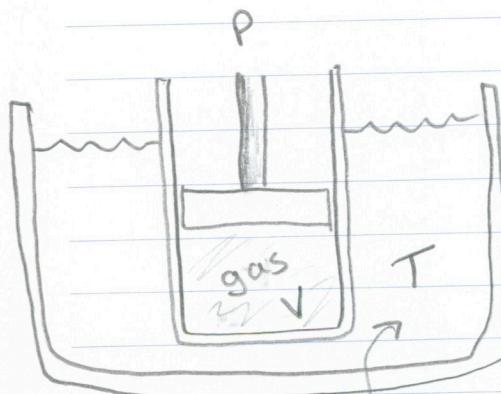


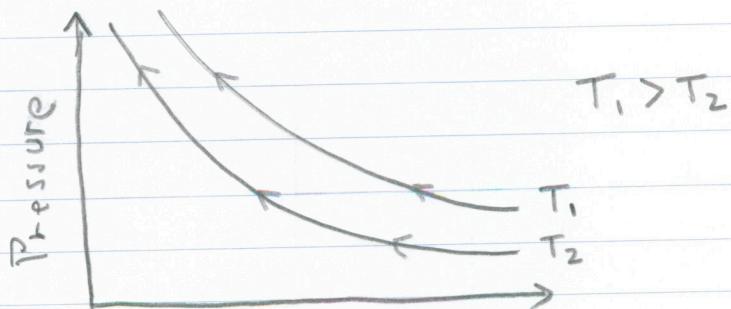
Gas/Liquid Phase Transition



const.
tempetative
bath.

Experiment

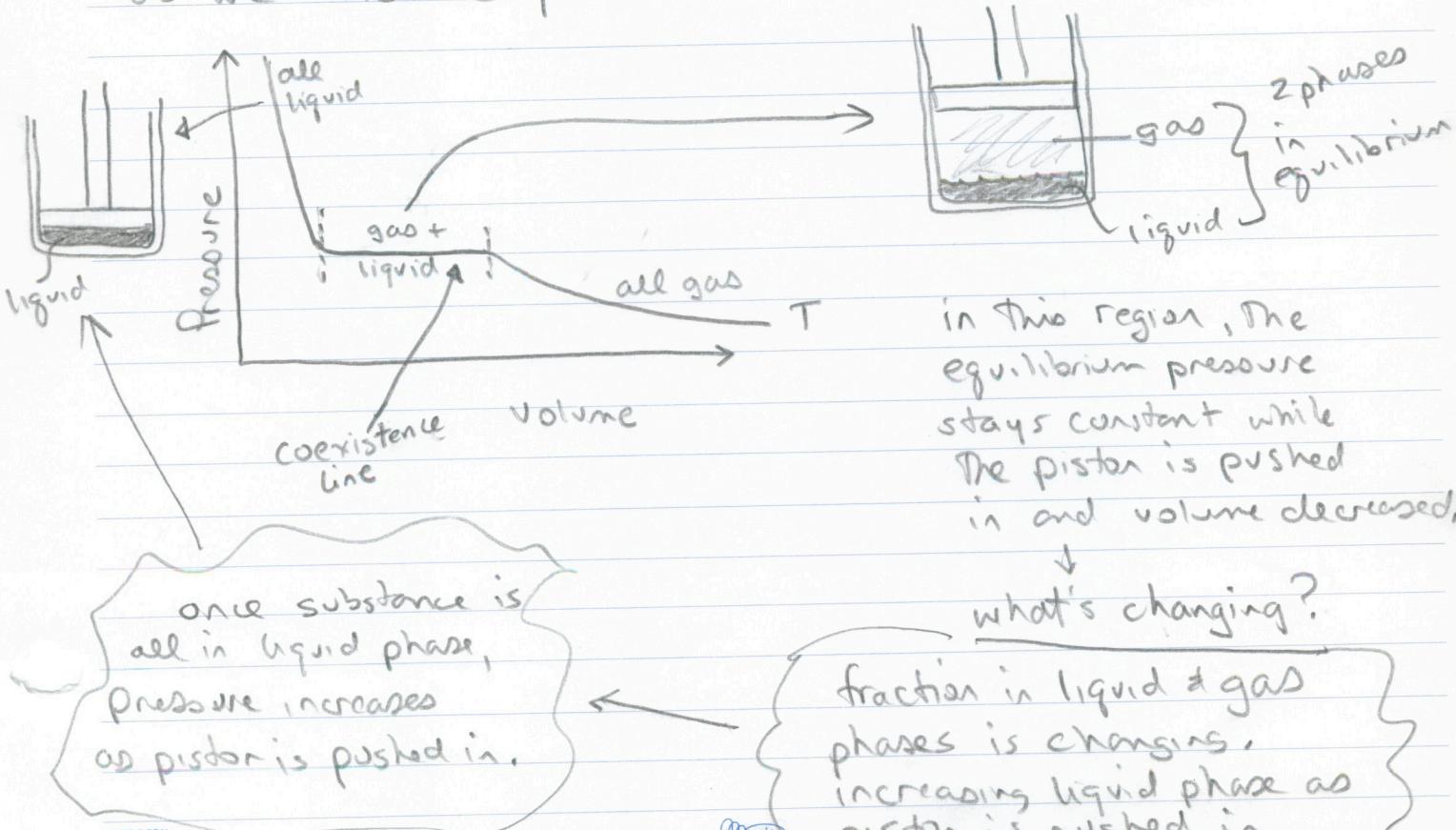
- (1) hold temperature constant
- (2) Push in Piston, measure equilibrium Pressure & Volume



Classic "Boyle's Law" Volume

when substance is always in the gas phase.

