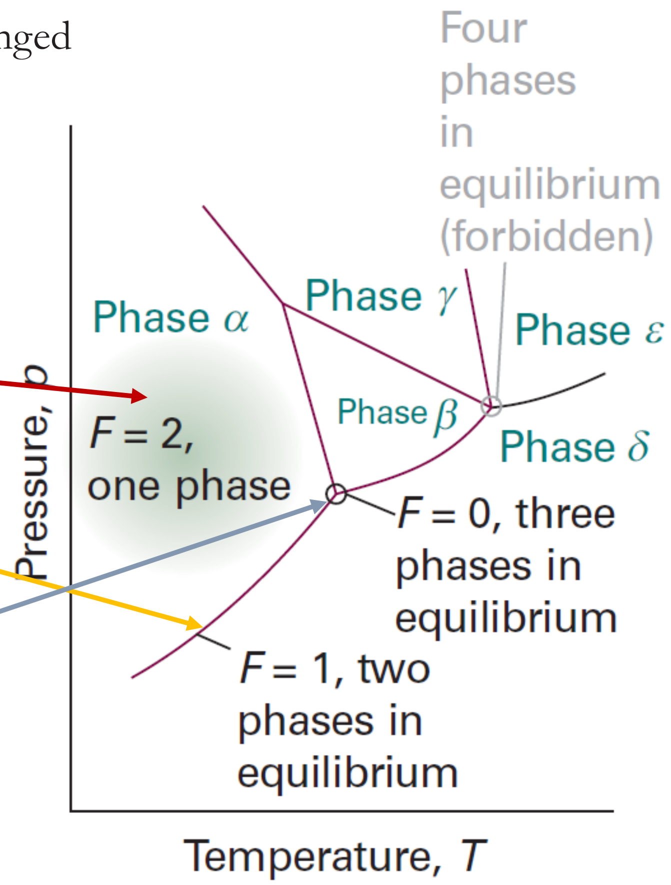
The **variance**, ***F***, of a system

number of **intensive variables** (e.g. pressure and temperature) that can be changed independently without disturbing the **number of phases in equilibrium**.

single-component, single-phase system ($C = 1$, $P = 1$),
***F* = 2**. system is **bivariant**, or that it has 2 **degrees of freedom**.

single-component, single-phase system ($C = 1$, $P = 2$),
***F* = 1**. system is **univariant**, or that it has 1 **degrees of freedom**.

single-component, single-phase system ($C = 1$, $P = 3$),
***F* = 0**. system is **invariant**, or that it has 0 **degrees of freedom**.



Phase diagrams

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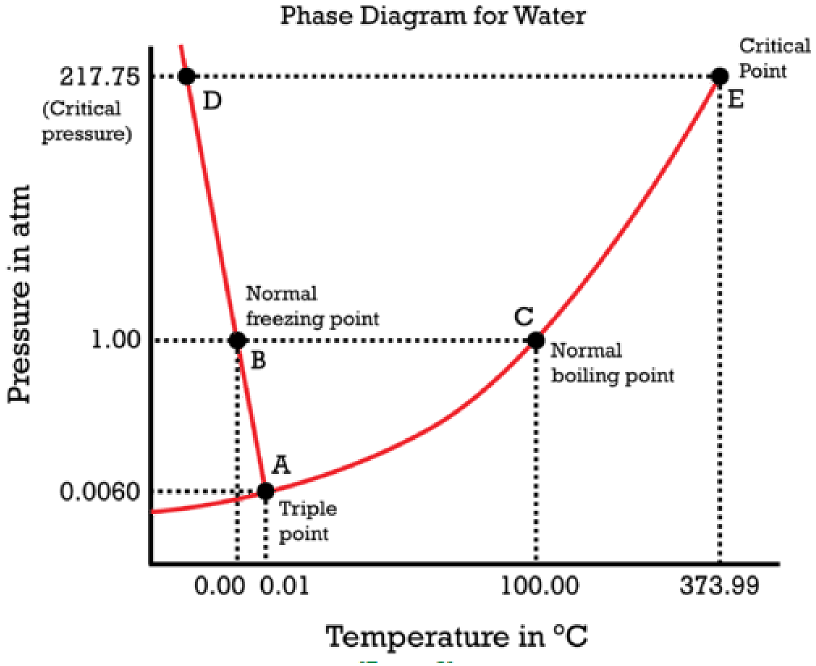
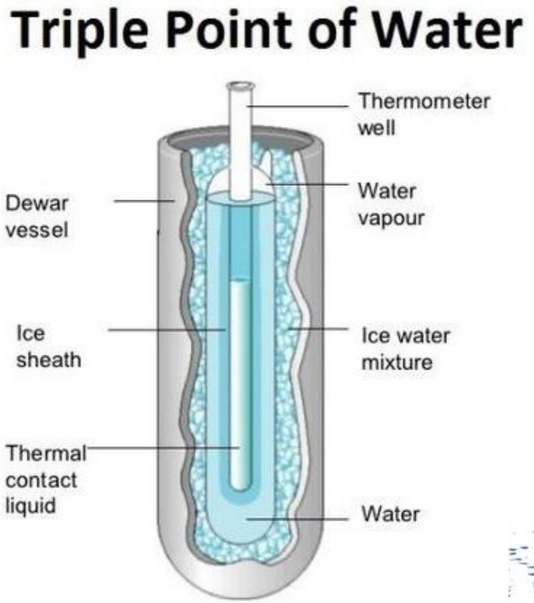


