

# Homework 1: Problem 2.51

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Define the system as the total amount of  $\text{H}_2\text{O}$  in the glass. No mass enters or exits the system, so it is closed. We're told it is adiabatic, so no heat is exchanged with the surrounding, so  $Q = 0$ . Assume for simplicity that the volume change due to ice melting is negligible, so  $W = 0$ . Finally, note that there is no change in kinetic or potential energy. Thus, the energy balance for the system simplifies to:  $\Delta U = 0$ . Similarly, since  $Pv$  remain constant, the entire energy balance simplifies to:

$$\Delta H = 0 \text{ [ +2 points ]}$$

(a) There are two ways you can solve the problem. The first method is perhaps more intuitive. The second method is important to understand and will be more useful later in the course. Throughout the solution, the subscript  $l$  refers to the liquid phase, and the subscript  $i$  refers to the solid phase.

## First Method

The total change in enthalpy is the balance between the change in enthalpy for the liquid and the change in enthalpy for the solid:

$$\Delta H = \Delta H_l + \Delta H_i$$

It follows that:  $\Delta H_l = -\Delta H_i$ . Next, recall the relationship between enthalpy and the heat capacity:  $\Delta h = \int_{T_1}^{T_2} c_p(T) dT$ . For condensed phases, the heat capacity often has a linear temperature dependence, so  $\Delta h = c_p(T_2 - T_1)$ . Thus we have:

$$\begin{aligned} \Delta H_l &= n_l \Delta h_l \\ &= n_l c_{p,l} (T_2 - T_1) \\ &= n_l c_{p,l} (T_{final} - T_{initial,l}) \text{ [ +2 point ]} \end{aligned}$$

where  $T_{initial,l} = 25^\circ\text{C}$ , and  $T_{final}$  is the unknown quantity we are asked to solve. A similar result holds for the solid phase:

$$\Delta H_i = n_i c_{p_i} (T_{final} - T_{initial,i})$$

where  $T_{initial,i} = -10^\circ\text{C}$ . Here, however, there is a complication: the ice will melt, so the heat capacity must change. Furthermore, we must include the latent heat. Thus, we separate the enthalpy change into three parts: the warming of the ice to its melting point (sensible heat); the melting of the ice (latent heat); and the warming of the freshly melted water to its final temperature (sensible heat):

$$\begin{aligned}\Delta H_i &= n_i c_{p_i} (T_{final} - T_{initial,i}) \\ &= n_i [c_{p_i} (T_{melt} - T_{initial,i}) + \Delta h_{melt} + c_{p_l} (T_{final} - T_{melt})] \quad [+2 \text{ point}]\end{aligned}$$

Combining these equations and solving for  $T_{final}$ , we get:

$$\begin{aligned}n_l c_{p_l} (T_{final} - T_{initial,l}) &= -n_i [c_{p_i} (T_{melt} - T_{initial,i}) + \Delta h_{melt} + c_{p_l} (T_{final} - T_{melt})] \\ (n_l + n_i) c_{p_l} T_{final} &= n_l c_{p_l} T_{initial,l} - n_i [c_{p_i} (T_{melt} - T_{initial,i}) + \Delta h_{melt} - c_{p_l} T_{melt}] \\ T_{final} &= \frac{n_l}{(n_l + n_i)} T_{initial,l} - \frac{n_i}{(n_l + n_i) c_{p_l}} [c_{p_i} (T_{melt} - T_{initial,i}) + \Delta h_{melt} - c_{p_l} T_{melt}]\end{aligned}$$

Using Table A.2.3, we find that the heat capacities for liquid and solid water are:

$$\begin{aligned}c_{p_l} &= 9.069R \\ &= 75.3997 \text{ [J/mol-K]} \\ c_{p_i} &= 4.196R \\ &= 34.6611 \text{ [J/mol-K]}\end{aligned}$$

where  $R = 8.314 \text{ J/mol-K}$ . Next, assume that the density of liquid water between 0 and  $25^\circ\text{C}$  is:  $\rho_l = 1 \text{ g/mL}$ , and that the molecular weight of water is  $MW = 18 \text{ g/mol}$ . Thus, we can determine the number of moles for liquid water and ice, respectively, as:

$$\begin{aligned}
n_l &= \frac{V_l \rho_l}{MW} \\
&= \frac{400 \text{ [mL]} \cdot 1 \text{ [g/mL]}}{18 \text{ [g/mol]}} \\
&= 22.22 \text{ [moles]} \\
n_i &= \frac{m_i}{MW} \\
&= \frac{100 \text{ [g]}}{18 \text{ [g/mol]}} \\
&= 5.55 \text{ [moles]}
\end{aligned}$$

Next, we are given the latent heat of fusion, but we need the latent heat of melting:  $\Delta h_{melt} = -\Delta h_{fus} = 6.0 \text{ kJ/mol}$ . Putting it all together, we get:

$$\begin{aligned}
T_{final} &= \frac{22.22 \text{ [moles]}}{27.77 \text{ [moles]}} 25^\circ\text{C} \\
&- \frac{5.55 \text{ [moles]}}{27.77 \text{ [moles]}} \frac{34.6611 \text{ [J/mol-K]}}{75.3997 \text{ [J/mol-K]}} (0 - -10^\circ\text{C}) \\
&- \frac{5.55 \text{ [moles]}}{27.77 \text{ [moles]}} \frac{6.0 \text{ [kJ/mol]}}{75.3997 \text{ [J/mol-K]}} \\
&+ \frac{5.55 \text{ [moles]}}{27.77 \text{ [moles]}} 0^\circ\text{C} \\
&= 3.18^\circ\text{C} \text{ [ +2 point ]}
\end{aligned}$$

