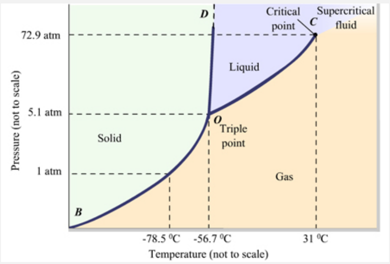
[TP] CO_2 gas at 1 atm, 0 °C
is heated to 1 atm, 60 °C;
then compressed to 75 atm, 60 °C;
then cooled to 75 atm, 0 °C;
then expanded to 65 atm, 0 °C.
At this point, the CO_2 will be a ...

25% 1. gas
25% 2. supercritical fluid
25% 3. liquid
25% 4. solid



BOSTON UNIVERSITY

0 of 0

10

Lecture 8 CH102 A2 (MWF 11:15 am)

Friday, February 8, 2019

- van der Waals equation
- Phase diagrams

Next: Begin ch12: Solutions and their behavior: Enthalpy change of solution: Ionic Solutes; $\Delta_{\text{latt}}H$, $\Delta_{\text{aq}}H$, and $\Delta_{\text{soln}}H$; Predicting relative values of $\Delta_{\text{latt}}H$ and $\Delta_{\text{aq}}H$

BOSTON UNIVERSITY

A gas law for "real" gases: van der Waals equation

We know the ideal gas law $pV = nRT$ where p does not account for inter-particle attractions ...

$$p = p_{\text{ideal}} = p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2$$

and V does not account for particle volume ...

$$V = V_{\text{empty}} = V_{\text{container}} - bn$$

Combine these two expressions into an equation relating p_{observed}, $V_{\text{container}}$, and T.

BOSTON UNIVERSITY

A gas law for "real" gases: van der Waals equation

We know the ideal gas law $pV = nRT$ where p does not account for inter-particle attractions and V does not account for particle volume ...

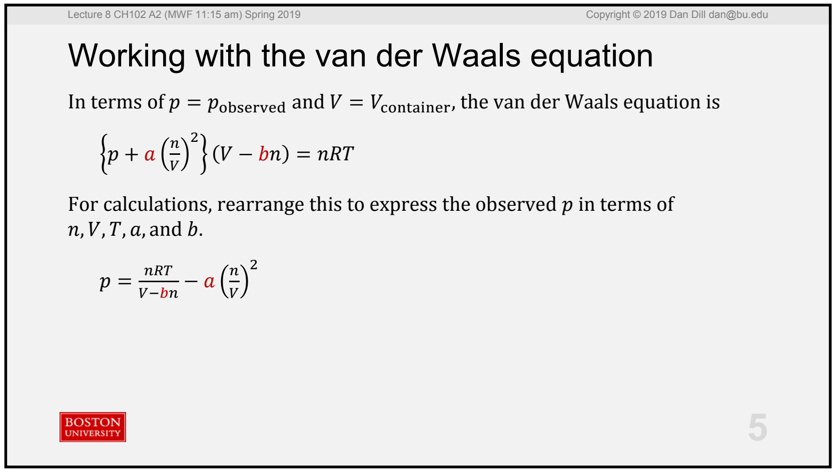
$$p = p_{\text{ideal}} = p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2$$

$$V = V_{\text{empty}} = V_{\text{container}} - bn$$

$$p_{\text{ideal}}V_{\text{empty}} = \left\{p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2\right\}(V_{\text{container}} - bn) = nRT$$

