Calorimetry

- One technique for measuring specific heat involves heating a material, adding it to a sample of water, and recording the final temperature
- This technique is known as **calorimetry**
  - A calorimeter is a device in which this energy transfer takes place

Calorimetry

- The system of the sample and the water is **isolated**
- Conservation of energy requires that the amount of energy that leaves the sample equals the amount of energy that enters the water
  - **Conservation of Energy** gives a mathematical expression of this:

$$Q_{\mathrm{cold}} = -Q_{\mathrm{hot}}$$

Calorimetry

- The negative sign in the equation is critical for consistency with the established sign convention
- Since each $Q = mc\Delta T$, c_{sample} can be found by:

$$c_s = \frac{m_w c_w \left(T_f - T_w\right)}{m_s \left(T_s - T_f\right)}$$

NOTE: the mass and c of the container should be included, but if $m_w >> m_{\text{container}}$ it can be neglected

Calorimetry, Example

- An ingot of metal is heated and then dropped into a beaker of water. The equilibrium temperature is measured

$$c_s = \frac{m_w c_w \left(T_f - T_w\right)}{m_s \left(T_s - T_f\right)}$$

$$= \frac{(0.400\,\text{kg})(4186\,\text{J/kg}\cdot{}^\circ\text{C})(22.4^\circ\text{C} - 20.0^\circ\text{C})}{(0.0500\,\text{kg})(200.0^\circ C - 22.4^\circ C)}$$

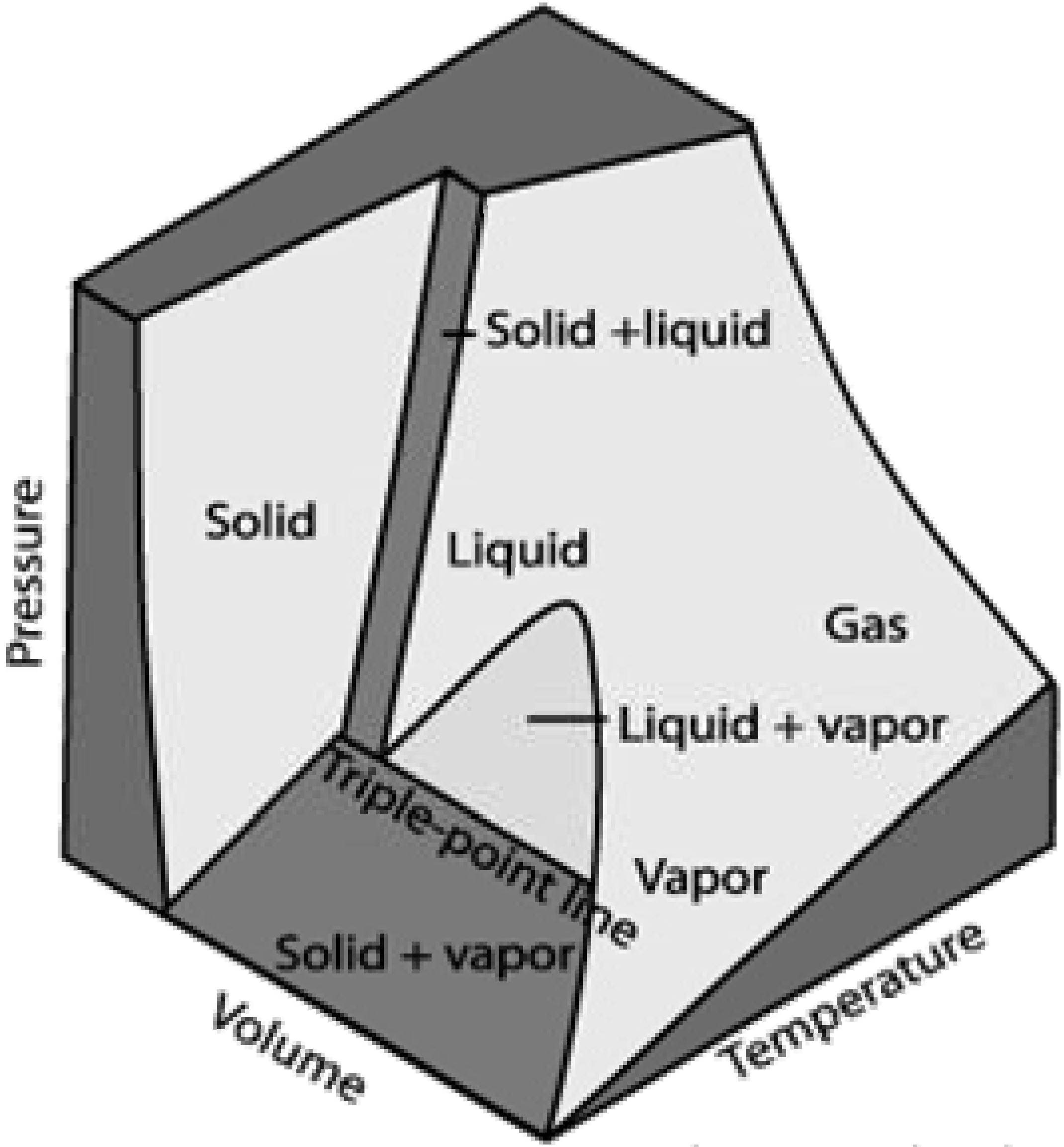
$$= 453\ \text{J/kg}\cdot{}^\circ\text{C}$$

