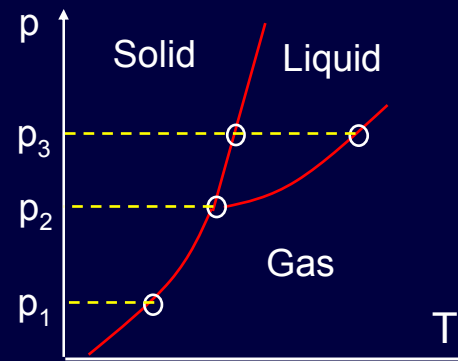


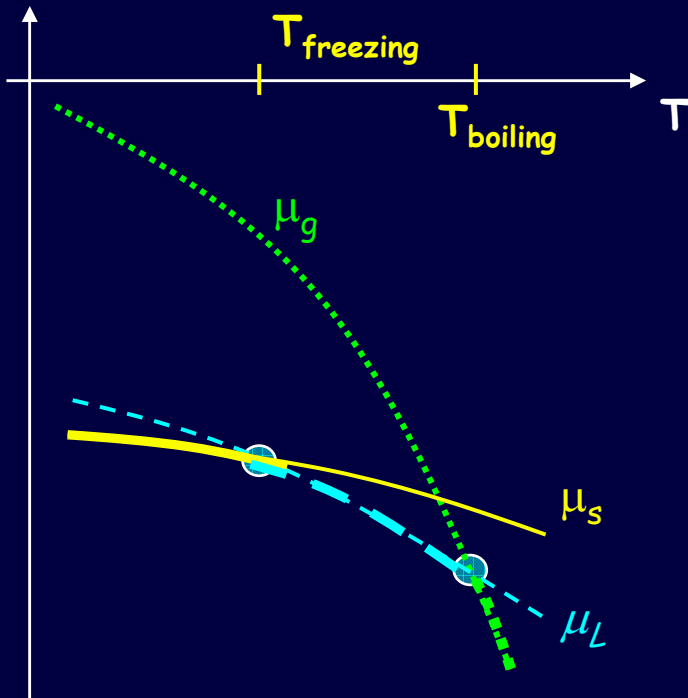
# Lecture 22

Freezing/boiling Point Elevation/depression  
Supercooling/superheating

Phase Diagram:



# Phase Transitions



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

For phase transitions:

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

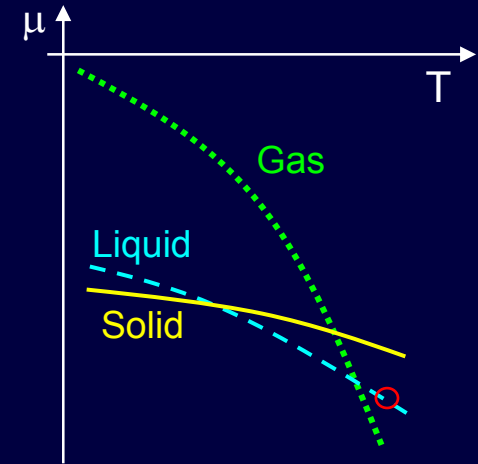
Except at coexistence points, the free energy is minimized by having all the molecules be in the phase with the lowest chemical potential at that temperature and pressure.

..... Gas  $\mu_g$   
- - - Liquid  $\mu_L$   
— Solid  $\mu_s$

# 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

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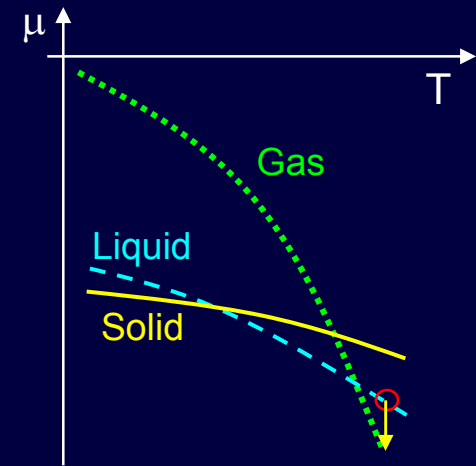
A) Substance freezes

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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?

