MSE-204 Thermodynamics for Materials Science

L7.2 Single Component Phase Diagrams

Thermodynamic Properties at Phase Transitions | First Order Phase Transitions | Critical Points

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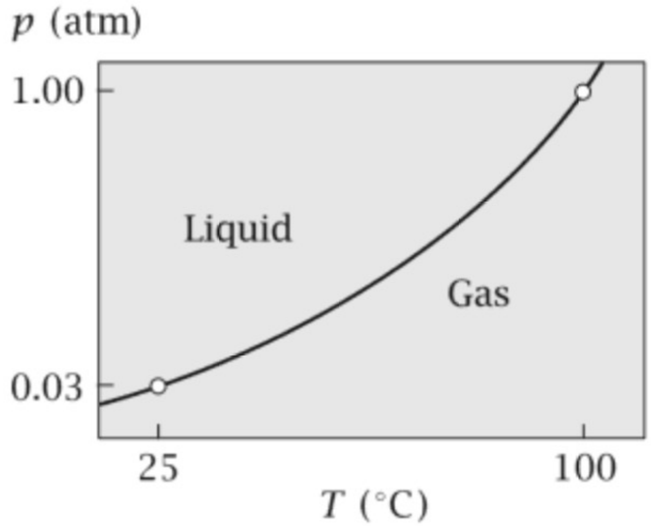
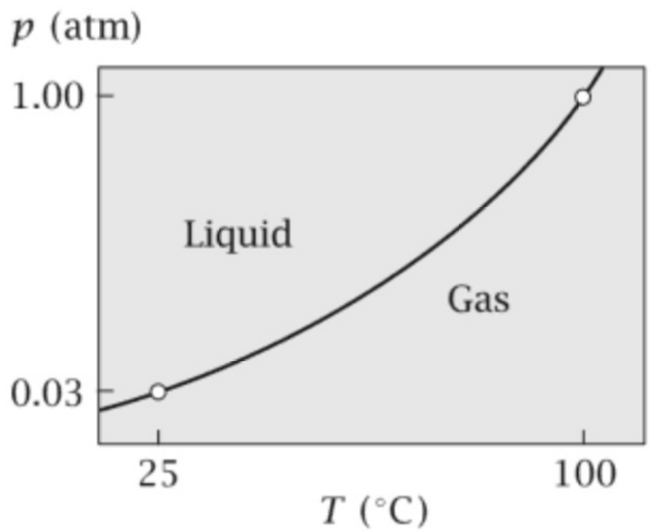
REMINDER FROM LAST TIME

EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE

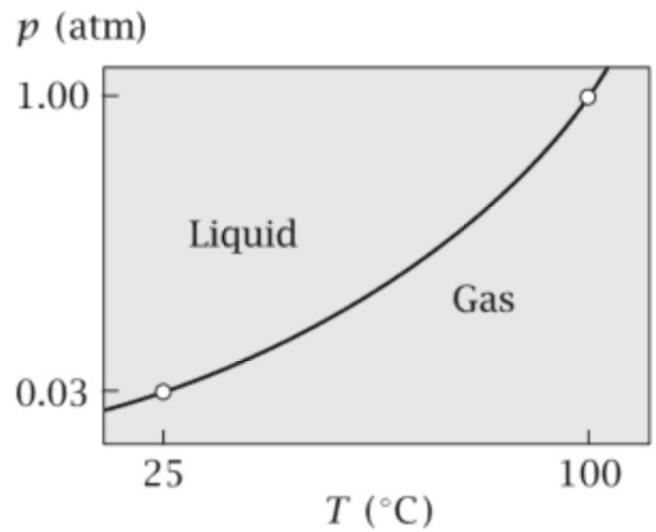
Each line on a phase diagram (also called a phase boundary) represents a set of (p,T) points at which two phases are equally stable. We can mathematically calculate these coexistence lines and then we can construct a phase diagram.



