Up to now we have dealt almost exclusively with systems consisting of a single phase. In this lecture, we will learn how more complicated, multi-phase systems can be treated by the methods of thermodynamics. The guiding principle will be the minimization of the Gibbs free energy in equilibrium for all systems, including the multi-phase ones.

The generic phase diagram of a substance in the *P-T* coordinates is shown above. Every point of this diagram is an equilibrium state; different states of the system in equilibrium are called **phases**. The lines dividing different phases are called the **coexistence curves**. Along these curves, the phases coexist in equilibrium, and the system is **macroscopically inhomogeneous**. All three coexistence curves can meet at the **triple point** – in this case, all three phases coexist at (T_{tr} , P_{tr}).
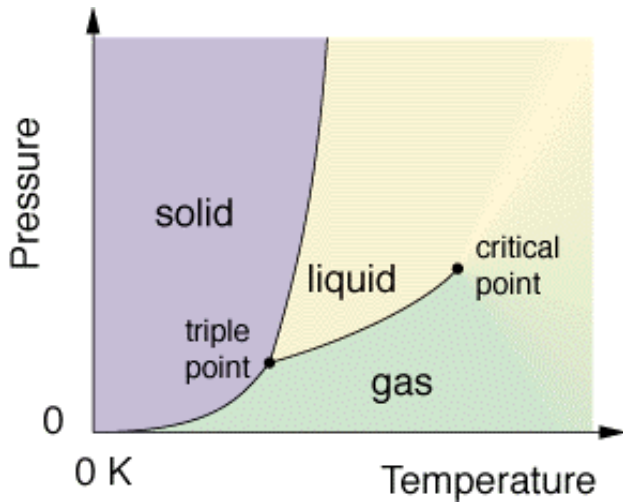
The Coexistence Curves

Along the coexistence curves, two different phases **1** and **2** coexist in equilibrium (e.g., ice and water coexist at $T = 0^0C$ and $P = 1bar$). The system undergoes phase separation each time we cross the equilibrium curve (the system is **spatially inhomogeneous** along the equilibrium curves).

Any system in contact with the thermal bath is governed by the **minimum free energy principle.** The shape of coexistence curves on the **P-T** phase diagram is determined by the condition:

$$\boxed{G_1(P,T) = G_2(P,T)} \quad \text{and, since} \quad G = N\mu \longrightarrow \boxed{\mu_1(P,T) = \mu_2(P,T)}$$

- otherwise, the system would be able to decrease its Gibbs free energy by transforming the phase with a higher μ into the phase with lower μ. Two phases are in a state of diffusive equilibrium: there are as many molecules migrating from **1** to **2** as the molecules migrating from **2** to **1**.

Also for equilibrium between the phases:

$$T_1 = T_2 \quad \text{- as for any two sub-systems in equilibrium}$$

$$P_1 = P_2 \quad \text{- the phase boundary does not move}$$

Though **G** is continuous across the transition, **H** demonstrates a step-like behavior:

$$G = N\mu = U + PV - TS = H - TS \longrightarrow \Delta H = T\Delta S \quad \text{(different phases have different values of the entropy)}$$

Example: the Gas-Liquid Transformation

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left[F \equiv U - TS\right] = \left(\frac{\partial U}{\partial N}\right)_{T,V} - T\left(\frac{\partial S}{\partial N}\right)_{T,V}$$

Gas: $\partial U/\partial N$ term is small and positive (kin. energy of a single molecule), $T(\partial S/\partial N)$ term is large and positive $\Rightarrow$ μ is negative, and **rapidly** decreases with increasing **T**.

Liquid: $\partial U/\partial N$ term is negative (attraction between molecules), $T(\partial S/\partial N)$ term is smaller than that in gas and positive $\Rightarrow$ μ is also negative, and **slowly** increases with decreasing **T** .

Table on page 404 (a very useful source of information) provides the values of **H** and **G** for different phases of many substances. The data are provided per mole, at **T**=298 K and **P**=1 bar. For example, let's check that at the boiling point, the values of G for liquid water and water vapor are equal to each other:

phase transformation
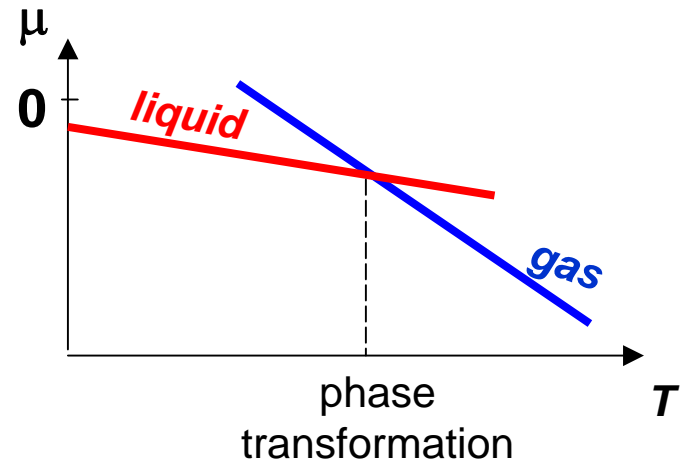
$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \longrightarrow \quad (G)_{P,N,T} \approx (G)_{P,N,T_0} - (T - T_0)S$$

S(water) = 70 J/K

$$\left(G_{liq}\right)_{T=373K} \approx -237 \times 10^3 J/mol - 75K \times 70J/(K \cdot mol) \approx 242 \times 10^3 J/mol$$

S(vapor) = 189 J/K

$$\left(G_{vap}\right)_{T=373K} \approx -2286 \times 10^3 J/mol - 75K \times 189J/(K \cdot mol) \approx 242 \times 10^3 J/mol$$

Phases of Carbon

The phase equilibrium on the *P,T*-plane is determined by

$$G_1(P,T) = G_2(P,T) \quad \text{or} \quad \mu_1(P,T) = \mu_2(P,T)$$

At normal conditions, graphite is more stable than diamond: **G**(graphite) = 0, **G**(diamond) = 2.9 kJ (diamonds are not forever...). What happens at higher pressures?