What does curve look like if gas condenses into liquid as we increase pressure?

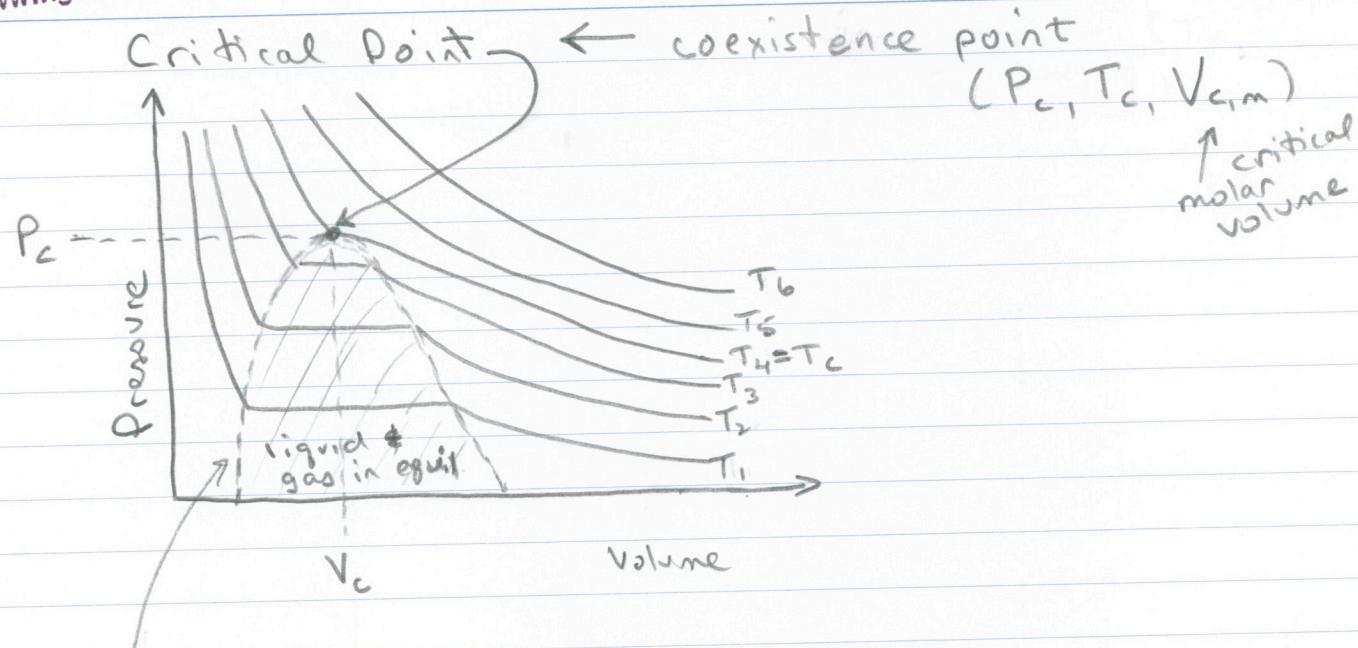


in this region, the equilibrium pressure stays constant while the piston is pushed in and volume decreased.

what's changing?

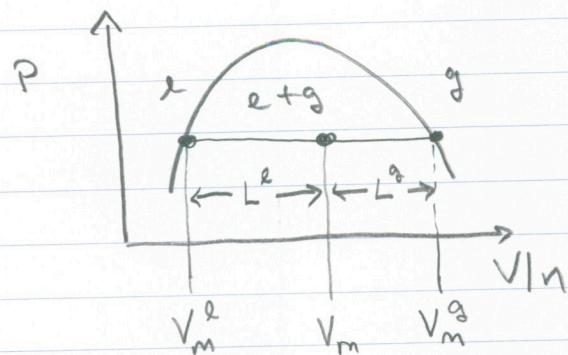
fraction in liquid & gas phases is changing, increasing liquid phase as piston is pushed in.

once substance is all in liquid phase, pressure increases as piston is pushed in.



co-existence curve

Lever Rule - determines fraction of system that exists in each of the 2 phases



$$V = n V_m = n [x_e V_m^L + x_g V_m^g]$$

$$x_e + x_g = 1$$

↑ ↑
mole fractions of liquid & gas

$$x_e = \frac{L^L}{L^g + L^L} \quad x_g = \frac{L^g}{L^g + L^L}$$

or

$$\boxed{x_e L^L = x_g L^g}$$

Lever Rule

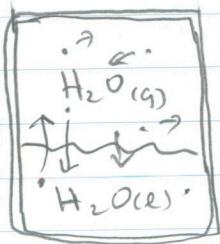
When both gas and liquid coexist at equilibrium the rate of evaporation and condensation are equal.

rate of
evaporation

= rate of
condensation

in a closed
container

for example
when H_2O
vapor and
liquid are
in equilibrium

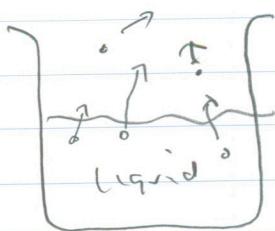


Vapor Pressure = pressure exerted by vapor in thermodynamic equilibrium with its condensed (liquid or solid) phase,

Volatility - tendency of a substance to vaporize.

When intermolecular attractive forces are strong, the liquid (or solid) is less volatile.

In an open container the liquid simply evaporates.



The vapor pressure of the liquid increases with temperature.

When the liquid vapor pressure is equal to the (external) atmospheric pressure the liquid will boil.