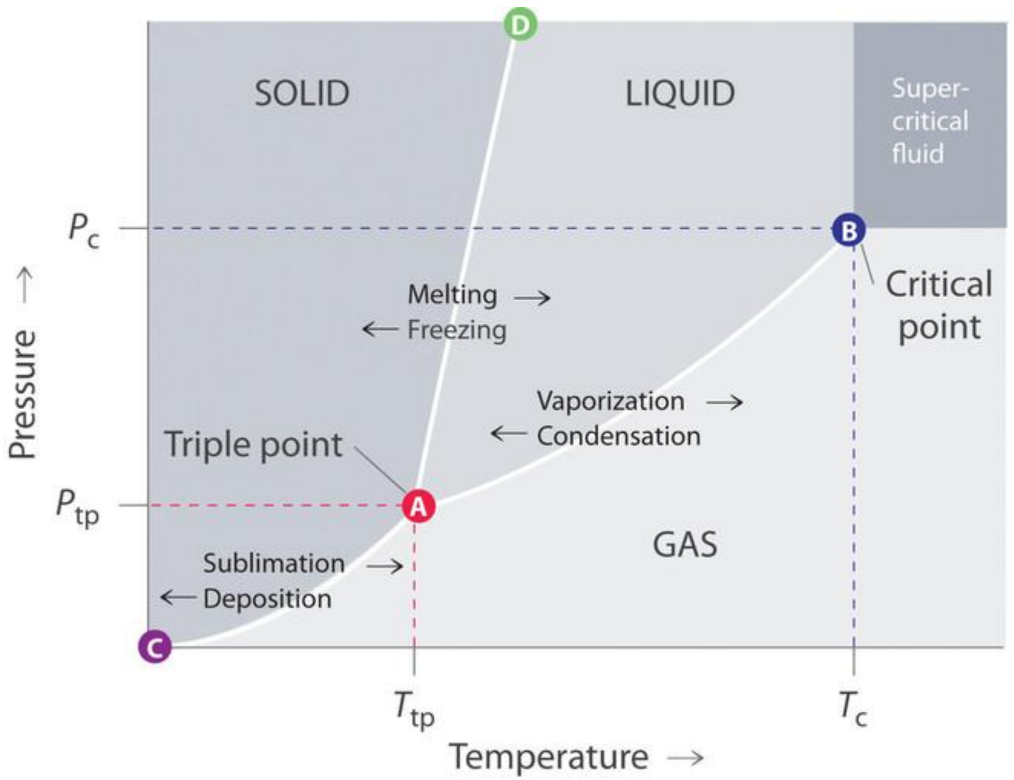
T= 0.01 °C; P=611.657 Pa

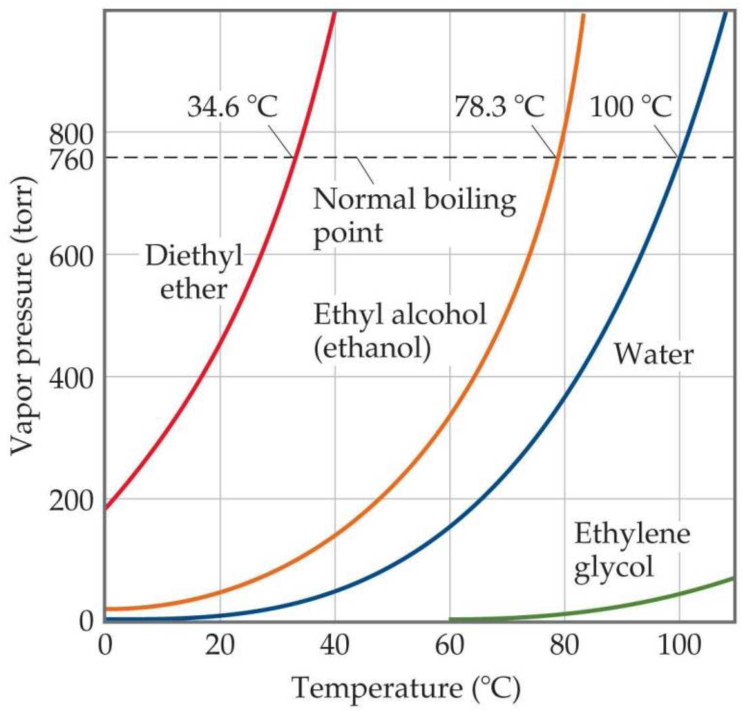


T= 0.00 °C; P=1 bar

https://www.nist.gov/video/triple-point-cell

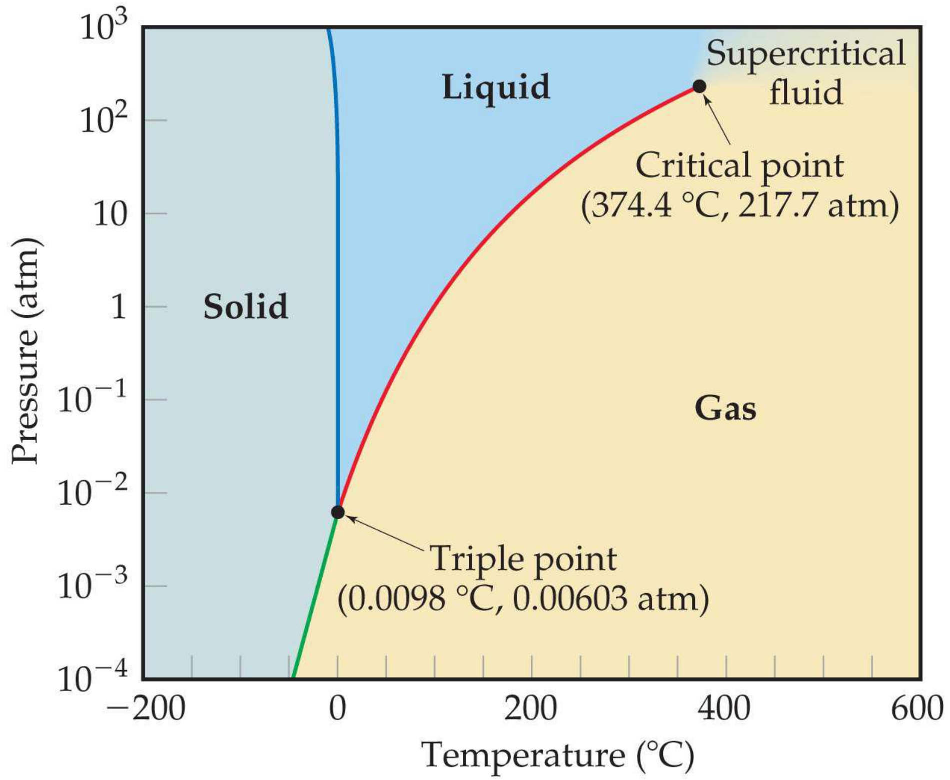
Phase diagrams



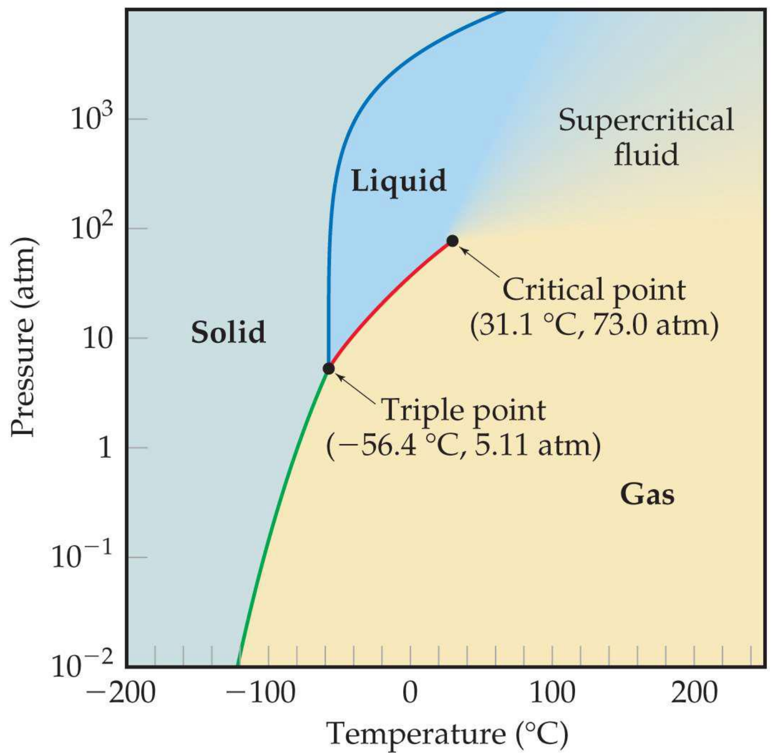


Phase diagrams

H_2O



CO_2

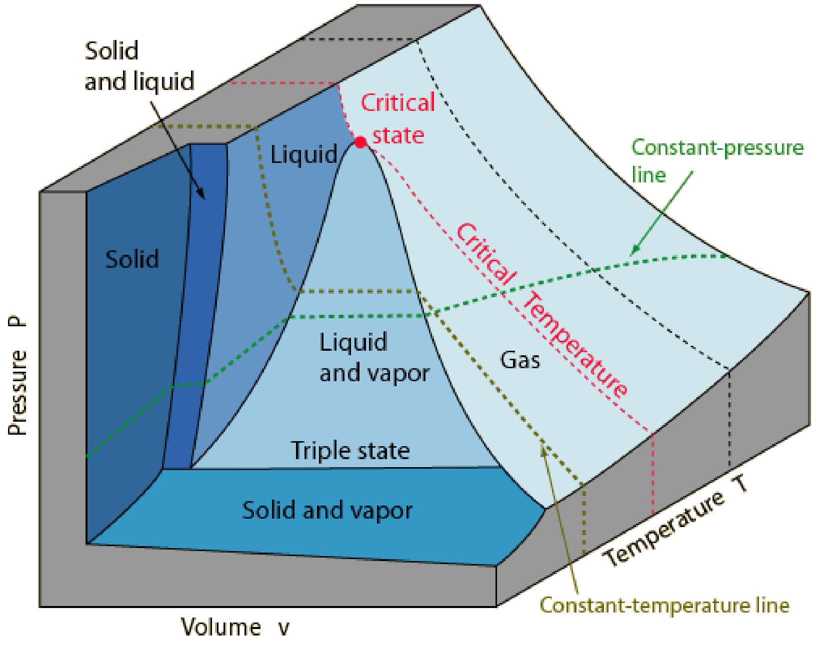


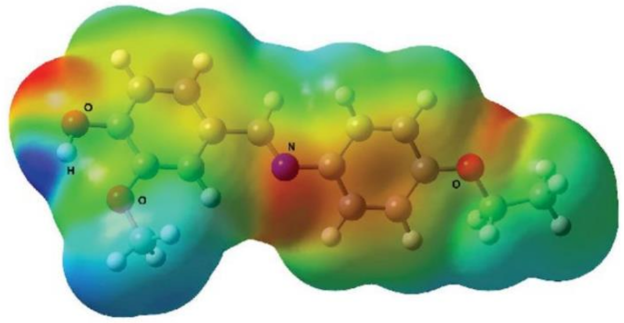
Pure substances & Mixtures

