## author: k.wodehouse

trying a diff method since other one doesn't quite work out. knowing that the  $\Delta_{mix}\underline{G}$  can be written as

$$\Delta_{mix} \underline{G} = G_{mixture} - \sum_{i=1}^3 x_i \underline{G}_i$$

this allows us to rearrange the given equation to be

$$G_{mixture} = \sum_{i=1}^{3} x_i \underline{G}_i + \sum_{i=1}^{3} \sum_{j=1}^{3} lpha_{ij} x_i x_j = \sum_{i=1}^{3} x_i \underline{G}_i + 2lpha_{12} x_1 x_2 + 2lpha_{13} x_1 x_3 + 2lpha_{23} x_2 x_3$$

and we need to remember our definition of the partial molar gibbs and relate it back to Beris's notes on the volterra derivative where he was nice enough to provide the second part of this relationship

$$\bar{G}_{i} = \left(\frac{\partial G}{\partial N_{i}}\right)_{T,P,N_{i\neq j}} = \underline{G}_{mixture} + \frac{\delta G}{\delta x_{i}} - \sum_{j=1}^{C} x_{i} \frac{\delta G}{\delta x_{j}}$$
(1)

so now we may take volterra derivatives (for maximum!!! symmetry!!! in equations)

$$rac{\delta G}{\delta x_1} = \underline{G}_1 + 2lpha_{12}x_2 + 2lpha_{13}x_3$$

I won't waste time typing out the other volterras since we can see it only depends on the  $\alpha_{ij}$  that corresponds to interactions the component would have (i.e. component 1 would not have a 2-3 interaction).

$$\frac{\delta G}{\delta x_i} = \underline{G}_i + 2\sum_{j \neq i} \alpha_{ij} x_j \tag{2}$$

now we can just go back to what beris gave us in his holy text (notes on volterra derivatives) for component 1. keeping things in the summation notation will be helpful to save some algebra time. (THIS COMES FROM eqn. (1) and (2) to make simple)

$$ar{G}_i = ar{G}_{mixture} + ar{G}_i + 2\sum_{j 
eq i}^C lpha_{ij} x_j - \left(\sum_{i=1}^C x_i ar{G}_i - \sum_{i=1}^3 \sum_{j=1}^3 lpha_{ij} x_i x_j
ight)$$

$$ar{G}_i = \underline{G}_{mixture} - \underline{G}_{mixture} + \underline{G}_i + 2\sum_{j 
eq i}^{C} lpha_{ij} x_j = \underline{G}_i + 2\sum_{j 
eq i}^{C} lpha_{ij} x_j$$

$$oxed{ar{G}_i = \underline{G}_i + 2\sum_{j 
eq i}^{C} lpha_{ij} x_j}$$

which, alas, gives us the desired result (thanks vasu!)

$$ar{G}_1 = \underline{G}_i + 2lpha_{12}x_2 + 2lpha_{13}x_3$$

$$ar{G}_2=\underline{G}_2+2lpha_{23}x_3+2lpha_{12}x_1$$

$$ar{G}_3=\underline{G}_3+2lpha_{13}x_1+2lpha_{23}x_2$$

b.

let's arbitrarily choose to hold  $x_3$  constants so that we don't need to shed tears over  $\frac{\partial x_2}{\partial x_1}$ . we essentially need to show this

$$\sum x_i rac{\partial ar{G}_i}{\partial x_1} + \sum x_i rac{\partial ar{G}_i}{\partial x_2} = 0$$

so, we evaluate the partials with respect to  $x_1, x_2$  and just let 3 be constant like a good boy

$$rac{\partial ar{G}_1}{\partial x_1} = -2lpha_{12}$$

$$rac{\partial ar{G}_2}{\partial x_1} = 2lpha_{12}$$

$$rac{\partial ar{G}_3}{\partial x_1} = 2lpha_{13} - 2lpha_{23}$$

$$rac{\partial ar{G}_1}{\partial x_2} = 2lpha_{12}$$

$$rac{\partial ar{G}_2}{\partial x_2} = -2lpha_{12}$$

$$rac{\partial ar{G}_3}{\partial x_2} = -2lpha_{13} + 2lpha_{23}$$

and now multiplying these by their respective mole fractions (and hoping to never see this problem ever ever again)

$$x_1rac{\partialar{G}_1}{\partial x_1}=-2lpha_{12}x_1$$

$$x_2rac{\partialar{G}_2}{\partial x_1}=2lpha_{12}x_2$$

$$egin{align} x_3rac{\partialar{G}_3}{\partial x_1}&=2lpha_{13}x_3-2lpha_{23}x_3\ &x_1rac{\partialar{G}_1}{\partial x_2}&=2lpha_{12}x_1\ &x_2rac{\partialar{G}_2}{\partial x_2}&=-2lpha_{12}x_2\ &x_3rac{\partialar{G}_3}{\partial x_2}&=-2lpha_{13}x_3+2lpha_{23}x_3 \end{aligned}$$

and now if we sum these and factor out all of the  $x_i$ s

$$x_{1}(2\alpha_{12}-2\alpha_{12})+x_{2}(2\alpha_{12}-2\alpha_{12})+x_{3}(2\alpha_{13}-2\alpha_{23}-2\alpha_{13}+2\alpha_{23})$$

which, obviously, simplifies to

$$x_1(0) + x_2(0) + x_3(0) = 0$$

which verifies the that these partials obey the gibbs-duhem