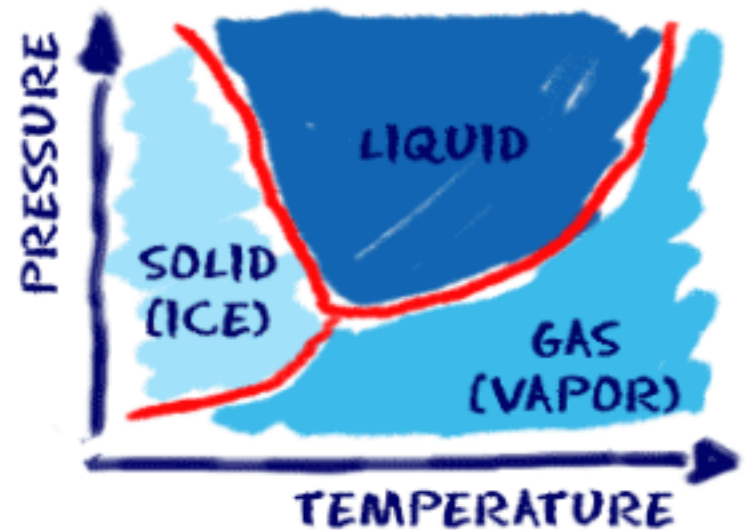


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# Lecture 28. *Phase transitions*

- In this lecture, we will dig deeper into phase transitions and will study how the thermodynamics of a phase transition can be characterized using various criteria
- Exceptionally, this lecture will be provided in two parts with the second part of the topic devoted to the so-called *Ising model*, an example of a simple system to study phase transition.



[http://www.chem4kids.com/files/matter\\_changes.html](http://www.chem4kids.com/files/matter_changes.html)

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# Latent heat

$$dU = TdS - pdV$$

To increase temperature of a substance, one needs to transfer heat

This is accompanied with an **increase in entropy**

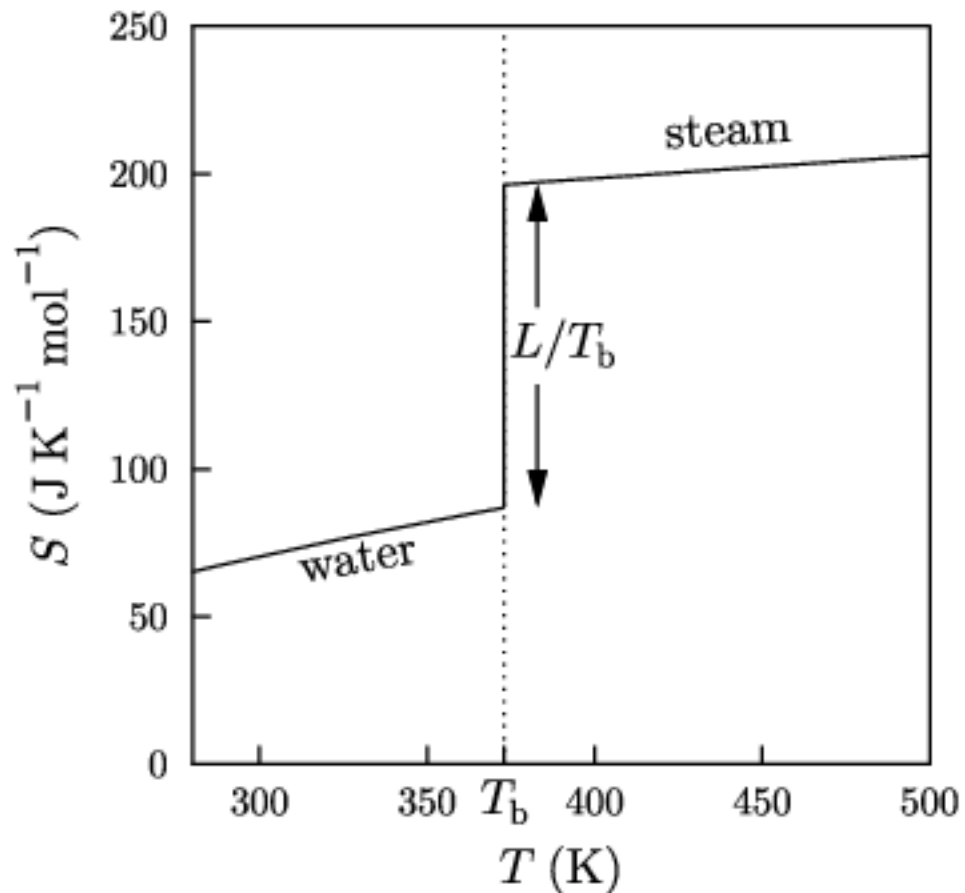
$$C_x = T \left( \frac{\partial S}{\partial T} \right)_x \quad x \text{ is a constraint (p, V, B, ...)}$$