Why each compound have a different PVT surface profile?

- C-H-π and π-π .. interactions
- H-bond
- Electrostatic .. interactions
- Molecular shape
- ...???

PVT diagram





Phase diagrams

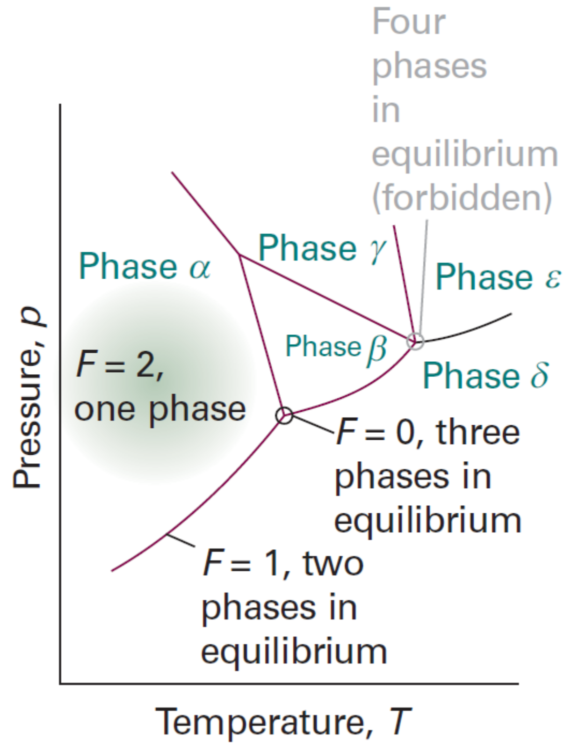
The **variance**, ***F***, of a system
is the number of **intensive variables** (e.g. pressure and temperature) that can be changed independently without disturbing the **number of phases in equilibrium**.

J.W. Gibbs deduced the **phase rule**

