

Lecture 5: 09.21.05 Heat storage and release in phase transitions

Today:

LAST TIME	2
<i>Calculation of internal energy changes</i>	3
HEAT STORED AND RELEASED DURING PHASE CHANGES	4
<i>Adding heat to materials</i>	4
<i>Adding heat to material... at a phase transition</i>	5
ACCOUNTING FOR THERMAL ENERGY IN A MATERIAL: ENTHALPY ¹	6
<i>A new thermodynamic function to help us analyze the heat storage/release in phase transitions</i>	6
<i>Enthalpies, phase fraction, and heat capacities at first-order phase transitions</i>	8
Phase fractions during a transformation	9
Heat capacity behavior at a first-order phase transition	9
<i>Determination of entropies of first-order phase transitions</i>	10
<i>Phase transitions of metastable and unstable materials</i>	10
APPLICATION EXAMPLE: PHASE CHANGE MATERIALS TECHNOLOGY	12
<i>Materials for solar energy storage</i>	12
EXTRA: DISCOVERY OF LATENT HEAT ⁵	13
REFERENCES	14

Reading: Engel and Reid: 2.8, 3.4, 4.6

Supplementary Reading: -

ANNOUNCEMENTS:

PS 2 POSTED, DUE FRI., SEPT. 30TH

Last time

- Heat Capacities: A quantity to measure the ability of a material to store energy transferred in the form of heat:

$$C \equiv \frac{dq_{rev}}{dT}$$

$$C_p = \left(\frac{dq_{rev}}{dT} \right)_p \quad \text{CONST. P}$$

$$C_v = \left(\frac{dq_{rev}}{dT} \right)_V$$

- We can make use of the defined zero-point of entropy (and heat capacities) to calculate absolute entropies: For example, if we change the temperature of an aluminum sample from $T=293\text{K}$ to $T=400\text{K}$ by a constant pressure process, we get:

$$C_p = \left(\frac{dq_{rev}}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$\rightarrow ds = \frac{dq_{rev}}{T}$

\rightarrow REARRANGING: $\frac{C_p(T)dT}{T} = dS$

\downarrow INTEGRATE

$$\int_{T_i}^{T_f} \frac{C_p(T)}{T} dT = \int dS = \Delta S$$

CALCULATE ENTROPY CHANGES \rightarrow STATE FUNCT

- ...Note that because the heat capacity approaches 0 at 0K, it would be unwise to assume C_p is a constant when integrating starting at $T=0\text{K}$.

Calculation of internal energy changes

- We've so far only been able to calculate changes in internal energy for ideal gases using the first law combined with the ideal gas law. The heat capacity gives us a means to determine changes in internal energy for arbitrary materials if we know the dependence of the heat capacity on temperature. For a constant volume process:

$$C_v = \left(\frac{dq_{rev}}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v$$

$$\begin{aligned} \hookrightarrow dU &= dq + dw \\ &= dq_{rev} - PdV \end{aligned}$$

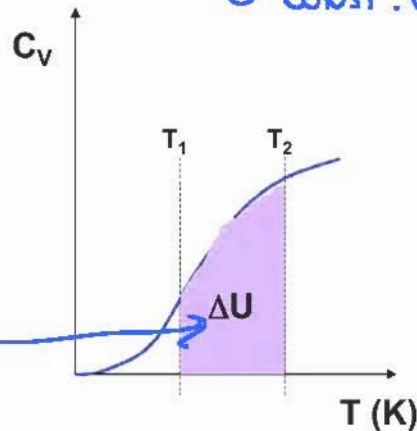
\downarrow
CONST. VOL!

REARRANGING:

$$dU = C_v dT$$

$$\int dU = \int_{T_1}^{T_2} C_v(T) dT$$

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$



TOTAL HEAT CAPACITY

$$\bar{C}_v = \frac{J}{\text{mole} \cdot K}$$

MOLAR
HEAT
CAPACITY

$$\Delta U = \int_{T_1}^{T_2} \bar{C}_v dT$$

\uparrow
 C_v

DIFFERENCES IN THERMO QUANTITIES

DEFINE THE BEHAVIOR OF REAL PROCESSES.

