Miscellaneous Notes

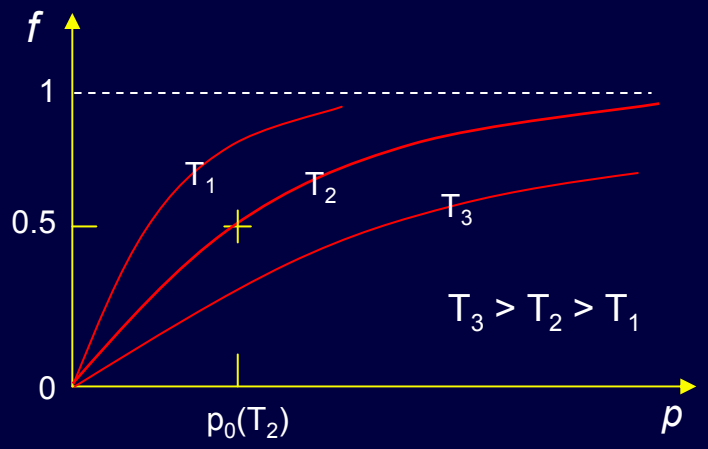
- The end is near – don't get behind.
- **All Excuses must be taken to 233 Loomis before noon, Thur, Dec. 13.**
- The PHYS 213 final exam times are
  * 8-10 AM, Monday, Dec. 17
  * 7-9 PM, Wed, Dec. 19

  The deadline for changing your final exam time is 5 pm, Friday, Dec. 7.

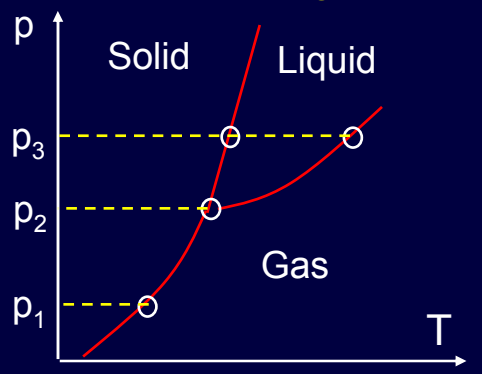
- Final review session: Sunday, Dec. 16, 3-6pm.
- Homework 6 is due Tuesday, Dec. 11 at 8 am. (NO late turn-in).
- Course Survey = 2 bonus points (accessible in SmartPhysics –Dec. 14 deadline)

Lecture 21

Review & Examples



Phase Diagram:



Chemical Equilibrium

Reactions like: $aA + bB \leftrightarrow cC$,
where A, B, and C are the particle types and a, b, and c are integers.

In equilibrium the total free energy, F, is a minimum.
We must have $\Delta F = 0$ when the reaction is in equilibrium,
for any reaction that takes us away from equilibrium:

Therefore: $a\mu_A + b\mu_B = c\mu_C$

Treating the components as ideal gases or solutes:

$$\mu_i = kT \ln \frac{n_i}{n_{Q_i}} - \Delta_i$$

← Internal energy per molecule

Plug these chemical potentials into the equilibrium condition,
$a\mu_A + b\mu_B = c\mu_C$, and solve for the density ratios:

$$\frac{n_C^c}{n_A^a n_B^b} = K(T), \text{ where } K(T) = \frac{n_{Q_C}^c}{n_{Q_A}^a n_{Q_C}^b} e^{+\Delta/kT} \qquad \Delta \equiv c\Delta_C - a\Delta_A - b\Delta_B$$

K(T) is called the "equilibrium constant".

ACT 1: Gases in Solution

1) Consider oxygen dissolving in a liquid. The reaction is $O_{2gas} \leftrightarrow O_{2liquid}$.
If you double the air pressure, keeping T constant, what happens to the density of the dissolved O_2? (Assume that the liquid itself is unaffected.)

A) Density is halved B) Density is unchanged C) Density is doubled

2) Now consider CO_2 being dissolved according to the approximate reaction: $CO_{2gas} \leftrightarrow CO_{2liquid}$ (here we neglect the chemistry that happens between the CO_2 and water after the dissolving occurs). If we increase the temperature, what will happen to the amount of CO_2 that can be 'kept' in the water?