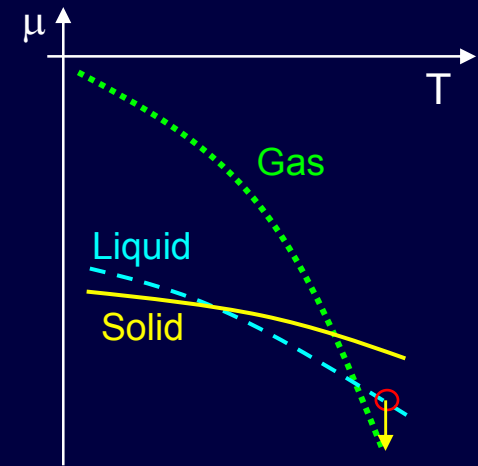


# Solution

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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.

So:

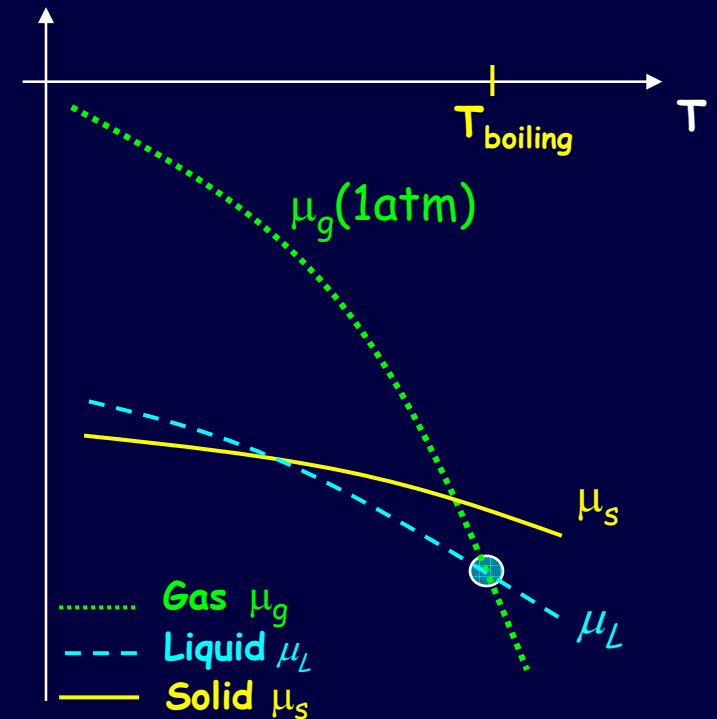
- We could increase  $T$ , because the gas curve falls faster than the liquid curve. That's why warm water evaporates more quickly.
  - We could decrease  $p$  (making the gas curve move to the left).
- Note: If several gases are present (as in air) we only need to lower the pressure of the one we are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

← I didn't justify this, so you'll have to take it on faith.

# ACT 2: Boiling Temperature

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

- A)  $T_{\text{boil}}(0.8 \text{ atm}) > T_{\text{boil}}(1 \text{ atm})$
- B)  $T_{\text{boil}}(0.8 \text{ atm}) = T_{\text{boil}}(1 \text{ atm})$
- C)  $T_{\text{boil}}(0.8 \text{ atm}) < T_{\text{boil}}(1 \text{ atm})$



# ACT 2: Boiling Temperature

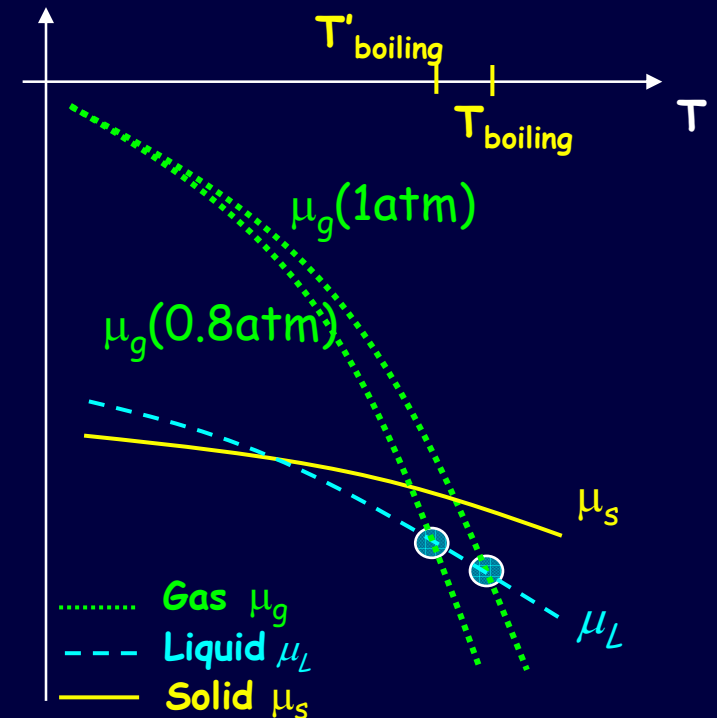
Compare the temperature of boiling water at 1 atm to the temperature at 0.8 atm.