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad \Longrightarrow \quad (G)_{T,N} \approx (G)_{T,N,P_0} + (P - P_0)V$$
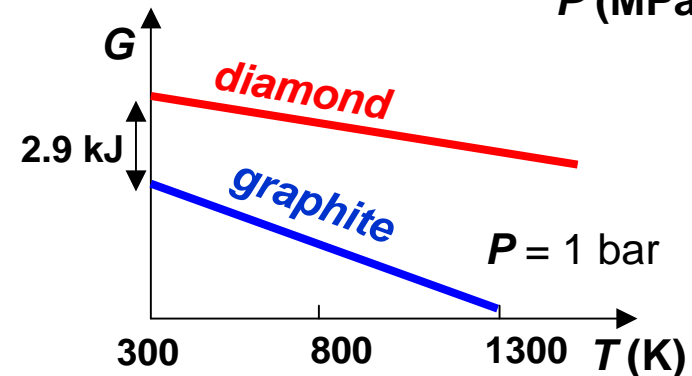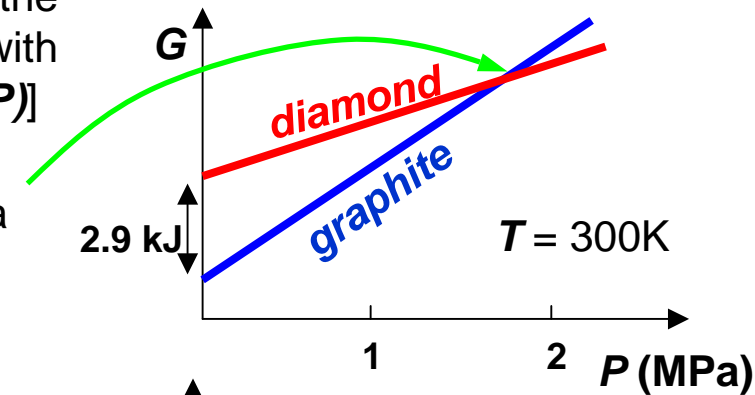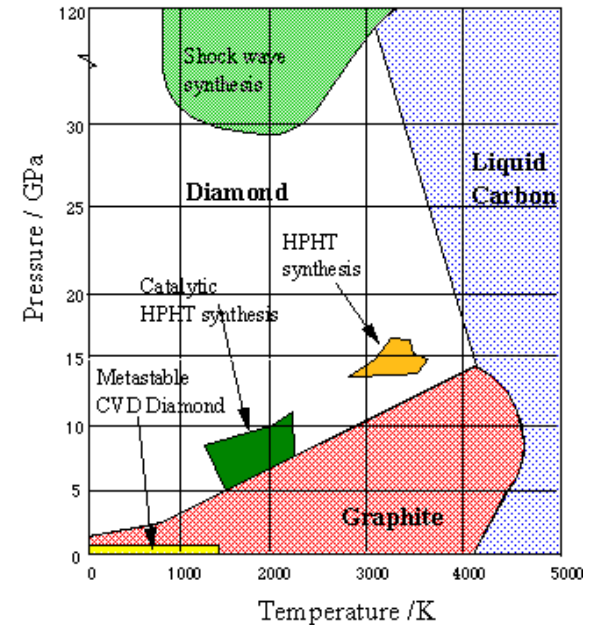
- since the molar volume of graphite is greater than the molar volume of diamond, **G**(graphite) will grow with pressure faster than **G**(diamond) [we neglected *V = V(P)*]

D. becomes more stable than G. only at **P** > 1.5 MPa

With increasing **T**, the pressure range of graphite stability becomes wider:

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \Longrightarrow \quad (G)_{P,N,T} \approx (G)_{P,N,T_0} - (T - T_0)S$$

**S**(graphite) = 5.74 J/K, **S**(diamond) = 2.38 J/K,
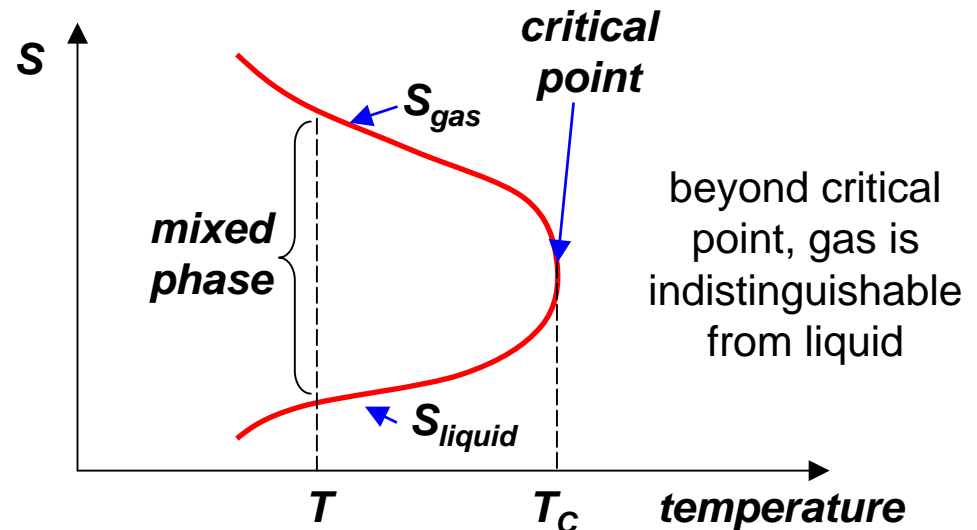
The First-Order Transitions

Because molecules aggregate differently in different phases, we have to provide (or remove) energy when crossing the coexistence curves. The energy difference is called the *latent heat*; crossing the coexistence curve, the system releases (absorbs) a *latent heat L*. The entropy of the system changes abruptly:

$$\Delta S = \frac{\delta Q}{T} = \frac{L}{T}$$

The transitions which displays a jump in entropy and a latent heat associated with this jump are called the *first-order phase transitions*.
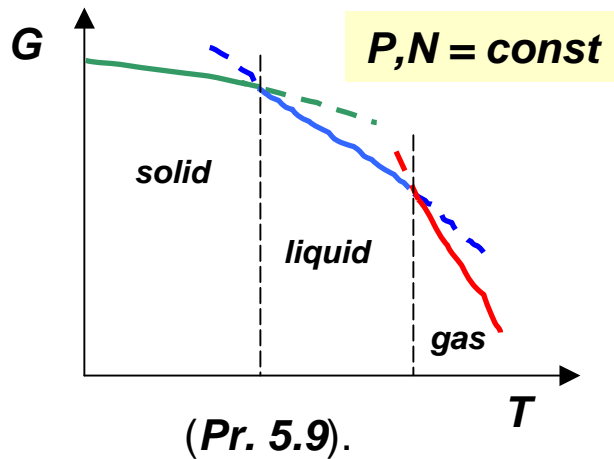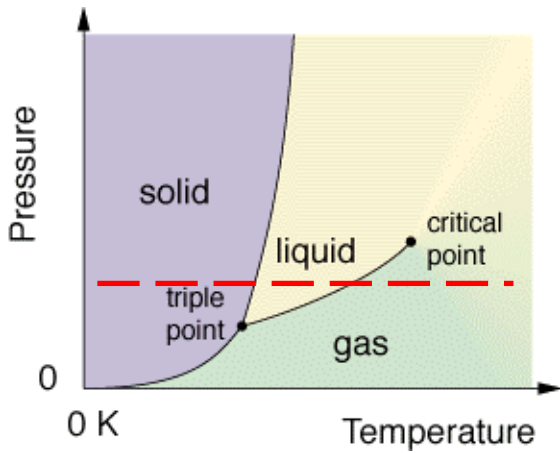

