## CHAPTER 25: PHASE TRANSITIONS

Consider stability of a single state with a degree of freedom *x*

Stable state at $x^*$ where *F(x)* is minimum

At phase coexistence, *F* has two minima

first-order phase transition $\rightarrow$ *F*: double minima

higher-order phase transition $\rightarrow$ F: broad minimum

boiling of $H_2O$ at *T* = 100 C, *P = 1 atm* is first-order phase transition

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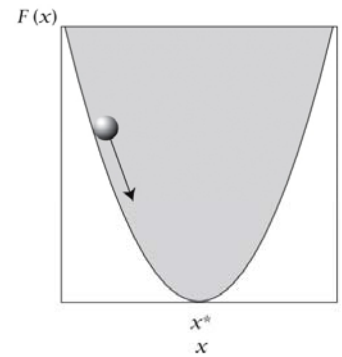
phase diagram

ice, liquid water, steam *vs*. *ρ, T*

Oil -water miscibility



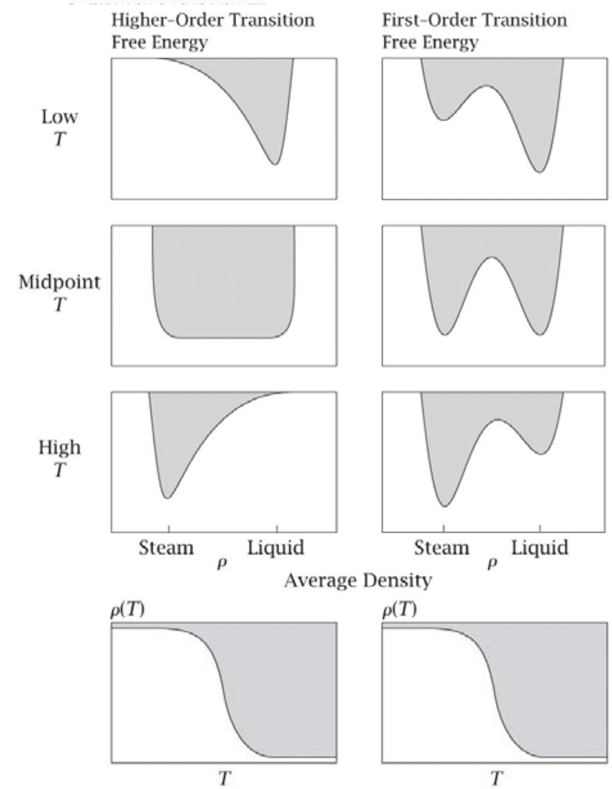




Figure 25.2 Molecular Driving Forces 2/e (© Garland Science 2011)

1. small amount of oil in water – one phase

2-5. two phases

6. small amount of water in oil – one phase

above $T_c$ only a single phase

heating facilitates solubility

Coexistence curve

At $T = T_o$

$x'$ (point 2)

$x''$ (point 5)