CALORIMETRY for high energy physics

A **calorimeter** is a device that helps scientists measure the energy of a particle. This triangular section is layered with sheets of **lead and plastic**. The lead is heavy and dense, so the particles have a hard time going through it. Scientists can tell how much energy a particle had by seeing how much lead it took to stop it.

Phase Changes

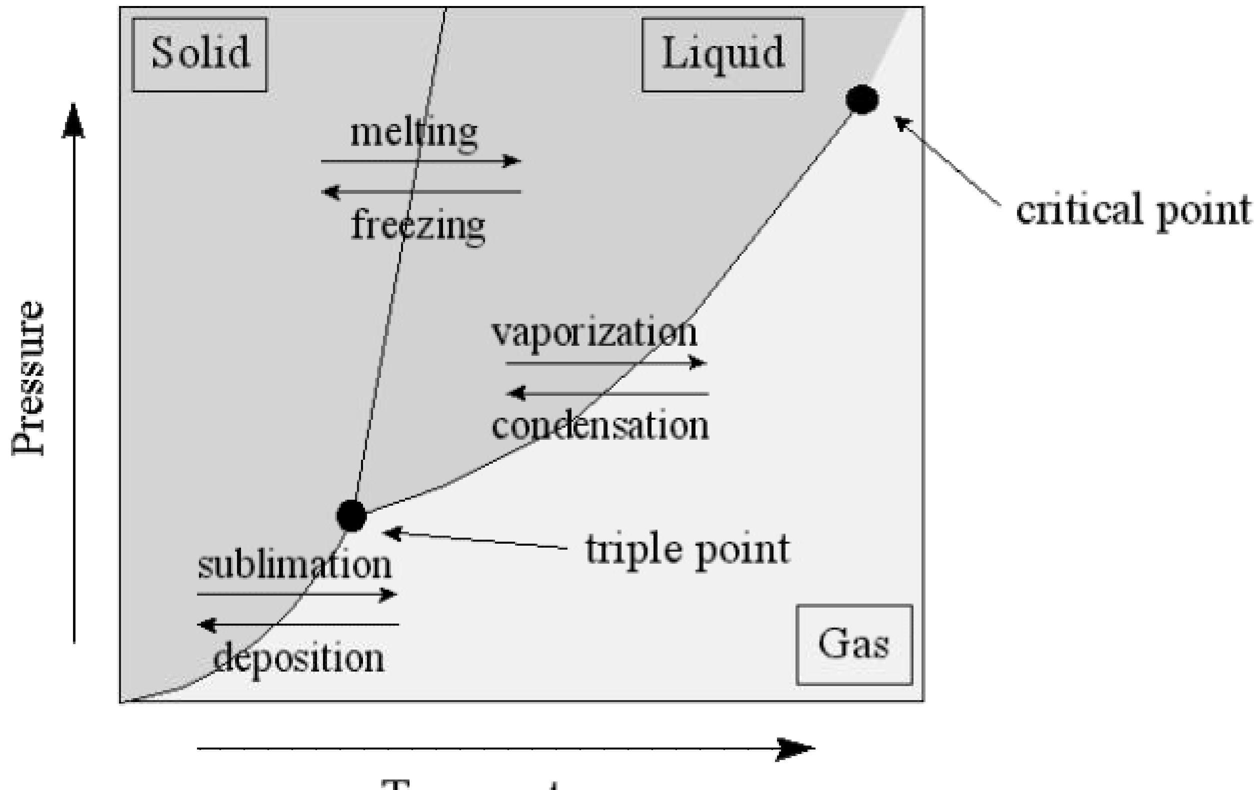
- A **phase change** is when a substance changes from one form to another
  - Two common phase changes are
    - Solid to liquid (melting)
    - Liquid to gas (boiling)
- **During a phase change, there is no change in temperature of the substance**


Solid +liquid
Solid
Liquid
Gas
Liquid + vapor
Triple-point line
Vapor
Solid + vapor
Pressure
Volume
Temperature
ThermoNet: John Wiley

Phase Diagrams (P,T)

Equilibrium can exist not only between the **liquid and vapor** phase of a substance but also between the **solid and liquid** phases, and the **solid and gas** phases of a substance.

