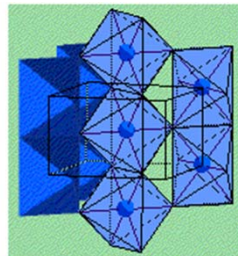
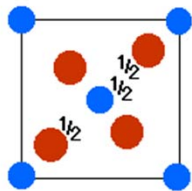
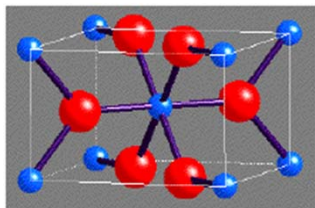
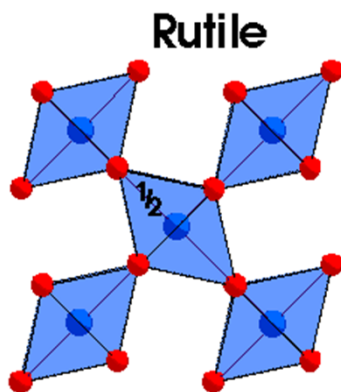


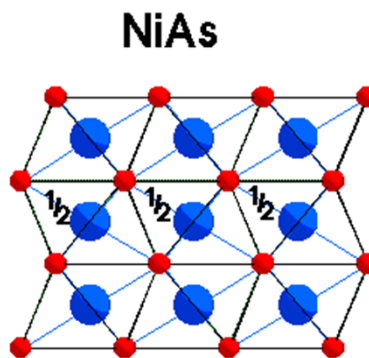
Oxide Structures & Networks



- **Unit Cell:** Primitive Tetragonal ($a = b \neq c$)
- **2TiO₂** per unit cell
- **Motif:** 2Ti at $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ & 4O at $\pm(0.3, 0.3, 0)$; $\pm(0.8, 0.2, \frac{1}{2})$
- **Ti:** 6 (octahedral coordination)
- **O:** 3 (trigonal planar coordination)
- **TiO₆** octahedra share edges in chains along c
- **Edge-sharing Chains** are linked by vertices
- **Examples:**
 - oxides: MO₂ (e.g. Ti, Nb, Cr, Mo, Ge, Pb, Sn)
 - fluorides: MF₂ (e.g. Mn, Fe, Co, Ni, Cu, Zn, Pd)



vs



i.e. Rutile is distorted hcp O with Ti in $\frac{1}{2}$ Octahedral holes.