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

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



Clausius-Clapeyron:

$$p = p_0 e^{-L/kT}$$

L = latent heat/molecule

$$L_{\text{water}} = 0.42 \text{ eV}$$

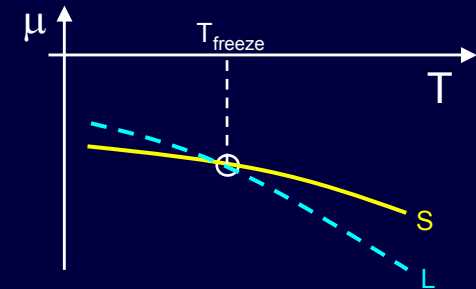
$$T_{\text{boil}}(\text{Champaign}) = 100^\circ\text{C}$$

$$T_{\text{boil}}(\text{Denver } [p = 0.82 \text{ atm}]) = 94.4^\circ\text{C}$$

$$T_{\text{boil}}(\text{Pressure cooker } [p = 2 \text{ atm}]) = 121^\circ\text{C}$$

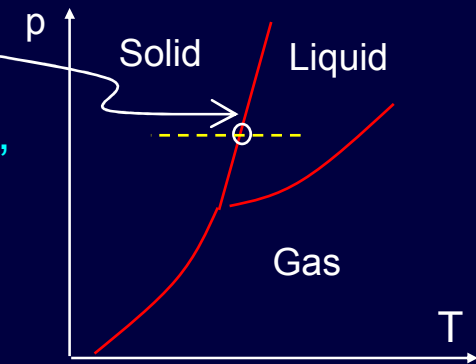
# Phase Transitions and Volume Change

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  $T_{\text{freeze}}$  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.**

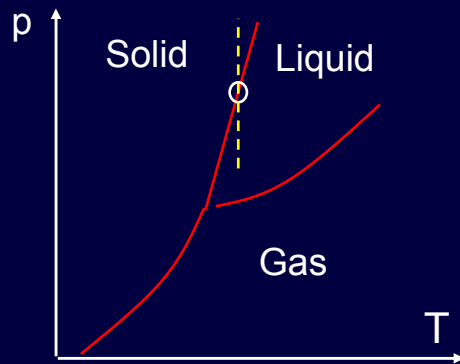


Suppose the volume change per mole is  $\Delta V$  (which means  $\Delta V/N_A$  per particle). Thus, (during melting) when a particle moves from solid to liquid, work is done by it (it's expanding):  $W = p\Delta V/N_A$ . This is a positive contribution to the liquid's chemical potential, and it increases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

