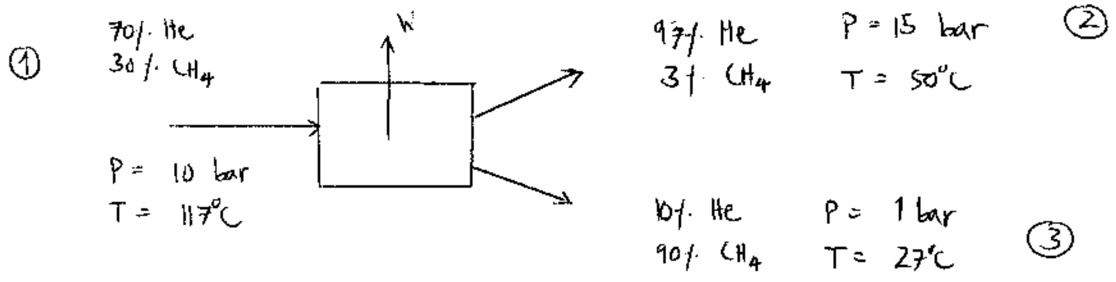
Problem Set H

Problem 26



Adiabatic, Q = 0

Material balances, using 1 mole of feed as a basis

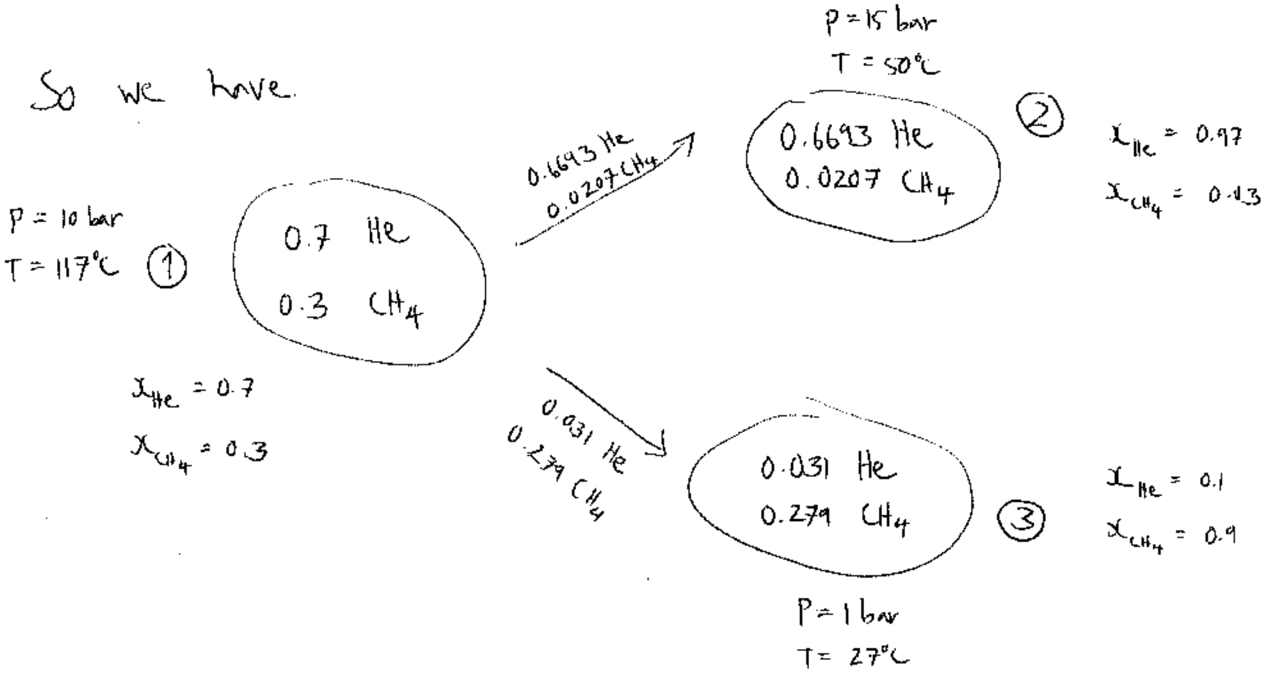
Balance on He : $0.7 = 0.97\,n_2 + 0.1\,n_3$