A) $CO_{2liquid}$ increases B) $CO_{2liquid}$ stays the same C) $CO_{2liquid}$ decreases

Solution

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$$\frac{n_{gas}}{n_{liquid}} = K(T)$$

K remains unchanged, so n_{liquid} must double.

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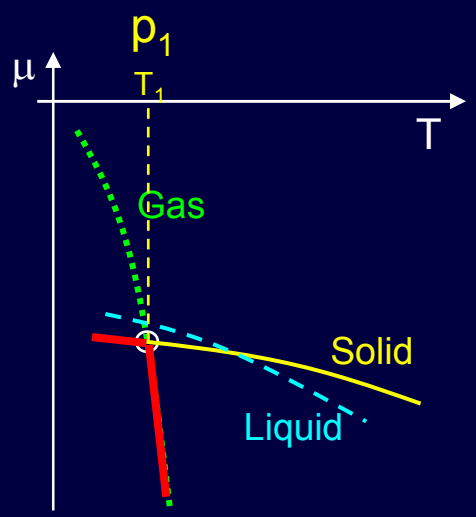
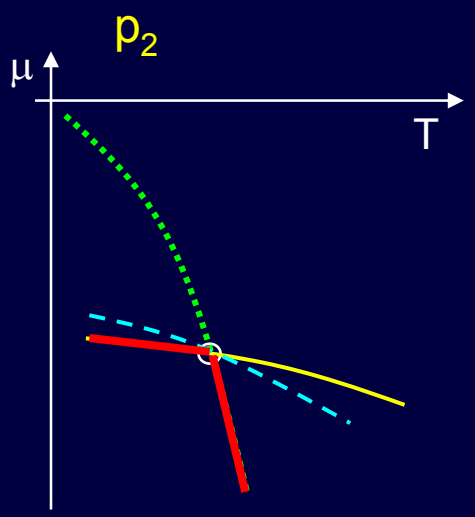
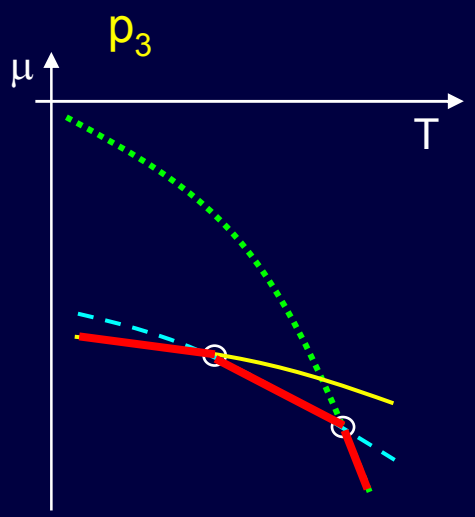
A) $CO_{2liquid}$ increases B) $CO_{2liquid}$ stays the same **C) $CO_{2liquid}$ decreases**

The CO_2 has more entropy in the atmosphere than in the water. So at high temperature that's where we find the CO_2. This means that global warming is doubly bad – it reduces the capacity of the ocean for CO_2, just when we'd like the ocean to take up more.

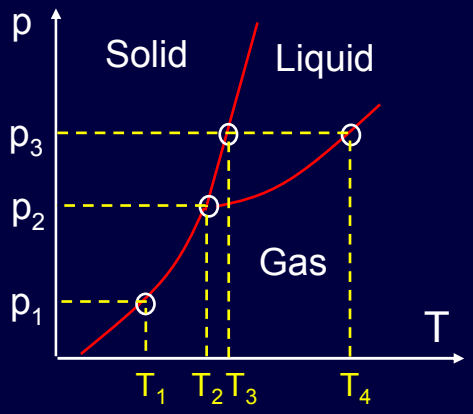
The p-T Diagram with Three Phases







Phase Diagram:



At low pressure, the liquid phase is not stable for any T. The substance sublimes at temperature T_1.

