Advanced Transport Phenomena II
ChE 548
Department of Chemical Engineering
University of Tennessee, Knoxville
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Final Examination
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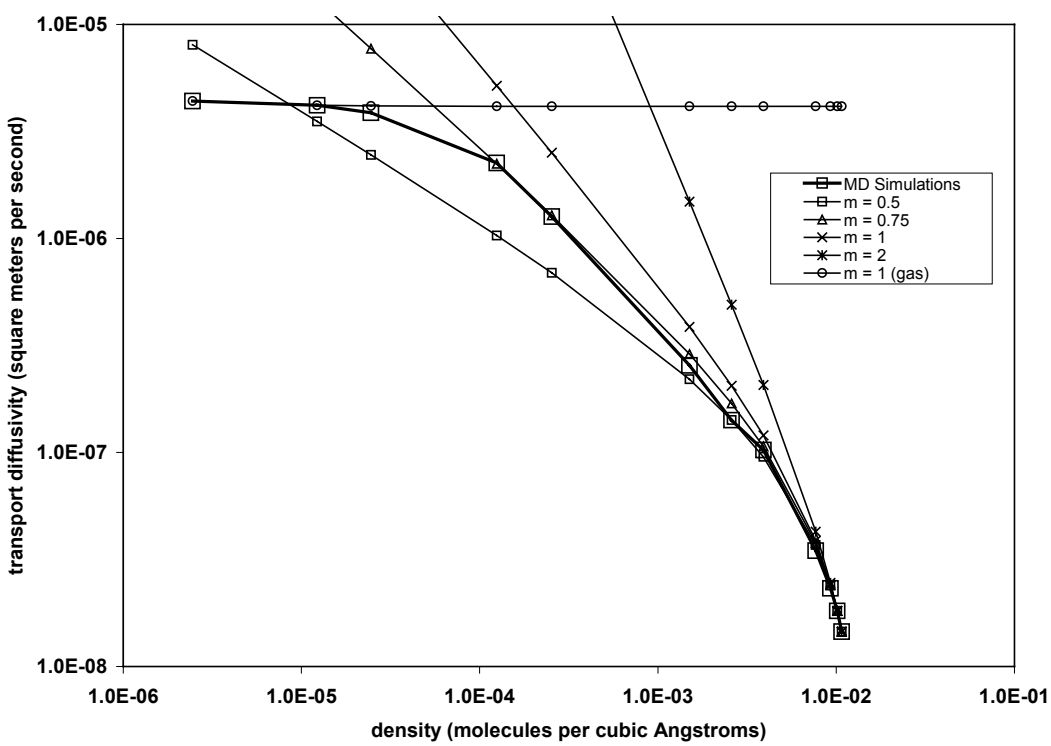
Problem 1. (30 points)
Kinetic theory tells us that the diffusivity of an ideal gas is proportional to the inverse of the total molar density,

$$D = b_0 + b_1\left(\frac{1}{n}\right)^m$$

so that in this case, the exponent, m, is one. (b_0 and b_1 are empirical constants.) Consider an equimolar binary mixture of methane and ethane at 300 K. The single, binary transport diffusivity, obtained by using MD simulations for the self-diffusivities and the Lennard-Jones equation of state for the thermodynamic correction factors, is plotted below as a function of total density (on a log-log scale). Also plotted are several asymptotes with the function form of the equation given above. At the low density (ideal gas limit), the m = 1 equation fits well. At the high density, several different values of m are plotted.



Answer the following questions based on this plot and on your understanding of the molecular-level mechanisms for diffusion in gases and liquids.
(a) What is the molecular-level mechanism for diffusion in gases that gives rise to m=1 behavior?
(b) What value of m models the high-density (liquid) density-dependence of the diffusivity best?
(c) What is the molecular-level mechanism for diffusion in liquids that gives rise to the m value selected in part (b)?

Problem 1. (30 points)

Solution:

(a) What is the molecular-level mechanism for diffusion in gases that gives rise to m=1 behavior?

Diffusion processes in dilute gases are governed by the rate of collisions between molecules, which is determined by the mean free path between molecules as well as by the temperature of the system. Since the mean free path is inversely proportional to the density, the diffusivity is inversely proportional to the density.

Additional information not explicitly required in the solution:

For a gas at low density, we can see the inverse relationship between self-diffusivity and density from kinetic theory:

$$D_{self,A} = \frac{2}{3}\sqrt{\frac{kT}{\pi m_A}}\frac{1}{\pi\sigma_A{}^2}\frac{1}{n} \qquad \text{(BSL 17.3-9)}$$

(b) What value of m models the high-density (liquid) density-dependence of the diffusivity best?

