CHEM 116

Phase Changes and Phase Diagrams

Lecture 4
Prof. Sevian

Please turn in extra credit assignments at the very beginning of class.

Today's agenda

Finish chapter 10

- Partial pressures
- Vapor pressure experiments
- When the assumptions fail: non-ideal behavior

Start chapter 11

- Compare the three most common phases of matter
- How to effect phase changes and what can be measured
- Particle level model of phase changes
- Reminder of polar vs. nonpolar molecules which you learned in first semester chemistry
- Phase diagrams

Announcements

FSG's

- FSG's will start next week on Sept 15
- Both FSG's will be on Mondays: one from 10:00-10:50am and the other from 11:00-11:50am
- Locations for the FSG's are undetermined yet – as soon as we know where they will be, I will post the locations on the Chem 116 website under Announcements on the front page

Pre-test

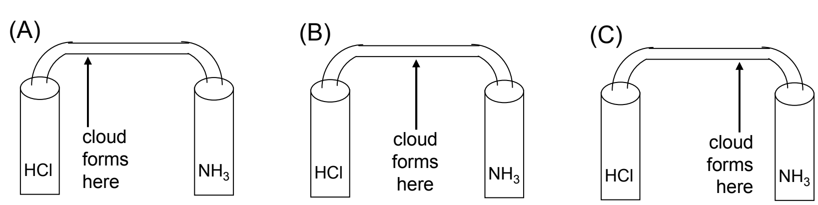
- You will take the pre-test during the first hour of lab on either Mon Sept 15 or Weds Sept 17 in M-1-417 from 1:00-2:00. Since this is at the very beginning of lab, you can go directly to the classroom in McCormack first.
- The pre-test is on material we will cover this semester, so I expect the scores to be very low (otherwise you wouldn't be in this course!). Please do not worry about how you do on the pre-test. You do not need to study for it. It is simply a test of your prior knowledge. Your score on the pre-test will not count toward your grade. It is simply an "attendance" grade to take the pre-test.
- If you are not enrolled in Chem 118, please attend lab for the first hour (1:00-2:00) on one of these days to take the pre-test
- If you can't take the pre-test at lab, please make arrangements with me to take the pre-test sometime during the week of Sept 15. After that week is up, it will not be possible to take the pre-test and you will get 0 out of 10 points for the pre-test grade.

i>Clickers

- On Tuesday next week (9/16), i>clicker questions will begin to count toward your grade. Bring your clicker to class with you every day.
- If you do not own an i>clicker and do not need one for another class this semester, I will loan you one. Come by my office (W-4-181) to get it. If you do not return it to me at the end of the semester, you will receive an INC for the course. If you lose it, you can buy another one on amazon.com for around $30.

A clicker question that asks about material we covered in class last time

When HCl (*g*) [M_w = 36.5 g/mol] and NH_3 (*g*) [M_w = 17.0 g/mol] react, they form NH_4Cl, an ionic compound which is a solid at room temperature. If this reaction is carried out in an evacuated tube, a cloudlike presence of NH_4Cl (*s*) can be detected in the tube when it forms. Which picture depicts what you should expect to see?



Gas mixtures

- All gases in a mixture spread out to occupy the entire space available
- Each component gas behaves as if it alone occupied the entire volume (which assumption of KMT supports this?)
- Each component exerts its own partial pressure, such that the sum of the partial pressures equals the total pressure
- Dalton's law of partial pressures

$$p_{total} = p_A + p_B + p_C + p_D + \ldots = \sum_i p_i$$

More about partial pressures

For a mixture with two gases (A and B):

$$\begin{aligned}
p_A + p_B &= p_{total} = \frac{nRT}{V} \\
&= \frac{(n_A + n_B)RT}{V} \\
&= (n_A + n_B)\frac{RT}{V} \\
&= (n_A + n_B)\frac{p_{total}}{n_{total}} \\
&= \underbrace{\frac{n_A}{n_{total}} p_{total}}_{p_A} + \underbrace{\frac{n_B}{n_{total}} p_{total}}_{p_B}
\end{aligned}$$

