

First Order Phase Transitions and Finding the Vapor Dome

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First Order Phase Transitions

- Consider the stability of a substance described by van der Waal's equation of state.

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

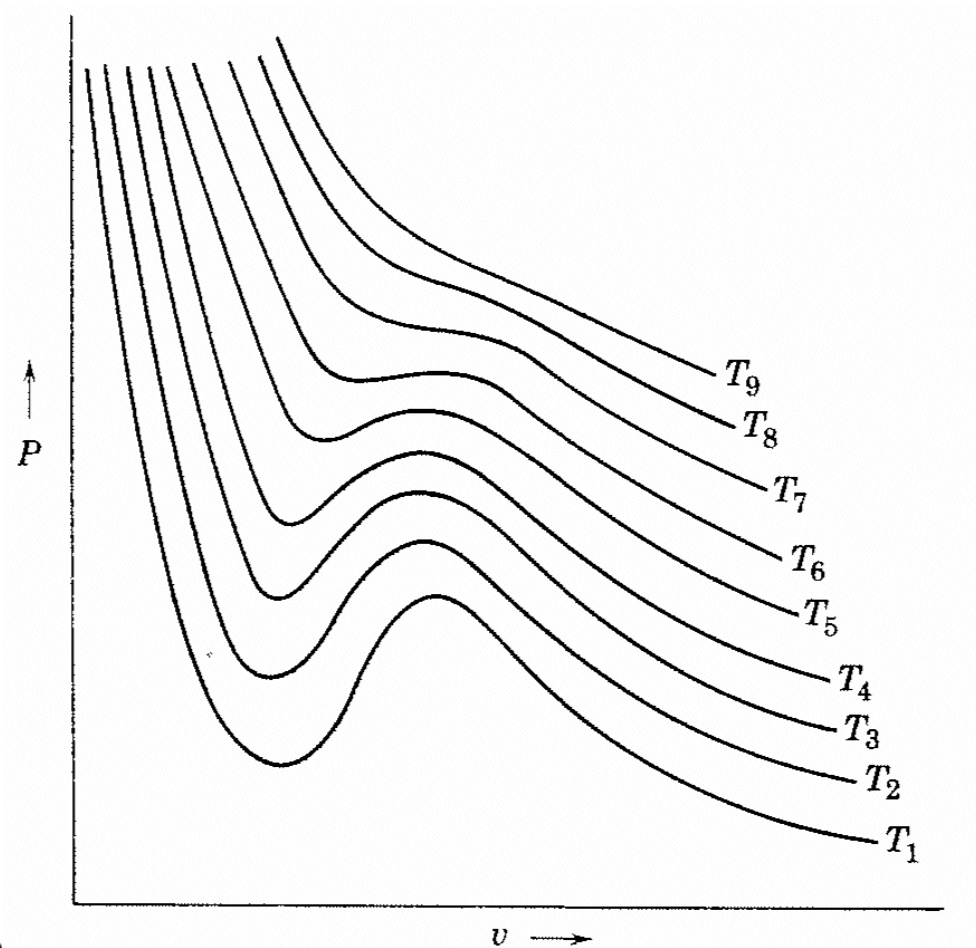
- Local stability requires