Heat stored and released during phase changes

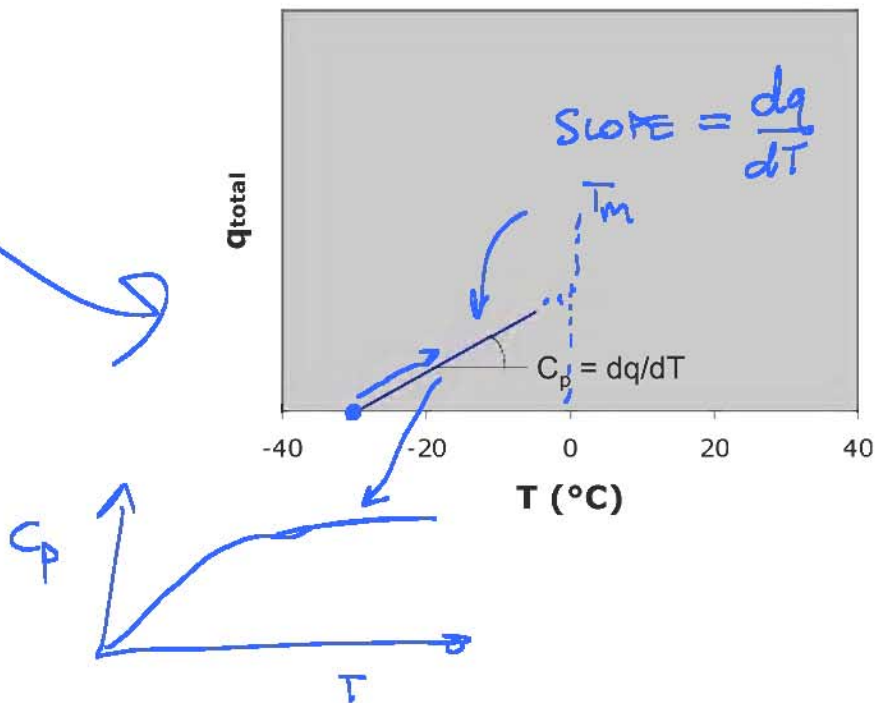
Adding heat to materials

- Thus, if we add heat to a material slowly (so that the temperature remains uniform in the material- a reversible process!) we can relate the temperature change in the material to the heat capacity:

$$C = \left(\frac{dq_{rev}}{dT} \right)_P \rightarrow dq_{rev} = C_p dT$$

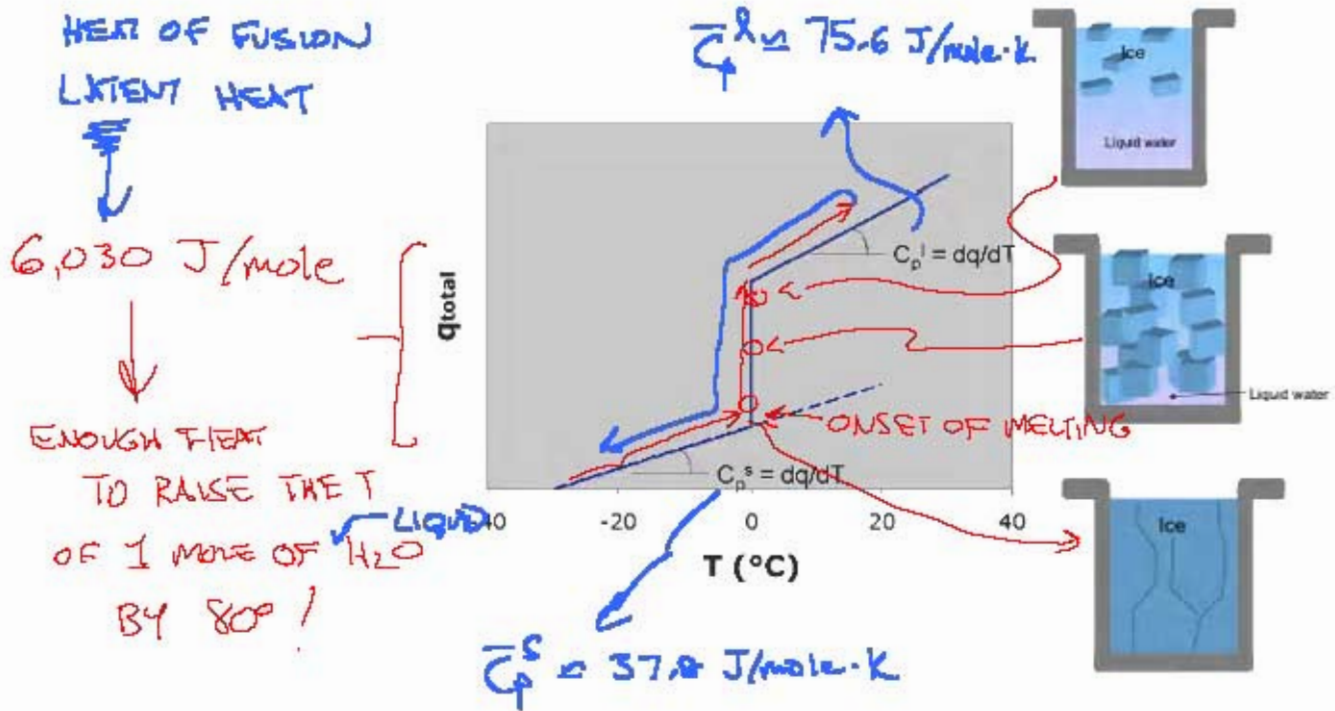
$$q_{rev} = \int_{T_i}^{T_f} C_p(T) dT$$

