Physical Chemistry (Chem 132A)

Lecture 8
Monday, October 16

New Homework #3 is due October 21

Note this assignment is a little longer/more challenging than the previous assignments---don't put it off until next Saturday.

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Temperature dependence of G?

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$G = H - TS \quad \text{so we have} \quad \left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

$$\left(\frac{\partial G/T}{\partial T}\right)_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz equation
See algebra on pg 144 of text

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

$$dG = Vdp - SdT$$

At constant T: dG = Vdp

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V \, dp$$

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m \, dp$$

For an ideal gas: $V_m = RT/p$

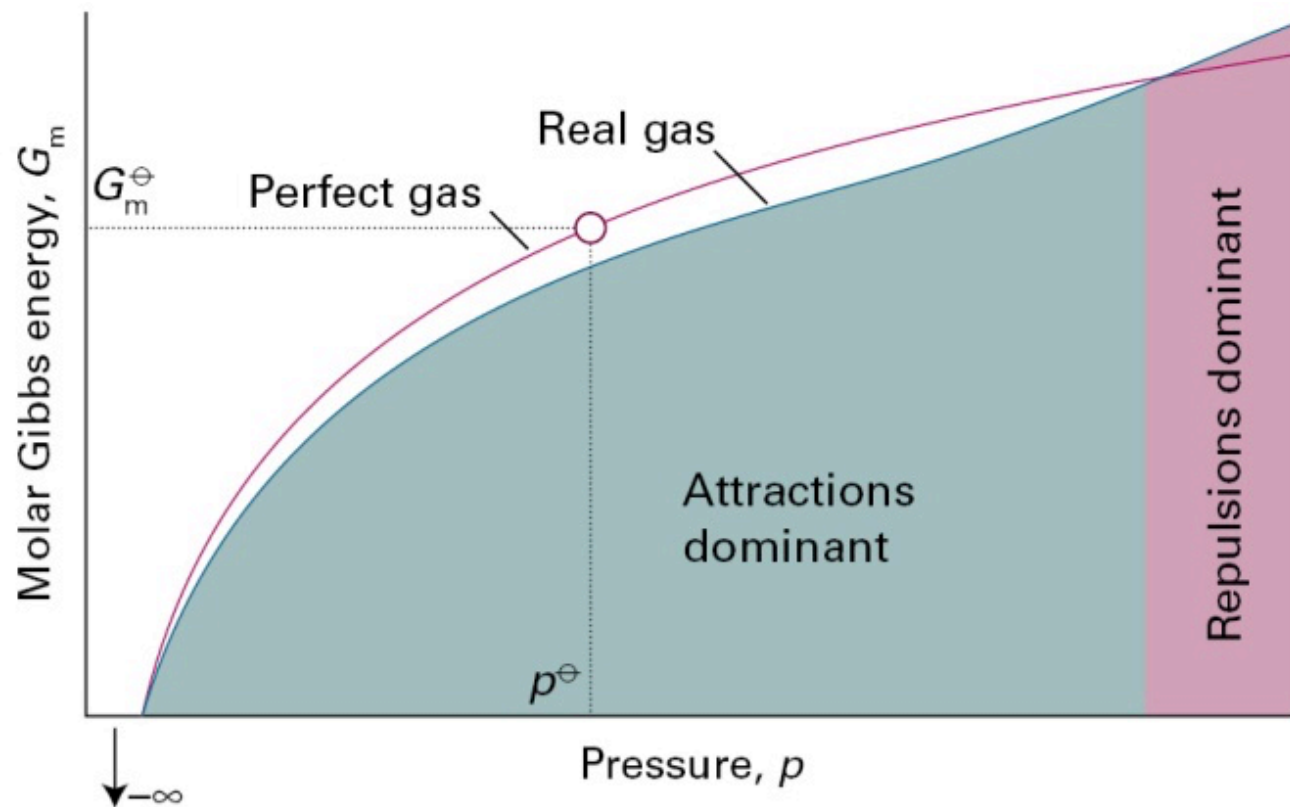$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} \, dp = G_m(p_i) + RT \ln\left(\frac{p_f}{p_i}\right)$$

$$G_m^0 = G_m^0 \left(p_i \right) + RT \ln \left(\frac{f}{p^0} \right)$$

This is the definition of f (the fugacity)

Usually take f = φp

φ is called the "fugacity coeficient"

Phases of a system (e.g. liquid, solid, vapor)

Phase transitions

Phase diagrams

Phase transitions

Consider a phase transition (e.g. melting)
At the normal transition temperature T_{trs}
This means the two phases are in equilibrium.
Equilibrium means the transition is reversible

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

$\Delta_{trs}S \approx 85 \ \text{JK}^{-1}\text{mol}^{-1}$
Trouton's rule.

