

I last time

II Clausius - Clapeyron

Equation

III Phases dumb, dumb, dumb.

Thermal Physics Nov 12th, 2014 P/5

Meeting

I. Ram argument 3 times:

Isolated: $P \propto e^{S/k}$

Equilibrium $\leftrightarrow S = \text{maximum}$

Heat bath: $P \propto e^{-F/kT}$

Equilib. $\leftrightarrow F = \text{minimum}$

Heat and pressure bath $P \propto e^{-G/kT}$

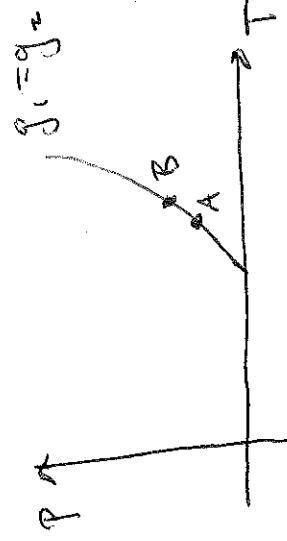
Equilib. $\leftrightarrow G = \text{minimum}$

• For constant T and P environment we found

Equilib between two phases $g_1 = g_2$

• For a displacement along the "phase equilibrium line"

$$dg_1 = dg_2$$



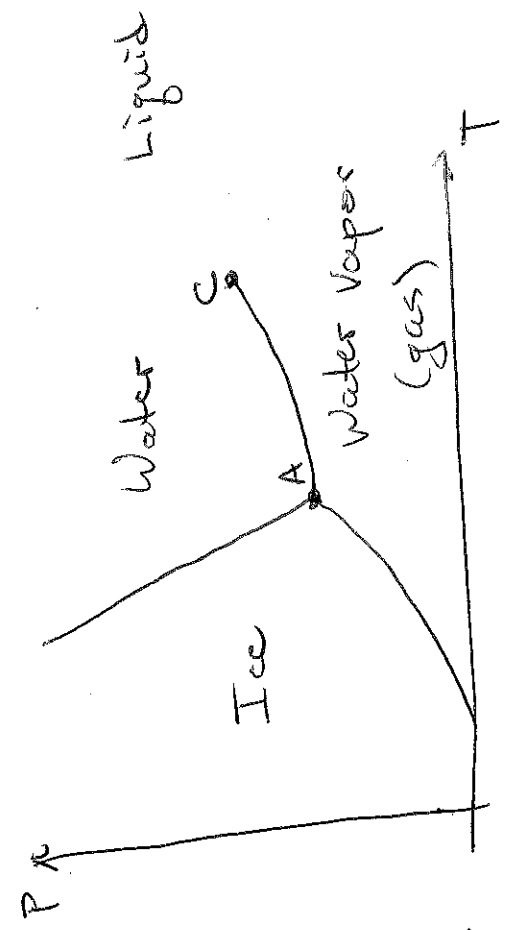
II. Now, $g = g(T, P)$ so

$$dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$$

While in molar form

$$d\epsilon = T ds - p dv$$

Phase diagram of water Pz/s



By definition

$$dg = d(e - Ts + pV) = -s dT + v dp$$

So $dg_1 = dg_2$ implies

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\Rightarrow (s_2 - s_1) dT = (v_2 - v_1) dp$$

or

$$\frac{df}{dT} = \frac{\Delta S}{\Delta V}$$

Prediction
Left

- a) Is this a 30% event
- b) a

Of course, ΔS and ΔV are the changes in S and V as you cross the line

$$\Delta S = S_2 - S_1$$

↑
two sides

and hence there must be a heat transfer in the process.

How much? $\Delta S = S_2 - S_1 \equiv \frac{L_{12}}{T}$ definition of L_{12}

Where L_{12} is the latent heat of transformation.