A **phase diagram** is a graphical way to depict the effects of pressure and temperature on the phase of a substance:



Latent Heat

- Different substances react differently to the energy added or removed during a phase change
  - Due to their different molecular arrangements
- The amount of energy also depends on the mass of the sample
- If an amount of energy Q is required to change the phase of a sample of mass m

$$L = Q / m \text{ or } Q = mL$$

Latent Heat

- The quantity L is called the **latent heat** of the material
  - Latent means “hidden”
  - The value of L depends on the substance as well as the actual phase change
- The energy required to change the phase is $Q = \pm mL$

Latent Heat

- The *latent heat of fusion* is used when the phase change is from solid to liquid
- The *latent heat of vaporization* is used when the phase change is from liquid to gas
- The **positive sign** is used when the energy is transferred **into** the system
  - This will result in melting or boiling
- The **negative sign** is used when energy is transferred **out** of the system
  - This will result in freezing or condensation

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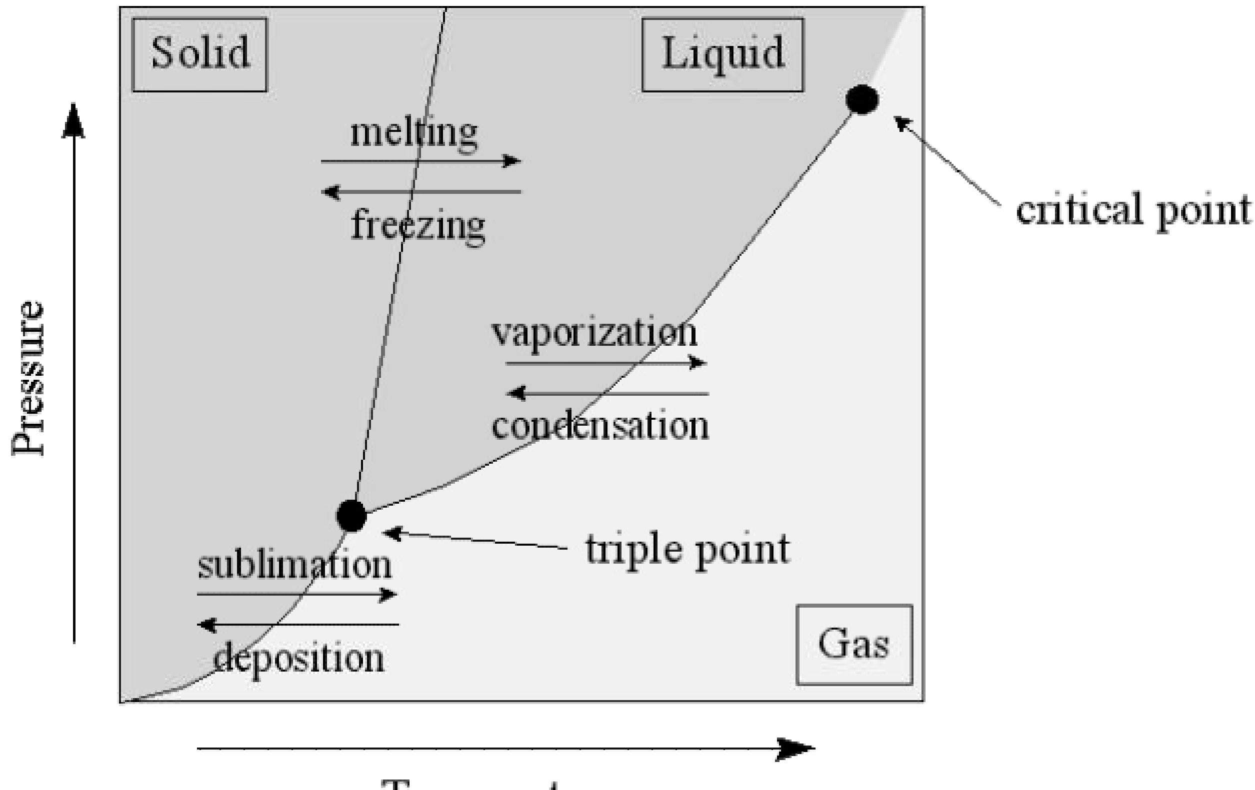
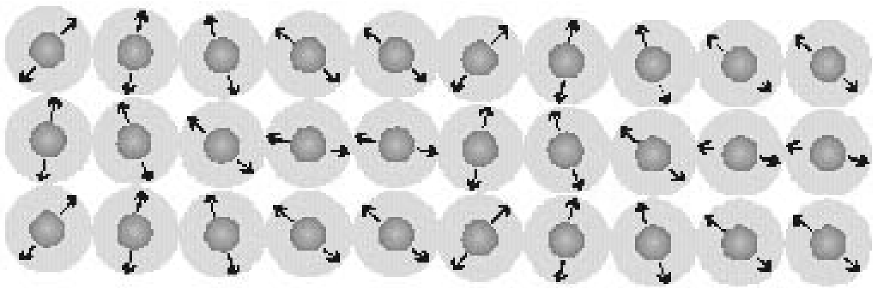


