MSE-204 Thermodynamics for Materials Science

L7.2 SINGLE COMPONENT PHASE DIAGRAMS

ENTHALPY AND ENTROPY ACCORDING TO BOLTZMANN | THERMODYNAMIC PROPERTIES AT PHASE TRANSITIONS | FIRST ORDER PHASE TRANSITIONS | CRITICAL POINTS

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WHY DO LIQUIDS BOIL? | LET'S DEFINE THE SYSTEM

solid → liquid → gas $\Rightarrow$ input heat $q = \Delta U - w$ $\Delta H = \Delta U - \Delta(pV)$

$h^s < h^l < h^g$

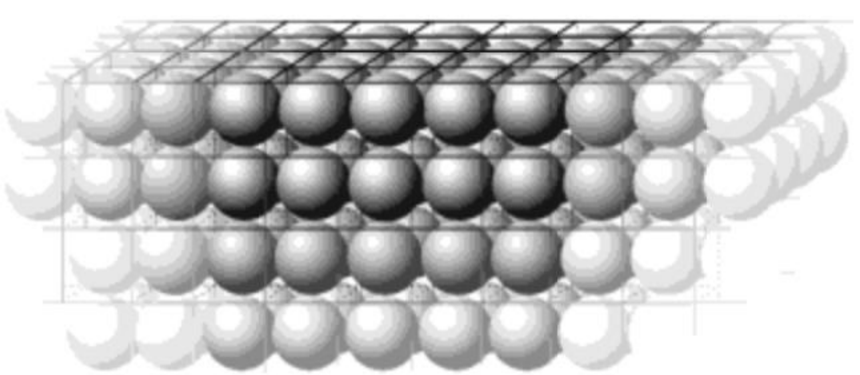
$s^s < s^l < s^g$

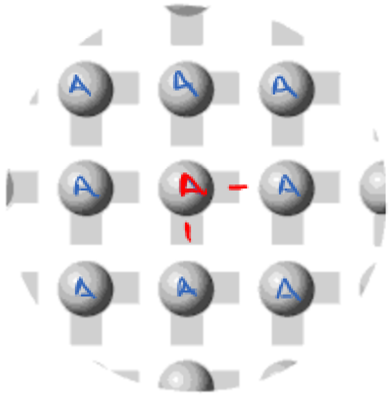
if $\mu^l < \mu^g$ the liquid is stable

$g^l < g^g \iff h^l - Ts^l < h^g - Ts^g \Rightarrow T(s^g - s^l) < h^g - h^l$

LATTICE MODEL FOR THE DESCRIPTION OF THE THERMODYNAMIC BEHAVIOR OF LIQUIDS/SOLIDS

We model a liquid (or a solid) as if its particles occupied a crystalline lattice, with every site occupied by one particle. For practical reasons the lattice is considered to be infinite. The main insight represented by the lattice model is that the most important energetic interactions for holding liquids together are the short-range interactions of its particle with its nearest neighbors, and that the number of nearest neighbors has a relatively well-defined average.





$U = \varepsilon_{AA} \cdot P_{AA}$

$U = \varepsilon_{AA} \cdot n \, \frac{z}{2}$

ε_{AA} : energy of the A-A bond

$P_{AA} = n \cdot \frac{z}{2}$

n : total number of atoms

z : nearest neighbors

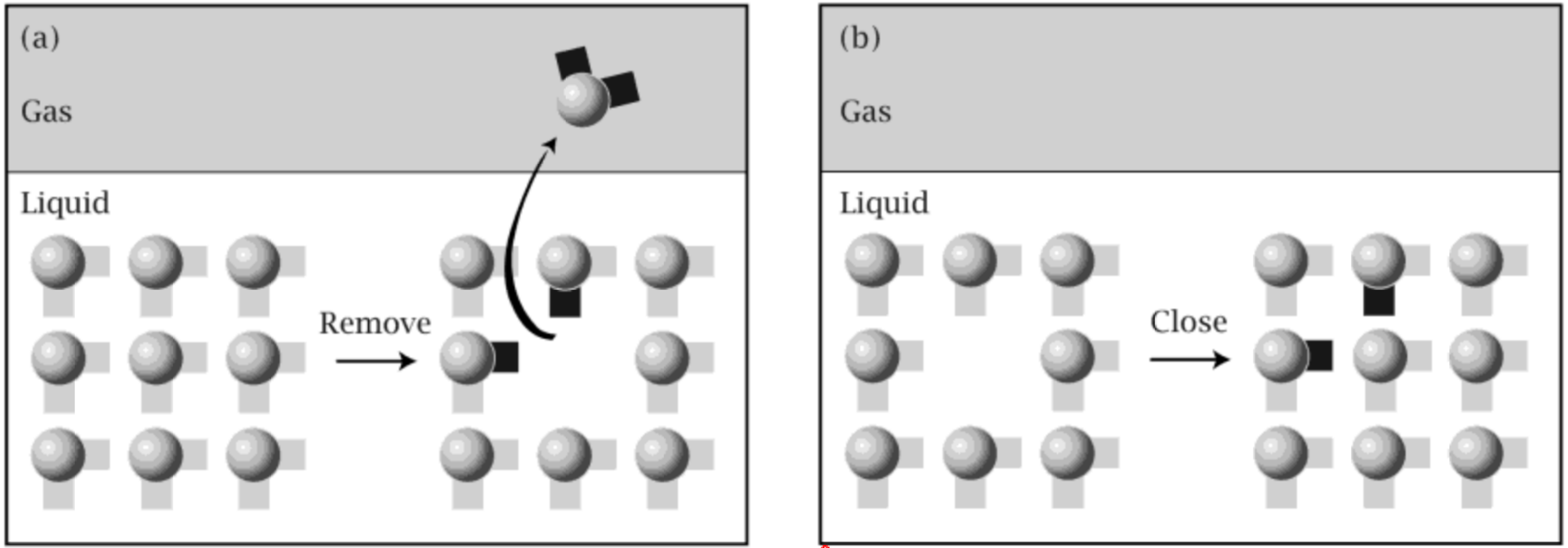
$S = k_B \ln \Omega$ where Ω : # of distinguishable configurations in the system

