

(1)

Lecture 9 - Stability

What are requirements of equilibrium?

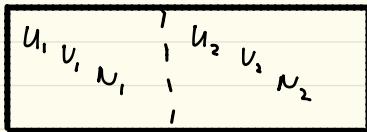
Entropy maximum principle
 (Postulate 2)

Equilibrium attains when entropy is maximized wrt internal dofs.

(Local) Conditions of maximum S

$$dS = 0 \quad d^2S \leq 0$$

Recall closed composite systems



$$S = S^{(1)} + S^{(2)} \quad \text{allow energy exchange}$$

$$dS = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right) dU^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right) (-dU^{(1)})$$

$$d^2S = \left(\frac{\partial^2 S^{(1)}}{\partial U^{(1)} \partial U^{(1)}}\right) dU^{(1)}^2 + \left(\frac{\partial^2 S^{(2)}}{\partial U^{(2)} \partial U^{(1)}}\right) (-dU^{(1)})^2 \leq 0$$

Thus, must have $\left(\frac{\partial^2 S}{\partial U^2}\right) \leq 0$ everywhere

for a system to be stable. A fully satisfactory fundamental eq must have this property.

(2)

$$\text{But } \left(\frac{\partial^2 S}{\partial u}\right) = \frac{1}{T}, \text{ so } \left(\frac{\partial^2 S}{\partial u^2}\right) = \left(\frac{\partial^2 S}{\partial u}\right)$$

$$= -\frac{1}{T^2} \left(\frac{\partial T}{\partial u}\right)_{v,n} = \frac{-1}{N C_v T^2} \leq 0$$

$\therefore C_v \geq 0$ is a requirement for a stable equilibrium.

Stability puts constraints on materials properties.

Same must apply to exchanging volume,

$$\left(\frac{\partial^2 S}{\partial v^2}\right) \leq 0$$

Consider variation of multiple dofs

$$d^2 S = \sum_{i,j=1}^2 \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right) dx_i dx_j \leq 0$$

Can write in matrix form

$$d^2 A = (dx_1, dx_2) \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} dx_1 \\ dx_2 \end{pmatrix} \leq 0, \quad S_{ij} = \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)$$

For the inequality to hold, determinant must be negative definite:

$$\begin{vmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{vmatrix} \leq 0 \Rightarrow \left(\frac{\partial^2 S}{\partial x_1^2}\right) \left(\frac{\partial^2 S}{\partial x_2^2}\right) - \left(\frac{\partial^2 S}{\partial x_1 \partial x_2}\right)^2 \leq 0$$

(3)

This condition is more stringent, requiring entropy to be concave wrt variations of BOTH $U + V$. Can be extended to more dimensions. NOT a saddle point.

What about energy? Showed long ago that entropy maximum implies energy minimum:

$$dU=0 \quad d^2U \geq 0 \quad \text{convex wrt } S, V$$

Other potentials?

$$F(T, V, N) = U - \left(\frac{\partial U}{\partial S}\right)S = U - TS$$

wrt extensive variables, same conditions apply:

$$dF=0 \quad \left(\frac{\partial^2 F}{\partial V^2}\right) \geq 0 \quad \begin{matrix} \text{not transformed} \\ \text{same curvature} \end{matrix}$$

wrt intensive, remember

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right) = -\left(\frac{\partial S}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial S}\right)_V} = -\frac{1}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V}$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right) \geq 0 \Rightarrow \left(\frac{\partial^2 F}{\partial T^2}\right) \leq 0$$

In general, for thermodynamic potentials

$$\left(\frac{\partial^2 A}{\partial \text{ext}^2}\right) \geq 0 \quad \left(\frac{\partial^2 A}{\partial \text{int}^2}\right) \leq 0$$

(5)

For entropy

$$\left(\frac{\partial^2 S}{\partial v_{ext}^2}\right) \leq 0 \quad \left(\frac{\partial^2 S}{\partial v_{int}^2}\right) \geq 0$$

These are the general conditions for the thermodynamic stability. All must be satisfied for a system to be stable.