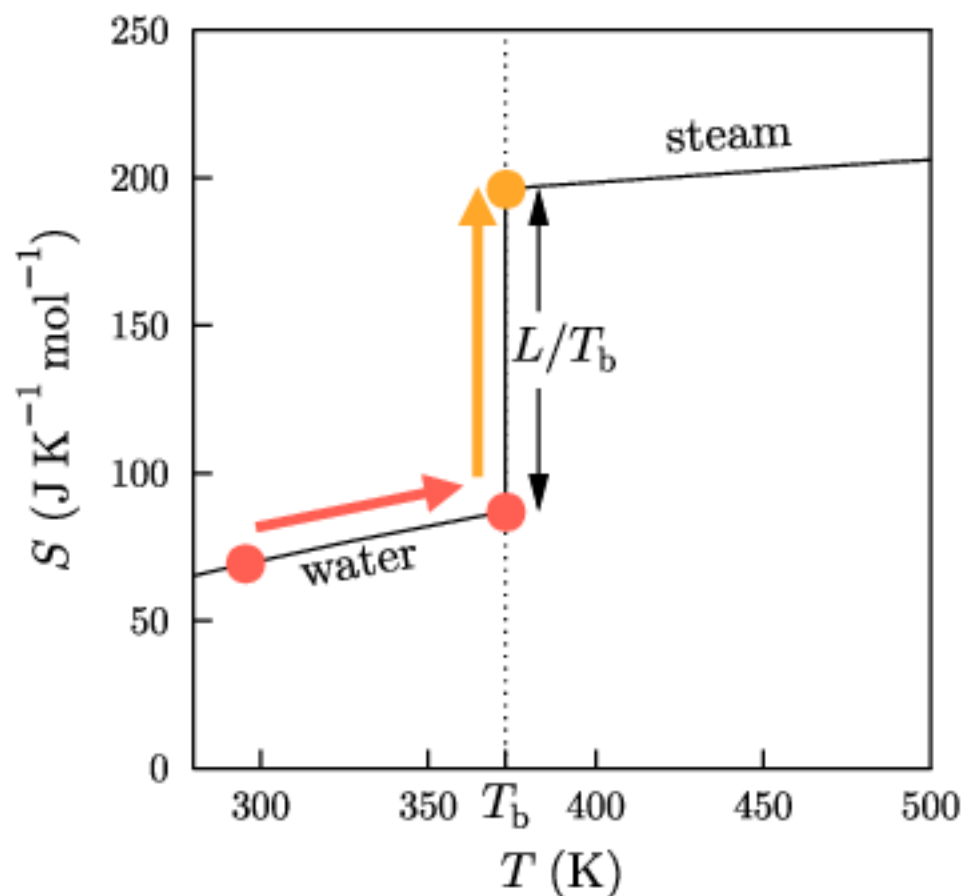
**Two phases in equilibrium** at critical temperature  $T_C$

Very often additional heat is necessary to be transferred to change from phase 1 to phase 2 (this is called the **latent heat**):

**Discontinuity in  $S$  as a function of  $T$ , thus spike in  $C_x$**

# Example





If it takes 3 min to boil water from 20C, how much longer does it take to make it dry?

$(100-20) \times 4.2 = 336 \text{ kJ/kg}$  (using value of heat capacity)

Energy to steam:  $L=2.26\text{MJ/kg}$

If 336 kJ/kg was delivered in 3 minutes, it would take  $3 \times 2.26 \times 10^6 / (336 \times 10^3)$  or 20 min to transform all the water into steam

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# Entropy discontinuity

The number of microstates available to a single gas molecule is proportional to its volume

$$\longrightarrow \frac{\Omega_{\text{vapor}}}{\Omega_{\text{liquid}}} = \left( \frac{V_{\text{vapor}}}{V_{\text{liquid}}} \right)^{N_A}$$

---

$$L \approx 10RT_b$$

Law of corresponding states:  $L/RT_b$  should be a constant

	Ne	Ar	Kr	Xe	He	H <sub>2</sub> O	CH <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>
$T_b$ (K)	27.1	87.3	119.8	165.0	4.22	373.15	111.7	353.9
$L$ (kJ mol <sup>-1</sup> )	1.77	6.52	9.03	12.64	0.084	40.7	8.18	30.7
$L/RT_b$	7.85	8.98	9.06	9.21	2.39	13.1	8.80	10.5

**Trouton's rule is observed, with some exceptions**

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# Chemical potential

- At constant  $p$  and  $T$ , we must minimize the Gibbs function

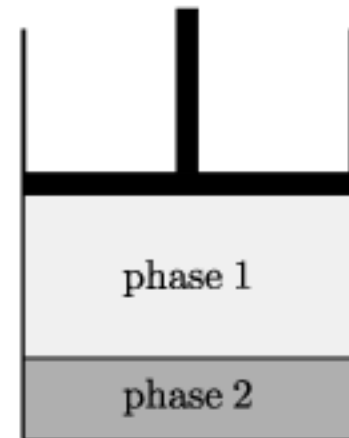
$$dG = Vdp - SdT + \sum_i \mu_i dN_i$$

- Since the *Gibbs function is the chemical potential per particle*, If  $N_1$  particles in phase 1 and  $N_2$  particles in phase 2, we have