Balance on CH_4 : $0.3 = 0.03\,n_2 + 0.9\,n_3$ ↖ no. of moles of gas in ③

↑ no. of moles of gas in ②

$n_2 = 0.69$ moles $n_3 = 0.31$ moles

So we have



Problem 27

a) At constant T and P

$$\sum_i x_i \, d\bar{M}_i = 0$$

see if $$x_1 \, d\bar{H}_1 + x_2 \, d\bar{H}_2 = 0$$

or $$x_1 \frac{d\bar{H}_1}{dx_1} + x_2 \frac{d\bar{H}_2}{dx_1} = 0$$

$$\bar{H}_1 = x_1(a_1 + b_1 x_1) \qquad \frac{d\bar{H}_1}{dx_1} = (a_1 + b_1 x_1) + b_1 x_1$$

$$= a_1 + 2 b_1 x_1$$

$$\bar{H}_2 = x_2(a_2 + b_2 x_2) \qquad \frac{d\bar{H}_2}{dx_1} = -a_2 + 2 b_2 (1 - x_1)(-1)$$

$$= a_2(1 - x_1) + b_2 (1 - x_1)^2$$

$$= -a_2 - 2 b_2 + 2 b_2 x_1$$

$$= -a_2 - 2 b_2 x_2$$

$$\therefore \quad x_1 \frac{d\bar{H}_1}{dx_1} + x_2 \frac{d\bar{H}_2}{dx_1} = x_1(a_1 + 2 b_1 x_1) + x_2(-a_2 - 2 b_2 x_2)$$

$$= x_1 a_1 + 2 b_1 x_1^2 - x_2 a_2 - 2 b_2 x_2^2$$

$$= -a_2 - 2 b_2 + (a_1 + a_2 + 4 b_1) x_1 + 2(b_1 - b_2) x_1^2$$

which in general $\neq 0$, $\bar{H}_i \neq x_i(a_i + b_i x_i)$

unless $b_1 = b_2 = b$

and $a_1 = a_2 = -2b$

for this special case $\bar{H}_i = x_i(a_i + b_i x_i)$

As $\bar{S}_i^{ig}(T, P) = S_i^{ig}(T, p_i)$

we therefore have $S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$ (eqn. 11.25)

$$\therefore \quad S_1 = 0.7 S_1^{He} + 0.3 S_1^{CH_4} - R(0.7 \ln 0.7 + 0.3 \ln 0.3)$$

$$S_2 = 0.97 S_2^{He} + 0.03 S_2^{CH_4} - R(0.97 \ln 0.97 + 0.03 \ln 0.03)$$

$$S_3 = 0.1 S_3^{He} + 0.9 S_3^{CH_4} - R(0.1 \ln 0.1 + 0.9 \ln 0.9)$$

$$\Delta S^{total} = (0.69 S_2 + 0.31 S_3) - S_1$$

$$= 0.6693(S_2^{He} - S_1^{He}) + 0.031(S_3^{He} - S_1^{He}) + 0.0207(S_2^{CH_4} - S_1^{CH_4})$$

$$+ 0.279(S_3^{CH_4} - S_1^{CH_4}) - 3.47$$

* Note here that we split $0.7 S_1^{He}$ into $0.6693 S_1^{He} + 0.031 S_1^{He}$ for convenient, same for $S_1^{CH_4}$

For ideal gas $\Delta S = \int C_p^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$

if C_p^{ig} is a constant $\Longrightarrow$ $\Delta S = C_p^{ig} \ln \frac{T}{T_0} - R \ln \frac{P}{P_0}$

$$\Delta S^{total} = 0.6693\left[\frac{5}{2} R \ln \frac{323}{390} - R \ln \frac{15}{10}\right] + 0.031\left[\frac{5}{2} R \ln \frac{300}{390} - R \ln \frac{1}{10}\right]$$

$$+ 0.0207\left[\frac{9}{2} R \ln \frac{323}{390} - R \ln \frac{15}{10}\right] + 0.279\left(\frac{9}{2} R \ln \frac{300}{390} - R \ln \frac{1}{10}\right) - 3.47$$