Table 3A.2* The standard enthalpies and entropies of vaporization of liquids at their normal boiling points

|	$\Delta_{vap}H^{\ominus}/(\text{kJ mol}^{-1})$	$\theta_b/°C$	$\Delta_{vap}S^{\ominus}/(\text{J K}^{-1}\text{mol}^{-1})$
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	−60.4	87.9
Methane	8.18	−161.5	73.2
Water	40.7	100.0	109.1

Chemical Potential (μ)

For a single component system $\mu = G_m$

For a system at equilibrium μ is is the same everywhere in the sample even if multiple phases are present.

Pure substances phase diagrams
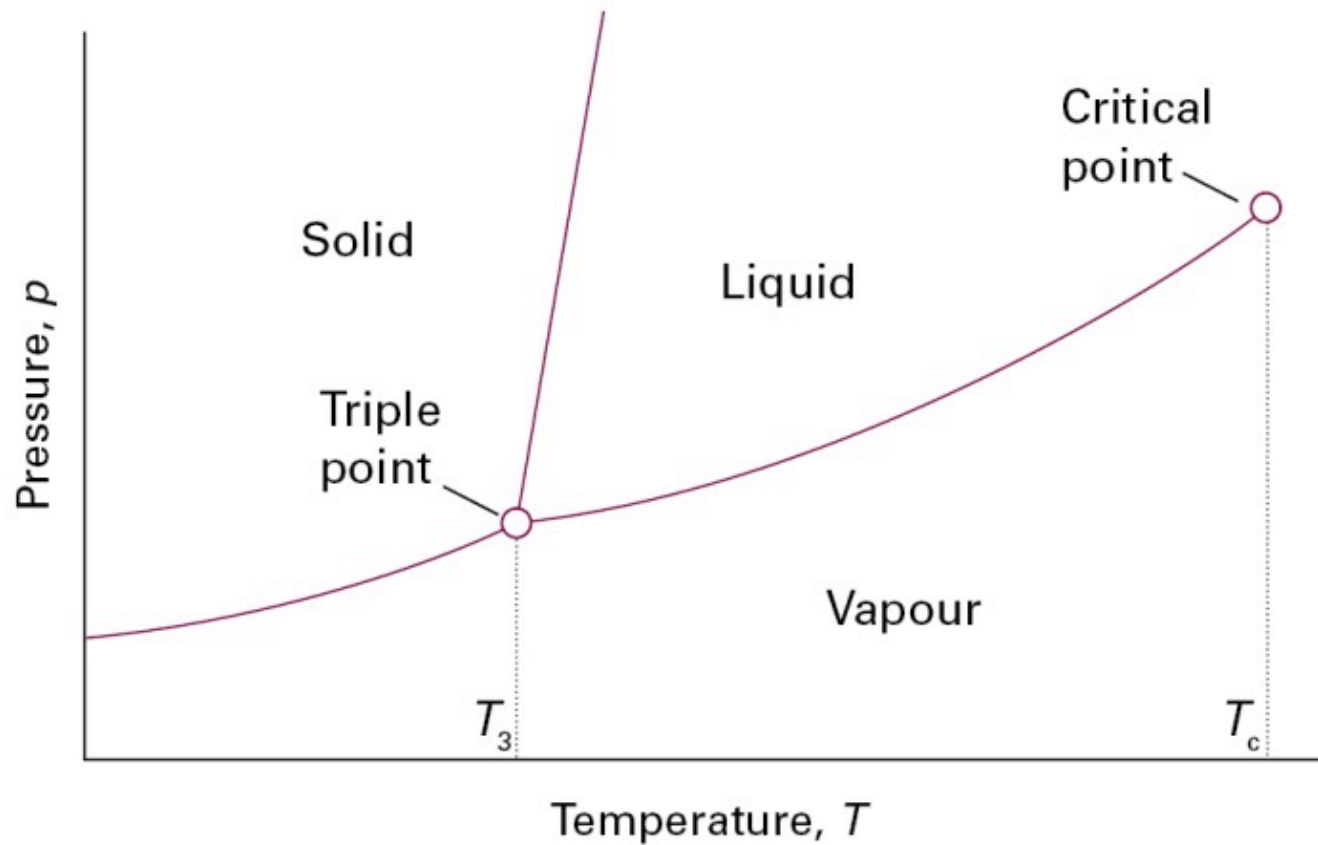
Pure substances phase diagrams
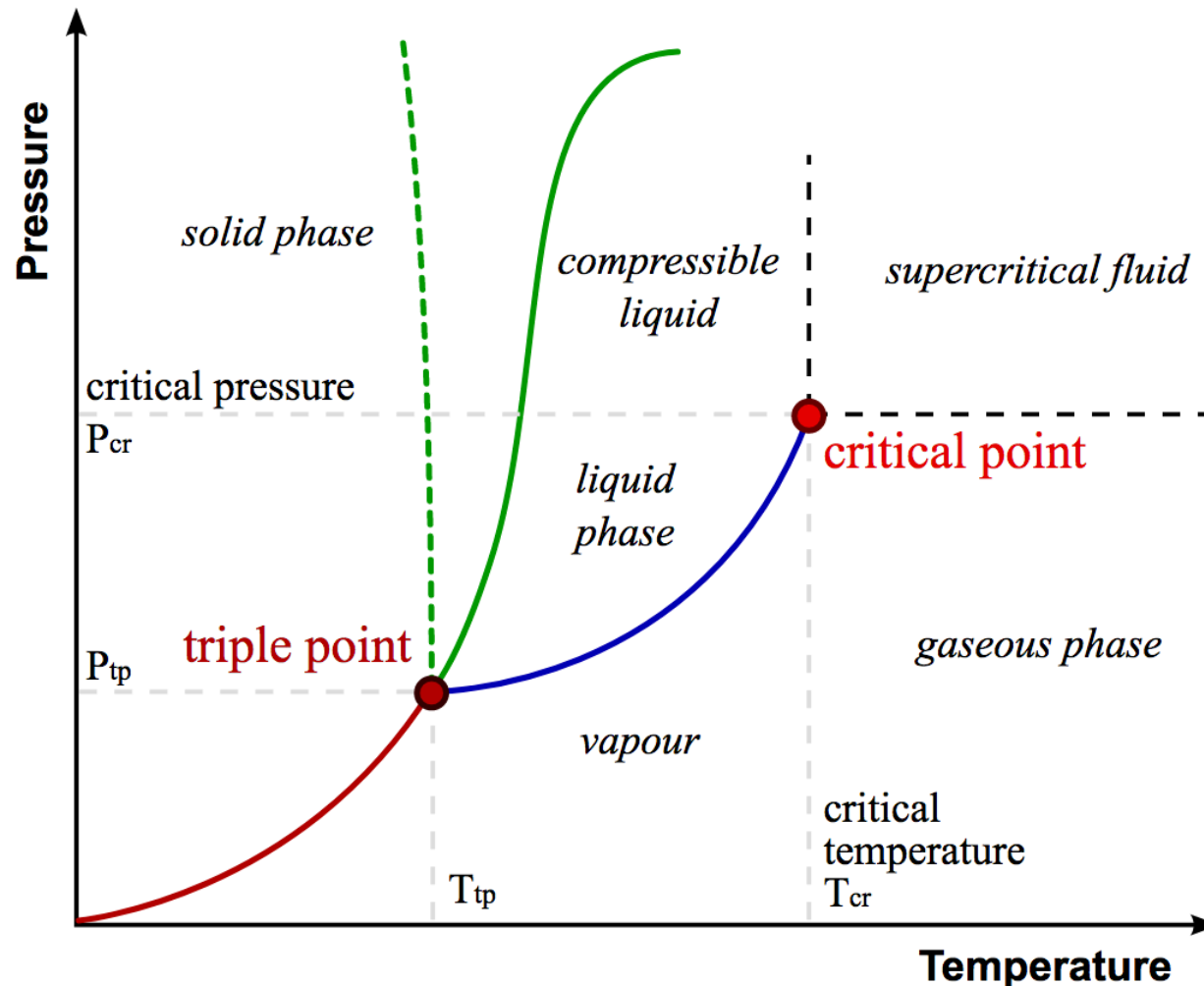
A typical phase diagram. The solid green line applies to most substances; the dotted green line gives the anomalous behavior of water. The green lines mark the freezing point and the blue line the boiling point, showing how they vary with pressure.