If we increase the pressure, the gas curve moves to the right. There is a critical pressure for which all three curves pass through a point. The three phases can coexist only at (T_2,p_2).

At high pressure, there are two phase transitions: solid-liquid at T_3, and liquid-gas at T_4.

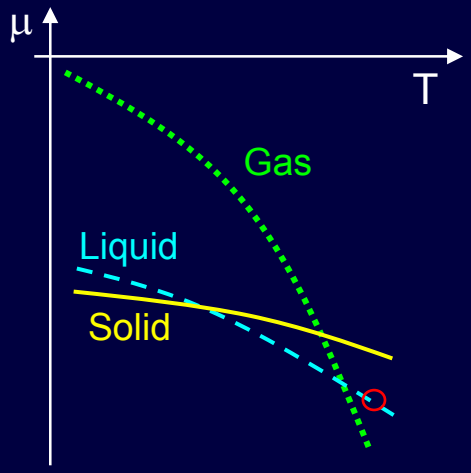
Act 2: Out of Equilibrium

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

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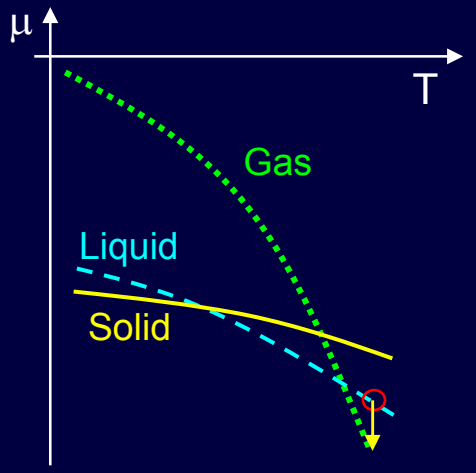
C) Substance evaporates

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).



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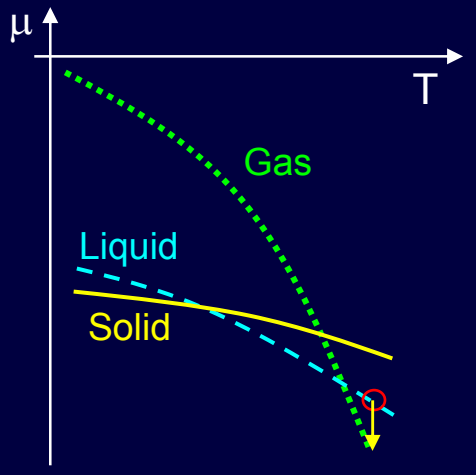


It's a liquid out of equilibrium. The chemical potential of the gas phase is lower, so the liquid evaporates (or boils, if the system is enough out of equilibrium).

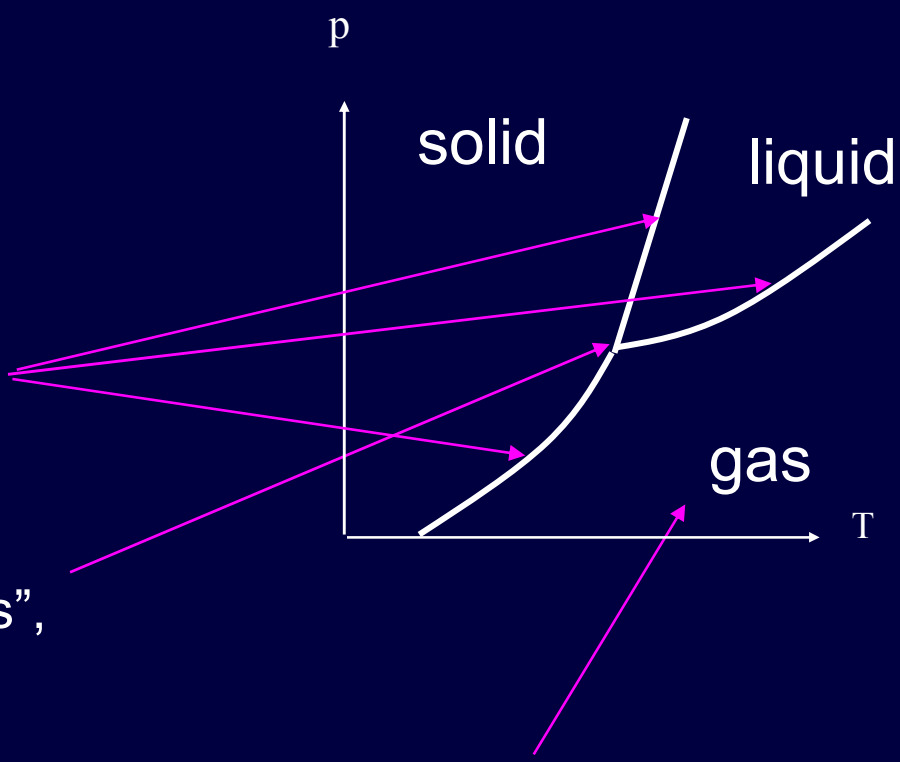
2) How could we make this happen more quickly?