$$\boxed{\Delta S^{total} = -5.535 \text{ J/K}}$$

as work is produced in the process, $\Delta S > 0$ is to be expected

$\boxed{\text{Violation of the 2nd law}}$

b) $$H = x_1(a_1 + b_1 x_1) + x_2(a_2 + b x_2)$$

$$= x_1(a_1 + b_1 x_1) + (1 - x_1)[a_2 + b_2(1 - x_1)]$$

$$= x_1 a_1 + b_1 x_1^2 + a_2 + b_2 - b_2 x_1 - x_1 a_2 - x_1 b_2 + b_2 x_1^2$$

$$= a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2$$

$$\frac{dH}{dx_1} = (a_1 - a_2 - 2b_2) + 2(b_1 + b_2) x_1$$

$$\bar{H}_1 = H + x_2 \frac{dH}{dx_1}$$

$$= a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2 + (a_1 - a_2 - 2b_2)$$

$$+ 2(b_1 + b_2) x_1 - (a_1 - a_2 - 2b_2) x_1 - 2(b_1 + b_2) x_1^2$$

$$= (a_1 - b_2) + 2(b_1 + b_2) x_1 - (b_1 + b_2) x_1^2$$

$$\bar{H}_2 = H - x_1 \frac{dM}{dx_1}$$

$$= a_2 + b_2 + (a_1 - a_2 - 2b_2) x_1 + (b_1 + b_2) x_1^2$$

$$- (a_1 - a_2 - 2b_2) x_1 - 2(b_1 + b_2) x_1^2$$

$$= (a_2 + b_2) - (b_1 + b_2) x_1^2$$

28)

For a mixture of n-octanol (1) and n-decane (2):

$$H = x_1x_2(A + B\,(x_1 - x_2))\ \text{J/mol}$$

where $A = -12{,}974 + 51.505\ T$ and $B = 8782.8 - 34.129\ T$ with T in K.

a) Wanted: H_1, H_2, $\overline{H}_1$, and $\overline{H}_2$.

$x_2 = 1 - x_1$ (binary)

Pure n-octanol enthalpy ($x_1 = 1$), $H_1 = H|_{x_1=1} = 1\cdot 0\cdot(A + B(1-0)) = 0$

Pure n-decane enthalpy ($x_2 = 1$), $H_2 = H|_{x_1=0} = 0\cdot 1\cdot(A + B(0-1)) = 0$ **(ans)**

We can use the following formulae for binary system:

$$\overline{H}_1 = H + x_2\frac{dH}{dx_1} \quad \textbf{(eq. 1)} \qquad \text{and} \qquad \overline{H}_2 = H - x_1\frac{dH}{dx_1} \quad \textbf{(eq. 2)}$$

We can also use the formal definition $\overline{H}_i = \left(\frac{\partial(nH)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

Let us calculate the yet unknown H and dH/dx_1 for $x_1 = 0.5$ and $T = 300$K

At 300 K, $A = -12974 + 51.505\ (300) = 2477.5$
$B = 8782.8 - 34.129\ (300) = -1455.9$

Writing H and dH/dx_1 in terms of x_1:

$$H = x_1(1-x_1)\left[A + B(x_1 - (1-x_1)\right]\ \text{J/mol}$$

$$H = (x_1 - x_1^2)\left[A + B(2x_1 - 1)\right]\ \text{J/mol} \qquad \textbf{(eq.3)}$$

Differentiating this with x_1 also gives us :

$$\frac{dH}{dx_1} = (1-2x_1)\left[A + B(2x_1-1)\right] + (x_1 - x_1^2)(2B)\ \text{J/mol} \qquad \textbf{(eq.4)}$$

At $x_1 = 0.5$ and $T = 300$K, $H = (0.5 - 0.5^2)\left[2477.5 - 1455.9(2\cdot 0.5 - 1)\right]\ \text{J/mol} = 619.38\ \text{J/mol}$

$$\frac{dH}{dx_1} = (1 - 2\cdot 0.5)\left[A + B(2\cdot 0.5 - 1)\right] + (0.5 - 0.5^2)(2\cdot(-1455.9)) = -727.95\ \text{J/mol}$$

Plugging in these values into eq.1 and eq.2, we get:

$$\overline{H}_1 = H + x_2\frac{dH}{dx_1} = 619.38 + 0.5\,(-727.95)\ \text{J/mol} = 255.4\ \text{J/mol}$$

$$\overline{H}_2 = H - x_1\frac{dH}{dx_1} = 619.38 - 0.5\,(-727.95)\ \text{J/mol} = 983.35\ \text{J/mol}$$

(ans)

b) Wanted : $Cp_1, Cp_2, \overline{C}p_1$, and $\overline{C}p_2$.

