$$\Rightarrow \boxed{\bar{M}_1 = M + X_2 \frac{dM}{dX_1}} \quad --- \quad 11.15$$

Similarly one can show:

$$\boxed{\bar{M}_2 = M - X_1 \frac{dM}{dX_1}} \quad --- \quad 11.16$$

Example 11.4 The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is represented by the equation

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J mol^{-1}. Determine expressions for $\bar{H}_1$ and $\bar{H}_2$ as functions of x_1, numerical values for the pure-species enthalpies H_1 and H_2, and numerical values for the partial enthalpies at infinite dilution $\bar{H}_1^\infty$ and $\bar{H}_2^\infty$.

<u>Solution</u>

We will evaluate $\bar{H}_1$ using two methods

<u>First Method</u>: $\bar{H}_1 = \left(\frac{\partial (nH)}{\partial n_1}\right)_{T,P,n_2}$

$$nH = 400\,n_1 + 600n_2 + n_1\,X_2\,(40X_1 + 20X_2)$$

multiply last term by $\frac{n^2}{n^2}$ $\quad (n = n_1 + n_2)$

$$\Rightarrow nH = 400n_1 + 600n_2 + \frac{n_1 n_2}{(n_1+n_2)^2}(40n_1 + 20n_2)$$

$$\Rightarrow \bar{H}_1 = 400 + \frac{n_2(n_1+n_2)^2 - n_1n_2\,2(n_1+n_2)}{(n_1+n_2)^4}(40n_1+20n_2)$$

$$+ \frac{n_1 n_2}{(n_1+n_2)^2}\,40$$

note $n = n_1 + n_2$, $x_1 = \frac{n_1}{n}$ & $x_2 = \frac{n_2}{n}$

simplify $\bar{H}_1$:

$$\bar{H}_1 = 400 + (x_2 - 2x_1x_2)(40x_1 + 20x_2)$$

$$+ 40x_1x_2$$

$$= 400 + 80x_1x_2 - 80x_1^2x_2 + 20x_2^2$$

$$-40x_1x_2^2$$

now $x_2 = 1 - x_1$

$$\Rightarrow \bar{H}_1 = 400 + 80x_1(1-x_1) - 80x_1^2(1-x_1)$$

$$+ 20(1-x_1)^2 - 40x_1(1-x_1)^2$$

$$= 400 + \cancel{80x_1} - 80x_1^2 - 80x_1^2 + 80x_1^3$$

$$+ 20 + 20x_1^2 - \cancel{40x_1} - \cancel{40x_1} - 40x_1^3$$

$$+ 80x_1^2$$

$$\boxed{\bar{H}_1 = 420 - 60x_1^2 + 40x_1^3}$$

second method: $\bar{H}_1 = H + x_2 \dfrac{dH}{dx_1}$ --- (11.15) 2

first find $\dfrac{dH}{dx_1}$ (note $\dfrac{dx_2}{dx_1} = -1$)

$$\downarrow$$

$$\frac{d(1-x_1)}{dx_1} = -1$$

$$\frac{dH}{dx_1} = 400 - 600 + (x_2 - x_1)(40x_1 + 20x_2)$$

$$+ x_1 x_2 (40 - 20)$$

$$x_2 = 1 - x_1$$

$$\Rightarrow \frac{dH}{dx_1} = -200 + (1 - 2x_1)(40x_1 + 20 - 20x_1)$$

$$+ 20(x_1 - x_1^2)$$

$$= -200 + \cancel{20x_1} + 20 - 40x_1^2 \cancel{- 40x_1}$$

$$+ \cancel{20x_1} - 20x_1^2$$

$$\Rightarrow \frac{dH}{dx_1} = -180 - 60x_1^2$$

substitute in 11.15

$$\Rightarrow \bar{H}_1 = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) +$$

$$x_2(-180 - 60x_1^2)$$

(6)

$$\bar{H}_1 = 400 X_1 + 600(1 - X_1) + (X_1 - X_1^2)(40X_1 + 20 - 20X_1)$$

$$- (1 - X_1)(180 + 60 X_1^2)$$

$$= 400X_1 + 600 - 600X_1 + 40X_1^2 + 20X_1 - 20X_1^2$$

$$- 40X_1^3 - 20X_1^2 + 20X_1^3 - 180 - 60X_1^2$$

$$+ 180X_1 + 60X_1^3$$

$$\bar{H}_1 = 420 - 60X_1^2 + 40X_1^3$$

$\Rightarrow$ Results by first and second methods are equivalant

Similarly $\bar{H}_2 = 600 + 40X_1^3$

<u>Now find H_1 & H_2</u>

$$H_1 = H(X_1 = 1 \;\&\; X_2 = 0)$$

$$= 400 \;(\mathrm{J/mol})$$

$$H_2 = H(X_1 = 0 \;\&\; X_2 = 1)$$

$$= 600 \;(\mathrm{J/mol})$$

now find H_1^{∞} & H_2^{∞} :

$$\overline{H}_1^{\infty} = \overline{H}_1 \, (x_1 = 0 \;\&\; x_2 = 1)$$ partial enthalpy at infinit dilution

$$= 420 \quad J/mol$$

$$\overline{H}_2^{\infty} = \overline{H}_2 \, (x_1 = 1 \;\&\; x_2 = 0)$$

$$= 640 \; (J/mol)$$