So we can also write

$$\frac{df}{dT} = \frac{\Delta S}{\Delta T} = \frac{L_{12}}{T \Delta V}$$

Recall that back in meeting XVI we showed that

$$dQ = \sum_r E_r dP_r$$

and

$$dW = - \sum_r P_r dE_r$$

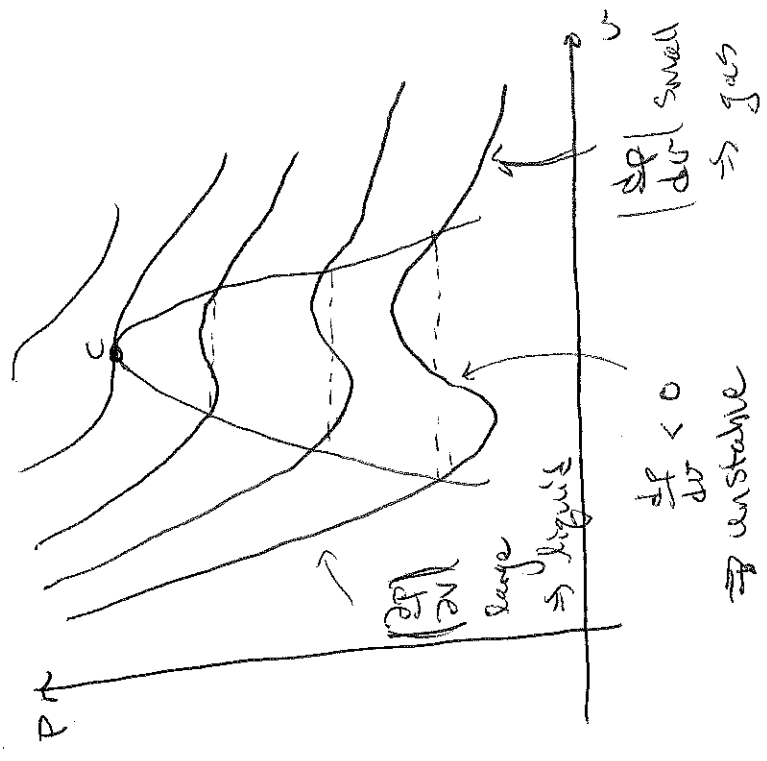
So the phase transition is reorganizing the probabilities and this comes as no surprise.

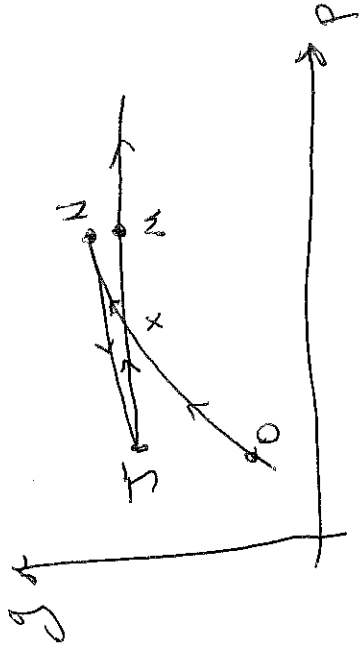
but simple enough to be analytic. It's not quantitatively accurate. \approx

$$(p + \frac{a}{v^2})(v-b) = RT$$

Recall b represents the excluded volume of a more realistic gas molecule, and a represents the long-range interaction

III Can we get a more P3/S detailed picture of all of this? Yes. In fact, the Van der Waals equation of state does a wonderful job. — it's complex enough to be interesting and give the qualitative picture





As the phase change proceeds the total fraction volume is shared between the phases.

Call the fraction in phase

Now, equilibrium is when

$$g_B = g_A$$

and this can be expressed as an integral (like at top left)

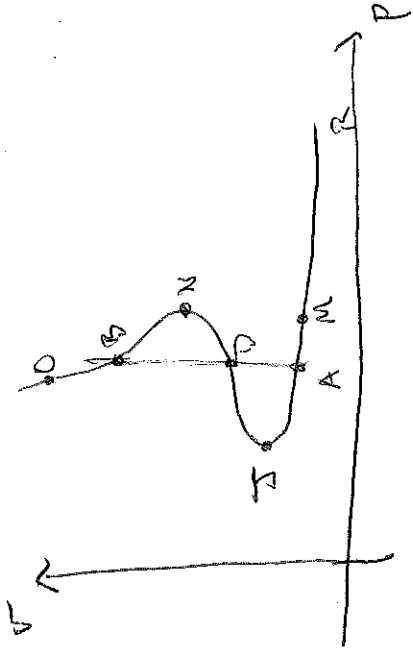
$$\int_{BNDIA} v dp = 0$$

If we break this up into pieces we get

isothermal

$$dg = v dp$$

$$\text{So } g - g_0 = \int_{P_0}^P v dp$$



A $(1-x)$ and the fraction in

phase B x then

$$V_{tot} = \sum v_B + (1-x)v_A$$

(The change of notation is

to make an easier comparison

with the above figures —

A is the liquid phase and B the gaseous one.)

line occurs is called the P5/5
 "Maxwell construction" or
 "equal area rule" by many.

$$\int_B^N v dp + \int_N^D v dp + \int_D^I v dp + \int_I^A v dp = 0$$

and swapping two limits

$$\left(\int_B^N v dp - \int_D^I v dp \right) + \left(- \int_I^D v dp + \int_I^A v dp \right) = 0$$

or

$$\text{area}(DNB) - \text{area}(AID) = 0$$

The result
 $\text{area}(DNB) = \text{area}(AID)$
 for where the phase transformation