Considering F gives another physical constraint:

$$\left(\frac{\partial^2 F}{\partial v^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right) = \frac{1}{V k_T} > 0 \geq 0$$

$K_T > 0$ isothermal compressibility

Total volume must go down when pressure is increased. Can show

$$C_p \geq C_v \geq 0 \quad K_T \geq K_S \geq 0$$

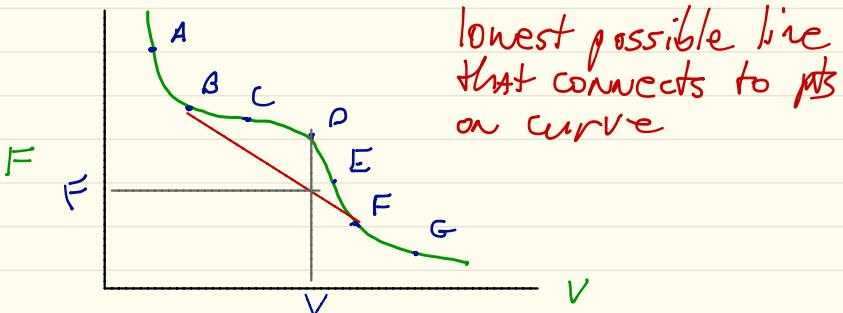
Why? Le Chatlier's principle. Small fluctuations in density or energy are damped, so e.g. $P \uparrow$, $P \uparrow$, $V \uparrow (x > 0)$, $P \downarrow$. Otherwise fluctuations would be amplified.

Interesting no such bound on $\alpha = \left(\frac{\partial v}{\partial T}\right)_P \cdot \frac{1}{V}$

A stable material could either expand or contract when heated. Think of a polymer. Mechanical & thermal fluctuations decoupled

(5)

So far focused on stability wrt infinitesimal variations. But stability criterion more general than that.



At points A, B, C and E, F, G, have

$$\left(\frac{\partial^2 F}{\partial V^2}\right) \geq 0 \quad \text{convex}$$

C and E are inflection points, $\left(\frac{\partial^2 F}{\partial V^2}\right) = 0$, so these define the ^V limits of stability. _{physical}

D is unstable and unreachable. What happens at D?



$$\text{Keep volume fixed, } N\bar{V}_0 = N[x_F \bar{V}_F + x_B \bar{V}_B]$$

Combined with mass balance, $x_F + x_B = 1$, can solve for $x_F + x_B$.

$$X_B = \frac{U_0 - U_F}{U_B - U_F} \quad \text{Lever rule}$$

point on the line

(6)

$$N[x_F F_F(v_F) + x_B F_B(v_B)] \leq N F_B(v_o) \quad \text{≡}$$

Free energy is lowered by the system at phase separating into B and F.

In general, points must be stable wrt infinitesimal or finite exchange

$$F(T, V + \Delta V, n) + F(T, V - \Delta V, n) \geq 2 F(T, V, n)$$

$$\text{Limit } \Delta V \rightarrow 0, \text{ this becomes } \left(\frac{\partial^2 F}{\partial V^2} \right) \geq 0$$

Construct tangents at every point along curve. Only globally stable points are those whose tangents lie above the curve.

Called common tangents construction, "convex hull"

BCDEF region all unstable by this criterion. Binodal region

BC and EF locally stable, globally not.

These are metastable, like a supersaturated solution. Will persist unless/until perturbed, relax to B + F. "spinodal" regions

CDE simply unstable

7

Compare pts B + F:

molar volumes different
free energies different
different extensive (molar) quantities

Temperature? same (isotherm)

Pressure? $\left(\frac{\partial F_F}{\partial V}\right) = \left(\frac{\partial F_B}{\partial V}\right) \rightarrow P_F = P_B$
mechanical equilibrium

Chemical potential?

$$\mu_F = f(T, v_F) + P v_F \quad (F = -PV + N\mu)$$

$$\mu_B = f(T, v_B) + P v_B$$

$$\mu_F - \mu_B = f(T, v_F) - f(T, v_B) + P(v_F - v_B)$$

$$\frac{f(T, v_F) - f(T, v_B)}{v_F - v_B} = -P \quad \text{finite difference}$$

$$\mu_F = \mu_B \quad \text{chemical equlibrium}$$

Intensive variables are unchanged by phase separation. Equilibrium maintained.