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.

Phase Diagrams



- On special transition lines, two phases are stable.
- At very special “triple points”, those line cross and three phases are stable.
- Notice that in almost all the (p.T) plane, only ONE phase is stable. Why is that?

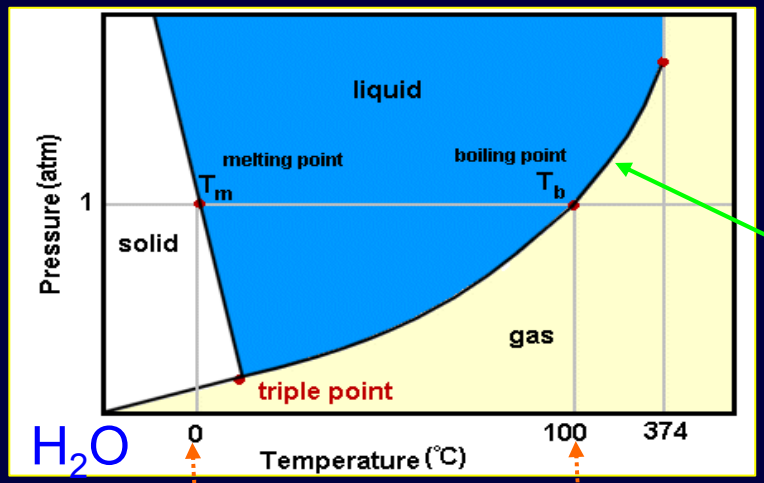
Why usually ONE stable phase?

- Ordinary chemical reaction equilibria:
  - *At low concentration n_i, μ_i* ***drops without limit*** (e.g. $kT\ln(n_i/n_T)$) until it matches the other μ's, at some particular ratio.
  - Therefore have positive concentrations of *every* possible molecular type.
    - »true at fixed p or at fixed V