This is known as the van der Waals equation

BOSTON UNIVERSITY



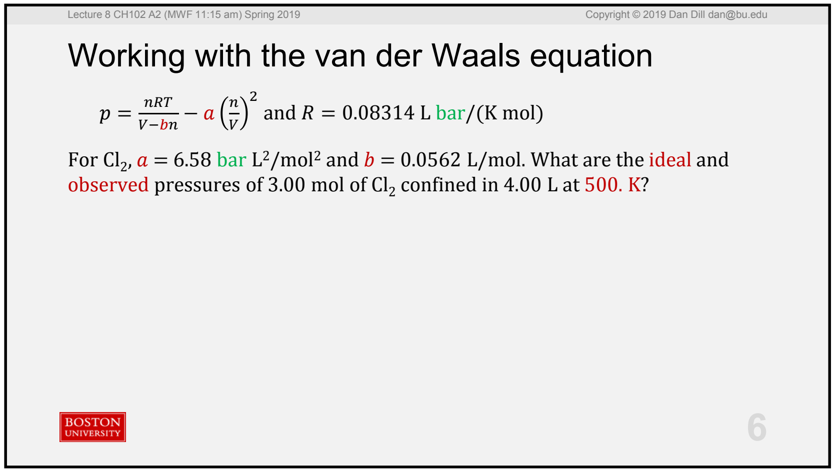
Working with the van der Waals equation

In terms of $p = p_{\text{observed}}$ and $V = V_{\text{container}}$, the van der Waals equation is

$$\left\{p + a\left(\frac{n}{V}\right)^2\right\}(V - bn) = nRT$$

For calculations, rearrange this to express the observed p in terms of $n, V, T, a,$ and b.

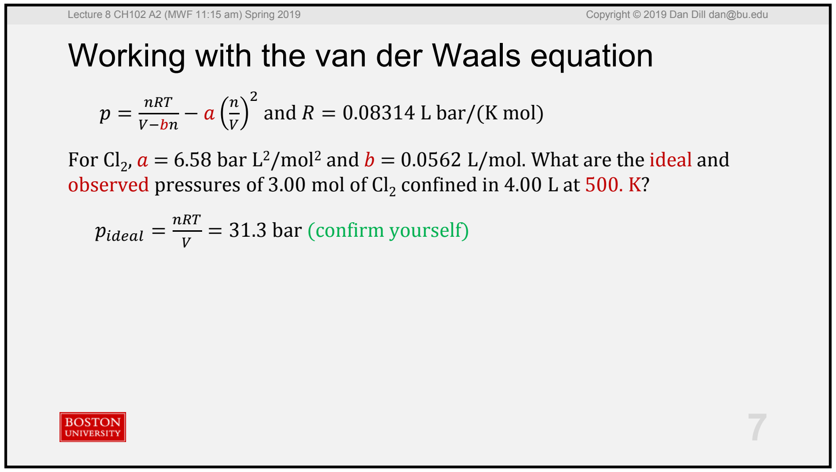
$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$$



Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

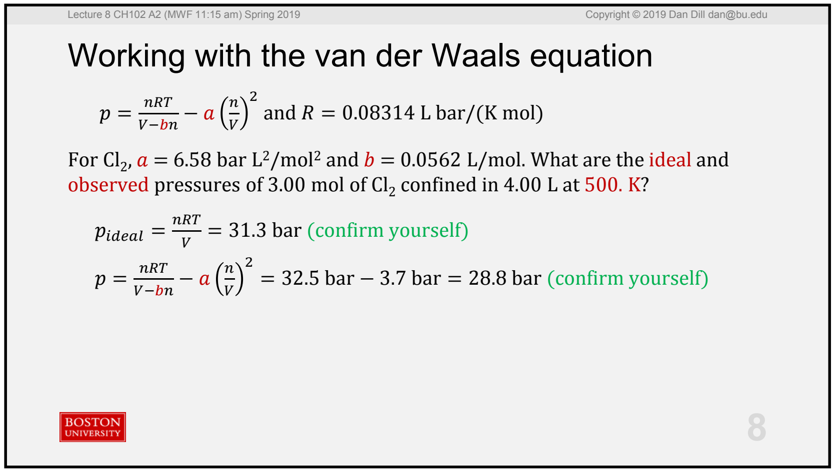


Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$p_{ideal} = \frac{nRT}{V} = 31.3 \text{ bar (confirm yourself)}$$