Mole fractions:

$$\chi_A = \frac{n_A}{n_{total}}$$

$$\chi_B = \frac{n_B}{n_{total}}$$

$$\chi_A + \chi_B = 1$$

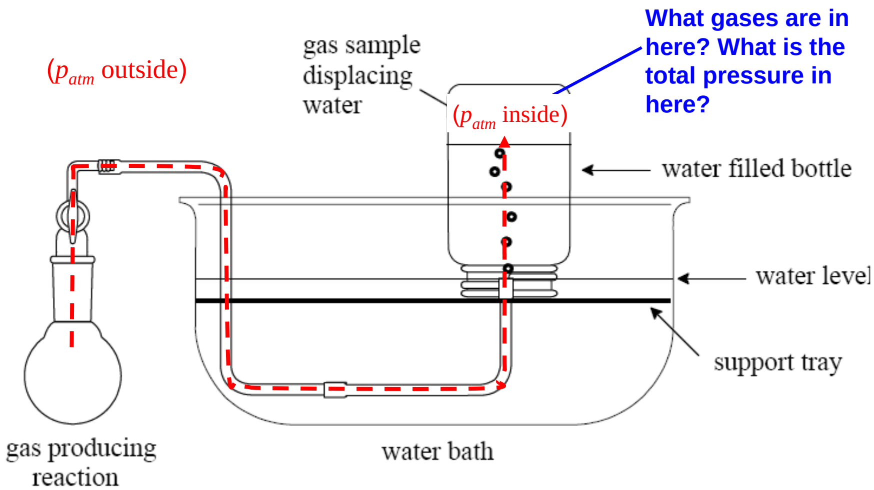
$$\text{and generally,} \sum \chi_i = 1$$

Partial pressure definition:

$$p_i = \chi_i p_{total}$$

For vapor pressures of water at different temperatures, see Appendix B in your text, p. 1122

What use are partial pressures?



Total pressure inside must equal sum of partial pressures of water vapor and the gas being collected: $p_{atm} = p_{water} + p_{gas}$

Collecting a gas over water

For vapor pressures of water at different temperatures, see Appendix B in your text, p. 1122. In this table, at 25ºC, the vapor pressure of water is 23.76 torr.

Example similar to additional question on Assignment 2

Zinc is reacted with excess hydrochloric acid in a vessel in such a way that the hydrogen gas produced is collected over water. In the laboratory, the atmospheric pressure is 755 mmHg and the water temperature is 25ºC. If the total volume of gas collected is 125 mL, what mass of zinc reacted?

$$Zn\ (s) + 2\ HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$$

What happens when the KMT assumptions break down?

1. No attractive forces between gas particles
2. Volume of individual particles is negligible compared to volume occupied by the gas
3. Particles are in constant motion
4. Particle travel in straight lines and change velocities only when they collide, either with other particles or with walls of container – all collisions are elastic (no loss of kinetic energy)
5. Pressure arises from particles hitting walls of container
6. Average kinetic energy is proportional to the temperature of the gas

Two major assumptions that break down

- Attractive forces
  - As particles become more massive, attractive forces increase
  - As pressure increases or when temperature decreases, particles get closer together and attractive forces increase
- Volume of particles
  - As particles become larger, their volume ceases to be negligible
  - When pressure increases or when temperature decreases, the fraction of the total volume that the particles occupy becomes less negligible
- Important indicators
  - High pressure
  - Low temperature
  - Mass/size of particles

van der Waals equation: the next mathematical step in the KMT theory (a series expansion)

$$\underbrace{\left(p + a\frac{n^2}{V^2}\right)}_{\text{}}\underbrace{(V - nb)}_{\text{}} = nRT$$

The actual pressure exerted by the gas is less than ideal because there are attractions that restrain the particles from causing pressure

$P_{ideal} = P_{actual}$

+ some amount that increases when density increases

Reflects that the actual volume for particles to move in is smaller than the volume the gas occupies

b **= volume occupied by the particles themselves (per mole)**

Which gases are more likely to deviate* from ideal gas behavior? Why?