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAPEYRON EQUATION | CONTINUED

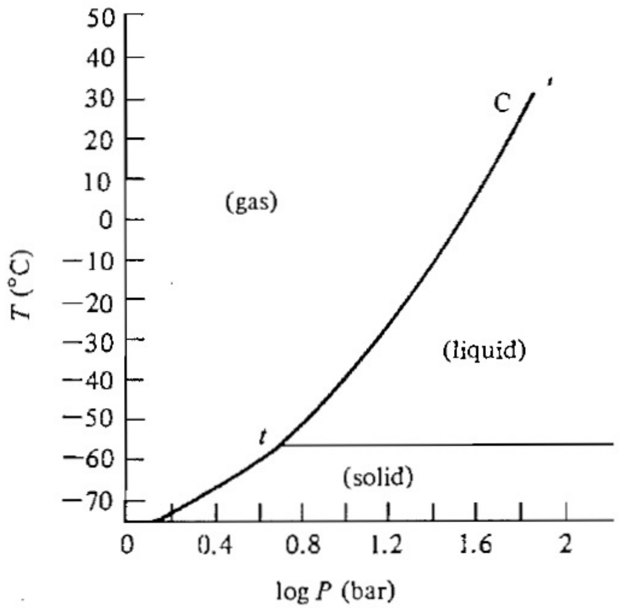


EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAUSIUS CLAPEYRON EQUATION | CONTINUED

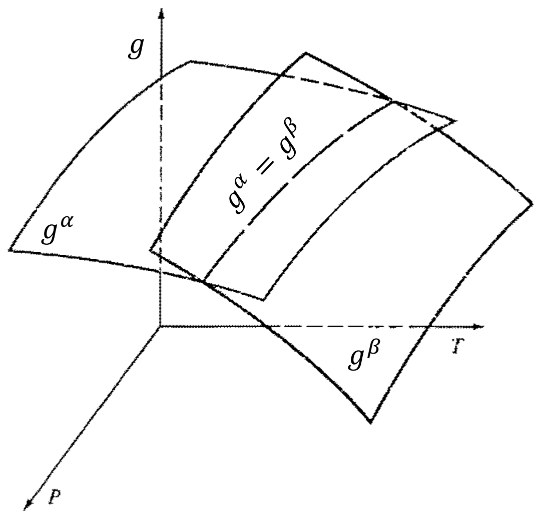


CONSTRUCTION OF A PHASE DIAGRAM OF A PURE SUBSTANCE

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.



Pressure – Temperature phase diagram for CO_2



Terminology

solid → gas: sublimation
gas → solid: deposition

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

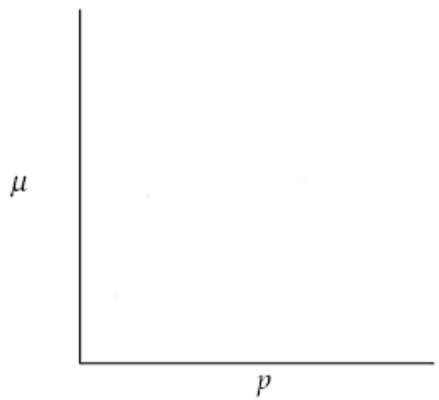
liquid → gas: vaporization
gas → liquid: condensation

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

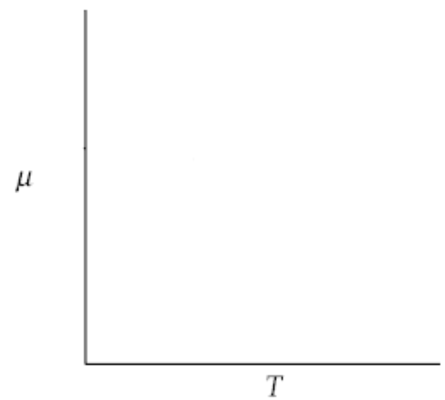
Simple kinds of phase change, such as melting and vaporization, are characterized by considerable changes in volume, and also of entropy and enthalpy, at the point of transition. The chemical potential of the phases are equal at equilibrium, however, their volumes, entropies, and enthalpies are far from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