Physical Equilibria

Let's go back to the 1st law of Thermodynamics

$$dU = dg + dw$$

which can be combined with the 2nd law to give

$$dU = Tds - pdV$$

for a closed system.

We also learned that U is an extensive property; it depends linearly on the amount of a substance.

so we can write

$$dU = Tds - pdV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

The rate that U changes as amount is increased is called the chemical potential, and is given the symbol

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

on close examination of the dU expression one could also define

$$T = \left(\frac{\partial U}{\partial S}\right)_{n,V} \quad \text{and} \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,n}$$

Remember the three types of equilibrium?

- ① Mechanical, ② Thermal, ③ Materials

~~required~~ ↑
uniform pressure

~~required~~ ↑
uniform temperature

~~source~~ ↑
uniform chemical potential

Similarly, we could start with

$$dG = -SdT + Vdp \quad \text{closed system}$$

and G is an extensive property, write

$$dG = -SdT + Vdp + \left(\frac{\partial G}{\partial n}\right)_{T,p} dn$$

The rate of change with amount is also
the chemical potential

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$$

For a pure substance in a single phase, for example, pure liquid H_2O or pure solid copper, the chemical potential is, by definition, the molar energy ...

$$G^*(p,T) = n \underset{P}{G}_m^*(p,T)$$

means pure substance

molar Gibbs free energy at p and T .

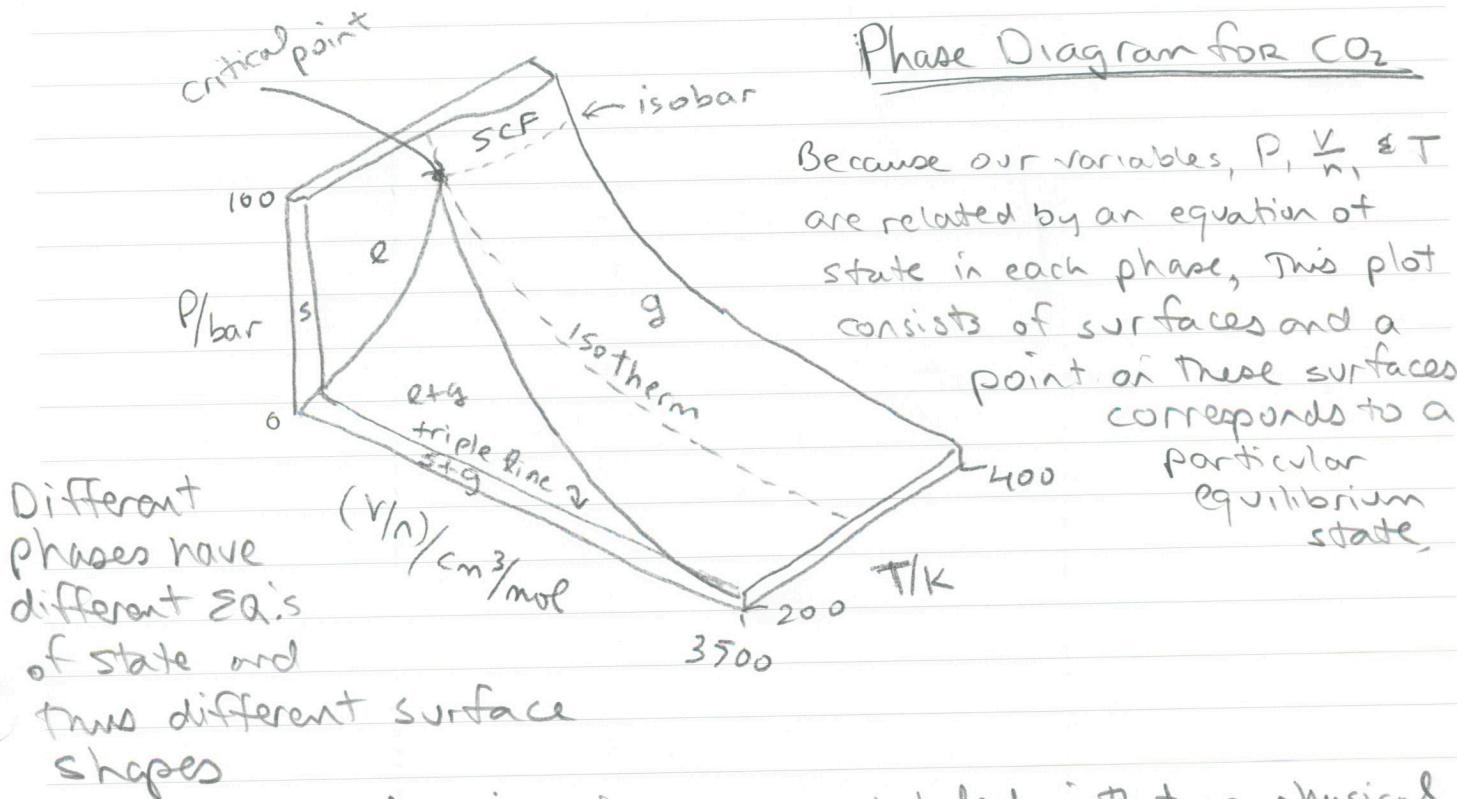
Gibbs Free energy for n moles at $p \neq T$

$$\text{so } \mu^* = \left(\frac{\partial G^*}{\partial n}\right)_{p,T} = G_m^*(p,T)$$

Warning: The chemical potential of each substance in a mixture, μ_i , is not equal to the chemical potential, μ_i^* , of the pure substance.

Phase Diagram of Pure Substances

For a pure substance at equilibrium we can make a 3 dimensional plot as a function of P , V/n , & T .