$$G_{\text{tot}} = N_1\mu_1 + N_2\mu_2$$

- At equilibrium  $dG_{\text{tot}} = dN_1\mu_1 + dN_2\mu_2 = 0$

- We find  $\mu_1 = \mu_2$



**During phase transition, the chemical potentials of the two phases are the same**

# Clausius-Clapeyron

On that line:  $\mu_1(p, T) = \mu_2(p, T)$

$$\longrightarrow \mu_1(p + dp, T + dT) = \mu_2(p + dp, T + dT).$$

$$\longrightarrow d\mu_1 = d\mu_2.$$

$$\mu = \frac{G}{N}$$

}



$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\downarrow$$

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

$$L = \Delta Q_{\text{rev}} = T_c(S_2 - S_1)$$

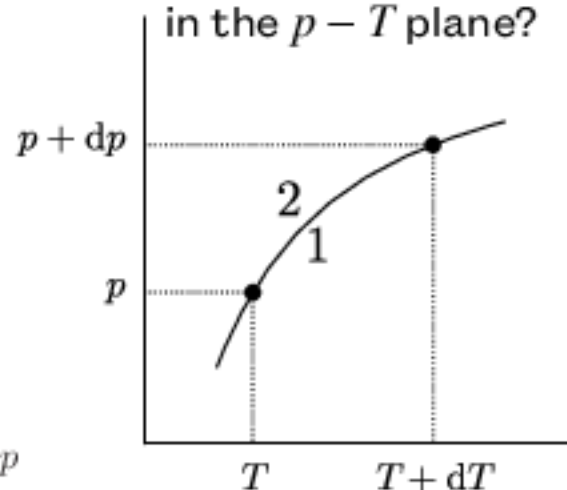


$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)}$$



$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

What's the phase boundary in the  $p - T$  plane?



**The slope is determined by the latent heat, the  $T$  at the phase boundary, and the volume**



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# Gas-liquid boundary at T-independent L

- **Assumptions:**

- $L$  does not depend on  $T$
- Gas can be treated as ideal gas
- Volume change is large

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad \longrightarrow \quad \frac{dp}{dT} = \frac{Lp}{RT^2}$$

$$\longrightarrow \quad \frac{dp}{p} = \frac{LdT}{RT^2}$$

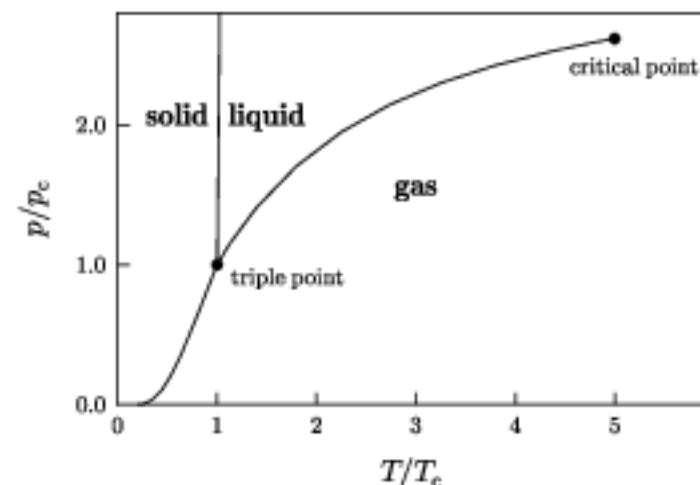
$$p(T) = p_0 \exp\left(-\frac{L}{RT}\right)$$

# Phase boundary between liquid and solid

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \longrightarrow dp = \frac{LdT}{T\Delta V}$$

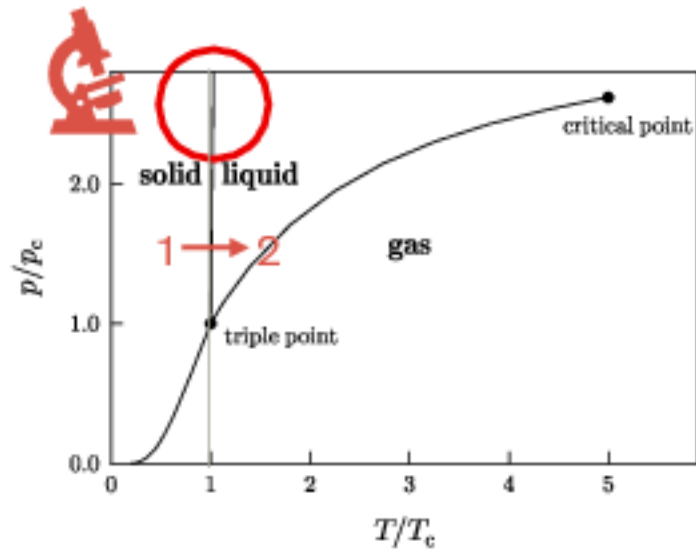
$$p = p_0 + \frac{L}{\Delta V} \ln\left(\frac{T}{T_0}\right)$$

