

## Phase diagrams

for a pure substance  $C=1$ , and The G.F.E is:

$$F = 3 - P \quad \begin{cases} \rightarrow P=1 \Rightarrow F=2 & P(v, T) \text{ surface} \\ \rightarrow P=2 \Rightarrow F=1 & P(T) \text{ line} \\ \rightarrow P=3 \Rightarrow F=0 & P_0 \text{ triple point} \end{cases}$$

so on a 3-D plot of  $(P, v, T)$  for a substance you have:

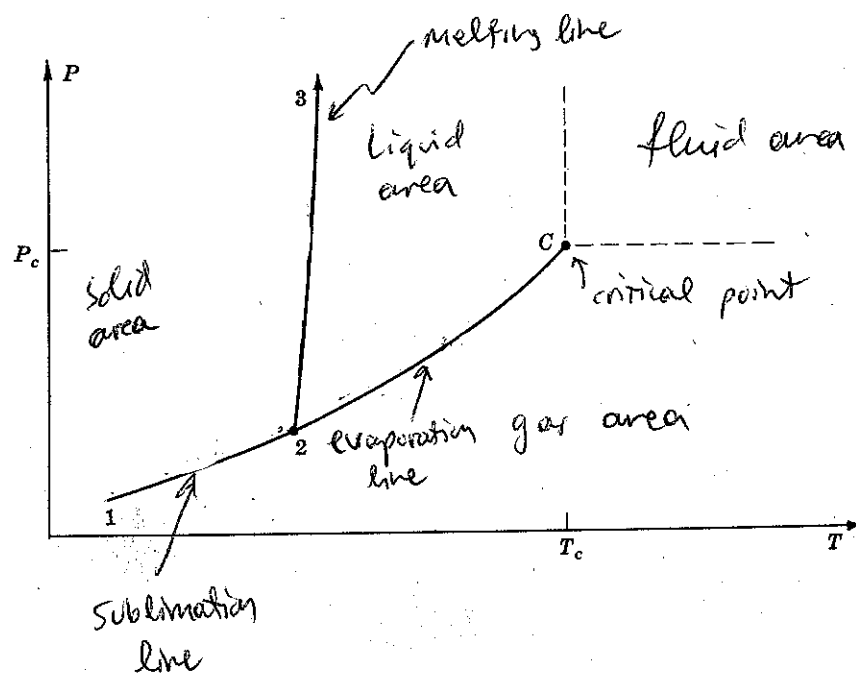
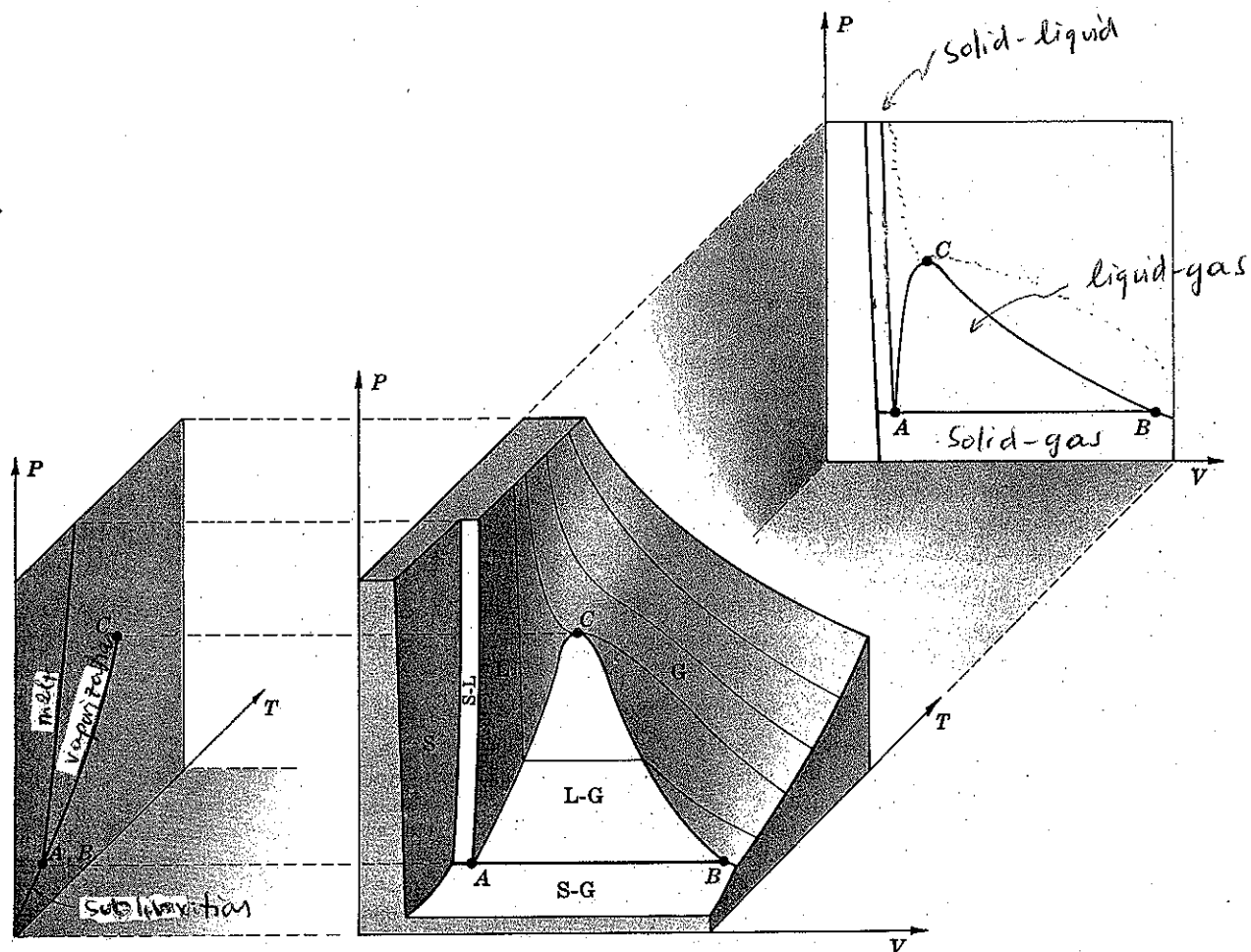
- a) areas of one phase  $\Rightarrow$  surface e.g.  $P(v, T)$
- b) areas of 2 phases  $\Rightarrow$  lines (curves) e.g.  $P(v)$   
 $P(T)$
- c) areas of 3 phases  $\Rightarrow$  point.

