Homework 6: Problem 6.26

April 3, 2008

We are given the following equation for the enthalpy of mixing for a binary mixture of cadmium and tin at 500 °C:

$$\Delta h_{mix} = 1.3 \times 10^4 X_{Cd} X_{Sn} \text{ [J/mol]}$$

For simplicity, we define $\alpha = 1.3 \times 10^4$ [J/mol] .

(a) Show that $\left(\overline{\Delta H}_{mix}\right)_{Cd} = \overline{H}_{Cd} - h_{Cd}$.

Start with the equation for the specific enthalpy of the mixture:

$$h = X_{Cd} h_{Cd} + X_{Sn} h_{Sn} + \Delta h_{mix}$$

Multiply by the number of moles:

$$\begin{aligned} nh &= nX_{Cd} h_{Cd} + nX_{Sn} h_{Sn} + n\Delta h_{mix} \\ H &= n_{Cd} h_{Cd} + n_{Sn} h_{Sn} + \Delta H_{mix} \end{aligned}$$

Differentiate with respect to the number of moles of Cd at constant T,P, and number of moles of Sn:

$$\begin{aligned} \left(\frac{\partial H}{\partial n_{Cd}}\right)_{T,P,n_{Sn}} &= h_{Cd} + \left(\frac{\partial \Delta H_{mix}}{\partial n_{Cd}}\right)_{T,P,n_{Sn}} \\ \overline{H}_{Cd} &= h_{Cd} + \left(\overline{\Delta H}_{mix}\right)_{Cd} \end{aligned}$$

Which can be rearranged to give the desired result. [+2 points]

(b) Calculate $\overline{H}_{Cd} - h_{Cd}$ and $\overline{H}_{Sn} - h_{Sn}$, given 3 moles of Cd and 2 moles of Sn.

From part (a), we have:

$$\overline{H}_{Cd} - h_{Cd} = \left(\overline{\Delta H}_{mix}\right)_{Cd}$$

So we need to calculate $\left(\overline{\Delta H}_{mix}\right)_{Cd}$. Begin with the equation given in problem statement, and multiply both sides by the total number of moles:

$$\begin{aligned}
n\Delta h_{mix} &= n\alpha X_{Cd} X_{Sn} \\
\Delta H_{mix} &= \alpha n_{Cd} X_{Sn} \frac{n}{n} \\
&= \alpha \frac{n_{Cd} n_{Sn}}{n_{Cd} + n_{Sn}}
\end{aligned}$$

Differentiate with respect to the number of moles of Cd at constant T,P, and number of moles of Sn:

$$\begin{aligned}
\left(\overline{\Delta H}_{mix}\right)_{Cd} &= \alpha \frac{n_{Sn}^2}{(n_{Cd} + n_{Sn})^2} \\
&= \alpha X_{Sn}^2
\end{aligned}$$

A similar results holds for $\left(\overline{\Delta H}_{mix}\right)_{Sn}$.

$$\begin{aligned}
\overline{H}_{Cd} - h_{Cd} &= \alpha 0.4^2 \\
&= 2080 \text{ [J/mol]} \\
\overline{H}_{Sn} - h_{Sn} &= \alpha 0.6^2 \\
&= 4680 \text{ [J/mol]}
\end{aligned}$$

[+3 points]

(c) The Gibbs-Duhem equation for this system states that

$$n_{Cd} d\overline{H}_{Cd} + n_{Sn} d\overline{H}_{Sn} = 0$$

We can substitute into this equation our results from part (a), differentiate with respect to n_{Cd}, and note that h_{Cd} and h_{Sn} are pure-species properties and thus do not change with respect to the number of moles.

$$\begin{aligned}
n_{Cd}\frac{d\overline{H}_{Cd}}{dn_{Cd}} + n_{Sn}\frac{d\overline{H}_{Sn}}{dn_{Cd}} &= n_{Cd}\frac{d\left(\left(\overline{\Delta H}_{mix}\right)_{Cd} + h_{Cd}\right)}{dn_{Cd}} + n_{Sn}\frac{d\left(\left(\overline{\Delta H}_{mix}\right)_{Sn} + h_{Sn}\right)}{dn_{Cd}} \\
&= n_{Cd}\frac{d\left(\overline{\Delta H}_{mix}\right)_{Cd}}{dn_{Cd}} + n_{Sn}\frac{d\left(\overline{\Delta H}_{mix}\right)_{Sn}}{dn_{Cd}} \\
&= n_{Cd}\frac{-2\alpha n_{Sn}^2}{\left(n_{Cd}+n_{Sn}\right)^3} + n_{Sn}\frac{2\alpha n_{Cd} n_{Sn}}{\left(n_{Cd}+n_{Sn}\right)^3} \\
&= 0
\end{aligned}$$

