2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 17

Room 3-442
Tuesday, April 9, 2:30pm - 4:30pm

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Liquid-vapor equilibria in non-ideal mixtures

stability and miscibility gap
liquid-liquid spinodal decomposition

Liquid-vapor equilibria for non-ideal binary mixtures

For a pure substance, MSE between f and g requires

$$\mu_{11\mathrm{f}}(T,p) = \mu_{11\mathrm{g}}(T,p) \;\Rightarrow\; p = p_{\mathrm{sat}}(T) \text{ or } T = T_{\mathrm{sat}}(p)$$

For a binary mixture

$$\begin{aligned}\mu_{1\mathrm{f}}(T,p,y_{1\mathrm{f}}) &= \mu_{1\mathrm{g}}(T,p,y_{1\mathrm{g}})\\ \mu_{2\mathrm{f}}(T,p,y_{1\mathrm{f}}) &= \mu_{2\mathrm{g}}(T,p,y_{1\mathrm{g}})\end{aligned} \;\Rightarrow\; \begin{aligned}y_{1\mathrm{f}} &= y_{1\mathrm{f}}(T,p)\\ y_{1\mathrm{g}} &= y_{1\mathrm{g}}(T,p)\end{aligned} \text{ or } \begin{aligned}p &= p_{\mathrm{bubble}}(T,y_{1\mathrm{f}})\\ p &= p_{\mathrm{dew}}(T,y_{1\mathrm{g}})\end{aligned} \text{ or } \begin{aligned}T &= T_{\mathrm{bubble}}(p,y_{1\mathrm{f}})\\ T &= T_{\mathrm{dew}}(p,y_{1\mathrm{g}})\end{aligned}$$

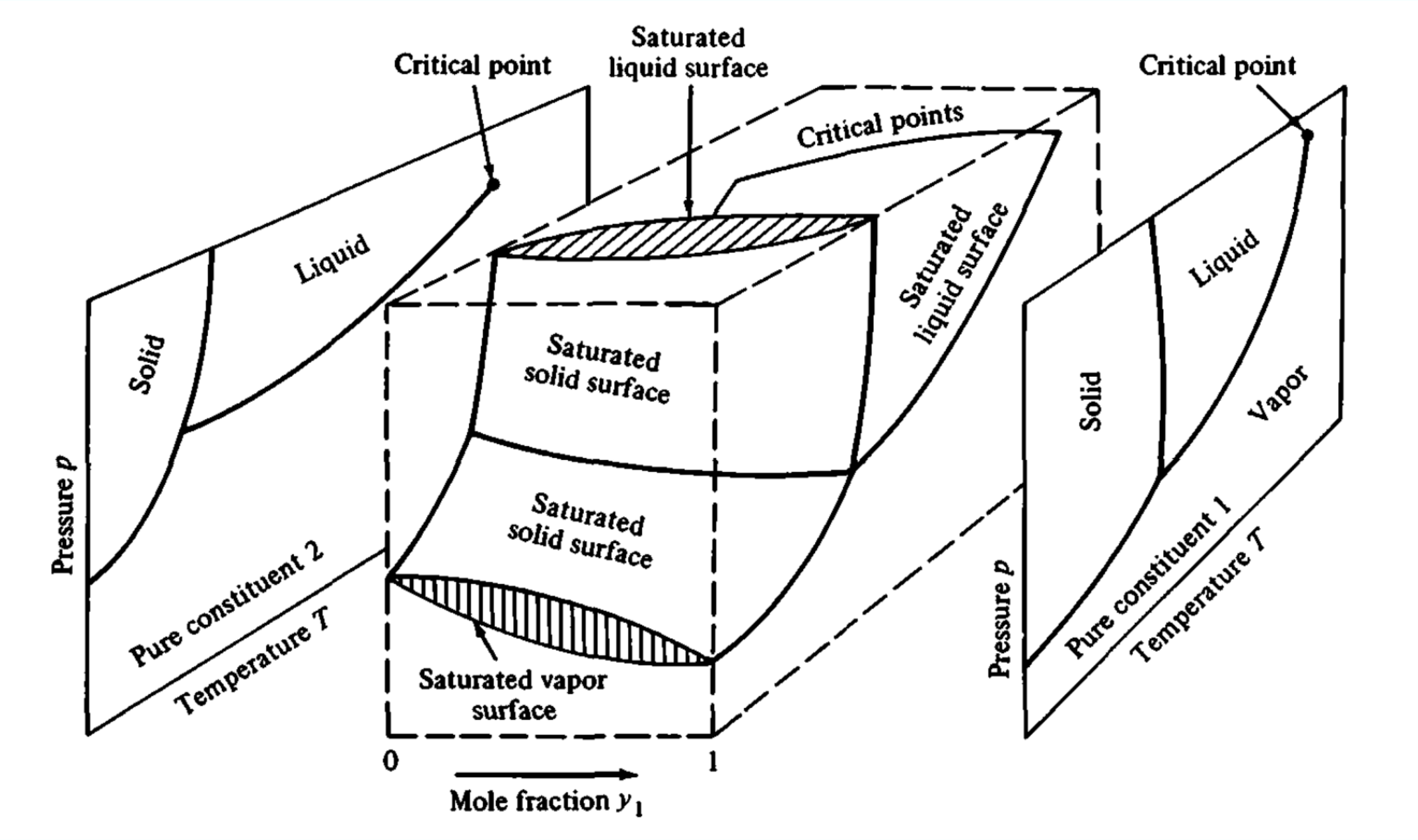


Figure from p.470 of Gyftopoulos, Beretta, Thermodynamics. Foundations and Applications, Dover, 2005

Henry's law for dilute non-ideal solutions

In the limit $y_{2\mathrm{f}} \ll 1$, the liquid phase is a dilute solution, and the solvent 1 always behaves as in an ideal solution, i.e.,

$$\mu_{1\mathrm{f}}(T,p,y_{1\mathrm{f}}) = \mu_{11\mathrm{f}}(T,p) + RT\ln y_{1\mathrm{f}} \quad \Rightarrow \quad \mathrm{d}\mu_{1\mathrm{f}}|_{T,p} = RT\frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}}$$

If the vapor behaves as a GD mix of ideal gases, Raoult's law applies for component 1, i.e.,

$$\mu_{1\mathrm{f}} = \mu_{1\mathrm{g}} \quad \Rightarrow \quad y_{1\mathrm{g}}\,p = y_{1\mathrm{f}}\,p^{\mathrm{fg}}_{\mathrm{sat},11}(T)$$

If the solution is ideal, then also component 2 satisfies a Raoult's law

$$\mu_{2\mathrm{f}} = \mu_{2\mathrm{g}} \quad \Rightarrow \quad y_{2\mathrm{g}}\,p = y_{2\mathrm{f}}\,p^{\mathrm{fg}}_{\mathrm{sat},22}(T)$$

