Lecture 20

Phase Transitions

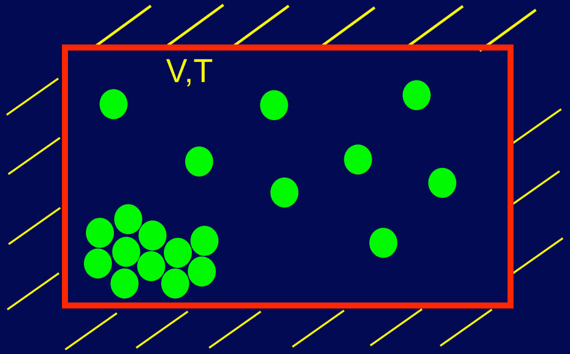
- Phase diagrams
- Latent heats
- Phase-transition fun

Reading for this Lecture:
Elements Ch 13

Solid-gas equilibrium: vapor pressure

Consider solid-gas equilibrium at constant volume and temperature. Some substances (e.g., CO_2) don't exist as liquids at atmospheric pressure.

The solid has negligible entropy (compared to the gas), so we'll ignore it. In that case:



$F_s = U_s - TS_s = -N\Delta \Rightarrow \mu_s = -\Delta$ Binding energy of an atom in the solid

The gas: $\mu_g = kT\ln(n/n_Q)$

Set them equal and solve for the equilibrium gas pressure:

$$kT\ln\left(\frac{n}{n_Q}\right) = kT\ln\left(\frac{p}{p_Q}\right) = -\Delta \Rightarrow p \equiv p_{vapor} = p_Q e^{-\Delta/kT}$$

The equilibrium pressure is called the "vapor pressure" of the solid at temperature T. If $p < p_{vapor}$, atoms will leave the solid until $p_{gas} = p_{vapor}$.
This is called sublimation. For liquids, it's called evaporation.

Examples: Si (28 g/mol): $p_{vapor} = (4.04\times10^4 \text{ atm})(28)^{3/2}\, e^{-3\text{eV}/.026\text{eV}} = 5\times10^{-44}$ atm
CO_2 (44 g/mol): $p_{vapor} = (4.04\times10^4 \text{ atm})(44)^{3/2}\, e^{-0.26\text{eV}/.026\text{eV}} = 535$ atm

Note the different Δ's

Some solids don't sublimate. Some do.
Question: Does water ice sublimate?

Chemical Potential of an Ideal Gas

Remember: $\mu_g = kT\ln\dfrac{n}{n_Q} = kT\ln\dfrac{p}{p_Q}$, where $p_Q = n_Q kT$

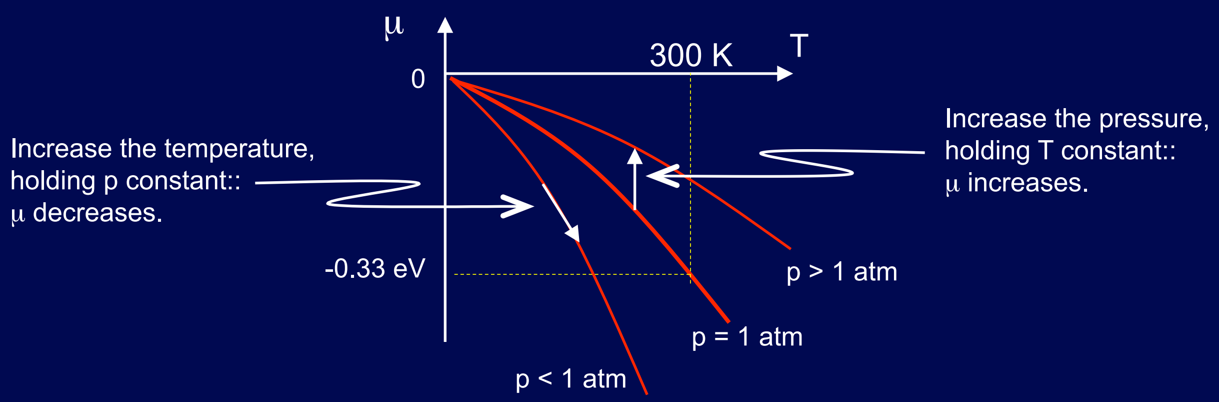
It's negative, because (unless highly compressed) $n_Q >> n$ and $p_Q >> p$.