$Cp = \left(\frac{\partial H}{\partial T}\right)_{P,n_i}$. So we can simply take the derivative with T of equations 3 and 4 above:

$$Cp = (x_1 - x_1^2)\left[A' + B'(2x_1 - 1)\right]\ \text{J/mol K} \qquad \textbf{(eq.5)}$$

$$\frac{dCp}{dx_1} = (1-2x_1)\left[A' + B'(2x_1-1)\right] + (x_1 - x_1^2)(2B')\ \text{J/mol K} \qquad \textbf{(eq.6)}$$

where $A' = \frac{dA}{dT} = 51.505$ and $B' = \frac{dB}{dT} = -34.129$

First, calculating the pure Cp's using eq. 5:
Pure n-octanol ($x_1 = 1$), $Cp_1 = Cp|_{x_1=1} = 1 \cdot 0 \cdot (A'+B'(1-0)) = 0$

Pure n-decane ($x_2 = 1$), $Cp_2 = Cp|_{x_1=0} = 0 \cdot 1 \cdot (A'+B'(0-1)) = 0$ **(ans)**

At $x_1 = x_2 = 0.5$ and T = 300K, using eq.5 and eq.6:

$$Cp = (0.5 - 0.5^2)[51.505 - 34.129(2 \cdot 0.5 - 1)] \text{ J/mol K} = 12.876 \text{ J/mol K}$$

$$\frac{dCp}{dx_1} = (1 - 2 \cdot 0.5)[A'+B'(2 \cdot 0.5 - 1)] + (0.5 - 0.5^2)(2 \cdot (-34.129)) = -17.065 \text{ J/mol K}$$

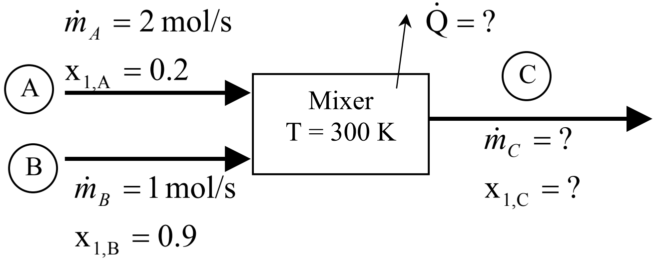
Since Cp is also a molar property, we can use expression similar to eq.1 and eq.2 (replacing H with Cp):

$$\overline{Cp}_1 = Cp + x_2 \frac{dCp}{dx_1} = 12.876 + 0.5 \cdot (-17.065) \text{ J/mol K} = 4.344 \text{ J/mol K}$$

$$\overline{Cp}_2 = Cp - x_1 \frac{dCp}{dx_1} = 12.876 - 0.5 \cdot (-17.065) \text{ J/mol K} = 21.408 \text{ J/mol K}$$

(ans)

c) Drawing the process (taking 2 mol/s of stream A as a basis)



Overall material balance: $\dot{m}_C = \dot{m}_A + \dot{m}_B = (2+1) \text{ mol/s} = 3 \text{ mol/s}$

Species 1 balance: $\dot{m}_C x_{1,C} = \dot{m}_A x_{1,A} + \dot{m}_B x_{1,B} \Rightarrow x_{1,C} = \frac{\dot{m}_A x_{1,A} + \dot{m}_B x_{1,B}}{\dot{m}_C} = \frac{(2 \text{ mol/s})(0.2) + (1 \text{ mol/s})(0.9)}{(3 \text{ mol/s})}$

$x_{1,C} = 0.433$

Energy balance: $\Delta(\dot{m}H) = \dot{Q} + \dot{W}_s = \dot{Q}$

$\dot{Q} = \dot{m}_C H_C - (\dot{m}_A H_A + \dot{m}_B H_B)$ **(eq.7)**

No shaft work in the mixer.