By visual inspection, the m=0.75 curve appears to best fit the high-density simulation diffusivities.

(c) What is the molecular-level mechanism for diffusion in liquids that gives rise to the m value selected in part (b)?

In dense gases and liquids, the mean free path arguments are no longer valid. In fact, some models assume the liquid is a disordered solid and model diffusion as if it occurred in a disordered solid. In a solid, diffusion is an activated process, with the following functional form:

$$D_{self,A} = D_o \exp\left(-\frac{E_a}{kT}\right)$$

If we assume that diffusion in a liquid has this sort of functionality, then, in order to obtain the density dependence of the diffusivity, we need to consider the density dependence of D_o and of E_a. The prefactor, D_o, incorporates various entropic effects, which include the separation between liquid molecules. In a liquid, the separation between molecules is not inversely proportional to the density. There is a peak in the pair correlation function at a fixed point. The magnitude of this peak changes with density, but not the position. Therefore, we can't get much density dependence from this argument.

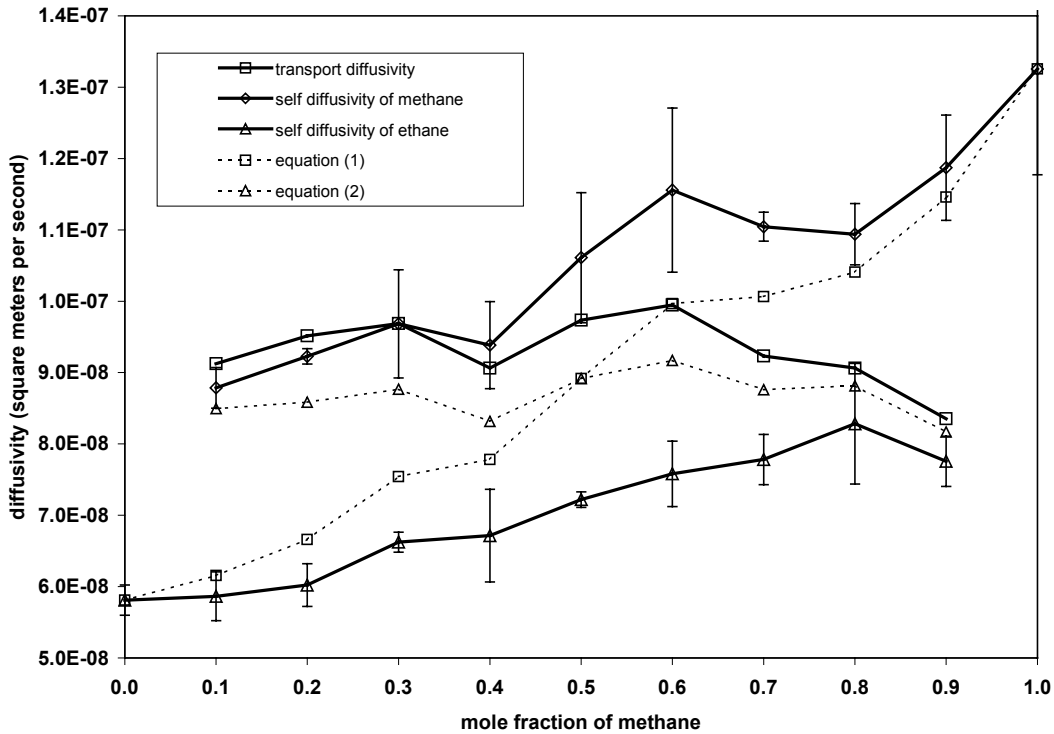
The activation energy, E_a, is also a function of density. The quantitative relationship between activation energy and density is unknown, but based on physical intuition we can hypothesize that as the density increases, it gets harder to diffuse, and thus the activation energy must increase. An increase in activation energy with density results in a decrease in the diffusivity with density.

Using this reasoning, we can determine that the value of m must be positive. The particular value of m, whether it is 0.5, 0.75, 1, or 2 is determined by the specifics of the diffusing species. In general, nothing more can be said without some experimental or simulation data.