Sample Latent Heat Values

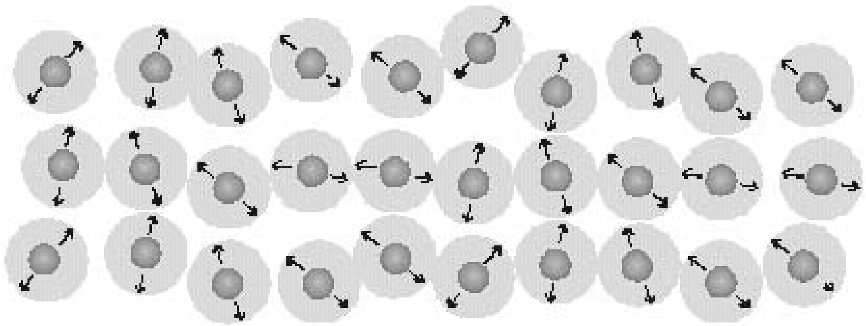
Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	−269.65	5.23×10^3	−268.93	2.09×10^4
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6



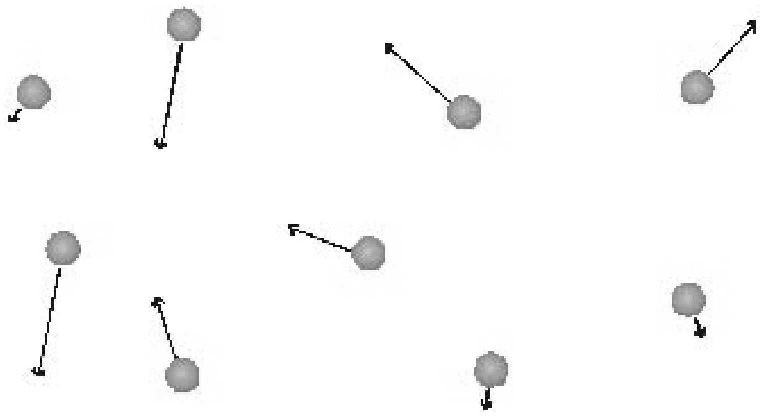
SOLIDS

The particles **vibrate around fixed positions**.
They are close together and so attract each other strongly. This is why solids maintain their shape.