$\Delta V$  is small and we thus have a steep change in pressure

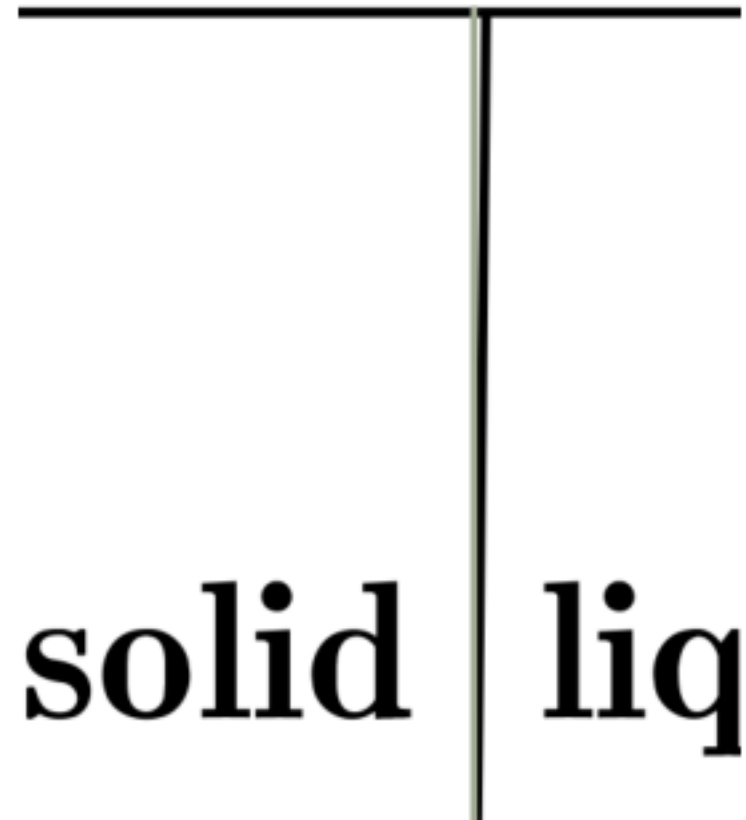


- The S-L phase boundary is **very steep** (large change in entropy and small change in volume)
- This phase boundary does not terminate, but continues indefinitely (no critical point!)
- Three phases coexist at the triple point
- At temperatures close to the triple point, the latent heat of sublimation (solid to gas) is the sum of the latent heat of melting (solid  $\rightarrow$  liquid) and the latent heat of vaporization (liquid  $\rightarrow$  gas)

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$



The gradient of the L-S coexistence line is usually positive because most substances **expand** as they melt.



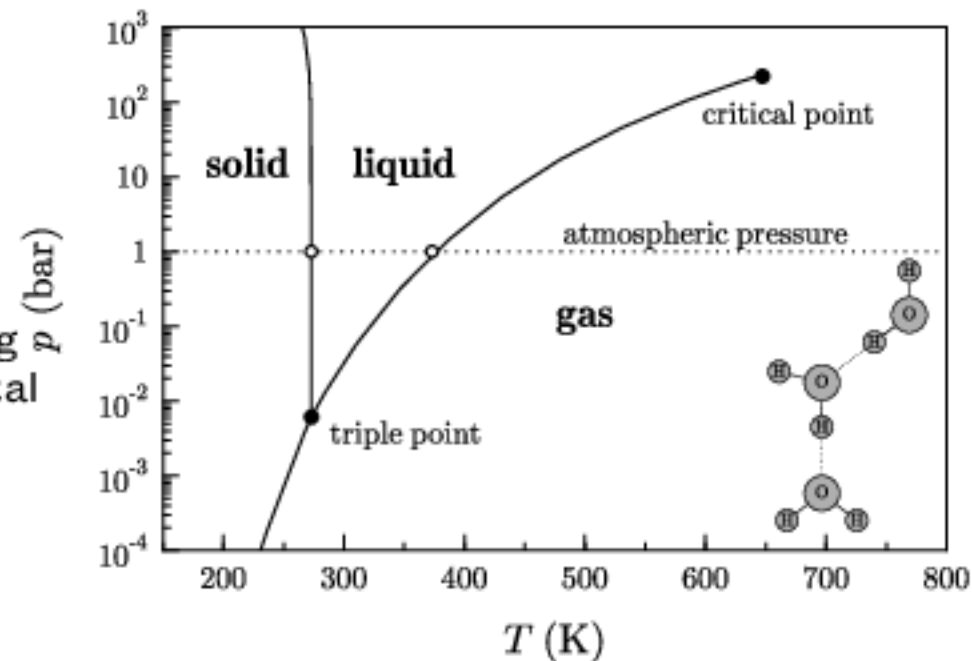
# Water

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

- **Water slightly shrinks when it melts.** The gradient of the ice-water coexistence line is negative.
- This effect occurs because of the hydrogen bonding in water leads to an open structure of the ice crystal lattice. This collapses on melting, resulting in a slightly denser liquid.

