3.020 Lecture 16

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1 Bookeeping for solutions

Partial molar properties

$$\overline{B}_k = \left.\frac{\partial B'}{\partial n_k}\right|_{T,P,n_{j\neq k}}$$

B' = extensive property, n_k = moles of k, $\overline{B}_k$ = partial molar property

- total differential

$$dB' = \left.\frac{\partial B'}{\partial T}\right|_{P,n_j} dT + \left.\frac{\partial B'}{\partial P}\right|_{T,n_j} dP + \sum_k \overline{B}_k dn_k$$

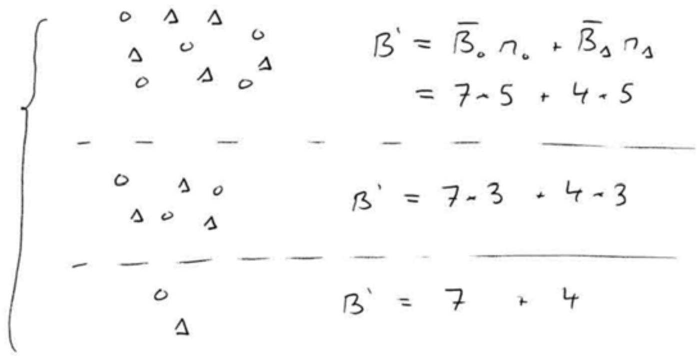
- for pure phase ($X_i = 1$), $\quad \overline{B}_i = B$

PMPs are intensive $\longrightarrow$ Independent of system size when all intensive properties are held constant.

e.g. $X_0 = X_\Delta = 0.5$

$\overline{B}_0 = 7,\ \overline{B}_\Delta = 4$

T, P **constant**



- Mathematical relations between extensive B' and intensive PMPs :
  - Consider scaling system size by scale factor λ

$$B' = B'(T, P, \lambda n_k) = \lambda B'(T, P, n_k)$$

  - Take derivative $\frac{d}{d\lambda}$ of both sides

$$\textbf{LHS:} \quad \frac{dB'}{d\lambda} = \sum_k \left.\frac{\partial B'}{\partial(\lambda n_k)}\right|_{T,P,n_{j\neq k}} \frac{d\lambda n_k}{d\lambda} = \overline{B}_k n_k$$

$$\textbf{RHS:} \quad \frac{d}{d\lambda}\lambda B^{'}(T,P,n_k) = B^{'}(T,P,n_k)$$

$B^{'}$ is a homogeneous function of n_k of order 1

- Comparing LHS = RHS we find

$$B^{'} = \sum \overline{B}_k n_k$$

this is called an Euler equation
$\longrightarrow$ Extensive properties at a solution phase are made up of the mole-weighted PMPs of the components
e.g.

$$G^{'} = \sum_k \frac{\partial G^{'}}{\partial n_k} n_k = \sum_k \mu_k n_k$$

Gibbs free energy PMP is the chemical potential

Euler and Gibbs-Duhem equations

- Euler eq'n: $B^{'} = \sum_k \overline{B}_k n_k$
- chain rule: $dB^{'} = \sum_k (\overline{B}_k dn_k + n_k d\overline{B}_k)$
- coefficient relation: $dB^{'}_{\ \ T,P} = \sum_k \overline{B}_k dn_k$
- Compare: $\sum_k n_k \ d\overline{B}_{k\ \ T,P} = 0$ this is called a Gibbs-Duhem equation

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- Gibbs-Duhem equations are a constraint on the variation of intensive properties (i.e. PMPs)
- Express how PMPs co-vary with system composition

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ex. Gibbs-Duhem for Gibbs free energy

- Euler: $G^{'} = \sum_k \mu_k n_k$
- chain rule: $dG^{'} = \sum_k (\mu_k dn_k + n_k d\mu_k)$

- combined statement : $dG^{'} = -S^{'}dT + V^{'}dP + \sum_k \mu_k dn_k$

$$\sum_k n_k d\mu_k = -S^{'}dT + V^{'}dP$$
$$\sum_k X_k d\mu_k = -SdT + VdP$$

this is a G-D equation

2 Partial molar properties of mixing

$$\begin{aligned}
\Delta B^{'}_{mix} &= B^{'}(solution) - B^{'}(pure\ starting\ materials) \\
&= \sum_k \overline{B}_k n_k - \sum_k \overline{B}^0_k n_k \\
&= \sum_k (\overline{B}_k - \overline{B}^0_k) n_k \\
&= \sum \Delta \overline{B}_{k,mix} n_k
\end{aligned}$$

change in PMPs due to mixing

ex. Gibbs free energy

$$G^{'} = \sum_k \overline{G}_k n_k = \sum_k \mu_k n_k = \sum (\mu^0_k + \Delta\mu_{k,mix}) n_k$$
$$G = \underbrace{\sum_k \mu^0_k X_k}_{sum\ of\ pure\ parts} + \underbrace{\sum_k \Delta\mu_{k,mix} X_k}_{this\ is\ \Delta G_{mix}\ from\ Lec.\ 15}$$

3 Calculating PMPs of mixing: Case of $\Delta\mu_k$, binary system

$$\Delta G_{mix} = \Delta\mu_i X_i + \Delta\mu_2 X_2$$
$$d\Delta G_{mix\ \ P,T} = \Delta\mu_1 dX_1 + \Delta\mu_2 dX_2 + \sum_k X_k d\Delta\mu_k$$

This summation is 0 by Gibbs-Duhem. Use $X_1 + X_2 = 1$ and $dX_1 = -dX_2$ to get:

$$\frac{d\Delta G_{mix}}{dX_2}_{p,T} = \Delta\mu_2 - \Delta\mu_1 \quad \textbf{eliminate } \Delta\mu_1 \textbf{ using this}$$

$$\Delta\mu_2 = \Delta G_{mix} + (1 - X_2)\frac{d\Delta G_{mix}}{dX_2}$$

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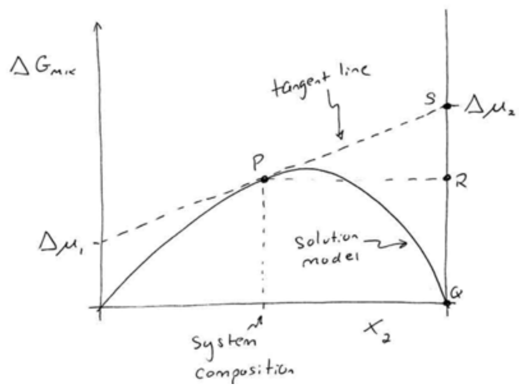
4 Graphical interpretation of PMPs using solution models

$\longrightarrow$ case of ΔG_{mix} and $\Delta\mu_k$'s



$$\Delta G_{mix} = \overline{QR}$$
$$1 - X_2 = \overline{PR}$$
$$\frac{d\Delta G_{mix}}{dX_2} = \frac{\overline{RS}}{\overline{PR}}$$
$$\Downarrow$$
$$\Delta\mu_2 = \overline{QR} + \overline{PR}\frac{\overline{RS}}{\overline{PR}} = \overline{QS}$$

likewise for $\Delta\mu_1$

3.020 Thermodynamics of Materials
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