Susceptibilities?

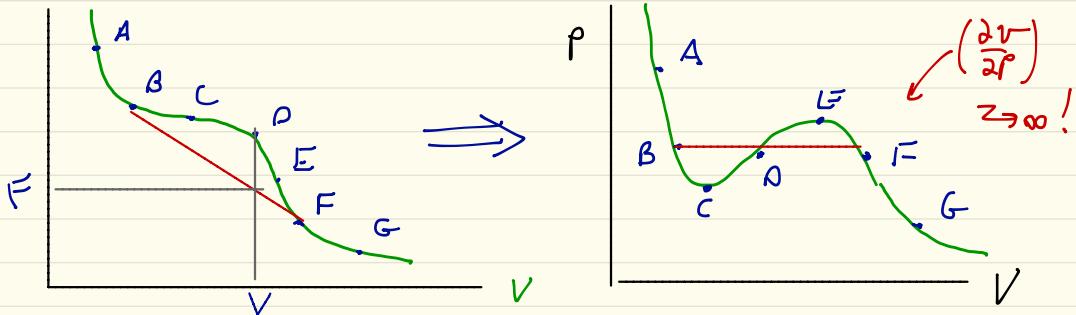
Like extensive quantities,

Susceptibilities different.

Characteristic of 1st order, discontinuous phase transition.

8

Because $(\frac{\partial F}{\partial V}) = -P$, can differentiate free energy curve to get P vs. V :

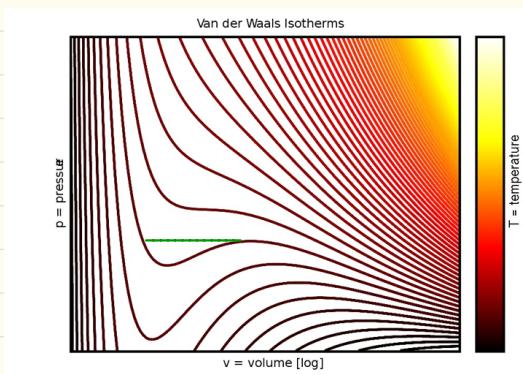


Looks like vdW isotherm! Characteristic shape of all fluid isotherms.

vanderWaals isotherms has right physics of intermolecular interactions

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Pretend this was all we knew



Focus on + lower T isotherms

$$CDE \quad \chi_T = \frac{1}{V} \left(\frac{\partial P}{\partial V} \right) < 0 \quad \text{unstable}$$

Chemical potential

(9)

Gibbs-Duhem tells us

$$d\mu = v dp - s dT \xrightarrow{\text{isotherm}}$$

$$\mu - \mu_G = \int_{v_G}^v v(p) dp$$

μ -p graph on its side to integrate

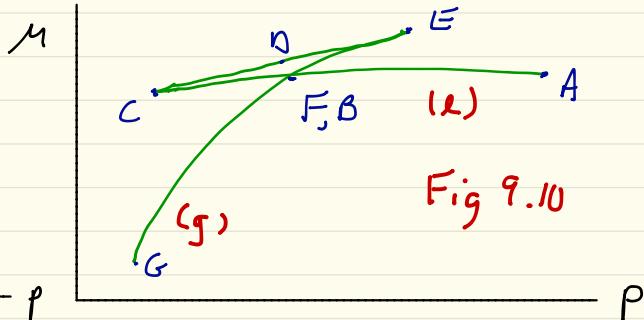
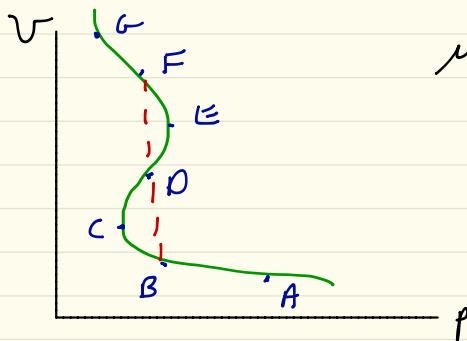


Fig 9.10

As we move along in pressure, systems will try to minimize $\mu(p)$.