## Consequences:

- Icebergs float on the ocean.
- Lakes only freeze from the top, preserving life in the cool liquid beneath. Water close to 4°C has the largest density, this sinks in the oceans, imposing the temperature of the deep oceans and facilitating the survival of life in the oceans.
- Pressing ice can cause it to melt



# Stability and metastability

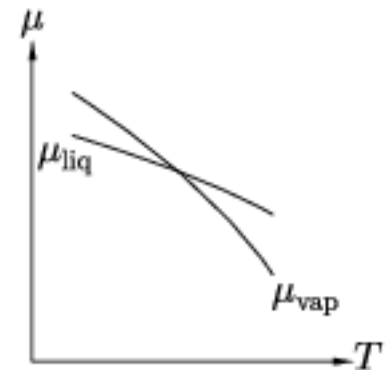
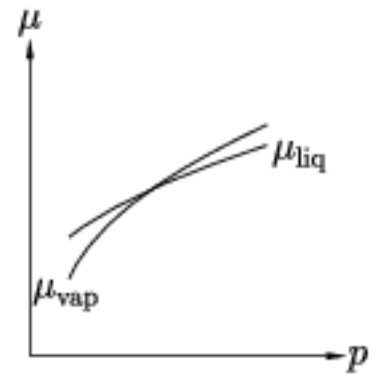
$$d\mu = -(S/N)dT + (V/N)dp$$

- Phase transition takes place towards lowest chemical potential
- We know that, on a per particle basis:  $\left(\frac{\partial\mu}{\partial p}\right)_T = v$

**Smallest volume is more stable at high pressure**

- We also know  $\left(\frac{\partial\mu}{\partial T}\right)_p = -s$ . (note:  $S$  positive)

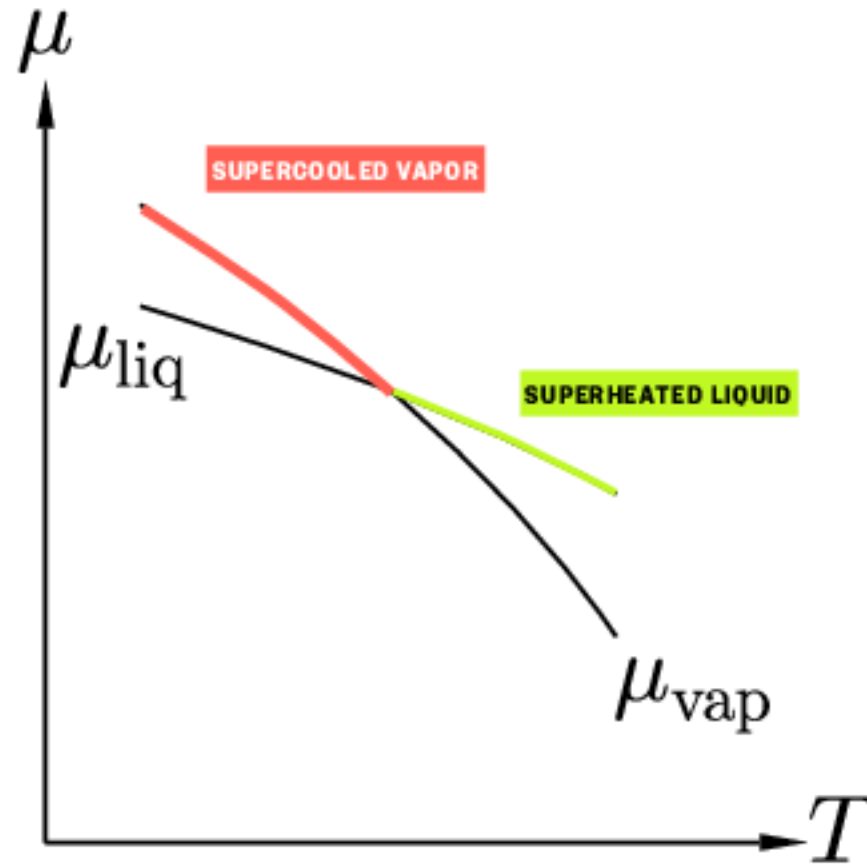
**At high  $T$ , the most stable has highest entropy**



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**Short-lived metastable states**

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



Why the thermodynamically most stable state sometimes does not form?  
We will look at the effect of droplet formation next, as an example

Imagine liquid at  $p_{\text{liq}}$  in equilibrium with a vapor at pressure  $p$ .

The chemical potential of liquid and vapor must remain equal when in equilibrium, if the pressure of the liquid increases, the pressure of the vapor increases as well



If we increase liquid pressure a bit, Imposing the chemical potentials to be equal leads to:

$$\left(\frac{\partial \mu_{\text{liq}}}{\partial p_{\text{liq}}}\right)_T dp_{\text{liq}} = \left(\frac{\partial \mu_{\text{vap}}}{\partial p}\right)_T dp$$

**Vapor pressure:** pressure in of vapor in equilibrium with the liquid (without excess pressure applied)

$$\longrightarrow v_{\text{liq}} dp_{\text{liq}} = v_{\text{vap}} dp \longrightarrow V_{\text{liq}} dp_{\text{liq}} = \frac{RT dp}{p} \quad (\text{Ideal gas})$$

$$p = p_0 \exp\left(\frac{V_{\text{liq}} \Delta p_{\text{liq}}}{RT}\right)$$

$\Delta p_{\text{liq}}$  is the extra pressure applied to the liquid and  $p_0$  is the vapor pressure of the gas

$$\text{Droplet: } \Delta p_{\text{liq}} = \frac{2\gamma}{r}$$

Lecture 17 for droplet of radius  $r$

$$p = p_0 \exp\left(\frac{2\gamma V_{\text{liq}}}{rRT}\right) \quad \text{Kelvin's formula}$$

