Lecture 14

Heat Stored during Phase Changes

Last Time

Second Law of Thermodynamics

Alternative Statements

Clausius

Kelvin

Ostwald

Parellelism between First and Second Laws

The Change of Temperature with the Addition of Heat

Question: What is the temperature of solid water (ice)?

a $\approx 0°$ C

b ≈ 273K

c Any of the above (a and/or b)

d $\approx 10°$ C

e $\approx -10°$

f any of the above (d and/or e and/or c)

Consider a mole of ice at $-100°$C that has heat added to it at a constant rate ($\dot{q}$ = constant) and a constant pressure. (Slow enough so that the body has a uniform temperature; i.e., reversibly at constant atmospheric pressure). What will be the temperature as a function of time?

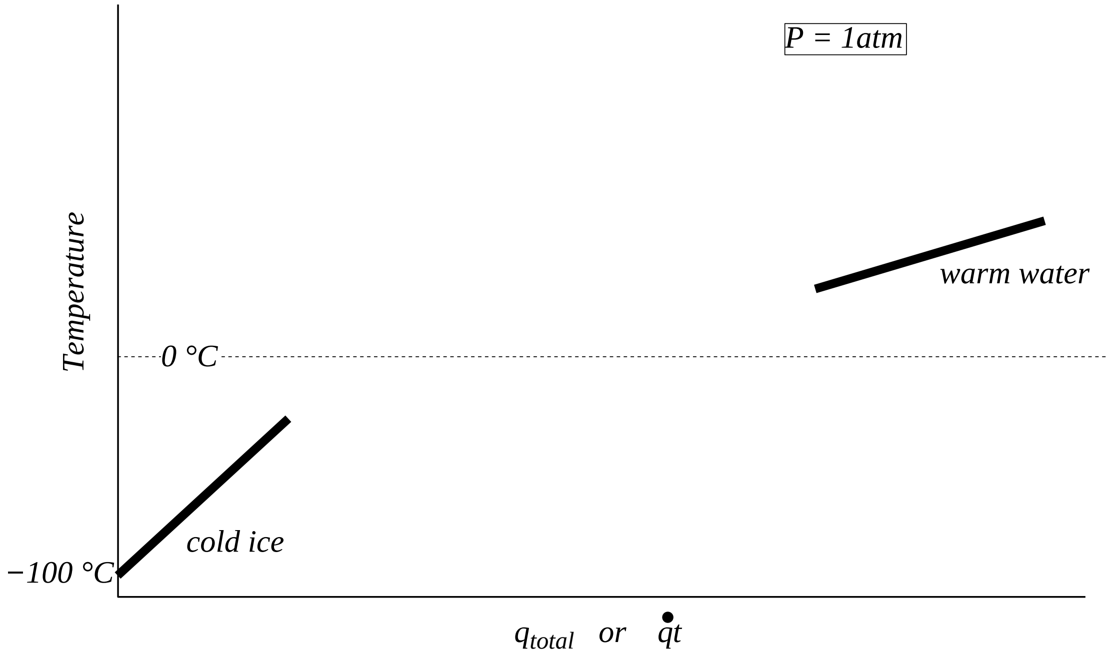

Figure 14-1: Heating up cold ice at a constant rate.

What is the slope of the initial part of the curve (Region I)?

$$\left(\frac{dq_{rev}}{dT}\right)_{P=\text{constant}} = C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{14-1}$$

Therefore the slope is $\frac{1}{C_P}$:

Region I Slope $= \frac{1}{C_{P(}\text{(solid)}}$

Region III Slope $= \frac{1}{C_{P(}\text{(liquid)}}$

Question: What is happening in Region II?

Question: What is the heat absorbed in Region II? Where does it go?

$$H(T = +0°) - H(T = -0°) > 0 \tag{14-2}$$

This is equivalent to the heat absorbed by the system at constant temperature—we identified this quantity with the state function enthalpy, $H = U + PV$. The change in the constant pressure heat state function ΔH, is the heat absorbed during the transformation.

Heat of Transformation

A positive ΔH means that heat was absorbed during the transformation, as in the case of melting (positive means that you have to add heat to make it happen). Reactions that have a positive ΔH are called "endothermic."

Let's consider the reverse transformation liquid → solid (solidification).

$$H(T = -0°) - H(T = +0°) = \Delta H_{\text{solidification}} = -\Delta H_{\text{melting}} \tag{14-3}$$

Solidification is typically "exothermic"—when something solidifies, heat is expelled (and has to be taken away as in the case of ice in the fridge).

Consider a plot the enthalpy as a function of T.