$$\left(\frac{\partial P}{\partial v} \right)_T \leq 0$$

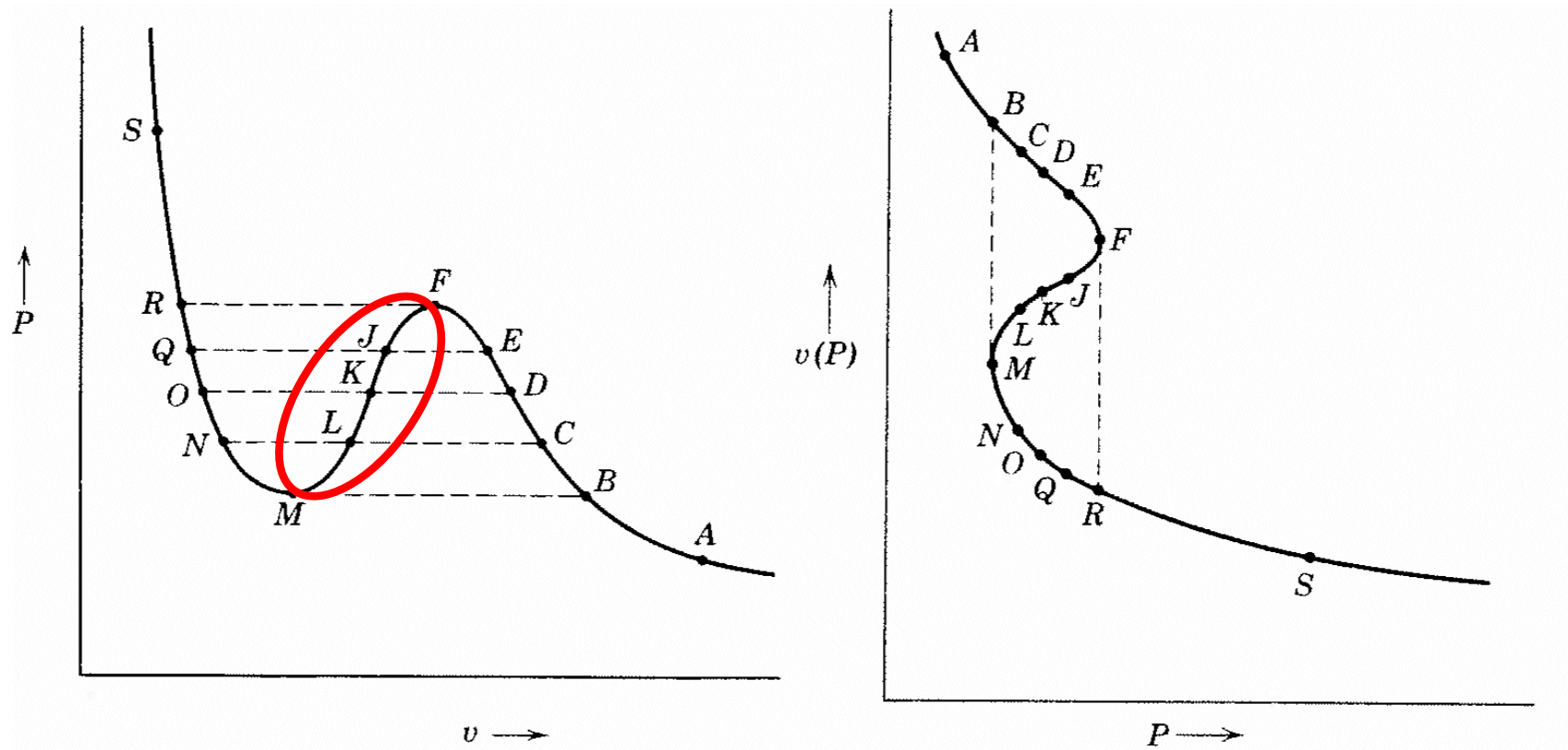


P-v-T Relation

- If we plotted this relation in the liquid-vapor region it would look like



- A given isotherm looks like:



- The local stability criterion is clearly violated over the region FKM .
- Therefore a phase transition must be involved.