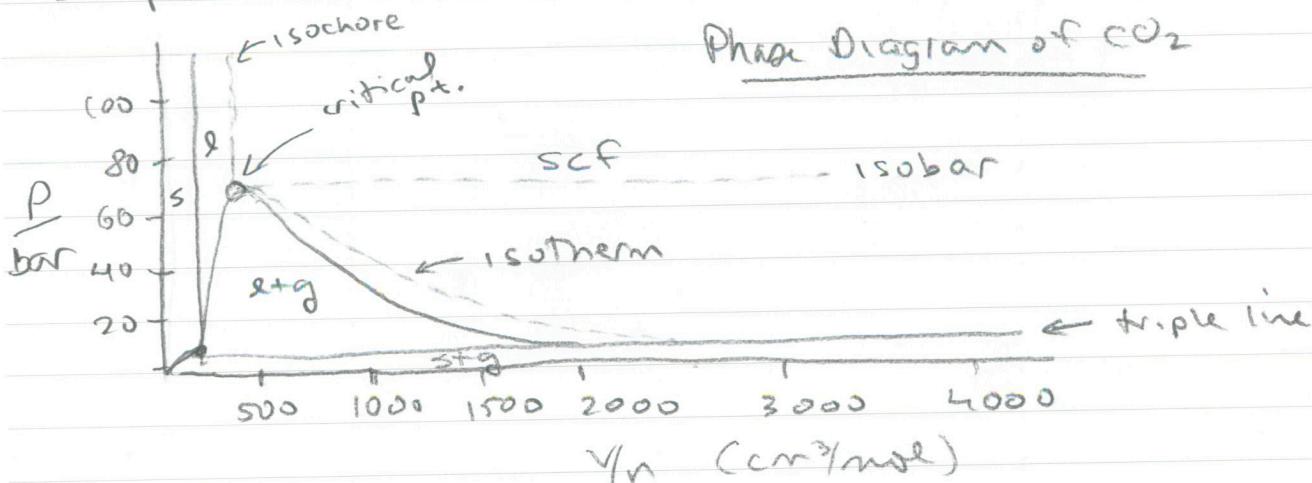
Phase Diagram for CO₂

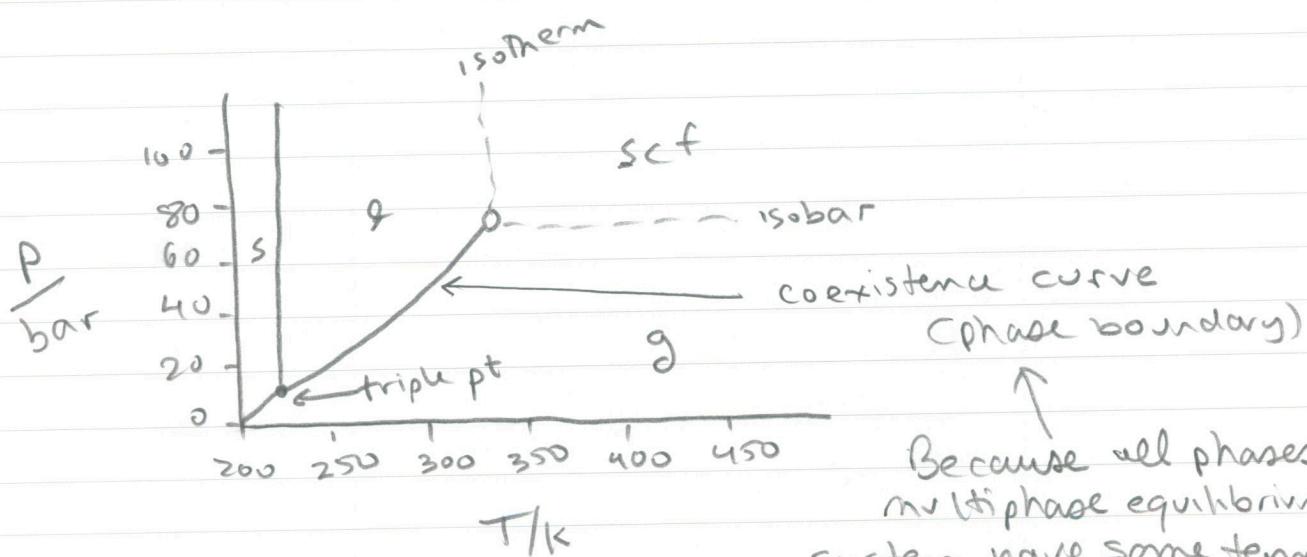
Because our variables, P , $\frac{V}{n}$, & T are related by an equation of state in each phase, this plot consists of surfaces and a point on these surfaces corresponds to a particular equilibrium state.

A point in an area labeled with two physical states corresponds to two coexisting phases.

A triple line is the locus of points for all possible equilibrium systems of 3 coexisting phases.

3D plots are hard to draw, so we use 2D projections





Because all phases of a multiphase equilibrium system have some temperature and pressure, the projection of each 2-phase area onto the pressure-temperature diagram is called a coexistence curve.

