

## Lecture 26

The Gibbs Phase Rule and its ApplicationLast Time**Symmetry and Thermodynamics**

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 **$Cf + 2$  Variables**

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 **$C(f - 1)$  Equations for Continuity of Chemical Potential**

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 **$f$  Gibbs-Duhem Relations (one for each phase)**

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 **$D = C - f - 2$  Degrees of Freedom Left Over**

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The Gibbs Phase Rule

$$D + f = C + 2 \quad (26-1)$$

The Gibbs phase rule is a very useful equation because it put precise limits on the number of phases  $f$  that can be simultaneously in equilibrium for a given number of components.

What does Equation 26-1 mean? Consider the following example of a single component (pure) phase diagram  $C = 1$ .

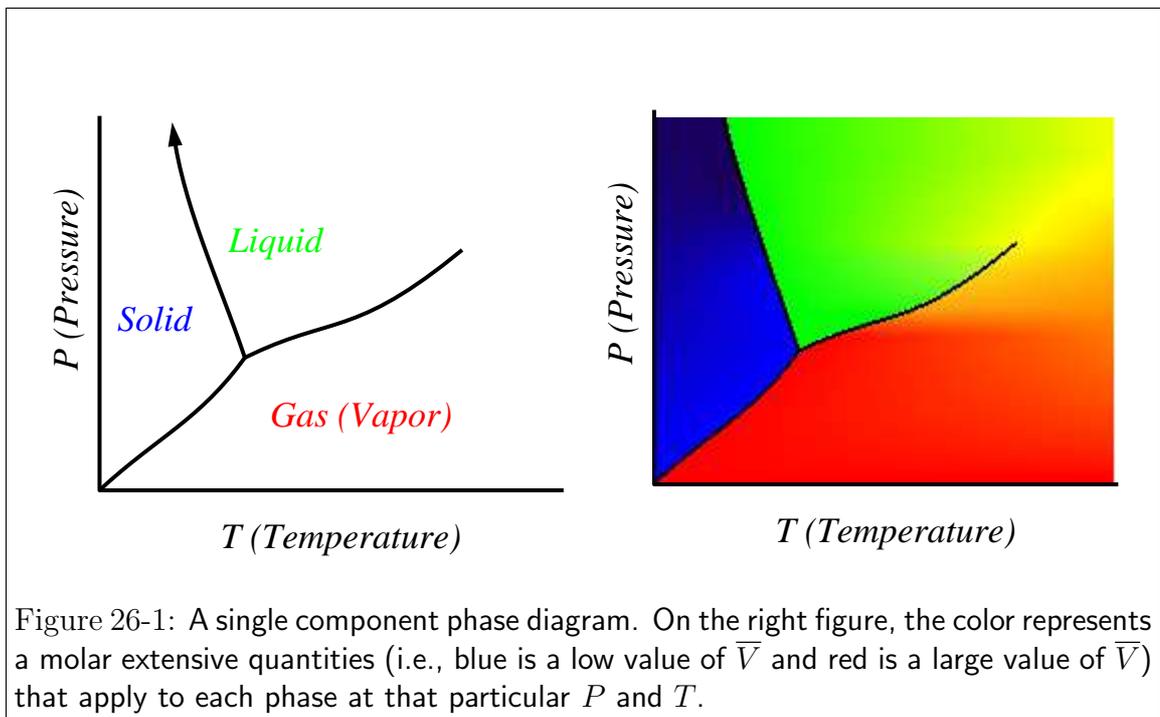


Figure 26-1: A single component phase diagram. On the right figure, the color represents a molar extensive quantities (i.e., blue is a low value of  $\bar{V}$  and red is a large value of  $\bar{V}$ ) that apply to each phase at that particular  $P$  and  $T$ .

Consider a single-phase region:

$$D = 2 - f + C = 2 - 1 + 1 = 2$$

This implies that two variables ( $P$  and  $T$ ) can be changed independently (i.e., pick any  $dP$  and  $dT$ ) and a single phase remains in equilibrium.

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Consider where two phases are in equilibrium:

$$D = 2 - f + C = 2 - 2 + 1 = 1,$$

There is only one degree of freedom—for the two phases to remain in equilibrium, one variable can be changed freely (for instance,  $dP$ ) but then the change in the other variable (i.e.,  $dT$ ) must depend on the change of the free variables:

$$\frac{dP}{dT} = f(P, T)$$

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Finally, consider where three phases are in equilibrium then:

$$D = 2 - 3 + 1 = 0.$$

There can be no change any variable that maintains three phase equilibrium.