For a pure substance that is also perfect (0 K)

$S(0) = 0$ because $\Omega = 1$

CAVITIES IN LIQUIDS AND SOLIDS

Does it matter whether an atom/molecule leaves from the surface or the bulk?

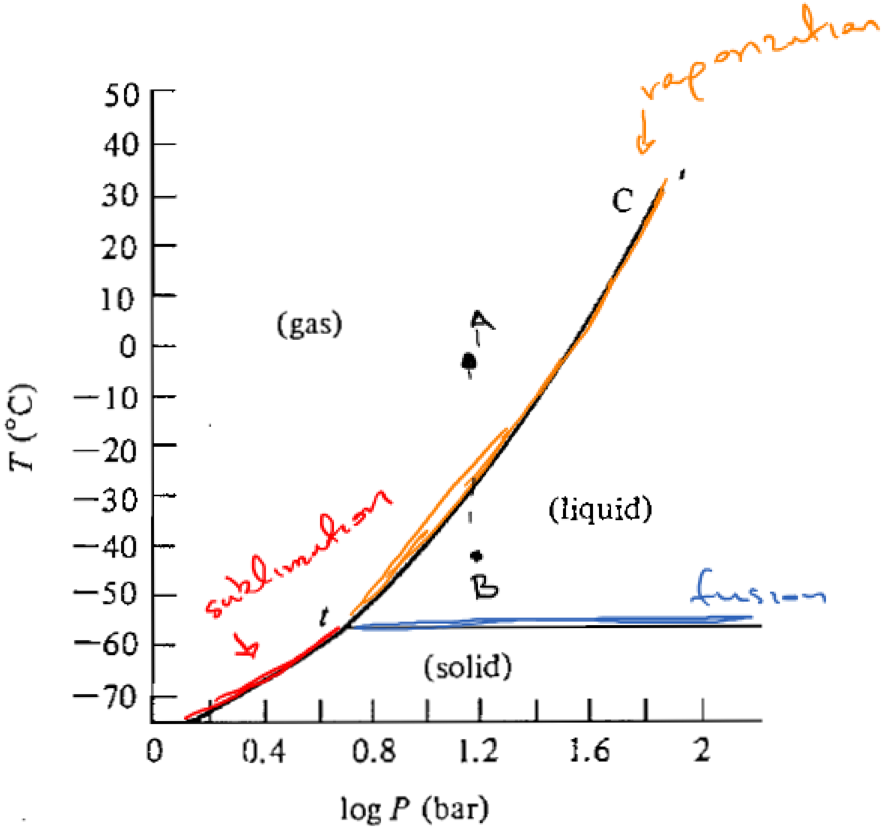


→ approximation is that the $\mu^{l}_{surface} = \mu^{l}_{bulk}$

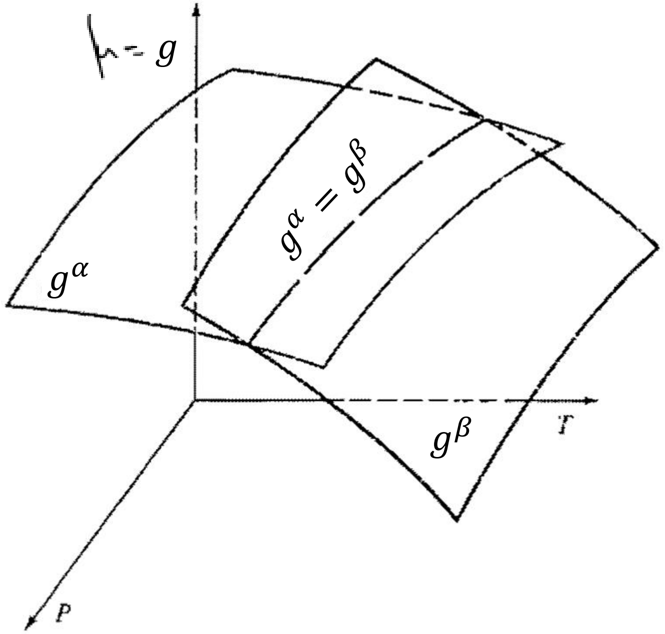
CONSTRUCTION OF A PHASE DIAGRAM OF A PURE SUBSTANCE

When the surfaces of the chemical potentials of two phases are constructed in the space (μ, p, T), the intersection line forms the coexistence line of the two phases. A phase transition occurs when the line is crossed. The phase with the lower chemical potential is always realized as the more stable phase.