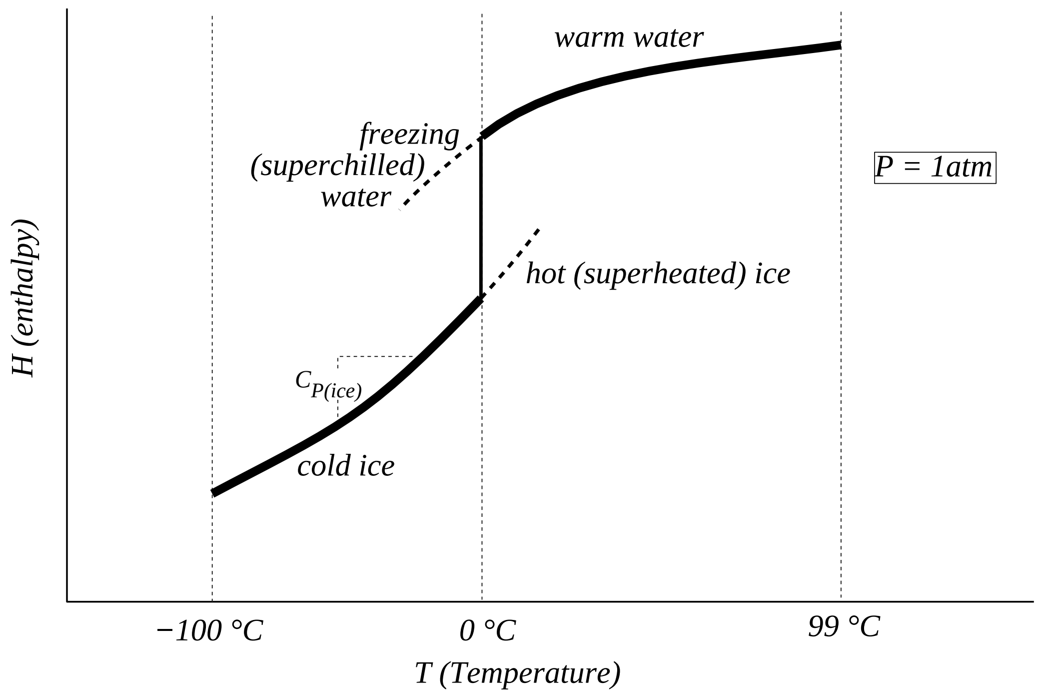

Figure 14-2: Enthalpy as a function of temperature at constant pressure.

Question: Where the "zero" is located on the ordinate axis.

Phase Fractions

Consider yet another way to characterize the system by introducing a parameter that is equal to the fraction of a particular phase that is present: the phase fraction:

$$
\begin{aligned}
f^{\text{solid}} &\equiv \text{fraction of system in solid state phase} \\
f^{\text{liquid}} &\equiv \text{fraction of system in liquid phase} \\
f^{\text{solid}} &= \frac{N^{\text{solid}}}{N^{\text{solid}} + N^{\text{liquid}}} = \frac{m^{\text{solid}}}{m^{\text{solid}} + m^{\text{liquid}}} \\
f^{\text{liquid}} &= \frac{N^{\text{liquid}}}{N^{\text{solid}} + N^{\text{liquid}}} = 1 - f^{\text{solid}}
\end{aligned}
\tag{14-4}
$$

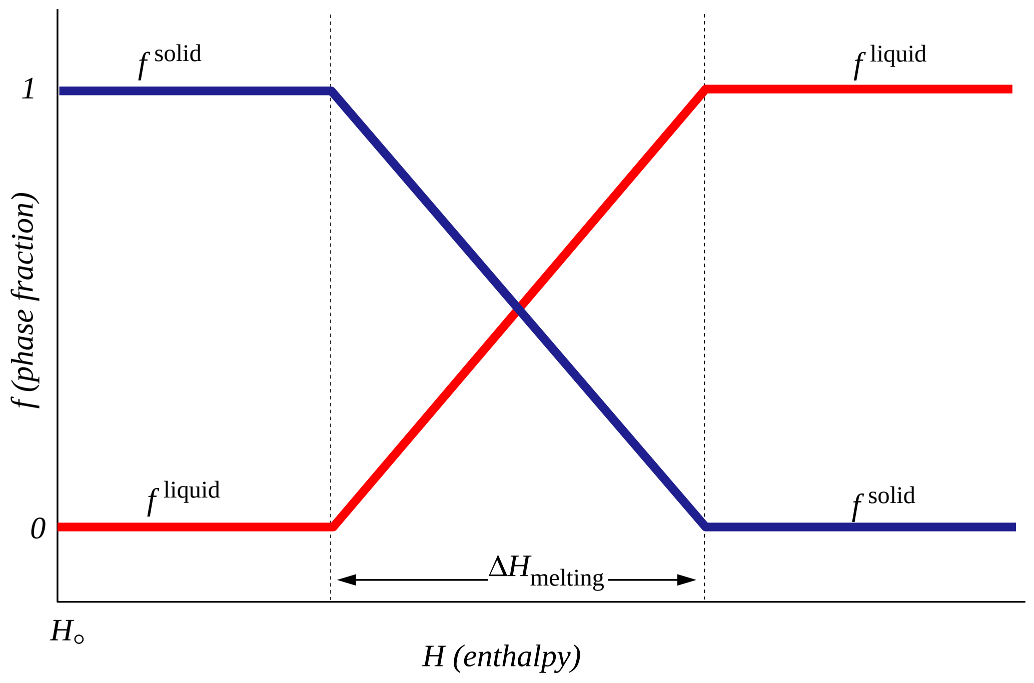

Figure 14-3: Phase fractions as function of total enthalpy of system.