Simplest case: for a pure substance with two phases

transition at constant T



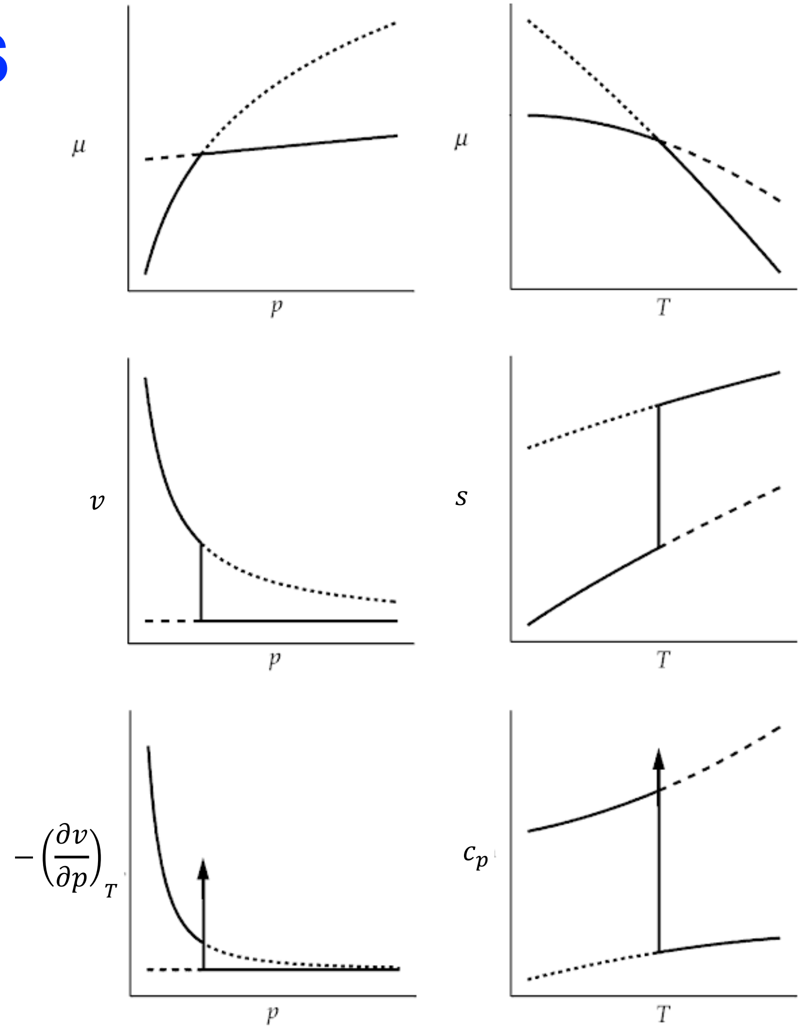
transition at constant p



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

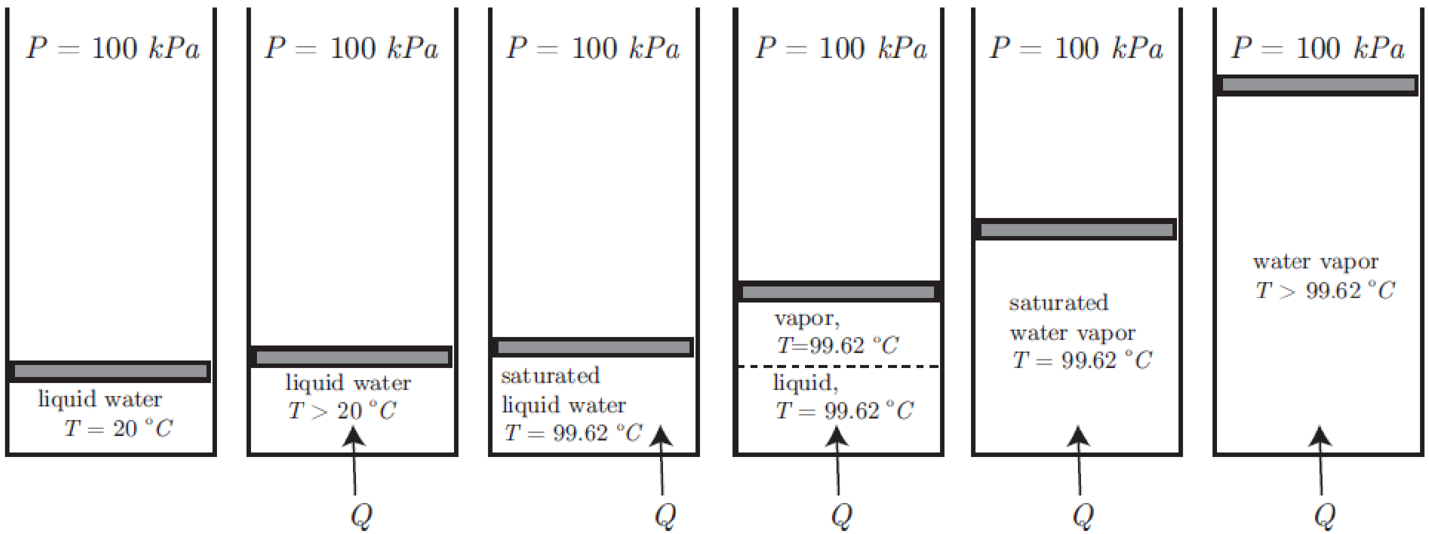
As a consequence, the observable physical properties of the material provide no information that a change of a rather drastic nature is about to happen.