T=T₁ = const
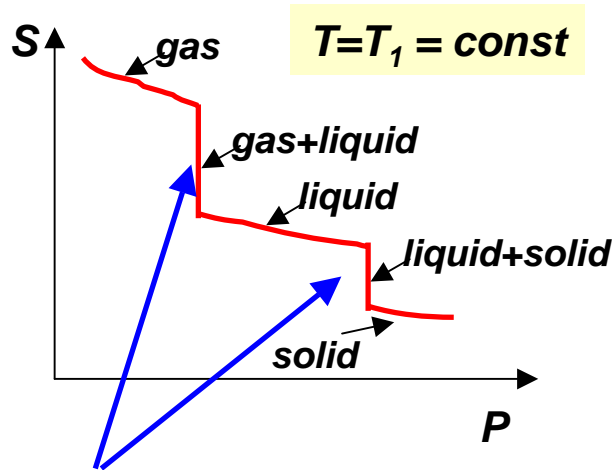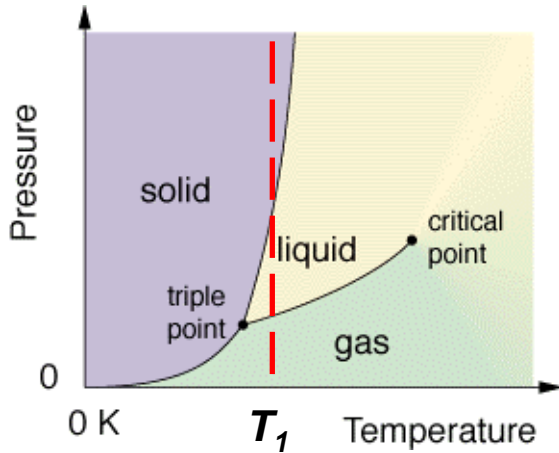
The "evaporation" *L* is generally greater than the "melting" *L* (the disorder introduced by evaporation is greater than that introduced by melting).

beyond critical point, gas is indistinguishable from liquid

Q: Can the critical point exist along the melting coexistence curve?

The First-Order Transitions (cont.)

Note that in the first-order transitions, the **G(T)** curves have a real meaning even beyond the intersection point, this results in **metastability** and **hysteresis**.

There is usually an energy barrier that prevents a transition occurring from the higher μ to the lower μ phase (e.g., gas, being cooled below T_{tr} does not immediately condense, since surface energy makes the formation of very small droplets energetically unfavorable).

L. water can exist at **T** far lower than the freezing temperature: water in organic cells can avoid freezing down to -20^0C in insects and down to -47^0C in plants.
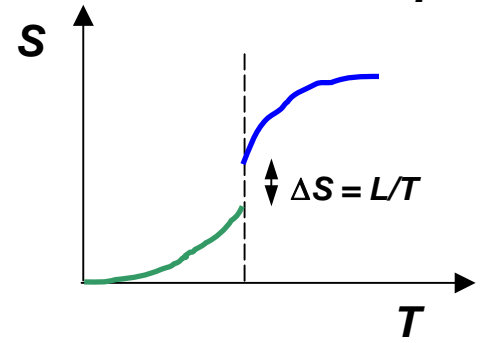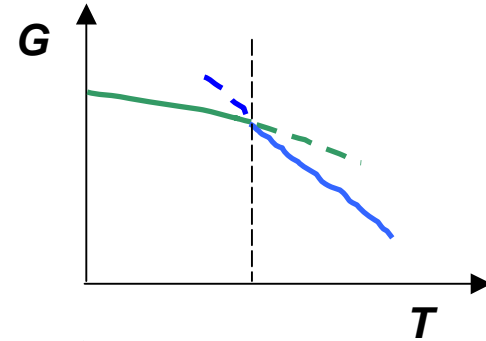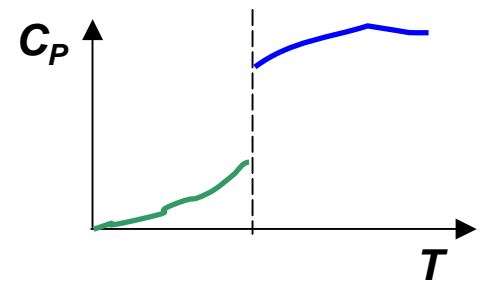

P,N = const

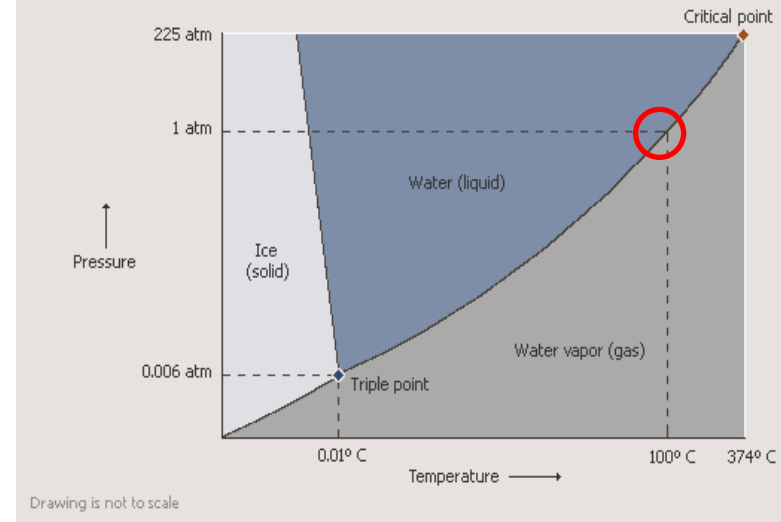(**Pr. 5.9**).

On the graph **G(T)** at **P,N** = const, the slope **dG/dT** is always negative:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$\Delta S = L/T$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

225 atm

1 atm

Pressure

0.006 atm

Critical point

Water (liquid)

Ice (solid)

Water vapor (gas)

Triple point

0.01° C

100° C

374° C

Temperature

Drawing is not to scale

Problem

The entropy of water at atmospheric pressure and 100^0C is 1.3 J/g·K, and the entropy of water vapor at the same T and P is 7.4 J/g K.

(a)   What is the heat of vaporization at this temperature?
(b)   The enthalpy of vapor under these conditions is
        2680 J/g. Calculate the enthalpy of water under these conditions.
(c)   Compute the Gibbs free energies of water and steam under these conditions.

(a)   The heat of vaporization: $L = T\Delta S$ = 373K×6.1 J/g·K=2275 J/g

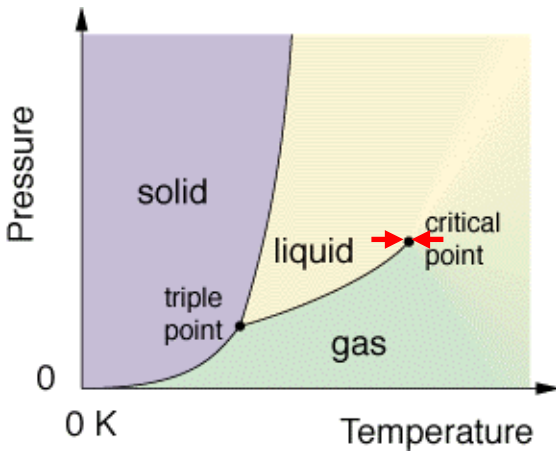(b)   The differential of enthalpy $dH = TdS + VdP$. Hence,

$$H_{water} = H_{vapor} - TdS = H_{vapor} - L = (2680-2275)\text{J/g} = 405 \text{ J/g}$$