Anatase: ccp version

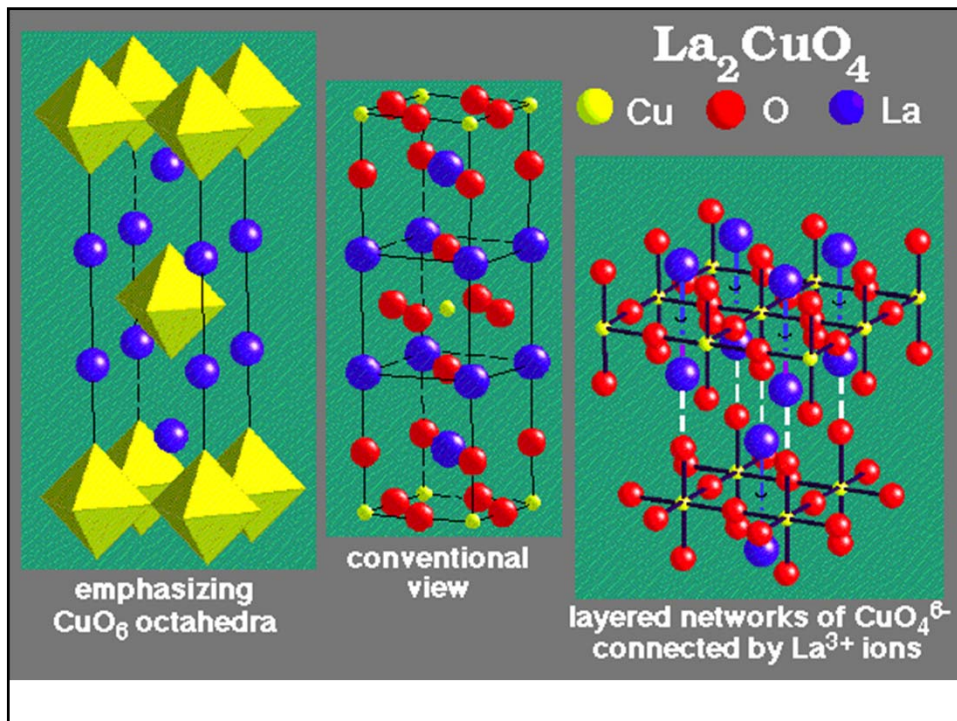
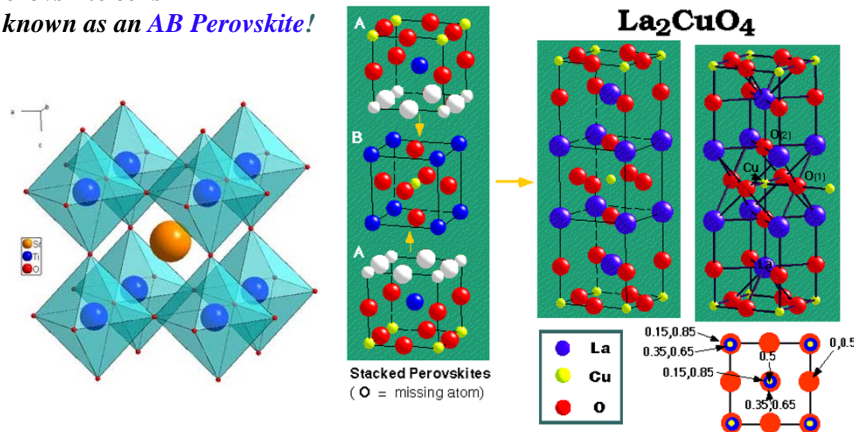
La_2CuO_4 { K_2NiF_4 structure}

Doped La_2CuO_4 was the first (1986) High- T_c Superconducting Oxide ($T_c \sim 40$ K)

Bednorz & Müller were awarded a Nobel Prize

La_2CuO_4 may be viewed as if constructed from an ABAB... arrangement of Perovskite cells

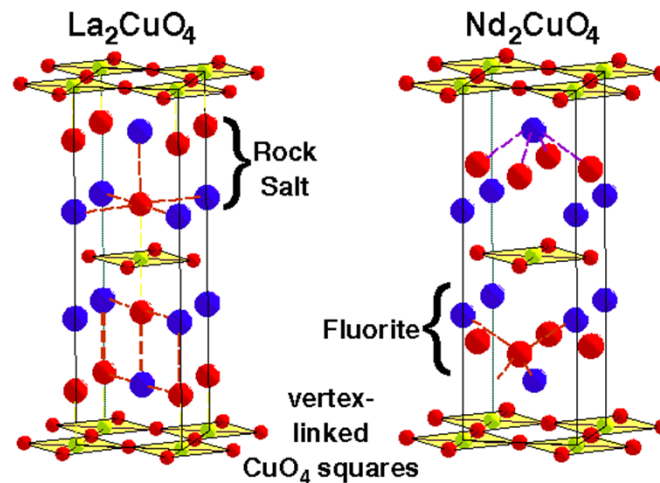
- known as an *AB Perovskite*!