$$F = C - P + 2$$

C **# Components**

P **# Phases,**



Phase diagrams

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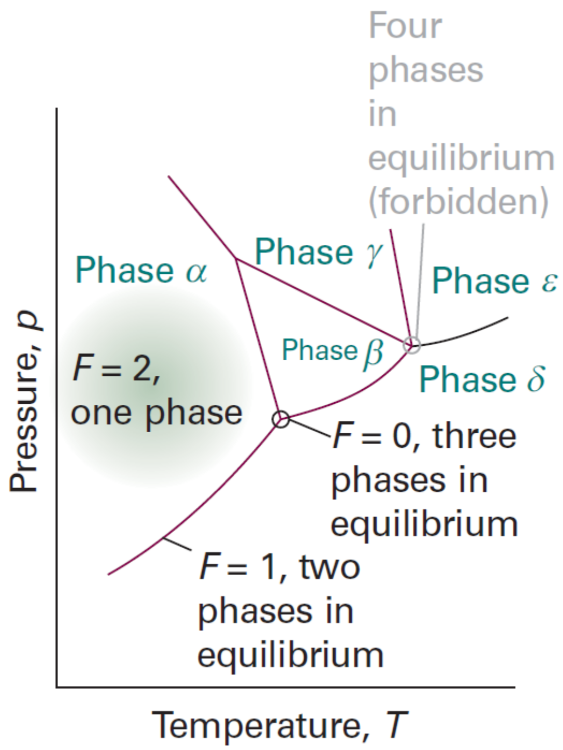

intensive variables

The pressure, $\boldsymbol{p}$, and temperature, $\boldsymbol{T}$, count as **2**.

composition of a phase

$\boldsymbol{P}(C-1)$ $\quad x_1 + x_2 + \cdots + x_C = 1, \ (C-1)$ *In each phase,* ***P***

$$F \ > \ P(C-1) \ +2$$

Minus the Restrictions !!