HEAT AS A FUNCTION OF TEMPERATURE: THE BOILING OF WATER

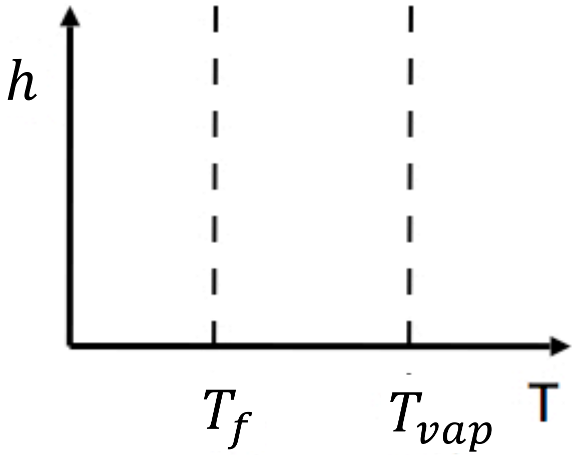
Let us consider a piston-cylinder arrangement for the boiling of water. Inside the cylinder, we begin with pure liquid water at T = 20ºC. The piston is free to move in the cylinder, but it is tightly sealed, so no water can escape. On the other side of the piston is a constant pressure atmosphere, which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

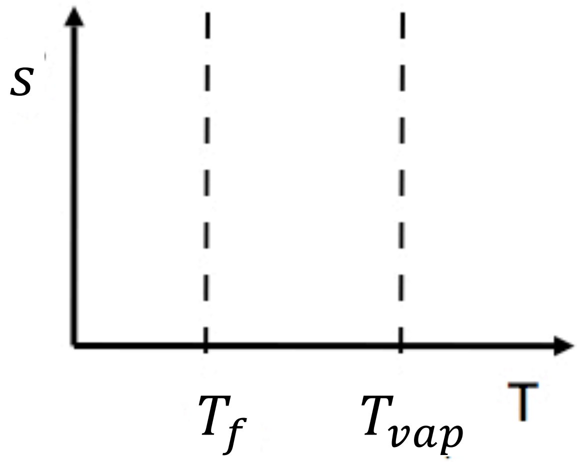
We slowly add heat to the cylinder, and observe a variety of interesting phenomena.

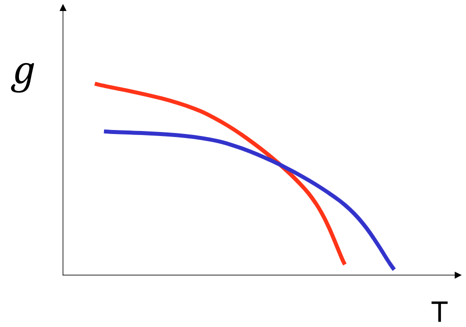


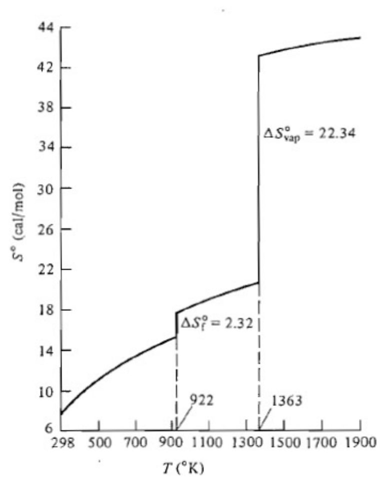
Molar Enthalpy and Entropy at the Phase Transition

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.





