EQUILIBRIO, ESTADOS ESTACIONARIOS Y ESTABILIDAD

TERMODINAMICA MOLECULAR - **2015739 – 1**
PROGRAMA DE INGENIERÍA QUÍMICA
UNIVERSIDAD NACIONAL DE COLOMBIA

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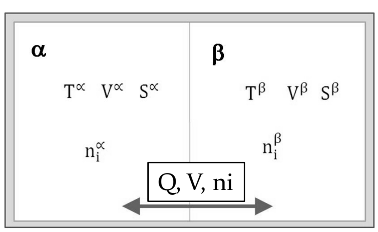
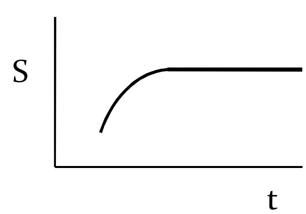
CRITERIOS DE EQUILIBRIO



$$dS^T = dS^{\propto} + dS^{\beta} \geq 0$$



En el equilibrio (aplica también para estados estacionarios) la entropía alcanza un máximo, siendo la primera derivada cero.

Ahora se van a considerar **perturbaciones** (δ) a estos estados de invariabilidad. Perturbaciones entendidas como cambios producidos en intervalos de tiempo cortos.

CRITERIOS DE ESTABILIDAD – PERTURBACIONES (δ) AL EQUILIBRIO

Series de Taylor:

$$\underline{f(x+\Delta x)} = \underline{f(x)} + \underline{f'(x)\cdot\Delta x} + \underline{f''(x)\cdot\frac{\Delta x^2}{2!}} + \cdots + f^{(n)}(x)\cdot\frac{\Delta x^n}{n!}$$

$$S = S_{Eq} + \cancel{\delta S} + \frac{1}{2}\delta^2 S + \cdots$$

Para la entropia en un sistema que se encuentra en equilibrio.

En el equilibrio la entropía alcanza un máximo, por lo que δS=0, haciendo que el término de segundo orden se vuelva importante.

Adaptado de Kondepudi y Prigogine

PERTURBACIONES (δ) AL EQUILIBRIO

$$S = S_{Eq} + \delta S + \frac{1}{2}\delta^2 S + \cdots$$

$$\delta S = \cancel{\frac{\delta U}{T}} + \frac{P}{T}\delta V$$

Considerando que solo hay perturbaciones mecánicas:

$$\delta V_1 = -\delta V_2 = \delta V$$

$$\delta S = \left(\frac{P_1}{T} - \frac{P_2}{T}\right)\delta V$$

Adaptado de Kondepudi y Prigogine

PERTURBACIONES (δ) AL EQUILIBRIO

$$\delta V_1 = -\delta V_2 = \delta V$$

$$\delta S = \left(\frac{P_1}{T} - \frac{P_2}{T}\right)\delta V$$

Para el segundo orden se tiene:

$$\delta^2 S = \frac{1}{T}\left(\frac{\partial P_1}{\partial V_1} + \frac{\partial P_2}{\partial V_2}\right)(\delta V)^2$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} \qquad \frac{\partial P}{\partial V} = -\frac{1}{V\kappa_T}$$

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$$\delta^2 S = -\frac{1}{T\kappa_T}\frac{(\delta V)^2}{V_1}\left(1 + \frac{V_1}{V_2}\right)$$

Adaptado de Kondepudi y Prigogine

PERTURBACIONES (δ) AL EQUILIBRIO

$$\delta^2 S = \frac{1}{T\kappa_T}\frac{(\delta V)^2}{V_1}\left(1 + \frac{V_1}{V_2}\right)$$

$$\delta^2 S = \frac{1}{T\kappa_T}\frac{(\delta V)^2}{V}$$

Ahora bien, si la entropía es máxima, las perturbaciones <u>estables</u> harán que la entropía tienda a disminuir, o sea que la concavidad sea hacia abajo:

$$\delta^2 S = -\frac{1}{T\kappa_T}\frac{(\delta V)^2}{V} < 0$$

Adaptado de Kondepudi y Prigogine

CRITERIOS DE ESTABILIDAD

$$\delta^2 S = -\frac{1}{T\kappa_T}\frac{(\delta V)^2}{V} < 0$$

Esto quiere decir que κ_T debe ser positivo, o sea que

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} > 0$$

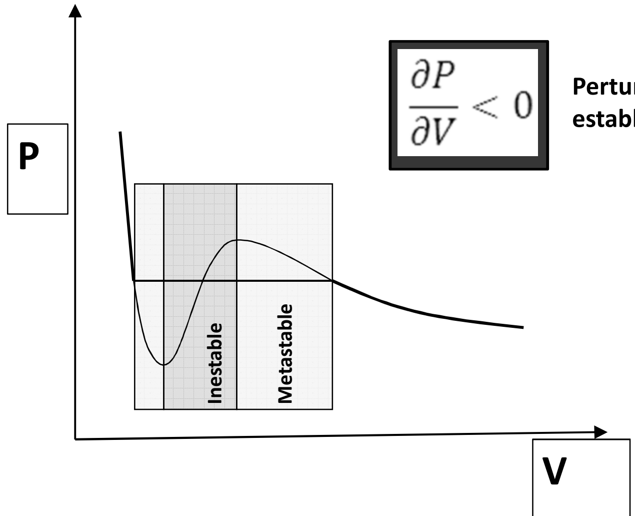
$$\frac{\partial V}{\partial P} < 0 \quad \text{Ó} \quad \boxed{\frac{\partial P}{\partial V} < 0}$$

Esto determina la estabilidad en una perturbación.

En el diagrama Presión – Volumen:

Adaptado de Kondepudi y Prigogine

REGIÓN DE ESTABILIDAD - ELV



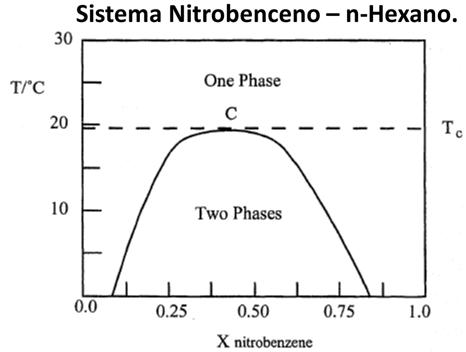
$$\frac{\partial P}{\partial V} < 0$$

Perturbaciones estables.

Adaptado de Kondepudi y Prigogine

REGIÓN DE ESTABILIDAD - ELL

Diagrama de Equilibrio
Sistema Nitrobenceno – n-Hexano.



Criterio: $$\frac{RT}{2\alpha} - x_1(1 - x_1) > 0$$

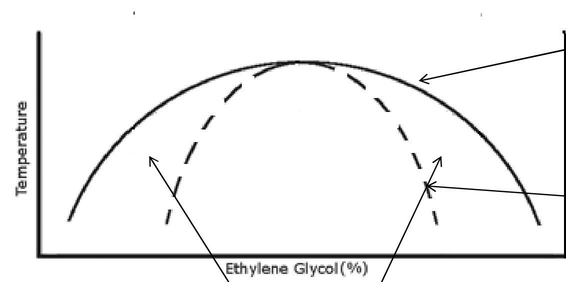
α es un parámetro de no-idealidad
Si α=0, es ideal.

Es estable fuera del equilibrio

Adaptado de Kondepudi y Prigogine

REGIÓN DE ESTABILIDAD - ELL

Sistema Etilen Glicol - Nitrometano



Curva binodal (Equilibrio)

Curva spinodal (Estado Estacionario ó Equilibrio metastable)

$$\frac{RT}{2\alpha} - x_1(1 - x_1) > 0$$

Es estable fuera del equilibrio

Bijel reinforcement by droplet bridging: a route to bicontinuous materials with large domains. Jessica Witt, Daniel Mumm and Ali Mohraz. Soft Matter, 2013, (9) p. 6773-6780.