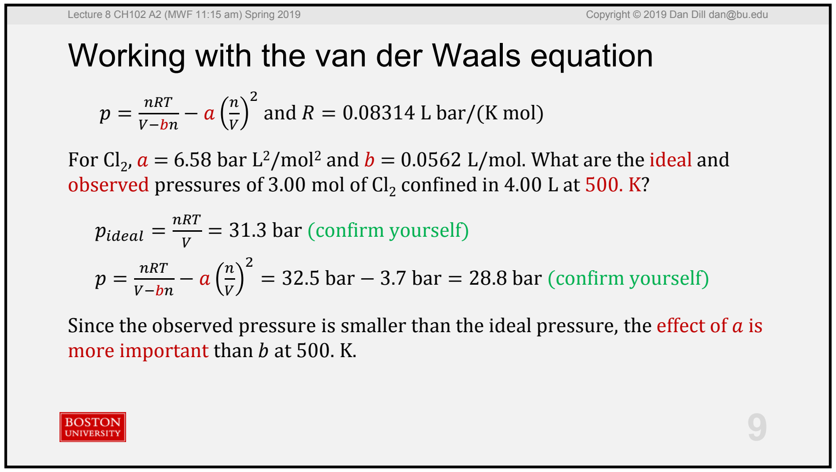
Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$p_{ideal} = \frac{nRT}{V} = 31.3 \text{ bar (confirm yourself)}$$

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8 \text{ bar (confirm yourself)}$$



Working with the van der Waals equation

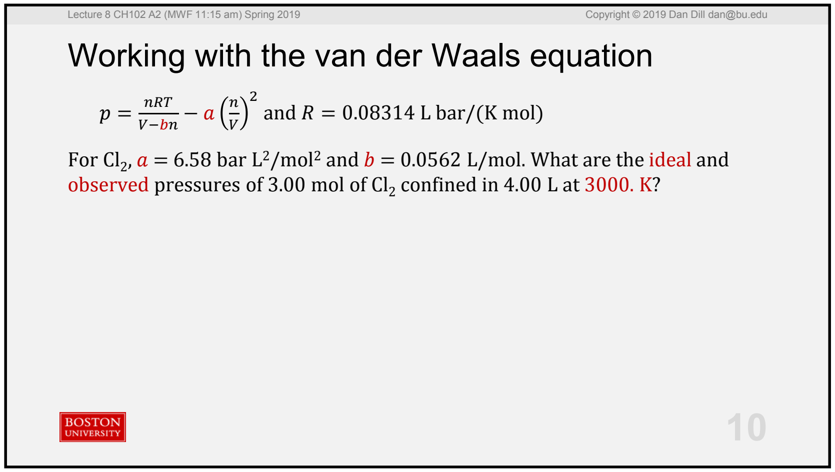
$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ L bar/(K mol)

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$p_{ideal} = \frac{nRT}{V} = 31.3$ bar (confirm yourself)

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8$ bar (confirm yourself)

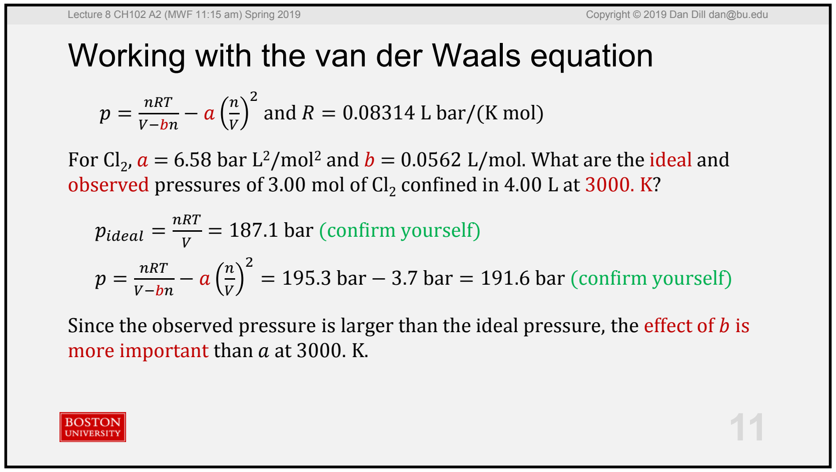
Since the observed pressure is smaller than the ideal pressure, the effect of a is more important than b at 500. K.



Working with the van der Waals equation

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ L bar/(K mol)

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?