$g = \mu = -s\,dT + v\,dp$



Pressure – Temperature phase diagram for CO_2



Terminology

solid → gas: sublimation
gas → solid: deposition

solid → liquid: fusion (melting)
liquid → solid: freezing

liquid → gas: vaporization
gas → liquid: condensation

CHANGES IN THERMODYNAMIC FUNCTIONS IN A NORMAL TYPE OF A PHASE TRANSITION

Simple kinds of phase change, such as melting and vaporization, are characterized by considerable changes in volume, and also of entropy and enthalpy, at the point of transition. The chemical potential of the phases are equal at equilibrium, however, their volumes, entropies, and enthalpies are far from equal.

Simplest case: for a pure substance with two phases gas liquid

$$\mu(T,p) : d\mu = \left(\frac{\partial\mu}{\partial T}\right)_p dT + \left(\frac{\partial\mu}{\partial p}\right)_T dp$$

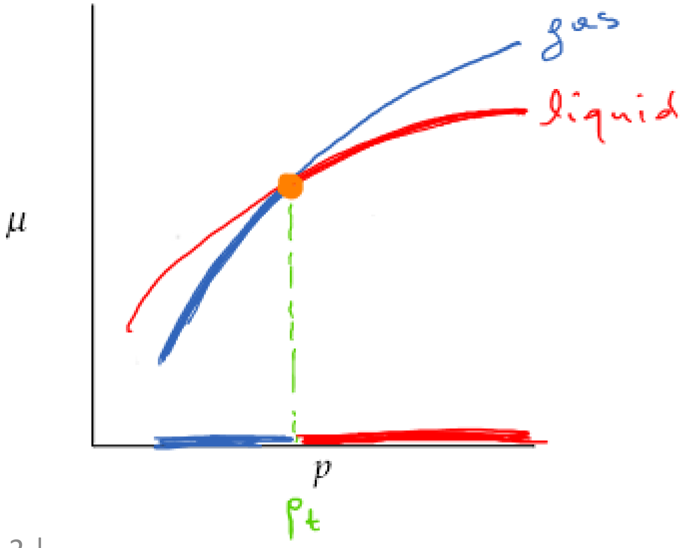
transition at constant T , $dT = 0$

$$d\mu = \left(\frac{\partial\mu}{\partial p}\right)_T dp \Rightarrow \frac{d\mu}{dp} = V \leftarrow \text{always positive (slope)}$$

transition at constant p , $dp = 0$

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_p dT \Rightarrow \frac{d\mu}{dp} = -S$$

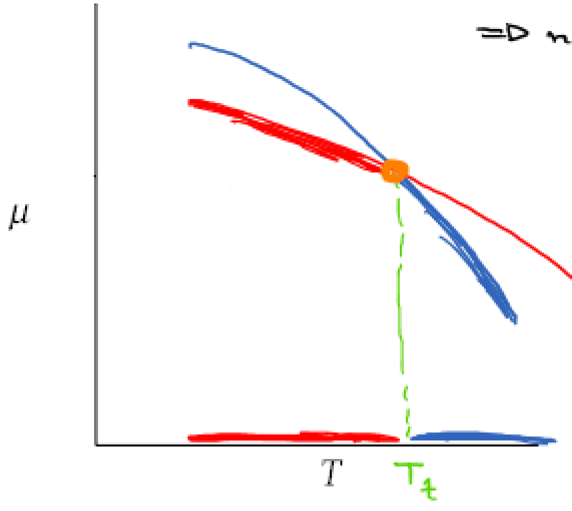
$\Rightarrow$ negative (slope)



At the transition point;

