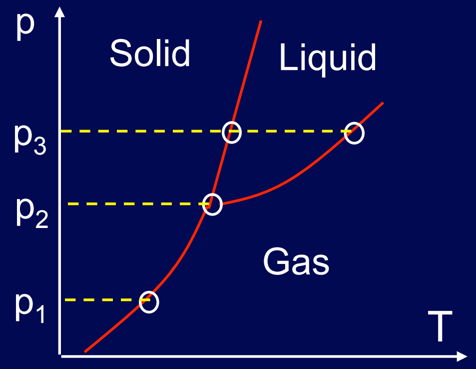
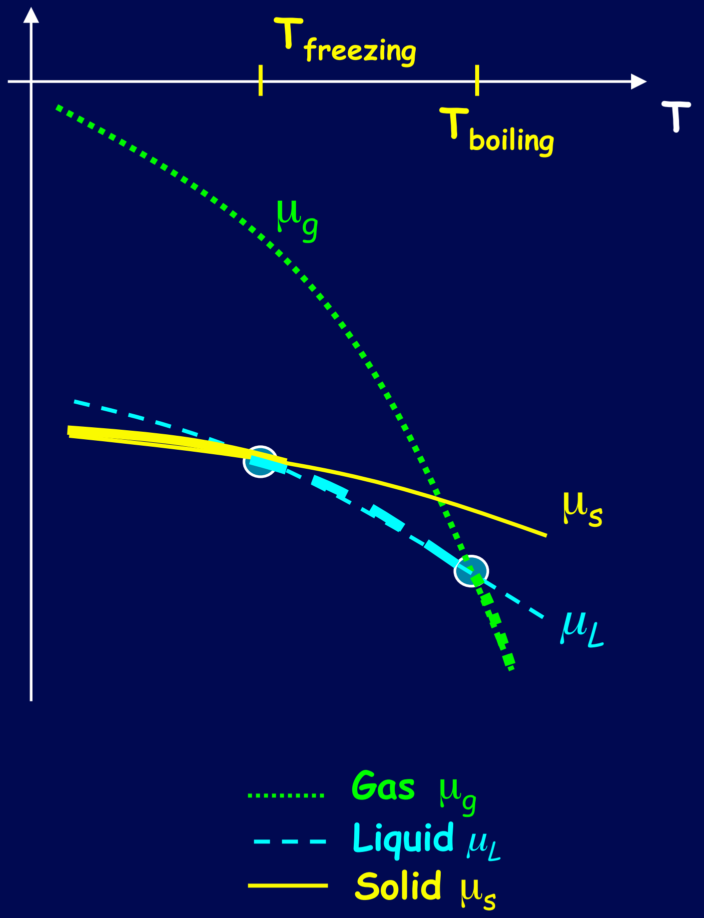
Lecture 22

Freezing/boiling Point Elevation/depression
Supercooling/superheating

Phase Diagram:



Phases of Matter



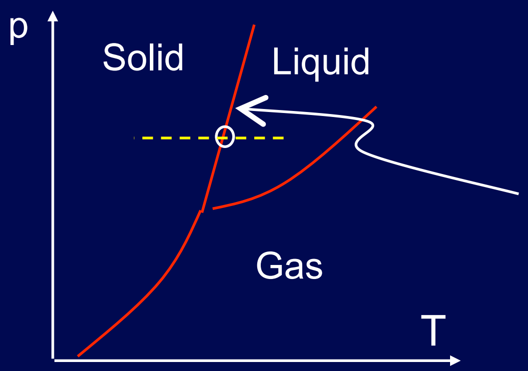
At constant pressure, the total entropy is maximized by minimizing the Gibb’s free energy: $G = U – TS + pV$

For phase transitions:

$$G = N_s \mu_s + N_l \mu_l + N_g \mu_g$$

Except at coexistence points, the free energy is minimized by having all the molecules be in the phase with the lowest chemical potential at that temperature and pressure.

