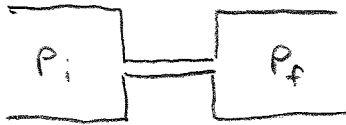


Lecture 6

Last time, started discussion of J-T effect



Free expansion out of insulated tube

Cooling or heating from intermolecular forces

Analyzed by determining that enthalpy $H = \text{const}$

$$\begin{aligned} \text{Get } \mu_J &= \text{J-T coeff} \equiv \left(\frac{\partial T}{\partial P}\right)_H \\ &= \frac{V}{C_p} (T\alpha_p - 1) \end{aligned}$$

$$\begin{aligned} C_p &= \text{heat capacity} \\ \alpha_p &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \\ &= \text{expansion coeff} \end{aligned}$$

For ideal gas, $\alpha_p = \frac{1}{T}$, so $\mu_J = 0$ as expected

Consider instead van der Waals gas:

$$NkT = \left(P + a \frac{N^2}{V^2}\right)(V - Nb)$$

a : attractive long range

b : repulsive short range

In hw, get to work out α_p exactly

I'll do in limit small a, b (or low density gas)

$$\text{So } NkT = PV + a \frac{N^2}{V} - bNP - a b \frac{N^3}{V^2}$$

drop

$$\left(\frac{\partial T}{\partial v}\right)_p = \frac{1}{Nk} \left[P - a \frac{N^2}{v^2} \right]$$

$$= \frac{1}{Nk} \left[P - \frac{a}{v^2} \right]$$

$$v \equiv \frac{V}{N} = \text{volume/particle}$$

Use $P = \frac{NkT}{V-Nb} - a \frac{N^2}{V^2}$

$$= \frac{kT}{v-b} - \frac{a}{v^2}$$

Taylor expand $\frac{1}{v-b} \rightarrow \frac{1}{v} \left(1 + \frac{b}{v}\right)$, get

$$\left(\frac{\partial T}{\partial v}\right)_p = \frac{1}{Nk} \left[\frac{kT}{v} + kT \frac{b}{v^2} - \frac{2a}{v^2} \right]$$

Then

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = \frac{Nk}{v} \frac{1}{\frac{kT}{v} + \frac{kTb}{v^2} - \frac{2a}{v^2}}$$

$$= \frac{1}{T} \frac{1}{1 + \frac{b}{v} - \frac{2a}{kTv}}$$

$$\approx \frac{1}{T} \left(1 - \frac{b}{v} + \frac{2a}{kTv}\right)$$

and

$$\mu_J = \frac{v}{C_p} (T\alpha_p - 1)$$

$$= \frac{v}{C_p} \left(-\frac{b}{v} + \frac{2a}{kTv}\right)$$

$$\boxed{\mu_J = \frac{N}{C_p} \left(\frac{2a}{kT} - b\right)} \quad (\text{weak interactions})$$

See that if a dominates, get heating,
 b dominates, cooling

Always get heating at high T , cooling at low

\Rightarrow need to start below inversion temp $T_{inv} = \frac{2a}{k_B b}$

Put in some numbers:

for N_2 gas, $a = 1.41 \frac{L^2 \text{ bar}}{\text{mol}}$

$b = 0.0391 \frac{L}{\text{mol}}$

$L = \text{liter} = 10^{-3} \text{ m}^3$

$\text{bar} = 10^5 \text{ Pa}$

$\text{mol} = 6.02 \times 10^{23} \text{ molecules} = N_A$

Often convenient to use $R = k_B \cdot N_A = 8.134 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

(Think of as k_B expressed in mols)

$$\text{So } T_{inv} = \frac{2 \cdot 1.41 \times 10^{-6} \text{ m}^6 \cdot 10^5 \text{ Pa} / \text{mol}^2}{8.134 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 0.0391 \times 10^{-3} \text{ m}^3 / \text{mol}}$$

$$= 886 \text{ K} \quad (\text{note } \text{Pa} \cdot \text{m}^3 = \text{J})$$

For He, $a = 0.0346 \frac{L^2 \text{ bar}}{\text{mol}}$ $b = 0.0237 \frac{L}{\text{mol}}$

get $T_{inv} = 36 \text{ K}$

(remember this is only in low density limit)

Get $\mu_J = \frac{N}{C_p} b \left(\frac{T}{T_c} - 1 \right)$

Assuming gas is almost ideal, $C_p \approx (\alpha+1)Nk_B T$

$$\begin{aligned}
 \text{N}_2: \quad \alpha &= \frac{5}{2} & \mu_J &= \frac{b}{\frac{7}{2}k_B} \left(\frac{T}{T_{inv}} - 1 \right) \\
 \text{say } T \ll T_{inv} & & &= -\frac{2}{7} \frac{0.037 \frac{\text{eV}}{\text{mol}}}{8.134 \frac{\text{J}}{\text{K mol}}} \\
 & & &= 1.4 \times 10^{-6} \frac{\text{K}}{\text{Pa}} \\
 & & &= 0.14 \frac{\text{K}}{\text{bar}}
 \end{aligned}$$