$\mu^g = \mu^l$

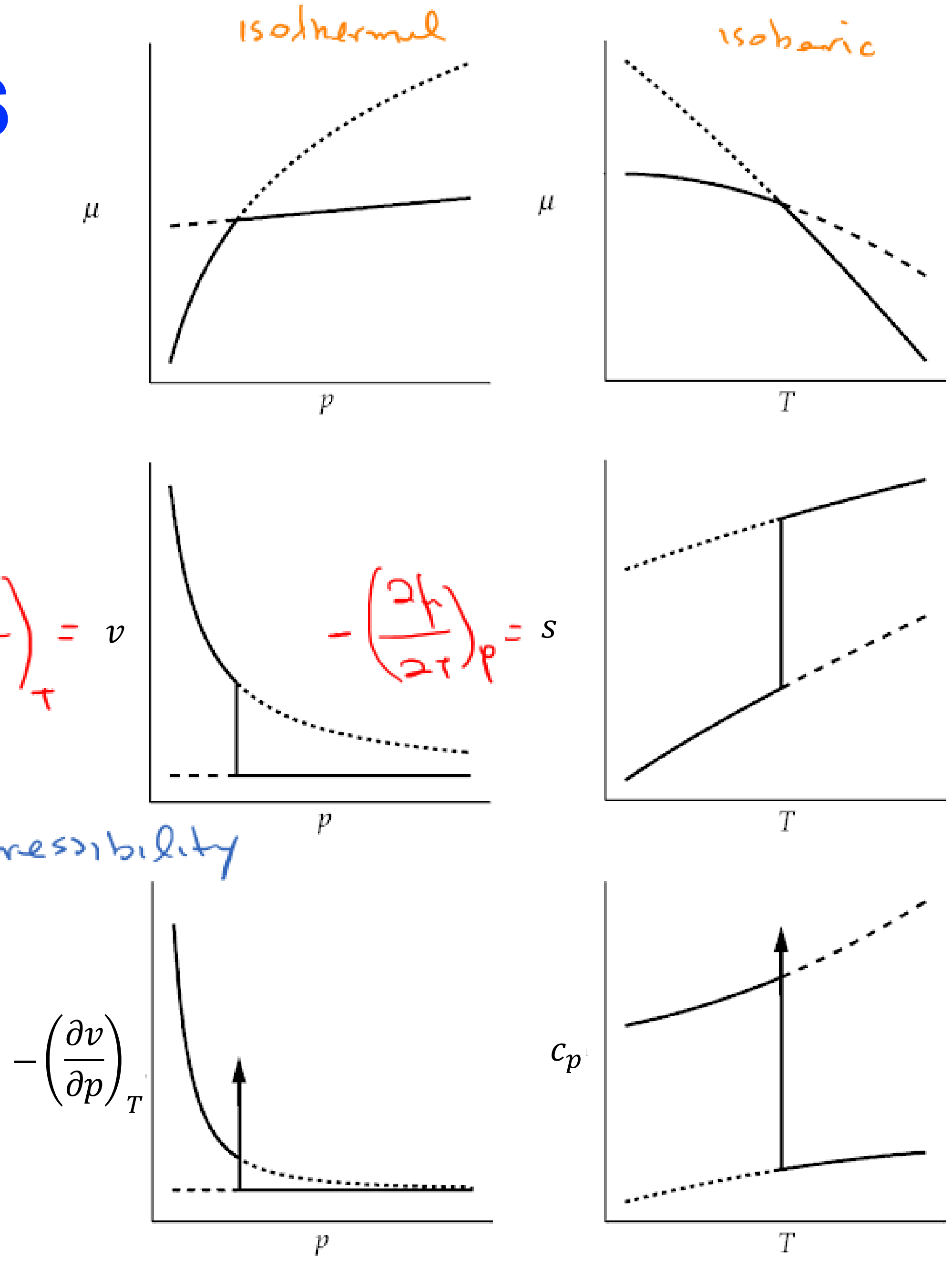
when we have the same phase transition



FIRST ORDER PHASE TRANSITIONS

First order phase transitions are defined by **a discontinuous change of the first derivatives of the chemical potential**, which are the molar quantities of entropy and volume

As a consequence, the observable physical properties of the material provide no information that a change of a rather drastic nature is about to happen.



$$\left(\frac{\partial f}{\partial p}\right)_T = v$$

$$-\left(\frac{\partial f}{\partial T}\right)_p = s$$

isothermal compressibility

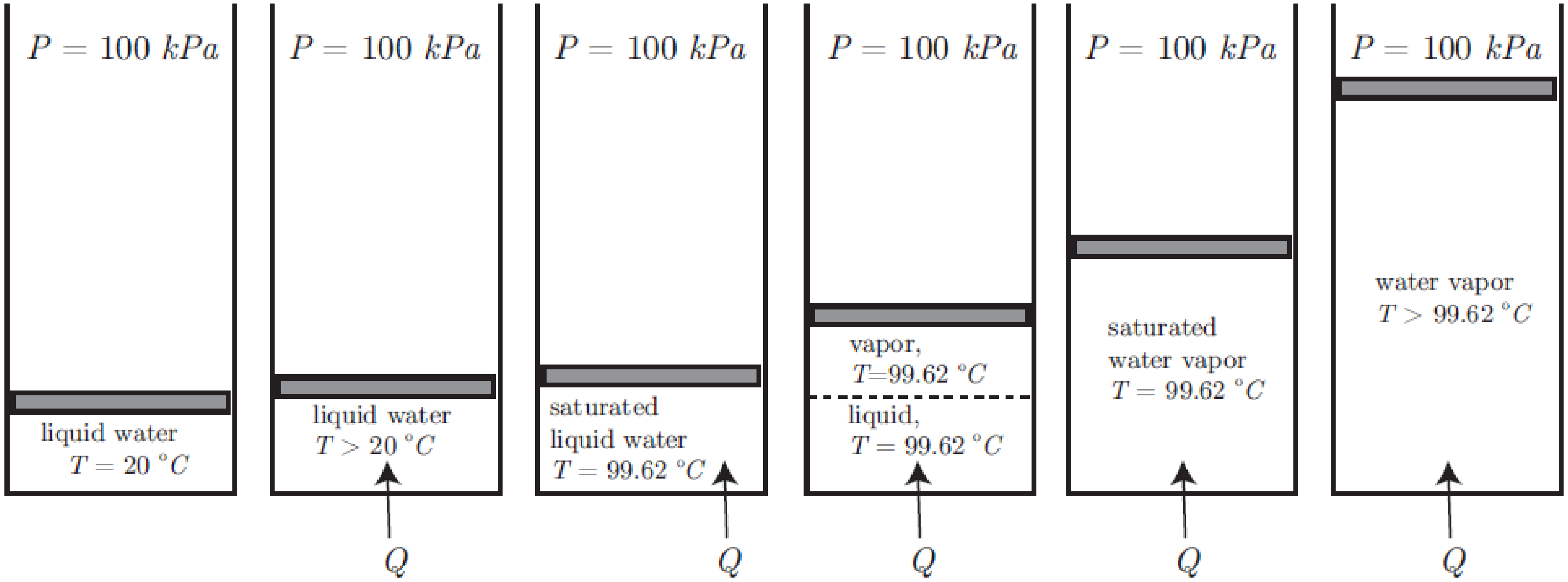
$$\left(\frac{\partial^2 f}{\partial p^2}\right)_T = \left(\frac{\partial v}{\partial p}\right)_T = -vB$$

