

Generalized Gibbs-Duhem relationship

$$dB = \left. \frac{\partial B}{\partial T} \right|_{P, \{N\}} dT + \left. \frac{\partial B}{\partial P} \right|_{T, \{N\}} dP + \sum_{i=1}^n \bar{B}_i dN_i$$

$B$  is extensive w.r.t.  $N_i$ 's only -  $B = \sum_{i=1}^n \bar{B}_i N_i$

The total Legendre transform gives

$$0 = \left. \frac{\partial B}{\partial T} \right|_{P, \{N\}} dT + \left. \frac{\partial B}{\partial P} \right|_{T, \{N\}} dP - \sum_{i=1}^n N_i d\bar{B}_i$$

This "generalized Gibbs-Duhem" relationship links changes of  $T, P, \bar{B}_i$ 's.

Usually expressed at const.  $T, P$  and dividing by  $N$ :

$$\boxed{\sum_{i=1}^n x_i d\bar{B}_i = 0 \text{ at const } T, P}$$

E.g. for binary mixtures, this implies that the two  $\bar{B}_i$ 's are not independent:

$$x_1 d\bar{B}_1 + x_2 d\bar{B}_2 = 0 \Rightarrow x_1 \frac{\partial \bar{B}_1}{\partial x_1} + x_2 \frac{\partial \bar{B}_2}{\partial x_1} = 0$$

Example 8.4: Application

$$\bar{V}_2 = a + bx_1^3 \quad \bar{V}_1 = ?$$

$$\text{at } x_1 = 0 \quad \bar{V}_2 = \underline{V}_2 \Rightarrow a = \underline{V}_2 \quad \left( \begin{array}{l} \text{pure} \\ \text{component} \\ \text{molar volume} \end{array} \right)$$

$$x_1 \frac{\partial \bar{v}_1}{\partial x_1} + x_2 \frac{\partial \bar{v}_2}{\partial x_1} = 0 \Rightarrow \frac{\partial \bar{v}_1}{\partial x_1} = - \frac{x_2}{x_1} \frac{\partial \bar{v}_2}{\partial x_1} =$$

$$- \frac{x_2}{x_1} \frac{\partial}{\partial x_1} (\bar{v}_2 + b x_1^3) = - \frac{x_2}{x_1} \cdot b \cdot 3x_1^2 = 3b x_1 (x_1 - 1)$$

$$\Rightarrow \bar{v}_1 = \int 3b (x_1^2 - x_1) dx_1 = b \left[ x_1^3 - \frac{3x_1^2}{2} \right] + C$$

↑  
integration const.

for  $x_1 = 1$   $\bar{v}_1 = \underline{v}_1 \Rightarrow \underline{v}_1 = -\frac{b}{2} + C \Rightarrow C = \underline{v}_1 + \frac{b}{2}$

$$\Rightarrow \bar{v}_1 = \underline{v}_1 + b \left[ x_1^3 - \frac{3x_1^2}{2} + \frac{1}{2} \right]$$

### $\bar{B}_i$ from Experimental Data

Partial molar properties are obtained from measurements of total or mixing functions,

e.g.  $\bar{v}_i$  from  $\underline{V}(x_1)$  or  $\Delta \underline{V}(\{x\})$

How do we get from  $\bar{B}_i = \left( \frac{\partial B}{\partial N_i} \right)_{T, P, N_{j \neq i}}$

to a derivative of  $\underline{B}$  or  $\Delta \underline{B}$  with respect to mole fractions?

$$\underline{B} = x_1 \bar{B}_1 + x_2 \bar{B}_2$$

$$\frac{\partial \underline{B}}{\partial x_1} = \bar{B}_1 + x_1 \frac{\partial \bar{B}_1}{\partial x_1} + \frac{\partial x_2}{\partial x_1} \bar{B}_2 + x_2 \frac{\partial \bar{B}_2}{\partial x_1}$$

↑ Gibbs-Duhem ↑

$$\frac{\partial x_2}{\partial x_1} = \frac{\partial(1-x_1)}{\partial x_1} = -1 \quad \therefore \frac{\partial \underline{B}}{\partial x_1} = \bar{B}_1 - \bar{B}_2 \cdot x_2$$