LIQUIDS

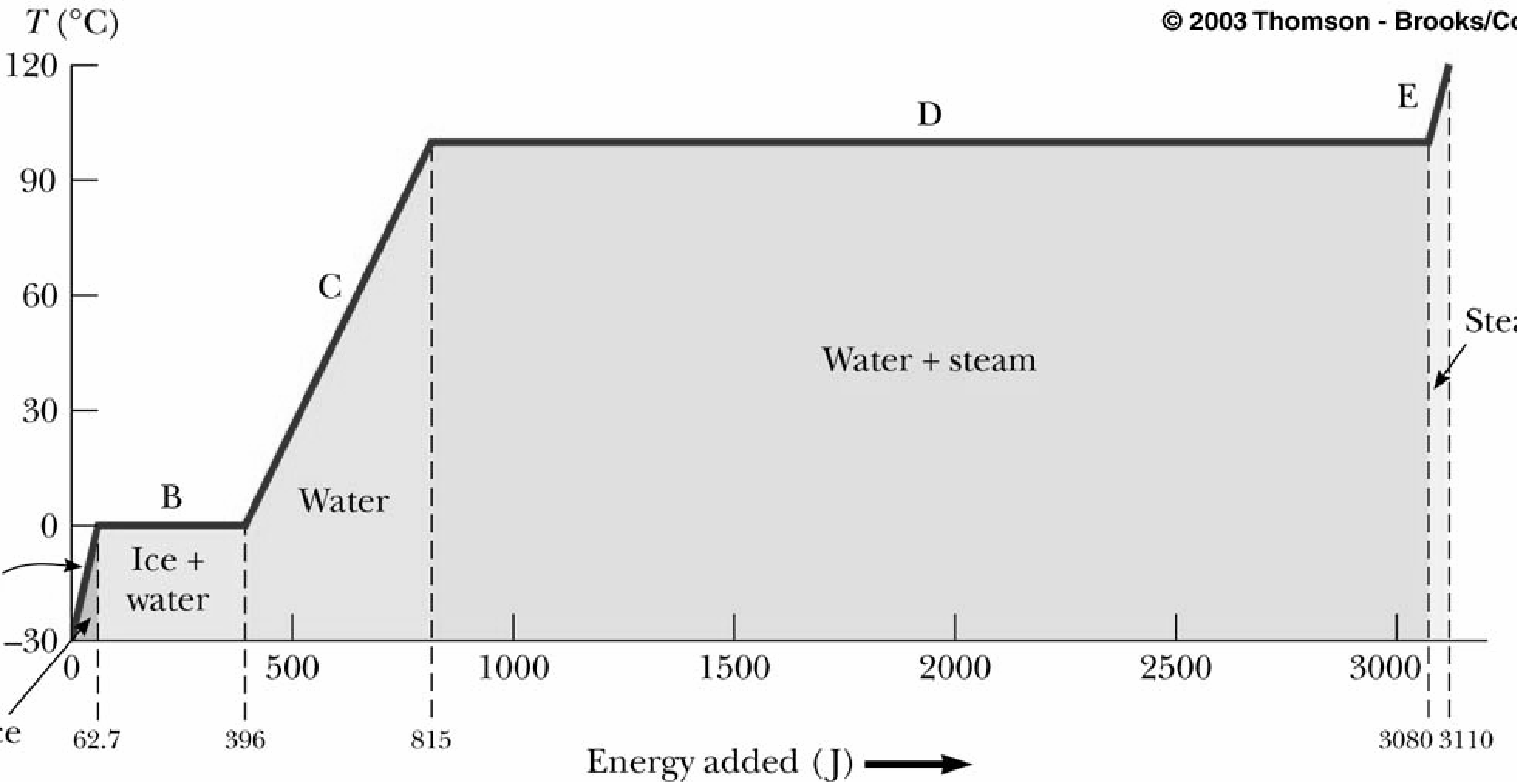
The particles are still relatively close together but now have **enough energy to "change places" with each other**. This is why liquids can **flow**.



GASES

Average distance between particles typically **10 times greater** than in solids and liquids. The particles now move **freely at random**, occupying all the space available to them.

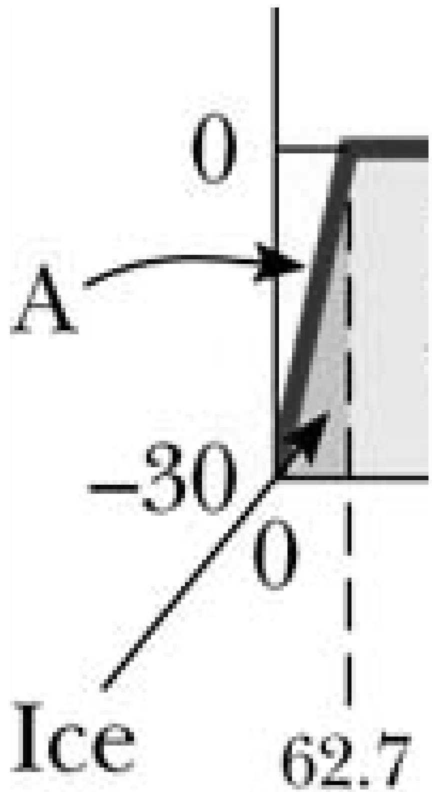
Graph of Ice to Steam



Note:all heat values are for 1 gram of water

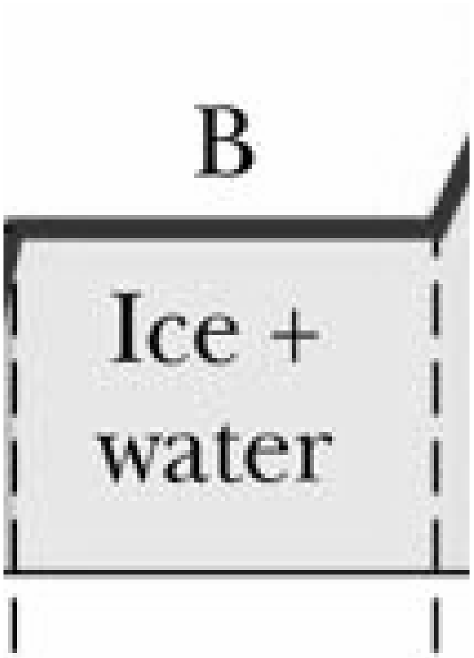
Warming Ice, Graph Part A

- Start with **one gram** of ice at –30.0ºC
- During phase A, the temperature of the ice changes from –30.0ºC to 0ºC
- Use $Q = m_i c_i ? T$
  – In this case, 62.7 J of energy are added