Working with the van der Waals equation

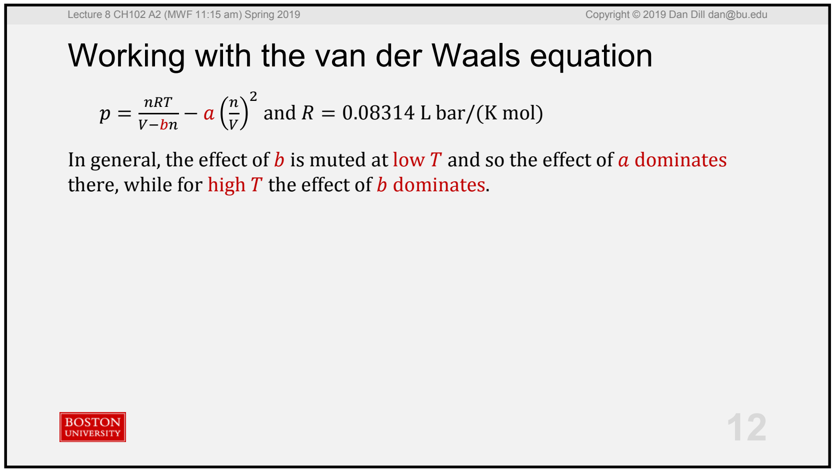
$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ L bar/(K mol)

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?

$p_{ideal} = \frac{nRT}{V} = 187.1$ bar (confirm yourself)

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 195.3 \text{ bar} - 3.7 \text{ bar} = 191.6$ bar (confirm yourself)

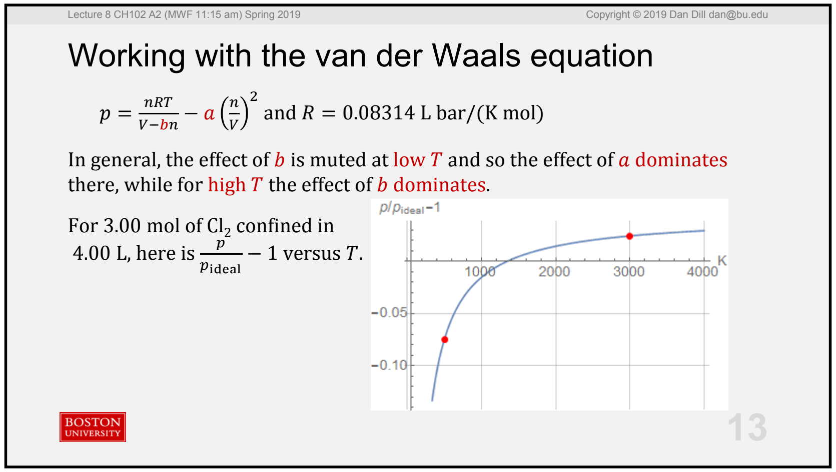
Since the observed pressure is larger than the ideal pressure, the effect of b is more important than a at 3000. K.



Working with the van der Waals equation

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ L bar/(K mol)

In general, the effect of b is muted at low T and so the effect of a dominates there, while for high T the effect of b dominates.