(c)   Since $G = H\text{-}TS$,

$$G_{water} = H_{water} - TS_{water} = 405\text{J/g} - 373\text{K} \times 1.3\text{J/g·K} = -80\text{J/g}$$

$$G_{vapor} = H_{vapor} - TS_{vapor} = 2680\text{J/g} - 373\text{K} \times 7.4\text{J/g·K} = -80\text{J/g}$$

The Second Order Transitions

The vaporization coexistence curve ends at a point called the **critical point** (T_C, P_C). As one moves along the coexistence curve toward the critical point, the distinction between the liquid phase on one side and the gas phase on the other gradually decreases and finally disappears at (T_C, P_C). The **T**-driven phase transition that occurs **exactly** at the critical point is called a **second-order phase transition**. Unlike the 1st-order transitions, the 2nd-order transition does not require any latent heat (**L**=0). In the **higher-order transitions** (**order-disorder transitions** or **critical phenomena**) the entropy is continuous across the transition. The specific heat $C_P = T(\delta S/\delta T)_P$ diverges at the transition (a cusp-like "λ" singularity).

Whereas in the 1st-order transitions the **G(T)** curves have a real meaning even beyond the intersection point, nothing of the sort can occur for a 2nd-order transition – the Gibbs free energy is a continuous function around the critical temperature.

Second-order transition

$\Delta S = 0$
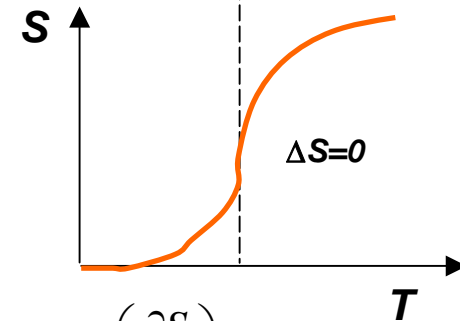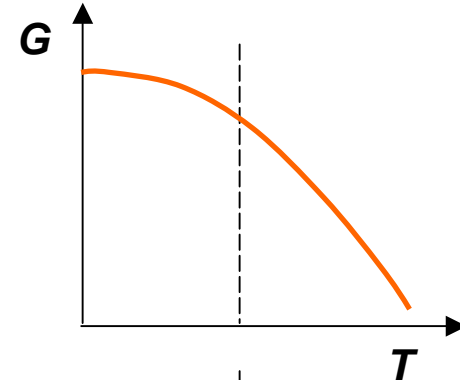
$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \to \infty$$

The Clausius-Clapeyron Relation
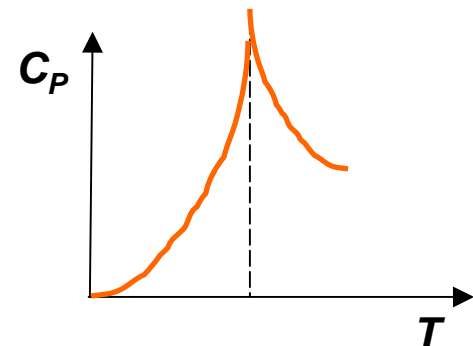
$$G_1(P,T) = G_2(P,T)$$

phase boundary

Along the phase boundary:

$$G_1(P,T) = G_2(P,T) \implies \mu_1(P,T) = \mu_2(P,T)$$

Consider two distinct displacements along the coexistence curve, one immediately above the curve (in phase 1), the other immediately below the curve, in phase 2. Because the chemical potentials remain equal along the curve, $d\mu_1 = d\mu_2$

For the slope of the boundary we have:

$$-S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$

$$\frac{dP}{dT} = \frac{S_1(P,T) - S_2(P,T)}{V_1(P,T) - V_2(P,T)}$$

- the slope is determined by the entropies and volumes of the two phases. The larger the difference in entropy between the phases – the steeper the coexistence curve, the larger the difference in molar volumes – the shallower the curve.

(compare the slopes of melting and vaporization curves)

Since $S_1 - S_2 = L/T$ (L is the latent heat), we arrive at the *Clausius-Clapeyron Relation* :

$$\frac{dP}{dT} = \frac{L(T)}{T\,\Delta V(T)}$$

(applies to all coexistence curves)

Example:

$$\frac{dT}{dP} = \frac{T\left[V_{gas}(T) - V_{liq}(T)\right]}{L(T)}$$

- since $V_{gas} > V_{liq}$, and $L > 0$ for the "liquid→gas" transformation, the boiling temperature increases with pressure. The "freezing" temperature with increasing pressure either increases or decreases, depending on the sign $V_{liq} - V_{solid}$ (exception – ^{3}He).
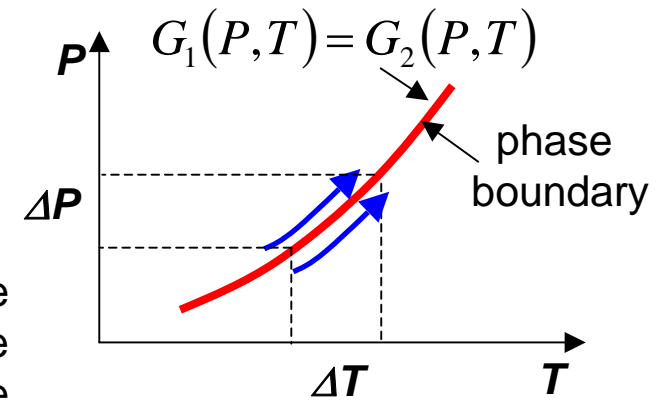
Problem

1 kg of water at 20⁰C is converted into ice at -10⁰C (all this happens at **P** = 1 bar). The latent heat of ice melting **L$_{melt}$** = 334 kJ/kg, the heat capacity of water at constant pressure is 4.2 kJ/(kg·K) and that of ice 2.1 kJ/(kg·K).
(a) What is the total change in entropy of the water-ice system?
(b) If the density of water at 0⁰C is taken as 10% greater than that of ice, what is the slope of the melting curve of ice at this temperature? Give both sign and size.