But, even if it is **not ideal**, the Gibbs-Duhem relations must hold. For the liquid phase,

$$\boxed{-s_{\mathrm{f}}\,\mathrm{d}T + v_{\mathrm{f}}\,\mathrm{d}p - y_{1\mathrm{f}}\,\mathrm{d}\mu_{1\mathrm{f}} - y_{2\mathrm{f}}\,\mathrm{d}\mu_{2\mathrm{f}} = 0} \quad \Rightarrow \quad \mathrm{d}\mu_{2\mathrm{f}}|_{T,p} = -\frac{y_{1\mathrm{f}}}{y_{2\mathrm{f}}}\mathrm{d}\mu_{1\mathrm{f}}|_{T,p} = -RT\frac{y_{1\mathrm{f}}}{y_{2\mathrm{f}}}\frac{\mathrm{d}y_{1\mathrm{f}}}{y_{1\mathrm{f}}} = RT\frac{\mathrm{d}y_{2\mathrm{f}}}{y_{2\mathrm{f}}}$$

so also the dependence of $\mu_{2\mathrm{f}}$ must be logarithmic in $y_{2\mathrm{f}}$. Indeed, integrating yields

$$\mu_{2\mathrm{f}} = \lambda_{2\mathrm{f}}(T,p) + RT\ln y_{2\mathrm{f}} \qquad [\text{for ideal solution behavior, of course, } \lambda_{2\mathrm{f}}(T,p) = \mu_{22\mathrm{f}}(T,p)]$$

and then, the MSE condition $\mu_{2\mathrm{f}} = \mu_{2\mathrm{g}}$ for component 2 yields

$$\lambda_{2\mathrm{f}}(T,p) + RT\ln y_{2\mathrm{f}} = \mu_{22\mathrm{g}}(T,p^{\mathrm{fg}}_{\mathrm{sat},22}(T)) + RT\ln\frac{y_{2\mathrm{g}}\,p}{p^{\mathrm{fg}}_{\mathrm{sat},22}(T)} \quad \Rightarrow \quad \boxed{y_{2\mathrm{g}}\,p = y_{2\mathrm{f}}\,\mathcal{H}_{2\mathrm{f}}(T,p)}$$

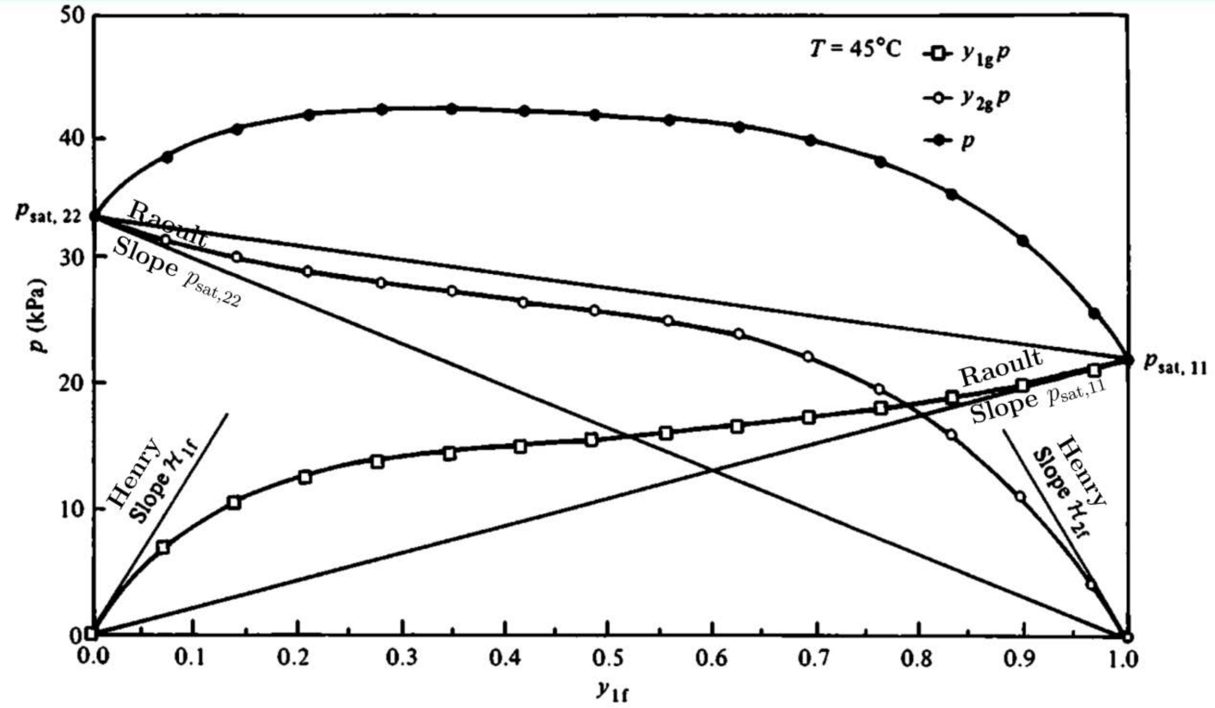
where $\mathcal{H}_{2\mathrm{f}}(T,p)$ is called **Henry's volatility constant**

$$\mathcal{H}_{2\mathrm{f}}(T,p) = p^{\mathrm{fg}}_{\mathrm{sat},22}(T)\exp\left[\frac{\lambda_{2\mathrm{f}}(T,p) - \mu_{22\mathrm{g}}(T,p^{\mathrm{fg}}_{\mathrm{sat},22}(T))}{RT}\right]$$

Henry's law for dilute non-ideal solutions

Diver's decompression sickness (”the bends”): As pressure increases with depth, according to Henry's law, the solubility of N2 in the bloodstream also increases. When the diver ascends to the surface, the pressure decreases, and the excess dissolved N2 needs time to be released through the lungs. However, if the diver ascends too rapidly from a dive, bubbles of N2 gas may form in the bloodstream, leading to decompression sickness (DCS). These bubbles can accumulate in major joints such as knees or elbows, causing severe pain and discomfort, which is why DCS is commonly referred to as ”the bends.”

Other applications: to characterize the transfer of trace species between the atmosphere and oceans, liquid cloud droplets, aerosol particles, and other bodies of water. To determine the vaporization of contaminants from rivers or wastewater treatment ponds.



Henry's constants (in atm) for acqueous solutions at 298 K of

SF_6	227×10^3
He	140×10^3
N_2	85×10^3
H_2	70×10^3
CO	56×10^3
O_2	42×10^3
CH_4	39×10^3
Ar	39×10^3
O_3	5.5×10^3
CO_2	1.6×10^3
Cl_2	0.9×10^3

Data from R. Sander, Atmos. Chem. Phys., 23, 10901 (2023).

Modeling non-ideal SES behavior of mixtures:

careful in taking derivatives!

$$G = G(T,p,\boldsymbol{n}) = \sum_{i=1}^{r} n_i\mu_i(T,p,\boldsymbol{y}) = n\,g(T,p,\boldsymbol{y}) \qquad \boxed{g(T,p,\boldsymbol{y}) = \sum_{i=1}^{r} y_i\mu_i(T,p,\boldsymbol{y})} \qquad n = \sum_{i=1}^{r} n_i$$

$$\frac{\partial \ln y_i}{\partial n_j} = \frac{\delta_{ij}}{n_i} - \frac{1}{n} \qquad \frac{\partial y_i}{\partial n_j} = y_i\frac{\partial \ln y_i}{\partial n_j} = \frac{y_i\delta_{ij}}{n_i} - \frac{y_i}{n} = \frac{1}{n}(\delta_{ij} - y_j)$$

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i}} = \left(\frac{\partial n\,g}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = g + n\left(\frac{\partial g}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = g + n\sum_{j=1}^{r}\left(\frac{\partial g}{\partial y_j}\right)_{T,p,\boldsymbol{y}'_j}\frac{\partial y_j}{\partial n_i}$$

$$= g + \sum_{j=1}^{r}\left(\frac{\partial g}{\partial y_j}\right)_{T,p,\boldsymbol{y}'_j}(\delta_{ij} - y_j) = \boxed{g(T,p,\boldsymbol{y}) + \left(\frac{\partial g}{\partial y_i}\right)_{T,p,\boldsymbol{y}'_i} - \sum_{j=1}^{r} y_j\left(\frac{\partial g}{\partial y_j}\right)_{T,p,\boldsymbol{y}'_j}} \qquad (1)$$

For example, consider $g^{\mathrm{id}}(T,p,\boldsymbol{y}) = \sum_{i=1}^{r} y_i\mu_i^{\mathrm{id}} = \sum_{i=1}^{r} y_i\mu_{ii}(T,p) + RT\sum_{i=1}^{r} y_i \ln y_i$

and notice that the derivative $(\partial g^{\mathrm{id}}/\partial y_i)_{T,p,\boldsymbol{y}'_i} = \mu_{ii} + RT(1 + \ln y_i) \neq \mu_i^{\mathrm{id}}$

but using it in Eq.(1) yields the correct expression $\mu_i^{\mathrm{id}} = \mu_{ii} + RT\ln y_i$.