For helium at T = 300K and p = 1 atm: $p_Q = \left(4.04\times10^4\ \text{atm}\right)\left(4\right)^{1.5} = 3.23\times10^5\ \text{atm}$

So, $\mu_{He} = kT\ln\dfrac{p}{p_Q} = kT\ln(3.10\times10^{-6}) = (.026\ \text{eV})(-12.69) = -0.33\ \text{eV}$

All ideal gases will behave similarly, with a logarithmic pressure dependence and an approximately linear temperature dependence. (The curvature is due to the T dependence of n_Q.)

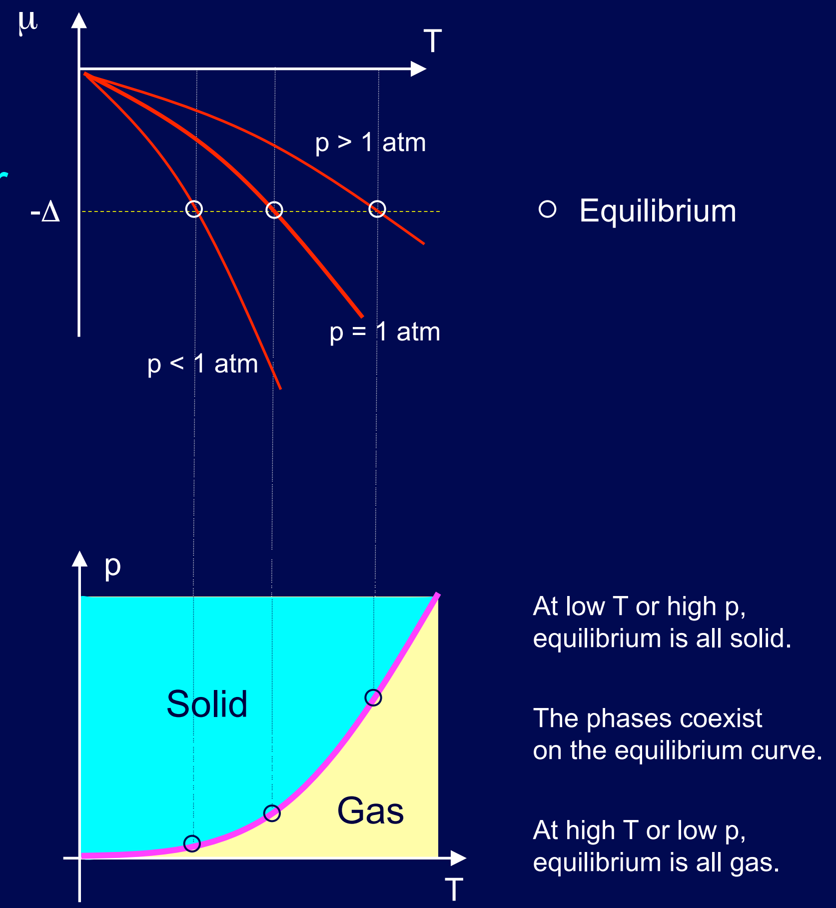
Here's a graph:



Vapor Pressure of a Solid and the p-T Phase Diagram

We saw that μ_{solid} is essentially constant ($-\Delta$). We can use this to determine graphically the equilibrium pressure (vapor pressure) of the solid as a function of T.

For a given temperature, at what pressure does the curve cross $\mu = -\Delta$?