Give out handouts of the PVT surface.

Shaded Surfaces S, L, G represent Solid, Liquid and gaseous regions.

Non-shaded (S-G), (S-L) and (L-G) represent regions of equilibrium between solid + gas, solid + liquid and liquid and gas.

Line that goes through A, B corresponds to a point where (S-G), (S-L), (L-G) all meet and is equilibrium between 3 phases. That is the critical point.



Lines of constant  $T$  (isotherms) pass thru (L-G) region until a certain point beyond which there is no (L-G) region. That is characterized by a  $(\bar{P}_c, \bar{T}_c, \bar{V}_c)$  and it is called critical point.

When  $P > P_c$   
 $T > T_c$  }  $\Rightarrow$  you cannot have equilibrium between liquid and gas, we have the potential of forming a liquid.

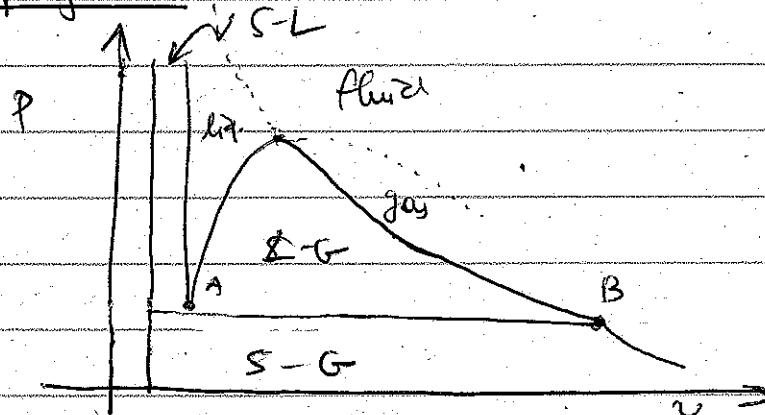
This is called "fluid" region.

when  $P < P_c$   
 $T > T_c$  } you have a gas that can condense if  $T \downarrow$