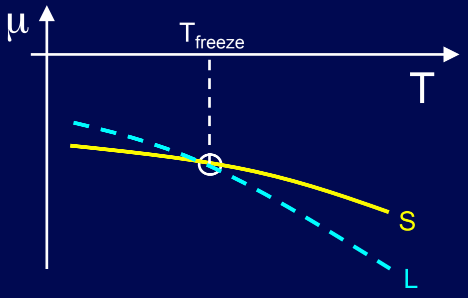
We can plot the coexistence points as a function of pressure and temperature → phase diagram



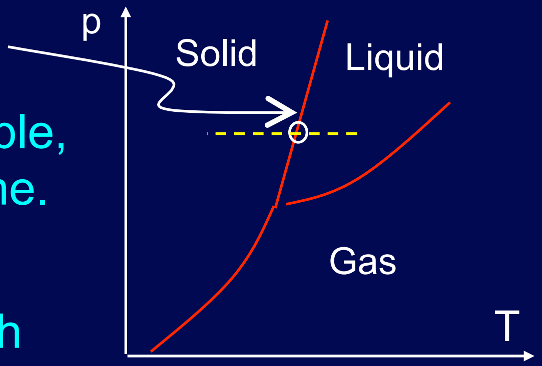
Question: Why isn’t this vertical?

Phase Transitions and Volume Change

So far, our liquid and solid $\mu(T)$ curves have been independent of pressure. We justified this with the fact that solids and liquids are nearly incompressible (which is true). This means that T_{freeze} should not depend on pressure. So:



Why is the line that separates the liquid and solid phases not vertical?

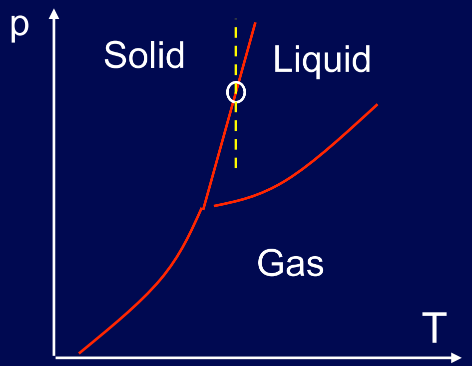


The reason is that, although they are incompressible, the volumes of the liquid and solid are not the same. Most substances expand when they melt.

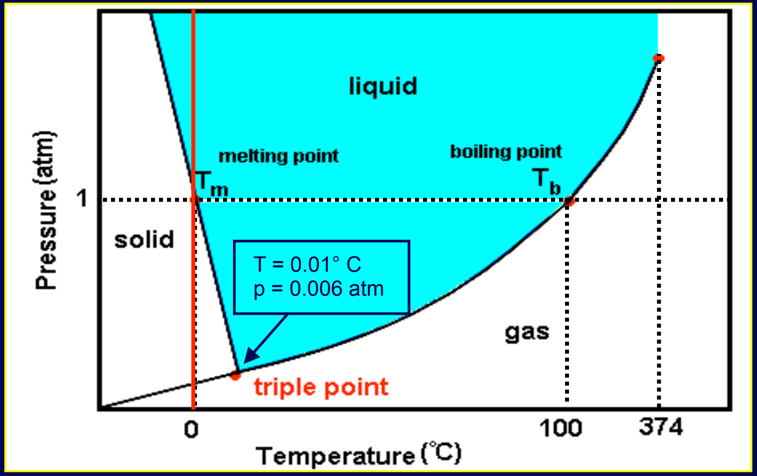
Suppose the volume change per mole is ΔV (which means $\Delta V/N_A$ per particle). Thus, (during melting) when a particle moves from solid to liquid, work is done by it (it's expanding): $W = p\Delta V/N_A$. This is a positive contribution to the liquid's chemical potential, and it increases with pressure. If you look at the chemical potential graph above, you'll see that this causes T_{freeze} to increase with pressure.

Water is Unusual

The typical phase diagram



The H_2O phase diagram



Most materials freeze if you push hard enough, but water melts!
This results from the fact that water expands when it freezes (ice floats).

Consequences:

- Fish can live in wintry lakes, because they don't freeze solid.

- Ice is slippery when you skate on it … NOT!