- Thinking of this reversible process graphically, the heat capacity is the slope dq/dT of a plot of the heat q_{total} added to a system vs. the system's temperature. Suppose we slowly add heat to a block of ice that started at -30°C :



Adding heat to material... at a phase transition

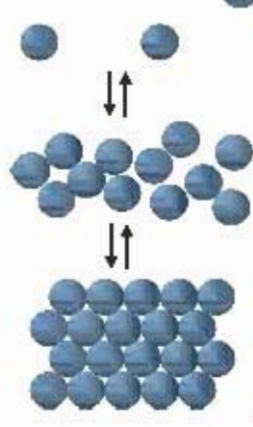
- Considering the previous graph again, what happens when we continue heating our block of ice to $T = 0^\circ\text{C}$ - the melting temperature (T_m) of ice? Experimentally, the following is observed:



- If we considered an inverse of this process and cooled a glass of water from 20°C very slowly down to -20°C , we would find that the temperature would vary as heat was removed from the glass following the curve above in reverse.
- The storage and release of heat is seen at many **first order phase transitions**:

- Solid \leftrightarrow liquid heat of melting
- Liquid \leftrightarrow gas heat of vaporization
- Solid \leftrightarrow gas heat of sublimation

SOLID \leftrightarrow SOLID SOLID-SOLID HEAT OF TRANSFORMATION
 α β



G HEAT ABSORBED AT PHASE TRANSITION IS THE ENERGY REQUIRED TO BREAK BONDS IN THE LOWER-T STATE



- NOT CHANGING TEMP. DURING THIS PROCESS
 ↓
 - NOT CHANGING KINETIC ENERGY OF SYSTEM

HEAT IS NOT A STATE FUNCTION → SO HOW DO WE ACCOUNT FOR

Accounting for thermal energy in a material: enthalpy¹

THERMAL ENERGY IN A MATERIAL?

A new thermodynamic function to help us analyze the heat storage/release in phase transitions

- Using the first law, we know we can write the following for a simple material that undergoes a reversible process:

$$dU = dq + dw = TdS - PdV$$

- The differential dU can either be thought of as a small change in the total internal energy of the system, or as the internal energy of a tiny portion of a large system, (illustrated below). Consider a material divided up into tiny subsystems such that each small subsystem obeyed the equation above. We could then integrate over all the subsystems to add up the total internal energy. What would be left in the total internal energy if we then subtracted out the 'compressive' energy- that portion of the internal energy arising from external pressure?

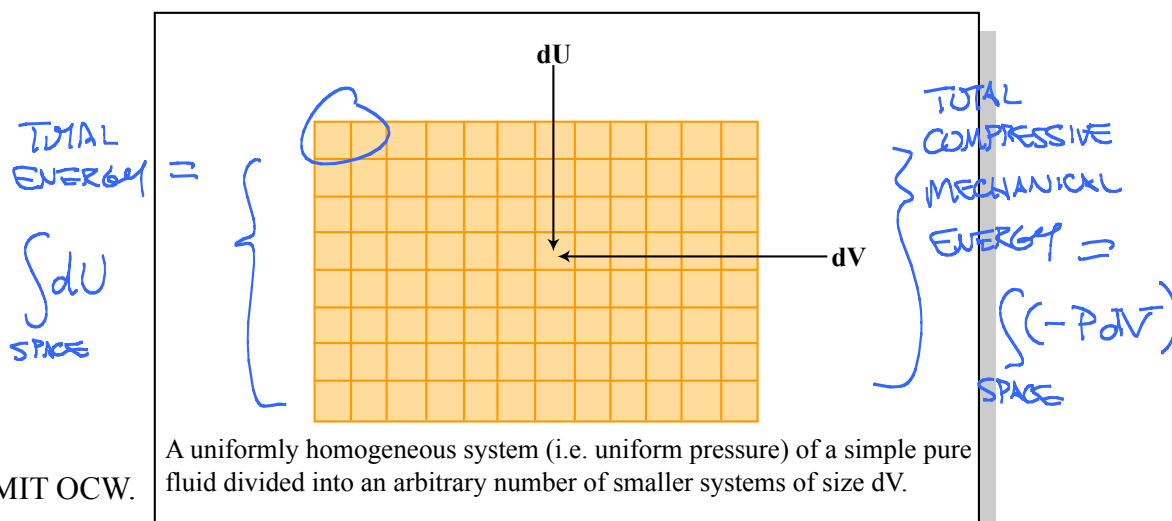


Figure by MIT OCW.