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### \_\_\_\_\_ Various Confusing Issues on Applications of $D + f = C + 2$ \_\_\_\_\_

Consider a pure liquid  $A$  in contact with the air. The degrees of freedom can be determined in several equivalent ways.

- A** Consider the system composed of two components, the pure liquid  $A$  and air and restrict that the total pressure is 1 atm.

$$(D + f = C + 2) \rightarrow (D + f = C + 1).$$

$$\text{Therefore, } D = 2 - 2 + 1 = 1.$$

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- B** Considering that the system consists of three components:  $A$ ,  $O_2$ ,  $N_2$  and has two additional restrictions: 1)  $\Sigma P = 1$   $P_{O_2}/P_{N_2} = \text{constant}$ , then  $(D + f = C + 2) \rightarrow (D + f = C + 0)$ .  $D = 3 - 2 + 0 = 1$  as before.

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**C** Disregard the air:  $C = 1$ ,  $f = 2$  and therefore  $D = 1$ . The liquid has an equilibrium vapor pressure which is a function of temperature. One can pick either the vapor pressure *or* the temperature independently, but not both.

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### Single Component Phase Equilibria

When there is only one degree of freedom in a single component phase diagram, it was shown above that there must be a relation between  $dP$  and  $dT$  for the system to remain in two phase equilibrium. Such a relation can be derived as follows:

$$\begin{aligned}
 0 &= S^{\text{liquid}} dT - V^{\text{liquid}} dP \\
 0 &= S^{\text{solid}} dT - V^{\text{solid}} dP \\
 \Rightarrow \left. \frac{dP}{dT} \right|_{\text{equilibrium}} &= \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T_{\text{eq.}} \Delta V}
 \end{aligned} \tag{26-2}$$

Equation 26-2 is the famous Clausius-Clapeyron equation.