Triple point of water is 273.16 K and 611 Pascal

$$F = C - P + 2$$

F = degrees of freedom
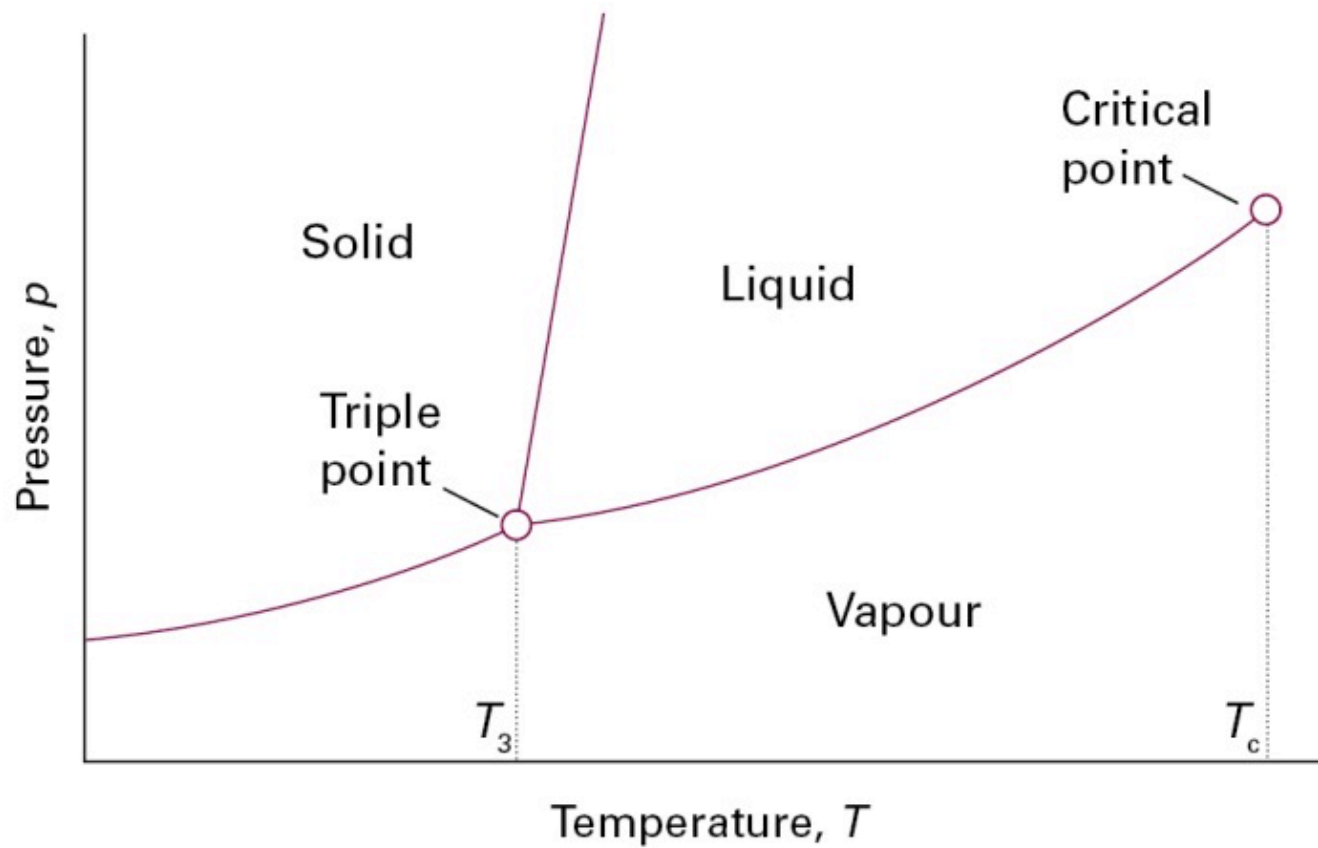
C = number of components