Let's apply the machinery of Thermodynamics to understand coexistence curves

Vaporization ($l \rightarrow g$)

$\Delta_{\text{vap}} H$

} enthalpy change for reversible

Sublimation ($s \rightarrow g$)

$\Delta_{\text{sub}} H$

} process at $P \& T$ in which 2 phases

Fusion ($s \rightarrow l$)

$\Delta_{\text{fus}} H$

} coexist at equilibrium

$$\Delta_{\text{vap}} H_m = H_m^g - H_m^l$$

intensive property of 2 phases at equilibrium, depends one intensive parameter (T or P).

all positive quantities change sign for reverse process.

remember that the chemical potential of a pure substance in phase α is just the molar Gibbs free energy $\mu^\alpha = \frac{G^\alpha}{n} = G_m^\alpha$

and at transfer equilibrium $\mu^\alpha = \mu^\beta$ between phases $\alpha \neq \beta$

$$\text{so } \mu^\beta - \mu^\alpha = G_m^\beta - G_m^\alpha = \Delta_{\text{trs}} G_m = 0 \text{ at equilibrium}$$

ΔG_m for transition $\alpha \rightarrow \beta$ $\neq 0$ if $\alpha \neq \beta$

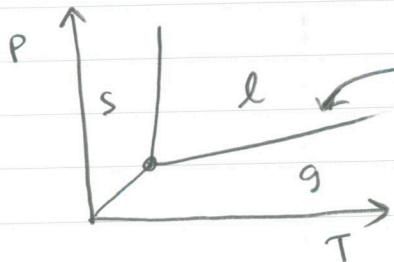
At the phase transition $\Delta_{trs} G_m = \Delta_{trs} H_m - T_{trs} \Delta_{trs} S_m = 0$

so

$$\Delta_{trs} S_m = \frac{\Delta_{trs} H_m}{T_{trs}}$$

we know this from earlier

Clapeyron EQUATION



What determines the slope of the coexistence curves in a phase diagram plot?

$$\frac{dp}{dT} = ?$$

On co-existence curve we know that $\mu^\alpha = \mu^\beta$
so it is also true that

$$d\mu^\alpha = d\mu^\beta$$

since we're considering a pure substance $d\mu^\alpha = dG_m^\alpha$
 $\& d\mu^\beta = dG_m^\beta$

then $dG_m^\alpha = dG_m^\beta$

becomes

$$-S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp$$

which rearranges to

$$S_m^\beta dT - S_m^\alpha dT = V_m^\beta dp - V_m^\alpha dp$$

$$(S_m^\beta - S_m^\alpha) dT = (V_m^\beta - V_m^\alpha) dp$$

which gives $\frac{dp}{dT} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha}$ or

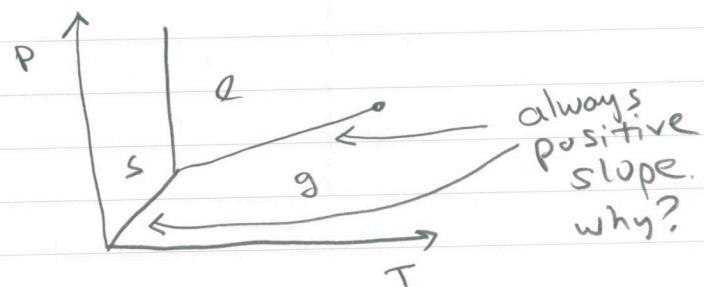
$$\frac{dp}{dT} = \frac{\Delta_{trs} S_m}{\Delta_{trs} V_m}$$

slope of
coexistence curve

Clapeyron EQ.

using $\Delta_{trs} S_m = \Delta_{trs} H_m / T_{trs}$
we get

$$\frac{dp}{dT} = \frac{\Delta_{trs} H_m}{T \Delta_{trs} V_m}$$



for $s \rightarrow g$ sublimation } both $\Delta_{trs} H_m$ & $\Delta_{trs} V_m$ are positive
 $\hookrightarrow g$ vaporization }

so $\frac{dp}{dT}$ is always positive along $s \rightarrow g$ & $l \rightarrow g$ curves

for $s \rightarrow l$ fusion, $\Delta_{fus} H_m$ is always positive
but $\Delta_{fus} V_m$ depends on substance.

what is sign of $\Delta_{fus} V_m = V_m^l - V_m^s$
for H_2O ?

MOST substances expand on melting, i.e., $V_m^s < V_m^l$,
so these substances have positive slope dp/dT curves.

exceptions with negative $\Delta_{fus} V_m$ & negative dp/dT

are H_2O , $RbNO_3$, Sn , Bi , Ga ← all expand on freezing

Variation of p with T is

$$dp = \frac{\Delta_{trs} H_m}{\Delta_{trs} V_m} \cdot \frac{dT}{T}$$

in case of fusion, $\Delta_{fus} V_m$ is relatively constant over small range
of p & T,

if $\Delta_{fus} H_m$ is independent of T, Then

$$P_2 - P_1 \approx \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \ln \frac{T_2}{T_1}$$

or

$$T_2 \approx T_1 \exp \left\{ \frac{\Delta_{fus} V_m (P_2 - P_1)}{\Delta_{fus} H_m} \right\}$$

melting point variation
w.r.t. pressure.

Clausius-Clapeyron EQ

Sublimation, Vaporization cases

for $s \rightarrow g$ or $l \rightarrow g$ transitions there is a large molar volume change. so large that...

$$\Delta_{\text{sub}} V_m = V_{m(g)} - V_{m(s)} \approx V_{m(g)}$$

$$\Delta_{\text{vap}} V_m = V_{m(g)} - V_{m(l)} \approx V_{m(g)}$$

$$\text{so } dp = \frac{\Delta_{\text{trs}} H_m}{V_{m(g)}} \cdot \frac{dT}{T}$$

and assuming $V_m \approx RT/p$ (ideal gas)
we get...

$$\frac{dp}{dT} \approx \frac{p \Delta_{\text{trs}} H_m}{RT^2}$$

Clausius-Clapeyron EQ.