For a binary mixture, $g = g(T,p,y_1) \qquad \mu_1 = g + (1 - y_1)\left(\dfrac{\partial g}{\partial y_1}\right)_{T,p} \qquad \mu_2 = g - y_1\left(\dfrac{\partial g}{\partial y_1}\right)_{T,p}$

so the MSE conditions between two phases, $\mu'_1 = \mu''_1$ and $\mu'_2 = \mu''_2$, imply

$$\boxed{\left(\frac{\partial g}{\partial y_1}\right)'_{T,p} = \left(\frac{\partial g}{\partial y_1}\right)''_{T,p}} \quad \text{and} \quad \boxed{g'' = g' + (y''_1 - y'_1)\left(\frac{\partial g}{\partial y_1}\right)'_{T,p}}$$

Non-ideal SES behavior of mixtures:

consequences of the stability conditions for a binary mixtures

$g = g^{\rm id} + g^{\rm ex}_{\rm M1} = g(T,p,y_1)$ **one parameter Margules, binary mixture**

$$g^{\rm id} = y_1\, g_{11}(T,p) + (1-y_1)\, g_{22}(T,p) + RT\,[y_1 \ln y_1 + (1-y_1)\ln(1-y_1)]$$

$$\mu_1^{\rm id} = g_{11}(T,p) + RT\ln y_1 \qquad \mu_2^{\rm id} = g_{22}(T,p) + RT\ln(1-y_1)$$

$$g^{\rm ex}_{\rm M1} = A(T,p)\, y_1\,(1-y_1) \qquad \mu^{\rm ex}_{1,\rm M1} = A(T,p)\,(1-y_1)^2 \qquad \mu^{\rm ex}_{2,\rm M1} = A(T,p)\, y_1^2$$

Stability requires $({\rm d}^2G)_{T,p} > 0$ therefore $({\rm d}^2G)_{T,p,n} = n\,({\rm d}^2g)_{T,p,n} \Rightarrow n\left(\frac{\partial^2 g}{\partial y_1^2}\right)_{T,p}({\rm d}y_1)^2 > 0$

$$\left(\frac{\partial g^{\rm id}}{\partial y_1}\right)_{T,p} = g_{11} - g_{22} + RT\,[1 + \ln y_1 - 1 - \ln(1-y_1)] \qquad \left(\frac{\partial g^{\rm ex}}{\partial y_1}\right)_{T,p} = RT\,(1-2y_1)A(T,p)$$

$$\left(\frac{\partial^2 g^{\rm id}}{\partial y_1^2}\right)_{T,p} = RT\left(\frac{1}{y_1} + \frac{1}{1-y_1}\right) = \frac{RT}{y_1\,(1-y_1)} \qquad \left(\frac{\partial^2 g^{\rm ex}}{\partial y_1^2}\right)_{T,p} = -2RT\,A(T,p)$$

$$\left(\frac{\partial^2 g}{\partial y_1^2}\right)_{T,p} = RT\left(\frac{1}{y_1\,(1-y_1)} - 2A(T,p)\right) > 0 \quad \forall y_1 \quad \Rightarrow \quad A(T,p) < 2$$

The mixture is stable at all compositions if $A(T,p) < 2$, whereas for $A(T,p) > 2$

$\left(\frac{\partial^2 g}{\partial y_1^2}\right)_{T,p} < 0$ for $y_1^2 - y_1 + \frac{1}{2A} < 0$, i.e., in the range $\frac{1-\sqrt{1-2/A}}{2} < y_1 < \frac{1+\sqrt{1-2/A}}{2}$

In the **spinodal range** the mixture is unstable and separates into two phases with different compositions. Stability also requires the MSE conditions between the two phases $'$ and $''$:

$$\mu_1' = \mu_1'' \qquad g_{11}'(T,p) + RT\ln y_1' + A(T,p)\,(1-y_1')^2 = g_{11}''(T,p) + RT\ln y_1'' + A(T,p)\,(1-y_1'')^2$$

$$\mu_2' = \mu_2'' \qquad g_{22}'(T,p) + RT\ln(1-y_1') + A(T,p)\,(y_1')^2 = g_{22}''(T,p) + RT\ln(1-y_1'') + A(T,p)\,(y_1'')^2$$

Non-ideal SES behavior of mixtures:

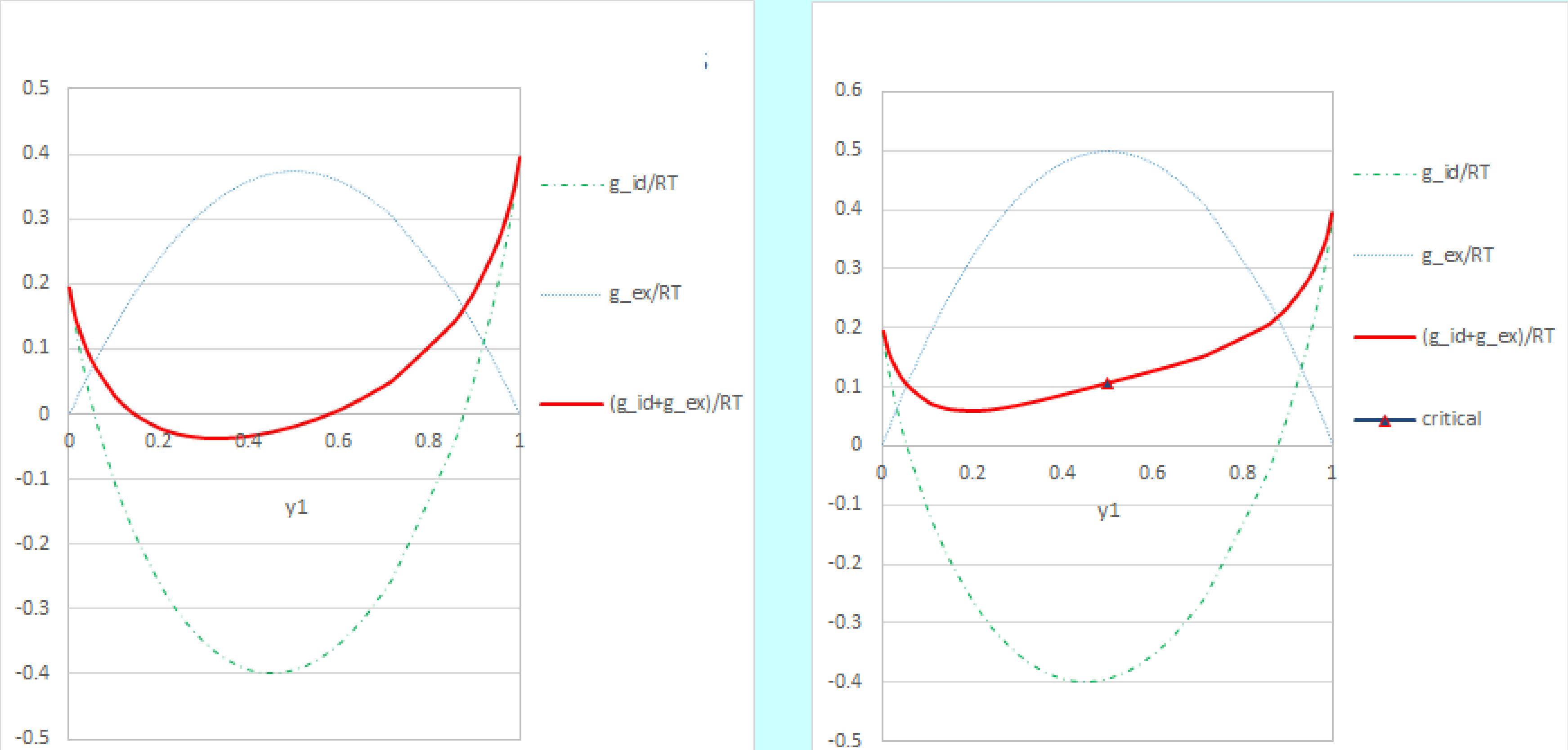
$A < 2$ (complete miscibility)