It's true that the melting/freezing temperature *does* decrease under pressure, but ice is not slippery for this reason - the pressure required is too large. Here's an article about it:

http://people.virginia.edu/~lz2n/mse305/ice-skating-PhysicsToday05.pdf

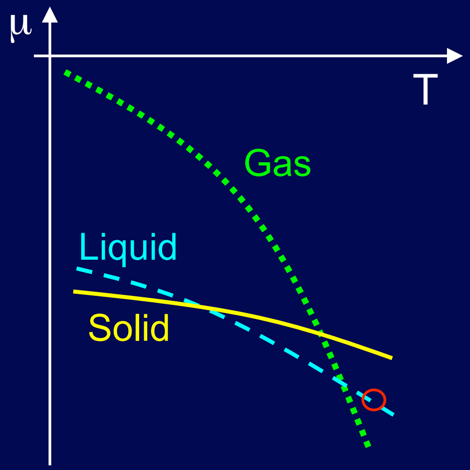
Act 1: Out of Equilibrium

1) A system starts in the state shown. What happens?

A) Substance freezes

B) Substance melts

C) Substance evaporates



2) How could we make this happen more quickly?

Solution

1) A system starts in the state shown. What happens?

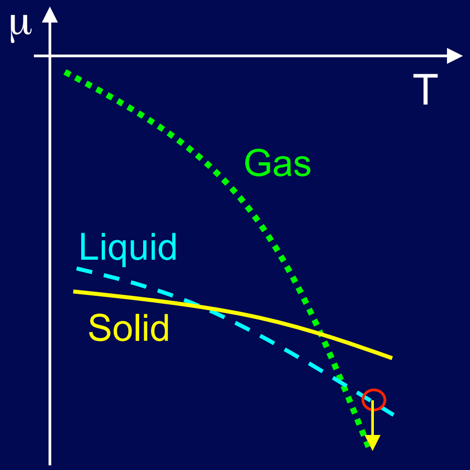
A) Substance freezes

B) Substance melts

C) Substance evaporates

It's a liquid out of equilibrium. The chemical potential of the gas phase is lower, so the liquid evaporates (or boils, if the system is enough out of equilibrium).

2) How could we make this happen more quickly?



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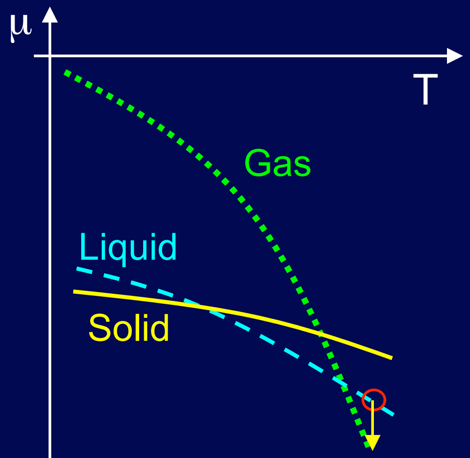


It's a liquid out of equilibrium. The chemical potential of the gas phase is lower, so the liquid evaporates (or boils, if the system is enough out of equilibrium).

2) How could we make this happen more quickly?

The rate depends on the chemical potential difference. ← I didn't justify this, so you'll have to take it on faith.

So:

- We could increase T, because the gas curve falls faster than the liquid curve. That's why warm water evaporates more quickly.
- We could decrease p (making the gas curve move to the left). Note: If several gases are present (as in air) we only need to lower the pressure of the one we are interested in.