To get significant cooling, use high pressures
(~100 bar)

Kittel & Kroemer, Ch 12 has nice discussion
of methods in practice

Now turn to biggest application: phase transitions

Most substances can exist in multiple configurations
= phases

Examples: water: solid, liquid, gas
magnet: ferromagnet or unmagnetized
metal: superconducting or normal
etc

Very general phenomenon

General principle: for given thermodynamic variables,
equilibrium determined by minimizing
free energy

As variables change, go from one phase
to mixture of phases
to new phase

Region of coexistence is interesting

Considering each phase separately,
need equal T , Y , and μ for equilibrium

But each phase has an equation of state,
so T , Y & μ are related
 \Rightarrow so write $\mu = \mu(Y, T)$

Can already say something interesting:
Gibbs phase rule

How many phases can coexist at once?

Denote phases I, II, III etc

For two phases coexisting, need

$$\mu_{\text{I}}(Y, T) = \mu_{\text{II}}(Y, T)$$

\Rightarrow coexistence curve $Y(T)$

For three phases, need $\mu_{\text{I}} = \mu_{\text{II}}$
 $\mu_{\text{II}} = \mu_{\text{III}}$

Two eqns, two variables

\Rightarrow one solution (Y, T) : "triple point"

With four phases, have 3 eqns, two variables
 \rightarrow can't satisfy, never happens

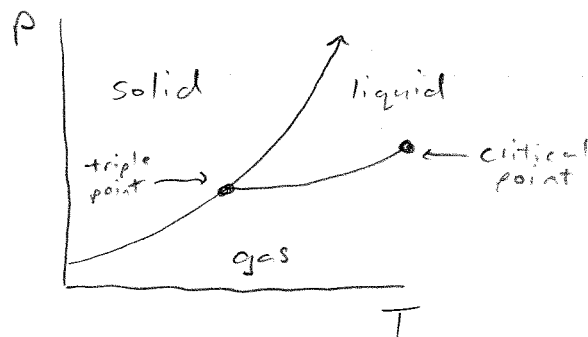
General statement:

If l different types of particles
 can have $l+2$ coexisting phases

Map out with phase diagram.

Example: water

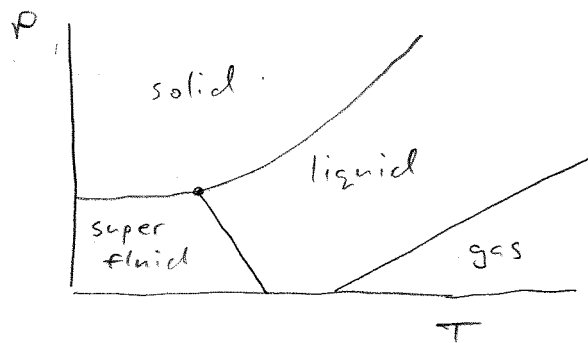
(Actually, several
 phases of ice)



Triple point: 3 phases coexist

Critical point: phase boundary disappears

Or He:



Analyze transition between phases

Since Y, T, N are constant,
 need to minimize Gibbs free energy

$$G = E - TS - XY =$$

$$dG = -SdT - XdY + \mu dN$$

So $\mu = \left(\frac{\partial G}{\partial N}\right)_{T, Y}$, equal for each phase

But $X = -\left(\frac{\partial G}{\partial Y}\right)_{T, N}$ and $S = -\left(\frac{\partial G}{\partial T}\right)_{Y, N}$

X and S can be different for each phase

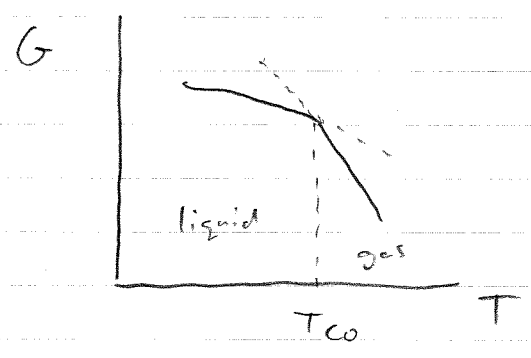
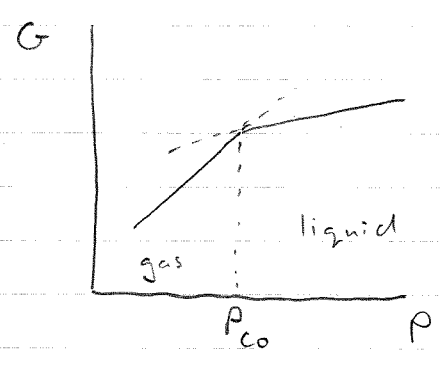
Call transition first order if $X + S$ are discontinuous across transition