With a little rearranging
this becomes

$$\frac{dp}{p} \approx \frac{\Delta_{\text{trs}} H_m}{R} \frac{dT}{T^2} = - \frac{\Delta_{\text{trs}} H_m}{R} d\left(\frac{1}{T}\right)$$

gives us an
approximate expression
for s/g & l/g coexistence

curves.

if $\Delta_{\text{sub}} H_m$ or $\Delta_{\text{vap}} H_m$ are constant over Temp. range

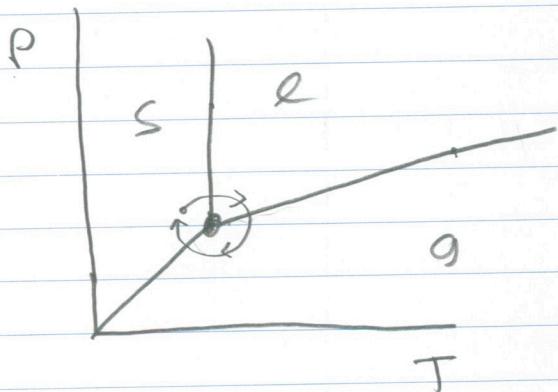
then

$$\ln \frac{P_2}{P_1} \approx - \frac{\Delta_{\text{trs}} H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

provides simple
way to get ΔH
without
calorimetry.

Finally, note that near triple point it is possible to go through all three phase transitions with little change in T and P.

Cyclic process around triple point



S \rightarrow R

L \rightarrow G

G \rightarrow S

$$\Delta_{\text{fus}} H_m + \Delta_{\text{vap}} H_m - \Delta_{\text{sub}} H_m = 0$$

(P)
always positive

$$\therefore \Delta_{\text{sub}} H_m = \Delta_{\text{fus}} H_m + \Delta_{\text{vap}} H_m$$

always positive
always the largest of the 3 $\Delta_{\text{trs}} H$'s

so slope of the S/G coexistence curve is always steeper than the L/G coexistence curve.

MIXTURES

Solution - mixture where one substance is the solvent and others are solutes

In Binary Solution A = solvent, B = solute

e.g. salt water; salt is solute
water is solvent

how much solute is dissolved in solvent?

Useful QUANTITIES

- mole fraction

$$x_B = \frac{n_B}{n_A + n_B}$$

↑ total # moles
solvent + solutes.

- amount concentration

$$c_B = \frac{n_B}{V}$$

↑ total volume
of solvent + solutes

- molarity

$$m_B = \frac{n_B}{n_A M_A}$$

↑ mass of solvent
↑ molar mass of solvent

Advantage of molarity is that it is independent of T and p, unlike amount concentration

Chemical Potential of Ideal gas

1st, let's look at the chemical potential of a pure ideal gas.

- for a fixed amount of a pure gas

$$dG^* = -SdT + Vdp$$

We can divide by n to get

$$d\mu^* = -S_m dT + V_m dp$$

↑ ↑
molar entropy molar volume

recall
 $\mu^* = \frac{G^*}{n}$
 for
 pure
 substance

at constant temperature we have

$$d\mu^* = V_m dp$$

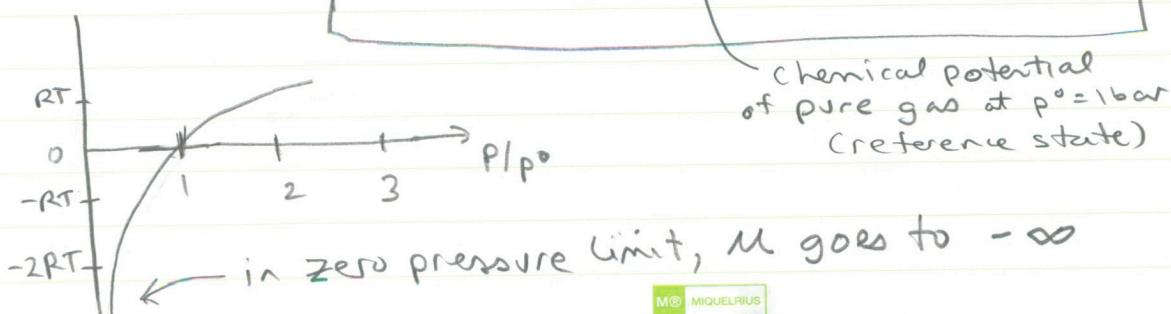
$$\text{for ideal gas } V_m = \frac{V}{n} = \frac{RT}{P}$$

$$\text{so } \int_{\mu_1^*}^{\mu_2^*} d\mu^* = RT \int_{P_1}^{P_2} \frac{dp}{P}$$