$A = 1.5$

the two liquids are completely miscible

$A = 2$ (critical value)

the two liquids are completely miscible but at $y_1 = 1/2$ it is at the edge of of instability, since $\left(\dfrac{\partial^2 g}{\partial y_1^2}\right)_{T,p} = 0$



g/RT vs y_1 assuming the Margules 1-parameter model with $g_{11}/RT = 0.4$, $g_{22}/RT = 0.2$

Non-ideal SES behavior of mixtures:

$A > 2$ (partial miscibility, miscibility gap)

For a binary mixture,

$$g = g(T, p, y_1)$$

$$\mu_1 = g + (1 - y_1)\left(\frac{\partial g}{\partial y_1}\right)_{T,p}$$

$$\mu_2 = g - y_1\left(\frac{\partial g}{\partial y_1}\right)_{T,p}$$

so the MSE conditions between two phases $'$ and $''$,

$$\mu_1' = \mu_1'' \text{ and } \mu_2' = \mu_2''$$

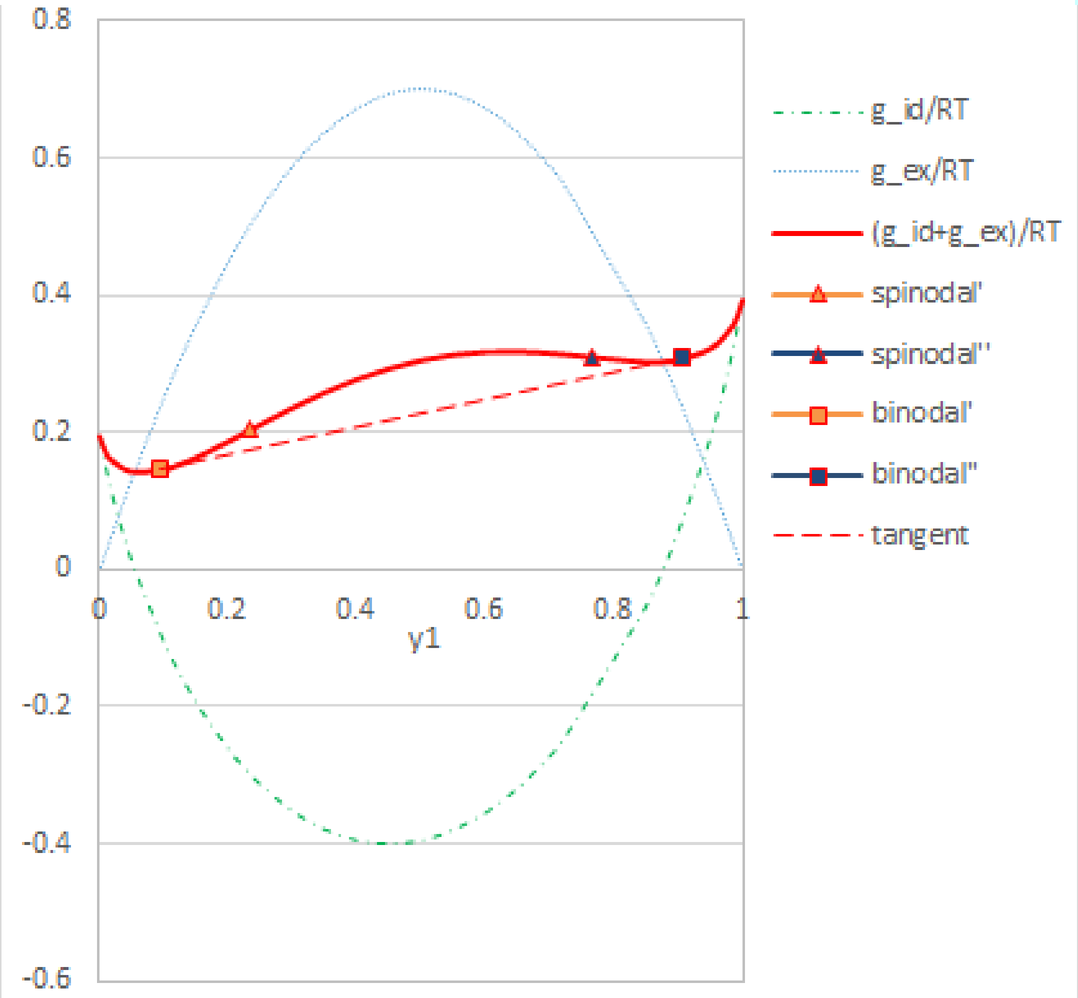
imply

$$\left(\frac{\partial g}{\partial y_1}\right)_{T,p}' = \left(\frac{\partial g}{\partial y_1}\right)_{T,p}''$$

and

$$g'' = g' + (y_1'' - y_1')\left(\frac{\partial g}{\partial y_1}\right)_{T,p}'$$

g/RT vs y_1 assuming the Margules 1-parameter model with $A = 2.8$, $g_{11}/RT = 0.4$, $g_{22}/RT = 0.2$



Solubility gaps and limit curves arise in liquid-liquid (and solid-solid) mixtures that are only partially miscible below (or above) an upper (lower) critical temperature: spinodal decomposition

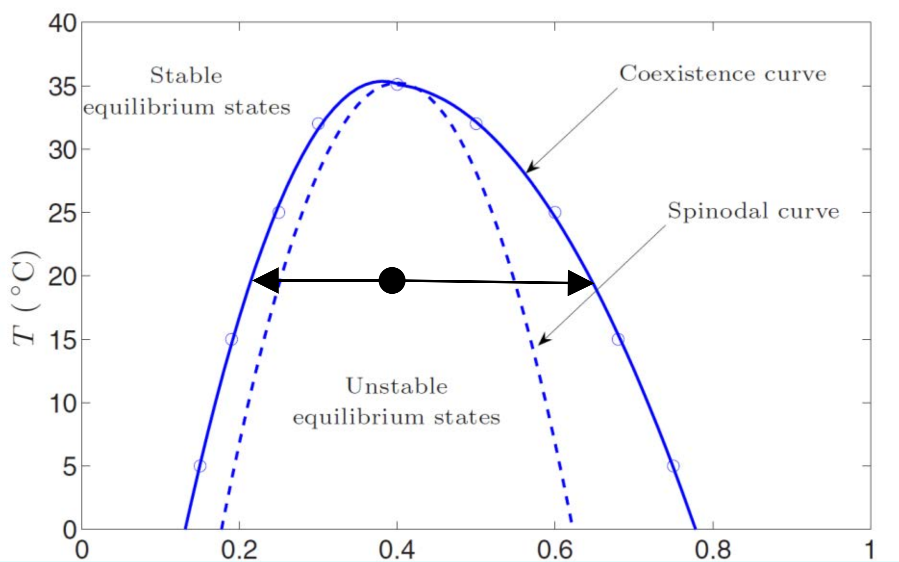
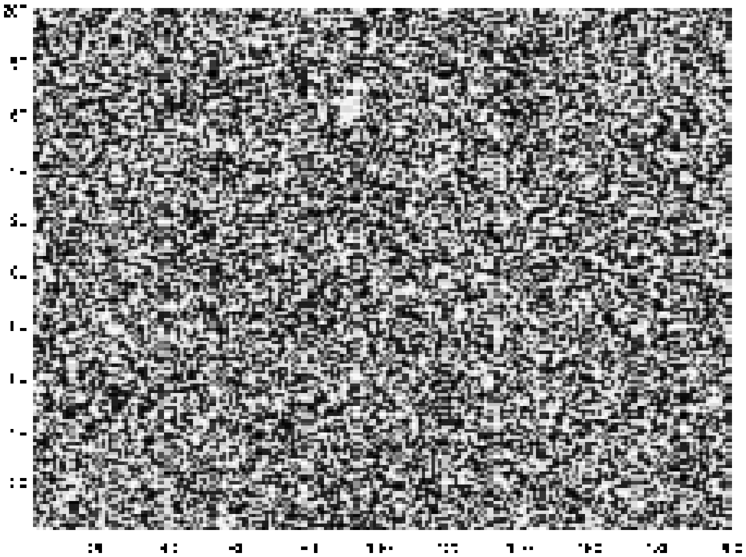