From this, we can plot the equilibrium curve, p(T), where the two phases can coexist.
This graph is called a p-T phase diagram.
It tells us what regions in the (p,T) plane make a gas and which make a solid.
The equilibrium curve separates them.

It's just a way to visualize the equilibrium equation:

$$\mu_g = \mu_s \rightarrow kT \ln \frac{p}{p_Q} = -\Delta \rightarrow p = p_Q e^{-\Delta / kT}$$

Solids and Liquids, More Accurately

We ignored the entropy of the solid, because the entropy of the gas was so much larger. When comparing solids and liquids, we can't ignore entropy. The entropy is small, but not completely negligible.

Compare solids and liquids (for a given substance):

- $\Delta_S > \Delta_L$. Atoms in the solid are more strongly bound.
- $S_S < S_L$. Atoms in the liquid have more available microstates (due to motion).

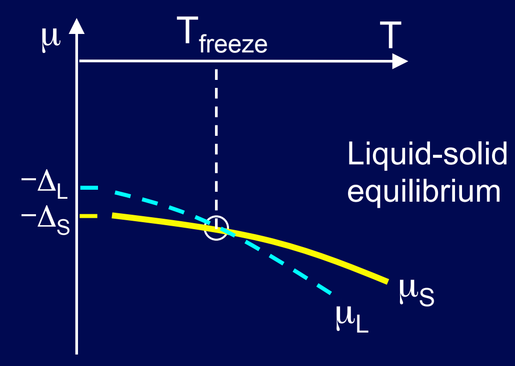
Compare the chemical potentials:

Remember that $F = U - TS$, and μ is the free energy per particle.

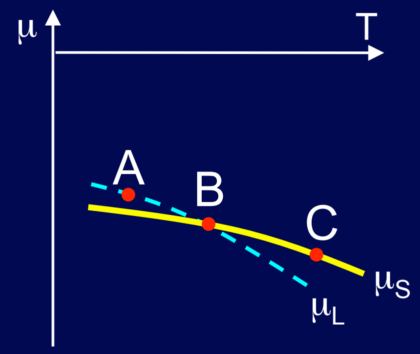
- At very low T, the entropy is not important, so $\mu_S < \mu_L$.
- As T increases, both chemical potentials decrease, but the liquid decreases faster.

Therefore, the solid phase is stable at low temperature, while the liquid phase is stable at high temperatures.

There is an equilibrium temperature, the melting/freezing temperature. As the substance passes through T_{freeze}, there is a phase transition.



Act 1: Solid-Liquid



1) Which point corresponds to a liquid?

A B C

2) The substance is in state C. What will happen?

A) The substance will melt

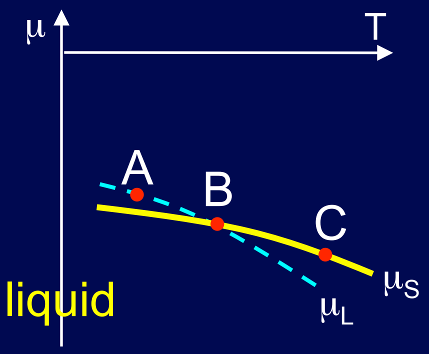
B) Free energy will minimize itself

C) Entropy will maximize

Solution

1) Which point corresponds to a liquid?

$\boxed{\text{A}}$ B C



Both points lie on the liquid's μ(T) curve.
Point A does not lie on the solid's curve, so it must be liquid

(but not one in equilibrium [lowest possible μ].

At point B the liquid and solid are in equilibrium.
We don't actually know how much of each there is.

FYI: Global equilibrium condition:

Minimum $G = N_g\mu_g + N_s\mu_s + N_l\mu_l$ G = Gibbs Free Energy

Except at a coexistence temperature, T_c, two of the N's will be zero in equilibrium.