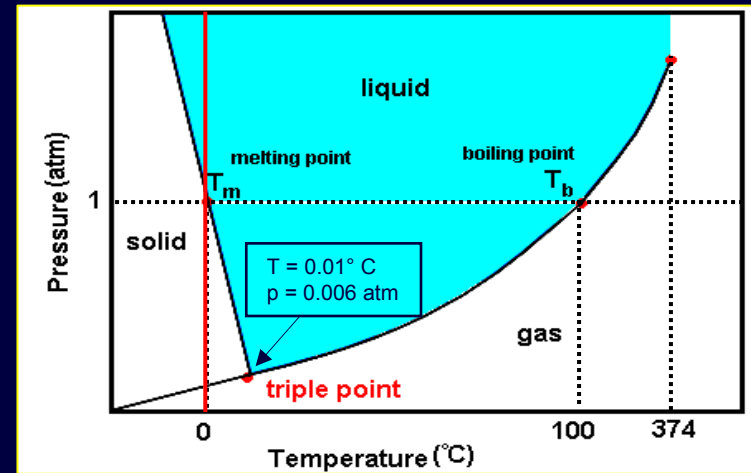


# Water is Unusual

The typical phase diagram



The H<sub>2</sub>O 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!**

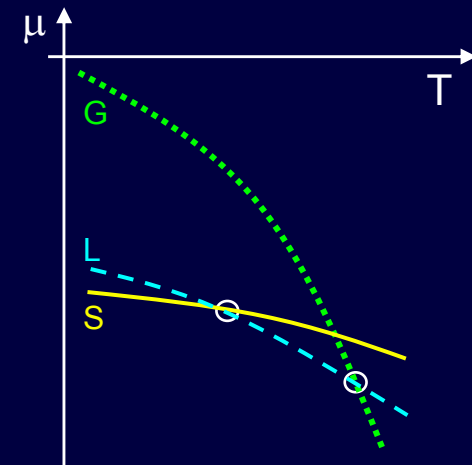
It's true that the melting/freezing temperature *does* decrease under pressure, but ice is not slippery for this reason - the pressure required is too large. Here's an article about it:

# Variation of Freezing/boiling Temperatures

Lowering the density of the gas lowers its chemical potential curve  $\mu_G$ . 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  $\mu_L$  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  $\mu$ ) of the remaining liquid  $H_2O$ . The salt does not easily penetrate the solid ice, so has little effect on its  $\mu$ .



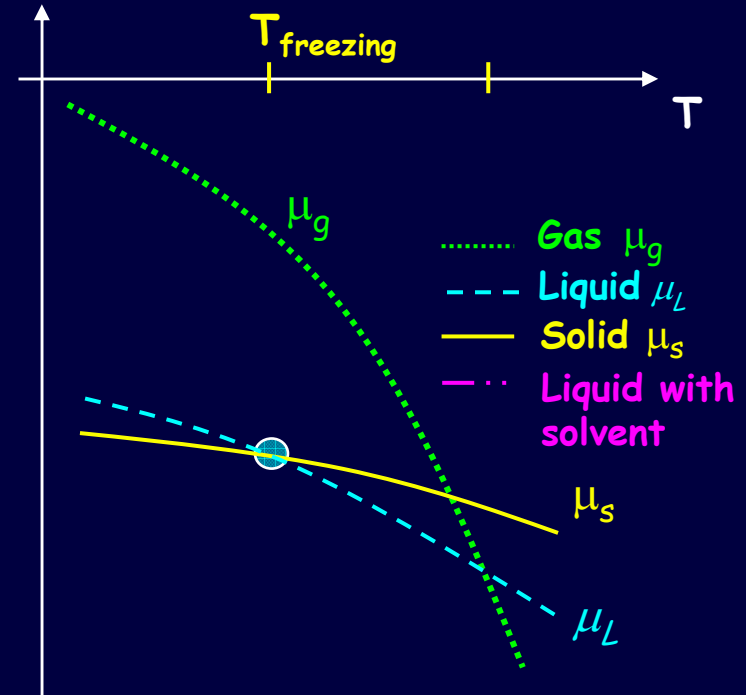
This illustrates a general principle: **Dissolving substance A in substance B lowers the chemical potential.** If the chemical potential weren't lowered, it wouldn't dissolve!

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

# Freezing point depression

Lowering the density of the gas lowers the chemical potential curve  $\mu_g$ .

We can similarly lower the  $\mu_L$  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  $\mu_g$ .

We can similarly lower the  $\mu_L$  curve by lowering the density of the molecules in the liquid. How do we lower the density of molecules?