- Total internal energy – total compressive mechanical energy

$$\text{TOTAL } U - \text{TOTAL 'MECHANICAL' ENERGY} = \int dU - \left(\int (-PdV) \right) = U + PV$$

- This new quantity is a thermodynamic state function, and is defined as the enthalpy $H(S,P,N)$:

ENTHALPY $H(S,P) \equiv U + PV$

- It is useful to write out the differential of the enthalpy and look at its components:

$$dH = dU + PdV + VdP$$

↓ REV. PROCESS

$$= TdS - PdV + PdV + VdP$$

$$dH(S,P) = TdS + VdP$$

- Looking at the differential expression for the enthalpy, we see that in a constant pressure process, the change in enthalpy of the system is equal to the thermal energy transferred to the system:

$$\text{CONST. } P: \quad dH = TdS + \cancel{VdP} = dq_{\text{rev}}$$

$$\Delta H = \int dH = q_{\text{rev}} (\text{CONST. } P)$$

- This expression is very useful since it states that we can experimentally measure the enthalpy by measuring the heat transfer occurring in a process at constant pressure.

- The enthalpy is thus also related to the constant pressure heat capacity:

$$C_p = \left(\frac{dq_{\text{rev}}}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$\hookrightarrow (dq_{\text{rev}})_p = dH$$

- Let's now return to our glass of ice/water and see what the enthalpy is doing during the phase transition solid \rightarrow liquid that occurs as we heat a block of ice.
 - Because we are considering a reversible, constant pressure process, $dH = dq_{rev}$:

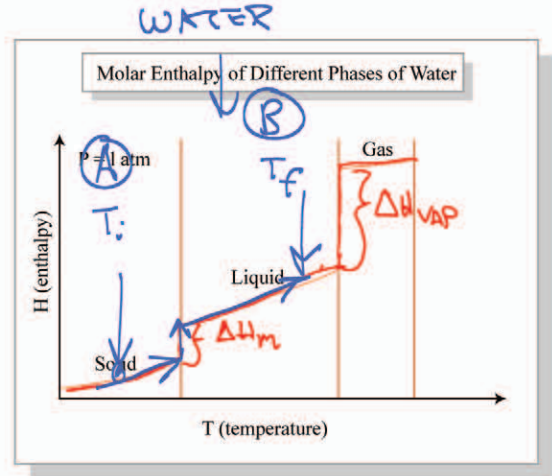
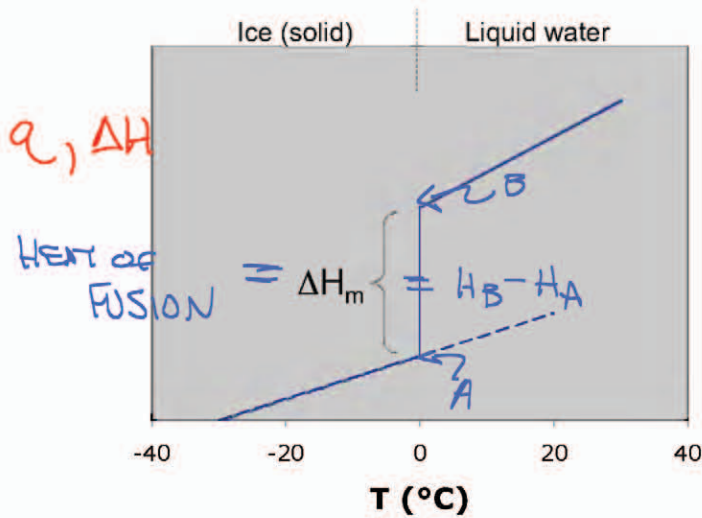


Figure by MIT OCW.