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_p = -\left(\frac{\partial s}{\partial T}\right)_T = -\frac{c_p}{T}$$

HEAT AS A FUNCTION OF TEMPERATURE: THE BOILING OF WATER

Let us consider a piston-cylinder arrangement for the boiling of water. Inside the cylinder, we begin with pure liquid water at T = 20ºC. The piston is free to move in the cylinder, but it is tightly sealed, so no water can escape. On the other side of the piston is a constant pressure atmosphere, which we take to be at P=100 kPa= 0.1MPa = 105Pa= 1 bar.

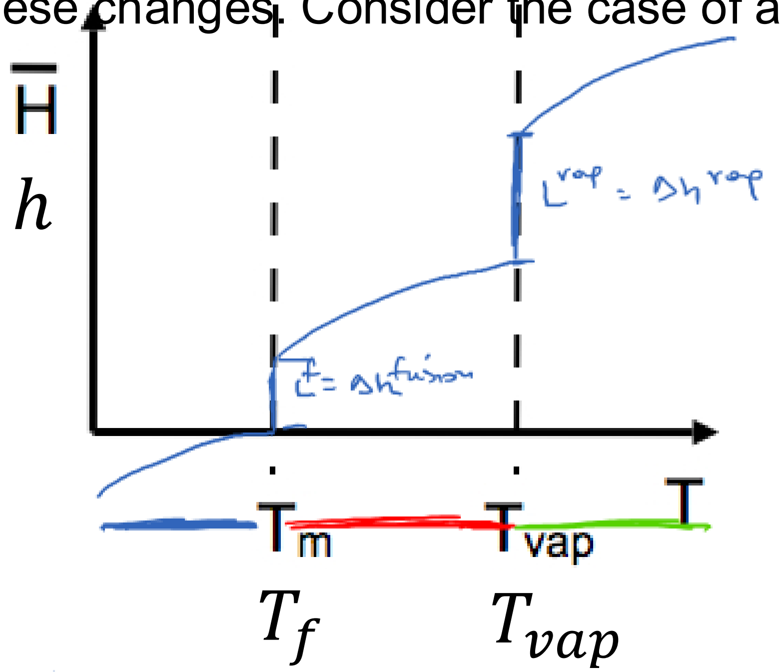
We slowly add heat to the cylinder, and observe a variety of interesting phenomena.

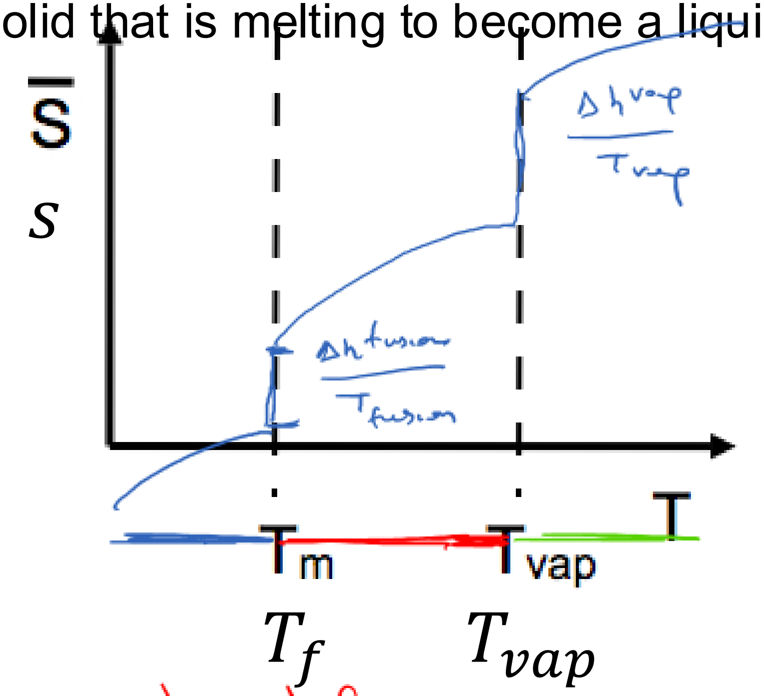


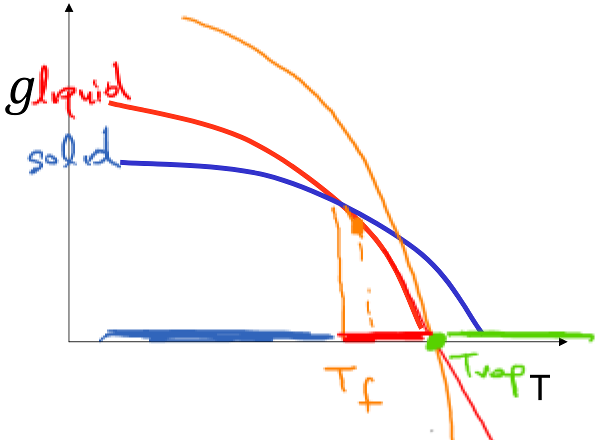
MOLAR ENTHALPY AND ENTROPY AT THE PHASE TRANSITION

Let's address what happens to the enthalpy and entropy at the phase transition, and how we can measure/calculate these changes. Consider the case of a solid that is melting to become a liquid at constant pressure.