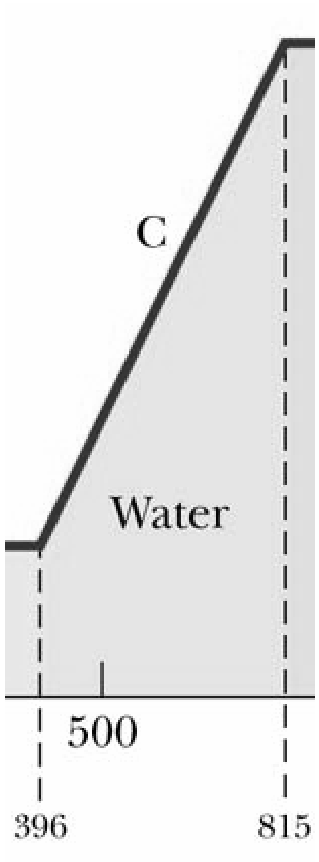
Melting Ice, Graph Part B

- Once at 0ºC, the phase change (melting) starts
- The temperature stays the same although energy is still being added
- Use $Q = m_i L_f$
  - The energy required is 333 J
  - On the graph, the values move from 62.7 J to 396 J



Warming Water, Graph Part C

- Between 0ºC and 100ºC, the material is liquid and no phase changes take place
- Energy added increases the temperature
- Use $Q = m_w c_w ?T$
  - 419 J are added
  - The total is now 815 J



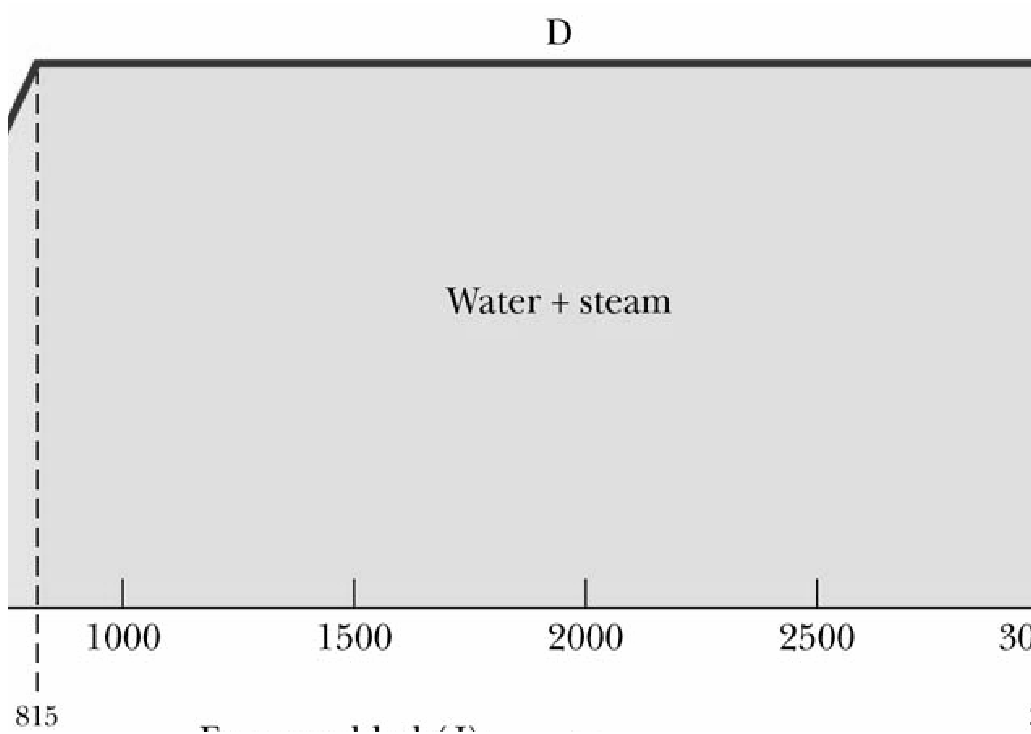
Boiling Water, Graph Part D

At 100ºC, a phase change occurs (boiling)