molar enthalpy of dif erent phases of water

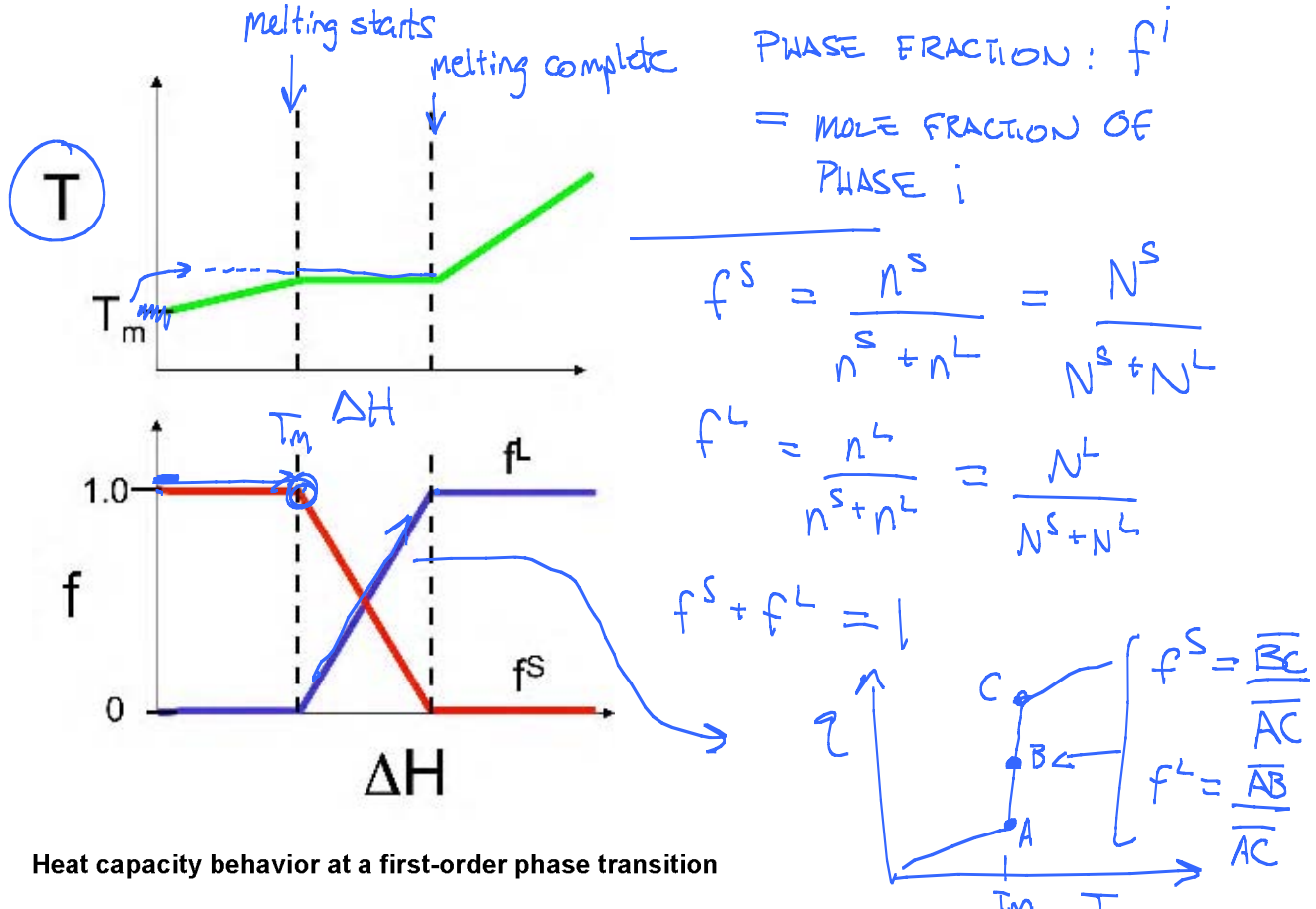
- The change in enthalpy at the phase transition ΔH_m is called the **enthalpy of melting**. (Some texts refer to it as a heat of transformation, heat of fusion, or latent heat of fusion). It is thermal energy that is stored in the solid upon freezing, and released again on melting.

Heat transfers, and thereby enthalpy changes, can be measured experimental y using devices known as calorimeters- you wil see this firsthand in 3.014.

$$q_{TOTAL} A \rightarrow B = \int_{T_i}^{T_m} C_p^s(T) dT + \Delta H_m + \int_{T_m}^{T_f} C_p^l(T) dT$$

Phase fractions during a transformation

- The enthalpy of melting measures the amount of heat needed at constant pressure to completely transform a sample from a solid to liquid- at intermediate amounts of heat transfer, the system is an equilibrium mixture of solid and liquid. If we plot the phase fraction f vs. the enthalpy:



Heat capacity behavior at a first-order phase transition

- Similar to the enthalpy, the heat capacity must show a discontinuity at the phase transition- since C_p is the derivative of the enthalpy with respect to temperature, it is **undefined** at the phase transition.