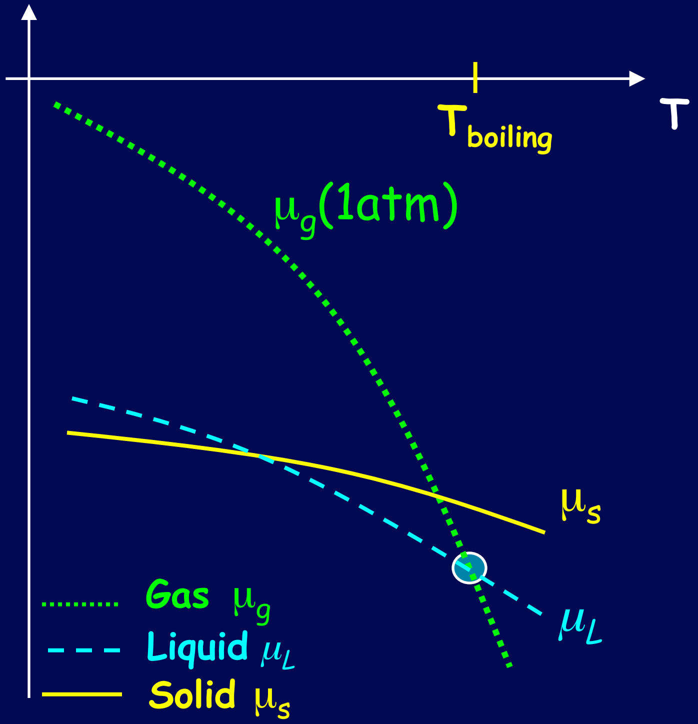
ACT 2: Boiling Temperature

Compare the temperature of boiling water at 1 atm to the temperature at 0.8 atm.

A) $T_{boil}(0.8\ \text{atm}) > T_{boil}(1\ \text{atm})$

B) $T_{boil}(0.8\ \text{atm}) = T_{boil}(1\ \text{atm})$

C) $T_{boil}(0.8\ \text{atm}) < T_{boil}(1\ \text{atm})$



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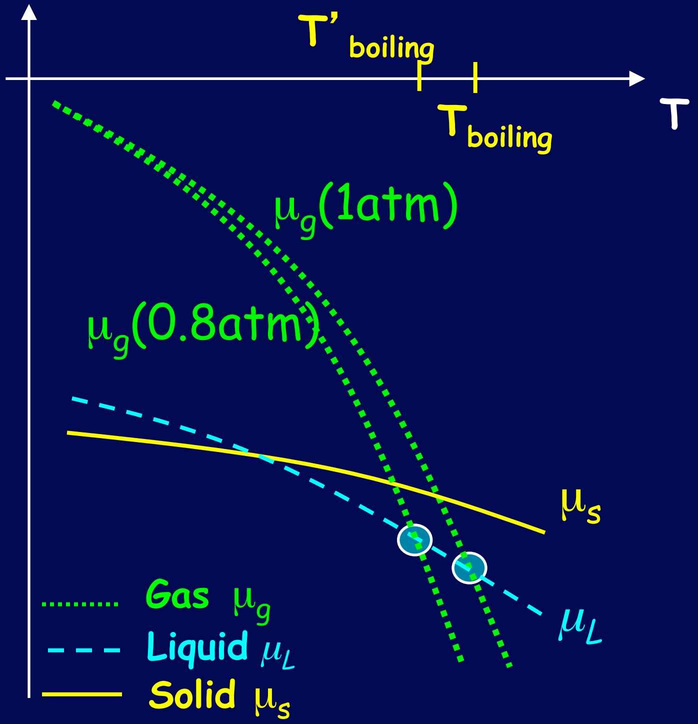


Lowering the density of the gas lowers its chemical potential curve μ_G. This will move the boiling transition to lower temperature. This is the reason water boils at lower T at high altitude.

Clausius-Clapeyron:

$p = p_o e^{-L/kT}$

L = latent heat/molecule

$L_{water} = 0.42$ eV

T_{boil}(Champaign) = 100ºC

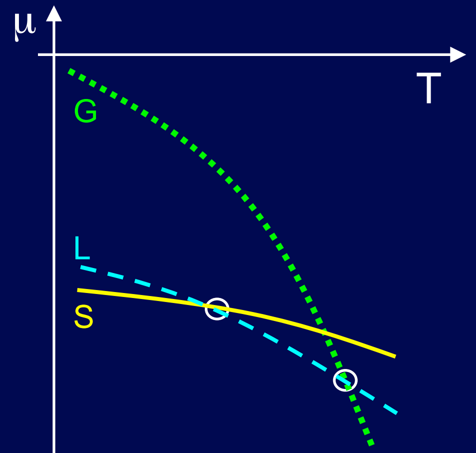
T_{boil}(Denver [p = 0.82 atm]) = 94.4ºC

T_{boil}(Pressure cooker [p = 2 atm]) = 121ºC

Variation of Freezing/boiling Temperatures

Lowering the density of the gas lowers its chemical potential curve μ_G. This will move the boiling transition to lower temperature. This is the reason water boils at lower T at high altitude.