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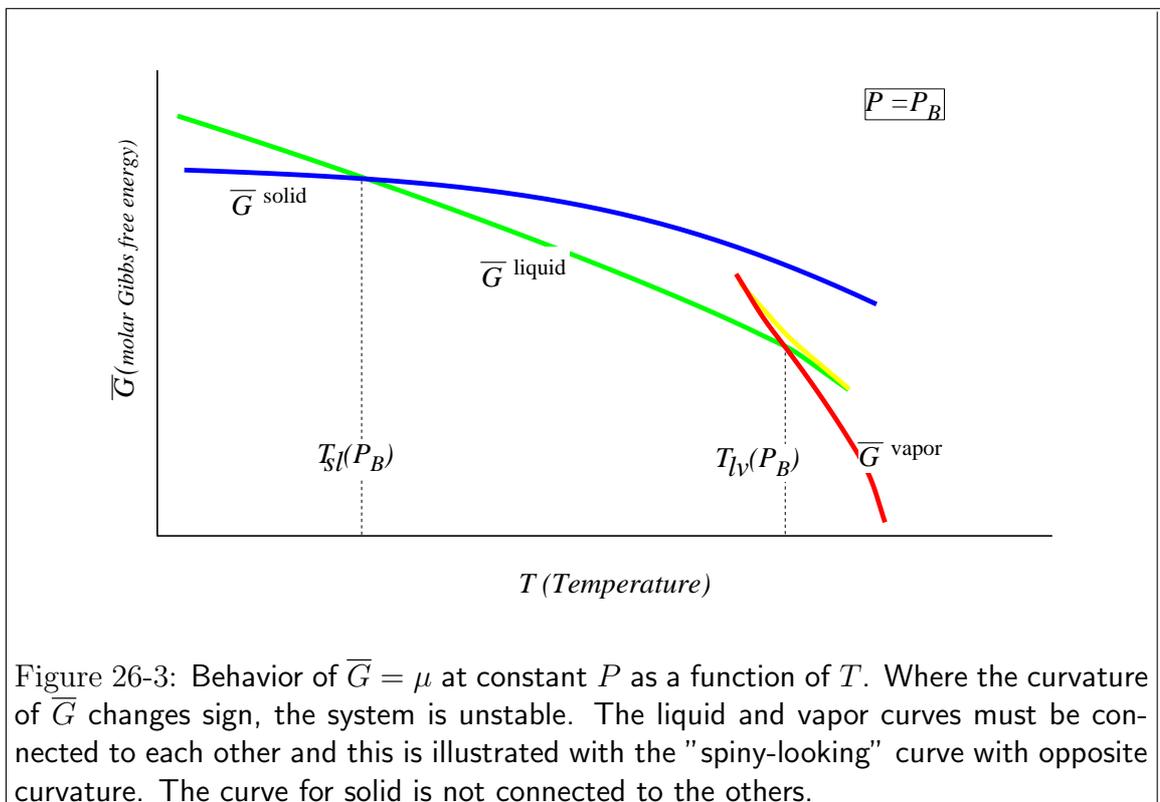
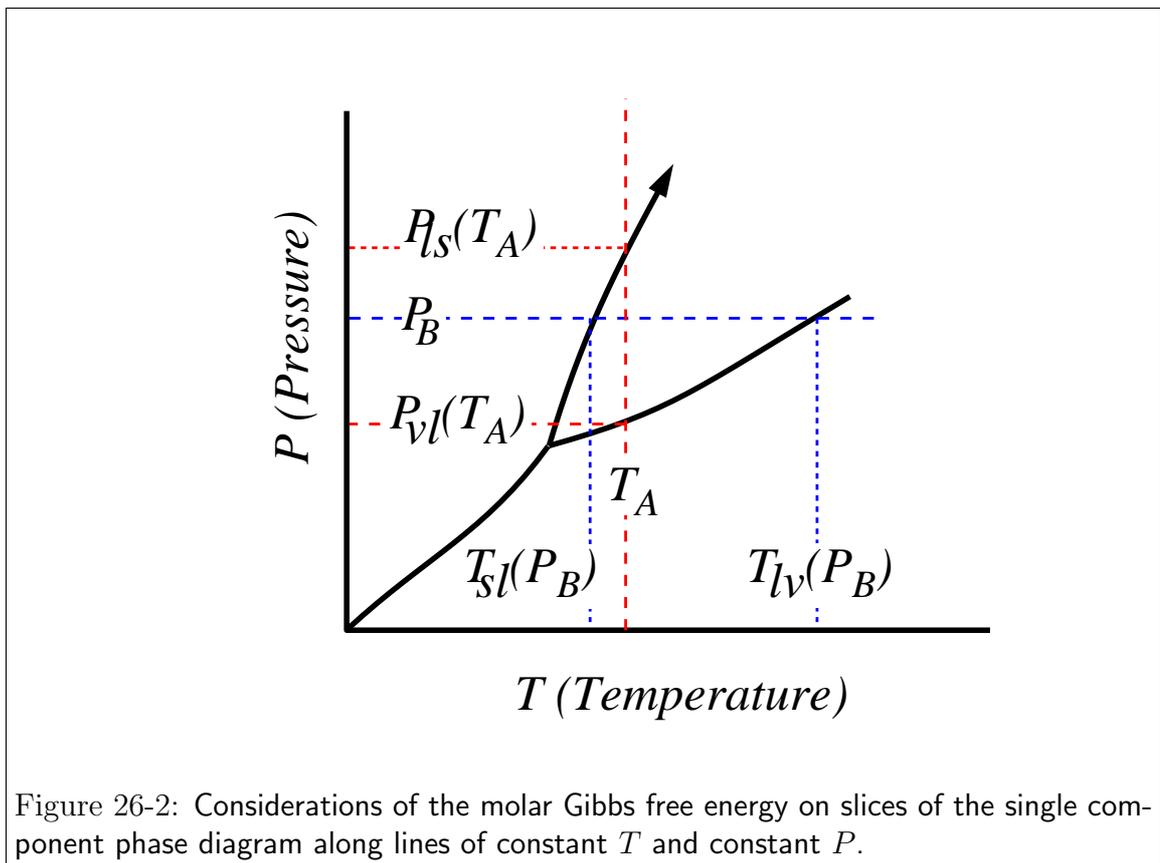