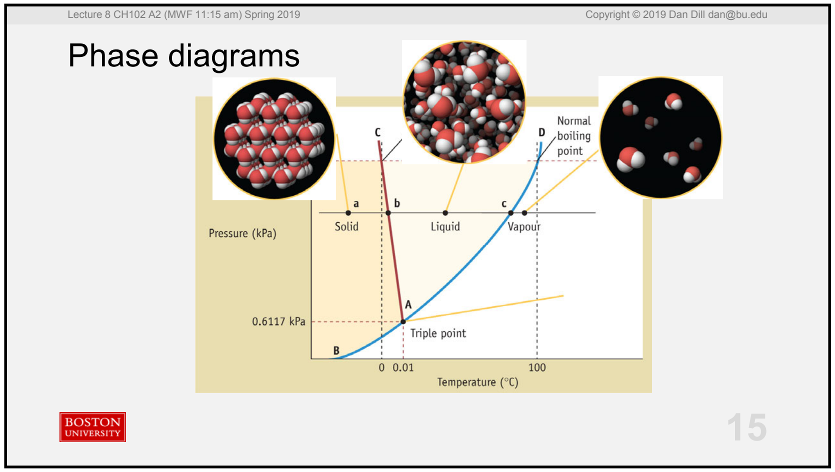


Working with the van der Waals equation

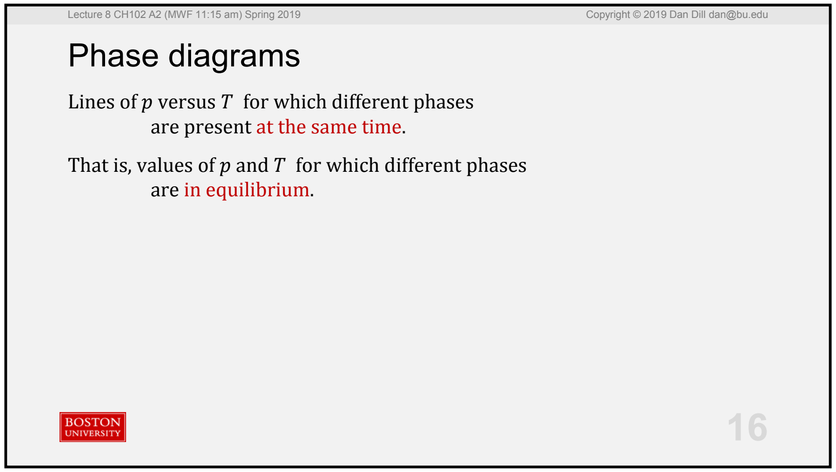
$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

In general, the effect of b is muted at low T and so the effect of a dominates there, while for high T the effect of b dominates.

For 3.00 mol of Cl_2 confined in 4.00 L, here is $\frac{p}{p_{\text{ideal}}} - 1$ versus T.



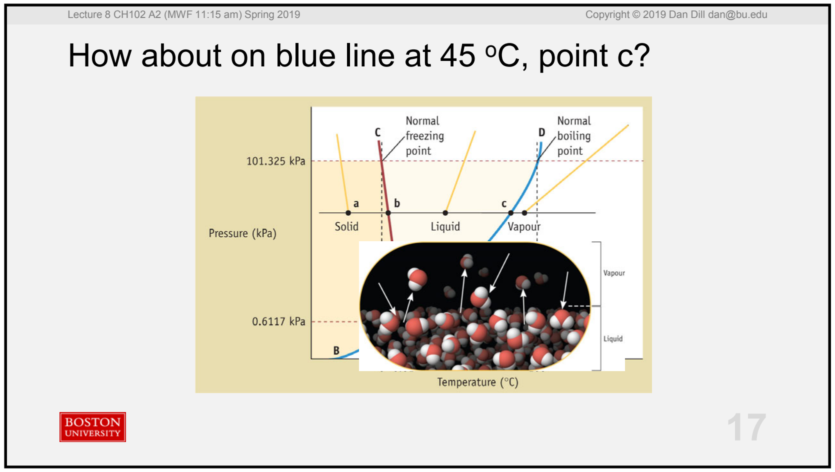
Phase diagrams



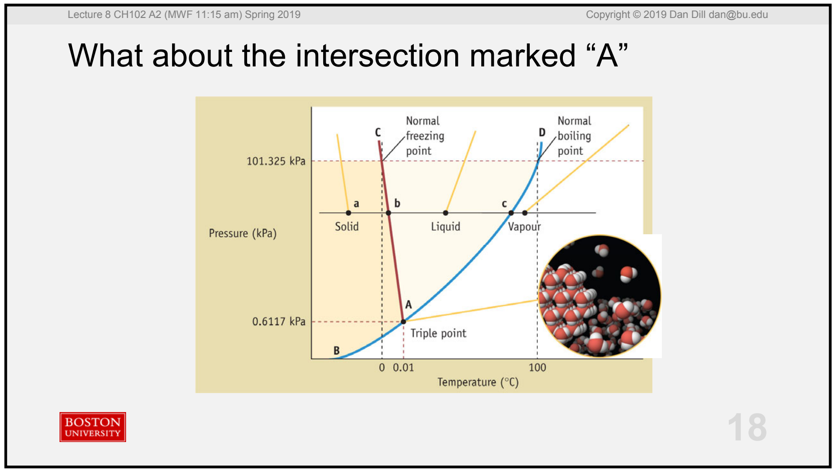
Phase diagrams

Lines of p versus T for which different phases are present at the same time.