We can similarly lower the μ_L curve by lowering the density of the molecules in the liquid. This will lower the freezing temperature of the liquid.



Example: Putting salt on ice lowers the melting point. Why? The salt dissolves in the liquid, lowering the density (and thus μ) of the remaining liquid H_2O. The salt does not easily penetrate the solid ice, so has little effect on its μ.

This illustrates a general principle: Dissolving substance A in substance B lowers the chemical potential. If the chemical potential weren't lowered, it wouldn't dissolve!

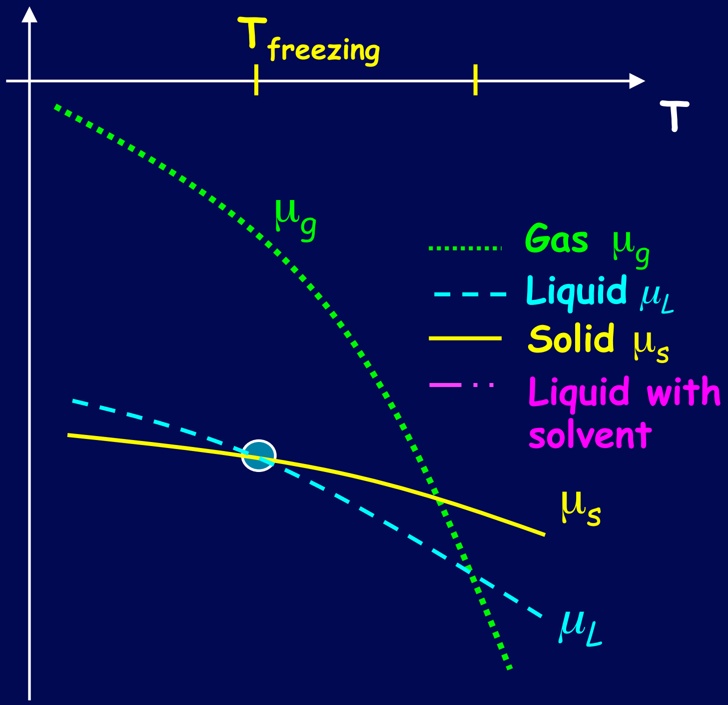
Note: The density argument we made above isn't always the important point. Sometimes, the energy change is also important (even dominant).

http://antoine.frostburg.edu/chem/senese/101/solutions/faq/thermo-explanation-of-freezingpoint-depression.shtml

Freezing point depression

Lowering the density of the gas lowers the chemical potential curve μ_g .

We can similarly lower the μ_L curve by lowering the density of the molecules in the liquid.



Freezing point depression

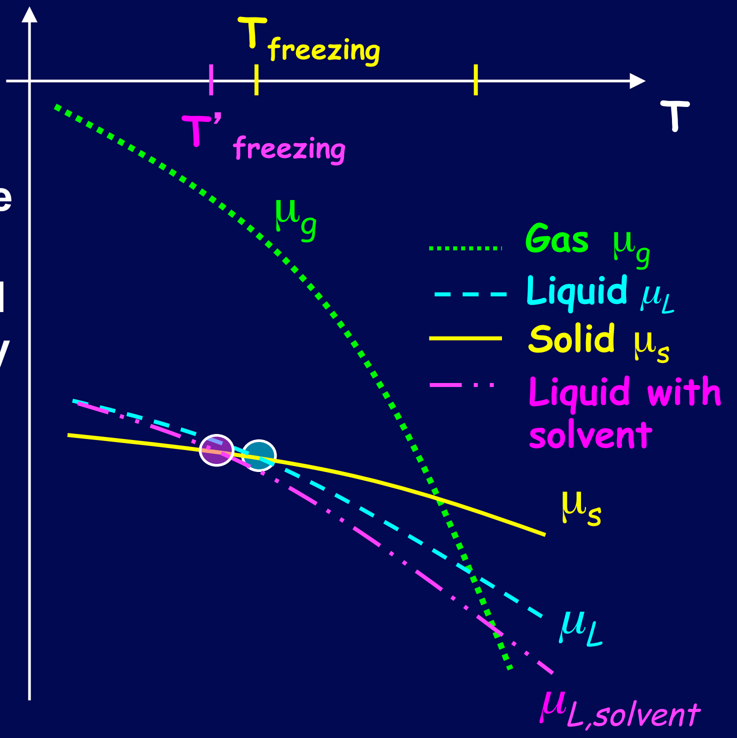
Lowering the density of the gas lowers the chemical potential curve μ_g .