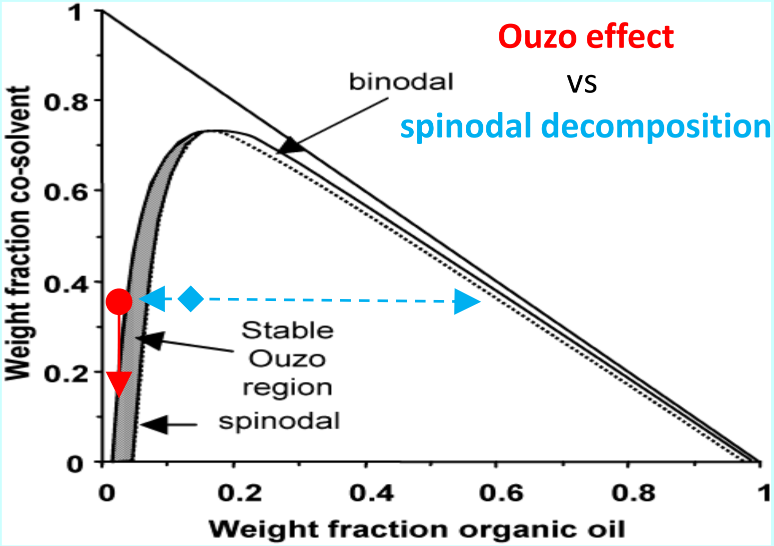
Fig. 1 from P. Poesio, A.M. Lezzi, G.P. Beretta, Evidence of convective heat transfer enhancement induced by spinodal decomposition, Physical Review E 75, 066306 (2007).

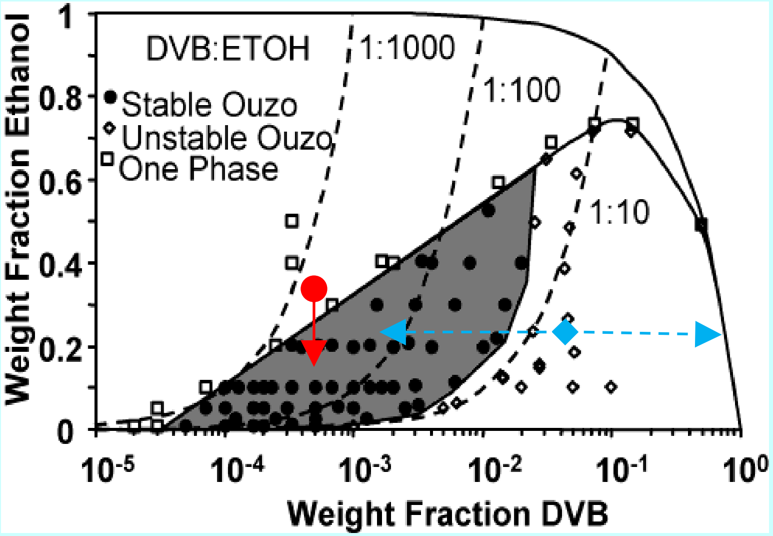


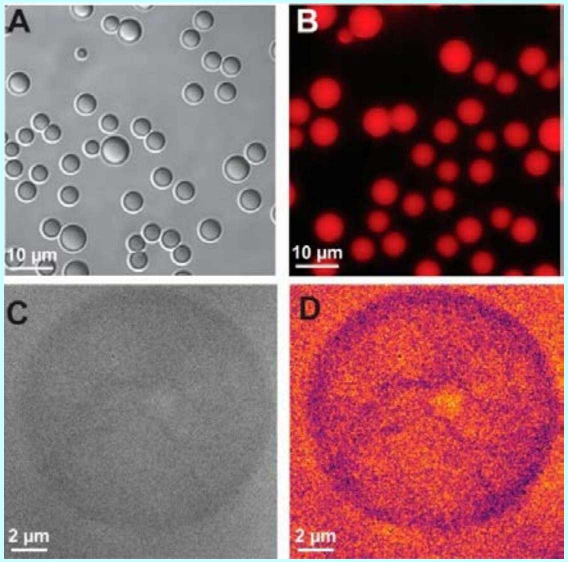
GIF by Yonatan Oren from Wikipedia

Spinodal decomposition is the spontaneous process whereby an unstable partially miscible liquid mixture relaxes toward a lower free energy (stable) equilibrium state. During this process, an initially homogeneous liquid solution of a given composition spontaneously changes from an unstable single-phase to a two-phase stable state consisting of two separated liquid phases, of different compositions, in mutual equilibrium. This is possible only if the overall Gibbs free energy of the two separated phases is lower than that of the initial single-phase mixture.

Solubility gaps and limit curves arise in liquid-liquid (and solid-solid) mixtures that are only partially miscible. They can produce metastable liquid-liquid dispersions: **”the Ouzo Effect”**







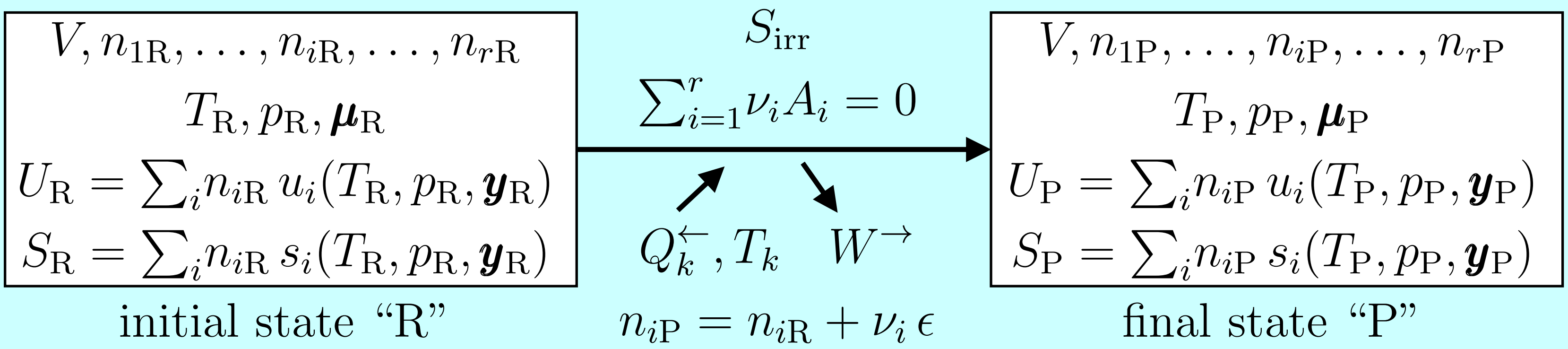
Figs. 1 and 2 adapted from S.A. Vitale and J.L. Katz. "Liquid droplet dispersions formed by homogeneous liquid– liquid nucleation:“The Ouzo Effect”." Langmuir 19, 4105 (2003).

Abstract and Fig. 2 from M.A. Vratsanos et al. "Ouzo effect examined at the nanoscale via direct observation of droplet nucleation and morphology." ACS Central Science 9, 457 (2023).