Phase diagrams

The **variance**, ***F***, of a system
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C # Components
P # Phases,

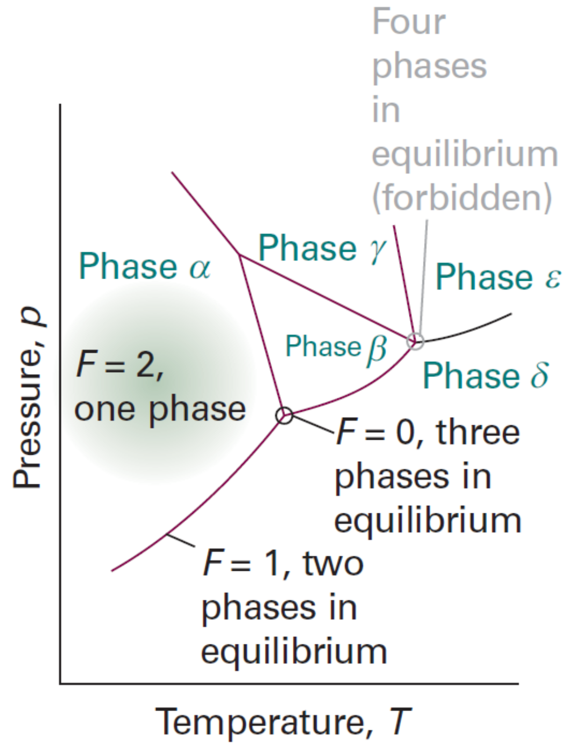
$$F \;>\; P(C-1) + 2$$

Minus the Restrictions !!

Relation due to of a phase equilibrium

$\boldsymbol{C}(P-1)$ $\mu_J(\alpha) = \mu_J(\beta) = \ldots$ for P phases *For each,* ***C***

$$F = P(C-1) + 2 - C(P-1) = C - P + 2$$



Phase diagrams

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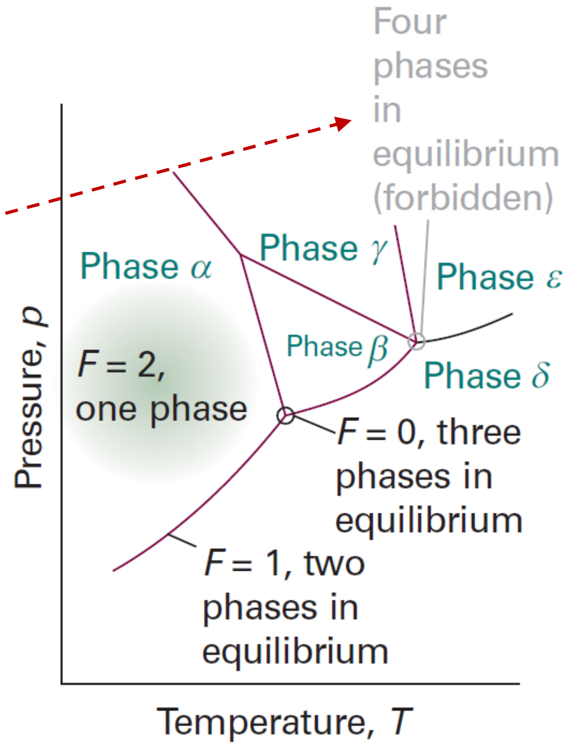
Minimum value of **variance**, ***F***, should be ***F*=0**

$C = 1$ $\qquad$ P # Phases Maximum?

$F = 1 - P + 2$ ..... $P \leq 3 - \mathbf{0}$ $\qquad$ ~~$P = 4$???~~

$\mu_J(\alpha; p,T) = \mu_J(\beta; p,T) \qquad \mu_J(\beta; p,T) = \mu_J(\gamma; p,T) \qquad \mu_J(\gamma; p,T) = \mu_J(\delta; p,T)$

three equations for two unknowns (p and T) are not consistent



$C = X$

$P \leq X + 2 - \mathbf{0}$

$C = 2$ $\qquad$ #max $P = 4$

$C = 3$ $\qquad$ #max $P = 5$

....