P = number of phases that can co-exist

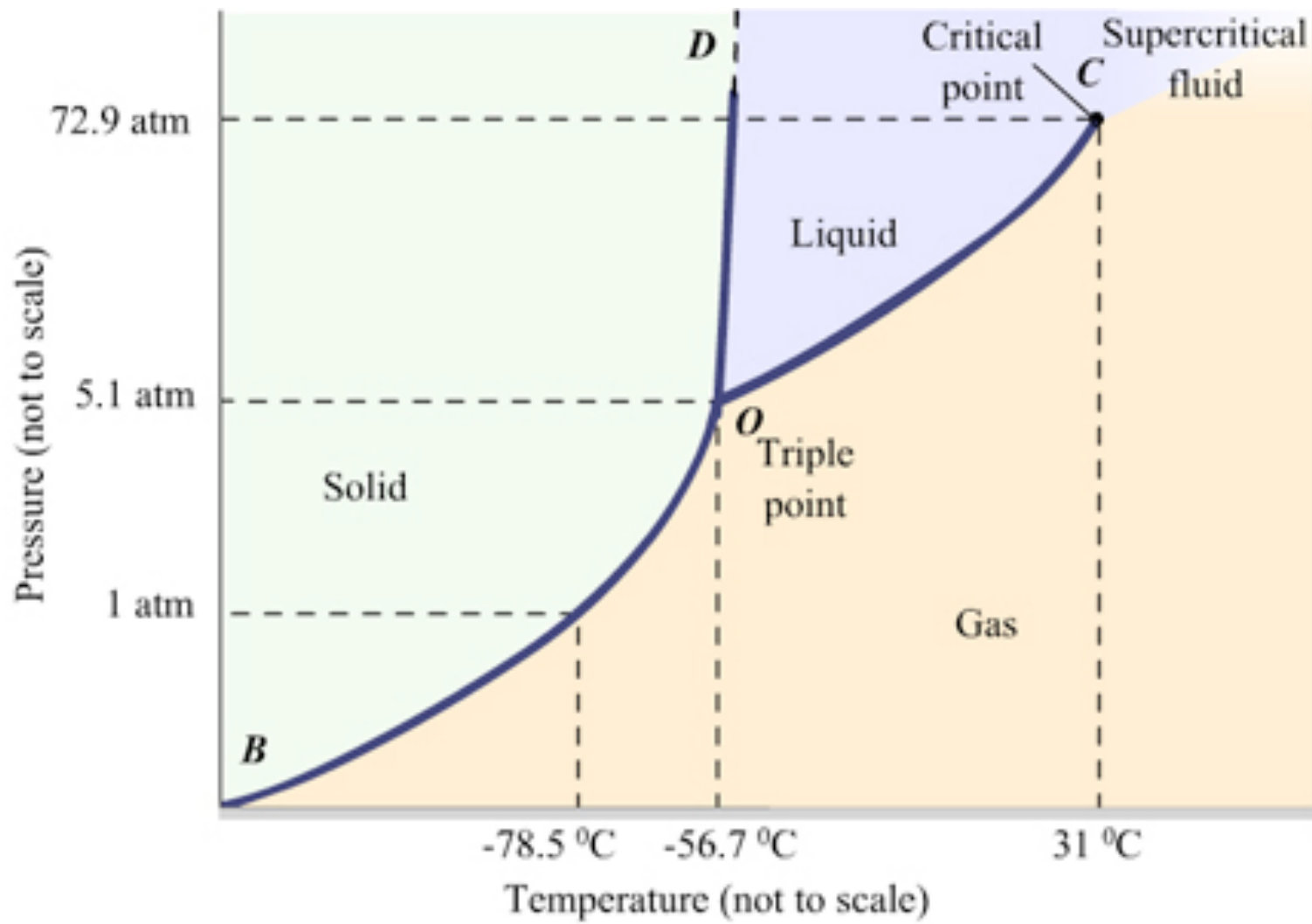