Systems with chemical reactions

energy and entropy balances
notation and stoichiometry

Energy and entropy balances for closed and open
systems with chemical reactions



$V, n_{1\mathrm{R}}, \dots, n_{i\mathrm{R}}, \dots, n_{r\mathrm{R}}$

$T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{\mu}_\mathrm{R}$

$U_\mathrm{R} = \sum_i n_{i\mathrm{R}}\, u_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$

$S_\mathrm{R} = \sum_i n_{i\mathrm{R}}\, s_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$

initial state “R”

S_irr

$\sum_{i=1}^r \nu_i A_i = 0$

$Q_k^\leftarrow, T_k$ $\quad W^\rightarrow$

$n_{i\mathrm{P}} = n_{i\mathrm{R}} + \nu_i\, \epsilon$

$V, n_{1\mathrm{P}}, \dots, n_{i\mathrm{P}}, \dots, n_{r\mathrm{P}}$

$T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{\mu}_\mathrm{P}$

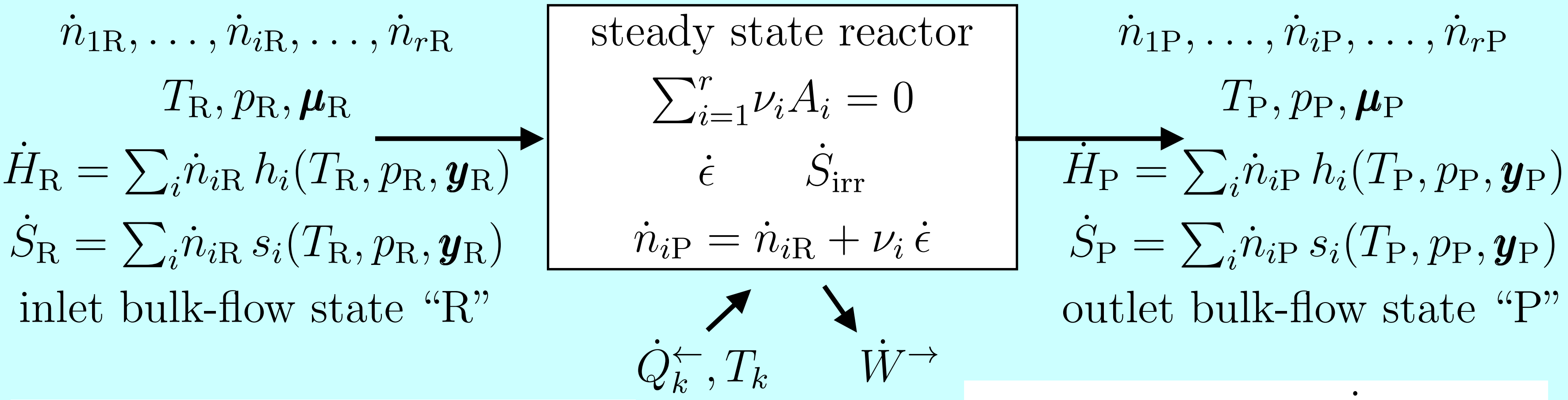
$U_\mathrm{P} = \sum_i n_{i\mathrm{P}}\, u_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$

$S_\mathrm{P} = \sum_i n_{i\mathrm{P}}\, s_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$

final state “P”

$$U_\mathrm{P} - U_\mathrm{R} = \sum_k Q_k^\leftarrow - W^\rightarrow$$

$$S_\mathrm{P} - S_\mathrm{R} = \sum_k \frac{Q_k^\leftarrow}{T_k} + S_\mathrm{irr}$$



$\dot n_{1\mathrm{R}}, \dots, \dot n_{i\mathrm{R}}, \dots, \dot n_{r\mathrm{R}}$

$T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{\mu}_\mathrm{R}$

$\dot H_\mathrm{R} = \sum_i \dot n_{i\mathrm{R}}\, h_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$

$\dot S_\mathrm{R} = \sum_i \dot n_{i\mathrm{R}}\, s_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$

inlet bulk-flow state “R”

steady state reactor

$\sum_{i=1}^r \nu_i A_i = 0$

$\dot\epsilon$ $\quad \dot S_\mathrm{irr}$

$\dot n_{i\mathrm{P}} = \dot n_{i\mathrm{R}} + \nu_i\, \dot\epsilon$

$\dot Q_k^\leftarrow, T_k$ $\quad \dot W^\rightarrow$

$\dot n_{1\mathrm{P}}, \dots, \dot n_{i\mathrm{P}}, \dots, \dot n_{r\mathrm{P}}$

$T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{\mu}_\mathrm{P}$

$\dot H_\mathrm{P} = \sum_i \dot n_{i\mathrm{P}}\, h_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$

$\dot S_\mathrm{P} = \sum_i \dot n_{i\mathrm{P}}\, s_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$

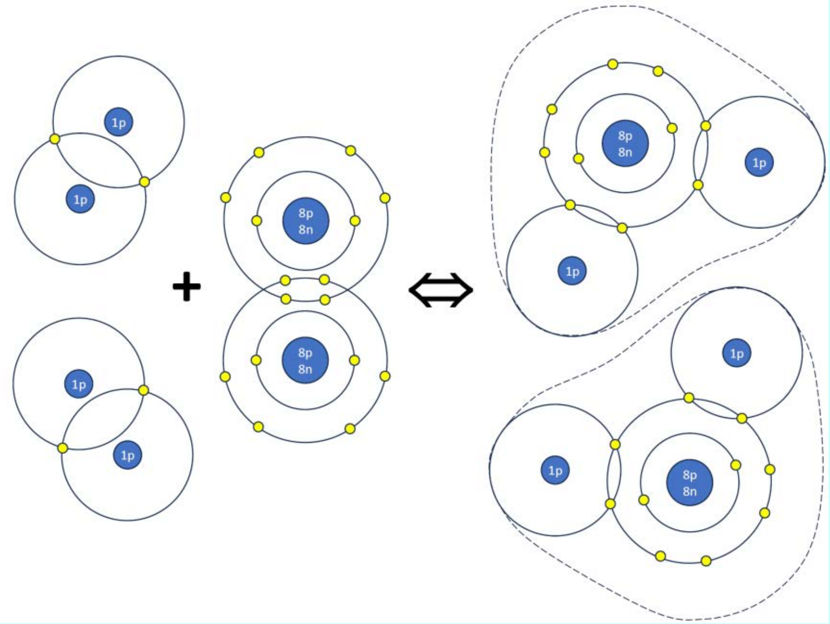
outlet bulk-flow state “P”

$$0 = \dot H_\mathrm{R} - \dot H_\mathrm{P} + \sum_k \dot Q_k^\leftarrow - \dot W^\rightarrow$$

$$0 = \dot S_\mathrm{R} - \dot S_\mathrm{P} + \sum_k \frac{\dot Q_k^\leftarrow}{T_k} + \dot S_\mathrm{irr}$$

Notation and stoichiometry:

proportionality relations, reaction coordinates



chemical reaction mechanism

$$2\mathrm{H}_2 + \mathrm{O}_2 = 2\mathrm{H}_2\mathrm{O} \quad \text{or} \quad -2\mathrm{H}_2 - \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} = 0$$

composition: $n_{\mathrm{H}_2},\ n_{\mathrm{O}_2},\ n_{\mathrm{H}_2\mathrm{O}}$

changes in composition: $\Delta n_{\mathrm{H}_2},\ \Delta n_{\mathrm{O}_2},\ \Delta n_{\mathrm{H}_2\mathrm{O}}$

proportionality relations

$$\frac{\Delta n_{\mathrm{H}_2}}{-2} = \frac{\Delta n_{\mathrm{O}_2}}{-1} = \frac{\Delta n_{\mathrm{H}_2\mathrm{O}}}{2} = \Delta\epsilon$$

