Solution to Problems | **10.213** | **04/18/02**
Concepts in the Topic of Ideal Mixture | Spring 2002 | YT

Please contact Yonathan (thio@mit.edu) if you find a typo, disagree with the solution, or have difficulty with the problems.

1) True / ***False*** $\overline{M}_i = \left(\frac{\partial(nM)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ *can also be written* $\overline{M}_i = \left(\frac{\partial M}{\partial x_i}\right)_{T,P,x_{j\neq i}}$

A common mistake when calculating $\overline{M}_i$. Since n also changes with n_i, we cannot take n out of the d(nM) term and divide n_i by n. To get $\overline{M}_i$ use the left equation or, for a binary system, the textbook's eqn 11.15 and 11.16.

Consider a mixture of A and B. $\overline{M}_A$, as defined in the left-hand equation, tells us how M changes when we add some small amount of A. So the total number of moles changes as well as the composition. The right-hand equation says: how would M change when we change the composition of the solution, *while maintaining total number of moles*? This means we have to take out some B while adding the A. Not the same.

2) True / ***False*** *For ideal gases: H = Σyi Hi where Hi is the enthalpy of pure species at some fixed reference temperature.*

Just a reminder. Be aware of what individual term means when writing out these equations. H is the enthalpy of the mixture at some T and P. As written above, H_i is the enthalpy of the pure species at the same T and P as the mixture that we are considering.

3) ***True*** */ False* *Ideal gases always form ideal mixtures.*

See section 11.4 in the textbook, particularly the paragraph on Gibbs's theorem, and the beginning of 11.8.
The ideal gas has no energetic interaction between different molecules and also has zero volume for each molecules. Therefore when we mix two ideal gases, the molecules still do not interact and no volume is taken by individual molecule. This fits the definition of an ideal mixture.

4) True / ***False*** *In an ideal mixture,* $\overline{M}_i = M_i$ *where M is any molar property.*

This is true for some properties, e.g. volume and enthalpy. As we saw in lecture, though, it's not true for entropy and Gibbs free energy.

Physical interpretation: See no 3) above for the explanation why $\overline{V}_i = V_i$ and $\overline{H}_i = H_i$ for an ideal gas. (To jog the mind, is $\overline{U}_i = U_i$?) Our idea for entropy, however, which is bound to the concept of reversibility, must be consistent when we mix two gases. Even if they were ideal gases, we know that once we mix them, they will never spontaneously unmix back, i.e. the process is irreversible. This irreversibility needs to be captured in a new term, which is the second term in $\overline{S}_i = S_i - R\ln y_i$ (eqn 11.24 in book). See 5) for more discussion on this.

5) *A and B are ideal gases. n_A moles of A and n_B moles of B are mixed adiabatically at some constant T and constant P. Let's call the fraction of A in the final mixture x_A. Find the expression for the change of entropy of the process in terms of n_A, n_B, x_A, T, P, and R. Is this process reversible?*

Note that all of the following is calculated at the given T and P.

Initial: n_A moles of A with some molar entropy S_A. n_B moles of B with some molar entropy S_B.
Therefore, at the beginning we have a total entropy of $S^t_{initial} = n_AS_A + n_BS_B$.

Final: $(n_A + n_B)$ moles of a mixture containing x_A fraction of A.
From material balance, we know $x_A = n_A / (n_A + n_B)$ and $x_B = 1–x_A = n_B/(n_A+n_B)$.
The molar entropy of the mixture is (eqn 11.15) $S_{final} = x_AS_A + x_BS_B – Rx_A\ln x_A – Rx_B\ln x_B$.
The total entropy at the end is then

$$\begin{aligned} S^t_{final} &= (n_A + n_B)\, S_{final} = (n_A + n_B)(x_AS_A + x_BS_B – Rx_A\ln x_A – Rx_B\ln x_B) \\ &= n_AS_A + n_BS_B – R(n_A\ln x_A + n_B\ln x_B) \end{aligned}$$

The change in entropy,

$$\begin{aligned} \Delta S^t &= S^t_{final} - S^t_{initial} \\ &= n_AS_A + n_BS_B – R(n_A\ln x_A + n_B\ln x_B) – (n_AS_A + n_BS_B) \\ &= – R(n_A\ln x_A + n_B\ln x_B) \end{aligned}$$

We can write x_B in terms of x_A, but we'll leave it at that.