Temperature does not change

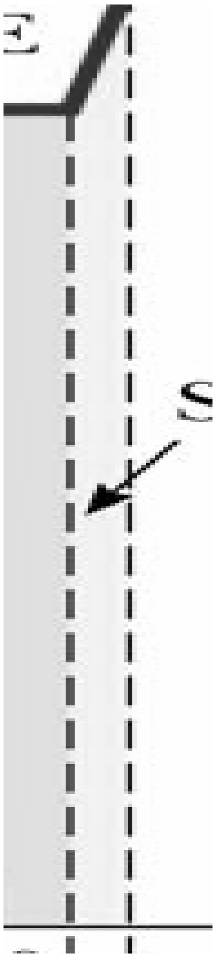
Use $Q = m_w L_v$

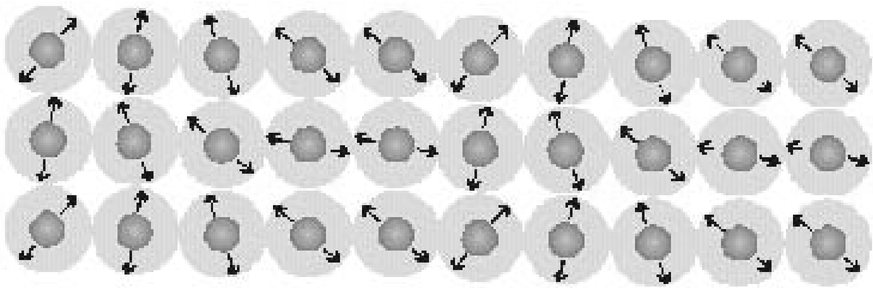
- This requires 2260 J
- The total is now 3070 J



Heating Steam

- After all the water is converted to steam, the steam will heat up
- No phase change occurs
- The added energy goes to increasing the temperature
- Use $Q = m_s c_s ?T$
  - In this case, 40.2 J are needed
  - The temperature is going to 120^o C
  - The total is now 3110 J





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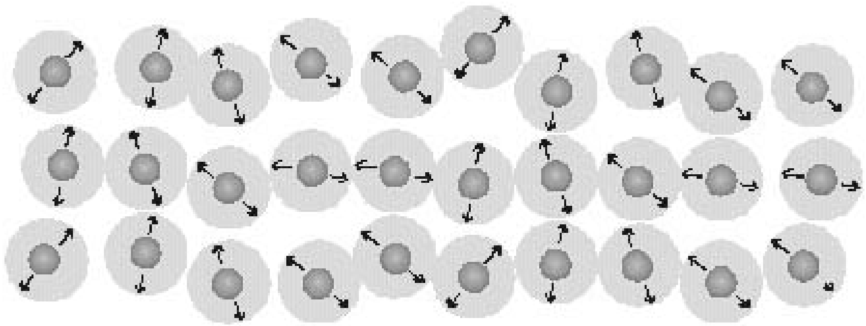

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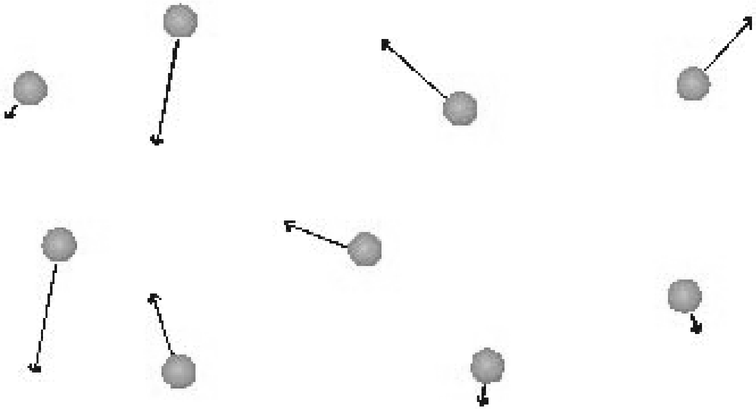

GASES

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Molecular View of Phase Changes

