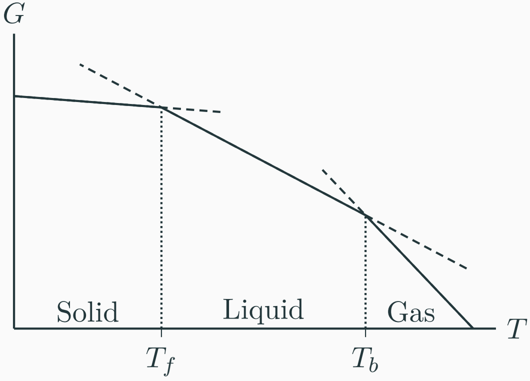
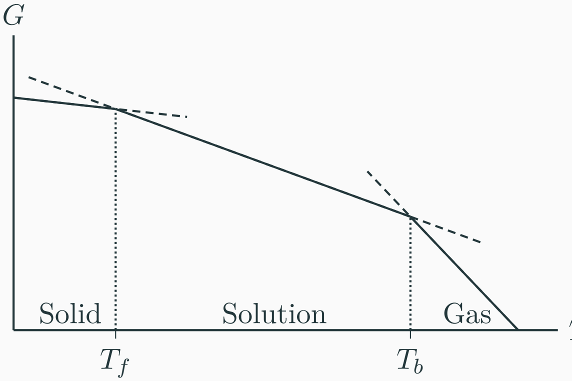
Lecture 30: G vs T, Liquid-Liquid Mixtures

Phase Transitions, Azeotropes

G vs T Diagram





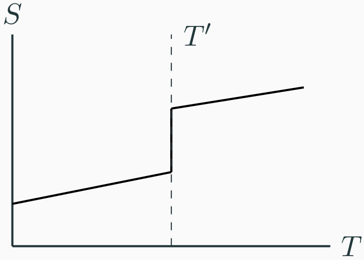
$$G = -ST + H$$
$$y = mx + b$$

Slopes are preserved, but T_f and T_b are moved due to colligative properties

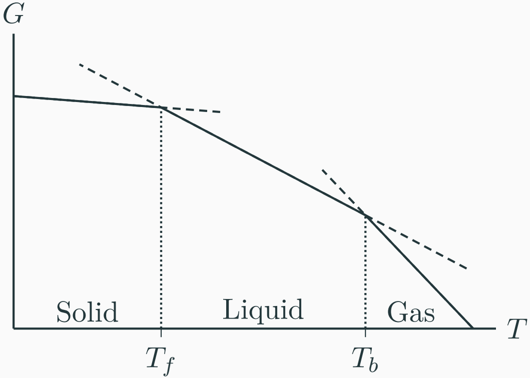
First Order Phase Transitions

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

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$



G is continuous, but slope is discontinuous at phase transitions



Phase Transitions

First vs Second Order

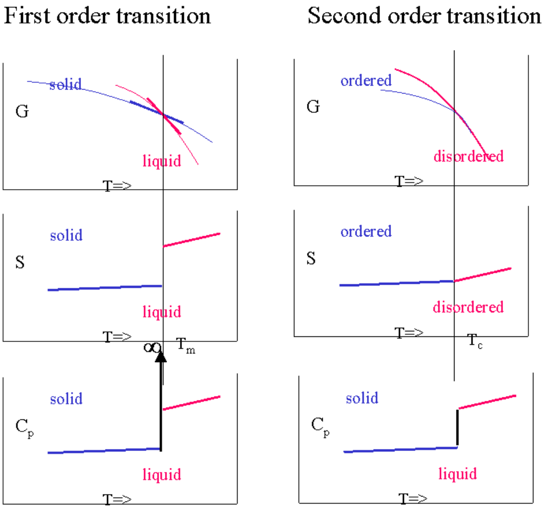
First Order (Typical)

- Continuous: G, T, P
- Discontinuous: S, V

Second Order (Continuous)

- Continuous: G, S, V, T, P
- Discontinuous: second derivatives of G: C_P, compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, thermal expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

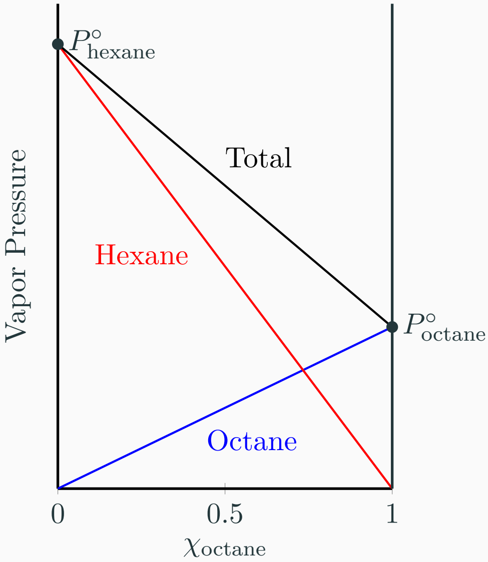
First vs Second Order



$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

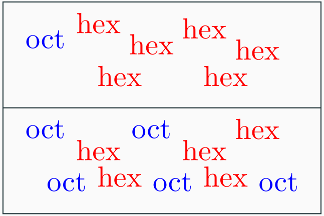
Ideal Liquid–Liquid Mixtures



Raoult's Law for Mixtures

Note the phases on mol fraction!