Otherwise, transition is continuous or second order

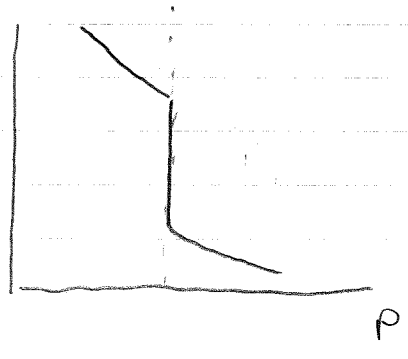
First order: solid-liquid, liquid-gas

Second order: Curie transition, superfluid transition

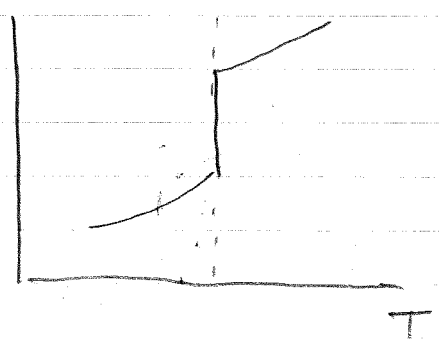
For example, look at liquid-gas:



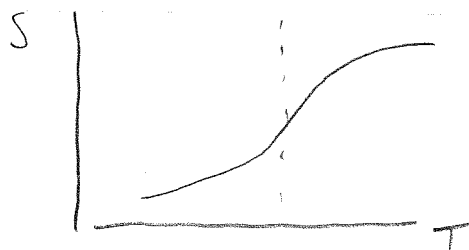
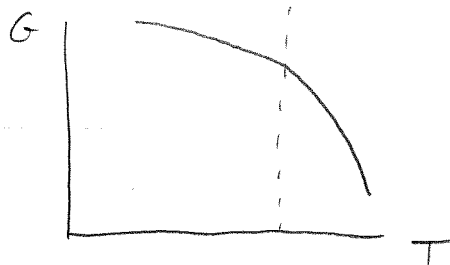
$$V = \frac{\partial G}{\partial p}$$



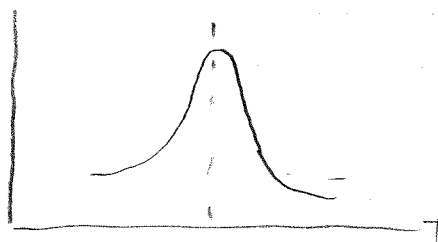
$$S = \frac{\partial G}{\partial T}$$



Compare 2nd order:



$$\frac{C_p}{T} = \frac{\partial S}{\partial T}$$



Note G always continuous

$$G = E - TS - XY = \mu N$$

N fixed

and $\mu_I = \mu_{II}$

But $H = G + TS$ discontinuous for 1st order

$$\Delta H = T \Delta S$$

= free energy required to drive transition in insulated system

= loosely, heat of transition

Can get general relation for coexistence curve:
Clausius-Clapeyron eqn

Know that on coexistence, $\mu_{\text{I}} = \mu_{\text{II}}$

Vary P & T , stay on curve:

$$\begin{aligned} d\mu_{\text{I}} &= \left(\frac{\partial \mu_{\text{I}}}{\partial P}\right)_T dP + \left(\frac{\partial \mu_{\text{I}}}{\partial T}\right)_P dT \\ &= d\mu_{\text{II}} = \left(\frac{\partial \mu_{\text{II}}}{\partial P}\right)_P dP + \left(\frac{\partial \mu_{\text{II}}}{\partial T}\right)_P dT \end{aligned}$$

But $\mu = \frac{G}{N}$

$$\text{So } \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{1}{N} \left(\frac{\partial G}{\partial P}\right)_{N,T} = \frac{1}{N} V = v$$

(volume/particle)

$$\left(\frac{\partial \mu}{\partial T}\right)_P = \frac{1}{N} \left(\frac{\partial G}{\partial T}\right)_{N,P} = -\frac{1}{N} S = -s$$

(entropy/particle)

$$\text{So } v_{\text{I}} dP - s_{\text{I}} dT = v_{\text{II}} dP - s_{\text{II}} dT$$

$$\text{Solve } \left(\frac{dP}{dT}\right)_{\text{coexist}} = \frac{s_{\text{I}} - s_{\text{II}}}{v_{\text{I}} - v_{\text{II}}}$$

$$\text{But } s_{\text{I}} - s_{\text{II}} = \frac{1}{N} (S_{\text{I}} - S_{\text{II}})$$

S_{I} = total entropy for all particles in I
 S_{II} = " " " " II

$$\text{So } S_{\text{I}} - S_{\text{II}} = \Delta S = \frac{1}{T} \Delta H$$

$$\text{Similarly, } v_{\text{I}} - v_{\text{II}} = \frac{1}{N} \Delta V$$

volume difference
between phases

$$\text{So } \left(\frac{dp}{dT} \right)_{co} = \frac{\Delta H}{T \Delta V}$$

Often define latent heat $L = \frac{\Delta H}{N}$

$$\left(\frac{dp}{dT} \right)_{co} = \frac{L}{T \Delta v}$$

$$\Delta v = v_{\text{I}} - v_{\text{II}}$$

Either form: Clausius-Clapeyron eqn