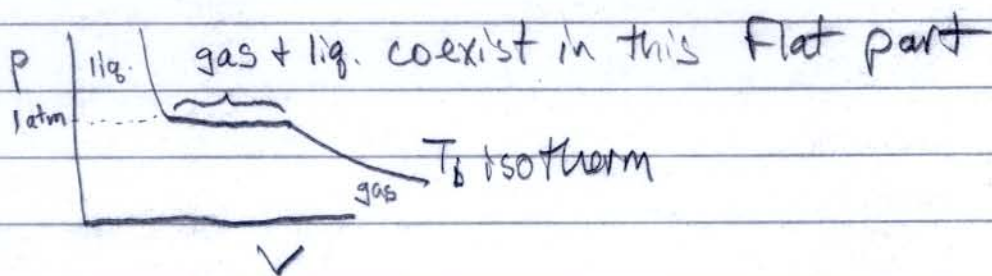
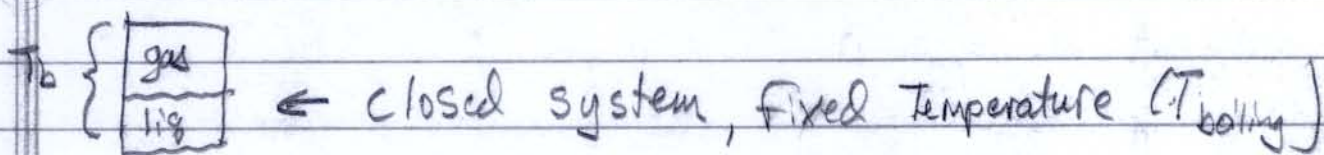


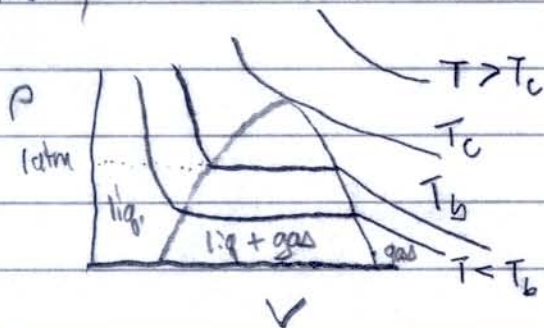
Chapter 7

7.1

First, let's work out the gas-liquid equilibrium:

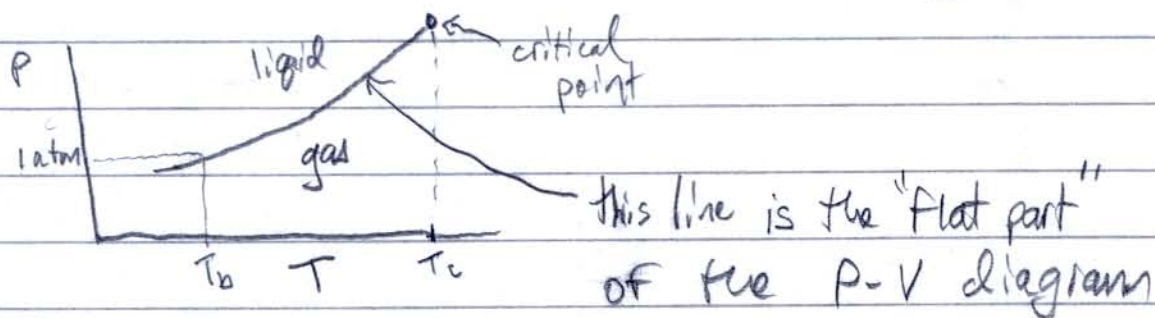


Now, let's consider other isotherms



Main point: after T_c there is no flat part
→ no difference between gas and liquid!

How does this look on a P vs T diagram?



Why is there only one line in the P-T diagram where gas and liquid coexist?

Answer: consider the chemical potential!

set up the chemical reaction: $\text{gas} \rightleftharpoons \text{liquid}$

At equilibrium, when gas + liquid coexist, the chemical potentials of products + reactants must be equal ($\Delta G_{\text{rxn}} = 0$, $A = 0$)

↑ Affinity

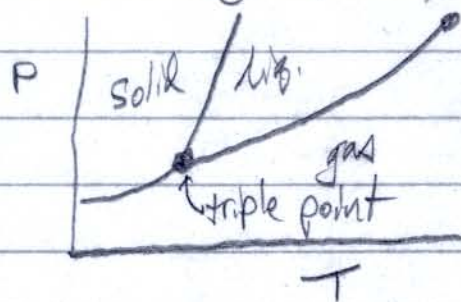
But chemical potential, μ , is a function of P + T

$$\text{so: } \mu_{\text{liq}}(P, T) = \mu_{\text{gas}}(P, T)$$

this is like when $z(x, y) = w(x, y)$

where z + w are surfaces above the x, y plane
 \rightarrow they intersect along a line!