Is the process reversible? Well, the above is the ΔS^t for our system. $\Delta S^t_{sys} = – R(n_A\ln x_A + n_B\ln x_B)$
What about ΔS^t for surrounding? (It's important to check this because we want ΔS of universe, not just the system, when considering reversibility). The process is stated to be adiabatic, so $Q_{sys} = 0$. Remember that $\Delta S^t_{surr} = –Q_{sys}/T_{surr}$. So $\Delta S^t_{surr} = 0$.

Therefore our $\Delta S^t_{universe} = \Delta S^t_{sys} + \Delta S^t_{surr} = \Delta S^t_{sys}$. Is ΔS^t_{sys} positive or negative?
$x_A \le 1$, $x_B \le 1 \rightarrow \ln x_A \le 0$, $\ln x_B \le 0 \rightarrow \Delta S^t_{sys} = – R(n_A\ln x_A + n_B\ln x_B) \ge 0$ for all x_A and x_B.
So $\Delta S^t_{universe} \ge 0$ for all x_A and x_B.

You can probably see that although we did this for two ideal gases, the concept can be extended to however many ideal gases we want to consider. This means that ideal gases will always mix. Furthermore, the process is irreversible, i.e. once they are mixed, they will not unmix.

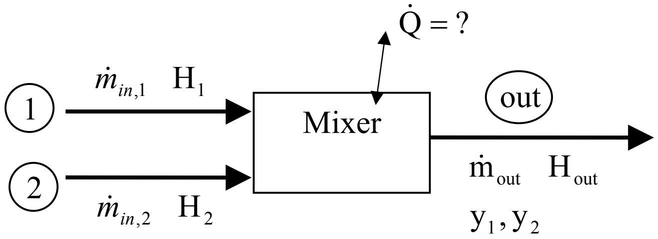
6) *When we mix two unknown liquids X and Y in the amount of 100 mL of X and 50 mL of Y, we get 148 mL of solution. What can we say about the relative magnitudes of* $\overline{V}_X, \overline{V}_Y, V_X$, and V_Y ?

$n_XV_X = 100$ mL; $n_YV_Y = 50$ mL. Or $n_XV_X + n_YV_Y = 150$ mL.
But $V^t_{mix} = n_{total}(x_X\overline{V}_X + x_Y\overline{V}_Y) = (n_X + n_Y)(x_X\overline{V}_X + x_Y\overline{V}_Y) = n_X\overline{V}_X + n_Y\overline{V}_Y = 148$ mL.

So all we can say is that $n_X\overline{V}_X + n_Y\overline{V}_Y < n_XV_X + n_YV_Y$.
It can be that $\overline{V}_X < V_X$, or $\overline{V}_Y < V_Y$, or both.

7) For a binary system of ideal gases 1 and 2, we are given $H = y_1H_1 + y_2H_2 + k^2y_1y_2$, where k is a constant. We mix some amount of gas 1 and some amount of gas 2 in a flow process, all at constant T = 298 K and P = 1 atm. Consider the case where no shaft work is done. To keep the mixture at 298 K and 1 atm, does heat need to be added or removed to the system? What if the final pressure is not 1 atm but 10 atm?

Before going to the solution, an additional question: is the mixture ideal or not?