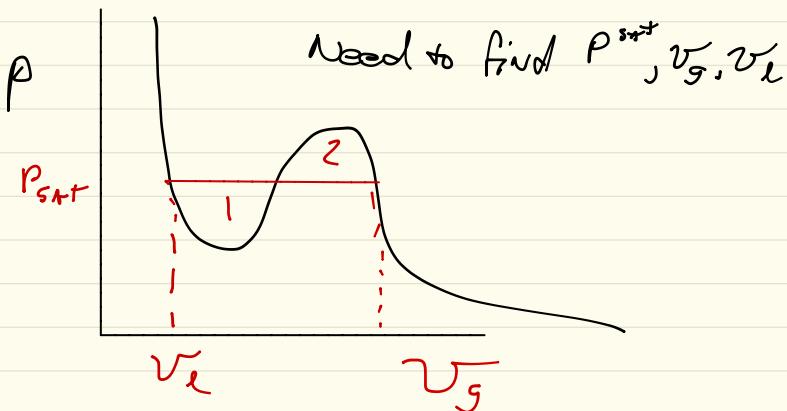
Starting @ G and isothermally increasing p , systems will follow $G \rightarrow F, B \rightarrow A$
 $(\partial\mu/\partial p)$ changes discontinuously @ F, B

Phase change

As noted before, P, T, μ all constant at transition point.

Because $\mu_B = \mu_F$, must have $\text{Area } BCD = \text{Area DEF}$. Equal areas construction

equal area construction



$$\int_{v_e}^{v_g} P dv = P_{\text{sat}}(v_g - v_e)$$

Have to simultaneously solve this and EOS

Ex. vdW In reduced variables

$$P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}$$

$$\int_{v_{e,r}}^{v_{g,r}} \left(\frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \right) dv_r$$

$$\frac{8T_r}{3} \ln(3v_r - 1) + \frac{3}{v_r} \Big|_{v_e}^{v_g} = P_r(v_g - v_e)$$

$$\text{Plus } P_r = \frac{8T_r}{3v_e - 1} - \frac{3}{v_e^2} \quad P_r = \frac{8T_r}{3v_g - 1} - \frac{3}{v_g^2}$$

Guess P , find $v_g + v_e$, plug into integral, adjust P to satisfy.

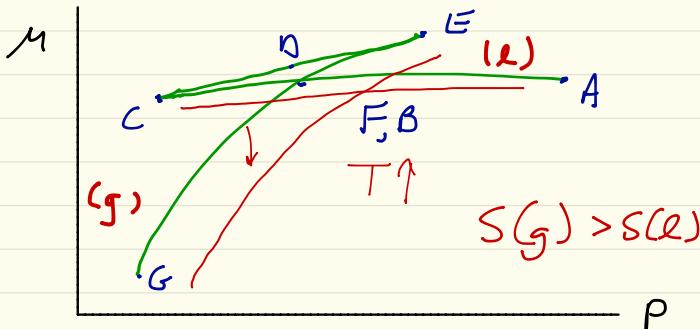
11

How do these curves move w/T?

$$d\mu = v dP - s dT$$

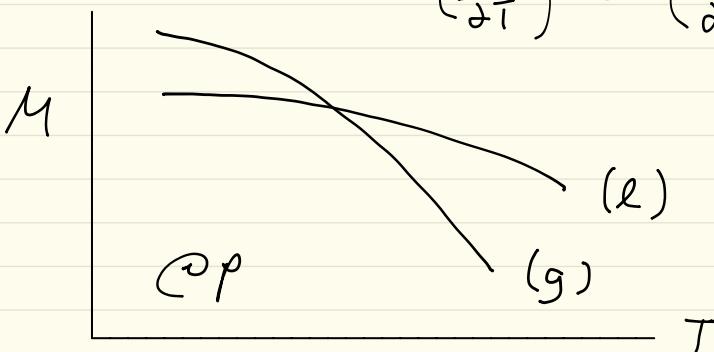
$$\left(\frac{\partial \mu}{\partial T}\right)_B = -s < 0$$

μ must decrease w/T, fastest for highest entropy phase.