Assume all these gases are being compared at STP

- H_2
- O_2
- H_2O
- Xe
- C_4H_{10}
- He
- Ne

- Attractive forces
  - As particles become more massive, attractive forces increase
  - As pressure increases or when temperature decreases, particles get closer together and attractive forces increase
- Volume of particles
  - As particles become larger, their volume ceases to be negligible
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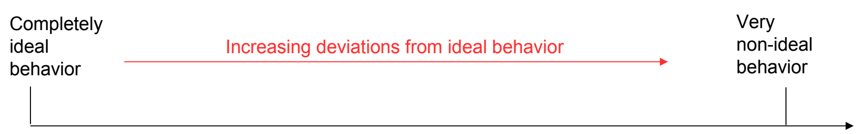
**to deviate = to be different from*

Rank the degree of deviation of each gas from ideal behavior



Key points so far

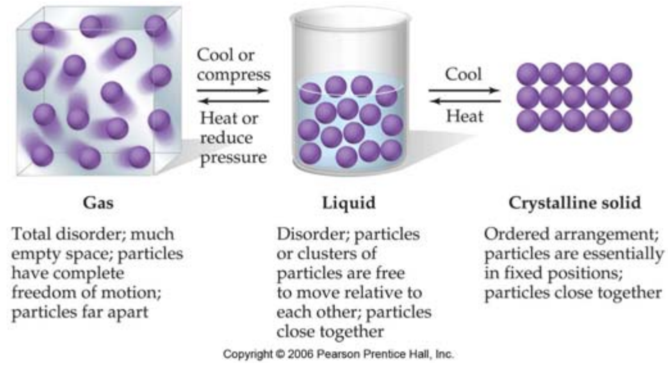
- pV/nT = constant
- $pV = nRT$ (ideal gas law)
- At STP, the molar volume of a gas is 22.4 L/mol
- Ideal gas law rests on assumptions. Model works best when a gas is under conditions that come close to assumptions being true.
- Celsius and Kelvin temperature scales:
  - Same degree sizes, Kelvin is shifted 273.15 degrees higher than Celsius
  - Different in that Celsius is relative to water freezing point, Kelvin is absolute temperature scale
- Always use Kelvin in gas law model/calculations
- If collecting a gas over water, the gas collected includes both the product of interest and water vapor

Common phases of matter

- Particle level
  - How are these three phases different?
  - How does a material change from one phase to another? What happens at the particle level?
- Macroscopic behavior
  - How do these particle behaviors manifest in different macroscopic behavior?

Three phases of matter: what do the particles do?

- Motion
- Proximity
- Density
- Interactions
- Timescale



Show simulations of methane (CH_4) gas.

Water behaves slightly differently due to H_2O to H_2O interactions being different than CH_4 to CH_4 interactions…we'll talk more about this next lecture (also in chapter 11).

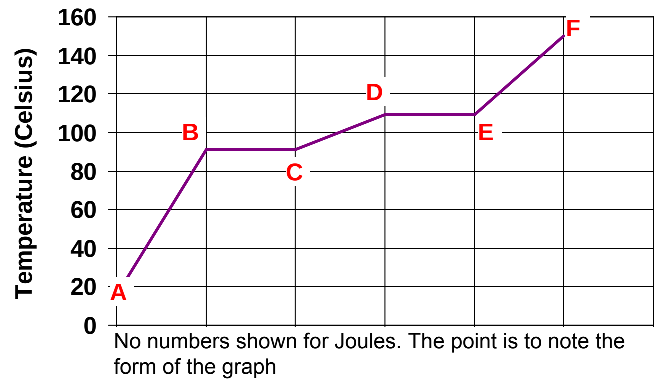
Particle level

Change from one phase to another

- What kinds of energy are involved?
  - Kinetic energy = motion
  - Potential energy = separation
- How do particles get from one phase to another? Surfaces!
- Some vocabulary
  - Solid to liquid: melting
  - Liquid to solid: fusion (freezing)
  - Liquid to gas: vaporization (boiling)
  - Gas to liquid: condensation
  - Solid to gas: sublimation
  - Gas to solid: deposition