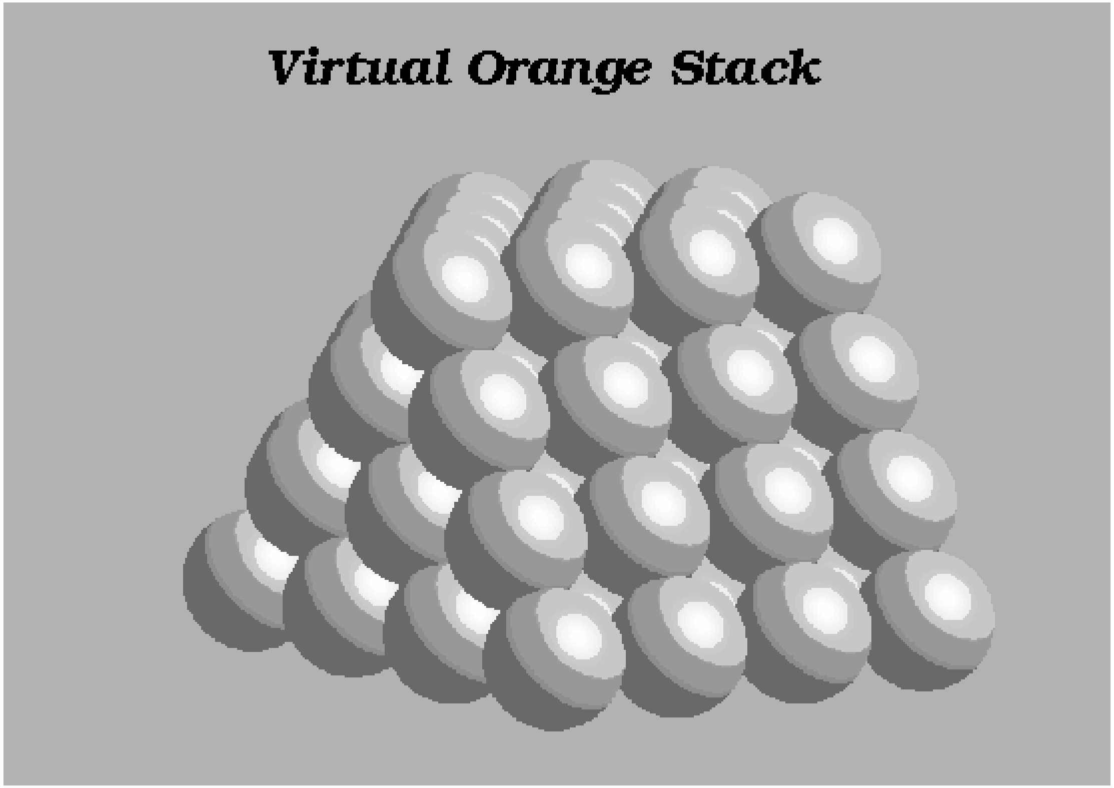
- Phase changes can be described in terms of the rearrangement of molecules (or atoms in an elementa substance)
- Liquid to Gas phase change
  - Molecules in a liquid are close together
  - The forces between them are stronger than those in a gas
  - Work must be done to separate the molecules
  - The latent heat of vaporization is the energy per unit mass needed to accomplish this separation

Molecular View of Phase Changes

- Solid to Liquid phase change
  - The addition of energy will cause the amplitude of the vibration of the molecules about their equilibrium position to increase
  - At the melting point, the amplitude is great enough to break apart bonds between the molecules
  - The molecules can move to new positions
  - The molecules in the liquid are bound together less strongly than those of the solid
  - They have less nearest neighbours
  - The latent heat of fusion is the energy per unit mass required to go from the solid-type to the liquid-type bonds

Molecular View of Phase Changes

- The latent heat of vaporization is greater than the latent heat of fusion
  - In the liquid-to-gas phase change, all bonds are broken
  - The gas molecules are essentially not bonded to each other
- It takes more energy to completely break the bonds than to change the type of bonds



Close-Packed Structures are the most efficient way to fill space with spheres

Features of Close-Packing:

- **Coordination Number** = 12
- 74% of space is occupied

Estimating melting and sublimation energies

There is the Avogadro number N_A of atoms in the mole of a solid.

We assume that each atom has ***n*** nearest neighbours and the strength of the pair-wise interaction between atoms is equal to e.

Then the energy required to melt one mole (latent heat of melting) is approximately equal:

L » **½** $\mathbf{N_A}$ ´ e ´ ***?n*,**

where ***?n*** is **the change of the number of nearest neighbours** from solid to liquid or vapour and ½ stands to avoid the double counting.

We can then use ***n*** = 12 for a solid and ***n*** ≈ 10 for a melt. Then

$\mathbf{L_{melt}}$ » **½**$\boldsymbol{N_A}$D***n****e*, where $\Delta n = 2$,

change of the coordination number from crystal to vapour $\Delta n = 12$

Calorimetry Problem-Solving Strategy

- Units of measure must be consistent
  - For example, if your value of *c* is in J/kg·^{o}C, then your mass must be in kg, the temperatures in ^{o}C and energies in J
- Transfers of energy are given by

  $Q = mc\,\Delta T$ only when no phase change occurs
- If there is a phase change, use $Q = mL$

Calorimetry Problem-Solving Strategy

- Be sure to select the correct sign for all energy transfers
- Remember to use $Q_{\text{cold}} = - Q_{\text{hot}}$
- The ΔT is always $T_f - T_i$