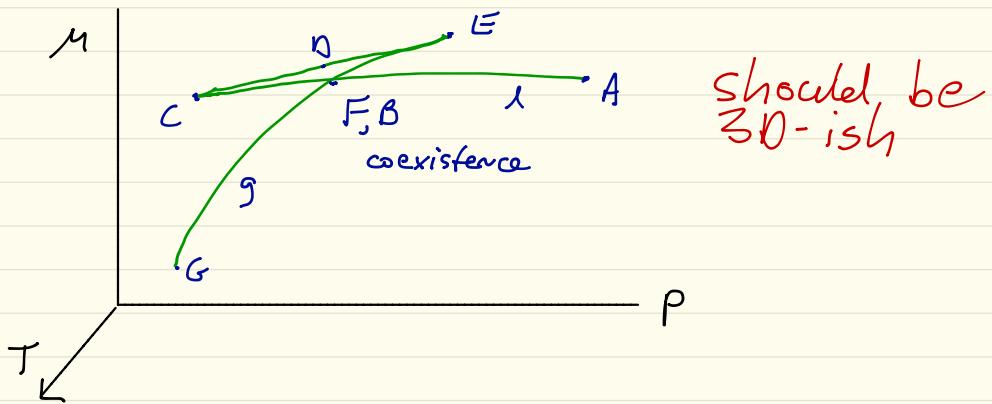


Points CDE move toward one another as $T \uparrow$

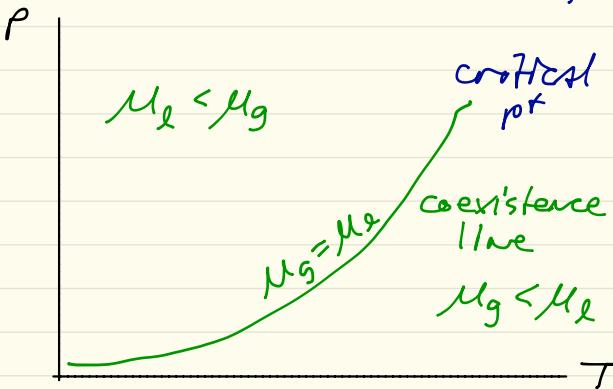
$$\left(\frac{\partial \mu}{\partial T}\right) < 0 \quad \left(\frac{\partial^2 \mu}{\partial T^2}\right) ?$$



If we compute for many T , get $\mu(T, P)$ surfaces.

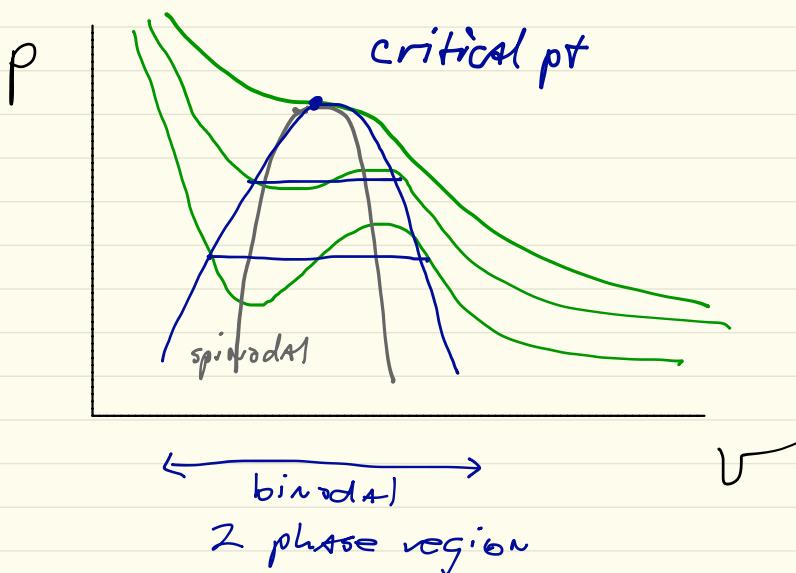


Visualize from below: Phase diagram



Pressure and temperature are continuous across transition, so coexistence becomes a line in T, P space.