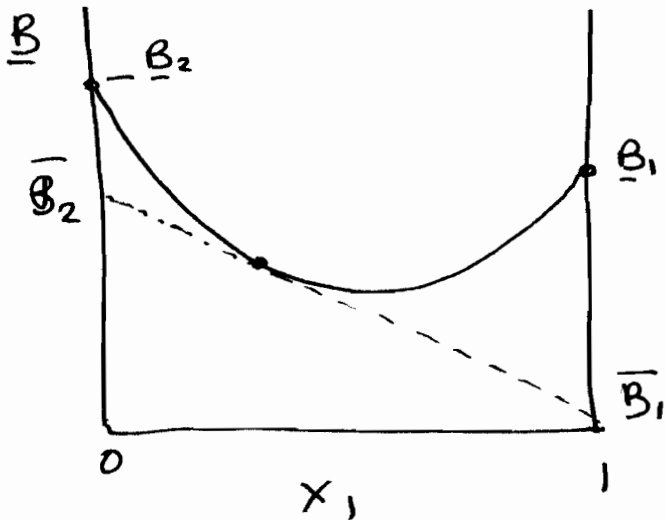
$$\underline{B} = x_1 \bar{B}_1 + x_2 \bar{B}_2$$

$$\text{add: } x_2 \frac{\partial \underline{B}}{\partial x_1} + \underline{B} = \bar{B}_1$$

$$\text{Similarly, } -x_1 \frac{\partial \underline{B}}{\partial x_1} + \underline{B} = \bar{B}_2$$

$$\text{Similarly, from } \Delta \underline{B}_{\text{mix}}: \quad \bar{B}_1 - \underline{B}_1 = \Delta \underline{B}_{\text{mix}} + x_2 \frac{\partial \Delta \underline{B}_{\text{mix}}}{\partial x_1}$$

$$\bar{B}_2 - \underline{B}_2 = \Delta \underline{B}_{\text{mix}} - x_1 \frac{\partial \Delta \underline{B}_{\text{mix}}}{\partial x_1}$$



$\underline{B}_1, \underline{B}_2$  are pure component properties (indep. of  $x$ )  
 $\bar{B}_1, \bar{B}_2$  are mixture properties, depend on where the tangent line is taken

### Example B.5

Worksheet can be downloaded from "Add-ons" in book web site.

Given  $\Delta \underline{H}_{\text{mix}}$ , obtain  $\bar{H}_1 - \underline{H}_1$   
 $\bar{H}_2 - \underline{H}_2$

for benzene-cyclohexane

CBE 246 Gibbs-Duhem,  $\bar{B}_i$  from data (4)

1<sup>st</sup> step is to postulate a functional form for  $\Delta \underline{H}_{mix}$  with the correct limit (=0) for  $x_1=0$  or  $x_1=1$

Assume 
$$\Delta \underline{H}_{mix} = x_1 x_2 \left[ a + b(x_1 - x_2) \right]$$

↑   ↑  
constants to be determined

Using "Solver" to optimize the sum-of-squares of deviations between model and data,

$a = 3.27 \text{ kJ/mol}$       $b = 0.21 \text{ kJ/mol}$

$$\bar{H}_1 - \underline{H}_1 = \Delta \underline{H}_{mix} + x_2 \frac{\partial \Delta \underline{H}_{mix}}{\partial x_1} =$$

$$= \Delta \underline{H}_{mix} + x_2 \frac{\partial}{\partial x_1} \left[ a x_1 (1-x_1) + b x_1 (1-x_1) (2x_1 - 1) \right]$$

$$= \Delta \underline{H}_{mix} + x_2 \left[ a - 2a x_1 + 6b x_1 - 6b x_1^2 - b \right]$$

$$\bar{H}_2 - \underline{H}_2 = \Delta \underline{H}_{mix} + x_1 \frac{\partial \Delta \underline{H}_{mix}}{\partial x_1} =$$

$$= \Delta \underline{H}_{mix} - x_1 \left[ a - 2a x_1 + 6b x_1 - 6b x_1^2 - b \right]$$