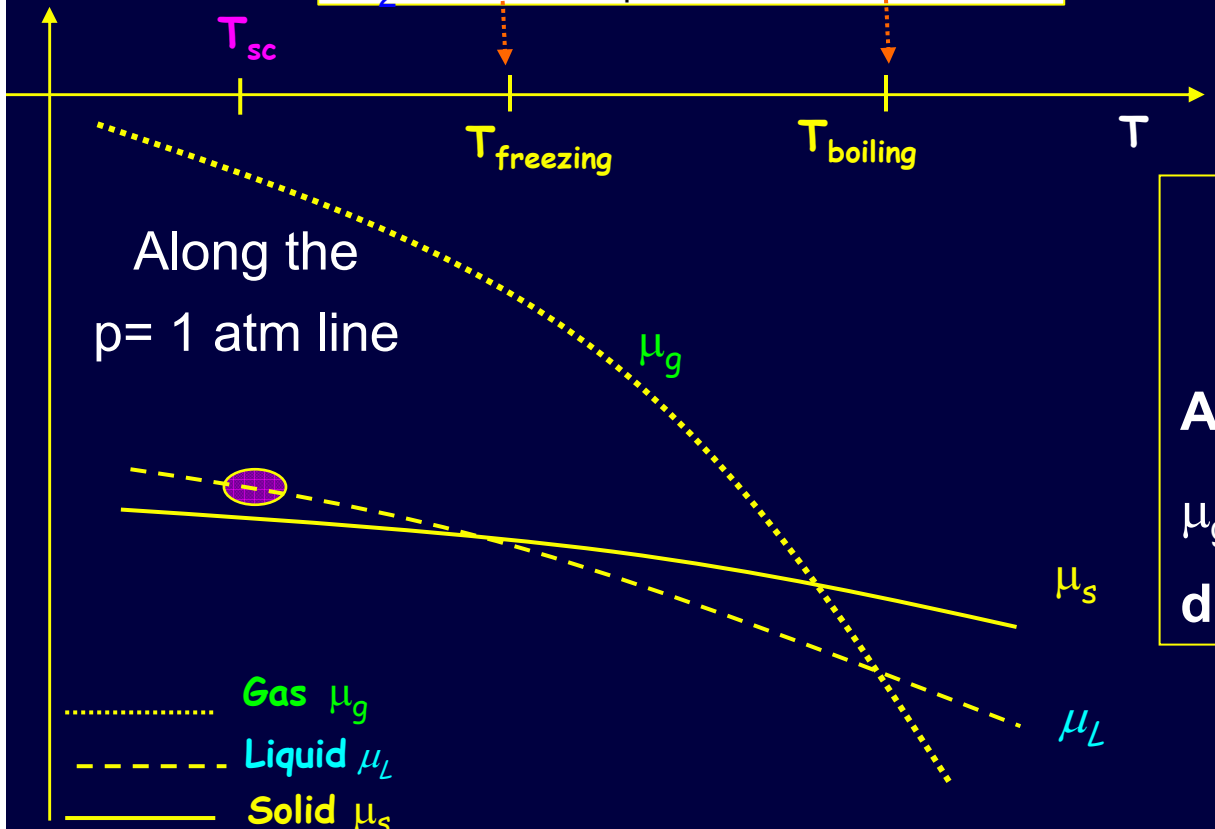
- Phase transitions:
  - *Each phase has a definite density* at a given (T,p) and hence a definite μ, regardless of how much is present!
    - Adding material changes the *volume* of the phase, not the *density*, so μ ***doesn't change***.

- Therefore at most (T, p) only ONE phase, with lowest μ, is stable.
  - At special (T, p), two can have the same μ, so they can coexist in any ratio.
  - Under constant V conditions, p, and thus μ, depends on the *amounts* of the phases, and thus there are some coexistence ranges, e.g., in a pres

μ vs. T at fixed p



Special lines where Two phases coexist



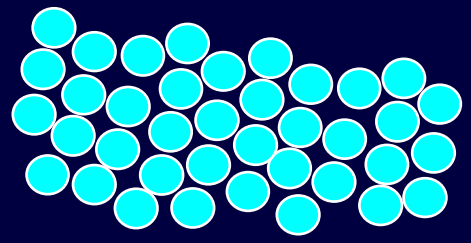
To minimize G

→ state with the lowest μ

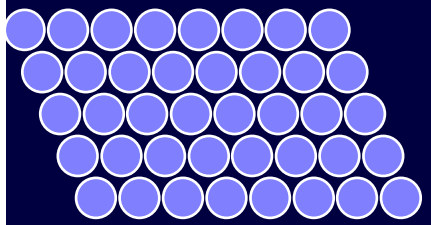
At *special values* of (p,T),

$\mu_g = \mu_L$ or $\mu_s = \mu_g$ or $\mu_s = \mu_L$ so **different phases coexist.**