[+2 points]
(d) To use the graphical method, we need an equation of the form:

$$\Delta h_{mix} = \text{intercept} + x_{Cd}\text{slope}$$

There are two ways we can derive this equation. The more rigorous way is described first. Start with the definition of Δh_{mix}

$$\begin{aligned}
\Delta h_{mix} &= h - X_{Cd}h_{Cd} - X_{Sn}h_{Sn} \\
&= h - X_{Cd}h_{Cd} - \left(1 - X_{Cd}\right)h_{Sn}
\end{aligned}$$

Next, we need to evaluate the term: $\left(\frac{\partial h}{\partial X_{Cd}}\right)_{T,P}$. We know from the text that $\overline{H}_{Sn} \neq \frac{1}{n}\left(\frac{\partial K}{\partial X_{Sn}}\right)_{T,P}$. However, after some algebra, it can be shown that

$$\overline{H}_{Sn} = h - X_{Cd}\left(\frac{\partial h}{\partial X_{Cd}}\right)_{T,P}$$

From which it follows that:

$$\left(\frac{\partial h}{\partial X_{Cd}}\right)_{T,P} = -\frac{\overline{H}_{Sn} - h}{X_{Cd}}$$

Next we differentiate the expression for Δh_{mix} with respect to X_{Cd}, then multiply by X_{Cd}, analogous to equations 6.60 - 6.64 in the text:

$$\begin{aligned}
\Delta h_{mix} &= h - X_{Cd}h_{Cd} - (1 - X_{Cd})\, h_{Sn} \\
\frac{d\Delta h_{mix}}{dX_{Cd}} &= \frac{dh}{dX_{Cd}} - h_{Cd} + h_{Sn} \\
X_{Cd}\frac{d\Delta h_{mix}}{dX_{Cd}} &= X_{Cd}\left(-\frac{\overline{H}_{Sn} - h}{X_{Cd}} - h_{Cd} + h_{Sn}\right) \\
&= -\overline{H}_{Sn} + h - X_{Cd}h_{Cd} + X_{Cd}h_{Sn} \\
&= -\overline{H}_{Sn} + h - X_{Cd}h_{Cd} - (1 - X_{Cd})h_{Sn} + h_{Sn} \\
&= -\overline{H}_{Sn} + \Delta h_{mix} + h_{Sn}
\end{aligned}$$

From which it follows that:

$$\Delta h_{mix} = \overline{H}_{Sn} - h_{Sn} + X_{Cd}\frac{d\Delta h_{mix}}{dX_{Cd}}$$

Alternatively, we can use Equation 6.65, and replace k with Δh_{mix}. The result is:

$$\left(\overline{\Delta H}_{mix}\right)_{Sn} = \Delta h_{mix} - X_{Cd}\frac{d\Delta h_{mix}}{dX_{Cd}}$$

which, when you substitute the result from part (a) into the left-hand side and rearrange, also yields:

$$\Delta h_{mix} = \overline{H}_{Sn} - h_{Sn} + X_{Cd}\frac{d\Delta h_{mix}}{dX_{Cd}}$$

Thus, the term in question, $\overline{H}_{Sn} - h_{Sn}$, is simply the intercept. A similar result holds for $\overline{H}_{Cd} - h_{Cd}$.

As long as you get this equation, [+2 point]

From graphical analysis, if we draw the tangent line at $X_{Cd} = 0.6$, the two intercepts are:

$$
\begin{aligned}
\overline{H}_{Cd} - h_{Cd} &= 2200 \text{ [J/mol]} \\
\overline{H}_{Sn} - h_{Sn} &= 4800 \text{ [J/mol]}
\end{aligned}
$$

which is pretty close to the values from part (b).
[+1 point]