Calculating the enthalpies of the stream (at T = 300 K and at each x_1), we can use the original eq'n:
$H = x_1 x_2(A + B(x_1 - x_2))$ J/mol. We calculated in part a), for 300 K: A = 2477.5 and B = -1455.9.

Stream A ($x_{1,A} = 0.2$): $H_A = (0.2)(0.8)(2477.5 - 1455.9(0.2 - 0.8))$ J/mol = 536.2 J/mol
Stream B ($x_{1,B} = 0.9$): $H_B = (0.9)(0.1)(2477.5 - 1455.9(0.9 - 0.1))$ J/mol = 118.2 J/mol
Stream C ($x_{1,C} = 0.433$): $H_C = (0.433)(0.567)(2477.5 - 1455.9(0.433 - 0.567))$ J/mol = 656.0 J/mol

Plugging in values into eq.7:

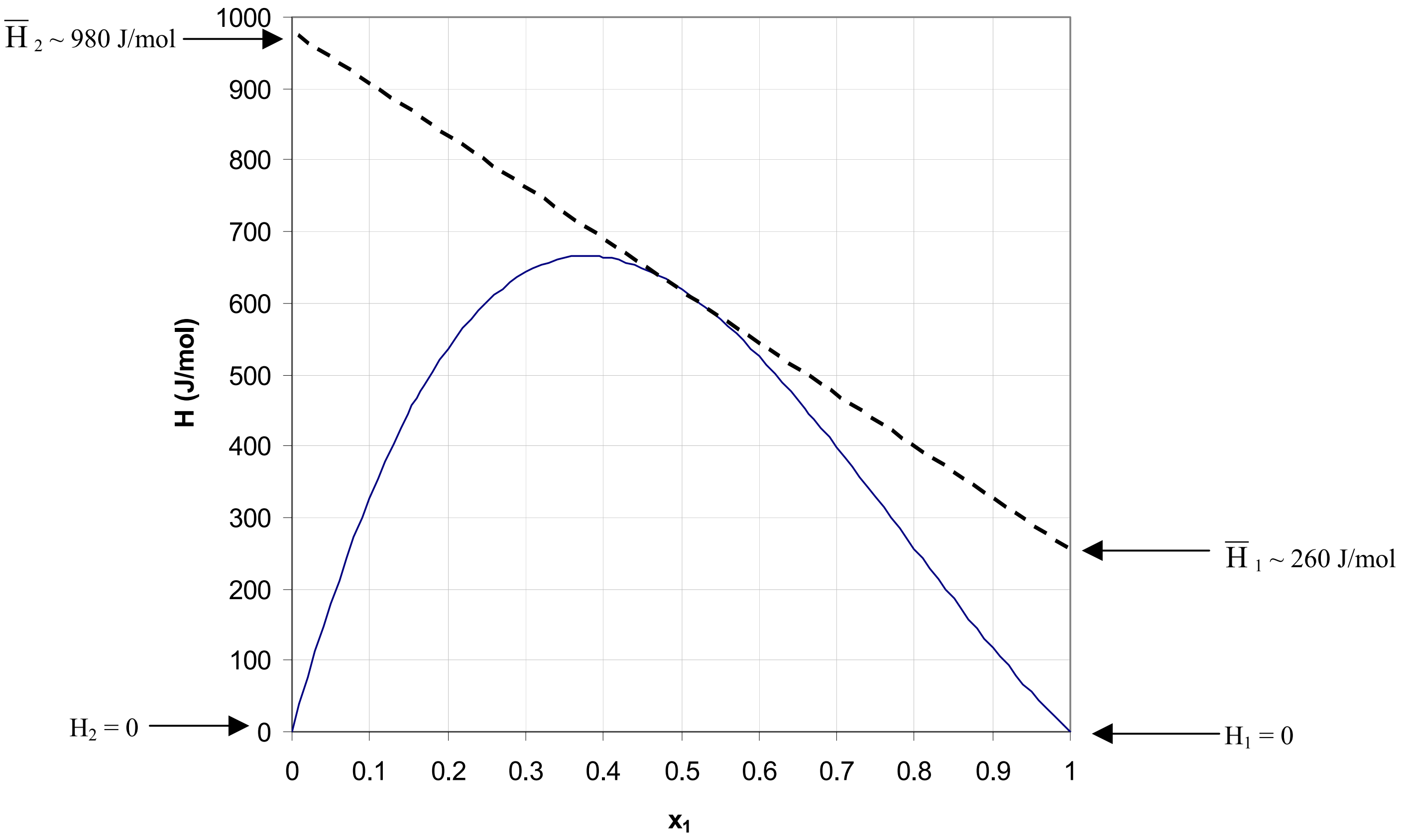
$$\dot{Q} = \dot{m}_C H_C - (\dot{m}_A H_A + \dot{m}_B H_B) = (3 \text{ mol/s})(656 \text{ J/mol}) - [(2 \text{ mol/s})(536.2 \text{ J/mol}) + (1 \text{ mol/s})(118.2 \text{ J/mol})]$$