Heating Curve of 1.00-gram Sample of Methane (CH_4) at Standard Pressure

Macroscopic



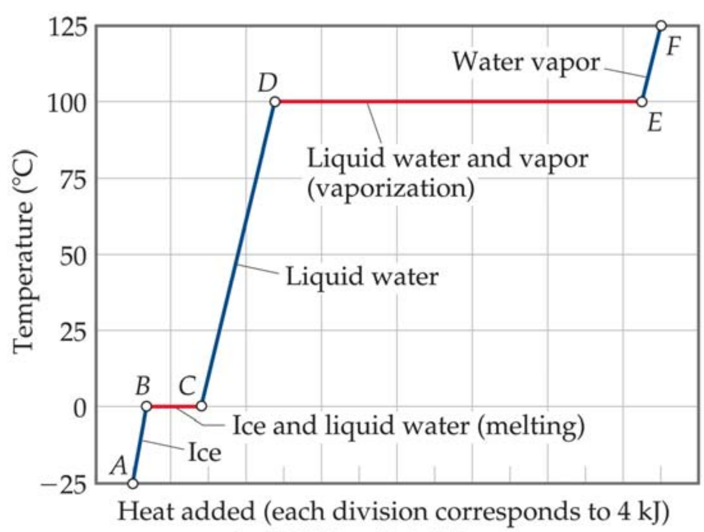
Energy added (Joules)

A = solid below melting*
B = solid has reached melting temperature, and is beginning to melt*
C = liquid at melting temperature, has just completed melting
D = liquid has reached boiling temperature, and is beginning to boil*
E = gas at boiling temperature, has just completed boiling*
F = gas above boiling temperature

Horizontal parts vs. sloped parts

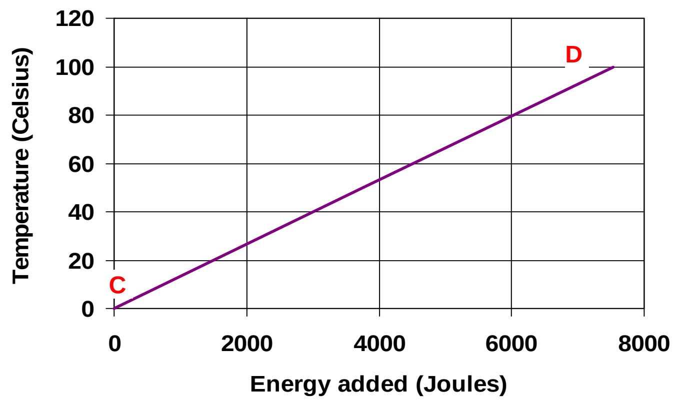
See http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/

Heating curve of water (1.00 mol at standard pressure)



Macroscopic

Focus on Liquid to Gas: For a 1.00-mol sample of liquid water



Particle level

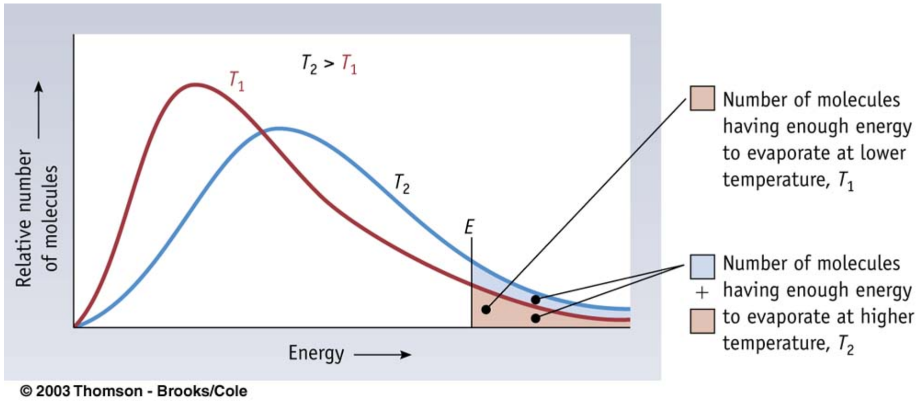
What happens if you add more heat energy to liquid water at 100ºC and 1 atm?