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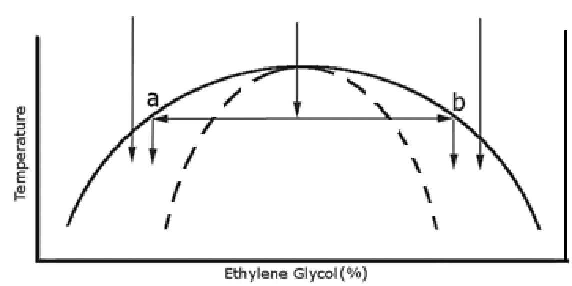

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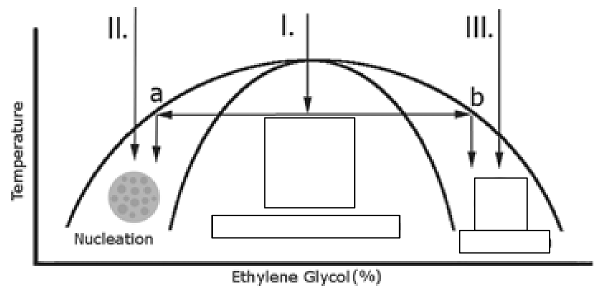

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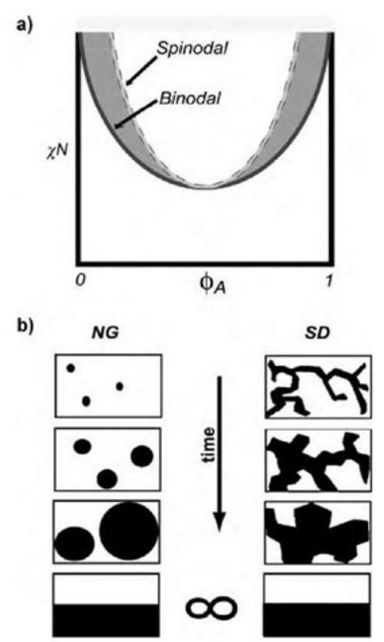
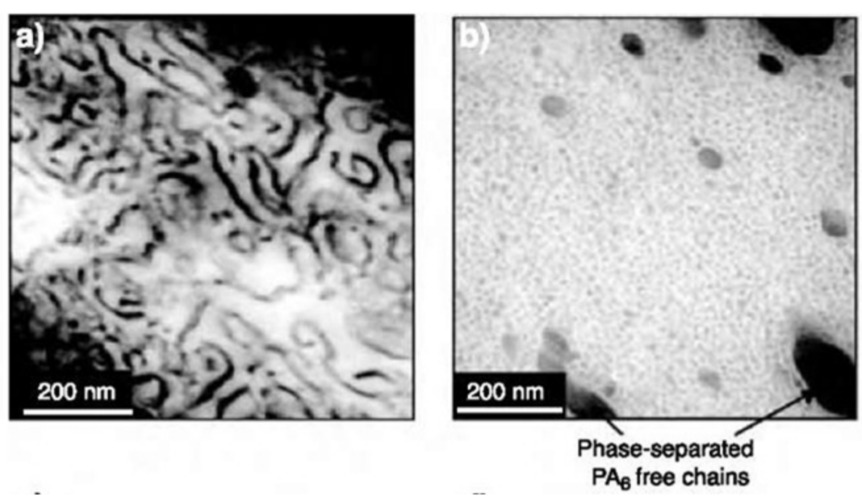
MECHANISMS OF PHASE SEPARATION IN HOMOPOLYMER BLENDS

There are two major mechanisms of phase separation that have been identified and that occur in different parts of the phase diagram as shown in Figure 1:

- **Nucleation and growth (NG)**. occurs in the metastable region of the phase diagram (the area between binodal and spinodal) and is characterized by the following steps: 1) initial formation of spherical fragments of the more stable phase (requires activation barrier); 2) growth of nuclei by first diffusion of material from the supersaturated continuum followed by droplet-droplet coalescence and Ostwald-ripening.
- **Spinodal Decomposition (SD)**, which is the commonly observed mechanism for phase separation in homopolymer blends, occurs in the unstable region of the phase diagram and is characterized by initial small-amplitude composition fluctuations that increase with time and result in interconnected phase morphologies at intermediate stages of phase separation.

Nanostructures Derived from Phase-Separated Polymers Part 1.
http://what-when-how.com/nanoscience-and-nanotechnology/nanostructures-derived-from-phase-separated-polymers-part-1-nanotechnology/


a)
Spinodal
Binodal
χN
0
ϕA
1
b)
NG
SD
time
∞


a)
200 nm
b)
200 nm
Phase-separated
PA6 free chains