$\dot{Q} = 777.8$ J/s. This was calculated for 3 mol/s of output stream. So for every mol of output stream we have:

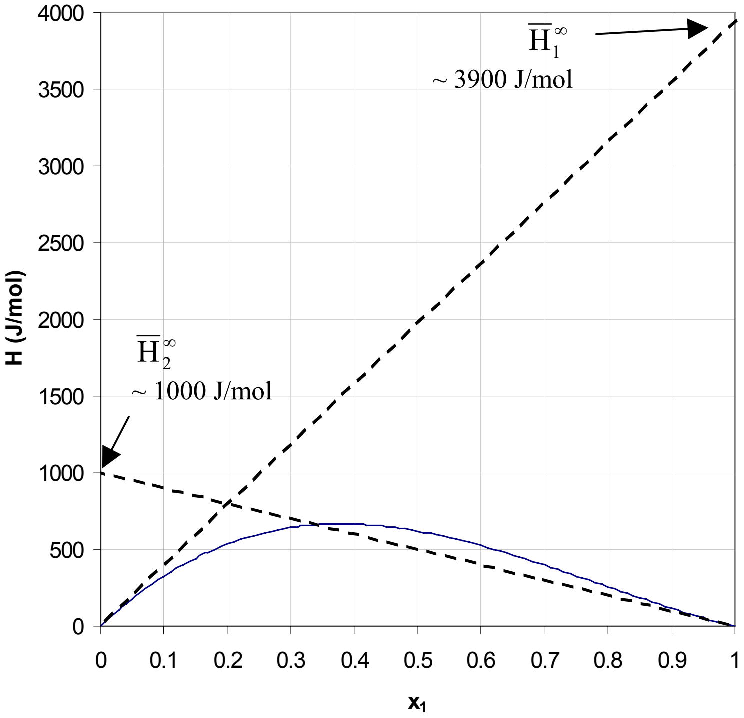
$$\dot{Q} = \frac{777.8 \text{ J/s}}{3 \text{ mol/s}} = \mathbf{259.3 \text{ J/mol output}} \quad \textbf{(ans)}$$

Since Q > 0, heat must be *added* into the system.

d) Plot of H vs x_1 at T = 300 K below. At $x_1 = 0.5$, H ~ 620 J/mol.
The partial molar enthalpies can be obtained graphically by drawing a tangent line at $x_1 = 0.5$.



e) To get the infinite dilution partial enthalpies, we draw tangent lines at $x_1 = 0$ and at $x_1 = 1$.



Graphical solution is easier, but we can confirm these values through calculation – not necessary in your solution – using eqns 1 to 4 (with appropriate x_1's):

$\overline{H}_1^\infty = H_1$ at $x_1 = 0$ or $x_2 = 1$.

At T = 300 K and $x_1 = 0$, using eq. 3 and eq.4 :

$$\frac{dH}{dx_1} = 3930 \text{ J/mol} \quad \text{and} \quad H = H_2 = 0$$

$$\overline{H}_1^\infty = H + x_2 \frac{dH}{dx_1} = 3930 \text{ J/mol}$$

$\overline{H}_2^\infty = H_2$ at $x_2 = 0$

At T = 300 K and $x_1 = 1$,

$$\frac{dH}{dx_1} = -1020 \text{ J/mol} \quad \text{and} \quad H = H_1 = 0$$

$$H_2 = \overline{H}_2^\infty = H - x_1 \frac{dH}{dx_1} = 1020 \text{ J/mol}$$