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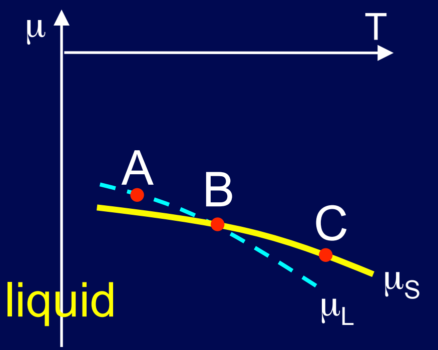

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2) The substance is in state C. What will happen?

A) The substance will melt
B) Free energy will minimize itself
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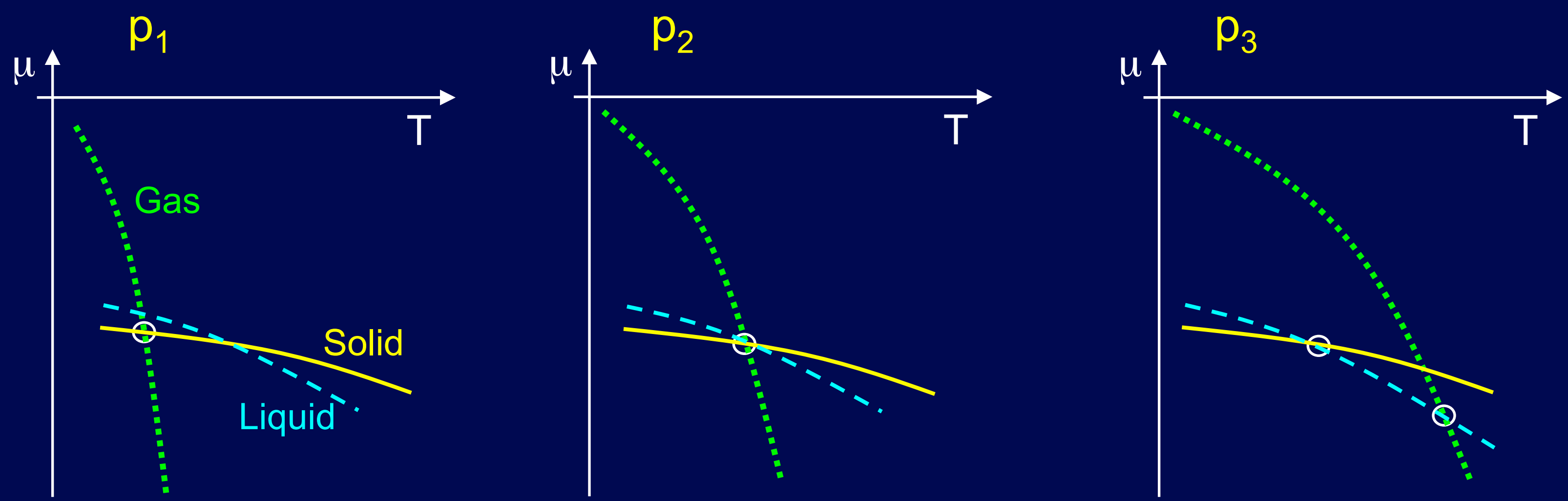
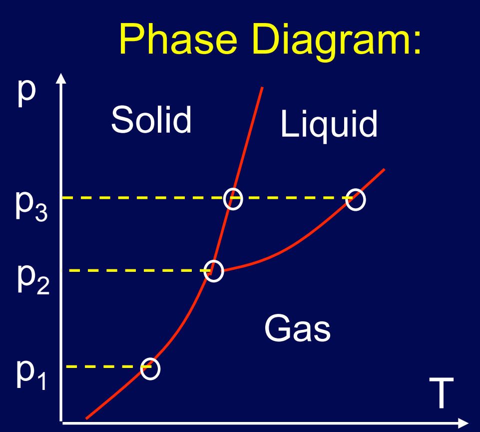
B and C are equivalent. That's what systems do unless we interfere.
A is also correct, because $\mu_L < \mu_S$ at that temperature.