**Vapor pressure of droplet of liquid**

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# Kelvin's formula

$$p = p_0 \exp\left(\frac{2\gamma V_{\text{liq}}}{rRT}\right)$$

- Small droplets have a very high vapor pressure
- The vapor sometimes doesn't condense when you cool it through the boiling temperature.
  - Small droplets initially begin to nucleate, but have a very high vapor pressure and therefore instead of growing can evaporate.
  - The thermodynamic driving force to condense is overcome by the tendency to evaporate.
- This effect occurs often in the atmosphere, which contains water vapor that has risen to an altitude where it is sufficiently cold to condense into water droplets, but the droplets cannot form owing to this tendency to evaporate.
- Clouds do form through the nucleation of droplets on minute dust particles, which have sufficient surface area for the liquid to condense and then grow above the critical size.

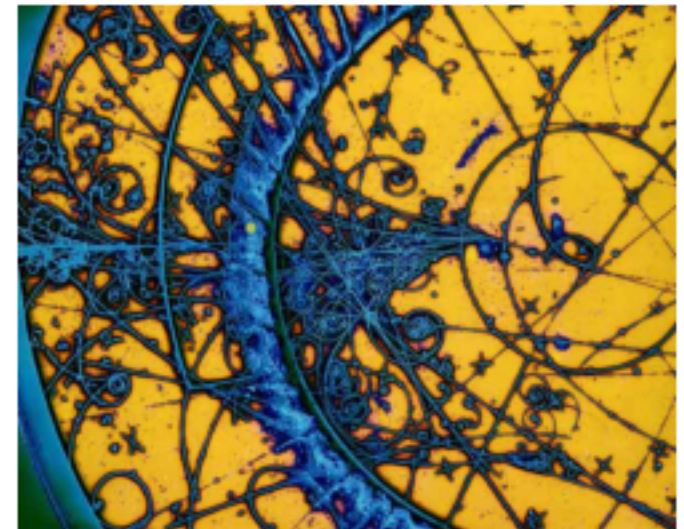


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# Similar effect in superheated liquid

- Vapor inside a cavity
- The vapor pressure in the cavity is lower than one might expect
- Bubbles of vapor (when we boil a liquid) tend to collapse and the liquid becomes superheated and kinetically stable above the boiling point
- The only bubbles that survive are the large ones

$$p = p_0 \exp\left(-\frac{2\gamma V_{\text{liq}}}{rRT}\right)$$



**Bubble chamber, CERN**

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# The Gibbs phase rule

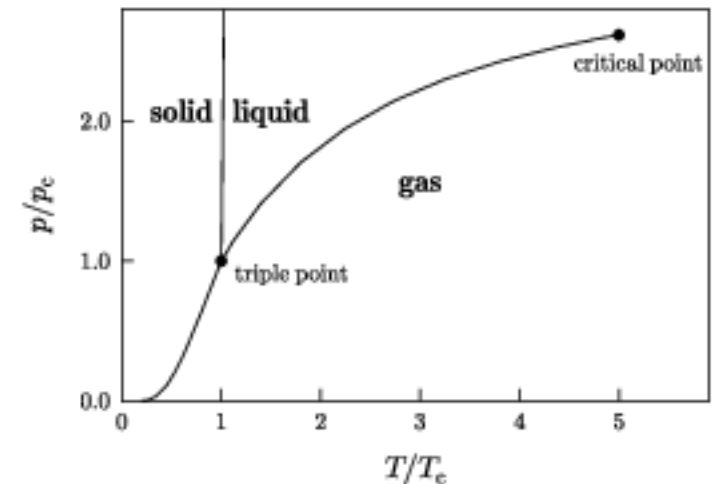
- **Component:** a chemically independent constituent of the system
- We use mole fraction  $x_i$  (ratio of number of moles)  $x_i = \frac{n_i}{n}$   $\sum x_i = 1$
- Each component can be in different phases
- $F$  degrees of freedom,  $P$  different phases, and  $C$  components
- **Intensive variables:**  $T, p$ , and mole fractions of the  $C - 1$  components.
  - Number of variables:  $2 + P(C - 1)$
- Total of  $C(P - 1)$  equations to solve  $\mu_i(\text{phase 1}) = \mu_i(\text{phase 2}) = \dots = \mu_i(\text{phase } P)$
- **Number of degrees of freedom,  $F$ ,** is thus:

$$F = C - P + 2$$

# Example of Gibbs phase rule: $C=1$

$$F = C - P + 2$$

- Single component, we have  $C=1$ , thus  $F = 3 - P$
- **One phase?** We have 2 degrees of freedom and the whole  $p - T$  plane is accessible
- **Two phases?**  $F = 1$ , the two phases can only coexist at a common line of coexistence in the  $p - T$  plane
- **Three phases?**  $F = 0$ , and the three phases can only coexist at a common point in the  $p - T$  plane (the triple point)