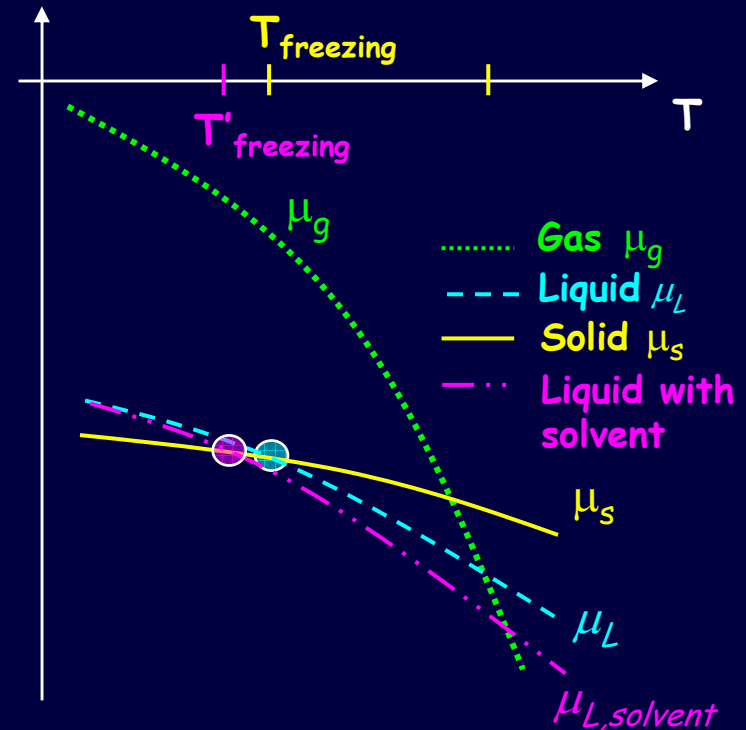
Replace them with other sorts of molecules (It is only the molecules of the same species as the solid that count toward equilibrium).

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  $\mu_g$  or  $\mu_s$ .

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



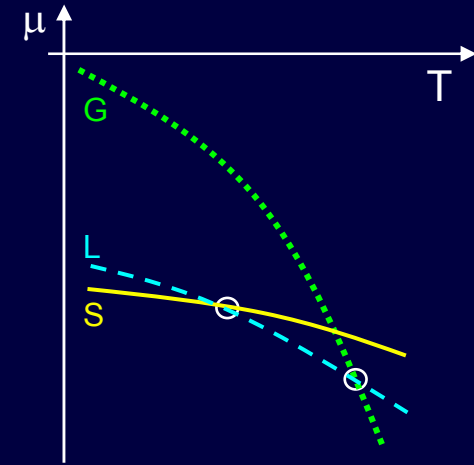
They always *lower*  $\mu_l$  (stabilize liquid in each case). So they lower  $T_f$ .