$$
\begin{aligned}
P_{\text{vap,soln}} &= P_{\text{vap,hex}} + P_{\text{vap,oct}} \\
&= \chi_{\text{hex(l)}}\, P^{\text{hex}}_{\text{vap}} + \chi_{\text{oct(l)}}\, P^{\text{oct}}_{\text{vap}} \\
P_{\text{hex}} &= \chi_{\text{hex (g)}}\, P_{\text{total}} = X_{\text{hex (l)}}\, P^{\text{pure}}_{\text{hex}}
\end{aligned}
$$



$$\chi_{\text{hex(g)}} = \frac{6}{7}$$

$$\chi_{\text{oct(g)}} = \frac{1}{7}$$

$$\chi_{\text{hex(l)}} = \frac{5}{10}$$

$$\chi_{\text{oct(l)}} = \frac{5}{10}$$

Example: Raoult's Law for Mixtures

Hexane and octane form an ideal mixture. The vapor pressure of pure hexane at 323 K is 0.55 atm. The vapor pressure of pure octane at 323 K is 0.09 atm. A mixture of hexane and octane has a total vapor pressure of 0.32 atm at 323 K. What is the mol fraction of hexane in the liquid phase and the mol fraction of hexane in the gas phase?

$$
\begin{aligned}
P_{\text{vap,soln}} &= \chi_{\text{hex (l)}}\, P_{\text{vap}}^{\text{hex}} + \chi_{\text{oct (l)}}\, P_{\text{vap}}^{\text{oct}} \\
&= \chi_{\text{hex (l)}}(0.55\,\text{atm}) + (1 - \chi_{\text{hex}(l)})(0.09\,\text{atm}) \\
0.32\,\text{atm} &= 0.55\chi_{\text{hex (l)}} + 0.09 - 0.09\chi_{\text{hex}} \\
0.23 &= 0.46\chi_{\text{hex (l)}} \\
\chi_{\text{hex (l)}} &= \boxed{0.50}
\end{aligned}
$$

Example: Raoult's Law for Mixtures

What is the mol fraction of hexane in the gas phase?

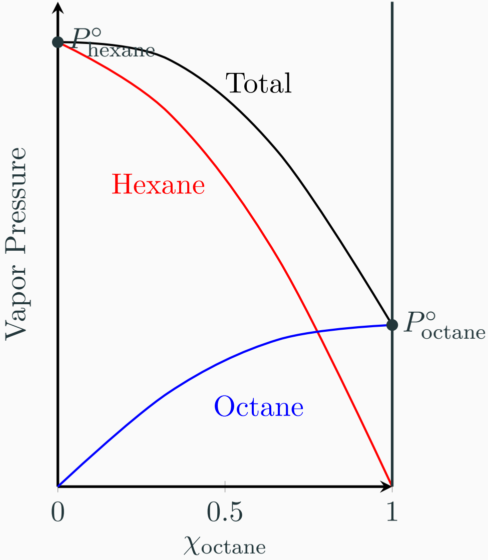
Raoult's Law (mol fraction solvent gives partial pressures)

$$P_{\text{hex}} = \chi_{\text{hex}\,(\text{l})}\, P_{\text{hex}}^{\text{pure}}$$

Dalton's Law (partial pressure of gas phase)

$$\begin{aligned} P_{\text{hex}} &= \chi_{\text{hex}\,(\text{g})} \cdot P_{\text{total}} \\ \chi_{\text{hex}\,(\text{g})} &= \frac{\chi_{\text{hex}\,(\text{l})}\, P_{\text{hex}}^{\text{pure}}}{P_{\text{total}}} \\ &= \frac{(0.50)(0.55\,\text{atm})}{0.32\,\text{atm}} \\ &= \boxed{0.86} \end{aligned}$$

Real Liquid–Liquid Mixtures

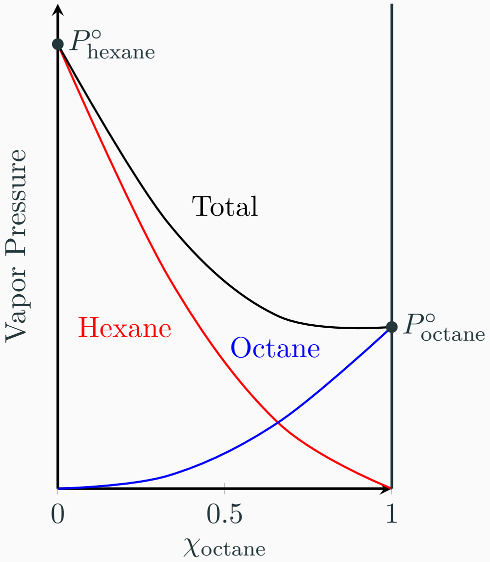


Positive Deviation

More favorable intermolecular interactions within pure solvent so molecules inclined to escape to vapor phase