The p-T Diagram with Three Phases





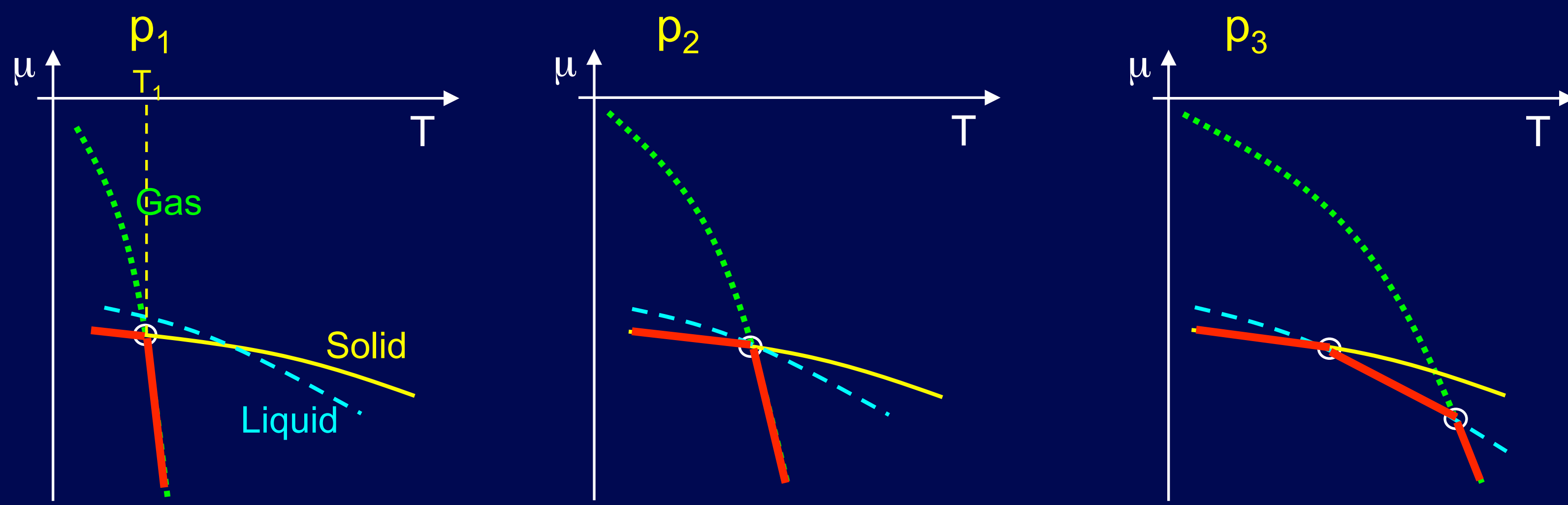
At a given p,T, the system will reside in the lowest μ.

Phase transitions occur where the μ(T) curves cross.

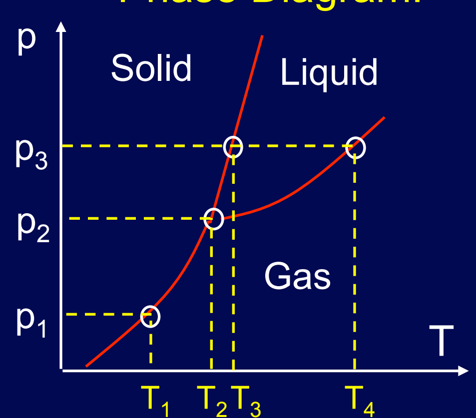
If we raise T at constant p, the sequence of phase transitions depends on the value of p.

The solid and liquid curves don't change with pressure,
because solids and liquids are nearly incompressible.

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.