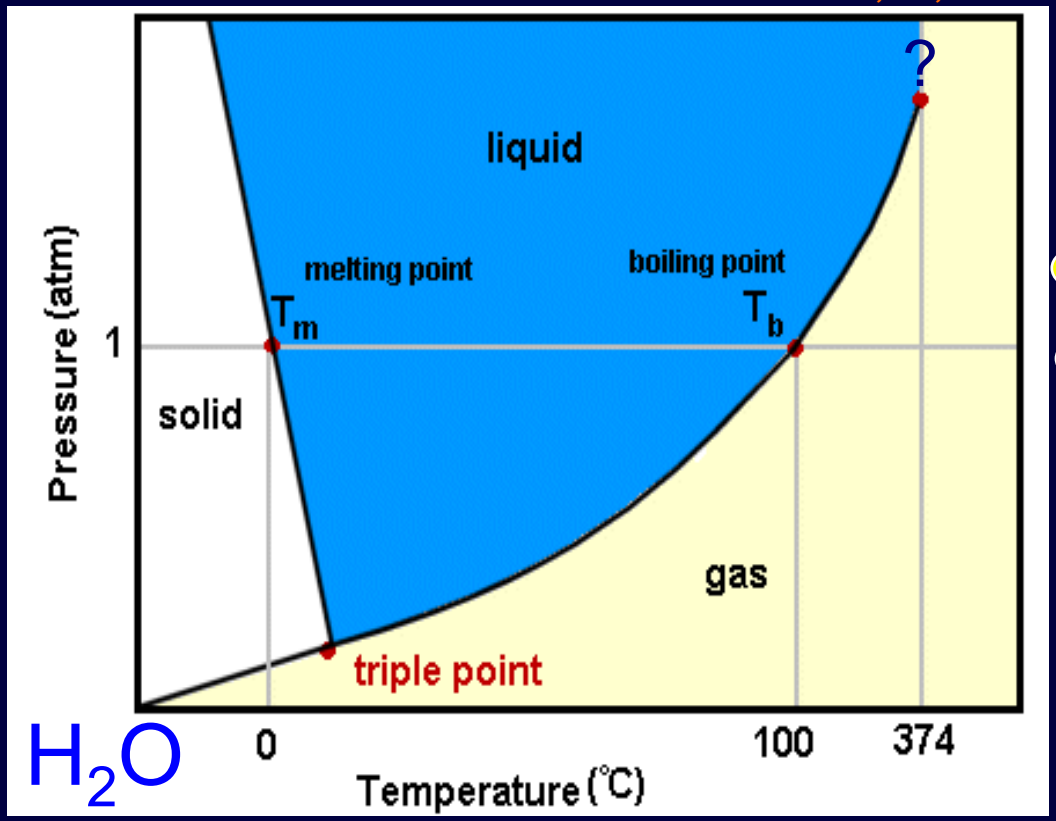
Phases: Solid, liquid, gas

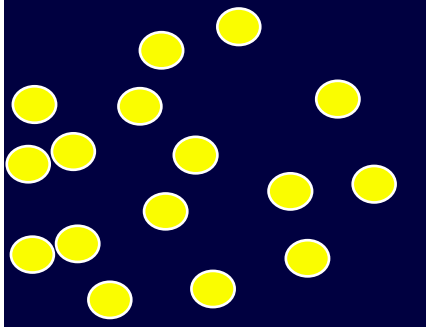


LIQUID:
Particles interact strongly,
But no regular pattern
Medium U, S, small V



SOLID:
Particles interact strongly,
Form regular pattern
Lowest U, S
Small V





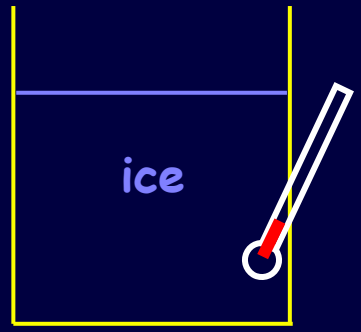
GAS:
Particles Scarcely Interact
Highest U, S, V

The stable phase at some (p, T) has the lowest μ. (G/particle)

Phase Transitions and Entropy

If $S_{gas} > S_{liguid} > S_{solid}$, why are different phases stable at different temperatures?