---

# Example of Gibbs phase rule: $C=2$

$$\underline{F = C - P + 2}$$

- Two components, we have  $C = 2$ , thus  $F = 4 - P$
- If we fix the pressure, the number of degrees of freedom left :  $3 - P$ ; we have two variables:  $T$  and the mole fraction of the first component ( $x_1$ )
- For 2 components, we thus have:
  - **One phase**,  $F = 2$ , the whole plane  $x_1 - T$  is accessible
  - **Two phases**,  $F = 1$ , the two phases can only coexist at a common line of co-existence
  - **Three phases**:  $F = 0$ , the three phases coexist at a single common point of co-existence.

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# Entropy of mixture: colligative properties

Adding a small quantity of solute to a solvent increases the entropy of the solvent

There is a weaker tendency to form a gas (this would increase entropy but the entropy is already increased)

**Therefore, the boiling point is increased**

**Likewise, increase in entropy in a liquid, opposes the tendency to freeze**

$$T - T^* = K_b x_B$$

**Ebullioscopic constant**

$$T^* - T = K_f x_B$$

**Cryoscopic constant**

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# Classification of phase transition

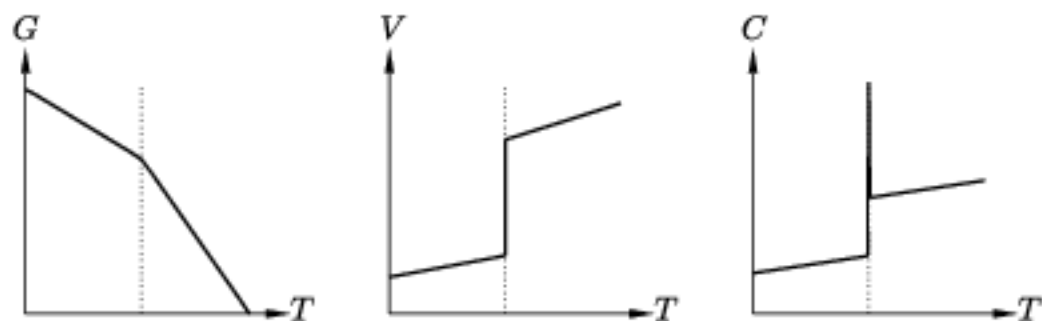
Paul Ehrenfest proposed a classification of phase transitions:

- **The order of a phase transition is the order of the lowest differential of  $G$  (or  $\mu$ ) that shows a discontinuity at  $T_c$** 
  - First-order phase transitions involve a latent heat because the entropy (a first differential of  $G$ ) shows a discontinuity.
  - The volume is also a first differential of  $G$  and this also shows a discontinuous jump.
  - The heat capacity is a second differential of  $G$  and thus it shows a sharp spike, as does the compressibility.
- Examples of first-order phase transitions include the solid-liquid transition, the solid-vapor transition, and the liquid-vapor transition.

$$S = - \left( \frac{\partial G}{\partial T} \right)_p$$

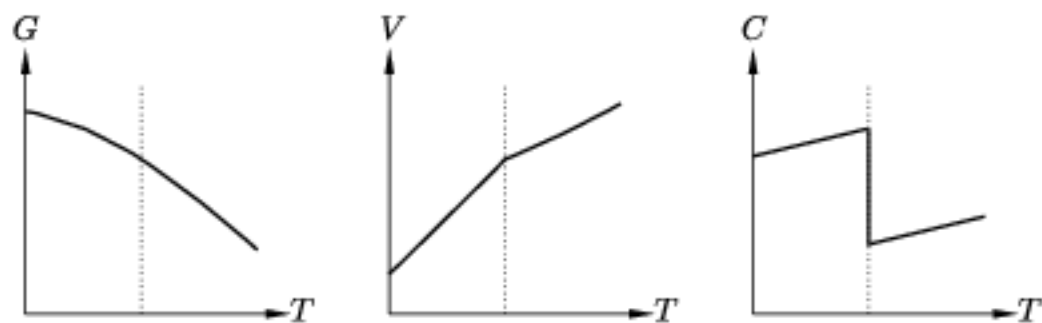
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### First order



$$S = - \left( \frac{\partial G}{\partial T} \right)_p$$

### Second order



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# Examples

- The liquid-gas phase transition is a first-order transition, except at the critical point where the phase transition involves no latent heat and is a continuous phase transition.
- A ferromagnet such as iron loses its ferromagnetism when heated to the Curie temperature,  $T_C$  (a particular example of a critical temperature).
  - This phase transition is a continuous phase transition, since there is no latent heat.
  - The magnetization is a first differential of the Gibbs function and does not change discontinuously at  $T_C$ . The specific heat  $C_B$ , at constant magnetic field  $B$ , has a finite peak at  $T_C$ .



