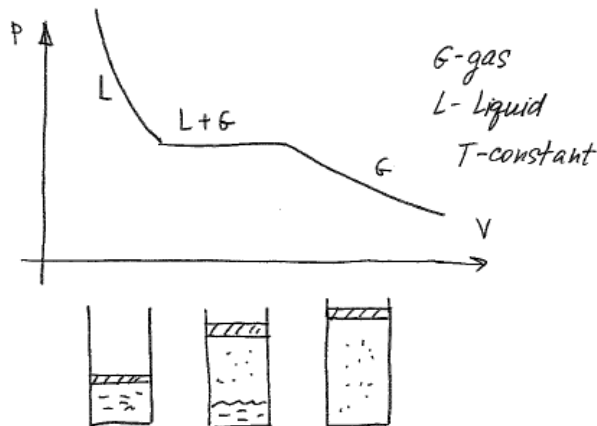


## Lecture #8

### Phase Transformations

Let's consider a pressure-versus-volume dependence for a real gas in which atoms and molecules interact with each other and under appropriate condition can associate together in a liquid or solid phase. A phase – is a portion of the system that is uniform in composition. Two phases may coexist, with a definite boundary between them.



Liquid and gas phase are in equilibrium in the some V range. If we do not change V and T, relative amounts of L and G do not change. Liquid and vapor (gas in equilibrium with its liquid or solid form) may coexist on the section of the isotherm only if the temperature of isotherm lies below a critical temperature  $T_c$ , above the critical temperature only a single phase – the fluid phase – exists no matter how great is the pressure. There is no more reason to call this phase a gas than a liquid, so we avoid the issues and call it a fluid.

Critical temperatures for some gases

	$T_c$ (k)	
He	5.2	
Ar	151	
O <sub>2</sub>	1543 k	
H <sub>2</sub> O	647.1	374 <sup>0</sup> C

The thermodynamic conditions for the coexistence of two phases are the conditions for the equilibrium of two systems that are in thermal, diffusion and mechanical contact.

$$T_L = T_G \quad \mu_L = \mu_G \quad P_L = P_G$$

The chemical potentials are equivalent at the common temperature and common pressure of the liquid and gas, so that  $\mu_L(P, T) = \mu_G(P, T)$ . At a arbitrary selected point in the P-T plane the two phases may not coexist. If  $\mu_G < \mu_L$  the gas phase is more stable. A

metastable state may have transient existence (super cooling and superheating), sometimes brief, sometimes long at temperature for which another more stable phase of the same substance has a lower chemical potential.

### Coexistence curve P vs T

Let  $P_0$  be the pressure for which two phases, L and G, coexist at temperature  $T_0$ . Suppose that the two phases also coexist at the nearby point  $P_0 + dP, T_0 + dT$ . We therefore have,

$$\mu_g(P_0, T_0) = \mu_L(P_0, T_0)$$

$$\mu_g(P_0 + dP, T_0 + dT) = \mu_L(P_0 + dP, T_0 + dT)$$

Expanding chemical potentials near the point  $P_0, T_0$  we have

$$\mu_g(P_0, T_0) + \left( \frac{\partial \mu_g}{\partial P} \right)_L dP + \left( \frac{\partial \mu_g}{\partial T} \right)_L dT + \dots = \mu_L(P_0, T_0) + \left( \frac{\partial \mu_L}{\partial P} \right)_T dP + \left( \frac{\partial \mu_L}{\partial T} \right)_T dT + \dots$$

When  $dP, dT \rightarrow 0$  we have

$$\frac{dP}{dT} = \frac{\left( \frac{\partial \mu_L}{\partial T} \right)_P - \left( \frac{\partial \mu_g}{\partial T} \right)_P}{\left( \frac{\partial \mu_g}{\partial P} \right)_T - \left( \frac{\partial \mu_L}{\partial P} \right)_T}, \text{ the differential equation for the coexistence of two phase.}$$

The above equation defines the vapor pressure curve. --- Why we may call it like that?