Problem 2. (30 points)
The single, binary transport diffusivity of a liquid is obviously a function of composition. Consider a binary mixture of methane and ethane at 300 K and at a density of 3.907×10^{-3} molecules/Å^3 (a liquid density). The single, binary transport diffusivity, obtained by using MD simulations for the self-diffusivities and the Lennard-Jones equation of state for the thermodynamic correction factors, is plotted below as a function of mole fraction of methane (on a log-log scale). Also plotted are the self diffusivities from MD simulations. Also plotted are two equations.

$$D = x_{Me} D_{self,Me} + x_{Et} D_{self,Et} \quad (1)$$

$$D = x_{Me} D_{self,Et} + x_{Et} D_{self,Me} \quad (2)$$



(a) Explain why the self diffusivity of methane is greater than the self diffusivity of ethane at the same temperature and density.
(b) The self diffusivities of methane and ethane generally increase with mole fraction of ethane. Why?
(c) The self diffusivities of methane and ethane are not strictly monotonically increasing with mole fraction of methane. In your opinion, do the local non-monotonicities reflect real trends or, rather, are they within the noise of the simulation?
(d) In this data, the transport diffusivity is bound by the two self-diffusivities at all compositions. Must this behavior always be true?
(e) If you believe that the approximate physics of your simulations (such as the approximation of the Lennard-Jones potential) are only good to generate transport properties to +/- 10%, is it a legitimate approximation to assume a constant mean value of the transport diffusivity for use in a process modeling application?
(f) The transport diffusivity is clearly better modeled by equation (2) than by the molar-weighted mean self diffusivity (equation (1)). Explain.

Problem 2. (30 points)
Solution:

(a) Explain why the self diffusivity of methane is greater than the self diffusivity of ethane at the same temperature and density.

From kinetic theory, we know that as the size of the molecule increases, the diffusivity decreases. Furthermore, we know that as the molecular weight of a molecule increases, the diffusivity decreases. Both of these factors serve to decrease the diffusivity of ethane, relative to methane.

(b) The self diffusivities of methane and ethane generally increase with mole fraction of ethane. Why?

The self diffusivities of methane and ethane generally increase with mole fraction of ethane because as the fraction of the faster diffusing species increases, the self-diffusivities of all species should increase based on the information given in (a).

(c) The self diffusivities of methane and ethane are not strictly monotonically increasing with mole fraction of methane. In your opinion, do the local non-monotonicities reflect real trends or, rather, are they within the noise of the simulation?

In my opinion, given the size of the error bars, I believe that the local non-monotonicities lie within the noise of the simulation.

(d) In this data, the transport diffusivity is bound by the two self-diffusivities at all compositions. Must this behavior always be true?

For ideal solutions, this should be true, especially since we know that for ideal gases,

$$D = x_{Me} D_{self,Et} + x_{Et} D_{self,Me} \tag{2}$$

which is always bounded by the self diffusivities. I suppose one could concoct a pathological case which contradicted this result. Right off the top of my head, I can't think of one.

(e) If you believe that the approximate physics of your simulations (such as the approximation of the Lennard-Jones potential) are only good to generate transport properties to +/- 10%, is it a legitimate approximation to assume a constant mean value of the transport diffusivity for use in a process modeling application?

The minimum value of the transport diffusivity is about 8.2 and the maximum value 9.8. The median is 9.0. Ten percent of 9.0 is 0.9. 8.2 and 9.8 are both within 10% of 9.0 so I would say that using a constant value of the transport diffusivity (with respect to composition—temperature is a different issue) is probably okay in this case.

(f) The transport diffusivity is clearly better modeled by equation (2) than by the molar-weighted mean self diffusivity (equation (1)). Explain.

This transport diffusivity is defined for a flux relative to a molar-average velocity. In fact, the flux can also be written as

$$J_A^* = c x_A (v_A - v^*)$$

If most of the mixture is A then v* and v_A are very similar and the diffusive flux of A is small. Thus we see in equation (2) that the self diffusivity of A is weighted very little (weighted by the mole fraction of B). The converse of the above statement is true for B, so that the self-diffusivity of B is heavily weighted. This oddity is due purely to the choice of reference state being the molar-average velocity.

Problem 3. (40 points)

Consider a two-component ideal mixture with constant molar volume in a perfectly insulated one-dimensional system of length L. The boundary conditions of the system are such that at z=0, the composition is fixed at $x_{\alpha,0}$, and at at z=L the composition is fixed at $x_{\alpha,L}$. Since the system is insulated, there is no heat flux at the boundaries, $q = 0$. Initially the temperature is constant. at the thermodynamic reference temperature. The enthalpy of component α at the reference temperature is positive (e.g. CH_4). The enthalpy of component β at the reference temperature is zero (e.g. N_2). In this system, no reaction takes place. You cannot ignore the enthalpy transfer due to the mass flux. (You must use the following form of the heat flux.)

$$q = -k\frac{\partial T}{\partial z} + \sum_{\alpha=1}^{n_c} \overline{H}_\alpha J_\alpha^*$$

As usual, q is the heat flux, k is the thermal conductivity, nc is the number of components (2), $\overline{H}_\alpha$ is the partial molar enthalpy of component α, and J_α^* is the molar flux of component α relative to the molar average velocity, v*.