An open system, 1st law:

$$\Delta(\dot{m}H) = \dot{Q} + \dot{W}_s = \dot{Q} + 0 = \dot{Q}$$

$$\dot{Q} = \dot{m}_{out}H_{out} - (\dot{m}_{in,1}H_1 + \dot{m}_{in,2}H_2)$$

Material balance: $\dot{m}_{out} = \dot{m}_{in,1} + \dot{m}_{in,2}$; $\quad y_1 = \dfrac{\dot{m}_{in,1}}{\dot{m}_{in,1} + \dot{m}_{in,2}}$; $\quad y_2 = \dfrac{\dot{m}_{in,2}}{\dot{m}_{in,1} + \dot{m}_{in,2}}$

According to the equation above: $H_{out} = y_1H_1 + y_2H_2 + k^2y_1y_2$.

$$\begin{aligned}\dot{m}_{out}H_{out} &= (\dot{m}_{in,1} + \dot{m}_{in,2})(y_1H_1 + y_2H_2 + k^2y_1y_2)\\ &= (\dot{m}_{in,1} + \dot{m}_{in,2})\left(\frac{\dot{m}_{in,1}}{\dot{m}_{in,1} + \dot{m}_{in,2}}H_1 + \frac{\dot{m}_{in,2}}{\dot{m}_{in,1} + \dot{m}_{in,2}}H_2 + k^2y_1y_2\right) \qquad \text{(we'll leave the last term as it is)}\\ &= \dot{m}_{in,1}H_1 + \dot{m}_{in,2}H_2 + (\dot{m}_{in,1} + \dot{m}_{in,2})k^2y_1y_2\end{aligned}$$

$$\dot{Q} = \dot{m}_{out}H_{out} - (\dot{m}_{in,1}H_1 + \dot{m}_{in,2}H_2) = \dot{m}_{in,1}H_1 + \dot{m}_{in,2}H_2 + (\dot{m}_{in,1} + \dot{m}_{in,2})k^2y_1y_2 - (\dot{m}_{in,1}H_1 + \dot{m}_{in,2}H_2)$$

$$\dot{Q} = (\dot{m}_{in,1} + \dot{m}_{in,2})k^2y_1y_2$$

Since $\dot{m}_{in,1}$, $\dot{m}_{in,2}$, k^2, y_1, and y_2 are all positive, $\dot{Q} > 0$. That means heat must be added into the system.

What if the final pressure is 10 atm? Since enthalpy of ideal gas only depends on T, the answer would be the same as above. Only if the final temperature is different would we get a different answer (which would have some Cp term in it).

Note:

The algebra above (and in problem 5) is to remind you how to deal with material balance, 1st law, and 2nd law for open system. You also did this problem 26 in pset H. You should be comfortable with writing out the equations and understanding what needs to go in each term. It's important to keep the following distinctions:

1) open vs. closed system;
2) number of moles vs. molar flow rate
3) molar property vs. total property (S vs S^t); [mind your units!];
4) property of a mixture, property of pure component, and partial property of a component in a mixture;
5) components and streams (may get confusing if you have many components in many streams)

8) ***True*** */ False* *The Gibbs-Duhem equation in the form of* $\sum x_i d\bar{M}_i$ *only applies at constant T and P.*

See p.374 of textbook for complete Gibbs-Duhem equation.

9) ***<u>True</u>*** */ False* *For an ideal gas mixture,* $\sum x_i \frac{d\overline{H}_i}{dx_1} - Cp\frac{dT}{dx_1} = 0$

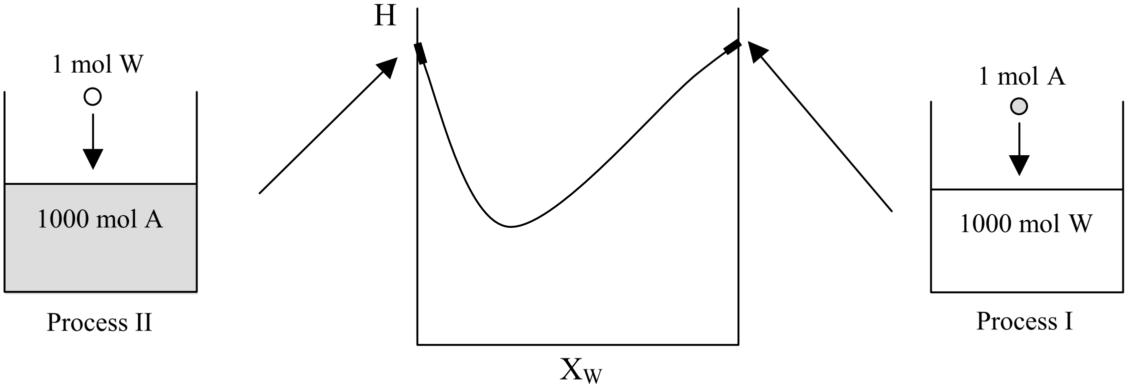
Gibbs-Duhem equation, writing out for enthalpy (M = H):