Phase diagrams

One-component systems

J.W. Gibbs deduced the **phase rule**

$$F = C - P + 2$$

$$C = 1$$

$$F = \mathbf{1} - P + 2 \quad ..... \quad \# \text{ P - } 1, 2, 3$$

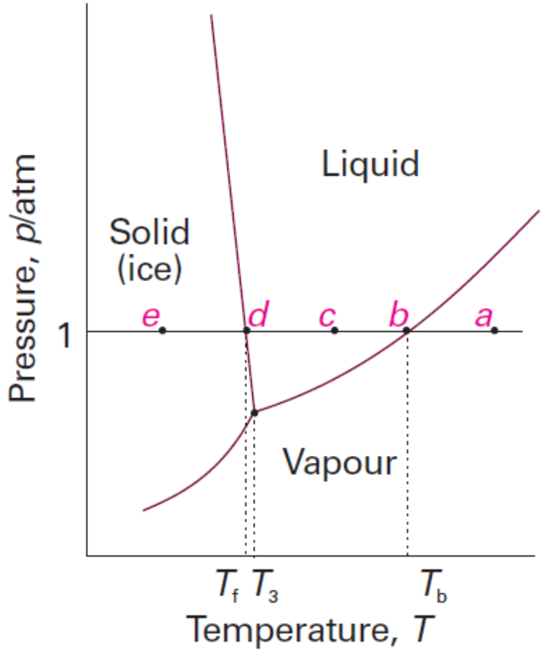
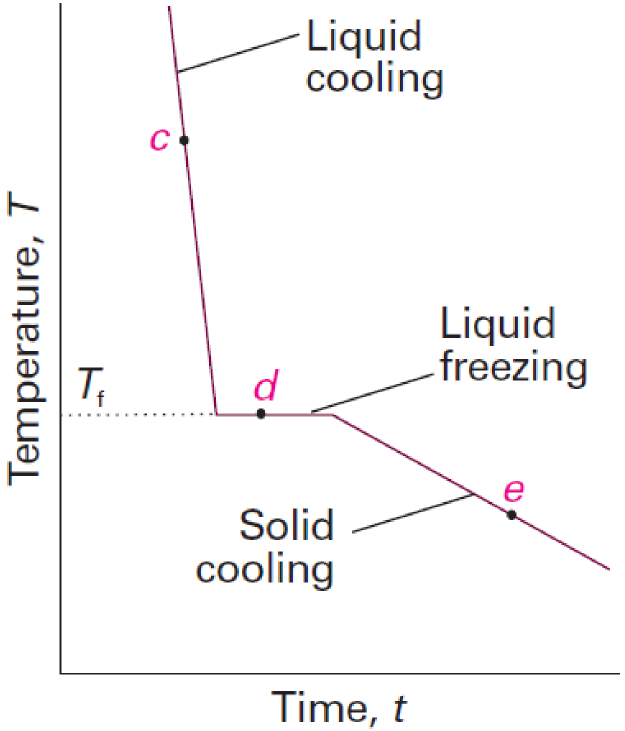


Fig. 6.3 The phase diagram for water, a simplified version of Fig. 4.5. The label T_3 marks the temperature of the triple point, T_b the normal boiling point, and T_f the normal freezing point.



Phase diagrams

Two-component systems $C = 2$

J.W. Gibbs deduced the **phase rule**

$$F = C - P + 2$$

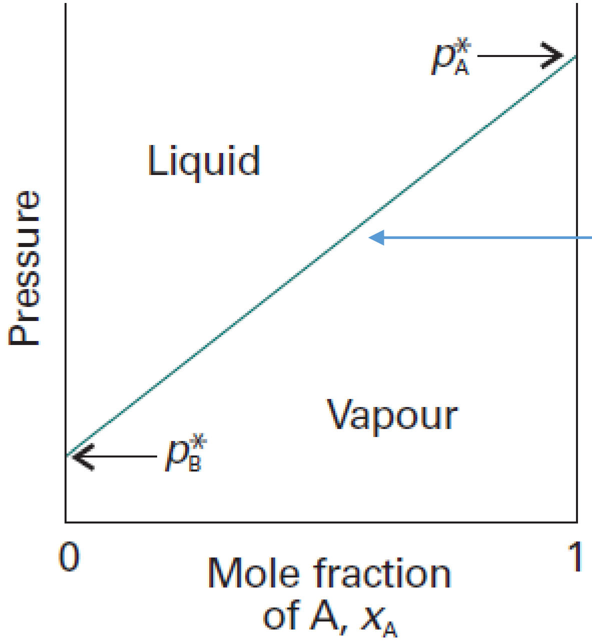


Fig. 6.6 The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult's law is obeyed.