Molecular dynamics simulation of water evaporating

- It boils
- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation (vapor pressure)
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase
- Normal boiling point is temperature at which vapor pressure reaches atmospheric pressure when p_{atm} = 1atm

Particle level

Comparing a liquid at two temperatures



The effect of temperature on the distribution of kinetic energies in a liquid

What we've learned about liquids and solids so far

- The same as in gases, there is a distribution of speeds of particles
- Both liquids and solids have *vapor pressure* at <u>every</u> temperature (even low temperatures)
- Vapor pressure is the pressure exerted by the gas particles that evaporate (L→G) or sublime (S→G) from a liquid or solid, respectively
- Evaporation and sublimation happen at the surface of the liquid or solid, where particles can escape from the surface
- When the vapor pressure reaches the pressure of whatever gas is surrounding the substance, we say that the substance is boiling (if it's changing from L→G) or subliming (S→G)

Heating curve vs. phase diagram vs. vapor pressure curve

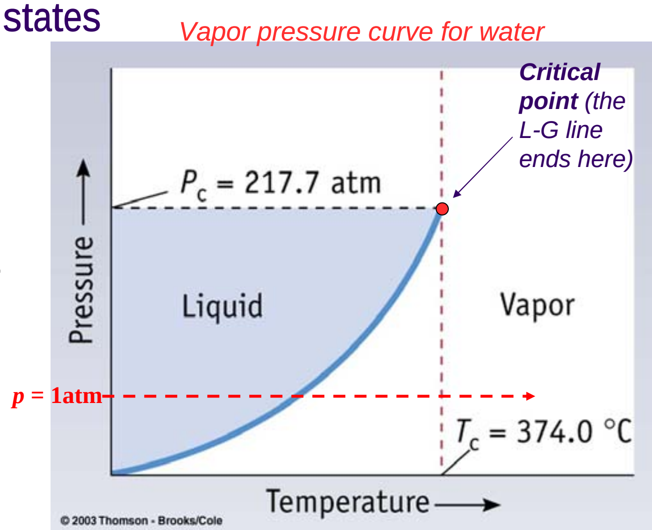
- Heating curve
  - Temperature vs. heat energy added
  - Characteristic up-across-up-across shape
  - Cooling curve is how temperature changes as you remove energy
- Phase diagram
  - Pressure vs. temperature
  - All 3 phases shown with boundaries between them
- Vapor pressure curve
  - The liquid-gas portion of the full phase diagram
  - Vapor pressure line is the boundary between L and G
  - All liquids (and solids too) have vapor pressure

Liquid to gas: As you add energy, the temperature changes. As the temperature changes, the vapor pressure changes.

Macroscopic

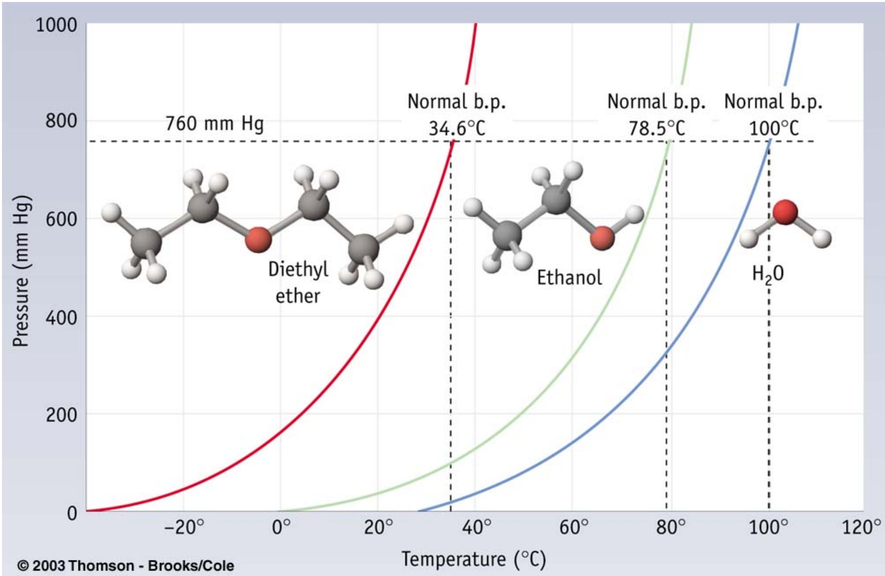
Phase diagram for water showing liquid and gas states

- Curve shows where phase change occurs
- All materials display a critical point, above which there is no interface between liquid and vapor
- Supercritical fluids are useful