oil phase: oil $x''$, water $1 - x''$

water phase: oil $x'$, water $1 - x'$

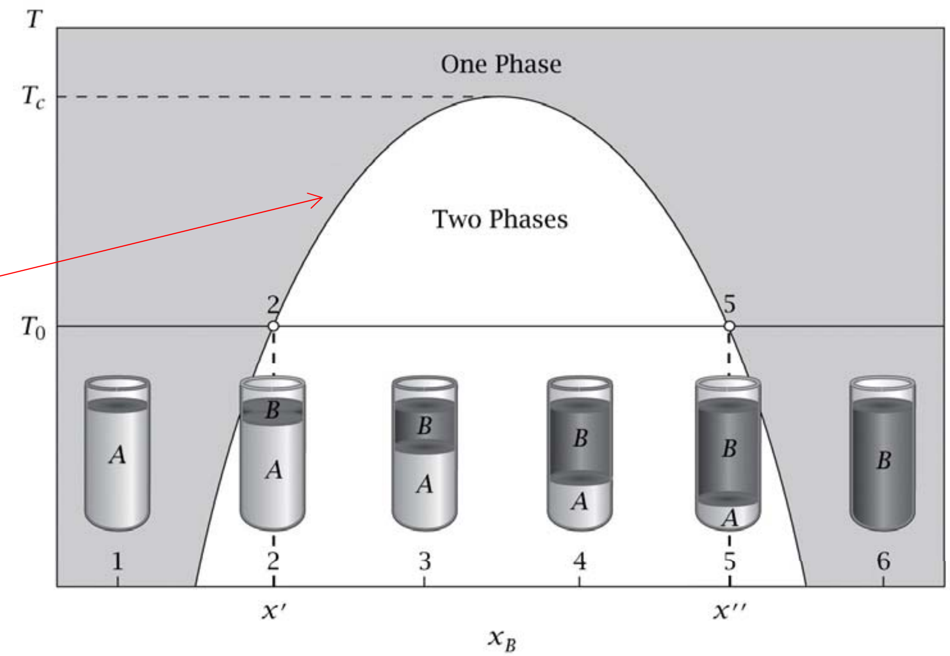



Figure 25.3 Molecular Driving Forces 2/e (© Garland Science 2011)

## lever rule

$$f = \frac{\text{\# of molecules in } A \text{ phase}}{\text{\# in both phases}}$$

$$1 - f = \text{ fraction in } B \text{ rich phase}$$

$$x' = \frac{\text{\# } B \text{ molecules in } A \text{ rich phase}}{\text{\# molecules in } A \text{ rich phase}}$$

$$x'' = \frac{\text{\# } B \text{ in } B \text{ rich phase}}{\text{\# molecules in } B \text{ rich phase}}$$

$$fx' = \frac{\text{\# } B \text{ molecules in } A \text{ rich phase}}{\text{total \# molecules in both phases}}$$

$$(1 - f)\,x'' = \frac{\text{\# } B \text{ molecules in } B \text{ rich phase}}{\text{total \# molecules in both phases}}$$

$$fx' + (1 - f)\,x'' = \frac{\text{\# } B \text{ molecules in both phases}}{\text{\# molecules in both phases}} = x_o$$

$$f\,(x' - x'') = x_o - x'' \Rightarrow f = \frac{x_o - x''}{x' - x''}$$

$$N_A^A \quad N_A^B \quad N_B^B \quad N_B^A$$

← phase
← species

$$f = \frac{N_A^A + N_B^A}{N_A^A + N_A^B + N_B^A + N_B^B}$$

$$x' = \frac{N_B^A}{N_A^A + N_B^A}$$

$$x'' = \frac{N_B^B}{N_B^B + N_B^A}$$

$$fx' = \frac{N_B^A}{N_A^A + N_A^B + N_B^A + N_B^B}$$

$$fx' + (1 - f)\,x'' = \frac{N_B^A + N_B^B}{N_A^A + N_A^B + N_B^A + N_B^B}$$

put $A$ and $B$ into a beaker and suppose $x_o = \frac{1}{2}$

The free energy diagram (Figure 25.8) indicates $F$ decreases if there is phase separation

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Common tangent strategy

if the two minima are different depths, $x'$ and $x''$ are not exactly the points that free energy is a local minima

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Why don't oil and water mix at low $T$?