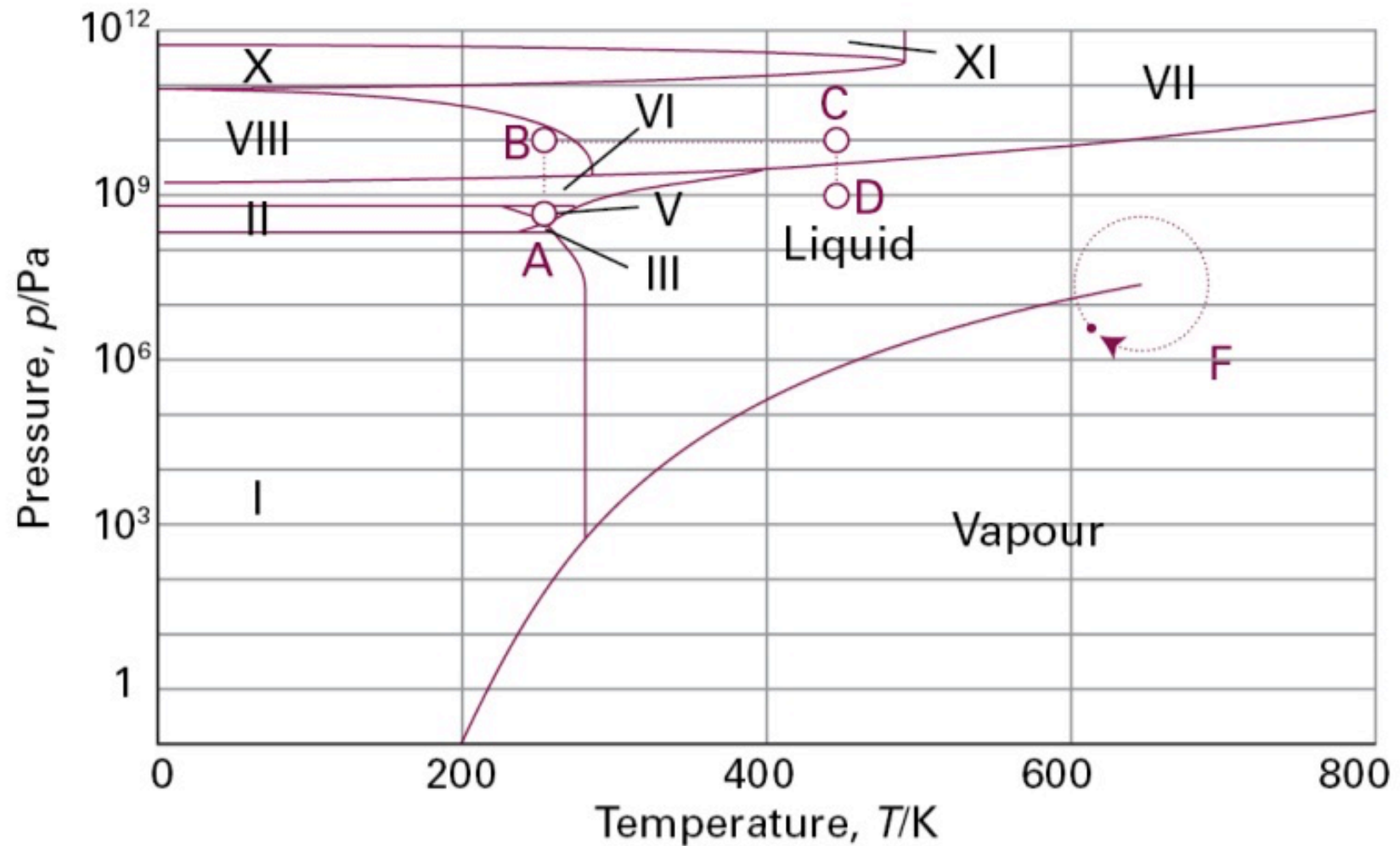**For a single component system: C = 1**