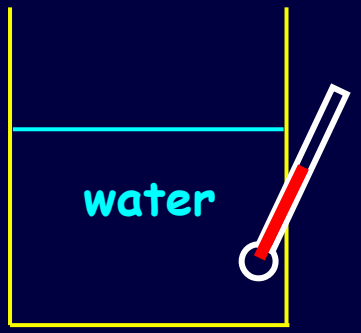
The answer is that we must also consider the entropy of the environment. That's what free energy and chemical potential do for us.



For example: At low enough temperatures a substance like water is a solid. Its entropy is lower than that of the liquid so it must give up enough energy to its environment to make the total entropy increase when ice forms:

Liquid $H_2O \rightarrow$ Solid: $\Delta S_{tot} = \underbrace{\Delta S_L + \Delta S_S}_{<0} + \underbrace{\Delta S_{env}}_{>0} \geq 0$

In order for this to work, enough heat must be given to the environment to make $\Delta S_{tot} \geq 0$.



OK. So, why is liquid H_2O favored at higher temperatures?

The relative sizes of the ΔS terms must be different.

Latent Heat

The heat required to convert the liquid entirely into gas is directly related to the entropy change of the material:

$$Q_{12} = T_1 \Delta S_{12} = \Delta U + p\Delta V \equiv \Delta H_{lg}$$

H = U + pV is defined as the Enthalpy ('heat content') of a material.

For phase transitions:

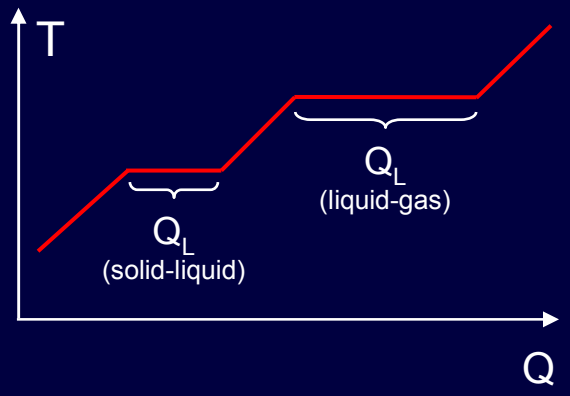
"Heat of vaporization" = "enthalpy change" = "latent heat":

$$\Delta H_{lg} = H_{gas} - H_{liquid} = \text{Latent Heat} = Q_L$$

Latent heats are typically given in units of J/mol or J/gram

Latent Heats of Evaporation

Gas	Boiling temp (K)	ΔH (J/mol)	ΔS (J/mol·K)
Helium	4.2	92	22
Nitrogen	77	5,600	72
Oxygen	90	6,800	76
H_2O	370	40,000	120



There is a similar latent heat for the solid-liquid transition.

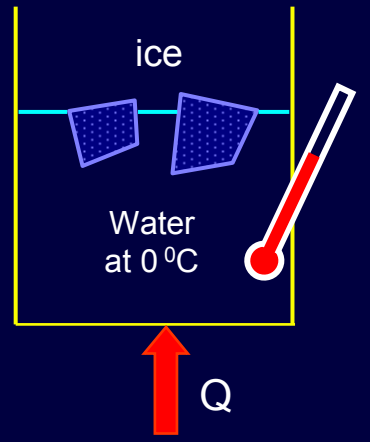
For H_2O at 1 atm:

Q_L(ice-liquid) = 80 cal/g = 333 kJ/kg

Q_L(liquid-steam) = 540 cal/g = 2256 kJ/kg

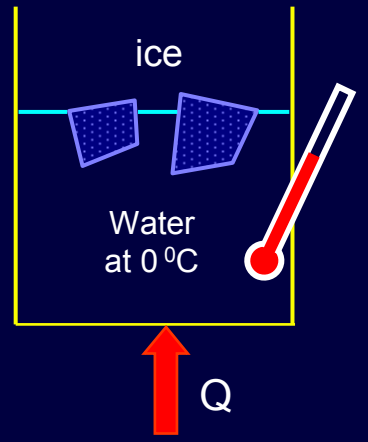
Exercise

What is the entropy change per mole of water when water freezes (at p = 1 atm)?