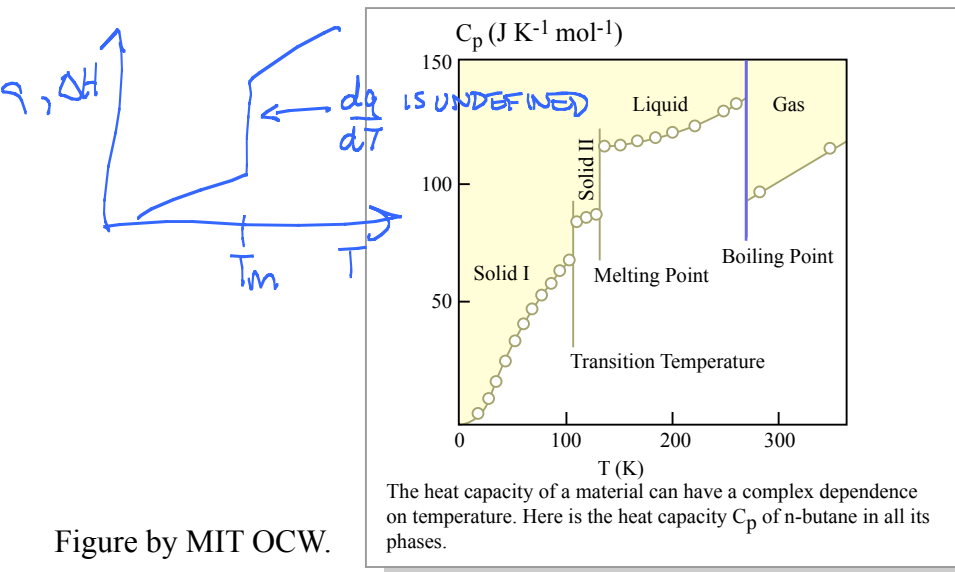


Figure by MIT OCW.

Determination of entropies of first-order phase transitions

- Measuring heat transfer gives us the enthalpy of phase transitions directly- but what about the entropy changes occurring in a system at these transitions? Suppose we perform a constant pressure experiment, heating a sample through its melting point. The heat released on melting is the enthalpy of melting:

TOTAL HEAT TO MELT $q_m = \Delta H_m @ \text{CONST. } P$

- But we also know from the reversible process definition of the entropy:

$$dq_{\text{rev}} = T ds$$

$$q_m = \int T ds = T_m \int ds = T_m \Delta S_m$$

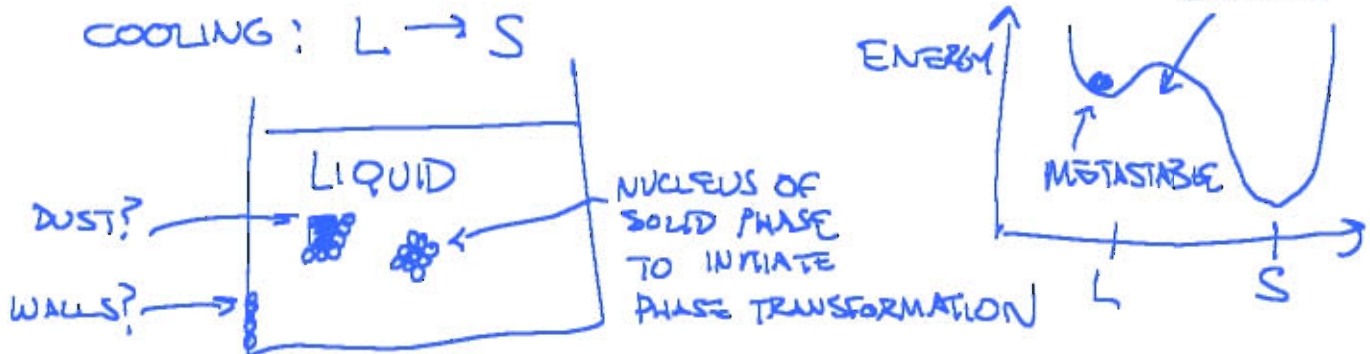
- Thus we find that the entropy of melting can be directly calculated from the enthalpy of melting and the melting temperature:

$$q_m = \Delta H_m = T_m \Delta S_m$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

Phase transitions of metastable and unstable materials

- Liquids can be **supercooled**- cooled to temperatures below their equilibrium freezing points. Likewise, solids can be **superheated**- heated to temperatures above the melting point. Such phases are unstable or metastable and will readily transform to the equilibrium state.
- Supercooling and superheating are possible when an energy barrier to formation of the stable phase exists (you will study this in detail next term):

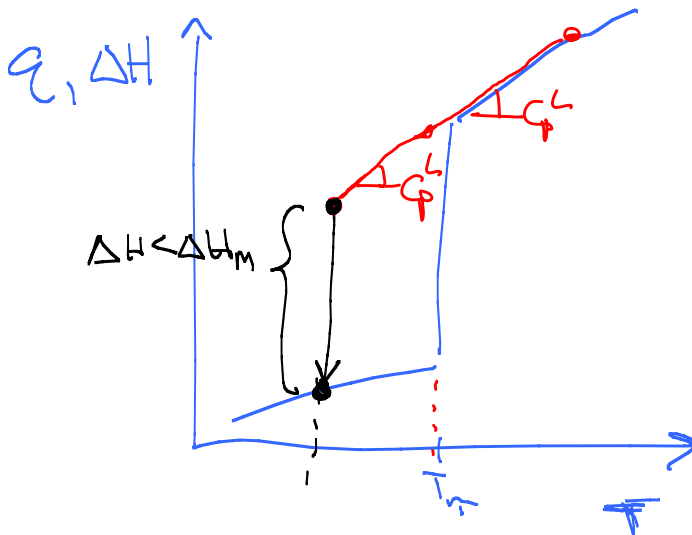


Substance	Maximum Observed Super-cooling (K)
Mercury	88
Cadmium	110
Silver	227
Iron	286
Nickel	365
Niobium	525 ←