We can similarly lower the μ_L curve by lowering the density of the molecules in the liquid. How do we lower the density of molecules? Replace them with other sorts of molecules (It is only the molecules of the same species as the solid that count toward equilibrium). There are very many solutes which:

- Dissolve easily in the liquid phase
- Don't fit well at all in the crystal
- Have very low vapor pressure (absent from gas)

These have almost no effect on H_2O's μ_g or μ_S.

- **anti-freeze**
- **salt on roads**
- **sugar would work too, but**
  - **doesn't have as many molecules/kg**
  - **costs more**
  - **would leave a sticky mess!**



They always *lower* μ_l (stabilize liquid in each case).
So they lower T_f.

What about T_b…

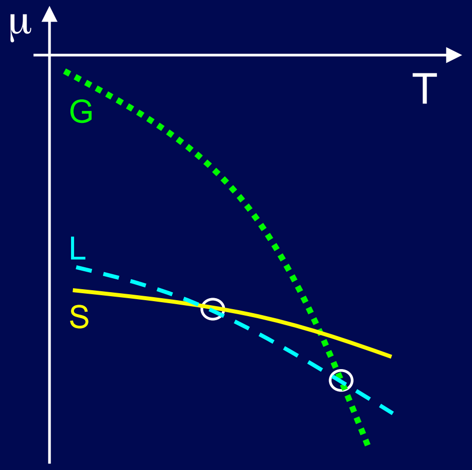
ACT 3: Boiling Temperature

What does the addition of salt to liquid water do to its boiling temperature?

A) Raises the boiling temperature

B) Lowers the boiling temperature

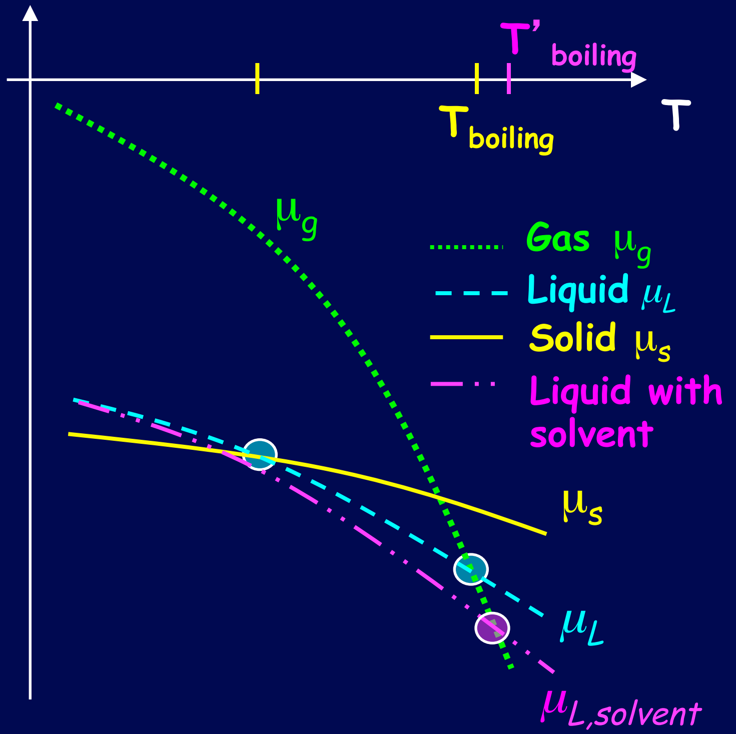
C) Does not change the boiling temperature



Solution

What does the addition of salt to liquid water do to its boiling temperature?