Solution

What is the entropy change per mole of water when ice freezes (at p = 1 atm)?



$Q_L = T\Delta S$

$\Delta S = -Q_L / T$

$= -333 \text{ J/g} / 273 \text{ K} * 18 \text{ g/mol}$

$= -22.0 \text{ J/K mol}$

That's a loss of σ of about 2.73 per molecule.
That is, there are about $e^{2.7}$, or 15×, as many microstates available to each molecule in the liquid.

Act 3: Entropy in freezing

We just saw that a mole of water loses entropy when it freezes. Consider a lake that freezes in winter. If the lake loses 10^6 J/K of entropy in the process, what is the change of entropy of the environment during this process?

A) $\Delta S = 0$ J/K mol

B) $\Delta S = +10^6$ J/K mol

C) $\Delta S > +10^6$ J/K mol

Solution

We just saw that a mole of water loses entropy when it freezes. Consider a lake that freezes in winter. If the lake loses 10^6 J/K of entropy in the process, what is the change of entropy of the environment during this process?

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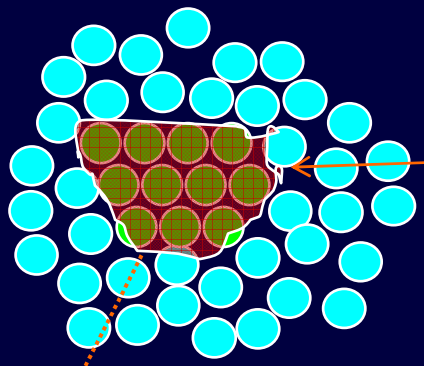
The entropy increase of the enviroment must at least balance the entropy loss of the water. Otherwise, the total entropy of the water-environment system would decrease, in violation of the 2nd law.

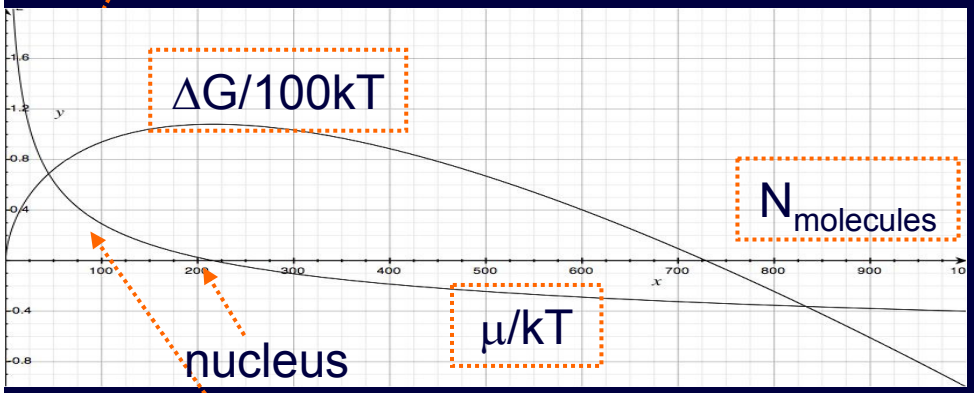
Since this is an open system, some of the energy extracted from the water will spread irreversibly into the environment, i.e., the net entropy must increase.

FYI: Why are phases separate?



Could liquids solidify gradually via little ordered clusters?

Those 11 molecules lost just about as much S as if they were in the middle of a big crystal. But they gained only 21 nice crystalline contacts (bonds), instead of the 33 they would gain in the *middle* of a crystal. So their G is much bigger than it would if they were part of a big crystal.



- The surfaces between phases add G
  - Extra G/area is called the surface tension
- Phases separate to lower G

Even below the freezing point,
- a small solid cluster is most likely to melt.
  - So it's hard for something to freeze even if $\mu_S < \mu_L$
    - Requires a rare "critical nucleus"