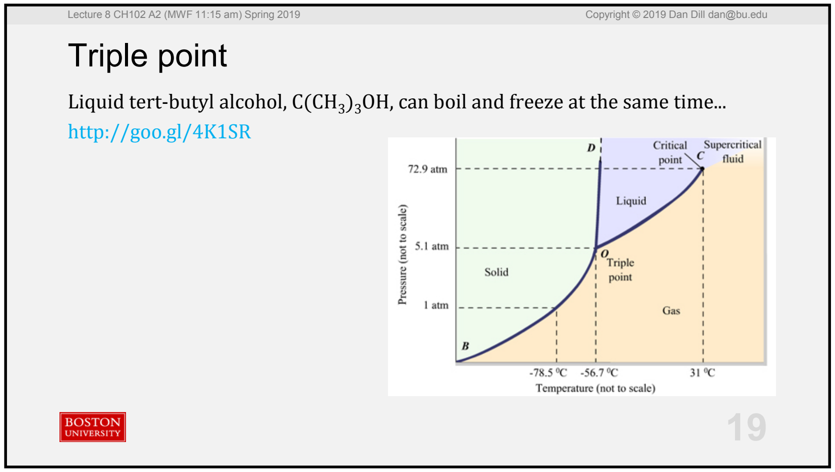
That is, values of p and T for which different phases are in equilibrium.



How about on blue line at 45 °C, point c?

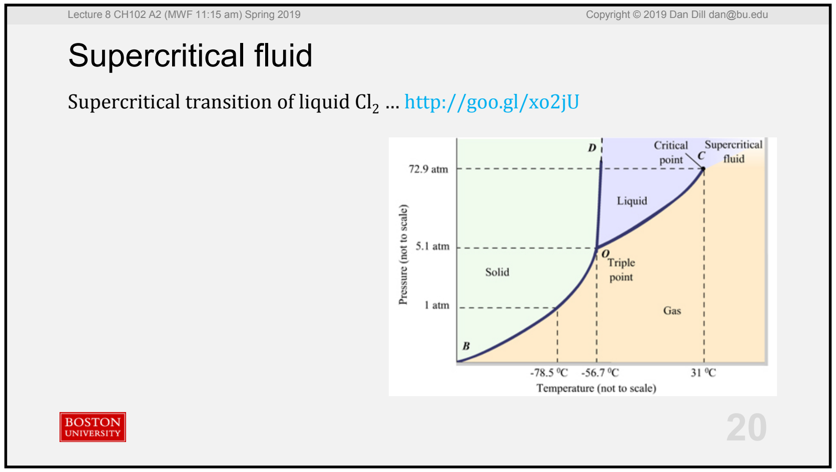


What about the intersection marked “A”



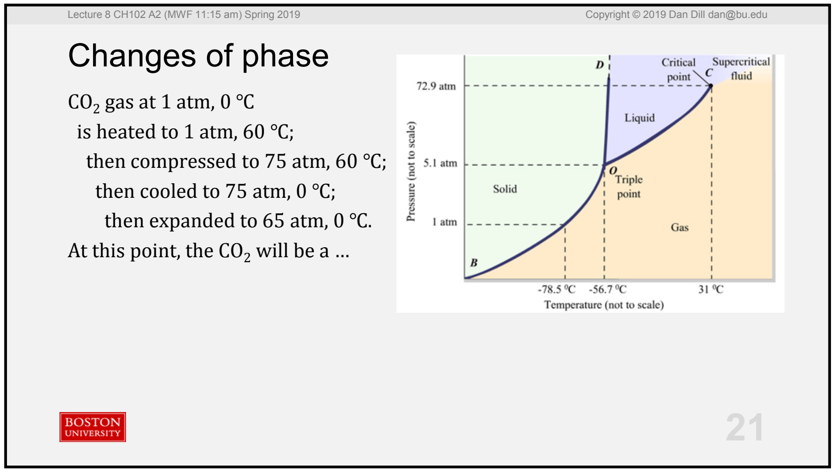
Triple point

Liquid tert-butyl alcohol, $C(CH_3)_3OH$, can boil and freeze at the same time…
http://goo.gl/4K1SR