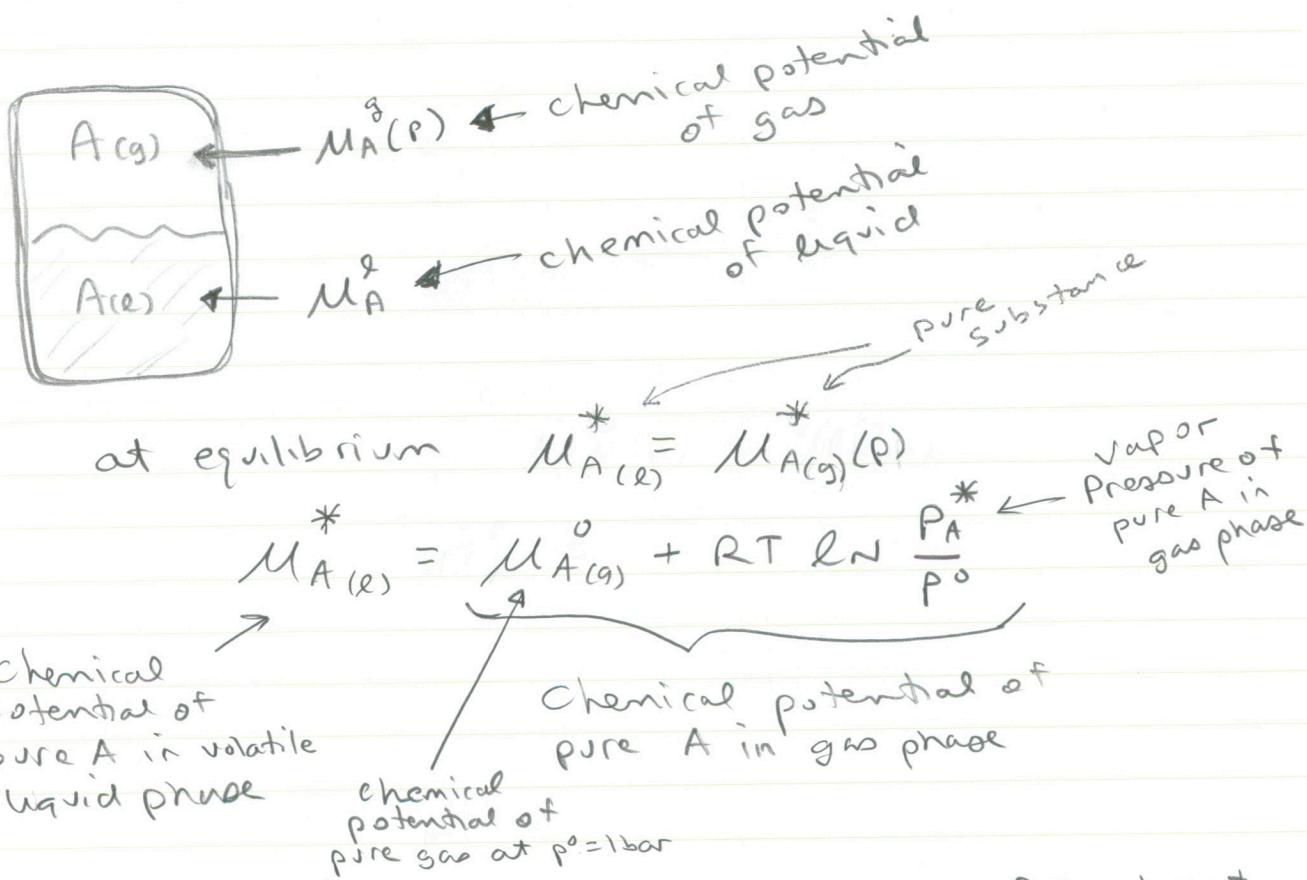
$$\text{and } \mu^*(T, P_1) - \mu^*(T_2, P_2) = RT \ln \left(\frac{P_2}{P_1} \right)$$

by convention, set $P_1 = P^o = 1 \text{ bar}$ ← standard pressure

& then $\mu^*(T) = \mu^o(T) + RT \ln \left(\frac{P}{P^o} \right)$

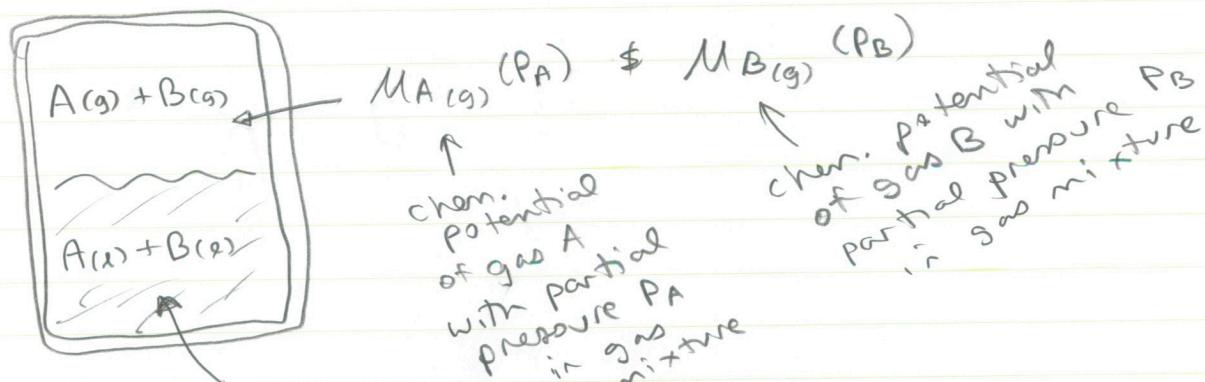


Gas and liquid in Equilibrium



Binary Mixture of Volatile liquids

$A \equiv \text{solvent}$
 $B \equiv \text{solute}$



$\mu_{A(l)} + \mu_{B(l)}$
chemical potentials of A + B in liquid mixture

at equilibrium $\mu_{A(l)} = \mu_{A(g)}(p_A)$

$\$ \quad \mu_{B(l)} = \mu_{B(g)}(p_B)$

Let's 1st focus on The solvent

It's 1st focus on The solvent

$$\mu_{A(l)} = \mu_{A(g)}^{\circ} + RT \ln \left(\frac{P_A}{P^{\circ}} \right)$$

↑ Partial pressure
of A in gas
mixture

↑ chemical potential
of Reference state

A in liquid
mixture

eliminate reference, $M_A^{(g)}$, with pure substance chem. pot.