We may view the structure as based on:

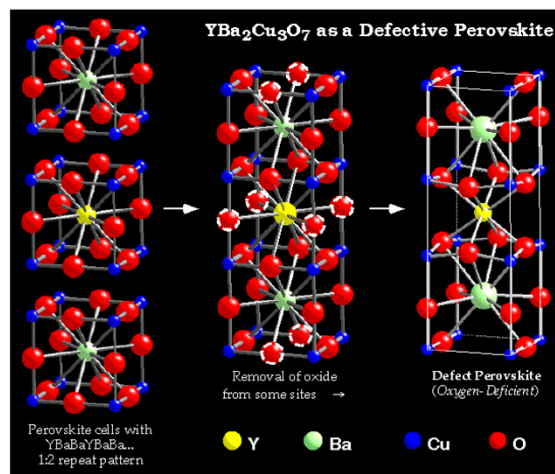
1. Sheets of elongated CuO_6 octahedra, sharing only vertices
2. Layered networks of CuO_4^{6-} , connected only by La^{3+} ions

Comparison of La_2CuO_4 with the related Nd_2CuO_4



- Common structural motif of **vertex-linked CuO_4 squares**.
- This motif occurs in all the high temperature superconducting copper oxides.
- The structures differ in the structure of the 'filling' in the 'sandwich' of copper oxide layers - known as **Intergrowth Structures**.

• $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be viewed as an **Oxygen-Deficient Perovskite**.

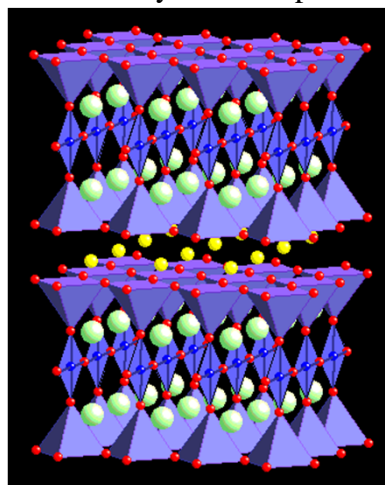


- Two types of Cu site

Layers of CuO_5 square pyramids (elongation \Rightarrow essentially *vertex-linked CuO_4 squares* again)