- The Gibbs potential can be calculated noting

$$d\mu = -sdT + vdP$$

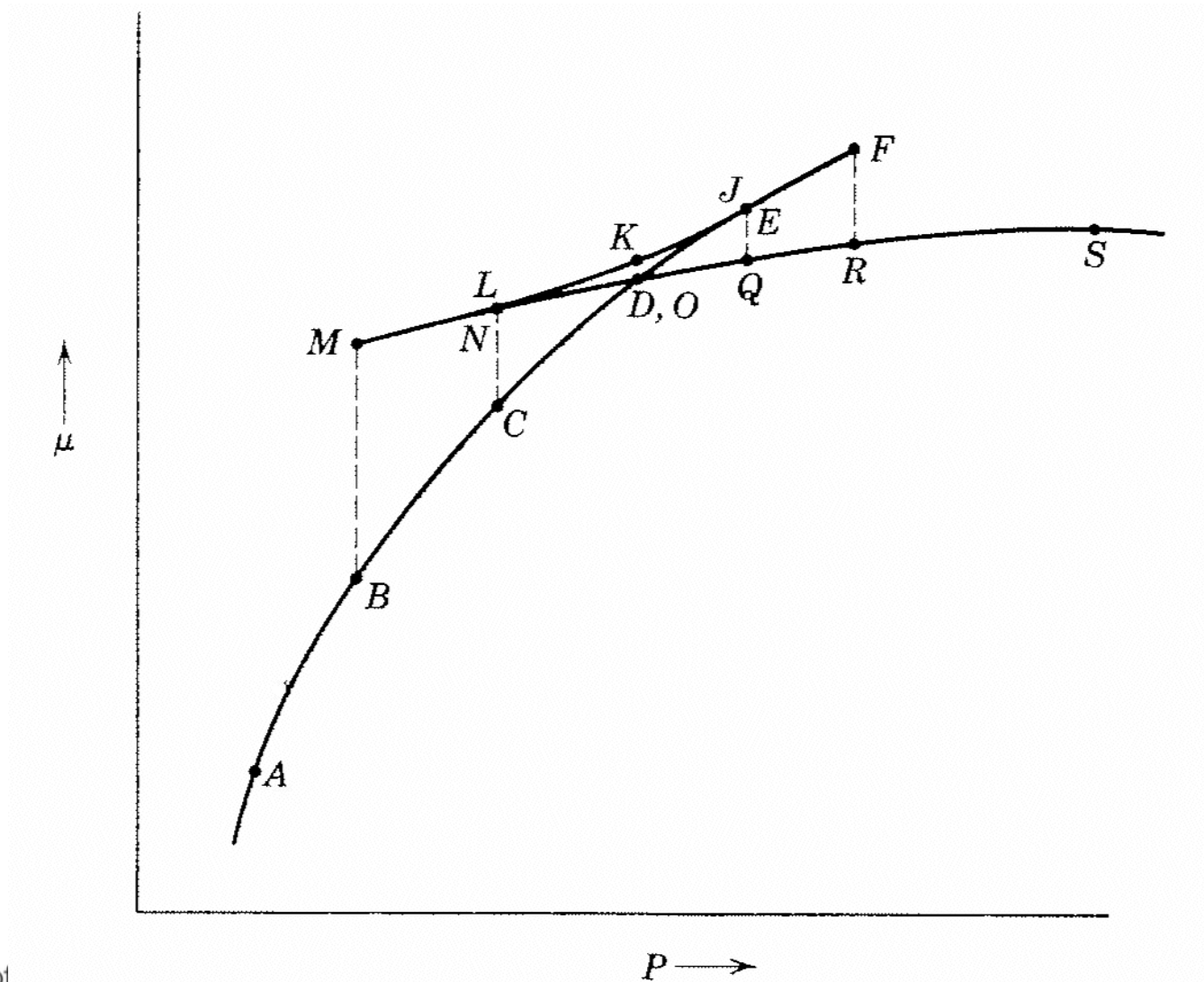
- Along a line of constant T

$$\mu = \int v dP + \phi(T)$$

- Thus the change in chemical potential along an isotherm is

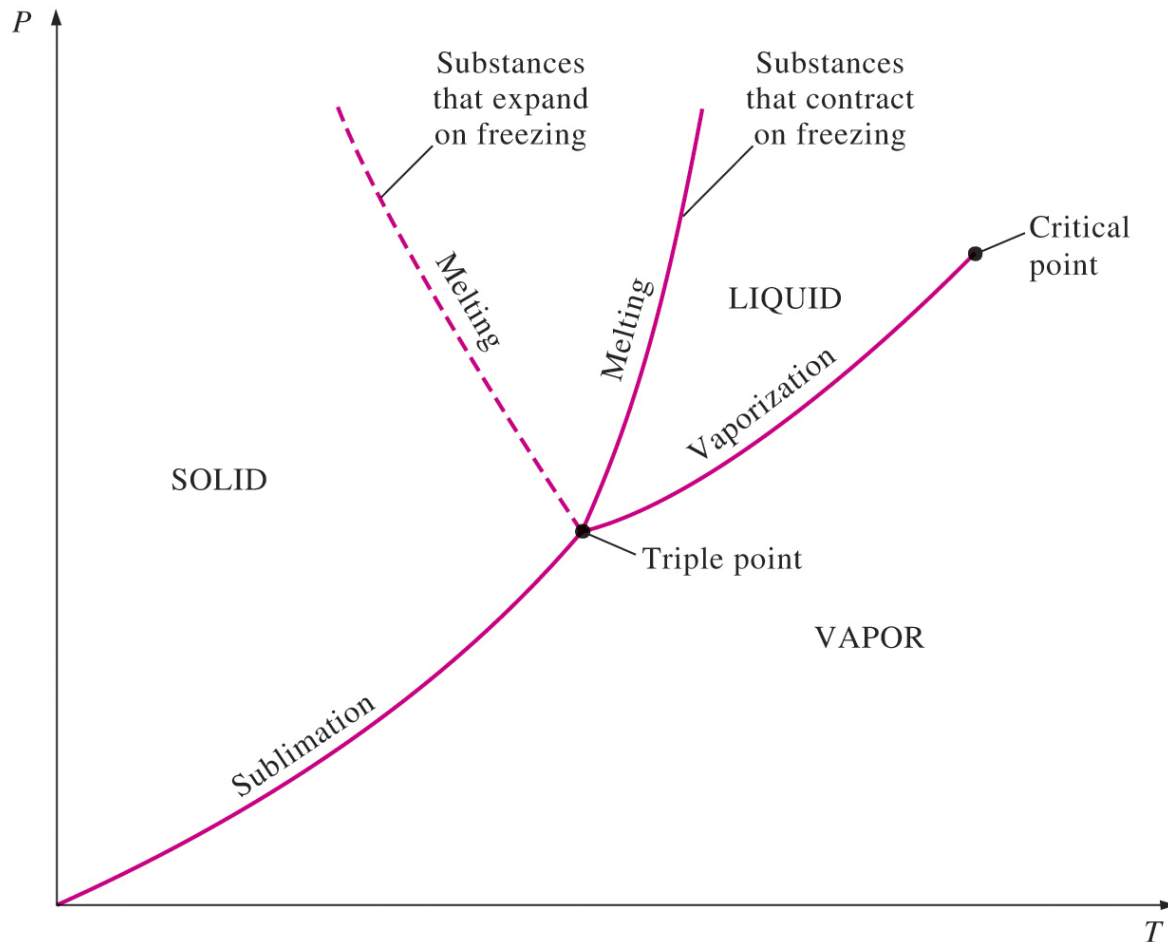
$$\mu_A - \mu_B = \int_A^B v(P) dP$$

- If we carried this integration out, it would look like

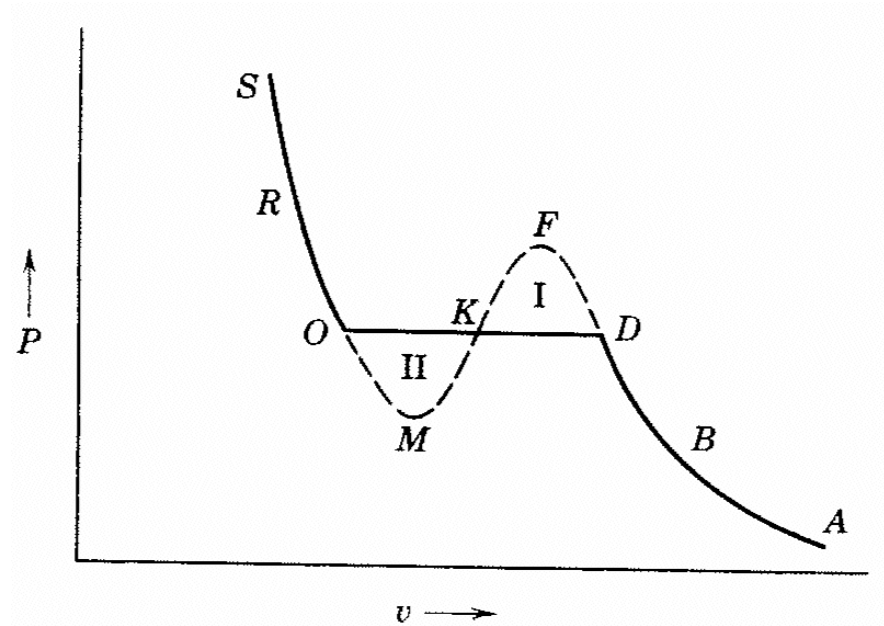


- Note that $\mu(T,P)$ is the FR per mole in the Gibbs Representation.
- Thus, stable points have minimum μ .
- As the pressure is increased, the physical state will be the one with minimum μ .
- At the points D,O where the two sides overlap, both liquid and vapor branches are at minimum μ .

Recall P-T Diagram



- Thus we expect the process to proceed as shown:



- The points OD are determined by:

$$\mu_D - \mu_O = \int_O^D v(P) dP = 0$$

- Thus, area I = area II.