In this problem, you may assume that the thermal conductivity and diffusivity are constants with respect to temperature, density, and composition. Assume the convection term is zero at steady state.

(a) Express q for an ideal mixture.
(b) Write out the total unsteady state mole balance, the balance on moles of α, and the energy balance.
(c) Derive the steady state profile of the concentration.
(d) Derive the steady state profile of the mole fraction of a. Sketch it.
(e) Derive the steady state profile of the temperature. Sketch it.
(f) If $x_{\alpha,L} > x_{\alpha,0}$, what is the relationship between T(z=L) and T(z=0)?

On the next page, you will find a list of equations, some of which you will certainly find useful in solving this problem.

Note: This problem is much easier to solve if you assume that the heat capacities of α and β are equal. It is acceptable to make this assumption for this problem.

Problem 3. (40 points)
Solution:

Solution:

(a) Express q for an ideal mixture.

$$q = -k\frac{\partial T}{\partial z} + \sum_{\alpha=1}^{n_c}\bar{H}_\alpha J_\alpha^*$$

$$q = -k\frac{\partial T}{\partial z} - \left[H_\alpha(T) - H_\beta(T)\right]\left(cD_{\alpha\beta}\frac{\partial x_\alpha}{\partial z}\right)$$

(b) Write out the total unsteady state mole balance, the balance on moles of α, and the energy balance.

The total mole balance.

$$\frac{\partial c}{\partial t} = -c\frac{\partial v^*}{\partial z} = 0$$

The mole balance on component α.

$$c\frac{\partial x_\alpha}{\partial t} = -cv^*\frac{\partial x_\alpha}{\partial z} - \frac{\partial J_\alpha^*}{\partial z}$$

$$\frac{\partial x_\alpha}{\partial t} = -v^*\frac{\partial x_\alpha}{\partial z} + D_{\alpha\beta}\frac{\partial^2 x_\alpha}{\partial z^2}$$

The energy balance.

$$c\frac{\partial H_{mix}}{\partial t} = -cv^*\frac{\partial H_{mix}}{\partial z} - \frac{\partial q}{\partial z}$$

$$c\frac{\partial H_{mix}}{\partial t} = -cv^*\frac{\partial H_{mix}}{\partial z} - \frac{\partial}{\partial z}\left(-k\frac{\partial T}{\partial z} + \sum_{\alpha=1}^{n_c}\bar{H}_\alpha J_\alpha^*\right)$$

$$c\frac{\partial H_{mix}}{\partial t} = -cv^*\frac{\partial H_{mix}}{\partial z} + k\frac{\partial^2 T}{\partial z^2} - \sum_{\alpha=1}^{n_c}\left(\bar{H}_\alpha\frac{\partial J_\alpha^*}{\partial z} + J_\alpha^*\frac{\partial \bar{H}_\alpha}{\partial z}\right)$$

(c) Derive the steady state profile of the concentration.

From the molar balance, the molar concentration, the inverse of the molar volume is constant. (Therefore, the molar average velocity, v*, is also constant.)

(d) Derive the steady state profile of the mole fraction of α. Sketch it.

$$0 = -v^* \frac{\partial x_\alpha}{\partial z} + D_{\alpha\beta} \frac{\partial^2 x_\alpha}{\partial z^2}$$

At steady state, the molar average velocity is zero.

$$0 = \frac{\partial^2 x_\alpha}{\partial z^2}$$

The solution of this is a straight line.

$$x_\alpha(z) = x_\alpha(z=0) + \frac{z}{L}\left(x_{\alpha,L} - x_{\alpha,0}\right)$$

$$\frac{\partial x_\alpha(z)}{\partial z} = \frac{\left(x_{\alpha,L} - x_{\alpha,0}\right)}{L}$$

The sketch of this is a straight line between the points ($z=0$, $x_\alpha=x_{\alpha,L}$) and ($z=L$, $x_\alpha=x_{\alpha,L}$).