Chains of vertex-linked CuO_4 squares

These are indicated in a Polyhedral Representation



CuO_2

BaO

CuO

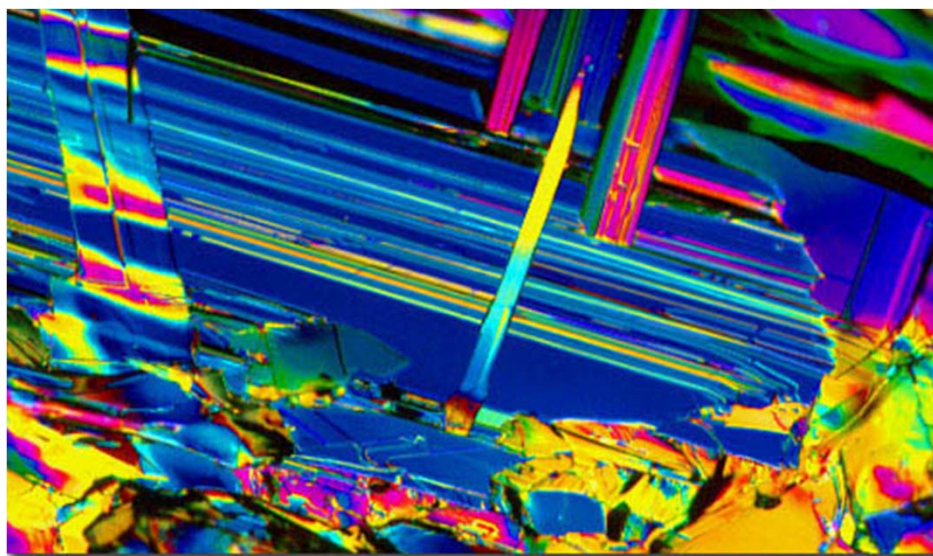
BaO

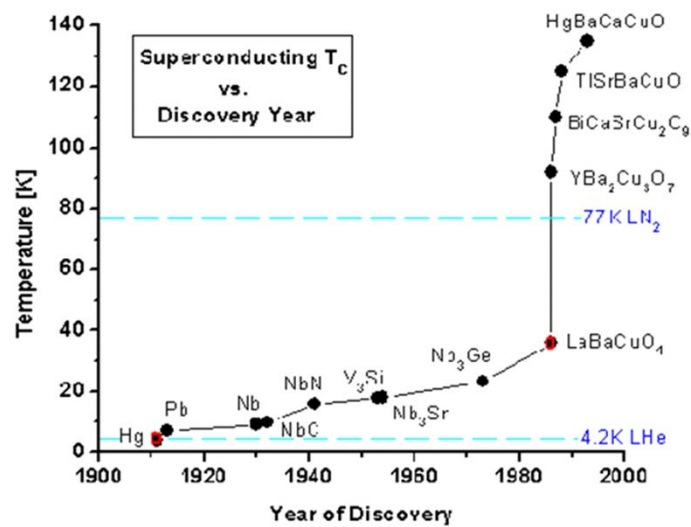
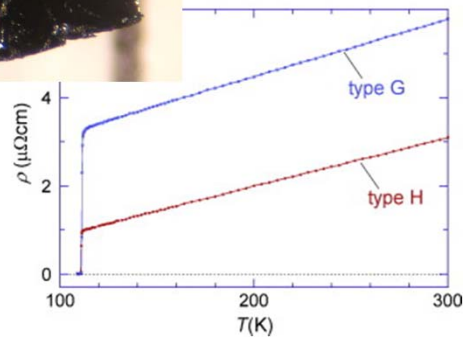
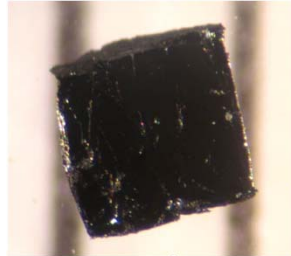
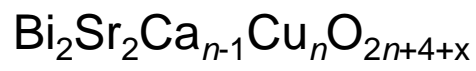
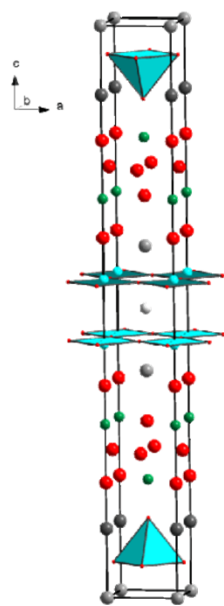
CuO_2

Y

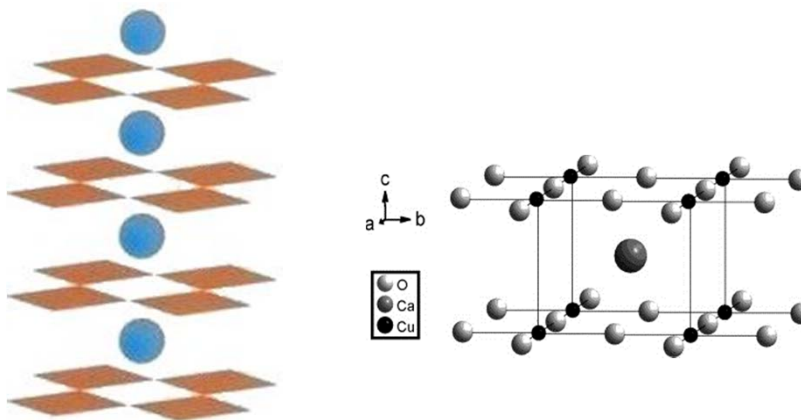
CuO_2

Chem 253, UC, Berkeley ● ● ●





Infinite-layer-structure oxide: SrCuO_2



Phase Diagram

- Also called equilibrium or constitutional diagram
- Represent the relationships between temperature and composition and quantities of phase at equilibrium
- Pressure also influences phase structure
 - Remains virtually constant in most applications
 - Most phase diagrams at 1 atm