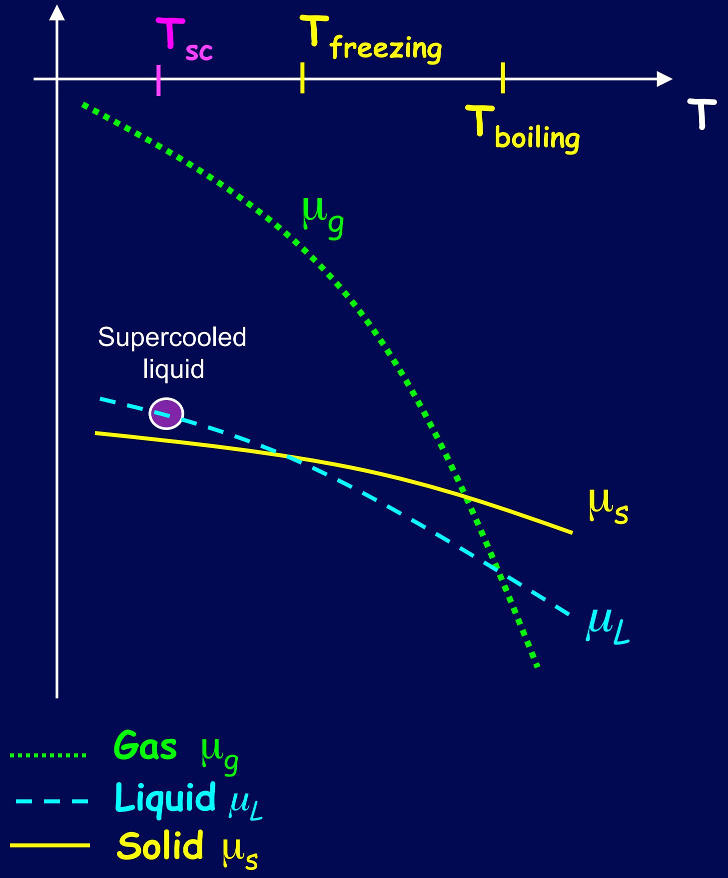
- A) Raises the boiling temperature
- B) Lowers the boiling temperature
- C) Does not change the boiling temperature



Adding salt to the liquid lowers the liquid's μ, (because it lowers the H_2O density) raising the boiling temperature.

However, we must be careful. What does the salt do to the gas's chemical potential? In this case, salt does not evaporate easily (it has a very low vapor pressure), so it has a negligible effect on μ_G. If we were to dissolve a more volatile substance (*e.g.*, alcohol) in the liquid, the answer might be different.

Supercooling & Superheating



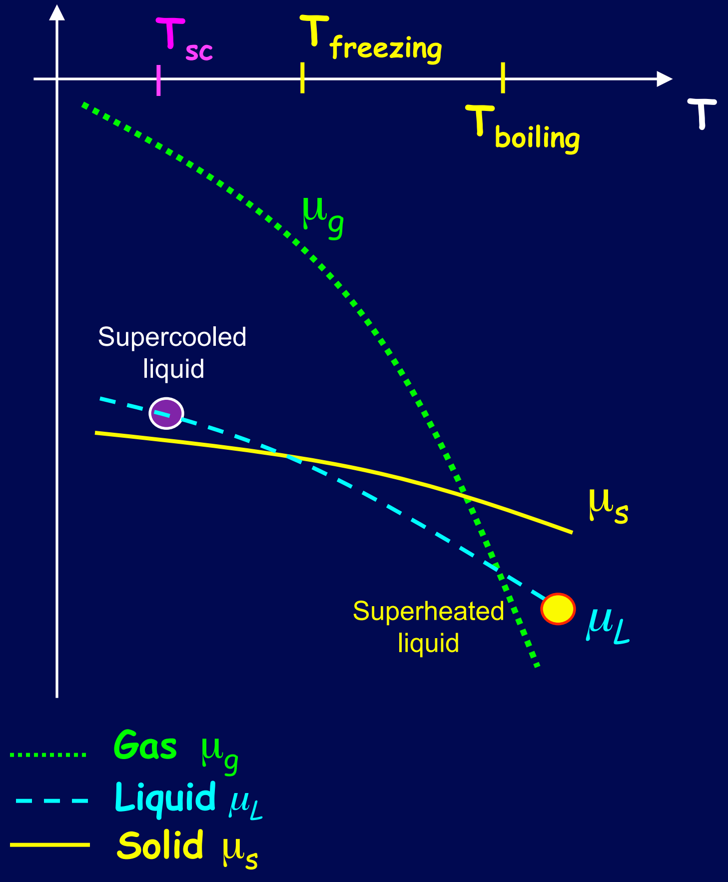
If we cool a liquid to $T_{freezing}$, normally it will freeze to lower its free energy.