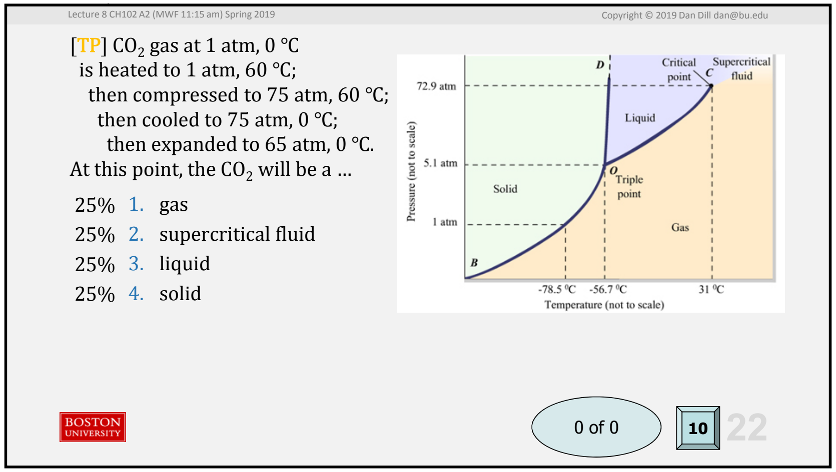
Supercritical fluid

Supercritical transition of liquid Cl_2 … http://goo.gl/xo2jU



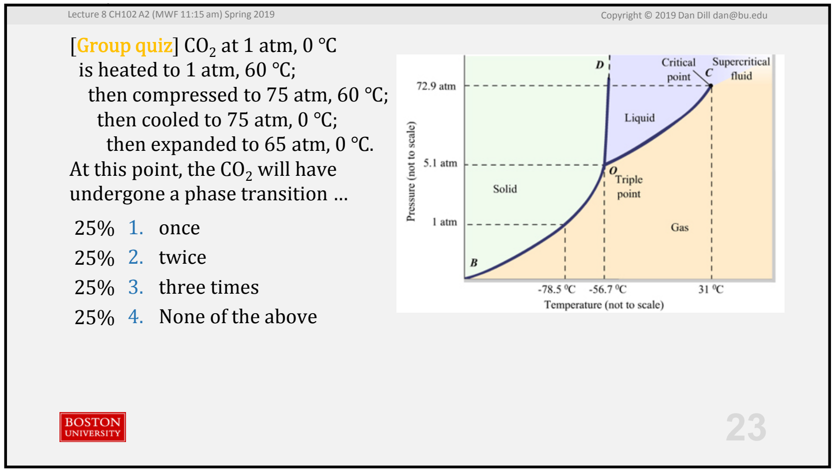
Changes of phase

CO_2 gas at 1 atm, 0 °C
is heated to 1 atm, 60 °C;
then compressed to 75 atm, 60 °C;
then cooled to 75 atm, 0 °C;
then expanded to 65 atm, 0 °C.
At this point, the CO_2 will be a …



[TP] CO_2 gas at 1 atm, 0 °C
is heated to 1 atm, 60 °C;
then compressed to 75 atm, 60 °C;
then cooled to 75 atm, 0 °C;
then expanded to 65 atm, 0 °C.
At this point, the CO_2 will be a ...

25% 1. gas
25% 2. supercritical fluid
25% 3. liquid
25% 4. solid



[Group quiz] CO_2 at 1 atm, 0 °C
is heated to 1 atm, 60 °C;
then compressed to 75 atm, 60 °C;
then cooled to 75 atm, 0 °C;
then expanded to 65 atm, 0 °C.
At this point, the CO_2 will have undergone a phase transition ...

25% 1. once
25% 2. twice
25% 3. three times
25% 4. None of the above