Can do this for a series of isotherms



Connecting coexistence points among isotherms gives coexistence curve. As T , binodal region narrows, culminates at the critical point.

Connecting stability boundaries gives spindal curve. Limit of metastability

Start at some large V and decrease V at constant T . P rises until you hit 2 phase boundary, bit of high density phase forms. As V decreases further, move into 2 phase region, low density phase gradually diminishing and high density phase growing according to lever

$\Delta h?$ $\Delta s?$

What's dP/dt ?

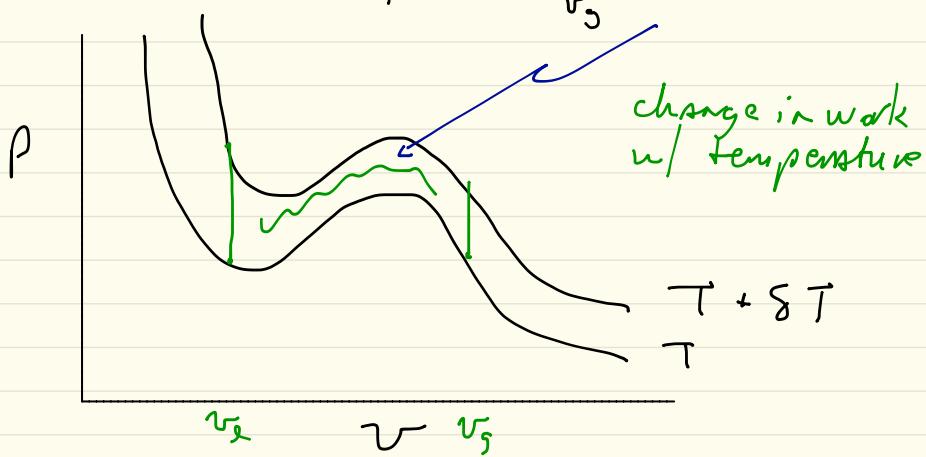
Along coexistence line, also have $d\mu_1 = d\mu_2$

From Gibbs-Duhem, $d\mu_1 = -S_g dT + V_g dP$

Equating, get $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

Can get from isotherms:

$$\Delta S = S_g - S_v = \int \left(\frac{\partial S}{\partial V} \right)_T dV = \int_{V_2}^{V_3} \left(\frac{\partial P}{\partial T} \right)_V dV$$



$$\Delta h = \Delta \mu^0 + T \Delta s$$

$$\approx \frac{1}{\Delta T} \int \Delta P dV \quad \text{Area}/\Delta T$$

Called latent entropy and latent heat

Not sensible, no change in T.

Equating, get

$$\frac{dP}{dT} = \frac{\Delta S}{4V} = \frac{\Delta h}{T\Delta V}$$

Clapeyron equation

Latent heat of vaporization

$$\Delta h_v = h_v - h_e = T(s_v - s_e)$$

$l, s \rightarrow g + s$ $\Delta V = V_g - V_{cond} \approx V_g \approx \frac{RT}{P}$ ideal approx.

$$\frac{dP}{dT} \approx \frac{\Delta h}{T \cdot (RT/P)} \rightarrow \boxed{\frac{d \ln P}{d(1/T)} = -\frac{\Delta h}{R}}$$

Clausius-Clapeyron eq.