Phases

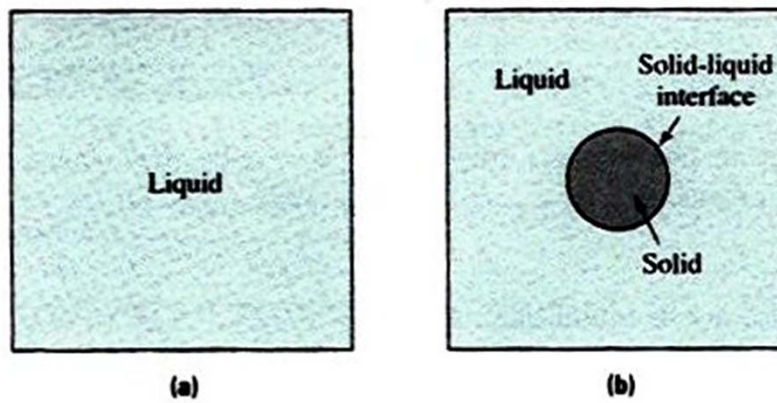
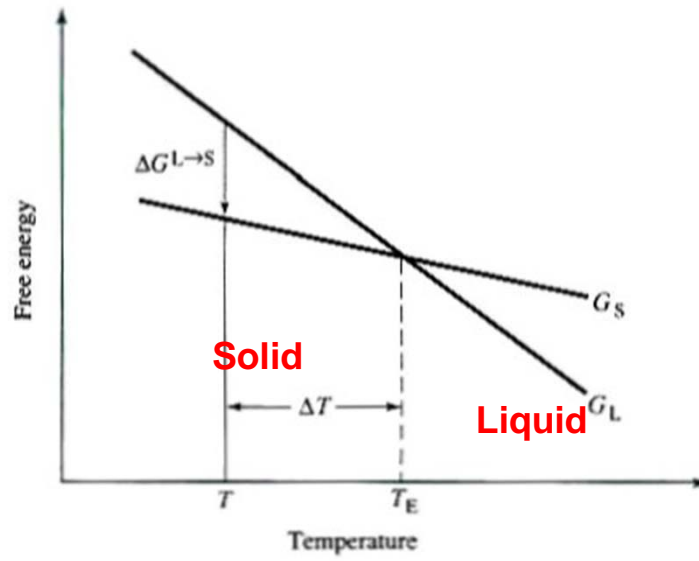
- Homogeneous portion of the system with uniform physical and chemical characteristics
 - Salt – water
 - Salt NaCl
- A difference in either physical or chemical properties constitutes a phase
 - Water and ice
 - FCC and BCC polymorphic forms of an element

Phase Equilibria

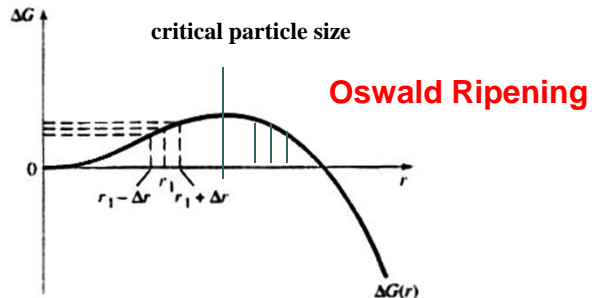
- Free energy
 - Function of internal energy and randomness
 - Equilibrium → free energy is at a minimum under some specified combination of temperature, pressure, and composition
 - spontaneous change to lower energy state
$$\Delta G = \Delta H - T \Delta S$$
- Reaction occurs only if it results in a reduction in total energy of the system

Driving Force for Phase Changes

- Depends on change in free energy
- If free energy of solid < free energy of liquid at a particular temperature, solid forms, or vice versa
- Both may coexist at T_E as they have the same free energy ($G_L = G_S$)