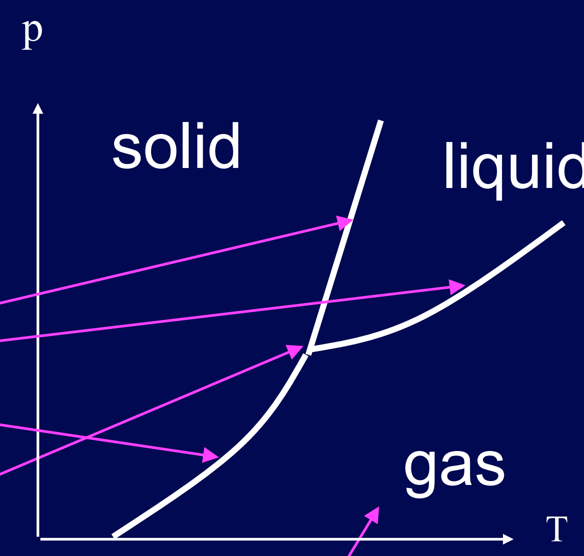
If we increase the pressure, the gas curve moves to the right. There is a critical pressure for which all three curves pass through a point. The three phases can coexist only at (T_2,p_2).

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

Phase Transitions: OOPS!

The photos below show the results of steam cleaning a railroad tank car, then sealing it before the steam had cooled

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.

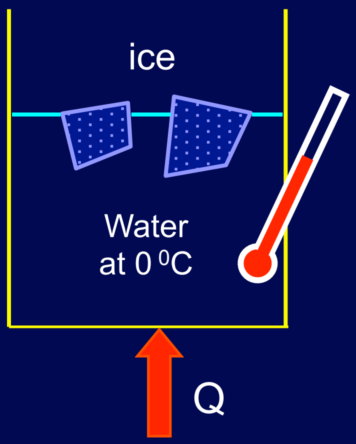
ACT 2: Phase Transitions

Let’s think a bit about energy flow during phase transitions.

Suppose heat flows slowly into 0^0 C water containing some ice cubes (maintaining equilibrium).

What happens to the energy added to the system?

A) It warms the ice.
B) It warms the water.
C) It breaks ice bonds.



Solution

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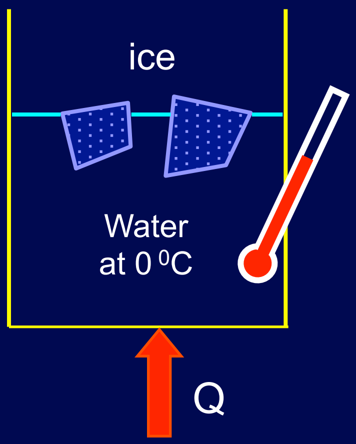
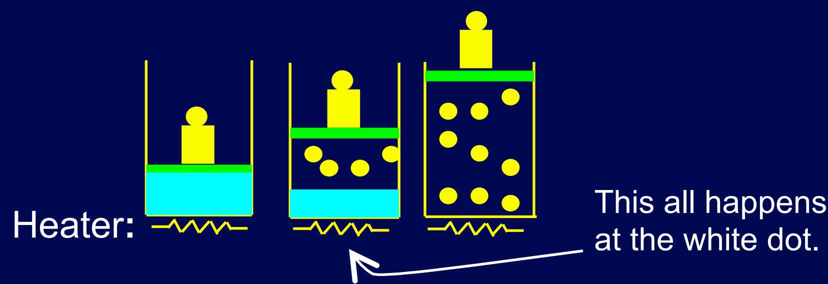
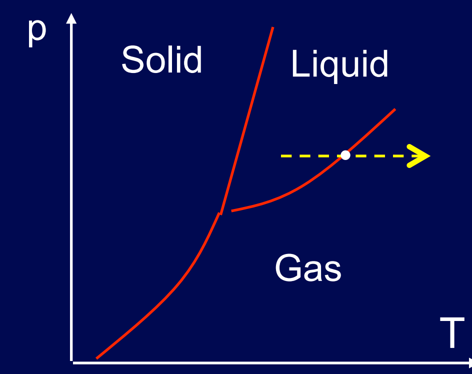


The temperature will remain constant until all the ice is melted.