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A$$

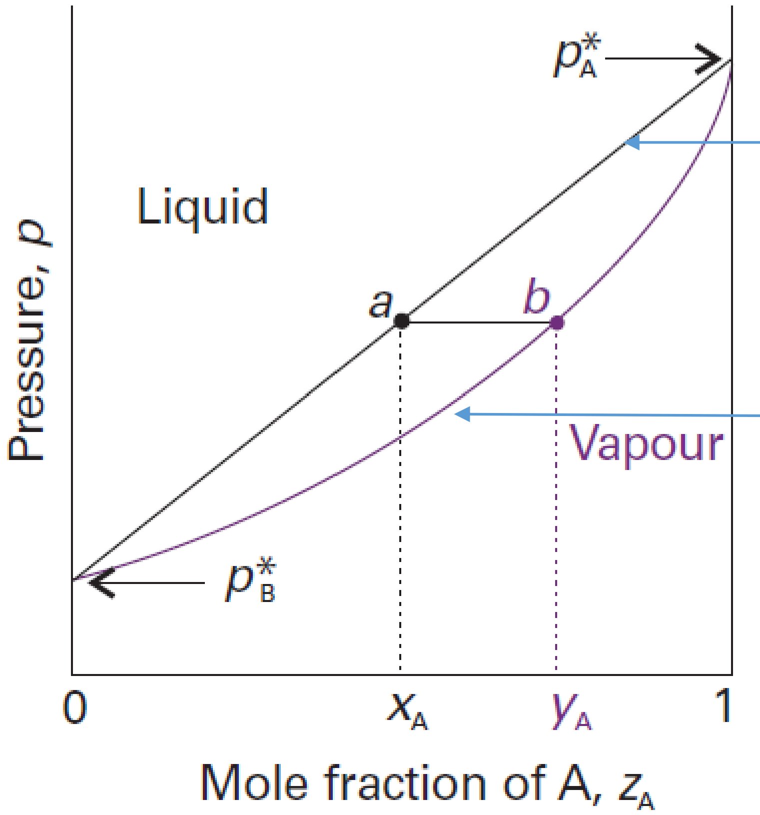
Composition of vapor

$$y_A = \frac{p_A}{p} \qquad y_B = \frac{p_B}{p}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \qquad y_B = 1 - y_A$$

Phase diagrams

Two-component systems $C = 2$

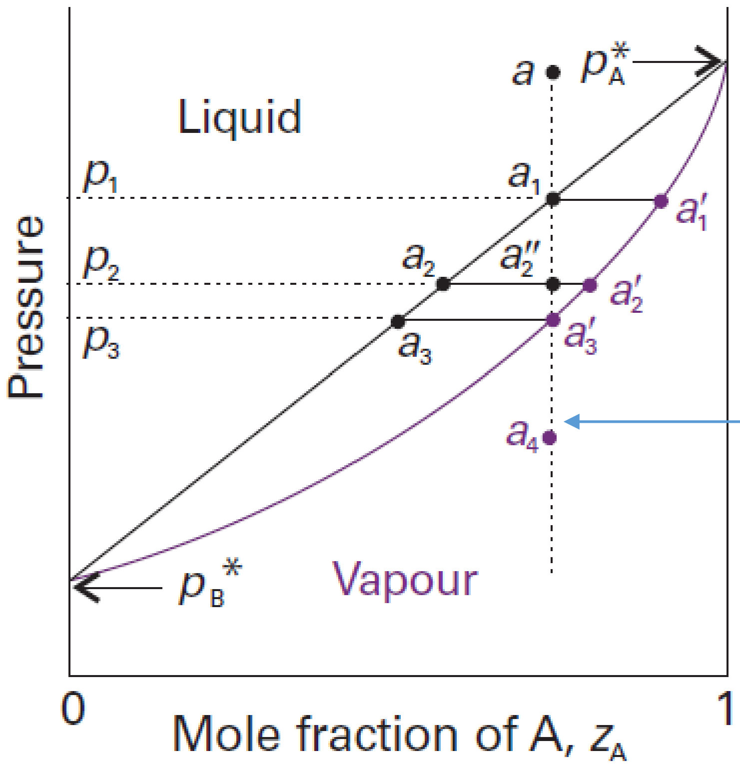


$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \qquad y_B = 1 - y_A$$

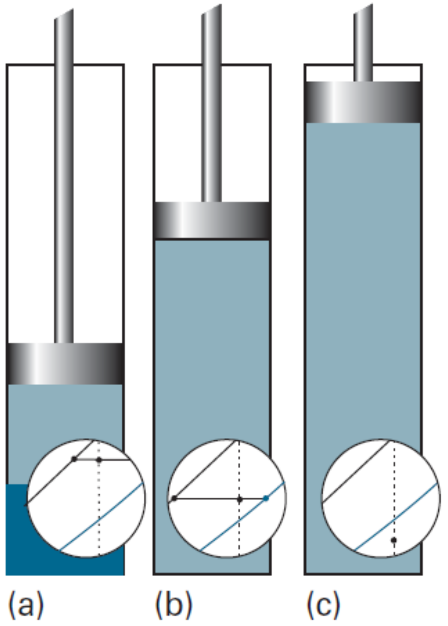
Phase diagrams

Two-component systems $C = 2$



isopleth,

Fig. 6.10 The points of the pressure–composition diagram discussed in the text. The vertical line through *a* is an *isopleth*, a line of constant composition of the entire system.