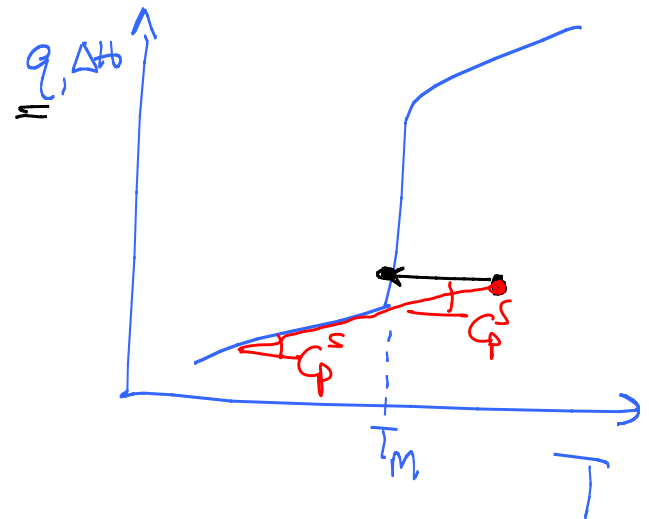
Figure by MIT OCW.

- Calculation of properties, such as enthalpy, entropy, or heat capacity of super-cooled or superheated phases is done by extrapolating the behavior of the relevant thermodynamic quantity to temperatures outside the equilibrium stability range:

SUPERCOOLING:



SUPERHEATING:



- Many solids cannot be superheated or only survive superheating of a few degrees, due to the perturbing influence of the free surface of the solid:

UNSATISFIED BONDS

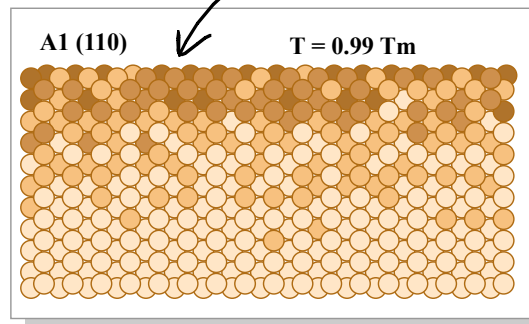
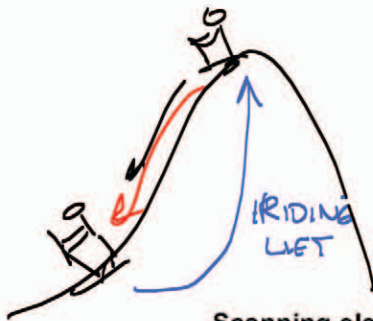


Figure by MIT OCW.

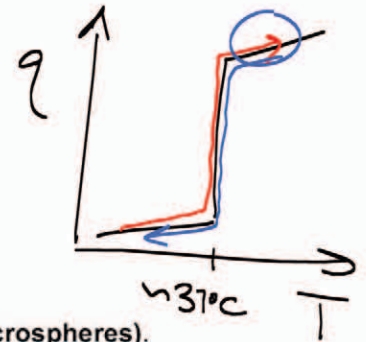
- Atoms at the surface of a material have many unsatisfied bonds, allowing much greater freedom to respond to thermal energy with vibrations.⁴ Surface energy thus drives the surface atoms to melt at a lower temperature than the bulk (the atoms away from the surface) material.

Application Example: Phase change materials technology

- Materials with phase transitions at convenient temperatures can be used, literally, to store and release heat under desired conditions.



Scanning electron micrograph of fabric with embedded PCM (microspheres).