(a)

1. From 20⁰C to 0⁰C: $dS = \dfrac{\partial Q}{T} \quad \partial Q = mcdT \quad \Delta S = \displaystyle\int_{293K}^{273K} \dfrac{mc_{water}dT}{T} = -mc_{water}\ln\left(\dfrac{293K}{273K}\right)$

2. Melting of ice $\Delta S = -m\dfrac{L_{melt}}{T_{melt}}$

3. From 0⁰C to -10⁰C: $\Delta S = \displaystyle\int_{273K}^{263K} \dfrac{mc_{ice}dT}{T} = -mc_{ice}\ln\left(\dfrac{273K}{263K}\right)$

$$\Delta S = 1kg\left(-4.2kJ/(kg\cdot K)\ln\left[\dfrac{293}{273}\right] - \dfrac{334kJ/kg}{273K} - 2.1kJ/(kg\cdot K)\ln\left[\dfrac{273}{263}\right]\right)$$

$$= -297\dfrac{J}{K} - 1231\dfrac{J}{K} - 78\dfrac{J}{K} = -1606\dfrac{J}{K}$$

(b) $\dfrac{dP}{dT} = \dfrac{(S_{water} - S_{ice})}{(v_{water} - v_{ice})} = \dfrac{1231J/(K\cdot kg)}{-0.1\times10^{-3}m^3} = -1.23\times10^{7}\, Pa/K$

The Vapor Pressure Equation

The differential Clausius-Clapeyron equation can be solved to find the shape of the entire coexistence curve (**Pr. 5.35**).

$$\left(\frac{dP}{dT}\right)_{vap} = \frac{S_{gas} - S_{liq}}{V_{gas} - V_{liq}} = \frac{L(T)}{T\,\Delta V(T)}$$
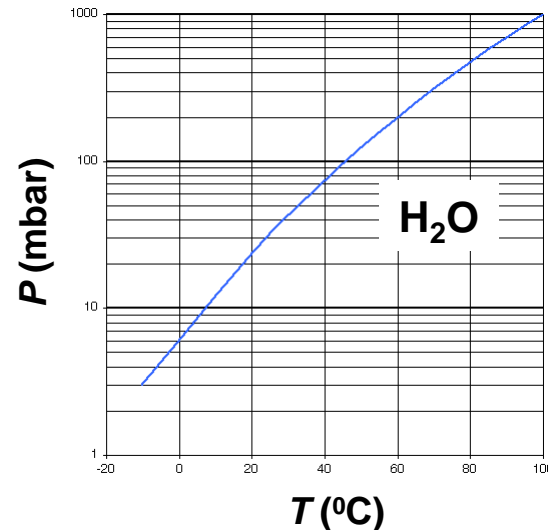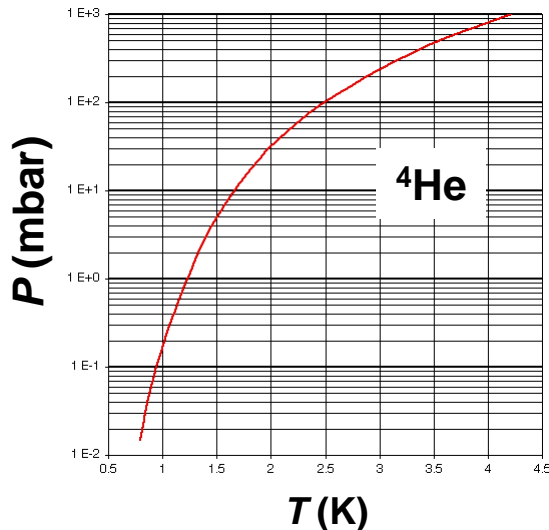
For the **liquid-gas** phase transition, we can make the following reasonable assumptions:
- the molar volume of the liquid is much smaller than that of the gas (neglect **V_{liquid}**)
- the molar volume of gas is given by the ideal gas law **$V = RT/P$**
- the latent heat is almost **T**-independent, **$L \neq L(T)$**

$$\left(\frac{dP}{dT}\right)_{vap} \approx \frac{L}{TV_{gas}} = \frac{LP}{RT^2} \qquad \frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2} \qquad \boxed{P_{vap} \propto \exp\left(-\frac{L}{RT}\right)}$$

Problem (The pressure cooker)

The boiling point of water at atmospheric pressure (1 bar) is 373 K, and the latent heat of vaporization at this T is 2.25 MJ/kg. Assuming the latent heat to be constant over the relevant temperature range, that water vapor is an ideal gas, and that the volume of the liquid is negligible relative to that of the vapor, find the temperature inside a pressure cooker operating at an absolute pressure of 2 bar.

$$\frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2} \qquad\qquad \ln\frac{P_2}{P_1} = -\frac{L}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$T_2 = \left[\frac{1}{T_1} - \frac{R}{L}\ln\frac{P_2}{P_1}\right]^{-1} = \left[\frac{1}{373} - 0.7\frac{8.3\,J/mol}{2.25\cdot 10^6\,J/kg \times 18\cdot 10^{-3}\,kg/mol}\right]^{-1} = 394K$$

Problem

For Hydrogen (H_2) near its triple point (T_{tr}=14K), the latent heat of vaporization L_{vap}=1.01 kJ/mol. The liquid density is 71 kg·m^{-3}, the solid density is 81 kg·m^{-3}, and the melting temperature is given by T_m =13.99+P/3.3, where T_m **and** P measured in K and MPa respectively. Compute the latent heat of sublimation
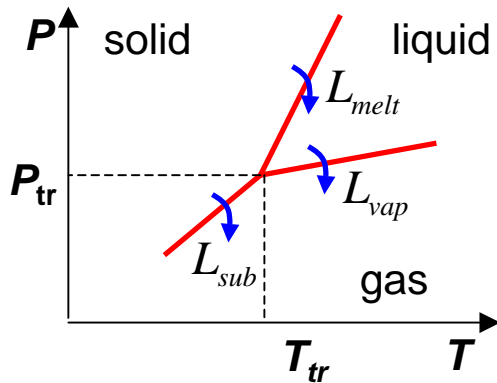
Near the triple point:

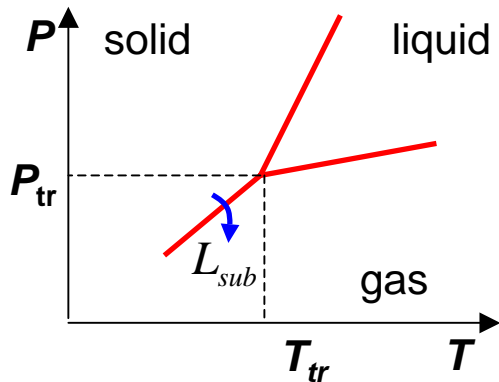$$L_{vap} = T_{tr}\left(S_G - S_L\right) \quad L_{melt} = T_{tr}\left(S_L - S_S\right) \quad L_{sub} = T_{tr}\left(S_G - S_S\right)$$

$$L_{sub} = T_{tr}\left(S_G - S_S\right) = L_{vap} + L_{melt} = \left(1010 + 162\right) \text{J/mol} = 1172 \text{J/mol}$$

solid   liquid

L_{melt}

P_{tr}

L_{vap}

L_{sub} gas

T_{tr} T

$$L_{melt} = \frac{T_{tr}\left(V_L - V_S\right)}{dT / dP} = \frac{14 \times \left(\dfrac{2 \cdot 10^{-3} \text{ kg/mol}}{71 \text{kg/m}^3} - \dfrac{2 \cdot 10^{-3} \text{ kg/mol}}{81 \text{kg/m}^3}\right)}{1/3.3 \cdot 10^6} \approx 162 \text{J}$$

$$V\left(\text{m}^3/\text{mol}\right) = \frac{\text{molar mass (kg/mol)}}{\text{density}\left(\text{kg/m}^3\right)}$$

The vapor pressure equation for H_2: $P = P_0 \exp\left(-\dfrac{L_{vap}}{RT}\right)$ where P_0 = 90 MPa .

Compute the slope of the vapor pressure curve (**dP/dT**) for the solid H_2 near the triple point, assuming that the H_2 vapor can be treated as an ideal gas.