$\Delta H_{mix} > 0$

Real Liquid–Liquid Mixtures



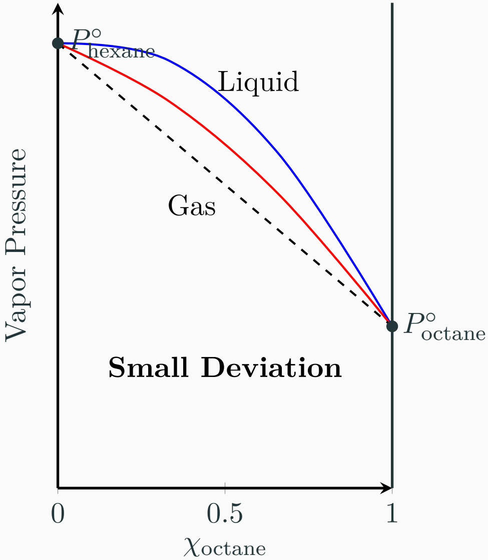
Negative Deviation

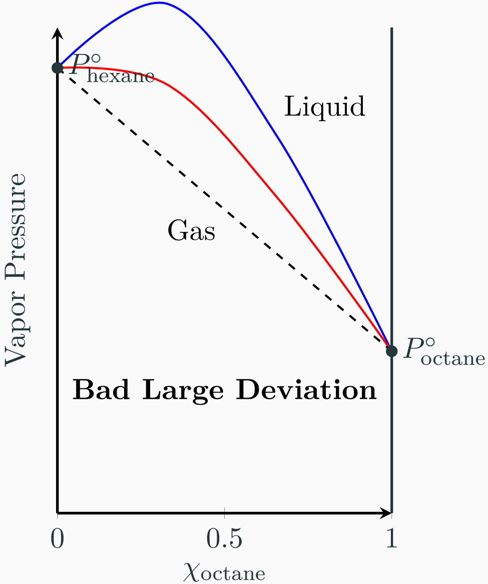
More favorable intermolecular interactions with other liquid than within pure solvent so molecules inclined stay in liquid phase

$\Delta H_{mix} < 0$

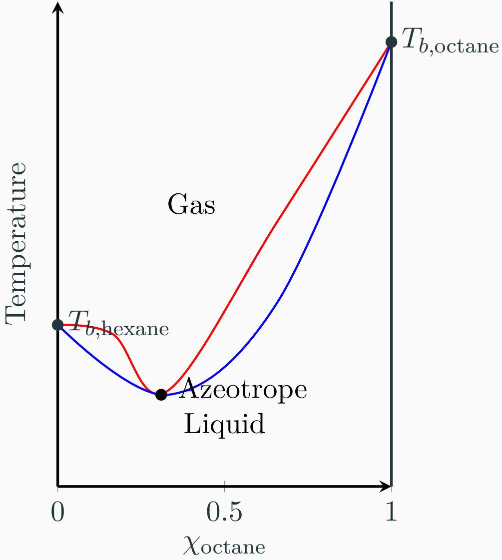
Note regions:
Below vapor pressure, liquid can't stay together, escape to gas phase
Above vapor pressure, gas molecules want to relieve pressure, goes to liquid

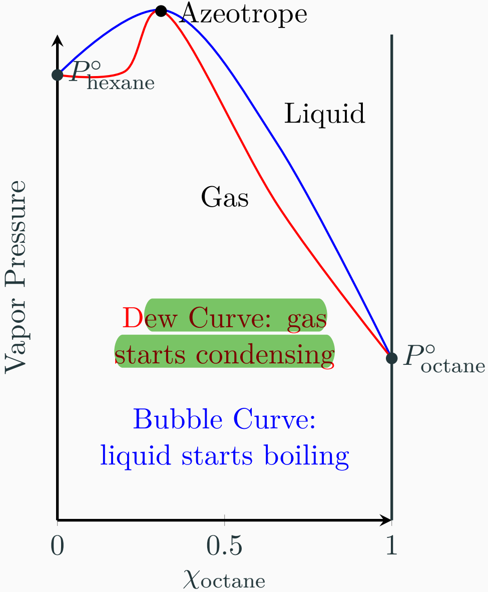
Formation of Azeotrope





Azeotrope Diagrams, positive deviation





Dew Curve: gas starts condensing

Bubble Curve: liquid starts boiling