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



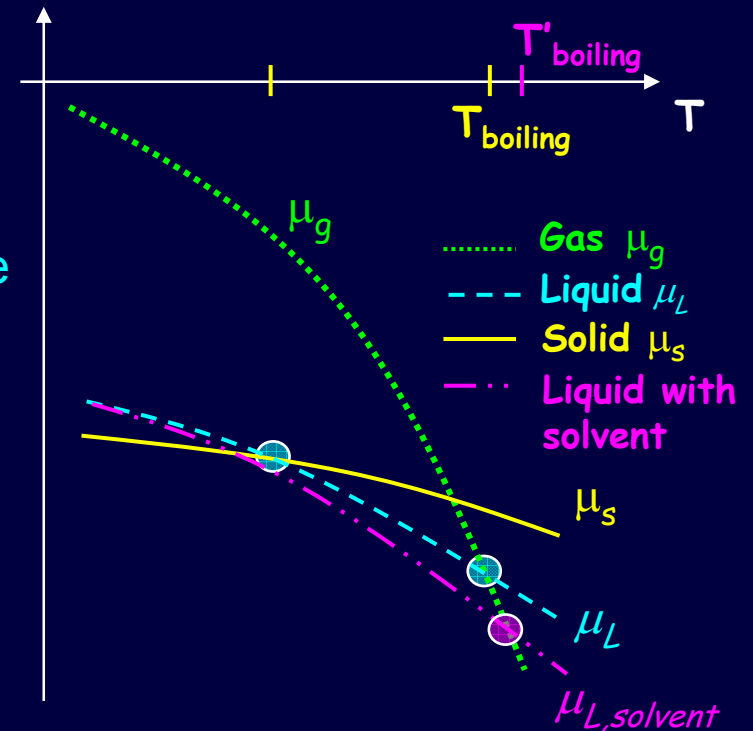
# Solution

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

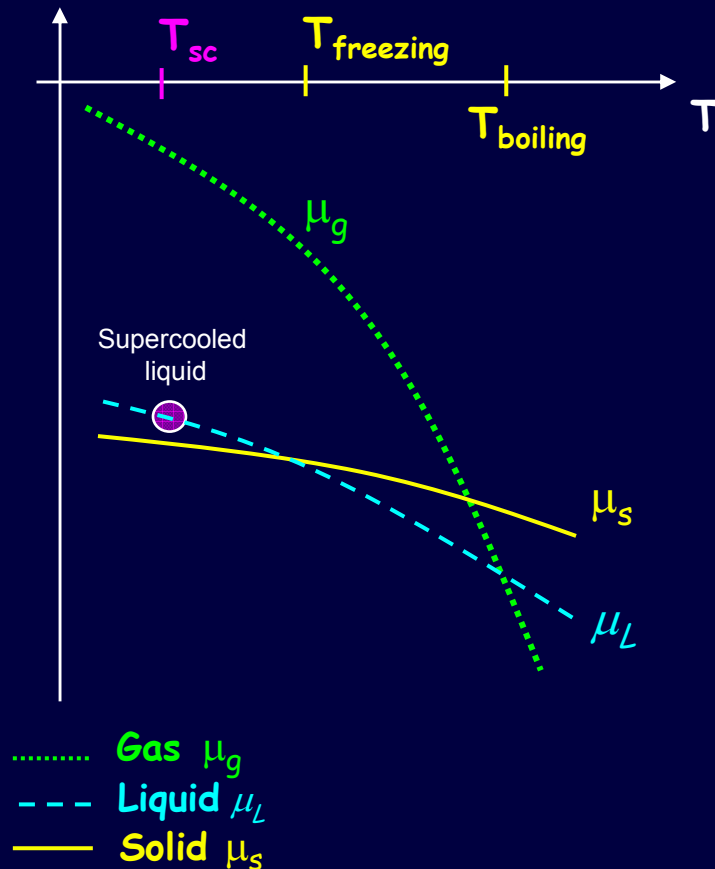
- A) Raises the boiling temperature
- B) Lowers the boiling temperature
- C) Does not change the boiling temperature

Adding salt to the liquid lowers the liquid's  $\mu$ , (because it lowers the  $\text{H}_2\text{O}$  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  $\mu_G$ . If we were to dissolve a more volatile substance (e.g., alcohol) in the liquid, the answer might be different.



# Supercooling & Superheating



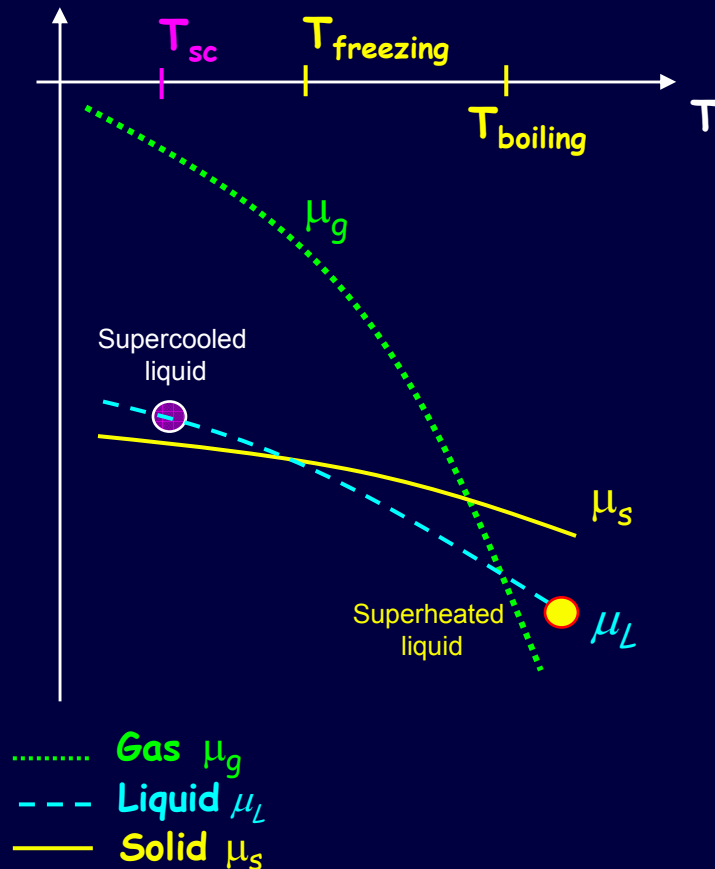
If we cool a liquid to  $T_{freezing}$ , normally it will freeze to lower its free energy.

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  $T_{\text{freezing}}$ , 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.



*Thank you,*

*Erika !!*

*Good Luck !!*