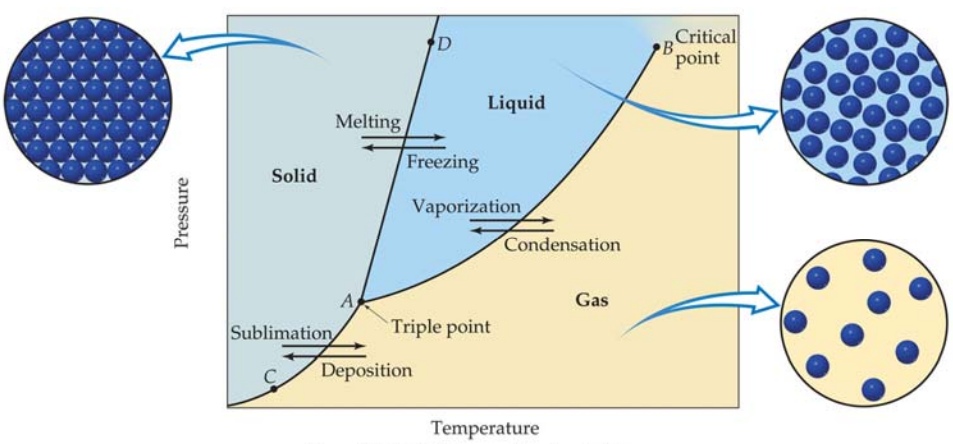


Comparison:
CO_2 T_c = 30.99ºC, P_c = 72.8 atm

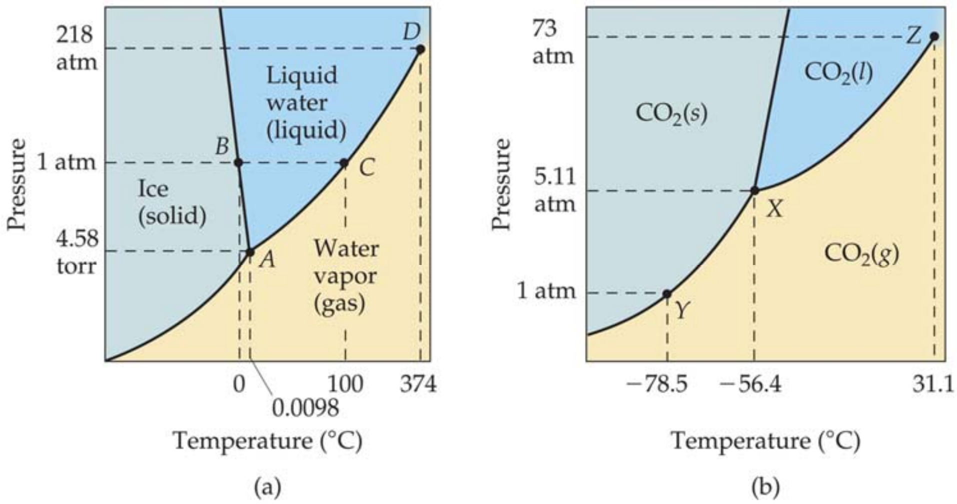
Compare vapor pressure curves for various materials