In the previous lecture we showed that  $G = \mu(P, T)N$

We also know that  $\left( \frac{\partial G}{\partial P} \right)_{N,T} = V$  and  $\left( \frac{\partial G}{\partial T} \right)_{P,N} = -S$

With the definitions:

$$v = \frac{V}{N} - \text{volume per molecule}$$

$$s = \frac{S}{N} - \text{entropy per molecule}$$

We have

$$\frac{1}{N} \left( \frac{\partial G}{\partial P} \right)_{N,T} = \frac{V}{N} = v = \left( \frac{\partial \mu}{\partial P} \right)_T$$

$$\frac{1}{N} \left( \frac{\partial G}{\partial T} \right)_{P,N} = -\frac{S}{N} = -s = \left( \frac{\partial \mu}{\partial T} \right)_P$$

Then we have

$$\frac{dP}{dT} = \frac{s_g - s_L}{v_g - v_L}$$

$s_g - s_L$  is the increase in the entropy of the system when we transfer one molecule from liquid to gas  
 $v_g - v_L$  - is the increase in the volume of the system when we transfer one molecule from liquid to gas.

It is important to understand that the derivative is not simply taken from the equation of state of a gas. The derivative refers to the very special interdependent change of P and T in which the number of molecules in each phase varies as the volume is varied subject only to the  $N_L + N_g = N$  constrain.

$$dQ = T(s_g - s_L) - \text{heat needed to evaporate one molecule}$$

$$L \equiv T(s_g - s_L) - \text{Latent heat of vaporization}$$

$$\Delta v = v_g - v_L$$

$$\frac{dP}{dT} = \frac{L}{T \Delta v} - \text{the Clausius- Clapeyron equation or vapor pressure equation}$$

**Please note that in the above derivation we have not used any specific information that one of the phases is a gas and the other in a liquid. We can apply this equation to describe the equilibrium between a solid and a liquid and a solid and a gas.**

For a gas- liquid co-existence a particular useful form of this equation can be obtained with two approximations.

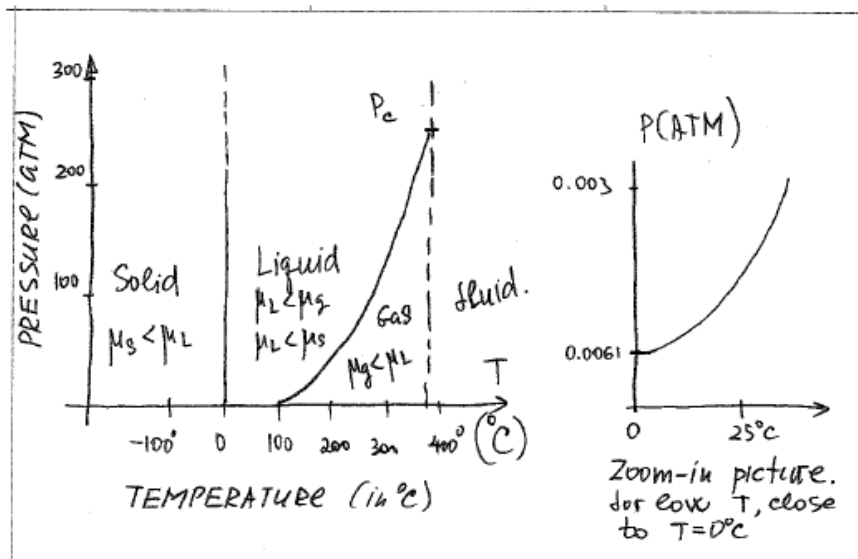
$$1) v_g \gg v_L \quad v_g = \frac{v_g}{N_g}$$

$$2) \text{ Ideal gas law } PV_g = N_g kT, \quad v_g = \frac{V_g}{N_g} = \frac{kT}{P}$$