(e) Derive the steady state profile of the temperature. Sketch it.

$$0 = \frac{\partial q}{\partial z}$$

$$q = q_o = \text{constant}$$

This constant is zero, because the boundary conditions state that there is no heat flux at either boundary.

$$-k\frac{\partial T}{\partial z} + \sum_{\alpha=1}^{n_c} \bar{H}_\alpha J_\alpha^* = q_0$$

$$-k\frac{\partial T}{\partial z} - \left[H_\alpha(T) - H_\beta(T)\right]\left(cD_{\alpha\beta}\frac{\partial x_\alpha}{\partial z}\right) = q_0$$

$$-k\frac{\partial T}{\partial z} - \left[H_\alpha(T) - H_\beta(T)\right]\left(cD_{\alpha\beta}\frac{\left(x_{\alpha,L} - x_{\alpha,0}\right)}{L}\right) = q_0$$

$$\partial T = -\frac{q_o + \left[H_\alpha(T) - H_\beta(T)\right]\frac{\left(x_{\alpha,L} - x_{\alpha,0}\right)}{L}}{k}\partial z$$

Approximate solution 1:
If we assume that the pure component heat capacities are the same for components α and β, we have

$$H_\alpha(T) - H_\beta(T) = H_\alpha(T_{ref}) - H_\beta(T_{ref})$$

then we can obtain a simple answer.

$$T(z) = T(z=0) - \frac{q_o + \left[H_\alpha(T_{ref}) - H_\beta(T_{ref})\right]\left(cD_{\alpha\beta}\frac{(x_{\alpha,L} - x_{\alpha,0})}{L}\right)}{k} z$$

The answer was simple because the reference enthalpies are not functions of temperature and can be pulled out of the integral.

Approximate solution 2:
If we assume that the enthalpies have a functional form such as

$$H_\alpha(T) = \int_{T_{ref}}^{T} C_{p,\alpha}(T)dT + H_\alpha(T_{ref})$$

where the heat capacities are simply a constant value but are different for each component, then

$$H_\alpha(T) = C_{p,\alpha}(T - T_{ref}) + H_\alpha(T_{ref})$$

With this case, we can rewrite the equation in the form

$$-k\frac{\partial T}{\partial z} - \left[C_{p,\alpha}(T - T_{ref}) + H_\alpha(T_{ref}) - C_{p,\beta}(T - T_{ref}) - H_\beta(T_{ref})\right]\left(cD_{\alpha\beta}\frac{(x_{\alpha,L} - x_{\alpha,0})}{L}\right) = q_0$$

$$-k\frac{\partial T}{\partial z} - T\left[C_{p,\alpha} - C_{p,\beta}\right]\left(cD_{\alpha\beta}\frac{(x_{\alpha,L} - x_{\alpha,0})}{L}\right)$$
$$= q_0 + \left[H_\alpha(T_{ref}) - H_\beta(T_{ref}) - (C_{p,\alpha} - C_{p,\beta})T_{ref}\right]\left(cD_{\alpha\beta}\frac{(x_{\alpha,L} - x_{\alpha,0})}{L}\right)$$

This ODE is a linear first order ODE with the form:

$$\frac{\partial y}{\partial x} + ay = b$$

This ODE has a solution of the form

$$y(x) = \left\{\left[ye^{\int a(x)dx}\right]_{x=x_o} + \int_{x=x_o}^{x} b(x)e^{\int a(x)dx}dx\right\}e^{-\int a(x)dx}$$

which for the case where a and b are constants (as is true in our problem) reduces to

$$y(x) = \left(y_o - \frac{b}{a}\right)e^{-a(x-x_o)} + \frac{b}{a}$$

With this form of the solution, our solution becomes

$$T(z) = \left(T(z=0) - \frac{b}{a}\right)e^{-az} + \frac{b}{a}$$

where

$$a = \frac{T\left[C_{p,\alpha} - C_{p,\beta}\right]\left(cD_{\alpha\beta}\frac{\left(x_{\alpha,L} - x_{\alpha,0}\right)}{L}\right)}{k}$$

$$b = -\frac{q_0 + \left[H_\alpha(T_{ref}) - H_\beta(T_{ref}) - \left(C_{p,\alpha} - C_{p,\beta}\right)T_{ref}\right]\left(cD_{\alpha\beta}\frac{\left(x_{\alpha,L} - x_{\alpha,0}\right)}{L}\right)}{k}$$

Both approximate solutions include $T(z=0)$. For either approximate solution we need to incorporate the second boundary conditions for T. The only way to obtain this is to consider the initial temperature. Given the initial temperature and the fact that the system is perfectly insulated, you can calculate T(z=0) by solving the P.D.E., I don't think you can get it otherwise.