Hot Ice Melts and Cold Water Freezes

To find the entropy change of the universe when **hot** ice melts, consider the following data:

Data for H_2O at 273°K and 1 atm		
Quantity	Symbol	Data
Molar Enthalpy of Melting	$\Delta \overline{H}_{\text{melt}}$	$6008 \frac{\text{J}}{\text{mole}}$
Molar Entropy of liquid H_2O	$\overline{S_{H_2O\,\text{liquid}}}$	$63.2 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Entropy of solid H_2O	$\overline{S_{H_2O\,\text{solid}}}$	$41.0 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Heat Capacity of liquid H_2O	$\overline{C_{P_{H_2O\,\text{liquid}}}}$	$75.44 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Heat Capacity of solid H_2O	$\overline{C_{P_{H_2O\,\text{solid}}}}$	$38.0 \frac{\text{J}}{\text{mole}^\circ\text{K}}$

As a first approximation, ignore difference in heat capacities:

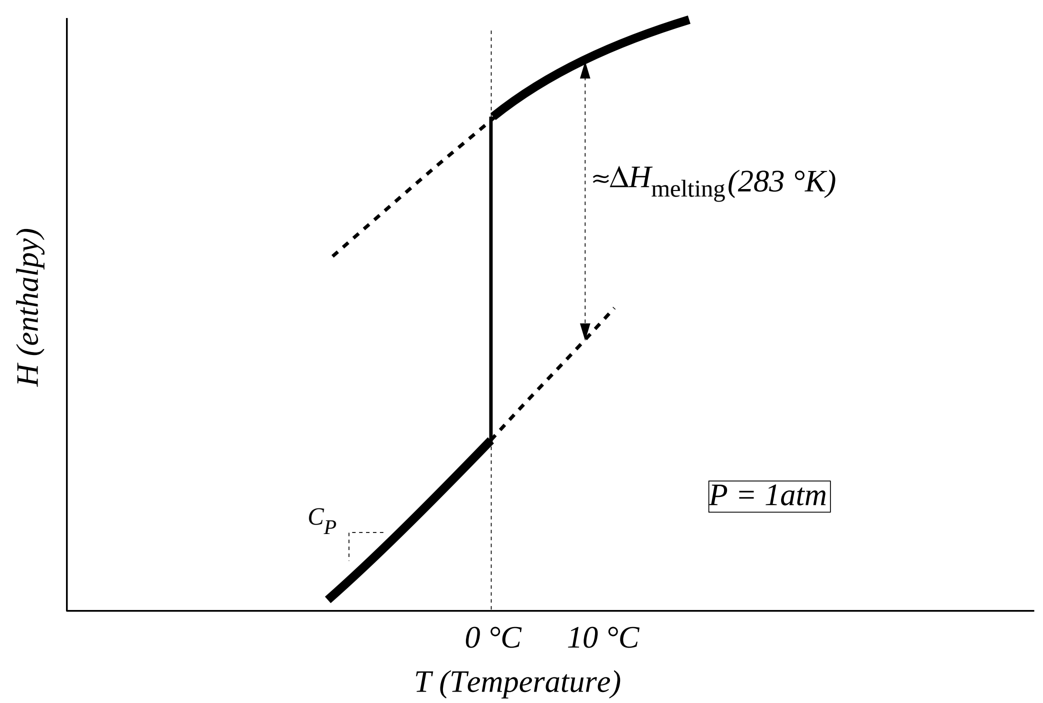

Figure 14-4: If the difference in heat capacities is ignored, $\Delta\overline{H}$ independent of temperature

Suppose our ice-system is enclosed in a giant reservoir at 10°C (the reservoir is so big that its temperature doesn't change, imagine cooling down the ocean with an ice-cube)

$$H^{\text{total}} = H_{\text{res.}} + H_{\text{H}_2\text{O}} \tag{14-5}$$

because P is constant and we suppose that no other heat is added to the system from any other source (constant pressure and adiabatic system).

Suppose the ice melts, then

$$\begin{aligned} \Delta H_{\text{res.}} &= -6008\text{J} \\ \Delta H_{\text{H}_2\text{O}} &= 6008\text{J} \end{aligned} \tag{14-6}$$

Therefore, $\Delta H_{total} = 0$ However,

$$\Delta S_{\text{res.}} = \frac{\Delta q}{T} = \frac{-6008}{283} = -21.3 \frac{\text{J}}{\text{mole}^\circ\text{K}} \tag{14-7}$$

The entropy of the reservoir **decreases.**

However the entropy change for our mole of ice that melts is:

$$\Delta S^{\text{total}} = 1.1 \frac{\text{J}}{^{\circ}\text{K}} \tag{14-8}$$

This corresponds to what we observe, hot ice would melt and the entropy of the universe increases.

Consider the melting of cold ice immersed in $-10°$C reservoir:

$$\Delta S_{\text{universe}} = \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{res.}} = \tag{14-9}$$

Entropy of the universe decreases and this is not observed to happen—good!

Hot ice melts and cold water freezes and the entropy of the universe always increases.