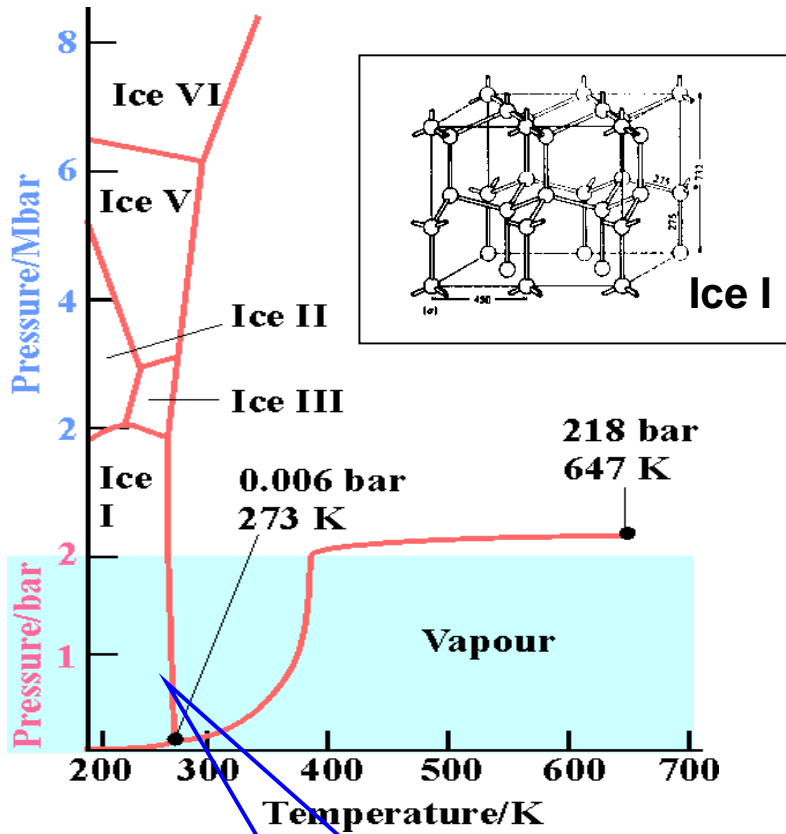At the solid-gas phase boundary: $\dfrac{dP}{dT} = \dfrac{L_{sub}}{T_{tr}(V_G - V_S)} \approx \dfrac{L_{sub}}{T_{tr}V_G}$

Assuming that the H_2 vapor can be treated as an ideal gas $\quad P_{tr}V_G = RT_{tr}$

$$V_G = \frac{RT_{tr}}{P_{tr}} = \frac{RT_{tr}}{P_0 \exp\left(-L_{vap}/RT_{tr}\right)} = \frac{8.3\,\text{J/K}\cdot\text{mol}\times 14\,\text{K}}{9\cdot 10^7\,\text{Pa}\times \exp\left[-1010\,\text{J}/\left(8.3\,\text{J/K}\cdot\text{mol}\times 14\,\text{K}\right)\right]}$$

$$= 7.69\cdot 10^{-3}\ \text{m}^3/\text{mol}$$

$$\frac{dP}{dT} = \frac{L_{sub}}{T_{tr}V_G} = \frac{1172\,\text{J/mol}}{14\,\text{K}\times 7.69\cdot 10^{-3}\,\text{m}^3/\text{mol}} = 1.09\cdot 10^4\,\text{Pa/K}$$

Phase Diagram of H$_2$O

For most "normal" substances, the slope of the melting curve is **positive** ($S_L > S_S$, $V_L > V_S$). The phase diagram for water shows the characteristic **negative** slope of the solid-liquid equilibrium curve. The ice is **less dense** than water ($V_L < V_S$): the hydrogen bonds determine the tetrahedral coordination and openness of the structure of ice. As ice melts into water the change in entropy (or the latent heat) is positive, while the change in volume is negative, hence the negative slope.

$$\frac{dT}{dP} = \frac{T\left(V_{liq} - V_{sol}\right)}{L} < 0$$

The negative slope of the solid-liquid coexistence curve makes ice skating possible: ice melts under the pressure exerted by the skate blade. The Clausius-Clapeyron equation provides the connection between ice skating and the observation that ice floats on water.
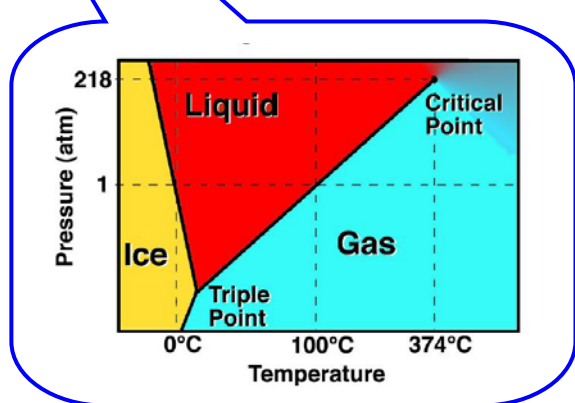
Problem

Ice skating becomes unpleasant if the weather is too cold so that the ice becomes too "hard". Estimate the lowest temperature for which ice skating is still enjoyable for a person of normal weight. The given data are that the latent heat of fusion of water is 333 J/g, that the density of liquid water is 1 g/cm^3, and that ice cubes float with ~9/10 of their volume submerged.
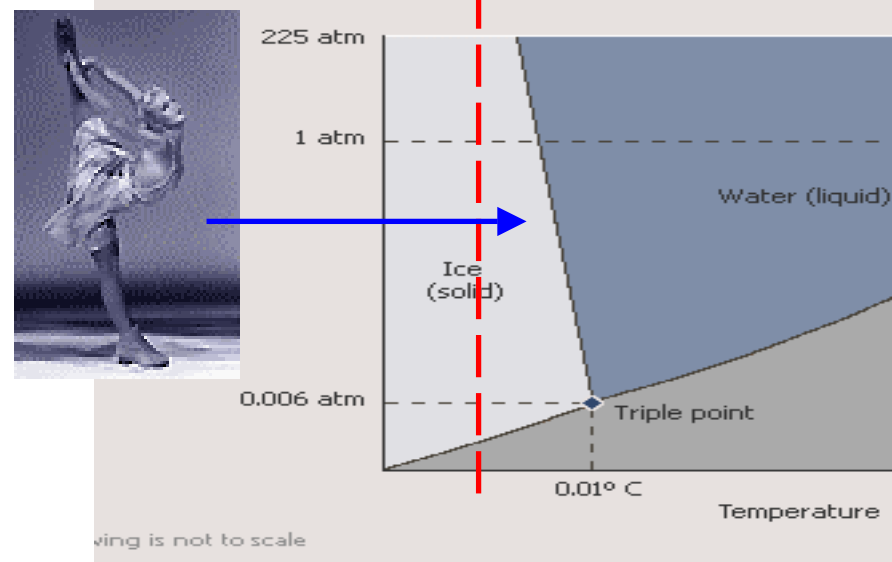
The lowest temperature for enjoyable skating is the temperature at which the pressure exerted by the skater on ice is equal to the pressure on the coexistence curve at this **T**. At **P₀** =1 bar, ice melts at **T₀** = 273.15K (=0⁰C).

pressure:

$$P = \frac{mg}{area} \approx \frac{100\,kg \times 10\,m/s^2}{0.1 \times 10^{-4}\,m^2} = 10^8\ kg \cdot s^2 m^{-1} = 10^8\ Pa\ \left(=1000\,atm\right)$$

$$\frac{dT}{dP} = \frac{T\left(V_{liq} - V_{sol}\right)}{L} \qquad \Delta T \approx \frac{T_0\left(V_{liq} - V_{sol}\right)}{L}\left(P - P_0\right) = -\frac{273\,K\left(0.1 \times 10^{-6}\,m^3/g\right)}{333\,J/g}10^8\,Pa \approx -8\,K$$

The lowest temperature: - 8⁰C, about right.