(f) If $x_{\alpha,L} > x_{\alpha,0}$, what is the relationship between T(z=L) and T(z=0)?

Approximate solution 1:
In the equation for T(z), q_o is zero. c, L, D, and k are all positive. The difference between the enthalpies of α and β are positive, as that was given in the problem statement. There is, however, a negative sign in front of the entire term. Therefore, if $x_{\alpha,L} > x_{\alpha,0}$, then T(z=L) < T(z=0). If $x_{\alpha,L} < x_{\alpha,0}$, then T(z=L) > T(z=0).

Approximate solution 2:
The answer here depends upon the specific values for the reference enthalpies and heat capacities. If you actually solved part (e) for approximate solution 2 (the case where the heat capacities are not equal), you did not have to do part (f).

molar flux: $J_\alpha^* = -cD_{\alpha\beta}\dfrac{\partial x_\alpha}{\partial z}$	$J_\beta^* = -cD_{\alpha\beta}\dfrac{\partial x_\beta}{\partial z}$
for binary systems: $x_\alpha + x_\beta = 1$ $N = N_\alpha + N_\beta$ $\left(\dfrac{\partial x_\alpha}{\partial N_\alpha}\right)_{T,p,N_\beta} = \dfrac{1}{N_\alpha + N_\beta} - \dfrac{N_\alpha}{(N_\alpha + N_\beta)^2} = \dfrac{N_\beta}{(N_\alpha + N_\beta)^2} = x_\beta \dfrac{1}{N}$	$\dfrac{\partial x_\beta}{\partial z} = -\dfrac{\partial x_\alpha}{\partial z}$ $x_\alpha = \dfrac{N_\alpha}{N} = \dfrac{N_\alpha}{N_\alpha + N_\beta}$ $\left(\dfrac{\partial N}{\partial N_\alpha}\right)_{T,p,N_\beta} = 1$
$\left(\dfrac{\partial x_\beta}{\partial x_\alpha}\right)_{T,p,N_\beta} = \left(\dfrac{\partial \dfrac{N_\beta}{N_\alpha + N_\beta}}{\partial N_\alpha}\right)_{T,p,N_\beta}$ $\left(\dfrac{\partial N_\alpha}{\partial x_\alpha}\right)_{T,p,N_\beta} = -\dfrac{N_\beta}{(N_\alpha + N_\beta)^2}\dfrac{1}{x_\beta \dfrac{1}{N}} = -1$	
pure component enthalpy $H_\alpha(T) = \int_{T_{ref}}^{T} C_{p,\alpha}(T)dT + H_\alpha(T_{ref})$	mixture enthalpy $H_{mix}(T,\underline{x}) = x_\alpha H_\alpha(T) + x_\beta H_\beta(T)$
partial molar enthalpy for an ideal mixture (derived) $\bar{H}_\alpha(T,\underline{x}) \equiv \left(\dfrac{\partial N H_{mix}}{\partial N_\alpha}\right)_{T,p,N_\beta} = N\left(\dfrac{\partial H_{mix}}{\partial N_\alpha}\right)_{T,p,N_\beta} + H_{mix}\left(\dfrac{\partial N}{\partial N_\alpha}\right)_{T,p,N_\beta}$ $\bar{H}_\alpha(T,\underline{x}) = N\left(\dfrac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta}\left(\dfrac{\partial x_\alpha}{\partial N_\alpha}\right)_{T,p,N_\beta} + H_{mix} = x_\beta\left(\dfrac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta} + H_{mix}$ $\left(\dfrac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta} = H_\alpha(T) + H_\beta(T)\left(\dfrac{\partial x_\beta}{\partial x_\alpha}\right)_{T,p,N_\beta} = H_\alpha(T) - H_\beta(T)$ $\bar{H}_\alpha(T,\underline{x}) = x_\beta\left[H_\alpha(T) - H_\beta(T)\right] + H_{mix} = (1 - x_\alpha)\left[H_\alpha(T) - H_\beta(T)\right] + H_{mix} = H_\alpha(T)$ $\bar{H}_\beta(T,\underline{x}) = x_\alpha\left[H_\beta(T) - H_\alpha(T)\right] + H_{mix} = \bar{H}_\alpha(T,\underline{x}) + \left[H_\beta(T) - H_\alpha(T)\right] = H_\beta(T)$	