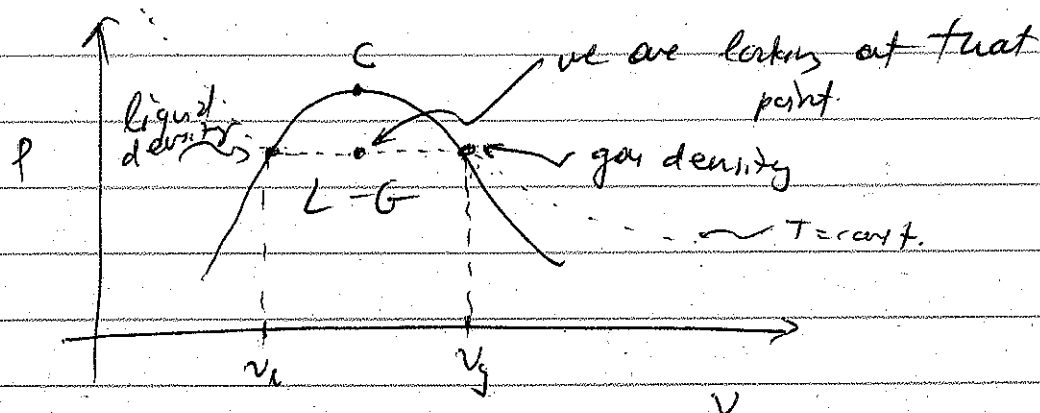
when  $T < T_c$   
 $P > P_c$  } you can have a fluid or a liquid if  $P \downarrow$

It is hard to deal with 3-D surfaces, so we can work with projections.

$\rightarrow$  P-V projections:



For example, when you are in a L-G region, the two phases have a density that we can calculate as:



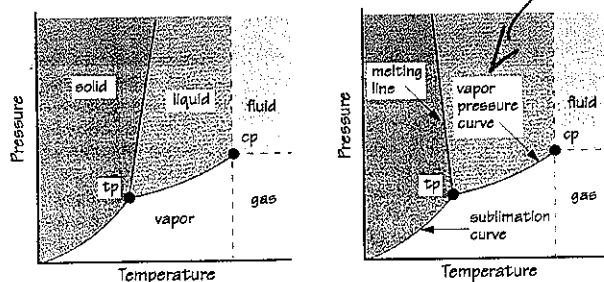
So, if we add a certain amount of mass of (water) into a vessel of volume  $V$  and under pressure  $P$ , then the system will separate into two phases with density  $v_l$  and  $v_g$ .

At critical point  $v_l = v_g$  i.e. they are indistinguishable. A mathematical way of defining C.P. is by the fact that it is an inflection point:

$$\left( \frac{\partial P}{\partial V} \right)_{T=\text{crit}} = 0 \quad \text{and} \quad \left( \frac{\partial^2 P}{\partial V^2} \right)_{T=\text{crit}} = 0$$

→ At conditions  $P \gg P_c$ ,  $T \gg T_c$  the isotherm approach  $P \sim \frac{1}{V}$  what is this?  
(ideal gas law)

## P-T projections:



**Figure 5.1** Schematic PT projections from the three-dimensional  $P$ - $T$  surfaces shown in the previous lecture. That on the left is from Figure 4.2; it applies to a material that expands on melting (its melting line has a positive slope). That on the right is from Figure 4.3; it applies to a material (such as water) that contracts on melting (its melting line has a negative slope). The SLV triple point is marked  $tp$  and the gas-liquid critical point is marked  $cp$ . Slopes of melting lines are exaggerated; on the scales of these plots, both melting lines would appear nearly vertical.

→ Point out regions of twophase coexistence and lines, and where the 3 phases "match" are at the triple point.

→  $P$ - $T$  is better for representing regions of  $(P, T)$  for phases → it is also good because we can then relate more easily to G.F. Energy.

## Phase changes

If we fix  $P$ , and heat a condensed phase, then  $T$  will change (why? because from G. Phase rule  $F=2$ , fixing  $P$  s.t.  $U$  gives us  $F=1$ , so  $T$  will change) until you have a phase change (e.g. solid starts melting).

Then, during the melting process,  $T$  will not change (why? look at G. Phase rule)

but heat is still added to system to melt the stuff. (why? where does heat go?). During this change entropy and specific volume changes.

The enthalpy change during the is a characteristic property and is called latent heat of (phase transition)  $L$

Sublimation/  
deposition  
(S-G)      evaporation  
or condensation  
(L-G)

fusion,  
freezing,  
melting  
(S-L)

Q: Which one is larger?

(consider density as a measure of internal energy)

→ when  $\rho = \rho_s$ , intra-molecular distances are small

↓ → add heat,  $L_{\text{fusion}}$

→ you "break" up a bit the interactions between molecules, so they move more freely.  $\rho = \rho_l$  (in general  $\rho_l < \rho_s$ )

↓ → add more heat

→ you "free" the molecules from each other, so they can go anywhere (i.e., gas). In that case  $\rho$  really drops, so you need to add alot of heat

A:  $L_{\text{melt}} < L_{\text{evap}} < L_{\text{subl}} (= L_{\text{melt}} + L_{\text{evap}})$

There is an entropy change as well:

$$\Delta S_{\text{phase change}} = \frac{L}{T_{\text{phase change}}}$$

Q: is disorder picture consistent with  $\Delta S$  sign?