$$U_A^*(e) = U_A^o(g) + RT \ln \left(\frac{P_A^*}{P_o} \right)$$

i.e.,

$$U_{A(e)} - RT \ln \left(\frac{P_A}{P_0} \right) = U_{A(e)}^* - RT \ln \left(\frac{P_A^*}{P_0} \right)$$

leads to

$$\mu_{A(l)} = \mu_{A(l)}^* + RT \ln \left(\frac{P_A}{P_A^*} \right)$$

↑ ↑

chemical potential of pure A liquid

vapor pressure of A above pure A liquid

Solvents often obey Raoult's Law

Partial pressure of A in gas mixture over liquid mixture \rightarrow

$$P_A = X_A P_A^*$$

↑ vapor pressure of A above pure A liquid

↑ mole fraction of A in liquid mixture

Solutions obeying Raoult's law at all concentrations are called ideal solutions

Then

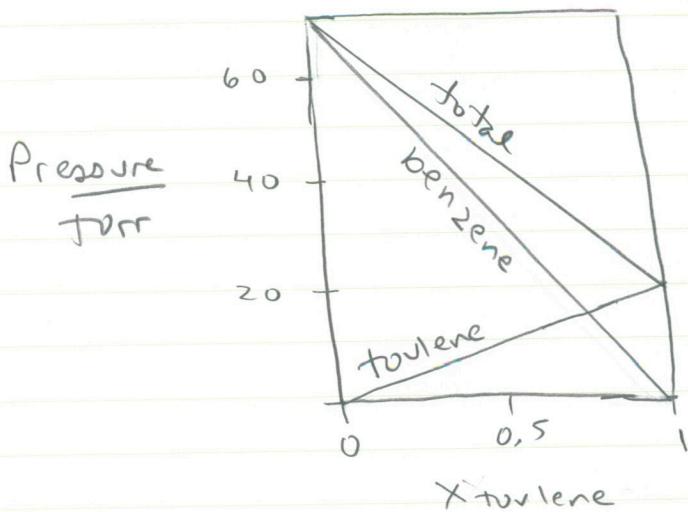
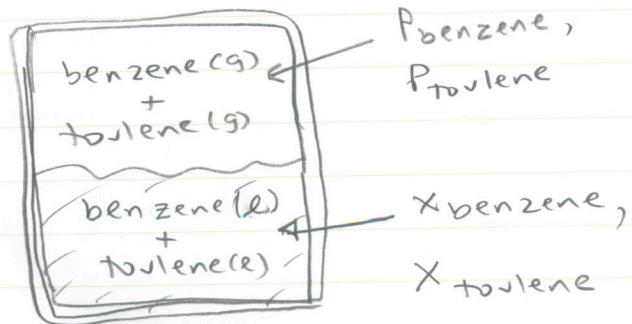
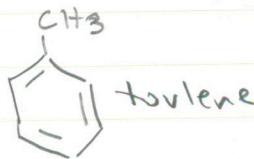
$$\boxed{M_{A(e)} = M_{A(e)}^* + RT \ln X_A}$$

When the molecular structure of two substances are similar there is good agreement w/ Raoult's law.

e.g.

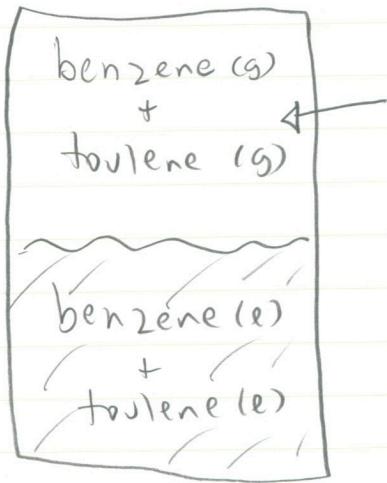


benzene



When substances have different interactions there will be deviations from Raoult's law.

Even then, for dilute solutions, $X_{\text{solute}} \ll X_{\text{solvent}}$
The solvent often follows Raoult's Law.



is the composition of the vapor phase the same as the liquid phase?

i.e., given $x_{\text{benzene}(l)}$, $x_{\text{toluene}(l)}$
and the vapor pressures of pure benzene & toluene, find

$x_{\text{benzene}(g)}$ and $x_{\text{toluene}(g)}$

$$\begin{aligned} P_{\text{benzene}}^* &= 94.6 \text{ Torr} \\ P_{\text{toluene}}^* &= 29.1 \text{ Torr} \end{aligned} \quad \left. \begin{array}{l} \text{at} \\ 25^\circ\text{C} \end{array} \right.$$

Try this at home. Hint: see bottom page 403.

Even if solutes do not obey Raoult's law, at low concentrations the partial pressure of the solute will still depend linearly (approximately) on its mole fraction in the liquid phase. This is called Henry's Law

$$P_B = K_{x,B} \times_B \quad \text{when } x_B \rightarrow 0$$

These are called ideal-dilute solutions



$$\mu_B(e) = \mu_B^{\circ(g)} = \mu_B^{\circ(g)} + RT \ln \frac{P_B}{P^{\circ}}$$

w/ Henry's law

$$\mu_B(e) = \mu_B^{\circ(g)} + RT \ln \frac{K_{x,B} x_B}{P^{\circ}}$$

Redefining our reference state

$$\mu_B(e) = \underbrace{\left[\mu_B^{\circ(g)} + RT \ln \frac{K_{x,B}}{P^{\circ}} \right]}_{\text{hypothetical reference state } \mu_{x,B}^{\text{ref}}(p,T)} + RT \ln x_B$$

$$\mu_B(e) = \mu_{x,B}^{\text{ref}}(p,T) + RT \ln x_B$$