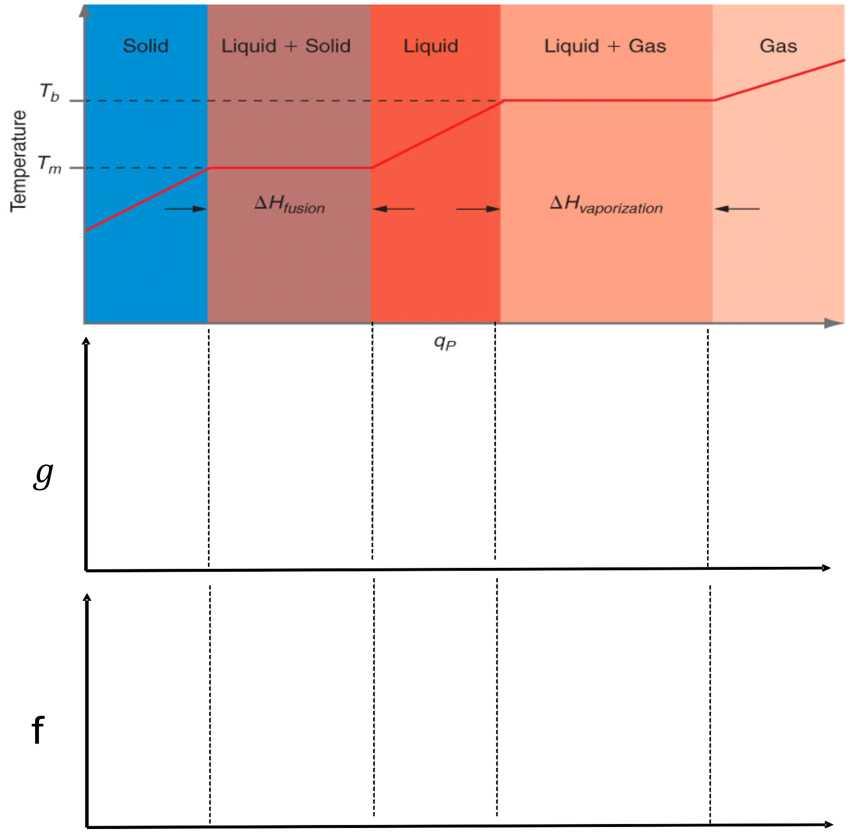




Temperature dependence of the entropy of magnesium at 1 atm.

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.



HEAT CAPACITIES OF TWO PHASES IN EQUILIBRIUM

Consider two phases of a single component in equilibrium. Suppose we move along the line of the coexistence of phases. The quantity of heat absorbed will be proportional to dT. For either of the two phases, we will have:

$$\delta q = C_{eq} dT$$

Where C_{eq} is the heat capacity at the two-phase equilibrium. The change is reversible, and therefore:

$$ds = \frac{c_{eq} dT}{T}$$

Heat Capacities of a Liquid and a Gas Phase in Equilibrium (Saturation)

Let's now see what the previous formula means for an equilibrium between a liquid phase and its vapor. The quantities c_{eq} are then called the molar heat capacities at saturation and are denoted c_{sat}. If we neglect the volume of the liquid compared to the gas, we have:

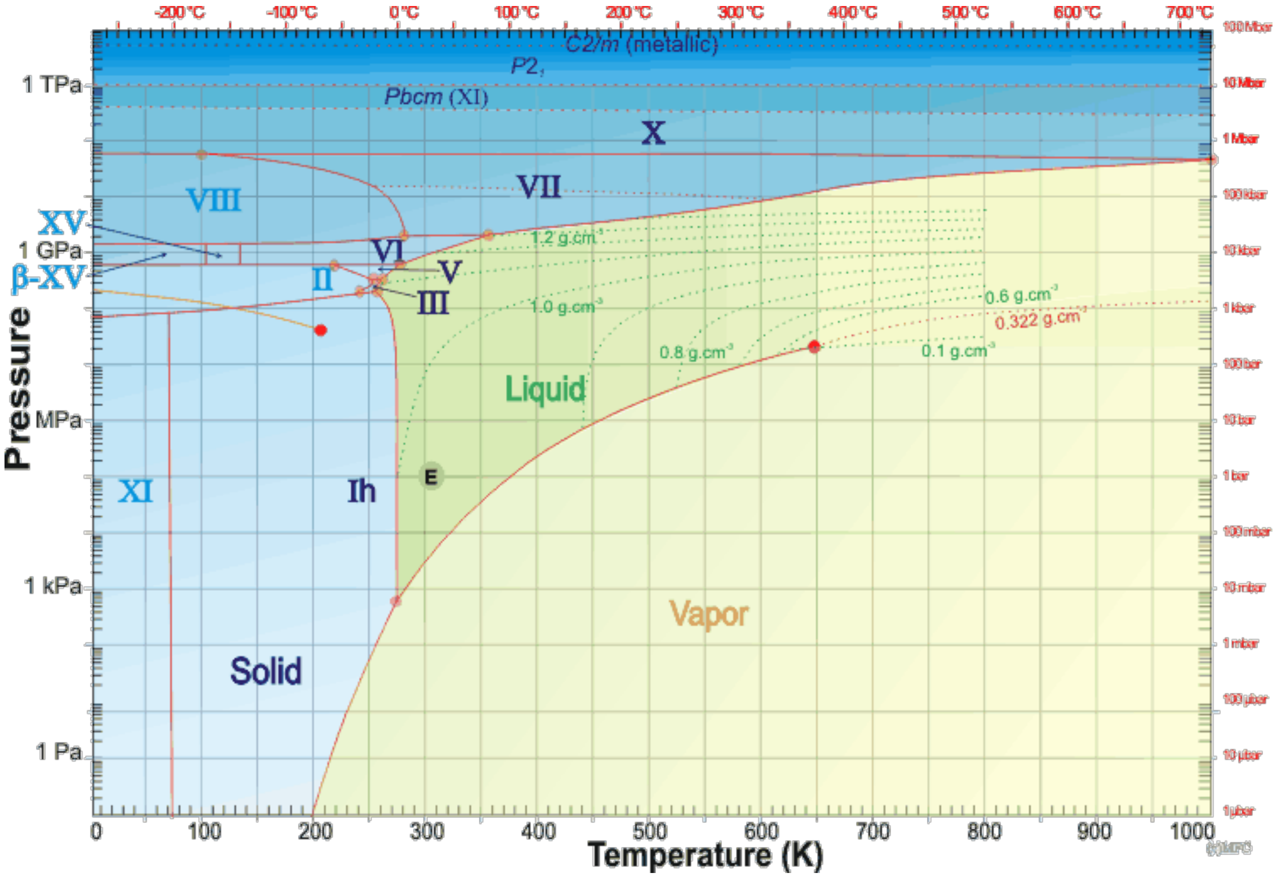
$$c_{sat} = c_p - \alpha \Delta h_{vap} \frac{pv}{RT}$$