A: Let them answer.

### Calculation of phase change properties

When two phases can co-exist, that means they are in chemical equilibrium:

$$G_1 = G_2 \Rightarrow dg_1 = dg_2 \quad \text{when we impose a change in } P \text{ or } T \text{ but still in the two phase region}$$

but:

$$\left. \begin{aligned} dg_1 &= -S_1 dT + V_1 dP \\ dg_2 &= -S_2 dT + V_2 dP \end{aligned} \right\} dg_1 = dg_2$$

$$-S_1 dT + S_2 dT = V_2 dP - V_1 dP \Rightarrow$$

$$\Rightarrow \frac{dP}{dT} = \left( \frac{S_2 - S_1}{V_2 - V_1} \right)$$

$$\left. \begin{aligned} \text{but } S_2 - S_1 \text{ is } \Delta S \text{ of phase change} &= \\ &= \frac{L}{T_{\text{phase change}}} \end{aligned} \right\}$$

$$\rightarrow \frac{dp}{dT} = \frac{L}{T} \cdot \frac{1}{(v_2 - v_1)} \quad (1)$$

also known as "Clapeyron eqn!"  
important. works for any phase change

→ Example: How does the melting temperature change with pressure (application: deep earth):

from (1):

$$\frac{dT_{\text{melt}}}{dp} = \frac{T_{\text{melt}}}{L_{\text{melt}}} \cdot (V_{\text{liquid}} - V_{\text{solid}})$$

for water, because  $V_{\text{liquid}} < V_{\text{solid}}$  that means  $\frac{dT_{\text{melt}}}{dp} < 0$  so melting T decreases with p.

→ Example: vapor-liquid equilibrium.

$$\frac{dp}{dT} = \frac{L}{T} \cdot \frac{1}{(v_{\text{gas}} - v_{\text{liquid}})}$$

but  $v_{\text{gas}} \gg v_{\text{liquid}}$

Pressure of ~~liquid~~ gas in equilibrium with liquid = vapor pressure

$$\Rightarrow \frac{dp}{dT} = \frac{L}{T_{\text{gas}}} \cdot \frac{1}{v_{\text{gas}}}$$

assuming gas behaves as ideal  $v = \frac{RT}{p}$



$$\Rightarrow \frac{dp^{\text{sat}}}{dT} = \frac{L_{\text{vap}} P}{R_{\text{vap}} T^2} \quad \text{Clausius - Clapeyron relationship} \quad (2)$$

$\uparrow$   
 specific gas const.

Example: How does boiling  $T$  change with pressure?  $T_{\text{boiling}}$  is when  $p^{\text{sat}} = P_{\text{atmosphere}}$   
 From (2), so  $dp^{\text{sat}} = dp_{\text{atmosphere}}$

$$\frac{dT_{\text{boiling}}}{dp} = \left( \frac{RT_{\text{boiling}}^2}{L_{\text{vap}} P} \right)^{>0}$$

so  $dT$  is in same direction of  $dp$  } so as  $p \downarrow$   $T_{\text{boiling}} \downarrow$

$\rightarrow$  If  $L_{\text{vaporization}} \neq f(T)$  then eq. 2 can be integrated between  $T_1, T_2$ :

$$\int_{p^{\text{sat}}(T_1)}^{p^{\text{sat}}(T_2)} dp^{\text{sat}} = \int_{T_1}^{T_2} \frac{L_{\text{vap}}}{R_v T^2} dT \quad \Rightarrow$$

$$\Rightarrow \ln \frac{P^{\text{sat}}(T_2)}{P^{\text{sat}}(T_1)} = - \frac{L}{R_v} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

assumptions: -  $U_g \gg U_l$   
 - ideal gas  
 -  $L = \text{const.}$

derive the sublimation vapor pressure curve  
(just like before)

Relative humidity RH:

$$\left( \frac{p_{\text{water vapor}}}{p_{\text{sat water vapor}}} \right) \times 100\% \rightarrow \begin{aligned} &100\% \Rightarrow p_{\text{vapor}} = p^{\text{sat}} \\ &50\% \Rightarrow p_{\text{vapor}} = 0.5 p^{\text{sat}} \end{aligned}$$

$$0\% \Rightarrow p_{\text{vapor}} = 0$$