Saturation Properties

- Entropy

$$s_{fg} = s_D - s_O = \int_{OMKFD} \left(\frac{\partial P}{\partial T} \right)_v dv$$

- Internal Energy

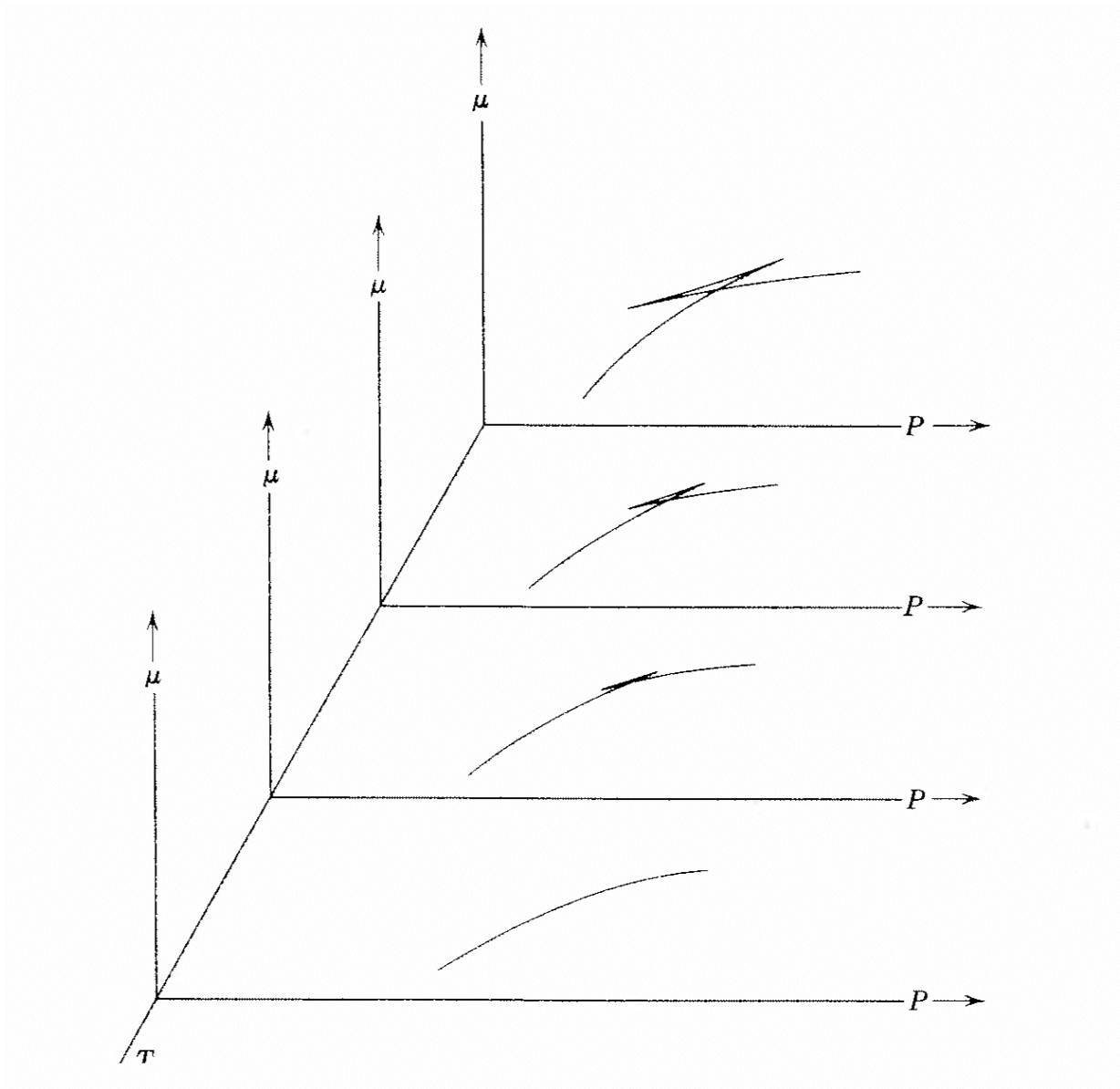
$$u_{fg} = u_D - u_O = Ts_{fg} - P(v_D - v_O)$$

- Enthalpy

$$h_{fg} = (u_D + P_D v_D) - (u_O + P_O v_O) = u_{fg} + P(v_D - v_O)$$



- The vapor dome is constructed from



Vapor Dome