*AA* and *BB* attractions strong compared to *Ab**B* interactions

since energy terms dominate at low $T$, oil and water don't mix

But at high $T$, entropy dominates and they do mix

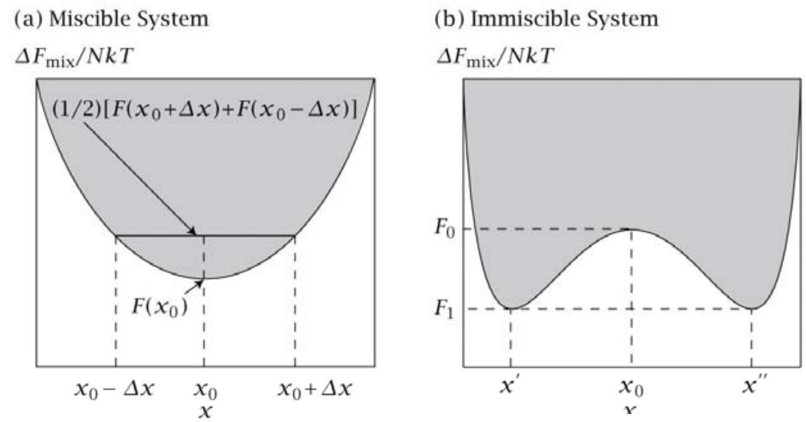



Figure 25.8 Molecular Driving Forces 2/e (© G

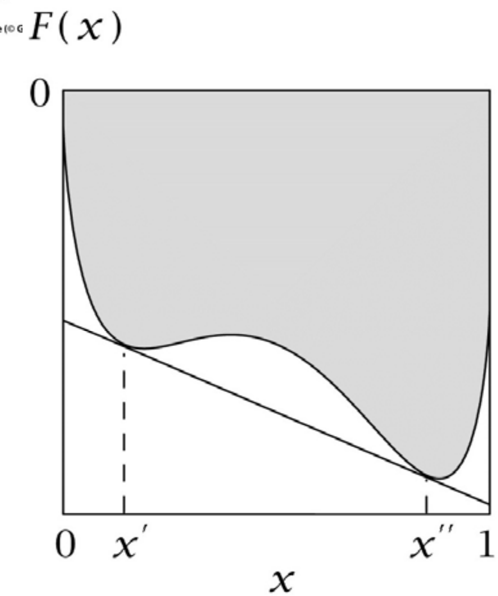
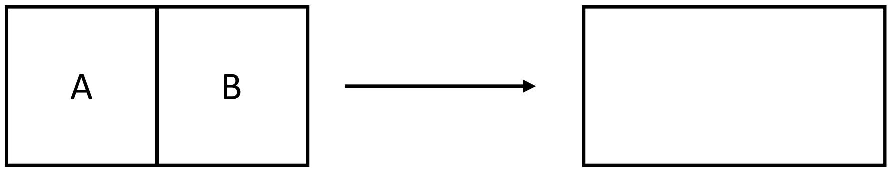



Figure 25.9 Molecular Driving Forces 2/e (© Garland Science 2011)




*x* of *B* in *A*

$$\frac{\Delta F}{NkT} = x\ell n x + (1-x)\,\ell n(1-x) + \chi_{AB}\,x(1-x)$$

$$N = N_A + N_B$$

$$\chi_{AB} = \frac{C_1}{T} = \frac{z}{k}\left( w_{AB} - \frac{w_{AA} w_{BB}}{2} \right)$$

$C_1$ is independent of *T*

So $>T, \quad < \chi_{AB}$

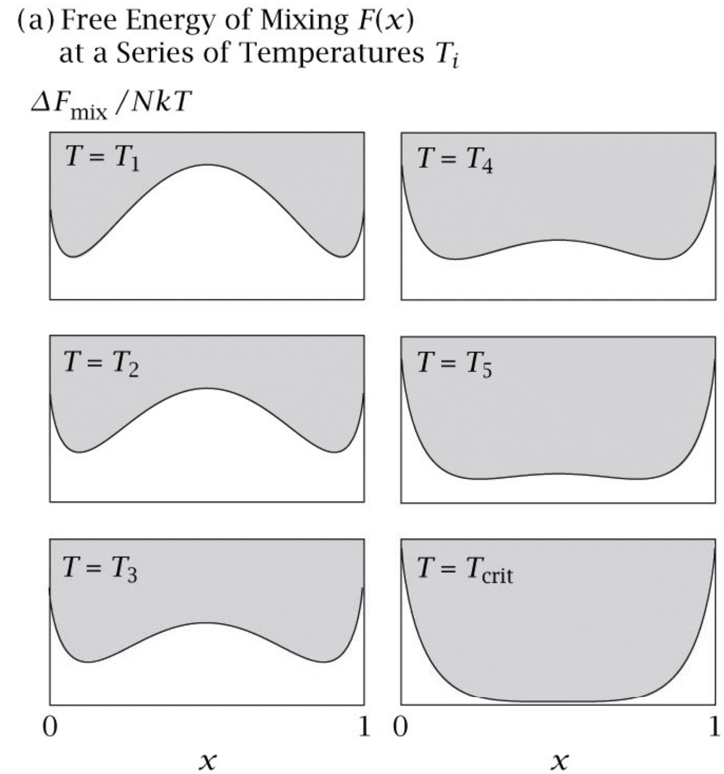



Figure 25.10 Molecular Driving Forces 2/e (© Garland Science 2011)