1 cal = 4.184 J







$g = f = h - Ts$

For fusion

$\Delta g = \Delta h^{fusion} - T_f \cdot \Delta s^{fusion} = 0$

$\Rightarrow \Delta s^{fusion} = \frac{\Delta h^{fusion}}{T_{fusion}}$

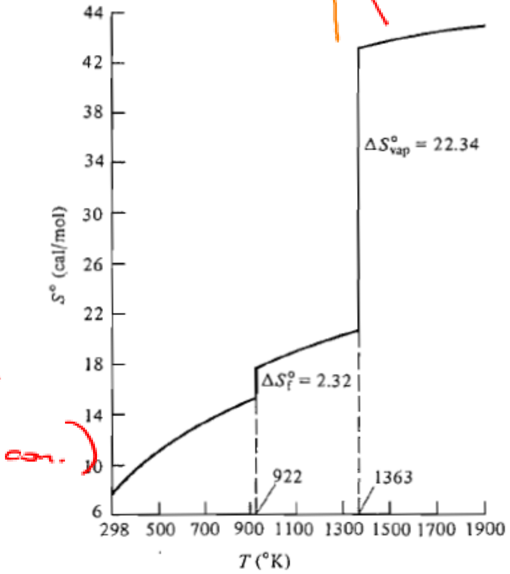
For most metals

Richard's Rule : $\Delta s^{f} = 2\text{-}3$ cal/K.mol

Trouton's Rule : $\Delta s^{vap} = 22$ cal/K.mol

Standard State of Entropy (atmospheric con.)

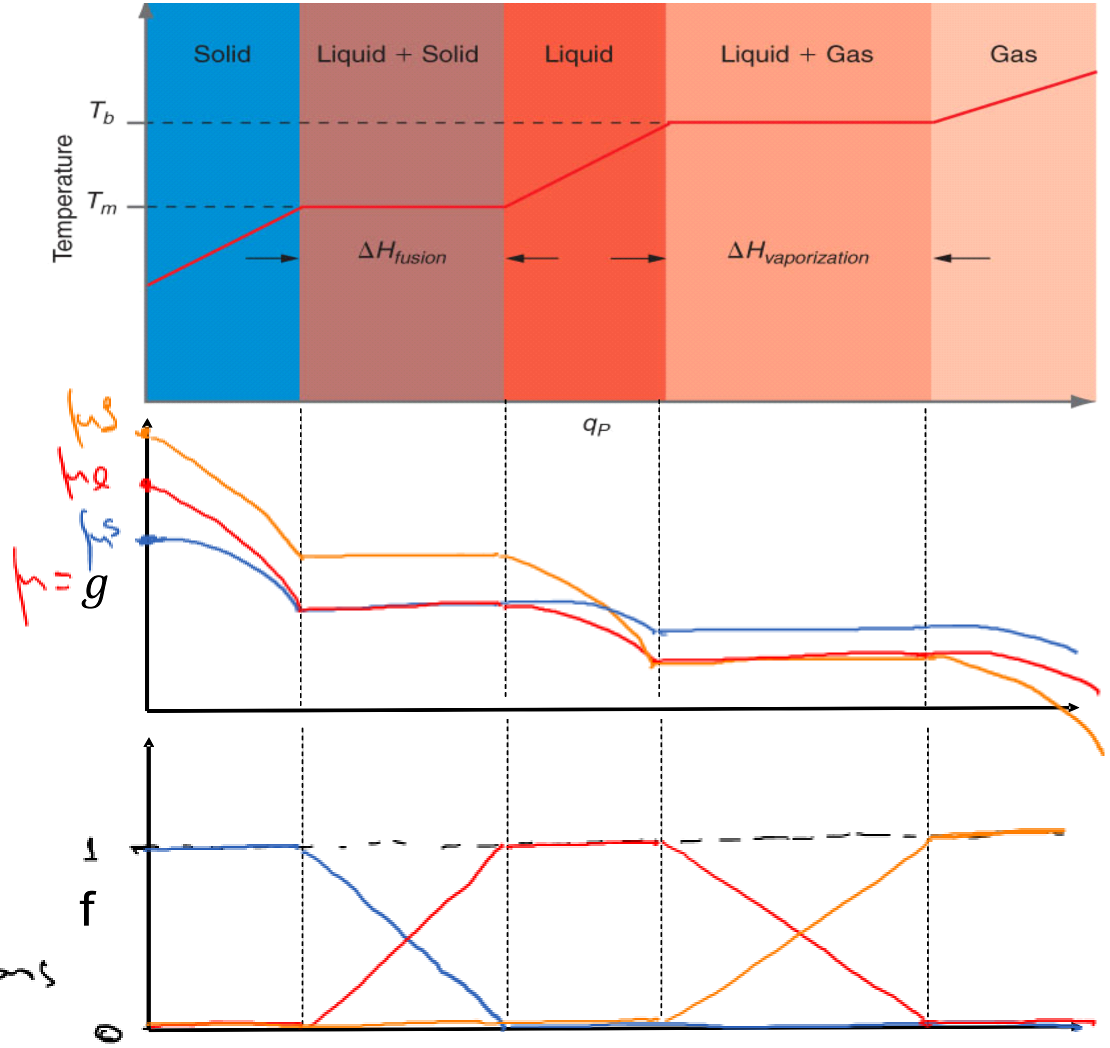
$\Delta S(298K) = \int_0^{298} C_p \, d\ln T$



Temperature dependence of the entropy of magnesium at 1 atm.

