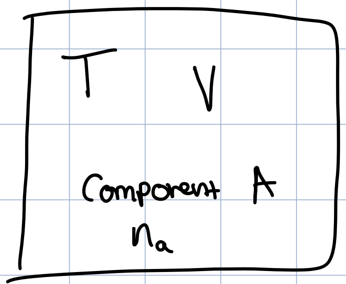
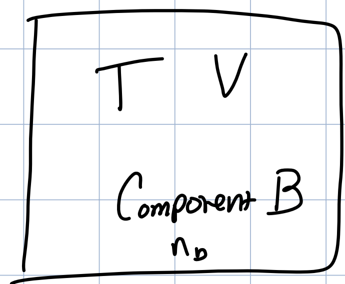
9.2 In Sec. 9.1 we considered the changes in thermodynamic properties on forming an ideal gas mixture from a collection of ideal gases at the same temperature and pressure. A second, less common way of forming an ideal gas mixture is to start with a collection of pure ideal gases, each at the temperature T and volume V, and mix and compress the mixture to produce an ideal gas mixture at temperature T and volume V.

a. Show that the mixing process described here is mixing at constant partial pressure of each component.

b. Derive each of the entries in the following table.

(a)

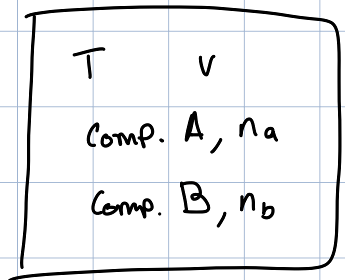




$P_a = \frac{n_a RT}{v}$ $\qquad$ $P_b = \frac{n_a RT}{v}$

for each of these the $P_{total} = P_{partial}$

since they are both pure components $(x=1)$



now,

$$P_a = \frac{n_a}{n_a+n_b} P_{total}$$

$$P_b = \frac{n_b}{n_a+n_b} P_{total}$$

and since

$$P_{total} = P_a + P_b = \frac{n_a RT}{V} + \frac{n_b RT}{V} = (n_a + n_b)\frac{RT}{V}$$

$$\left.\begin{aligned} P_a &= n_a P_{total} = \frac{n_a RT}{V} \\ P_b &= n_b P_{total} = \frac{n_b RT}{V} \end{aligned}\right\} \text{same partial pressure as before}$$

(b)

Ideal Gas Mixing Properties* at Constant Temperature and Partial Pressure of Each Species

1	Internal energy	$\bar{U}_i^{IG}(T, x_i) = \underline{U}_i^{IG}(T)$	$\Delta_{mix}\underline{U}^{IG} = 0$
2	Volume†	$\bar{V}_i^{IGM}(T, P, x_i) = x_i \underline{V}_i^{IG}(T, P_i)$	$\Delta_{mix}\underline{V}^{IGM} = (1 - \mathcal{C})V / \sum_{i=1}^{\mathcal{C}} N_i$
3	Enthalpy	$\bar{H}_i^{IGM}(T, x_i) = \underline{H}_i^{IG}(T)$	$\Delta_{mix}^{IGM}\underline{H} = 0$
4	Entropy	$\bar{S}_i^{IGM}(T, P, x_i) = \underline{S}_i^{IG}(T, P_i)$	$\Delta_{mix}\underline{S}^{IGM} = 0$
5	Helmholtz energy	$\bar{A}_i^{IGM}(T, P, x_i) = \underline{A}_i^{IG}(T, P_i)$	$\Delta_{mix}\underline{A}^{IGM} = 0$
6	Gibbs energy	$\bar{G}_i^{IGM}(T, P, x_i) = \underline{G}_i^{IG}(T, P_i)$	$\Delta_{mix}\underline{G}^{IGM} = 0$

*For mixing at constant temperature and partial pressure of each species, we have the following

$$\Delta_{mix}\underline{\theta}^{IGM} = \sum_i x_i[\bar{\theta}_i(T, P, x_i) - \underline{\theta}_i(T, P_i)]$$

†$\mathcal{C}$ = number of components.

Remembering our partial molar definition

$$\bar{\theta}_i = \left.\frac{\partial \theta_i}{\partial N_i}\right|_{T,P,N_{j\neq i}}$$

<u>internal energy</u>

$$\bar{U}_i^{IGM} = \left.\frac{\partial U^{IGM}}{\partial N_i}\right|_{P,T,N_{j\neq i}} = \left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} N_i \underline{U}_i^{IGM} = \underline{U}_i^{IGM} \quad \textcircled{1}$$

$$\Delta_{mix}\underline{U}^{IGM} = \sum_{i=1}^{C} x_i\left(\underline{U}^{IGM} - \underline{U}^{IGM}\right) = 0$$