Crystal Nucleation and Growth

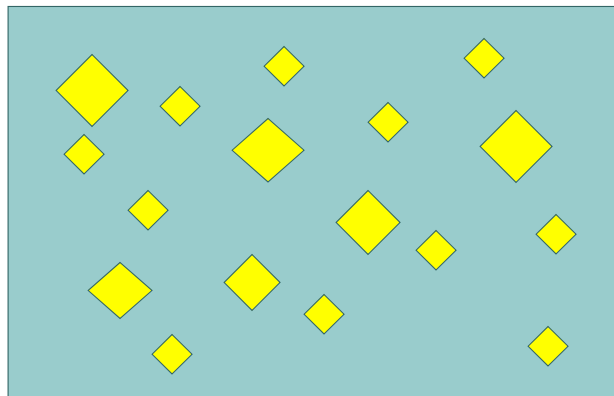


All particles with $r < r^$ are unstable. For a particle of size r_1 to grow an amount Δr represents an increase in Free energy, not a spontaneous process.*

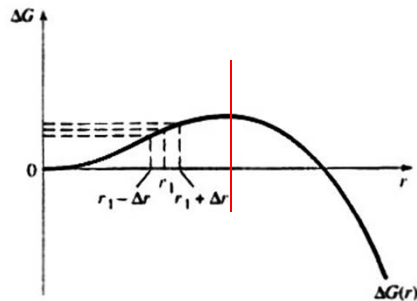
The spontaneous process would be the dissolution of a particle of radius r_p , which lower the energy (subcritical nuclei).

$R = r^*$ is a critical particle size since either growth or dissolution decreases the free energy. Beyond r^* , only growth reduces free energy.

Oswald Ripening



Critical size of nuclei



ΔG_v The free energy per unit volume of the Nucleus relative to the parent phase

ΔG_s The surface free energy per unit area of the nucleus.

$$\Delta G_n = 4\pi r^2 \Delta G_s - \frac{4}{3}\pi r^3 \Delta G_v$$

$$\frac{d\Delta G}{dr} = 8\pi r \Delta G_s - 4\pi r^2 \Delta G_v$$

$$r_c = \frac{2\Delta G_s}{\Delta G_v}$$

$$\Delta G_c = \frac{16}{3} \frac{\pi \Delta G_s^3}{\Delta G_v^2}$$

Nucleation is difficult at temperature close to T_E

Phase Rule

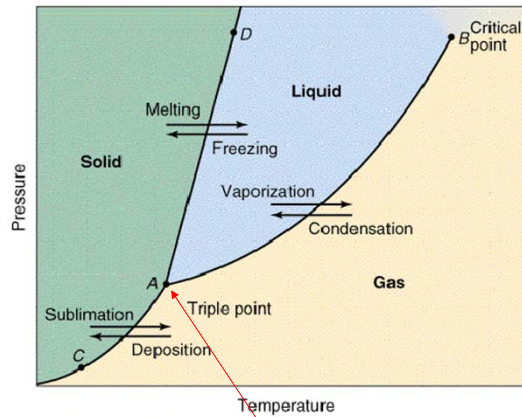
$$P + F = C + 2$$

P: number of phases present in equilibrium

C: number of components need to describe the system

F: number of degrees of freedom, e.g. T, P, composition

One component phase diagram



Largest number of phases that can occur at equilibrium:

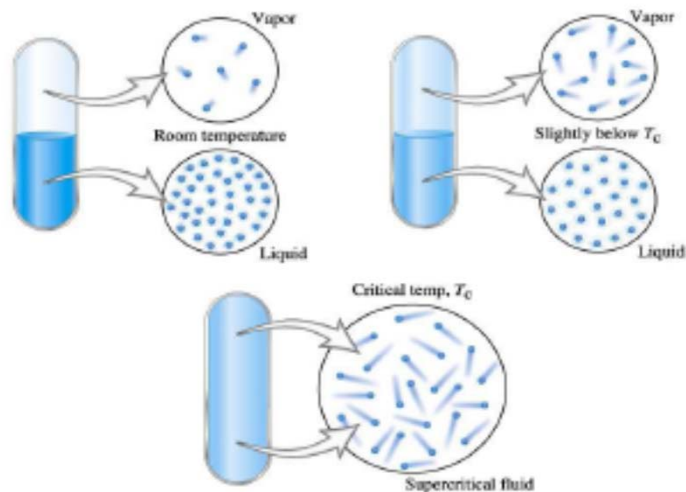
$$P + 0 = 1 + 2 = 3$$

Two phase: (lines)

One phase region.