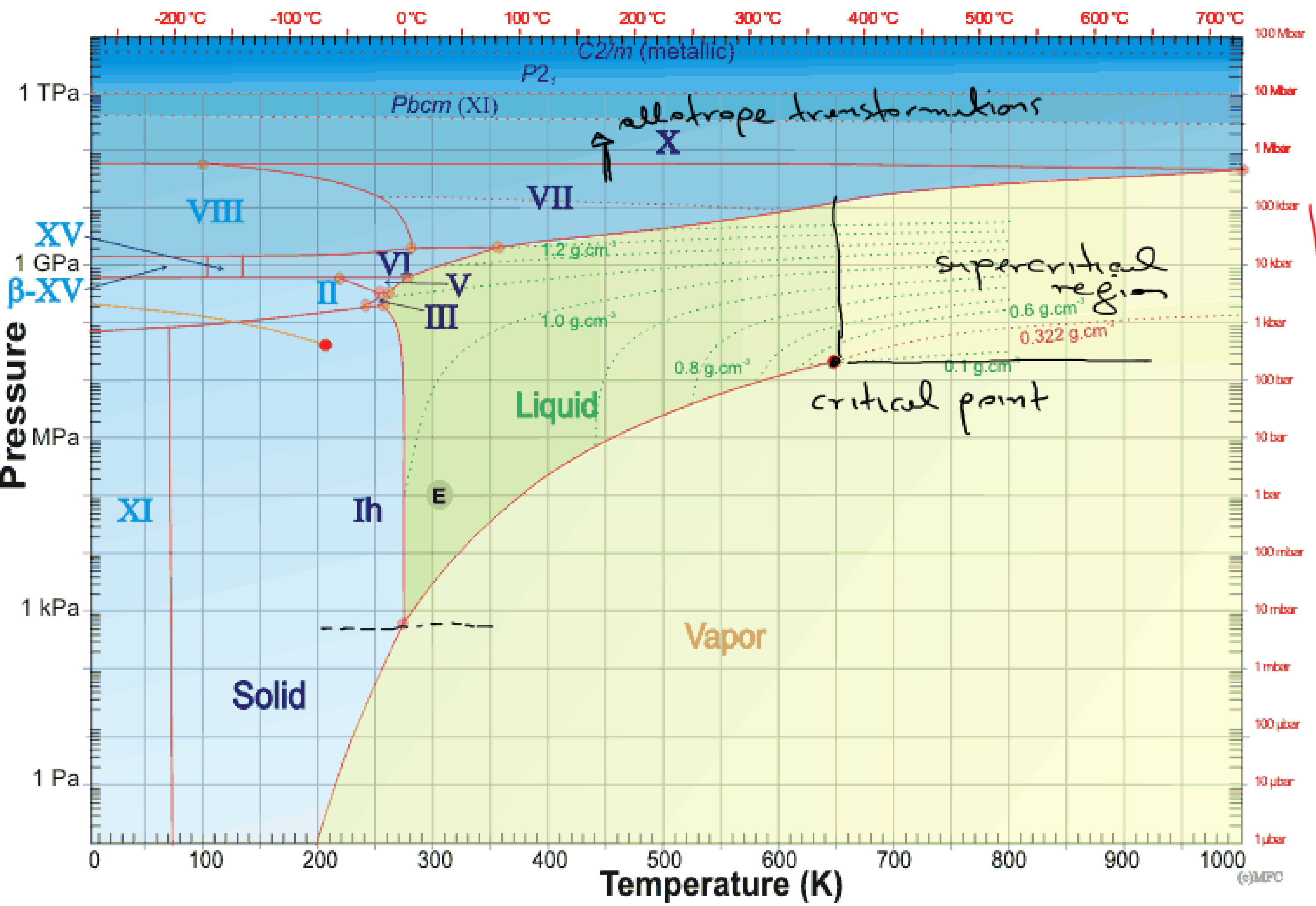
BEHAVIOR OF THE CHEMICAL POTENTIAL DURING TRANSITIONS

We will now see graphically what happens to the chemical potential of the single component going through all three phase transformations, starting from the solid, as we increase the heat in our system.



fraction of each phase changes during transitions

EXAMPLE OF SINGLE COMPONENT PHASE DIAGRAM: H_2O

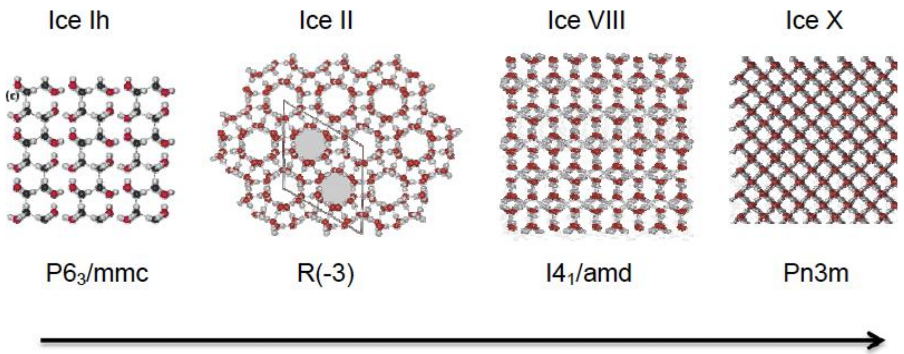


① negative slope between liquid & solid

$$\left[\frac{dp}{dT} = \frac{L}{T \cdot \Delta V}\right]_{\text{fusion}} \Rightarrow \boxed{V_\ell < V_s}$$