Volume

from Ideal Eos

$$\bar{V}^{IGM} = \frac{\partial}{\partial N_i}\bigg|_{T,P,N_{j\neq i}} \frac{\sum N_i RT}{P}$$

$$= \frac{RT}{P} = x_i \frac{RT}{P_i}$$

now assuming $V^{IG}(P_i, T) = \frac{N_i RT}{P_i} \longrightarrow \frac{V^{IG}(P_i,T)}{N_i} = \frac{RT}{P_i}$

$$\bar{V}^{IGM} = x_i \frac{V^{IG}(P_i,T)}{N_i} = x_i \underline{V}^{IG}(P_i,T)$$

now for $\Delta_{mix} \underline{V}^{IGM}$

$$\Delta_{mix}\underline{V}^{IGM} = \sum_{i=1}^{C} x_i \left[\bar{V}_i^{IGM} - \underline{V}_i\right]$$

$$= \sum^{C} x_i \left[x_i \underline{V}_i - \underline{V}_i\right]$$

$$= \sum^{C} x_i (x_i - 1)\underline{V}_i$$

same V for both comp

$$= \sum^{C} x_i (x_i - 1)\frac{V}{N_i} \leftarrow = x_i N$$

$$= \sum_{i=1}^{C} (x_i - 1)\frac{V}{N} = \frac{V}{N}\sum_{i=1}^{C}(x_i - 1)$$

by rules of sum

$$= \frac{V}{N}\left(\sum_{i=1}^{C} x_i - \sum_{i=1}^{C} 1\right)$$

$$\Delta_{mix}\underline{V}^{IGM} = \frac{V}{N}(1 - C)$$

enthalpy

$$\bar{H}_i^{IGM} = \bar{U}^{IGM} + P\bar{V}^{IGM}$$

from earlier ① $\bar{U}_i^{IGM} = \underline{U}_i^{IG}$ and $\bar{V}_i^{IGM} = x_i \underline{V}_i^{IG}$

$$\bar{H}_i^{IGM} = \underline{U}^{IG} + P x_i \underline{V}_i^{IG}$$

$$\bar{H}_i^{IGM} = \underline{U}^{IG} + P_i \underline{V}_i^{IG}$$

$$= \underline{H}_i^{IG}$$

using this result

mixing now

$$\Delta_{mix} \underline{H}^{IGM} = \sum_{i=1}^{C} x_i \left(\underline{H}_i^{IG} - H_i^{IG} \right) = 0$$

entropy

Since constant partial pressure, this gets interesting

$$\bar{S}^{IGM} - \underline{S}^{IG} = -R \ln\left(\frac{p_i}{P}\right) \qquad (9.1\text{-}7)$$

as shown in part a

$$P_{i,final} = P_{initial}$$

So

$$\bar{S}_i^{IGM} - \underline{S}_i^{IG} = -R \ln(1) = 0$$

$$\bar{S}_i^{IGM} = \underline{S}_i^{IG}$$

and since this is true for all components

$$\Delta_{mix} \underline{S}^{IGM} = \sum x_i \left(\bar{S}_i^{IGM} - \underline{S}_i^{IG} \right)$$

$$= 0$$

<u>helmholtz free energy</u>

$$A = U - TS$$

$$\Longrightarrow \bar{A}_i^{IGM} = \bar{U}_i^{IGM} - T\bar{S}_i^{IGM}$$

as shown earlier

$$\bar{U}_i^{IGM} = \underline{U}_i^{IG}$$

$$\bar{S}_i^{IGM} = \underline{S}_i^{IG}$$

$$\therefore \quad \bar{A}_i^{IGM} = \underline{U}_i^{IG} - T\underline{S}_i^{IG} = \underline{A}_i^{IG}$$

$$\Delta_{mix} \bar{A}_i^{IGM} = \sum_{i=1}^{c} x_i \left[\bar{A}_i^{IGM} - \underline{A}_i^{IG} \right]$$

$$= \sum_{i=1}^{c} x_i \left[\underline{A}_i^{IG} - \underline{A}_i^{IG} \right]$$

$$= 0$$

<u>gibbs energy</u>

could do from $H - TS$ or $\underline{A + PV}$

$$\bar{G}_i^{IGM} = \bar{A}_i^{IGM} + P\bar{V}^{IGM}$$

using results from earlier

$$\bar{G}_i^{IGM} = \underline{A}_i^{IG} + P x_i \underline{V}_i^{IG}$$

$$= \underline{A}_i^{IG} + P_i \underline{V}_i^{IG}$$

$$= \underline{G}_i^{IGM}$$

or alternatively

$$\bar{G}_i^{IGM} = \bar{H}_i^{IGM} - T\bar{S}_i^{IGM}$$

and from earlier as well

$$\bar{G}_i^{IGM} = \underline{H}_i^{IG} - T\underline{S}_i^{IG}$$

$$\bar{G}_i^{IGM} = \underline{G}_i^{IG}$$

$$\Delta_{mix}\bar{G}_i^{IGM} = \sum_{i=1}^{c} x_i\left[\bar{G}_i^{IGM} - \underline{G}_i^{IG}\right]$$

$$= \sum_{i=1}^{c} x_i\left[\underline{G}_i^{IG} - \underline{G}_i^{IG}\right]$$

$$= 0$$