$$\frac{dP}{dT} = \frac{L}{T} \frac{P}{kT}; \quad \int \frac{dP}{P} = L_0 \int \frac{dT}{T^2} \cdot \frac{1}{k}; \quad \ln \frac{P}{P_0} = -\frac{L_0}{kT}$$

$$P = P_0 \exp\left(-\frac{L_0}{kT}\right), \text{ where } L_0 \text{ is a latent heat of vaporization of one molecule.}$$

$$P = P_0 \exp\left(-\frac{L_0}{RT}\right), \text{ where } L_0 \text{ is a latent heat of vaporization of one mole.}$$



How do we measure vapor pressure?

### Triple Point

The triple point of a substance is that point  $P_t, T_t$  in the  $P - T$  plane at which all three phases, vapor, liquid, and solid are in equilibrium that is

$$\mu_L = \mu_g = \mu_s$$

Consider an equilibrium mixture of liquid and solid phases enclosed in a volume somewhat large that that occupied by the mixture alone. The remaining volume will contain only the vapor in equilibrium with the vapor pressure of both phases. This pressure is triple point pressure.

Water triple point  $T_t = 0.01^\circ C$   $P_t = 0.006 \text{ atm}$

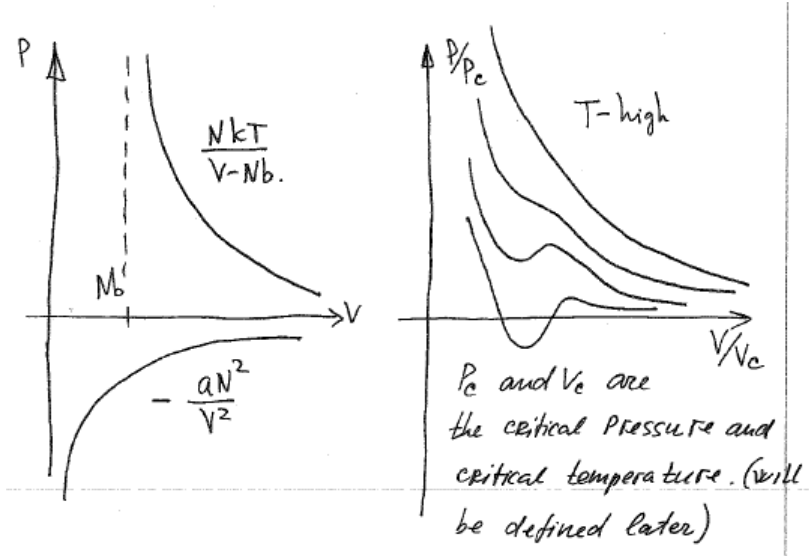
Carbon dioxide  $T_t = -56.6^\circ C$   $P = 5.2 \text{ atm}$

So at ambient pressure carbon dioxide does not melt it dries.

For carbon dioxide pressure increases melting temperature, for water pressure decreases melting temperature (unusual properties density of ice is larger than the density of water). Another similar examples are silicon and germanium. Liquid silicon has larger density and has better conductivity than a crystalline silicon.

### **Phase transformation in Van der Waals gas**

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$



Let us compute Gibbs free energy for VDW fluid

$$dG = -SdT + VdP + \mu dN$$

If we keep N and T constant, then

$$dG = +VdP \Rightarrow \left( \frac{\partial G}{\partial V} \right)_{NT} = V \left( \frac{\partial P}{\partial V} \right)_{N,T}$$

$$\left( \frac{\partial G}{\partial V} \right)_{N,T} = -\frac{NkTV}{(V-N)^2} + \frac{2aN^2}{V^2}$$