Materials for solar energy storage

'PHASE CHANGE DRYWALL'
ROADS THAT DON'T ICE AT NIGHT

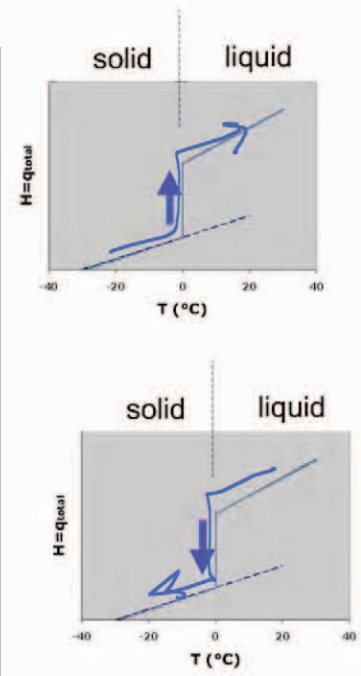
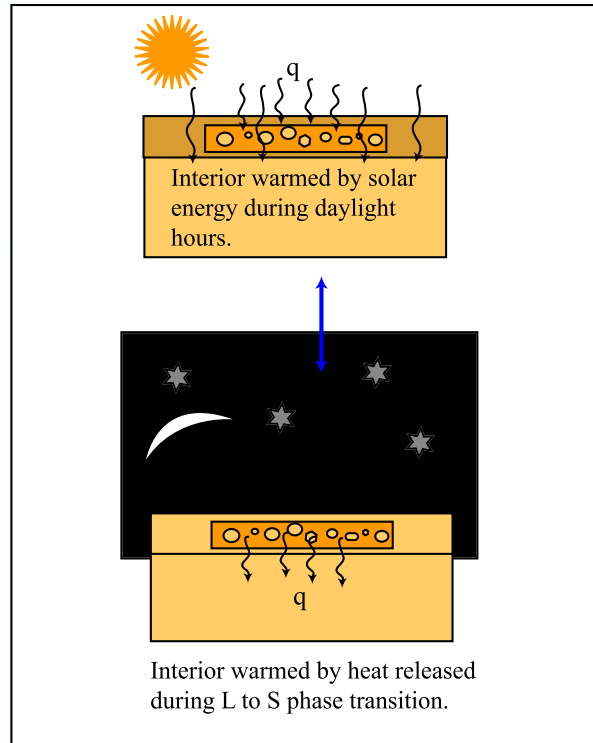
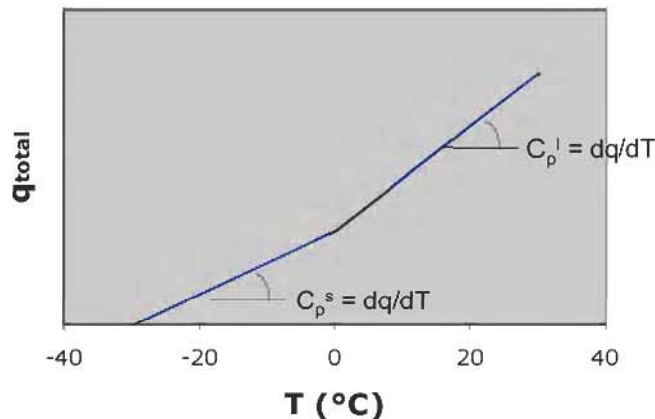


Figure by MIT OCW.

Extra: Discovery of latent heat⁵

- In the 1700's, it was thought that once a material was uniformly heated to its melting point, addition of only a tiny additional amount of heat would melt the entire sample- in other words, as soon as heat was added to raise the temperature of the material above T_m , the phase transformation spontaneously occurred with no extra input. Joseph Black (1728-1799) wrote the following observation in response to this idea:⁵
 - "If we attend to the manner in which ice and snow melt when exposed to the air of a warm room, or when a thaw succeeds to frost, we can easily perceive that, however cold they might be at first, they soon warm up to their melting point and begin to melt at their surfaces. And if the common opinion had been well founded- if the complete change of them into water required only the further addition of a very small quantity of heat- the mass, though of a considerable size, ought all to be melted within a very few minutes or seconds by the heat incessantly communicated from the surrounding air. Were this really the case, the consequences of it would be dreadful in many cases; for, even as things are at present, the melting of large amounts of snow on dice occasions violent torrents and great inundations in the cold countries or in the rivers that come from them. But, were the ice and snow to melt suddenly, as they would if the former opinion of the action of heat in melting them were well founded, the torrents and inundations would be incomparably more irresistible and dreadful. They would tear up and sweep away everything, and this so suddenly that mankind would have great difficulty in escaping their ravages. This sudden liquefaction does not actually happen..."!
- Immediate transformation of (for example) a solid to a liquid at the melting temperature, as was commonly believed to happen at that time, would imply that a plot of the temperature of an iceberg that starts at -30°C vs. heat transferred into it would look like:

1700's view of melting ice



- Remember that the heat capacity of the solid and liquid states will differ- hence the break in slope at the melting point of the ice.
- Black went on to perform experiments where he found that melting ice appeared to absorb much more heat than was required to raise the temperature from 31 to 32°C . In effect, he performed measurements that revealed the enthalpy of melting.

References

1. Carter, W. C. (2002).
2. Dil, K. & Bromberg, S. Molecular Driving Forces (New York, 2003).
3. Reed-Hill, R. E. & Abbaschian, R. Physical Metallurgy Principles (PWS Publishing, Boston, 1994).
4. Tartaglino, U., Zykova-Timan, T., Ercolessi, F. & Tosatti, E. Melting and nonmelting of solid surfaces and nanosystems. Physics Reports-Review Section of Physics Letters 411, 291-321 (2005).
5. Bent, H. A. The Second Law (Oxford University Press, New York, 1965).