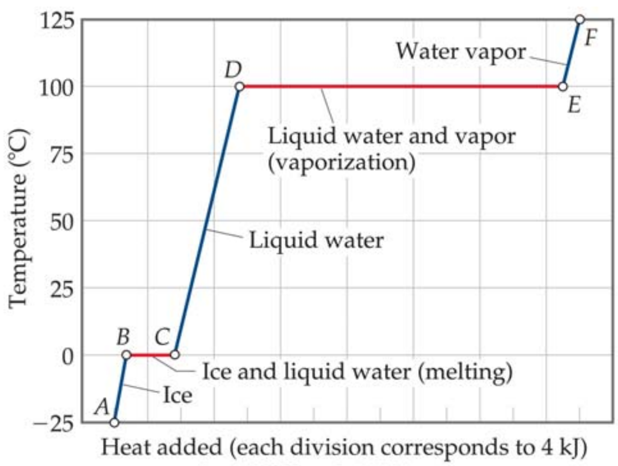
Phase diagram showing all 3 phases



Compare phase diagrams of H_2O and CO_2

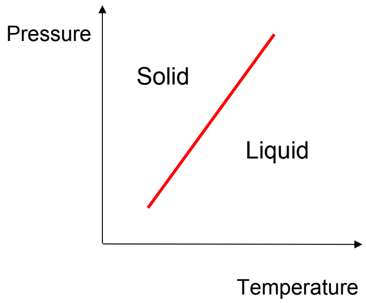


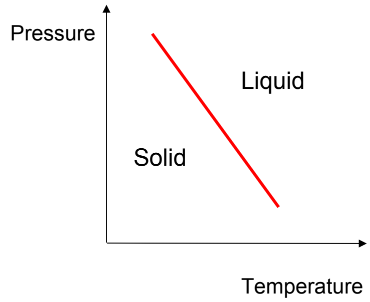
Focus on solid to liquid: A to B



- Vapor pressure still exists (Solid-Gas)
- Phase diagrams for S-L change can differ

Solid-liquid transition at various pressures





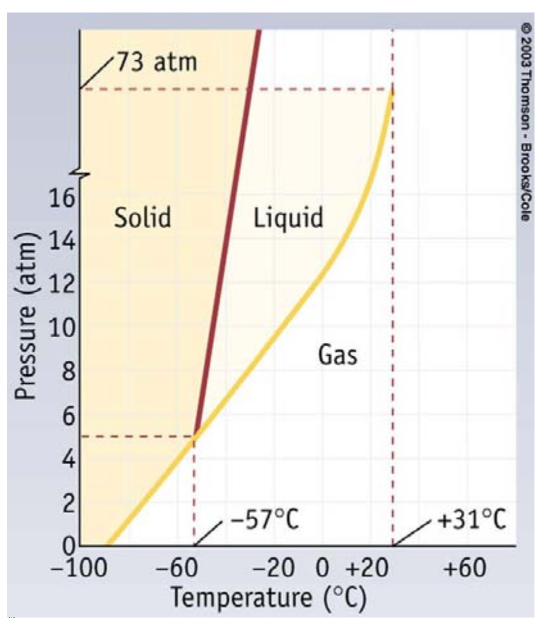
- Typical behavior
- At same T, as you increase p, substance changes from liquid to solid
- Solid more dense than liquid

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid

Consequence: solid melts when pressure exerted on it

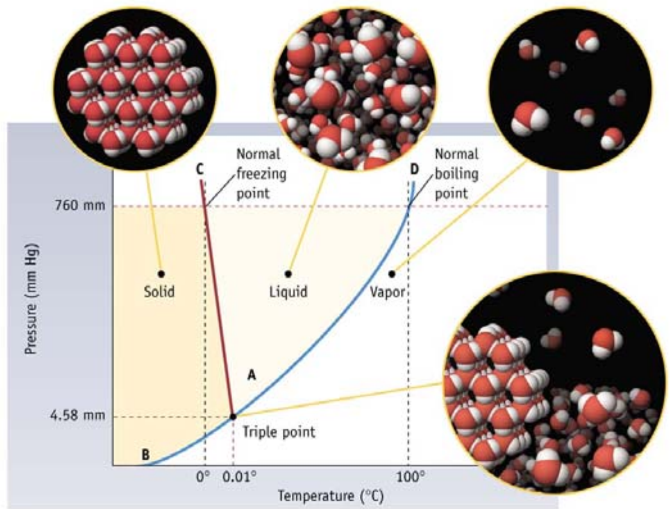
CO_2: a typical phase diagram

- Typical behavior
- At same T, as you increase p, substance changes from liquid to solid
- Solid more dense than liquid
- Exhibits triple point where all three phases coexist



H_2O: an unusual phase diagram

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid
- Exhibits triple point where all three phases coexist



Key points from today

- Two gases at the same temperature have the same average kinetic energy
  - Particles of the less massive gas travel faster on average
- The same gas at different temperatures has different distributions of particle speeds
  - At higher temperature, average velocity is larger and distribution of velocities is wider
- If collecting a gas over water, the gas collected includes both the product of interest <u>and</u> water vapor
- All solids and liquids have some vapor pressure. Vapor pressure increases as temperature increases (L-G line in phase diagram always has a positive slope). If the temperature is high enough that the vapor pressure equals atmospheric pressure, then the substance boils.
- Phase diagrams show p vs. T for all three phases, with lines indicating where phase transition occurs.
- S-L line can have either a positive (usual) or negative (unusual) slope. Water is unusual.