$\epsilon =$ reaction coordinate

chemical symbols

$$A_1 = \mathrm{H}_2,\ A_2 = \mathrm{O}_2,\ A_3 = \mathrm{H}_2\mathrm{O}$$

stoichiometric coefficients

$$\nu_1 = -2,\ \nu_2 = -1,\ \nu_3 = 2$$

rewrite the mechanism as

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 = 0$$

$$\boxed{\textstyle\sum_i \nu_i A_i = 0}$$

proportionality relations

$$\frac{\Delta n_1}{\nu_1} = \frac{\Delta n_2}{\nu_2} = \frac{\Delta n_3}{\nu_3} = \Delta\epsilon$$

$$\Delta n_i = \nu_i\,\Delta\epsilon \quad \forall i$$

$$\boxed{n_{i\mathrm{P}} = n_{i\mathrm{R}} + \nu_i\,\epsilon}$$

where $\epsilon = \epsilon_\mathrm{P} - \epsilon_\mathrm{R}$

$$\dot n_i = \nu_i \dot\epsilon \quad \forall i$$

$$\boxed{\dot n_{i\mathrm{P}} = \dot n_{i\mathrm{R}} + \nu_i\,\dot\epsilon}$$

Properties of reaction

The balance equations require these differences: $U_\mathrm{P}-U_\mathrm{R}$, $S_\mathrm{P}-S_\mathrm{R}$, $\dot H_\mathrm{P}-\dot H_\mathrm{R}$, $\dot S_\mathrm{P}-\dot S_\mathrm{R}$. For example,

$$U_\mathrm{P}-U_\mathrm{R}=\sum_i n_{i\mathrm{P}}\,u_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}})-\sum_i n_{i\mathrm{R}}\,u_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}})=\quad\text{add and subtract }u_{ii}(T,p_o)$$

$$=\sum_i n_{i\mathrm{P}}\underbrace{\left[u_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}})-u_{ii}(T,p_o)\right]}_{\substack{\Delta u_i^\mathrm{mix}|_{T_\mathrm{P},p_\mathrm{P}}+\\+u_{ii}(T_\mathrm{P},p_\mathrm{P})-u_{ii}(T,p_o)}}-\sum_i n_{i\mathrm{R}}\underbrace{\left[u_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}})-u_{ii}(T,p_o)\right]}_{\substack{\Delta u_i^\mathrm{mix}|_{T_\mathrm{R},p_\mathrm{R}}+\\+u_{ii}(T_\mathrm{R},p_\mathrm{R})-u_{ii}(T,p_o)}}+\underbrace{\sum_i\underbrace{(n_{i\mathrm{P}}-n_{i\mathrm{R}})}_{\nu_i\,\epsilon}u_{ii}(T,p_o)}_{\epsilon\sum_i\nu_i\,u_{ii}(T,p_o)=\epsilon\,\Delta u^o(T)}$$

$$\dot H_\mathrm{P}-\dot H_\mathrm{R}=\sum_i \dot n_{i\mathrm{P}}\,h_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}})-\sum_i \dot n_{i\mathrm{R}}\,h_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}})=\quad\text{add and subtract }h_{ii}(T,p_o)$$

$$=\sum_i \dot n_{i\mathrm{P}}\underbrace{\left[h_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}})-h_{ii}(T,p_o)\right]}_{\substack{\Delta h_i^\mathrm{mix}|_{T_\mathrm{P},p_\mathrm{P}}+\\+h_{ii}(T_\mathrm{P},p_\mathrm{P})-h_{ii}(T,p_o)}}-\sum_i \dot n_{i\mathrm{R}}\underbrace{\left[h_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}})-h_{ii}(T,p_o)\right]}_{\substack{\Delta h_i^\mathrm{mix}|_{T_\mathrm{R},p_\mathrm{R}}+\\+h_{ii}(T_\mathrm{R},p_\mathrm{R})-h_{ii}(T,p_o)}}+\underbrace{\sum_i\underbrace{(\dot n_{i\mathrm{P}}-\dot n_{i\mathrm{R}})}_{\nu_i\,\dot\epsilon}h_{ii}(T,p_o)}_{\dot\epsilon\sum_i\nu_i\,h_{ii}(T,p_o)=\dot\epsilon\,\Delta h^o(T)}$$

So, we defined the properties of reaction

at T and standard pressure $p_o = 1\,\mathrm{atm}$:

$$\Delta u^o(T)=\sum_i\nu_i\,u_{ii}(T,p_o)$$
$$\Delta s^o(T)=\sum_i\nu_i\,s_{ii}(T,p_o)$$
$$\Delta h^o(T)=\sum_i\nu_i\,h_{ii}(T,p_o)$$
$$\Delta g^o(T)=\sum_i\nu_i\,g_{ii}(T,p_o)$$
$$\Delta g^o(T)=\Delta h^o(T)-T\,\Delta s^o(T)$$
$$\Delta v^o(T)=\sum_i\nu_i\,v_{ii}(T,p_o)$$
$$\Delta h^o(T)=\Delta u^o(T)+p_o\,\Delta v^o(T)$$

at STP: $T_o = 298.15\,\mathrm{K}$ and $p_o = 1\,\mathrm{atm}$:

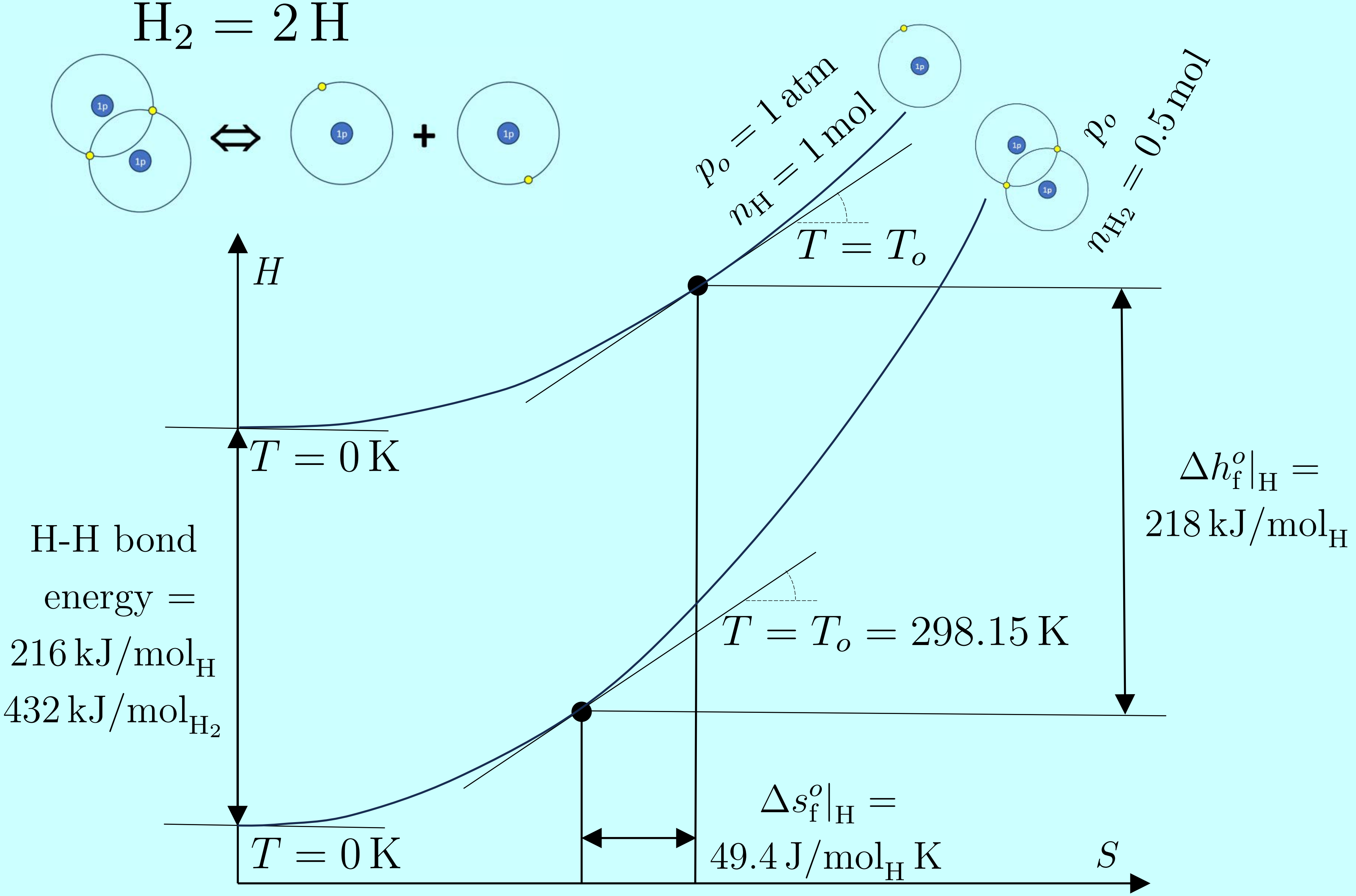
$$\Delta u^o=\sum_i\nu_i\,u_{ii}(T_o,p_o)$$
$$\Delta s^o=\sum_i\nu_i\,s_{ii}(T_o,p_o)$$
$$\Delta h^o=\sum_i\nu_i\,h_{ii}(T_o,p_o)$$
$$\Delta g^o=\sum_i\nu_i\,g_{ii}(T_o,p_o)$$
$$\Delta g^o=\Delta h^o-T_o\,\Delta s^o$$
$$\Delta v^o=\sum_i\nu_i\,v_{ii}(T_o,p_o)$$
$$\Delta h^o=\Delta u^o+p_o\,\Delta v^o$$