Let's verify that from two points on the melting curve, (0.006 bar 273.16K) and (1 bar 273.15K) we can get a reasonable estimate for **L**:

$$L(273K) = \frac{T\left(V_{liq} - V_{sol}\right)\left(P_1 - P_2\right)}{\left(T_1 - T_2\right)} = \frac{273\text{K} \times 0.1 \times 10^{-6}\ \text{m}^3/\text{g} \times 0.994 \times 10^5\ \text{Pa}}{0.01\text{K}} \approx 271\text{J/g}$$

Why Is Ice Slippery? (R. Rosenberg, Physics today, Dec. 2005)

Pressure melting does not explain why skating is possible in climates as cold as –30°C. This popular explanation of the thermodynamics of ice skating is not the whole story (the experiments by Robert Wood and other researchers). The mechanism(s) is much more complicated.

The physicists interested in the problem: Faraday, Gibbs, etc.

Two other important factors:

Frictional heating. S. Colbeck in his experiments (1988-1997) attached a thermocouple to a skate blade (and to the bottom of skis) and showed that the increase in temperature with velocity was consistent with frictional heating.

Liquid layer on ice surface below zero. There is a disordered (liquid-like) layer on the surface of ice (its thickness - ~ 10 nm) down to ~ -30°C.

# Phase Diagrams of ^{4}He

^{4}He
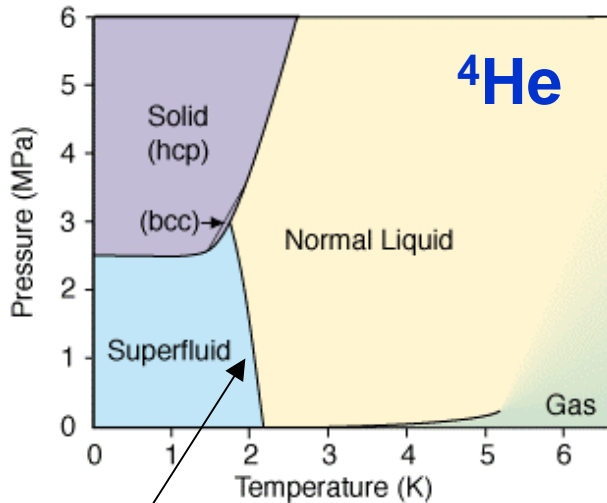
the "λ" transition

He is the only element that remains a liquid at **T**=0 and **P** =1 bar because (a) the zero-point oscillations of light atoms are large, and (b) the binding forces between the atoms are very weak. The zero-point energy of *He* is larger than the latent heat of evaporation of liquid helium; the zero-point vibration amplitude is ~1/3 of the mean separation of atoms in the liquid state. As a result, the molar volume of ^{4}He (^{3}He) is more than a factor of two (three) larger than one would calculate for a corresponding classical liquid. Also, the latent heat of evaporation is unusually small - ~1/4 of its value for the corresponding classical liquid.

According to Nernst's theorem, for any processes that bring a system at **T = 0** from one equilibrium state to another, Δ**S = 0**. If, at the same time, Δ**V ≠ 0**, then **dP/dV = 0**, and the slope of the coexistence curve "solid-liquid" must approach zero as **T → 0**.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

The slope of the phase boundary solid helium – **superfluid** liquid helium is essentially 0 at **T < 1K**: the entropy change must be zero, and **the liquid must be as ordered as the solid**! While the phase diagram shows that the solid and liquid II are equally ordered, x-rays reveal that only the solid has a long-range order in "real" space. Therefore, we arrive at a conclusion that **liquid II must be more ordered in the momentum space!**
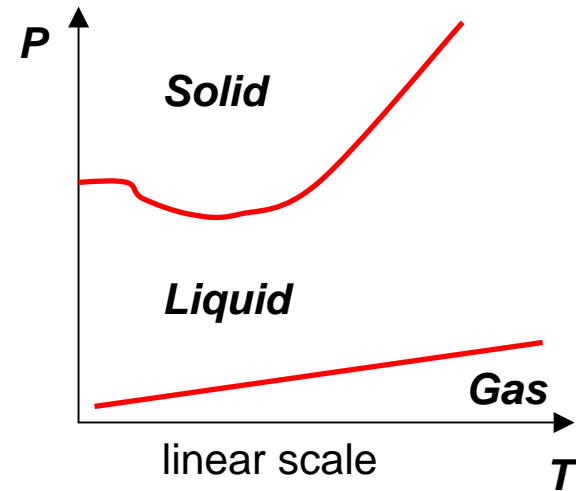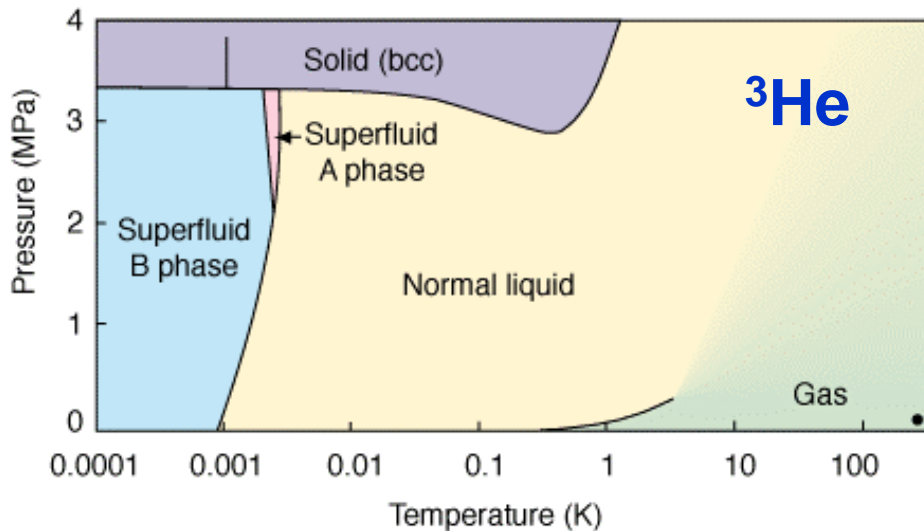
Below 0.3K the slope of the ³He solid-liquid phase boundary is **negative**. This negative slope tells us that ΔS and ΔV have opposite signs. The denser phase is always the one that is stable at high **P** – its molar volume is smaller, and at sufficiently high **P**, its **G** is smaller. When we move from liquid ³He to solid ³He, **V** decreases - thus, **S** must increase!!