Phase diagrams

Two-component systems $C = 2$

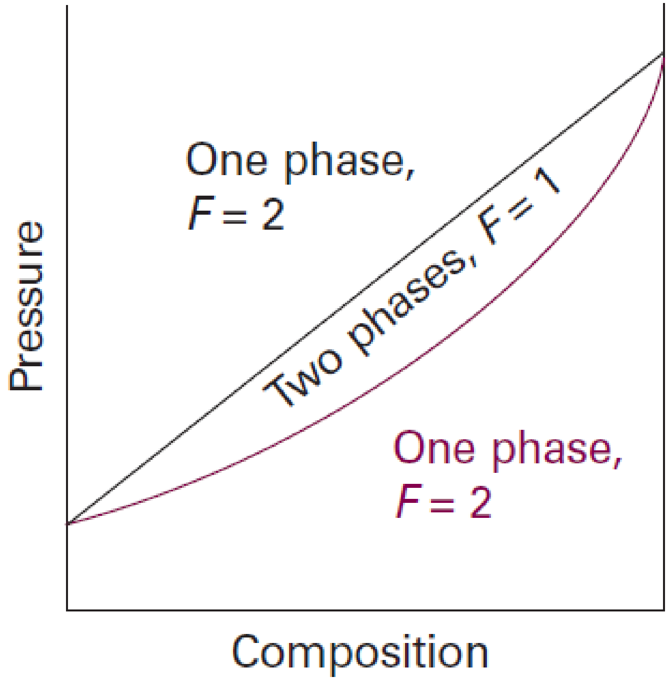
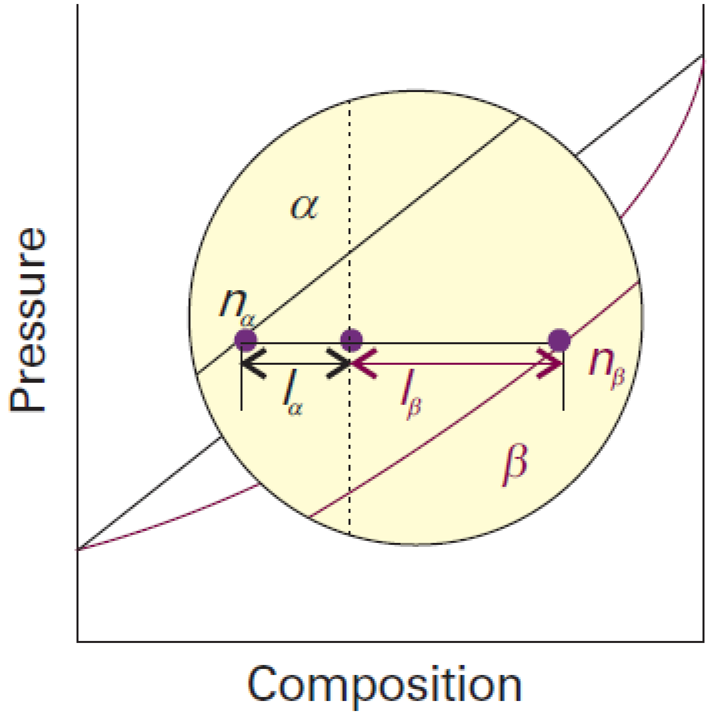


Fig. 6.12 The general scheme of interpretation of a pressure–composition diagram (a vapour pressure diagram).



Lever rule

The distances l_α and l_β are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium.

$$n_\alpha l_\alpha = n_\beta l_\beta$$

Lever rule

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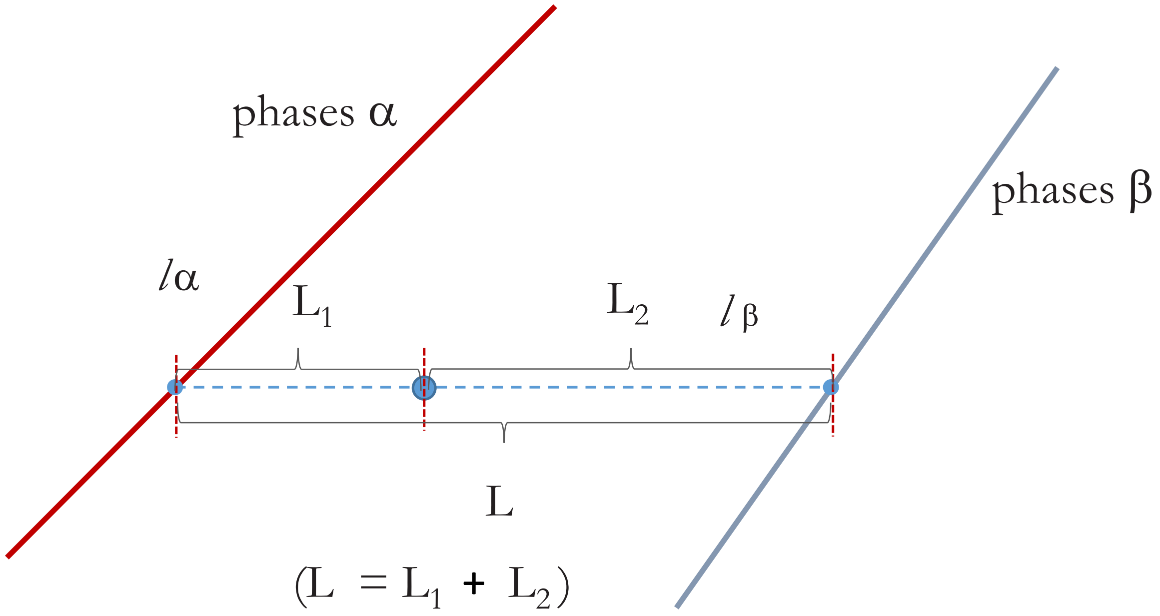

Proportions of the amounts

phase α = L_2 / L
phase β = L_1 / L

e.g. L=0.50 ; L_1 = 0.20 ; L_2 = 0.30;

phase α = 0.3/0.5 = 0.60 ... 60%
phase β = 0.2/0.5=0.40 ... 40%