recall the significance of $\mu_i \equiv \frac{\partial G}{\partial n_i}$ the change in energy associated with the change in the amount of mass in the system.

The Gibbs-duhem expression arises from the fact that intensive properties are <u>not</u> affected by the size of the system, <u>but</u> extensive properties are... So, for each phase we can write

dG, the change in the Gibbs energy is

$$dG = \underbrace{\sum_{i=1}^{j} n_i d\mu_i}_{\text{extensive}} + \underbrace{\sum_{i=1}^{j} \mu_i dn_i}_{\text{the intensive part}}$$

using the expression for $dG = -SdT + VdP + \sum_i \mu_i dn_i$ we get the Gibbs duhem expression for each phase

$$-SdT + VdP - \sum_i n_i d\mu_i = 0$$

thus, for any group of coexisting phases we can write the following relation for <u>each</u> phase in the system.

$$\sum_i n_i d\mu_i = \bar{V}dP - \bar{S}dT$$

10/31/01 ⑧ ②

so — first let's consider a 2 component system and a univariant equilibrium —

recall that in a one component system at a univariant equilibrium we showed that

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} \ldots$$

for two components and 3 phases (A, B and C) the Gibbs-Duhem looks like the following....

$$X_{1A}\, d\mu_1 + X_{2A}\, d\mu_2 = \bar{V}_A\, dP - \bar{S}_A\, dT$$

$$X_{1B}\, d\mu_1 + X_{2B}\, d\mu_2 = \bar{V}_B\, dP - \bar{S}_B\, dT$$

$$X_{1C}\, d\mu_1 + X_{2C}\, d\mu_2 = \bar{V}_C\, dP - \bar{S}_C\, dT$$

rearranging...

$$\bar{S}_A = \bar{V}_A \left.\frac{dP}{dT}\right|_{3\phi} - X_{1A} \left.\frac{d\mu_1}{dT}\right|_{3\phi} - X_{2A} \left.\frac{d\mu_2}{dT}\right|_{3\phi}$$

$$\bar{S}_B = \bar{V}_B \left.\frac{dP}{dT}\right|_{3\phi} - X_{1B} \left.\frac{d\mu_1}{dT}\right|_{3\phi} - X_{2B} \left.\frac{d\mu_2}{dT}\right|_{3\phi}$$

$$\bar{S}_C = \bar{V}_C \left.\frac{dP}{dT}\right|_{3\phi} - X_{1C} \left.\frac{d\mu_1}{dT}\right|_{3\phi} - X_{2C} \left.\frac{d\mu_2}{dT}\right|_{3\phi}$$

— we can solve this system of equations using Cramer's rule because μ's are equal,

$$\left.\frac{dP}{dT}\right|_{3\phi} = \begin{vmatrix} \bar{S}_A & X_{1A} & X_{2A} \\ \bar{S}_B & X_{1B} & X_{2B} \\ \bar{S}_C & X_{1C} & X_{2C} \end{vmatrix} \Bigg/ \begin{vmatrix} \bar{V}_A & X_{1A} & X_{2A} \\ \bar{V}_B & X_{1B} & X_{2B} \\ \bar{V}_C & X_{1C} & X_{2C} \end{vmatrix}$$

← ratio of these determinants

note that for a one component system the equivalent expression would be

$$\frac{dP}{dT} = \frac{\begin{vmatrix} \bar{S}_A & X_{1A} \\ \bar{S}_B & X_{1B} \end{vmatrix}}{\begin{vmatrix} \bar{V}_A & X_{1A} \\ \bar{V}_B & X_{1B} \end{vmatrix}}$$

since $X_{1A} = X_{1B} = 1$ this reduces to

$$\frac{dP}{dT} = \frac{\Delta S_{rxn}}{\Delta V_{rxn}}$$

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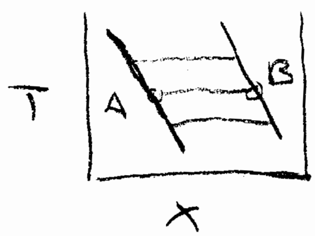
now consider the case where we have a 2 phase coexistence in a binary system

for example



we use the relation $X_{1A} = 1 - X_{2A}$ and substitute

these are the Gibbs Duhem equations for each phase

$$(1 - X_{2A})\,d\mu_1 + X_{2A}\,d\mu_2 = \bar{V}_A\,dP - \bar{S}_A\,dT$$

$$d\mu_1 + X_{2A}\,d(\mu_2 - \mu_1) = \bar{V}_A\,dP - \bar{S}_A\,dT$$

we have 4 unknowns $d\mu_1$, $d(\mu_2 - \mu_1)$, dP & dT

we also

the total differential in $d(\mu_2 - \mu_1)$ can also be written as:

$$dG_A = \left.\frac{\partial G}{\partial P}\right)_{T,X} dP + \left.\frac{\partial G}{\partial T}\right)_{P,X} dT + \left.\frac{\partial G}{\partial X_2}\right)_{T,P} dX_2$$

$$= \Delta\bar{V}_* \, dP - \Delta\bar{S}_* \, dT + G_{XXA}$$

> 0 for coexisting phases

$$dG_A = (\bar{V}_{2A} - \bar{V}_{1A})dP - (\bar{S}_{2A} - \bar{S}_{1A})dT + A_{xx}dX_2$$

$dG_A = d(\mu_2 - \mu_1)_A$) slopes of tangent planes are the same. for two phases in equilibrium

so rearrange & solve

$$d(\mu_2-\mu_1) = (\bar{V}_{2A} - \bar{V}_{1A})dP - (\bar{S}_{2A} - \bar{S}_{1A})dT + A_{xx}dX_2$$

$$d\mu_1 + X_{2A}\, d(\mu_2-\mu_1) = -\bar{S}_A\, dT + \bar{V}_A\, dP$$

$$d\mu_1 + X_{2B}\, d(\mu_2-\mu_1) = -\bar{S}_B\, dT + \bar{V}_B\, dP$$

$$d\mu_1 = -X_{2A}\, d(\mu_2-\mu_1) - \bar{S}_A\, dT + \bar{V}_A\, dP$$

$$d\mu_1 = -X_{2B}\, d(\mu_2-\mu_1) - \bar{S}_B\, dT + \bar{V}_B\, dP$$

$$0 = (X_{2B} - X_{2A})\, d(\mu_2-\mu_1) + (\bar{S}_B - \bar{S}_A)dT - (\bar{V}_B - \bar{V}_A)dP$$

plug in the expression for

$d(\mu_2 - \mu_1)$

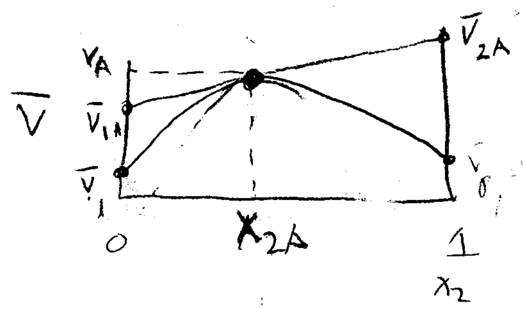
$$(x_{2B} - x_{2A})\, \underline{\underline{d(\mu_2 - \mu_1)}} = (\bar{V}_B - \bar{V}_A)\, dP - (\bar{S}_B - \bar{S}_A)\, dT$$

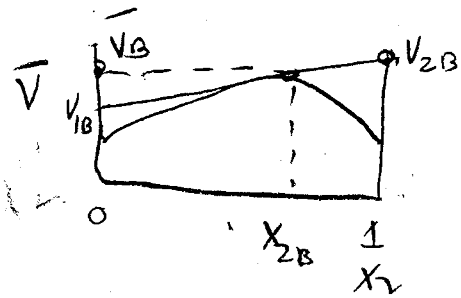
⑤

$$(x_{2B} - x_{2A})\left[(\bar{V}_{2A} - \bar{V}_{1A})\, dP - (\bar{S}_{2A} - \bar{S}_{1A})\, dT + A_{xx}\, dx_2\right] = (\bar{V}_B - \bar{V}_A)\, dP - (\bar{S}_B - \bar{S}_A)\, dT$$

$$(x_{2B} - x_{2A})\, A_{xx}\, dx_2 = \left[(\bar{V}_B - \bar{V}_A) - (\bar{V}_{2A} - \bar{V}_{1A})(x_{2B} - x_{2A})\right] dP + \left[(\bar{S}_{2A} - \bar{S}_{1A})(x_{2B} - x_{2A}) - (\bar{S}_B - \bar{S}_A)\right] dT$$

2nd deriv
of G
wrt comp
goes to zero
since $dx_2 = 0$


$\bar{V}$
V_A
$\bar{V}_{1A}$
$\bar{V}_1$
$\bar{V}_{2A}$
0
X_{2A}
1
x_2


$\bar{V}$
$\bar{V}_B$
V_{1B}
V_{2B}
0
X_{2B}
1
x_2

Walker et al, discussion

7

concerned with crystal/melt buoyancy

& effects of multi-component equilib.

p. 318 bottom left last sent.

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p. 319 - changes in slope of liquidus - why not important

left-hand side 2nd para - several points