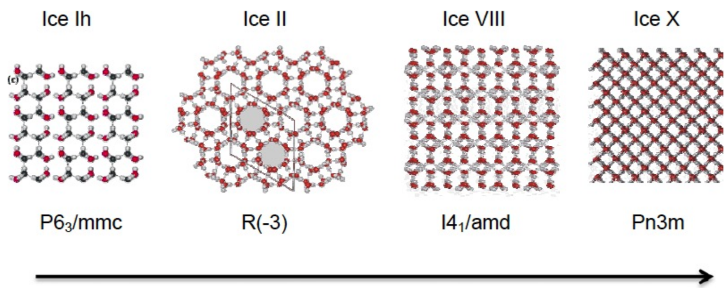
This equation is applicable to both gas and liquid.

For the gas, we have:

For the liquid, we have:

EXAMPLE OF SINGLE COMPONENT PHASE DIAGRAM: H_2O

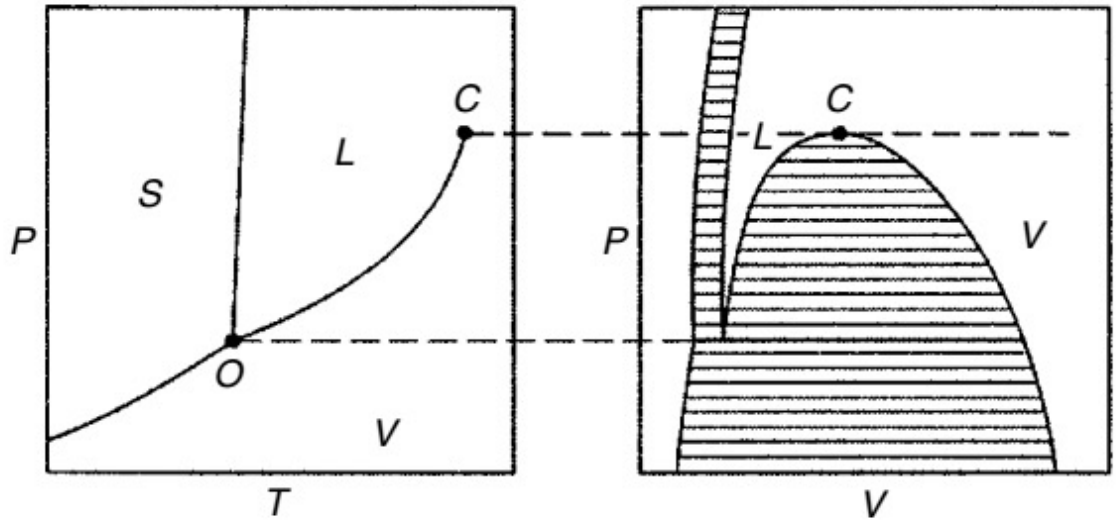




ALTERNATIVE REPRESENTATIONS OF SINGLE COMPONENT PHASE DIAGRAMS

The two phase coexistence in a p, T diagram is a line (i.e., a region of zero width) because the pressure and temperature of the alpha phase in the two phase system is required to be the same as that of the beta phase. The corresponding states of the two equilibrated phases are represented by the same point in the p,T space. Thus the phase boundaries for the alpha phase, and that for the beta phase, coincide.