By the same logic, the intersection of 3 surfaces is a single point, i.e. the triple point:



Since P & T are dependent when $\mu_{\text{liq}} = \mu_{\text{gas}}$
 we can find the equation that relate them;

$$\mu_{\text{liq}} = \mu_{\text{gas}}$$

$$\bar{G}_{\text{liq}} = \bar{G}_{\text{gas}} \quad \leftarrow \bar{\mu} \text{ is molar Gibb Energy}$$

$$-\bar{S}_{\text{liq}} dT + \bar{V}_{\text{liq}} dP = -\bar{S}_{\text{gas}} dT + \bar{V}_{\text{gas}} dP \quad \leftarrow \text{fund, Eq}$$

$$(\bar{V}_{\text{liq}} - \bar{V}_{\text{gas}}) dP = (\bar{S}_{\text{liq}} - \bar{S}_{\text{gas}}) dT \quad \leftarrow \text{group } dP \text{ + } dT \text{ terms}$$

$$\frac{dP}{dT} = \frac{\bar{S}_{\text{liq}} - \bar{S}_{\text{gas}}}{\bar{V}_{\text{liq}} - \bar{V}_{\text{gas}}} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \quad \leftarrow \begin{array}{l} \text{divide by } dT \\ \text{divide by } (\bar{V}_{\text{liq}} - \bar{V}_{\text{gas}}) \end{array}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap, melt}}}{T_m \Delta \bar{V}_{\text{vap, melt}}} \quad \leftarrow \Delta S = \frac{\Delta H}{T} \text{ @ const. } T}$$

(i.e., for any phase change, eg melting)

$$\int_{P_1}^{P_2} dP = \int_{T_m(P_1)}^{T_m(P_2)} \frac{\Delta \bar{H}_{\text{melt}}}{T_m \Delta \bar{V}_{\text{melt}}} dT \quad \leftarrow \text{set up integral for melting: solid} \rightarrow \text{liq}$$

$$\Delta P = \frac{\Delta \bar{H}_{\text{melt}}}{\Delta \bar{V}_{\text{melt}}} \ln \left(\frac{T_m(P_2)}{T_m(P_1)} \right) \quad \leftarrow \text{integrate}$$

$$\Delta P \approx \frac{\Delta \bar{H}_{\text{melt}}}{\Delta \bar{V}_{\text{melt}}} \frac{\Delta T_{(P_2-P_1)}}{T_m} \quad \leftarrow \text{since } T_m(P_2) \approx T_m(P_1) \text{ (} \ln a/b \approx a-b/b \text{ for } a \approx b \text{)}$$

for vaporization this approximation doesn't hold
 so we leave the Clapeyron Eq. in this form:
 or we obtain the Clausius-Clapeyron Eq. (next page)

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{T \Delta \bar{V}_{\text{vap}}}$$

← Clapeyron Eq
liq → gas

$$\approx \frac{\Delta \bar{H}_{\text{vap}}}{T \bar{V}_{\text{gas}}}$$

← all volume change
is due to gas phase

$$\frac{1}{P} \frac{dP}{dT} \approx \frac{\Delta \bar{H}_{\text{vap}}}{T(RT)}$$

← $\bar{V}_{\text{gas}} = RT/P$, multiply by $\frac{1}{P}$

$$\frac{d(\ln P)}{dT} \approx \frac{\Delta \bar{H}_{\text{vap}}}{RT^2}$$

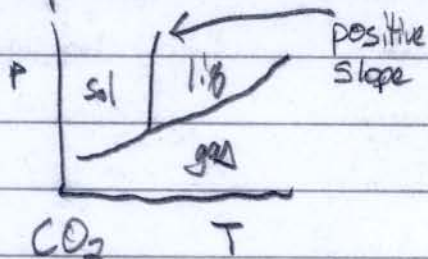
← $\frac{1}{P} dP = d(\ln P)$

$$\int_{P_1}^{P_2} d(\ln P) \approx \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} dT \quad \leftarrow \text{set up integral}$$

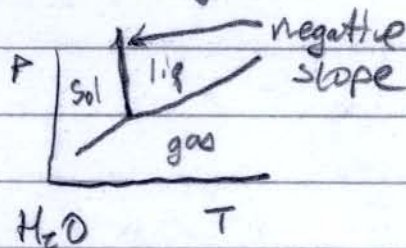
$$\ln P_2 - \ln P_1 \approx -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \leftarrow \text{integrate}$$

We'll use this Clausius - Clapeyron Eq for prob. 7.1

The derivative form (i.e. the Clapeyron eq) tells us the slope of the line in our phase diagrams:



or



The integrated form (i.e. the Clausius Clapeyron eq for gas → liq or the $\Delta P = \frac{\Delta \bar{H} \Delta T}{\Delta \bar{V} T}$ for solid → liq) is used to find the phase change Temp. or Pres. when ΔH is known,

What is the rules for coexistence when more than one component (e.g. molecule, atom) is involved?