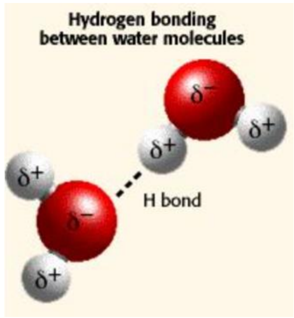
The volume of liquid water is SMALLER than that of solid water

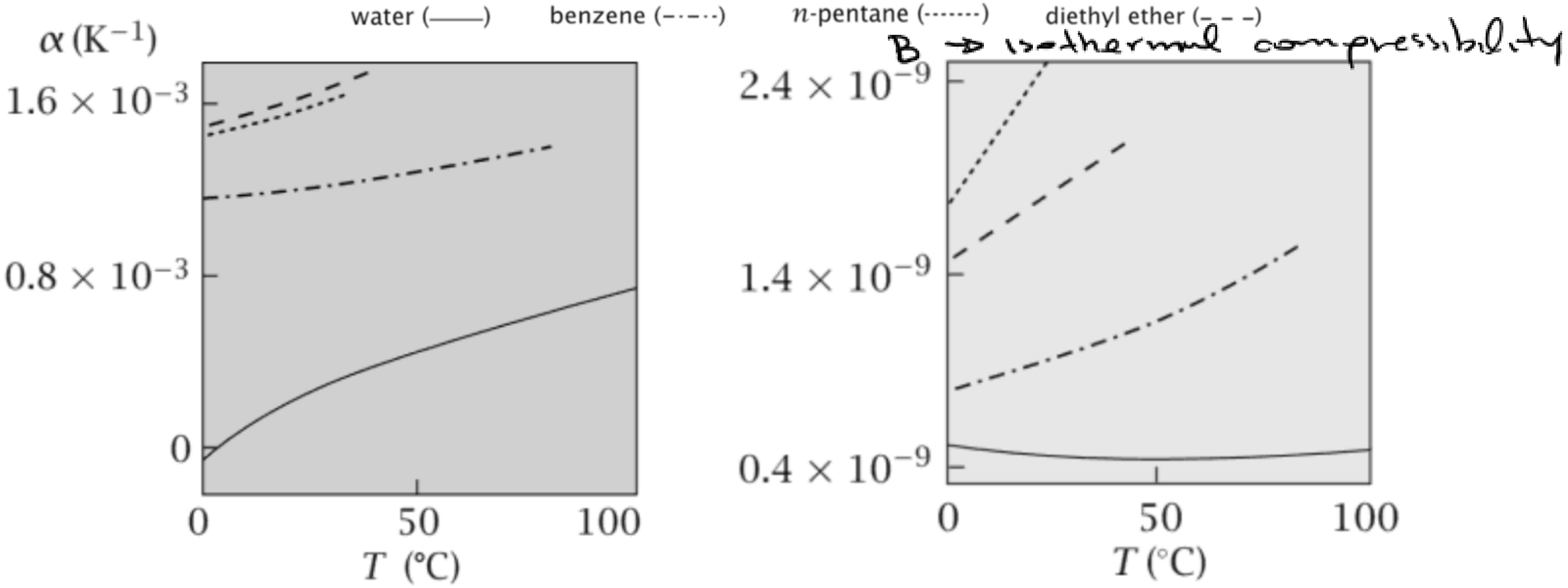
As one of your colleagues said, water expands when frozen



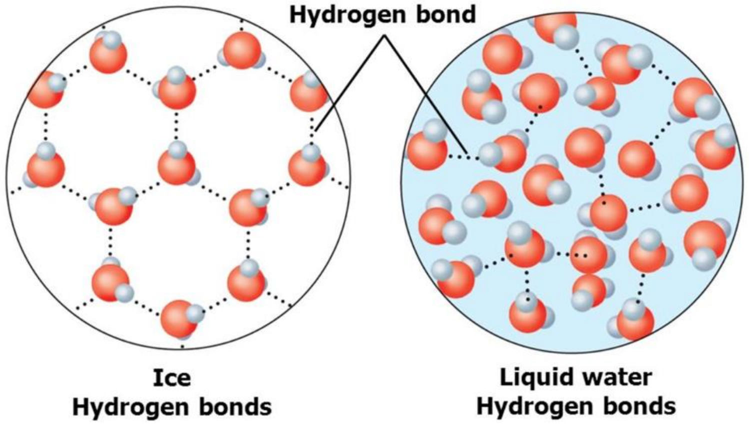
WATER DIFFERS FROM SIMPLE LIQUIDS: ENTROPY, VOLUME, & STRUCTURE

The thermal expansion coefficient and the isothermal compressibility are small for water, which is hydrogen bonded, than for simpler liquids like benzene which are not.





B → isothermal compressibility



$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$: thermal expansion coefficient