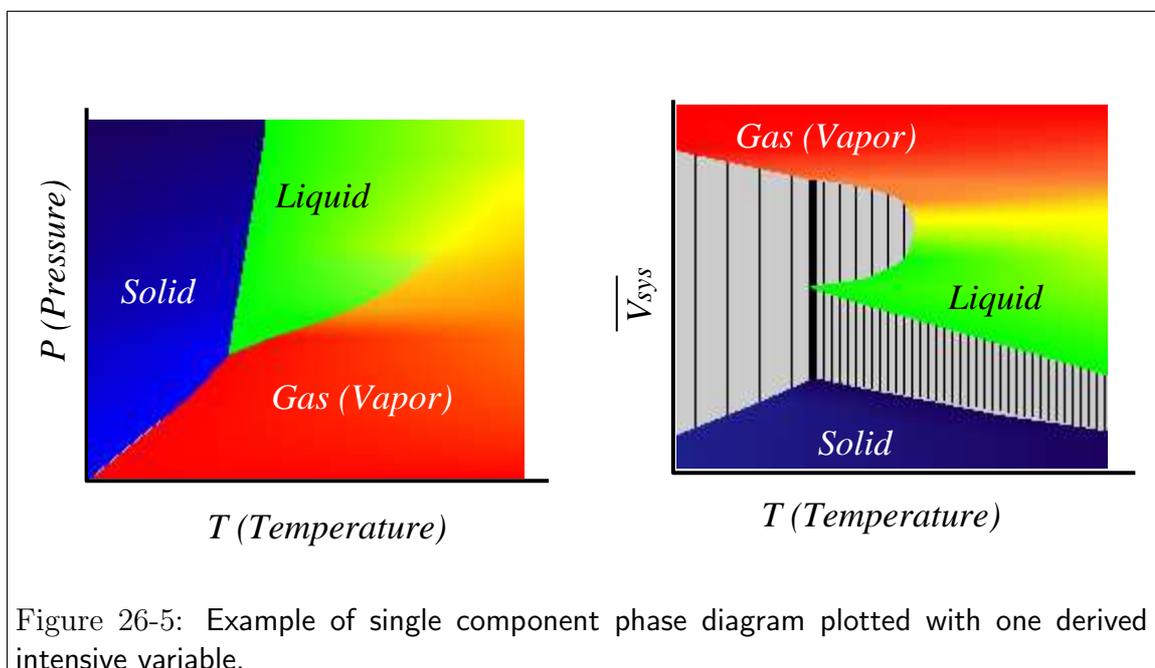
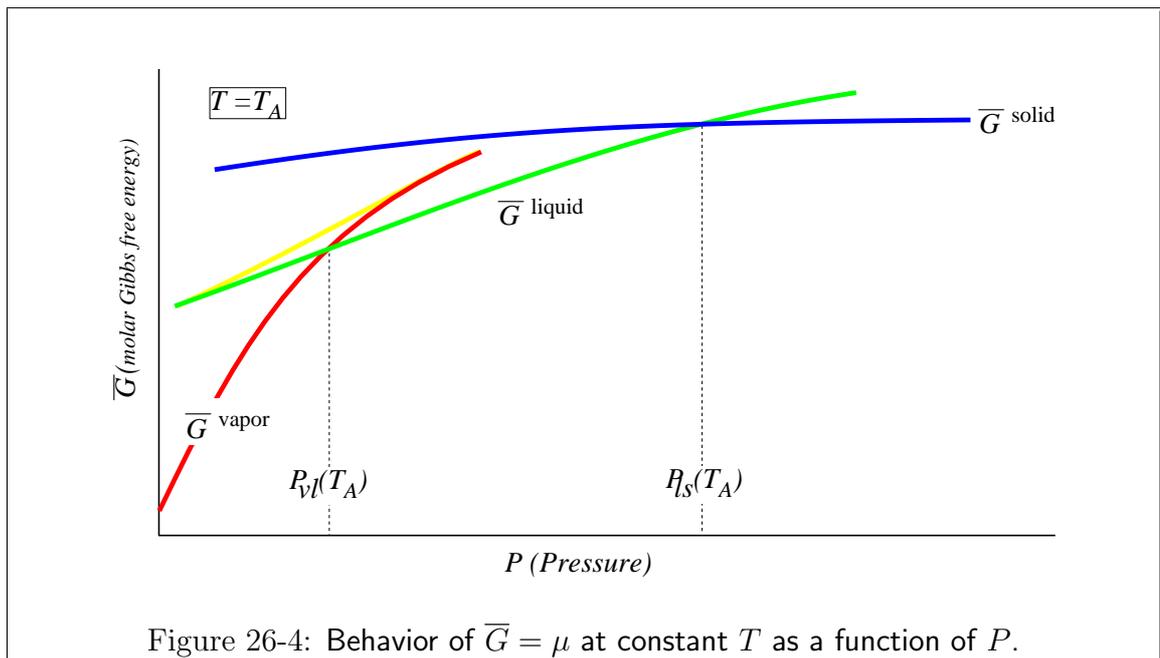
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Consider the behavior of the molar free energy (or  $\mu$ ) on slices of Figure 26-1 at constant  $P$  and  $T$ :





What would the plot look like with two extensive variables plotted?