If Δh constant over a small range, can integrate

$$\int d \ln P = -\frac{\Delta h}{R} \int d \frac{1}{T}$$

$$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta h}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Says coexistence p goes up exponentially w/T

$$p_{sat} \approx A e^{-\Delta h_{vap}/RT}$$

ex benzene $T_b = 353.2 \text{ K}$ @ 760 torr

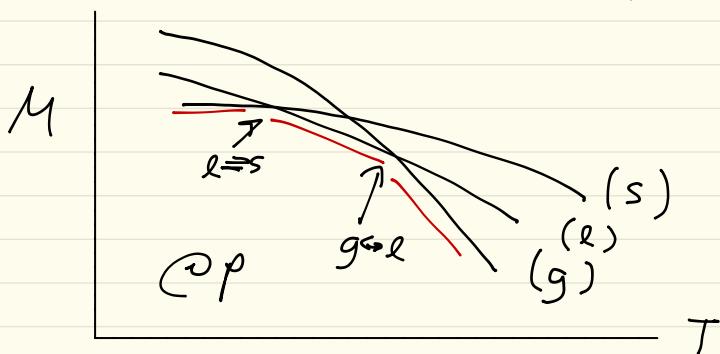
$$\Delta h_{vap} = 30.8 \text{ kJ/mol}$$

P_{sat} @ 373.2 K?

$$\ln \left(\frac{P_{sat}}{760} \right) = -\frac{30.8}{R} \left(\frac{1}{373} - \frac{1}{353} \right)$$

$$P_{sat} \approx 1360 \text{ torr} \quad \text{exp}^t 1360 \text{ torr}$$

Focused on VLE so far. Other phases?



Gibbs Phase Rule

Properties of a pure fluid determined by two variables
 $g = g(T, P)$, for instance

At phase boundary, dof's reduce to 1. Why?

Requirement that $M^\alpha = M_\beta$.

Consider a system of c components and π phases

$$M_i^\alpha(T, P, x_1^\alpha, x_2^\alpha, \dots, x_n^\alpha)$$

Independent variables $T, P, \pi (c-1) x_i^\alpha$ comp
 $\pi c - \pi + 2$ total variables variables

If π phase equilibria,

$$M_i^\alpha = M_i^\beta = \dots = M_i^\pi \quad \pi - 1 \text{ equalities/component}$$