### Second Method

This method might be less intuitive, but it will better serve you for further problem sets. Instead of comparing the change in enthalpy between the liquid and solid phase, we compare the total initial enthalpy to the total final enthalpy:

$$\begin{aligned}
\Delta H &= 0 \\
H_{initial} &= H_{final}
\end{aligned}$$

In order to calculate the enthalpy of liquid water at  $25^\circ\text{C}$ , we must first define a reference temperature. Why? Recall the expression relating the enthalpy to the heat capacity:  $\Delta h = \int_{T_1}^{T_2} c_p(T) dT$ . If we want to know the enthalpy at  $h(T = T_2)$ ,

it must be relative to some other temperature  $h(T = T_1)$ . That temperature is the reference temperature. You'll spend a lot of time this semester using reference states, so get used to the idea now. We will drop the  $\Delta$  for convenience and just write the initial enthalpy of liquid water as:  $h_{initial,l} = c_{p_l}(T_{initial,l} - T_{ref})$ . Similarly,  $h_{initial,i} = c_{p_i}(T_{initial,i} - T_{ref})$ . The initial enthalpy is:

$$\begin{aligned} H_{initial} &= n_l h_{initial,l} + n_i h_{initial,i} \\ &= n_l c_{p_l}(T_{initial,l} - T_{ref}) + n_i c_{p_i}(T_{initial,i} - T_{ref}) \quad [ +2 \text{ point } ] \end{aligned}$$

The final enthalpy contains the enthalpy of the initial liquid water, cooled to its final state, plus the enthalpy of the warmed ice, plus the enthalpy of the melted ice, plus the enthalpy of the warmed freshly melted liquid. As in the previous problem, we separate the change in enthalpy for the ice into the sensible and latent heat. In all cases, these enthalpies MUST be calculated to the same reference state. In other words, if you choose one reference state for the left-hand side of an equation, you must choose the same reference for the right-hand side:

$$\begin{aligned} H_{final} &= n_l h_{final,l} + n_i h_{final,i} \\ &= n_l c_{p_l}(T_{final} - T_{ref}) + n_i [c_{p_i}(T_{melt} - T_{ref}) + \Delta h_{melt} + c_{p_l}(T_{final} - T_{melt})] \quad [ +2 \text{ point } ] \end{aligned}$$

Equating the initial and final enthalpy yields:

$$\begin{aligned} n_l c_{p_l}(T_{initial,l} - T_{ref}) + n_i c_{p_i}(T_{initial,i} - T_{ref}) &= n_l c_{p_l}(T_{final} - T_{ref}) \\ &+ n_i [c_{p_i}(T_{melt} - T_{ref}) + \Delta h_{melt} + c_{p_l}(T_{final} - T_{melt})] \end{aligned}$$

Solving the equation for the final temperature yields:

$$\begin{aligned} (n_l + n_i) c_{p_l} T_{final} &= -n_l c_{p_l} T_{ref} \\ &+ n_i [c_{p_i}(T_{melt} - T_{ref}) + \Delta h_{melt} + c_{p_l}(T_{final} - T_{melt})] \\ &- n_l c_{p_l}(T_{initial,l} - T_{ref}) - n_i c_{p_i}(T_{initial,i} - T_{ref}) \end{aligned}$$

Note that all the terms with  $T_{ref}$  cancel. If you don't like carrying those terms around, a convenient choice for this problem is  $T_{ref} = 0^\circ\text{C}$ . Either way, the equation reduces once again to:

$$\begin{aligned}
T_{final} &= \frac{n_l}{(n_l + n_i)} T_{initial,l} - \frac{n_i}{(n_l + n_i) c_{p_i}} [c_{p_i} (T_{melt} - T_{initial,i}) + \Delta h_{melt} - c_{p_l} T_{melt}] \\
&= 3.18^\circ\text{C} \text{ [ +2 point ]}
\end{aligned}$$

(b) As described in part (a), there are three effects that contribute to the total cooling of the initial 400 mL of liquid water: The warming of the ice from -10 to 0 ° C; the latent heat required to melt the ice; and the warming of the newly melting water from 0 to 3 ° C. As we saw in the first method, the total cooling of the water is balanced by the total warming of the ice, and the total cooling of the water is simply the heat capacity times time temperature change:

$$\begin{aligned}
Q_{total} &= n_l \Delta \hat{H}_l \\
&= n_l c_{p_l} (T_{final} - T_{initial}) \\
&= 22.22 \text{ [moles]} 75.3997 \text{ [J/mol-K]} (3.18 - 25)^\circ\text{C} \\
&= -36.557 \text{ [kJ]}
\end{aligned}$$

The initial 400 mL of water gave off 36.5 kJ of energy to warm the ice. Next, the cooling due to the melting is:

$$\begin{aligned}
Q_{latent} &= n_i \Delta h_{melt} \\
&= 5.55 \text{ [moles]} 6.0 \text{ [KJ/mol]} \\
&= 33.30 \text{ [kJ]}
\end{aligned}$$

Thus, the fraction of cooling achieved by the latent heat is:

$$\begin{aligned}
\frac{Q_{latent}}{Q_{total}} &= \frac{33.3}{36.557} \\
&= 91.1\% \text{ [2 points]}
\end{aligned}$$

The remainder of the cooling is attributed to the sensible heat absorbed by the 100 g H<sub>2</sub>O as it warms up first to the melting temperature and then to the final temperature.