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

In other words, the liquid is more "ordered" than the solid, and therefore it takes heat to change the liquid to a solid! **The Pomeranchuk effect**: as the solid-liquid mixture is compressed, heat is removed from the liquid phase as crystals form. The latent heat associated with converting 1 mole of ³He liquid into solid is 0.42J. Cooling: from ~ 20 mK to 2 mK.
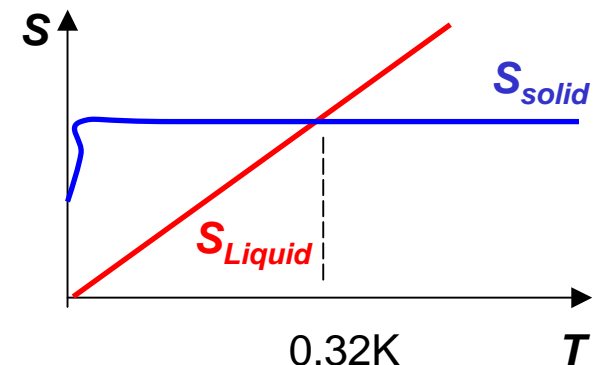
Problem

At the atmospheric pressure, ^{3}He remains liquid even at T=0. The minimum pressure of ^{3}He solidification is P_{min}= 28.9 bar. At low temperatures, the entropy of 1 mole of liquid ^{3}He is $S_L = RT/T_0$, where T_0=0.22 K, the entropy of solid ^{3}He is temperature-independent: $S_S = R \ln 2$. The difference between the molar volumes of liquid and solid ^{3}He $\Delta V = V_L - V_S = 1.25$ cm^3/mol

   (a) Find the temperature of solidification T_{min} at $P = P_{min}$
   (b) Find the temperature dependence of the latent heat of melting L_{melt}.
   (c) Find the pressure of solidification of ^{3}He at $T = 0$.

(a) $\left(\dfrac{dP}{dT}\right)_{melt} = \dfrac{L_{melt}}{T(V_L - V_S)}$ The minimum on the solid-liquid coexistence curve ($P = P_{min}$) corresponds to $dP/dT = 0$, and, thus, $L_{melt}(T_{min}) = 0$.

$$L_{melt}(T_{min}) = T_{min}\left[S_L(T_{min}) - S_S(T_{min})\right] \qquad T_{min} = T_0 \ln 2 \approx 0.15K$$

**(b)** $L_{melt}(T) = T\left[S_L(T) - S_S(T)\right] = \dfrac{RT^2}{T_0} - RT\ln 2$ - a parabola that goes through 0 at $T = T_{min}$.
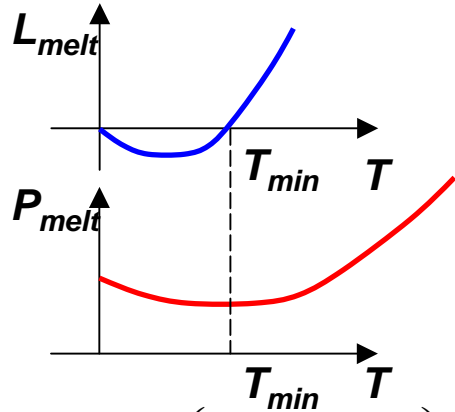
The negative sign of L_{melt} for ^{3}He is a unique phenomenon (the Pomeranchuk effect). Over the range of T where $L_{melt} < 0$, the slope of the L-S coexistence curve is negative. (Note that, in contrast to $dP_{melt}/dT < 0$ on the phase diagram for water, here the negative slope is observed for $V_L - V_S > 0$).

(c) By integrating the Cl.-Cl. eq. $dP = \dfrac{R}{\Delta V}\left(\dfrac{T}{T_0} - \ln 2\right)dT$

$$P = \dfrac{R}{\Delta V}\left(\dfrac{T^2}{2T_0} - T\ln 2\right) + const \qquad const = P(T=0) = P_{min} - \dfrac{R}{\Delta V}\left(\dfrac{T_0}{2} - T_0\ln 2\right) = 31.7\cdot 10^5 \text{ Pa}$$
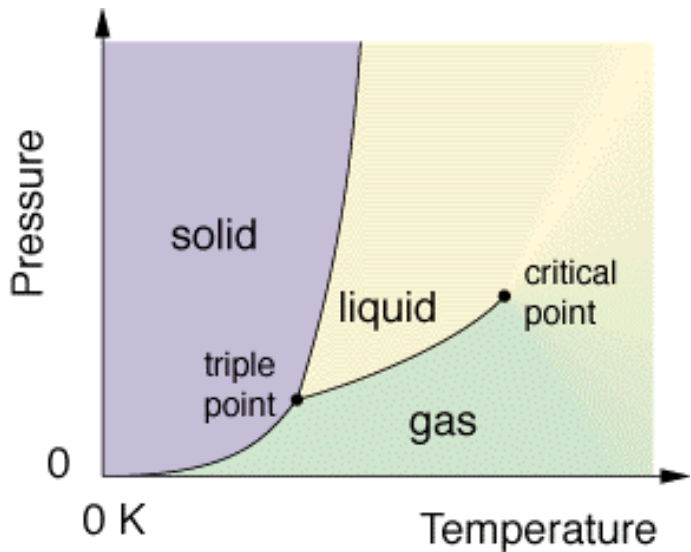
1. The shape of coexistence curves on the **P-T** diagram:

$$G_1(P,T) = G_2(P,T)$$

2. The latent heat in the 1st order phase transitions:

$$\Delta S = \frac{\delta Q}{T} = \frac{L}{T}$$

$$G = N\mu = U + PV - TS = H - TS \quad \longrightarrow \quad \Delta H = T\Delta S = L$$

3. The slope of the coexistence curve is given by the *Clausius-Clapeyron Relation:*

$$\frac{dP}{dT} = \frac{L(T)}{T\,\Delta V(T)}$$

By integrating the CC relation, one can restore the shape of the coexistence curve, **P(T)**

4. For the gas-liquid transition, we can replace the CC relation with the vapor equation:

$$\left(\frac{dP}{dT}\right)_{vap} \approx \frac{L}{TV_{gas}} = \frac{LP}{RT^2} \qquad \frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2} \qquad P_{vap} \propto \exp\left(-\frac{L}{RT}\right)$$

5. The triple point:

$$G_{liq}(P_{tr},T_{tr}) = G_{gas}(P_{tr},T_{tr}) = G_{sol}(P_{tr},T_{tr})$$

$$L_{vap} = T_{tr}(S_G - S_L) \quad L_{melt} = T_{tr}(S_L - S_S) \quad L_{sub} = T_{tr}(S_G - S_S) \quad \longrightarrow \quad L_{melt}(T_{tr}) + L_{vap}(T_{tr}) = L_{sub}(T_{tr})$$