$$c(\pi - 1) \text{ total equalities}$$

$$\pi c - \pi + 2 - c(\pi - 1) = \boxed{c - \pi + 2 \text{ DOFs}}$$

ex. 1 component, 1 phase

$$DOF = 1 - 1 + 2 = 2 \quad T, P$$

1 component, 2 phases

$$DOF = 1 - 2 + 2 = 1 \quad T \text{ or } P$$

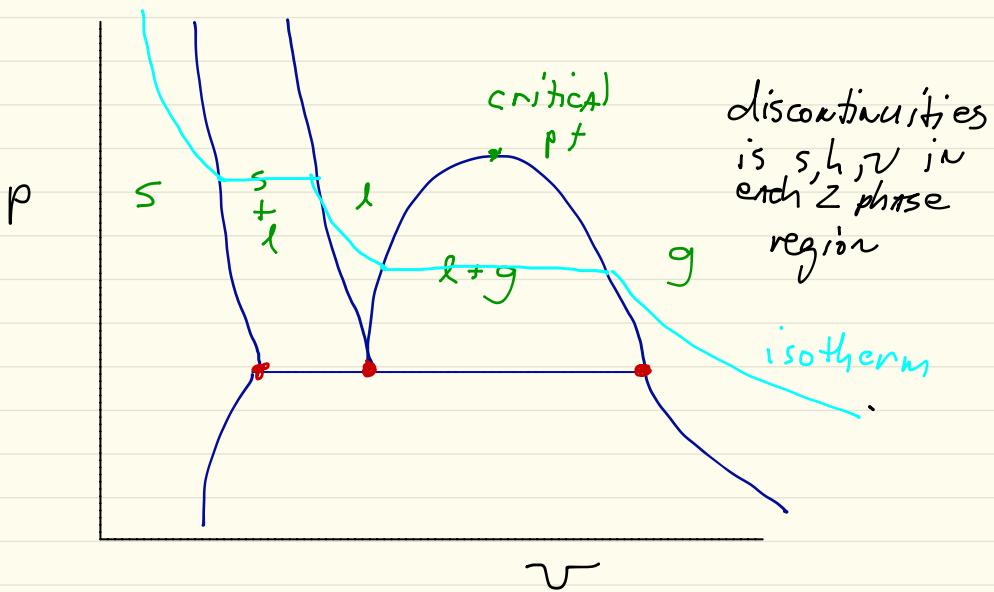
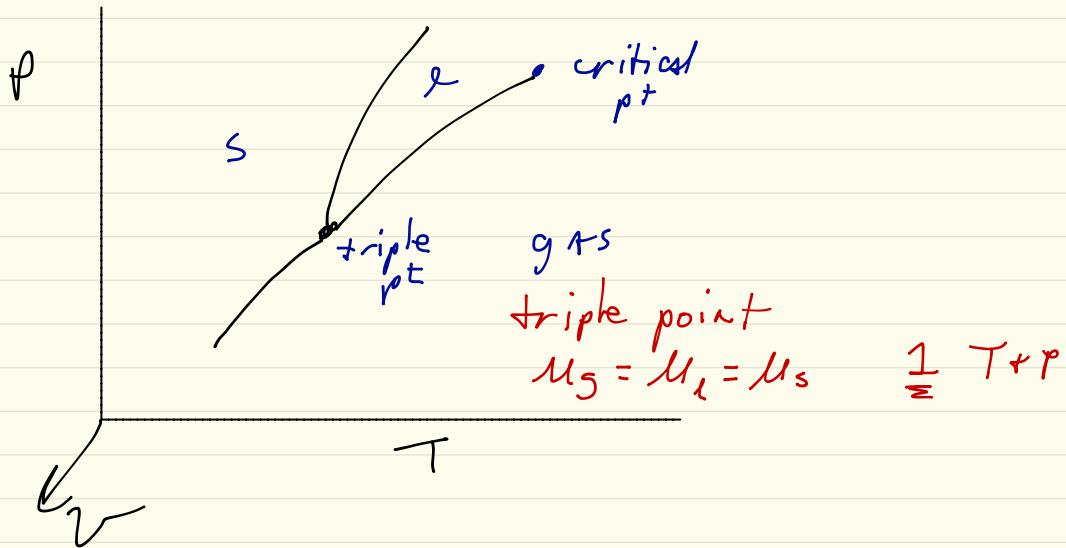
ex 1 component, 3 phases

$$DOF = 1 - 3 + 2 = 0 \quad T, P \text{ determined}$$

triple point

Phase diagram view

17



fusion $l \rightarrow s$

(18)

latent quantities

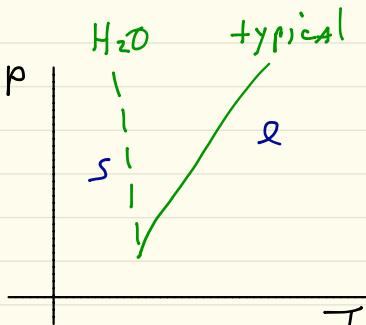
$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta V}$$

$$\frac{\Delta p}{\Delta T} \approx \frac{\Delta h}{T\Delta V}$$

often ok since l, s so incompressible

$$\Delta V < 0 \quad \Delta h < 0$$

typically



Ex. $P = 1 \text{ atm}$, $\Delta P = 1000 \text{ atm}$

<u>T_{fus}</u>	<u>Δh_{fus}</u>	<u>ΔV</u> (cm^3/g)	<u>ΔT_{cav}</u>	<u>$\Delta T_{exp't}$</u>
AcOH 289.8	44.7	0.01595	25.0	24.4
Sn 505	14.0	0.00389	3.40	3.28
H ₂ O 273.2	79.8	-0.0906	-7.5	-7.4

Water exhibits anomalous increase in volume upon freezing.

ex 2 component

2 phase	2 dof	plane
3 phase	1 dof	line
4 phase	0 dof	pt

Recall each equilibrated rxn provides another constraint on chemical potentials w/i each phase, so in total

$$\text{dof} = c - \pi - r + 2$$

Defines topology of phase diagrams.