However, if there are no nucleation sites, it is possible to "supercool" the liquid well below the freezing temperature.

This is an unstable equilibrium.

What happens when the system suddenly freezes?

Solution



If we cool a liquid to $T_{freezing}$, normally it will freeze to lower its free energy.

However, if there are no nucleation sites, it is possible to "supercool" the liquid well below the freezing temperature.

This is an unstable equilibrium.

What happens when the system suddenly freezes?

The free energy drops.
This "latent heat" is suddenly released.

It is similarly possible to superheat a liquid above its boiling temperature; adding nucleation sites leads to rapid (and often dangerous!) boiling.

Supercooling/superheating Demos

Liquid water can be

- heated above 100°C
  - http://www.animations.physics.unsw.edu.au/jw/superheating.htm
- Cooled well below 0°C
  - http://www.youtube.com/watch?v=13unrtlvfrw

Why does the water only partly boil or freeze (slush)?
What is T of the leftover water?
Boiling: 100°C
Freezing: 0°C

Supercooling/superheating Demos (2)

Freezing: warmed to 0°C.
The molecules U* dropped as they joined the ice, releasing U* that warmed things up to 0°C

At which point freezing stopped,
leaving slush.

*To be precise, it's U+pV (enthalpy, H) here at constant p

Boiling: cooled to 100°C.
U+pV (enthalpy, H) increased as molecules joined the gas, soaking up H from surroundings, cooling them to 100°C

At which point boiling stopped
leaving some liquid.

Thank you,

Erika !!

Good Luck !!

FYI: Quantitative Freezing Point Depression, H_2O

How it works (exact for dilute solutions):
A solvent molecule entering from another phase
gives extra V for each solute molecule to roam in.
That increases the solute's S, reduces $\Delta G = \Delta U + p\Delta V - T\Delta S$.
Smaller ΔG on adding a solvent particle *means* reduced μ of solvent.

- At low solute concentration, $n = N/V$,
  the *only* effect of the solute on μ is via getting more S when the solvent volume increases.
  (too few solutes to interact, solute-H_2O interaction doesn't change when you get more H_2O)

- We can calculate the effect exactly via state counting!
  This result *does not depend on the type of solute particle!*
  - At higher solute concentrations other terms (solute-solute interactions) also matter

- Adding 1 molecule of water increases the solution volume V by $\delta V = 3 \times 10^{-29}$ m^3.
  - So V available to each solute molecule increases by a factor $(1+\delta V/V)$.
  - So its S increases by $k \ln(1+\delta V/V) = k\,\delta V/V$
  - This happens to nV molecules.
  - So $\Delta S = knV\,\delta V/V = nk\delta V$.
  - At 1 Molar solute, $n = 6 \times 10^{26}/\text{m}^3$: $\Delta S = nk\delta V = 2.5 \times 10^{-25}$ J/K
  - ΔS of freezing = Latent Heat/T= (6000 J/Mole) /273K ~ 22 J/K-Mole, ~$3.7\ 10^{-23}$ J/K-molecule
  - So a 1M solute increases the melting ΔS by ~ 0.7% ($2.5 \times 10^{-25} / 3.7\ 10^{-23}$)
    - To keep the $T\Delta S$ term in ΔG balancing ΔH at T_F,
      T_F must *drop* by about 0.7%/M or 1.9 K/M (works well experimentally)