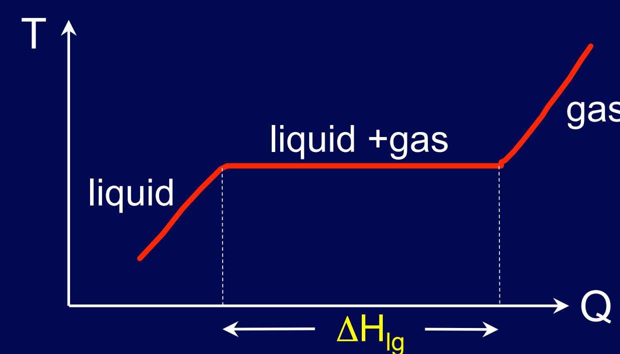
Latent Heat

Consider a liguid-gas phase transition at constant pressure. The phase diagram doesn't tell the whole story. Look at how the system changes as we add heat:





Plot temperature *vs* the amount of heat added:



Heat of transformation
≡ Latent Heat

Remember the 1st law: $Q = \Delta U + p\Delta V$.
Some of the energy goes into breaking the bonds (ΔU), and some goes into raising the weight ($p\Delta V$).

The p-T diagram doesn't show either of these changes.

The heat we need to add to effect the phase change is called "latent heat".

Latent Heat (2)

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

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

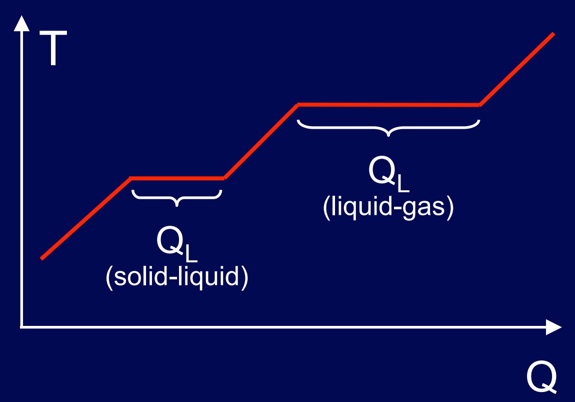
H = U + pV is defined as the Enthalpy (‘heat content’) of a material.
For phase transitions:
“Heat of vaporization” = “enthalpy change” = “latent heat”:

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

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

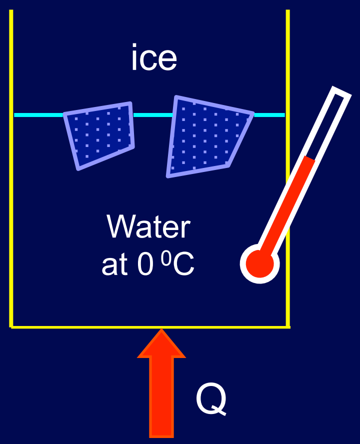


There is a similar latent heat for the solid-liquid transition.

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

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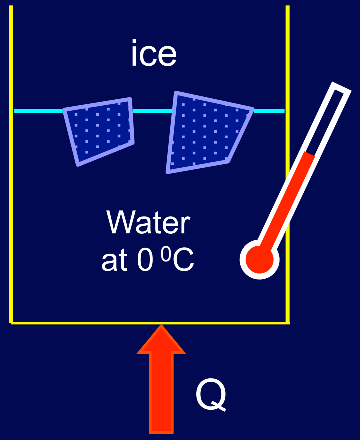

$$Q_L = T\Delta S$$

$$\Delta S = -Q_L / T$$

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

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

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

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

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$\boxed{\text{C) } \Delta S > +10^6 \text{ J/K mol}}$

The entropy increase of the environment 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.