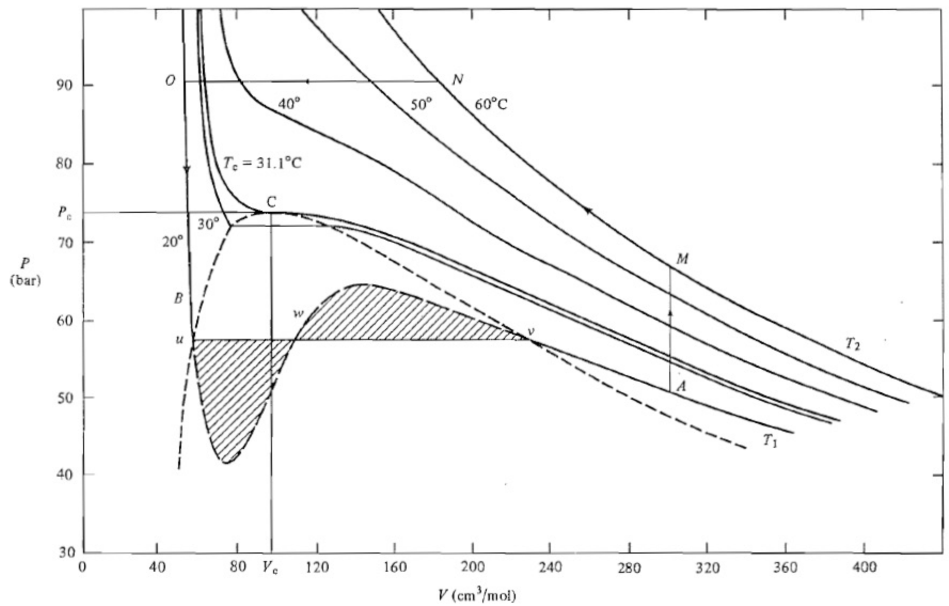
This will not be true of some property other than p or T is used in the description of the state of the two phases. Suppose the properties of the participating phases are described in terms of their pressure, P; and molar volume, v. While the conditions for equilibrium require the pressure to be the same in both phases, the molar volumes will not, in general, be the same. The resulting plot of the phase relationships is very different in appearance from the simple p,T.



CRITICAL POINTS

Under certain conditions of temperature and pressure, the liquid and gas phases are indistinguishable.

Moreover, even under ordinary conditions where they are quite distinguishable, it is possible to pass from one to another by processes in which the substance remains perfectly homogeneous.