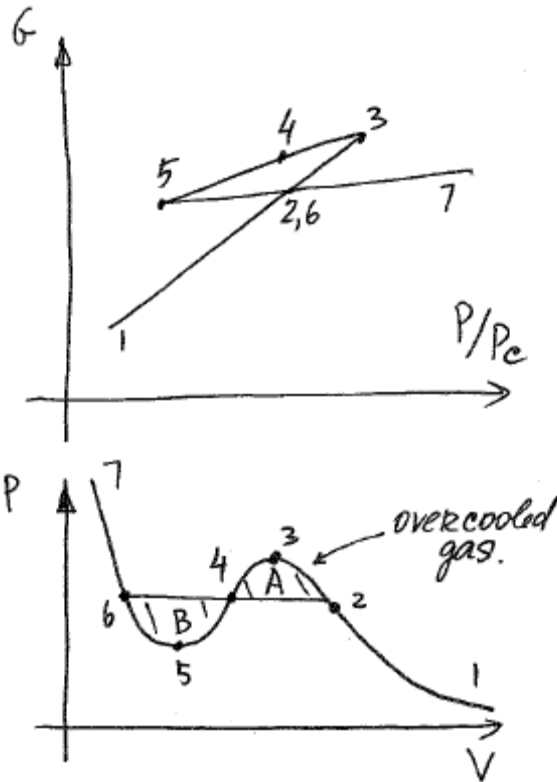
$$G = \int \left( \frac{\partial G}{\partial V} \right) dV = \int \left[ -\frac{NkT(V-Nb) + Nb}{(V-Nb)^2} + \frac{2aN^2}{V^2} \right] dV =$$

$$= -NkT \ln(V-Nb) + \frac{(NkT)(Nb)}{V-N} - \frac{2aN^2}{V} + c(T)$$

The above equation gives us the Gibbs free energy  $G(V)$  as a function of  $V$

The state equation  $P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}$  gives us  $P$  as a function of  $V$ .

Now we plot  $G$  versus  $P$  using  $V$  as a parameter. So we get  $V$ , compute corresponding  $G$  and  $P$  and put point on graph.



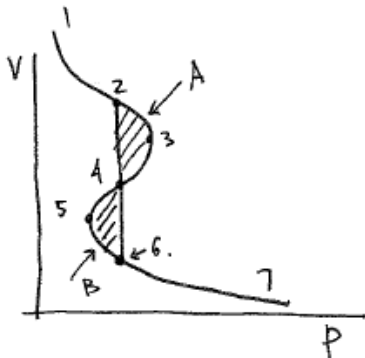
Although the VdW equation associates same pressure with more than one volume (lower figure) the thermodynamically stable is the state with the lowest Gibbs free energy; In the sections (1-2) fluid is a gas, in section (6-7) fluid is a liquid.

At intermediate volumes between 2 and 6 the thermodynamically stable is actually a combination of part gas and part liquid, still at transition pressure. There is a clever method of determination of the position of straight line in PV diagram.

Note that the net change in  $G$  as we go around triangular loop (2-3-4-5-6)

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left( \frac{\partial G}{\partial P} \right)_T dP = \int_{\text{loop}} V dP$$

This integral is equal: area A minus area B.



The critical temperature correspond to isotherm that still has a point of deflection but no phase coexistence line at temperature  $T > T_c$  only one phase (fluid) exist.

Mathematically  $T_c$  can be found from condition that equation  $\frac{dP}{dV}=0$  has only one root.

That also means that the second derivative  $\frac{d^2P}{dV^2}=0$ . Using these facts we may find

$$kT_c = \frac{8}{27} \frac{a}{b} \quad V_c = 3Nb \quad P_c = \frac{1}{27} \frac{a}{b^2}$$

The VdW equation may be then re-written in the reduced form

$$\left( \hat{P} + \frac{3}{\hat{V}^2} \right) \left( \hat{V} - \frac{1}{3} \right) = \frac{8}{3} \hat{T}$$

$$\hat{P} = \frac{8/3 \hat{T}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}$$

where  $\hat{P} = \frac{P}{P_c} \quad \hat{V} = \frac{V}{V_c} \quad \hat{T} = \frac{T}{T_c}$ .