Critical Temperature

Critical Temperature, T_c



Supercritical fluid

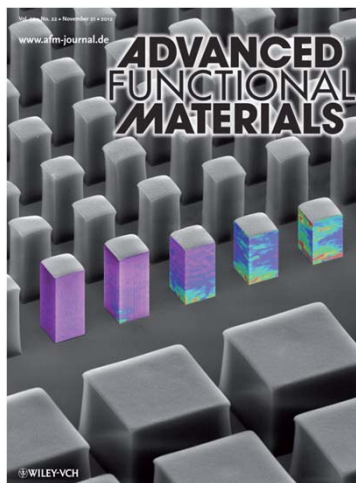
A **supercritical fluid** is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid.

| Solvent | Molecular weight g/mol | Critical temperature K | Critical pressure Mpa (atm) | Critical density g/cm ³ |
|-----------------------------------|---------------------------|---------------------------|--------------------------------|---------------------------------------|
| Carbon dioxide (CO ₂) | 44.01 | 304.1 | 7.38 (72.8) | 0.469 |
| Water (H ₂ O) | 18.015 | 647.096 | 22.064 (217.755) | 0.322 |

Supercritical fluid

- There is no surface tension in a supercritical fluid, as there is no liquid/gas phase boundary.
- Supercritical drying is a method of removing solvent without surface tension effects. As a liquid dries, the surface tension drags on small structures within a solid, causing distortion and shrinkage. Under supercritical conditions there is no surface tension, and the supercritical fluid can be removed without distortion. Supercritical drying is used for manufacture of aerogels.

Supercritical drying



Example: a system of boiling water

$$P + F = C + 2$$

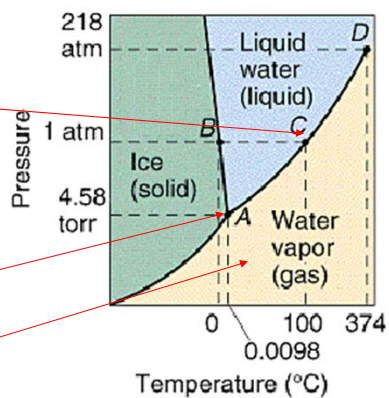
$C=1$ (water)

$P=2$ (Vapor + Liquid)

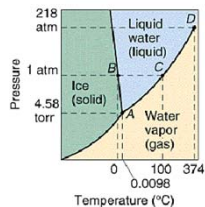
$F=1$ (either T or P,
but not both)

$F=0$

$F=2$



Clausius-Clapeyron Equation



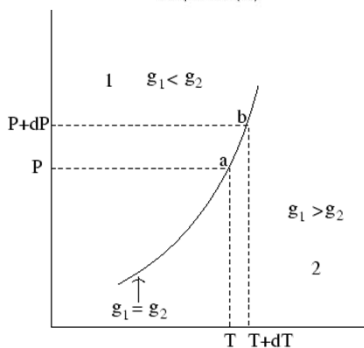
From a to b:

$$dg_1 = -s_1 dT + v_1 dP$$

$$dg_2 = -s_2 dT + v_2 dP$$

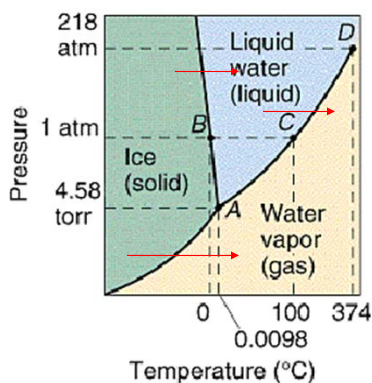
$$dg_1 = dg_2$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \quad \Delta S = \frac{\Delta H}{T}$$