$$\left(\frac{\partial H}{\partial P}\right)_{T,x} dP + \left(\frac{\partial H}{\partial T}\right)_{P,x} dT - \sum x_i d\overline{H}_i = 0 \quad \Rightarrow \quad \left(\frac{\partial H}{\partial P}\right)_{T,x} \frac{dP}{dx_1} + \left(\frac{\partial H}{\partial T}\right)_{P,x} \frac{dT}{dx_1} - \sum x_i \frac{d\overline{H}_i}{dx_1} = 0.$$

$\left(\frac{\partial H}{\partial T}\right)_{P,x} = Cp.$ For ideal gas, H only depends on T, therefore $\left(\frac{\partial H}{\partial P}\right)_{T,x} = 0.$

$$Cp\frac{dT}{dx_1} - \sum x_i \frac{d\overline{H}_i}{dx_1} = 0 \quad \text{or} \quad \sum x_i \frac{d\overline{H}_i}{dx_1} - Cp\frac{dT}{dx_1} = 0 \quad \text{for ideal gas mixture}$$

10) The enthalpy diagram for a mixture of A and W is given below. Consider two processes depicted next to the diagram. In each process, 1 mol of one substance is added to 1,000 mol of the other substance. Which process, I or II, will generate more heat?



Process I starts at $X_W = 1$ and ends at some $X_W = (1 - \delta)$ where δ is some small number (=1/1001). On the diagram, it's represented by that small strip near $X_W = 1$. Process II starts at $X_W = 0$ and ends at some $X_W = \delta$, as represented by the small strip near $X_W = 0$. Since the slope of the H-curve at $X_W = 0$ is steeper than the slope at $X_W = 1$, the change in enthalpy is larger for process II. Thus, we expect more heat generation in process II. (Is it justifiable for me to claim that the heat generated is the same as the enthalpy change of the process?)

Note 1: Infinite dilution

This is one instance where the infinite dilution concept is useful. The change in enthalpy in each process per mole of mixture can be *approximated* using $\overline{H}_A^\infty$ and $\overline{H}_W^\infty$: $\Delta H_I \approx x_A(\overline{H}_A^\infty - H_A)$ and $\Delta H_{II} \approx x_W(\overline{H}_W^\infty - H_W)$. Do the calculation to convince yourself that this approximation is true. If we estimate $\overline{H}_A^\infty$ and $\overline{H}_W^\infty$ using the diagram above (can you?) we'll see that $\left|\overline{H}_W^\infty - H_W\right| > \left|\overline{H}_A^\infty - H_A\right|$. And therefore the heat generated in process II is larger.

For some particular systems, we usually deal with small concentrations (e.g. solution of CO_2 in water – useful in designing carbonated drinks… I suspect we'll see a problem with this soon enough). In these cases, the infinite dilution properties can be used to approximate the change in properties. Basically, we take the portions of the curve near x=0 and near x=1 to be linear.

Note 2: Lab safety revisited

Consider W as water and A as acid. The above can be used as one argument why you always add acid to water rather than water to acid. The enthalpy-concentration diagram for acid-water system does indeed look like what I drew above, e.g. see Figure 12.17 in the book. Adding a small amount of water to acid generates much more heat than a small amount of acid to water. (Why this is so is another question altogether). While this thermodynamic argument is valid, there is also the practical argument of "if it splatters, I'd rather have water, not acid, splattering on my face".