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# Effect of fluctuations

- One key approximation made in thermodynamics is that the number of particles is so large that average properties such as pressure and density are well defined.
- This breaks down at a phase transition
- **Fluctuations build up near a phase transition and the behavior of the system does not follow the expectations of our analysis very close to the phase transition temperature**

For example, when a saucepan of water is heated, the water warms quite quietly and unobtrusively until near the boiling point, when it makes a great deal of noise and bubbles violently.

*A more modern approach to classifying phase transitions simply distinguishes between those that show a latent heat (like Ehrenfest's term "first-order phase transition" in contrast to those with a continuous phase transition (and include Ehrenfest's phase transitions of second order, third order, fourth order, etc., all lumped together).*

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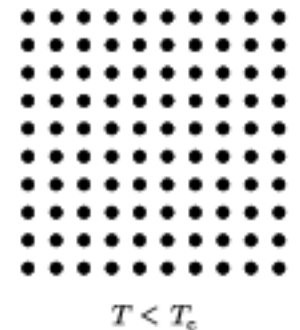
# Symmetry breaking

The figure shows atoms in a liquid and in a solid. As a liquid cools there is a very slight contraction of the system but it retains a very high degree of symmetry. However, below the melting temperature, the liquid becomes a solid and that symmetry is broken.

This may at first sight seem surprising because the picture of the solid "looks" more symmetrical than that of the liquid. The atoms in the solid are all symmetrically lined up while in the liquid they are all over the place.

Any point in a liquid is, on average, exactly the same as any other. If you average the system over time, each position is visited by atoms as often as any other. There are no unique directions or axes along which atoms line up. In the solid, however, this high degree of symmetry is nearly all lost. The solid still possesses some residual symmetry.

Therefore not all symmetry has been lost but the high symmetry of the liquid state has been *broken*. **It is impossible to change symmetry gradually.** Either a particular symmetry is present or it is not. Hence, phase transitions are sharp and there is a clear delineation between the ordered and disordered states.



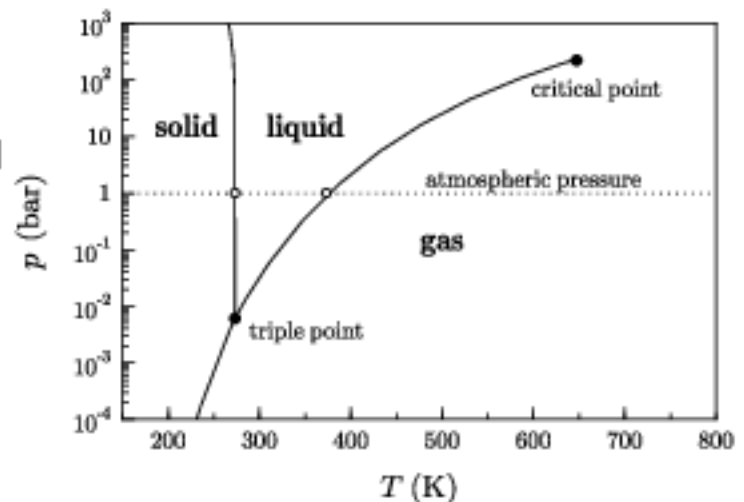
# Not all phase transitions involve a change of symmetry

The boundary line between the liquid and gas regions is terminated by a critical point.

It is possible to "cheat" the sharp phase transition by taking a path through the phase diagram that avoids a discontinuous change. For temperatures above the critical temperature the gaseous and liquid states are distinguished only by their density.

The transition between a gas and a liquid involves no change of symmetry and therefore it is possible to avoid it by working round the critical end point.

In contrast, the solid-liquid transition involves a change of symmetry and consequently there is no critical point for the melting curve.



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## Other examples of symmetry breaking during phase transition

Symmetry-breaking phase transitions include

- those between the ferromagnetic and paramagnetic states (in which the low-temperature state does not possess the rotational symmetries of the high-temperature state)
- those between the superconducting and normal metal states of certain materials (in which the low-temperature state does not possess the same symmetry in the phase of the wavefunction as the high-temperature state).

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# More about broken symmetry

The concept of broken symmetry is very wide ranging and is used to explain how the electromagnetic and weak forces originated.

In the early Universe, when the temperature was very high, it is believed that the electromagnetic and weak forces were part of the same, unified, electroweak force. When the temperature cooled to below about  $10^{11}$  eV a symmetry was broken and a phase transition occurred, via what is known as the Higgs mechanism, and the W and Z bosons (mediating the weak force) acquired mass while the photon (mediating the electromagnetic force) remained massless.

At even earlier times, when the temperature of the Universe was around  $10^{21}$  eV, the electroweak and strong forces were unified, and as the Universe expanded and its temperature lowered, another symmetry-breaking transition caused them to appear as different forces.

# Summary

- The latent heat is related to the change in entropy at a first-order phase transition.
- The Clausius-Clapeyron equation can be used to determine the shape of the phase boundary. 
$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$
- The Kelvin formula states that the pressure in a droplet is given by
- The Gibbs phase rule states that
- Dissolving a solute in a solvent results in the elevation of the solvent's boiling point and a depression of its freezing point.
- A first-order phase transition involves a latent heat while a continuous phase transition does not.
- Certain phase transitions involve the breaking of symmetry.