$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

One component phase diagram



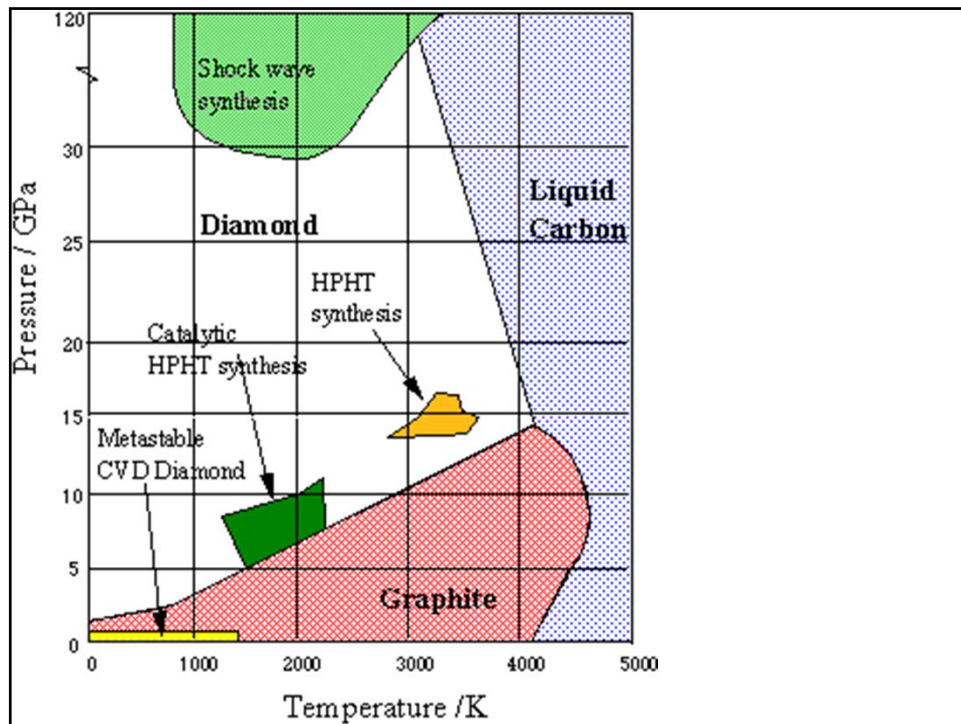
Slope of the phase-boundary
Curves:

Clausius-Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

ΔH always positive

ΔV

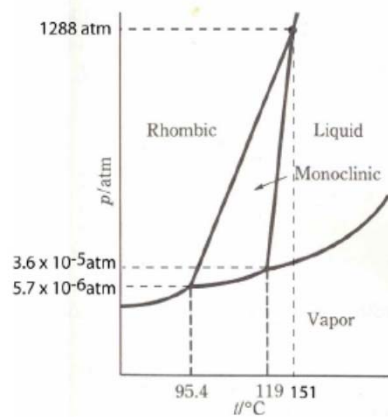


Chem 253, UC, Berkeley ● ● ●

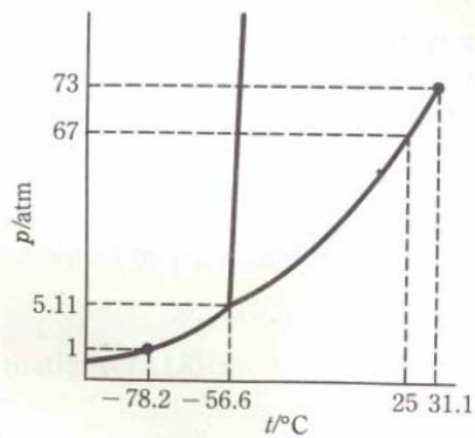
More than 100 tons of the stones is produced annually worldwide by firms like Diamond Innovations (previously part of General Electric), Sumitomo Electric, and De Beers.



Gemesis, GE, Sumitomo Electric, and De Beers



Sulfur



CO_2