$$F = 3 - P$$
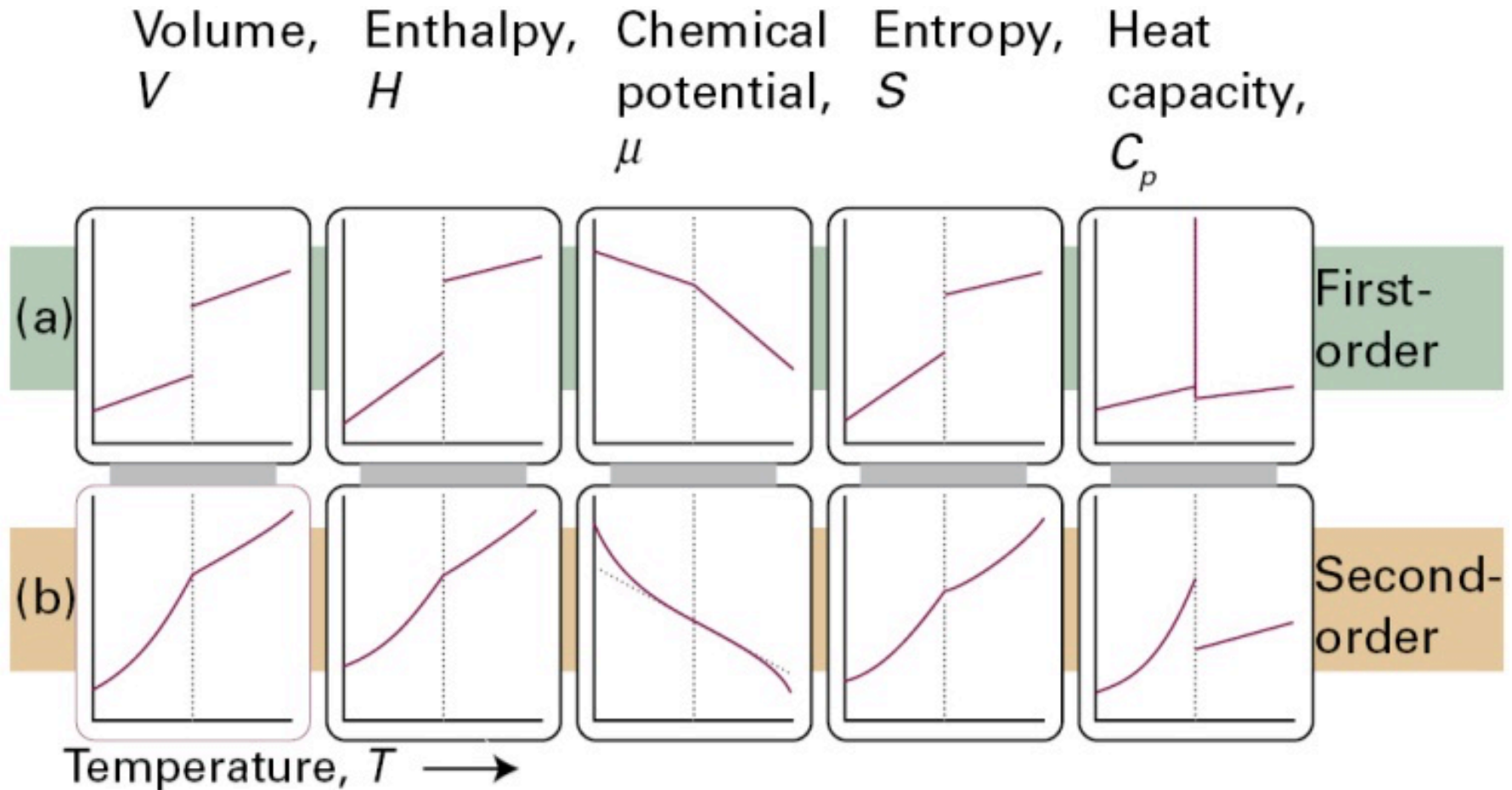
F = 3 − P

Phase Diagram for Carbon Dioxide

Phase Diagram for Water

Classification of Phase Transitions

Note: Modern terminology uses "first order transitions" and "continuous transitions"

THE END

SEE YOU Wednesday