Pressure – Volume phase diagram for CO_2

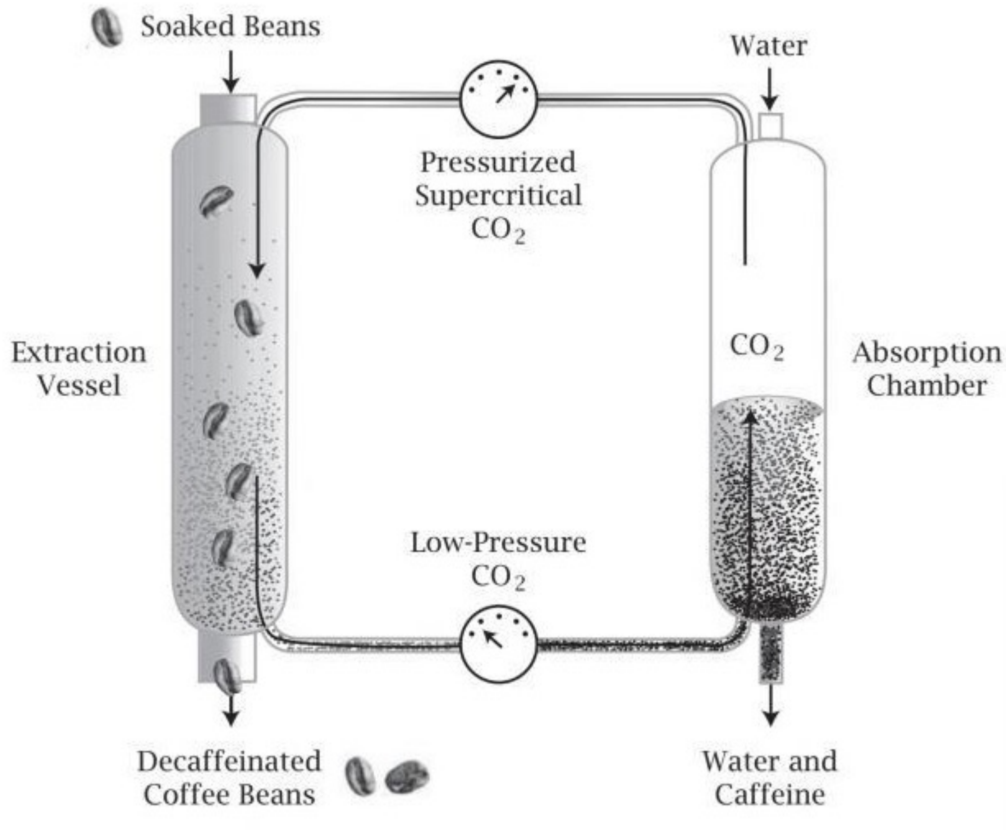
USE OF SUPERCRITICAL FLUIDS: DECAFFEINATION OF COFFEE BEANS

To remove caffeine from coffee, coffee is mixed with CO_2 at a temperature and pressure above the critical point of the CO_2.

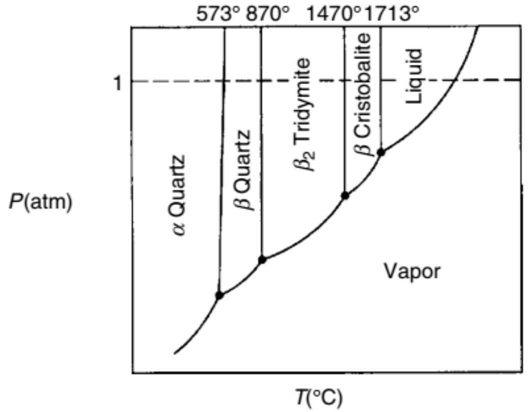
The supercritical CO_2 dissolves the caffeine (small black dots), decaffeinating the coffee beans.

The fluid mixture of CO_2 with caffeine then flows into a chamber where the pressure is lowered below the critical point so caffeine partitions into water.

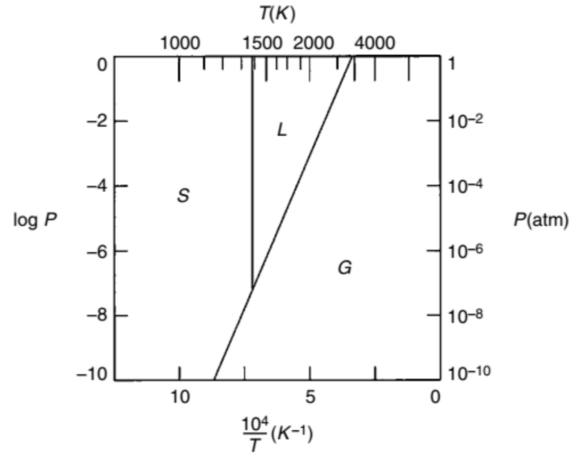
The carrier CO_2 is recaptured and the caffeine is dumped into the aqueous phase.



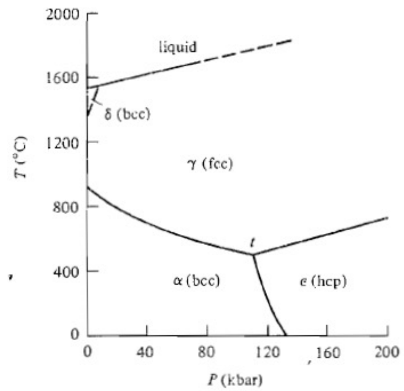
FURTHER EXAMPLES OF SINGLE COMPONENTS PHASE DIAGRAMS



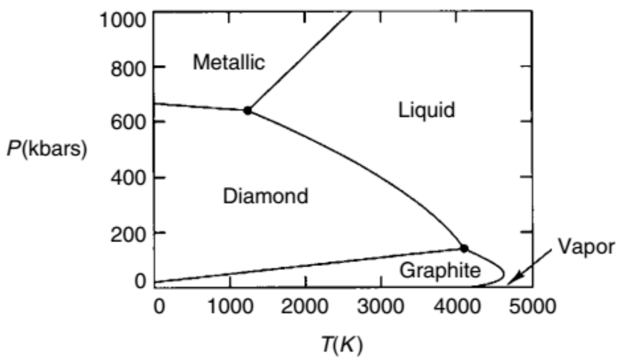
Phase diagram of silicon (Si)



Phase diagram of copper (Cu)



Phase diagram of iron (Fe)



Phase diagram of carbon (C)