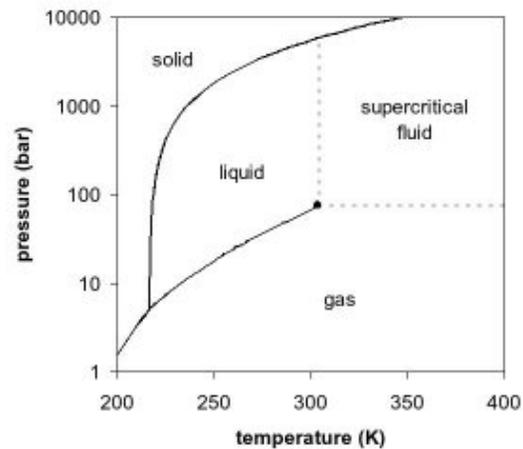
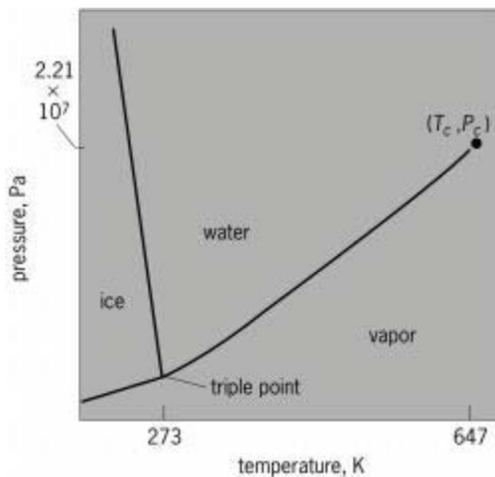


Lecture 25

Physics 404

Phases are distinct forms of matter with uniform composition. Examples of phases include solid, liquid, gas and plasma. Within solids there can be many phases, such as crystalline and amorphous. Carbon has many solid phases, including graphite, diamond, Buckyball, carbon nanotube, and graphene. More phases could be discovered in the future.

Today we are concerned with the coexistence of two phases in equilibrium. Examples include the liquid-to-vapor transition, the solid-to-liquid transition, and the solid-to-vapor transition. We examined the specific case of liquid nitrogen changing to gaseous nitrogen at a temperature of $T_0 = 77$ K and a pressure of $P_0 = 1$ atmosphere. Such systems are in thermal, diffusive and mechanical contact. Mechanical contact means that the two phases can exert forces on each other. The condition of equilibrium coexistence of gas and liquid can be stated as: $\tau_g = \tau_l, \mu_g = \mu_l, P_g = P_l$. In the case of coexistence at temperature T_0 and pressure P_0 , we have: $\mu_g(P_0, \tau_0) = \mu_l(P_0, \tau_0)$. There are nearby points in the pressure-temperature plane where coexistence also exists. The locus of all such points constitute the phase boundaries and define a phase diagram, as shown for the case of H_2O and CO_2 below.



Pressure-Temperature phase diagrams for H_2O (left) and CO_2 (right).

Coexistence can occur at a nearby point in the phase diagram so that $\mu_g(P_0 + dP, \tau_0 + d\tau) = \mu_l(P_0 + dP, \tau_0 + d\tau)$. This statement essentially constrains how one can move in the $P - \tau$ plane and maintain coexistence. Expanding this in a Taylor series, taking the limit as dP and $d\tau$ go to zero, rearranging, one finds: $\frac{dP}{d\tau} = \left(\frac{\partial \mu_l}{\partial \tau} \Big|_P - \frac{\partial \mu_g}{\partial \tau} \Big|_P \right) / \left(\frac{\partial \mu_g}{\partial P} \Big|_\tau - \frac{\partial \mu_l}{\partial P} \Big|_\tau \right)$. This is a differential equation for the coexistence curve in the $P - \tau$ plane. How to calculate these derivatives of the chemical potential? We introduce the Gibbs free energy.

The Gibbs free energy is defined as the $G \equiv U - \tau\sigma + PV$. With the help of the thermodynamic identity, one finds that the total differential of G is $dG = \mu dN - \sigma d\tau + V dP$. G is minimized for

systems with fixed N at constant pressure and temperature. As such it is useful for determining the equilibrium phase of a material at a given pressure and temperature. From dG , one finds the following differential relations, $\frac{\partial G}{\partial N}|_{\tau,P} = \mu$, $\frac{\partial G}{\partial \tau}|_{N,P} = -\sigma$, $\frac{\partial G}{\partial P}|_{\tau,N} = V$. The Gibbs free energy G , energy U , entropy σ , volume V , number N are all examples of extensive quantities. They scale with the number of particles present in the system, i.e. the amount of "stuff". On the other hand, the temperature τ , the pressure P , and the chemical potential μ are intensive quantities. Their values do not change if the system is suddenly sliced in half. We can write the Gibbs free energy $G(P, \tau, N)$ simply as $G(P, \tau, N) = N \mu(P, \tau, N)$. This satisfies the derivative equation $\frac{\partial G}{\partial N}|_{\tau,P} = \mu$, and it correctly expresses G as an extensive quantity, while including the appropriate dependence on the intensive quantities μ, P , and τ .

Returning to the coexistence differential equation, we can now evaluate the derivatives of the chemical potential using the Gibbs free energy to arrive at: $\frac{dP}{d\tau} = \frac{s_g - s_l}{v_g - v_l}$, where $s = \sigma/N$ and $v = V/N$ are the entropy and volume per particle. This result is known as the Clausius-Clapeyron equation. It relates the local slope of the coexistence curve in the $P - \tau$ plane to the entropy difference and volume difference of molecules in the gas and liquid phases. The numerator is directly related to the latent heat L of the phase transition: $L = \tau(s_g - s_l)$, so the equation becomes $\frac{dP}{d\tau} = \frac{L}{\tau \Delta v}$, where $\Delta v = v_g - v_l$. Under most circumstances the volume per particle in the gas phase is far larger than that in the liquid phase, and the gas will obey the ideal gas law, so that the C-C equation becomes approximately $\frac{dP}{d\tau} = \frac{L}{\tau^2} P$, or equivalently as $\frac{d}{d\tau} \log P = \frac{L}{\tau^2}$. If $L(\tau)$ is measured, this equation can be integrated to find the coexistence line $P(\tau)$ in the $P - \tau$ plane. If the latent heat is constant, $L = L_0$, the integration can be done to yield $P(\tau) = P_0 e^{-L_0/\tau}$. Some representative data for benzene showing a phase boundary like this between liquid and vapor, and between solid and vapor, is shown on the class web site.