using the Hess relation and the properties of formation at STP:

$$\Delta u^o=\sum_i\nu_i\,\Delta u_\mathrm{f}^o|_i$$
$$\Delta s^o=\sum_i\nu_i\,\Delta s_\mathrm{f}^o|_i$$
$$\Delta h^o=\sum_i\nu_i\,\Delta h_\mathrm{f}^o|_i$$
$$\Delta g^o=\sum_i\nu_i\,\Delta g_\mathrm{f}^o|_i$$
$$\Delta v^o=\sum_i\nu_i\,\Delta v_\mathrm{f}^o|_i$$

Enthalpy of formation of H and H-H bond energy

$$H_2 = 2\,H$$



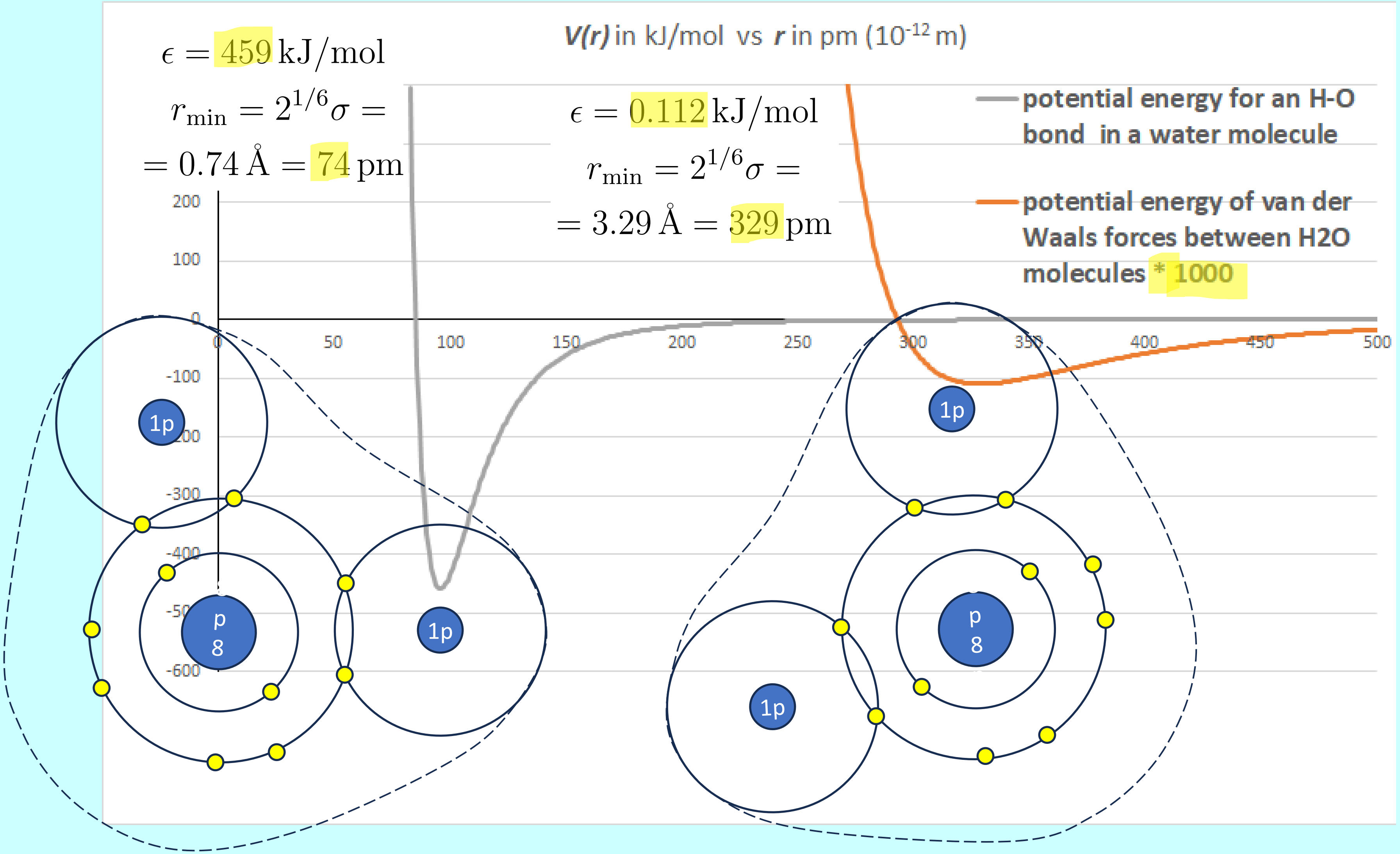
H-H bond energy $=$ $216\,\mathrm{kJ/mol_H}$ $432\,\mathrm{kJ/mol_{H_2}}$

$\Delta h_\mathrm{f}^o|_\mathrm{H} =$ $218\,\mathrm{kJ/mol_H}$

$\Delta s_\mathrm{f}^o|_\mathrm{H} =$ $49.4\,\mathrm{J/mol_H\,K}$

van der Waals forces vs covalent bonds

van der Waals forces have a significant impact on the physical properties of substances, such as boiling points, melting points, and solubility. But they are very weak compared to ionic or covalent bonds.



$$\epsilon = 459\,\mathrm{kJ/mol}$$

$$r_{\min} = 2^{1/6}\sigma =$$

$$= 0.74\,\text{Å} = 74\,\mathrm{pm}$$

$$\epsilon = 0.112\,\mathrm{kJ/mol}$$

$$r_{\min} = 2^{1/6}\sigma =$$

$$= 3.29\,\text{Å} = 329\,\mathrm{pm}$$

Image Credits

Slide 3:

Image showing liquid-vapor equilibria for non-ideal binary mixtures from the book *Thermodynamics: Foundations and Applications* © Dover Publications. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

Slide 10:

- Phase diagram of a partially miscible binary mixture with upper critical solution temperature © American Physical Society. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.
- Gif animation showing evolution under the Cahn-Hilliard equation is in the public domain.

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