We saw for 1 component, coexistence happen on a line for 2 phases and at a point for 3 phases.

In general, 2 variables are required to specify a 1-component syst with no constraints, (Pressure + Temp). Each new component needs 1 more variable, (mole fraction). Each new phase that must coexist reduces the number of variables by 1. So we have;

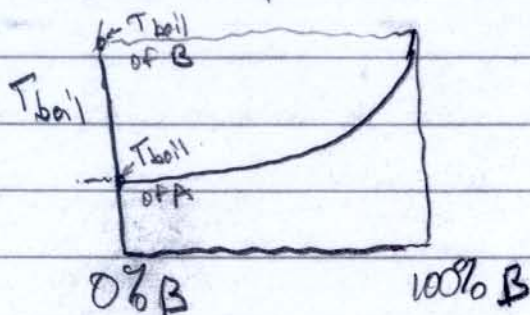
$$\# \text{ of variables} = 2 + C_{\text{new}} - P_{\text{new}}$$

but $C_{\text{new}} = C_{\text{Total}} + 1$ and $P_{\text{new}} = P_{\text{Total}} + 1$ SO:

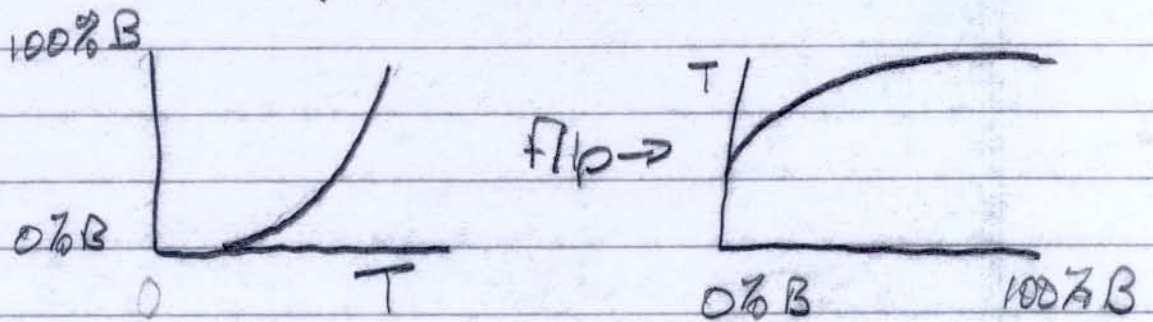
$$\# \text{ of variables} = C_{\text{Total}} - P_{\text{Total}} + 2$$

For an ideal mixture of 2 components that are in 2 phases (vapor + liquid) we need $2 - 2 + 2 = 2$ variables, which are the pressure and the mole fraction.

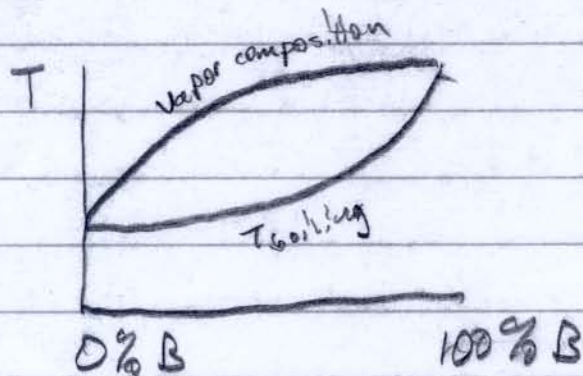
at constant pressure we can graph T_{boil} vs mole fraction



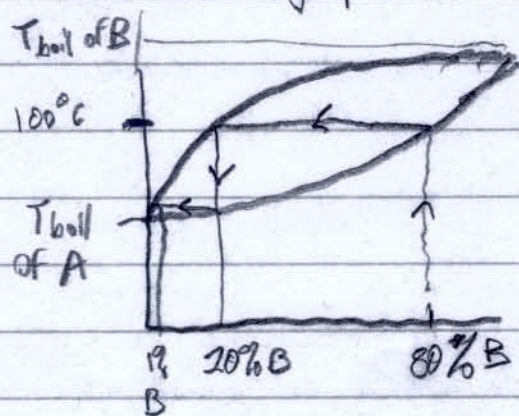
We can also graph Vapor composition as a function of T



combining the two graphs



This combined graph shows how distillation works



an 80% solution of B
boils at 100°C , the vapor
phase is enriched in A
(it has a lower boiling point)
when the vapor condenses
it is only 20% B!

Repeat this process to get pure A \rightarrow except when
you hit an azeotrope.