

Thermal Physics

PHYS/BMME 441

Gökçe Başar

Lectures 12 - 15

When & Where: Mon. / Wed. 8:45- 10:00 AM, Phillips 247

Textbook: *An Introduction to Thermal Physics*, Daniel V. Schroeder

Website: sakai.unc.edu

Outlook for the next few weeks

Chapter 5: Free Energy and Chemical Thermodynamics (chapters 5.1 to 5.6)

read chapters:

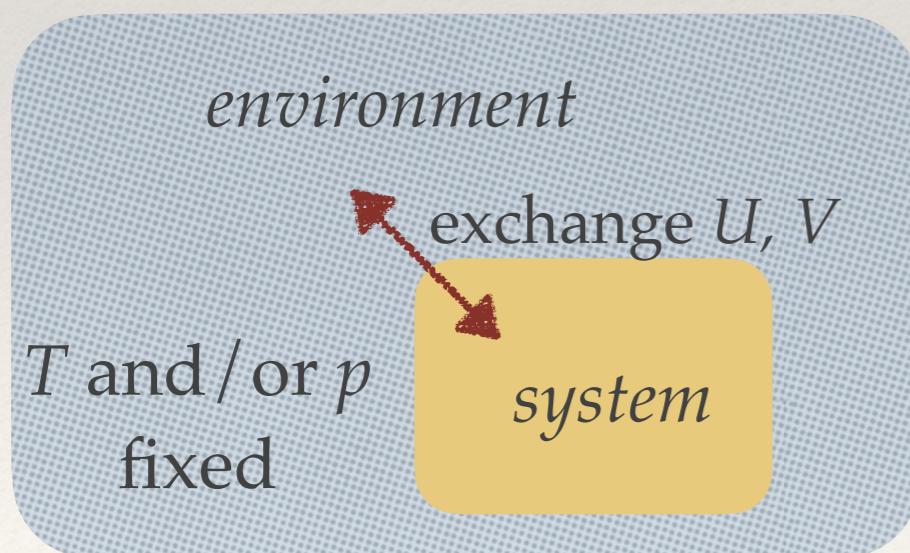
- 5.1 Free Energy as Available Work
- 5.2 Free Energy as a Force Towards Equilibrium
- 5.3 Phase Transformations of Pure Substances
- 5.4 Phase Transformations of Mixtures
- 5.5 Dilute Solutions
- 5.6 Chemical Equilibrium

Non Cyclic Processes

So far we have seen *cyclic* processes where the system returns to its original state. Energy, entropy,... of the system remains unchanged

There are many processes for which this is not the case (phase transitions, chemical reactions). State functions such as energy, volume, typically change due to interaction with the environment.

Temperature or pressure (or both) remains fixed.



Thermodynamic Free Energies:
tools to tackle constant T and / or p
processes

Free Energy as Available Work

recall

Enthalpy:

$$H = U + pV$$

energy content of the system

work needed to make room for it ``tax''

Constant pressure



total energy needed to *create* a system with internal energy U at *constant p*

pV = *the work needed to make room ("tax")*

total energy gain after *annihilating* a system with internal energy U at *constant p*

pV = *the work environment does ("subsidy")*

Helmholtz Free Energy

Consider a *constant temperature* environment

Helmholtz Free Energy:

$$F = U - TS$$

energy content of the
system

Heat from the
environment "subsidy"

total energy needed to *create* a system with internal energy U at *constant T*

$-TS$ = *heat you get for free from the environment ("subsidy")*

total energy gain after *annihilating* a system with internal energy U at *constant T*

$-TS$ = *heat you have to dump to get rid of the entropy of the system ("tax")*

The name *free energy* comes from this point of view:
You only get energy F that can be converted to work

Gibbs Free Energy

$$G = U + pV - TS = H - TS$$

↑ ↓ ↓
energy content of the system work needed to make room for it ``tax'' Heat from the environment ``subsidy''



total energy needed to *create* a system with internal energy U at *constant* p and T

pV : tax, $-TS$: subsidy

total energy gain after *annihilating* a system with internal energy U at *constant* p and T

pV : subsidy, $-TS$: tax

The name *free energy* comes from this point of view

Infinitesimal Changes

constant T: $dF = dQ + dW - TdS$

If no new entropy is produced in the process: $dQ = TdS \Rightarrow dF = dW \longrightarrow$ Includes
expansion work

If new entropy is produced in the process: $dS > dQ/T \Rightarrow dF < dW$

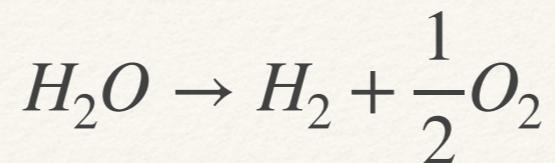
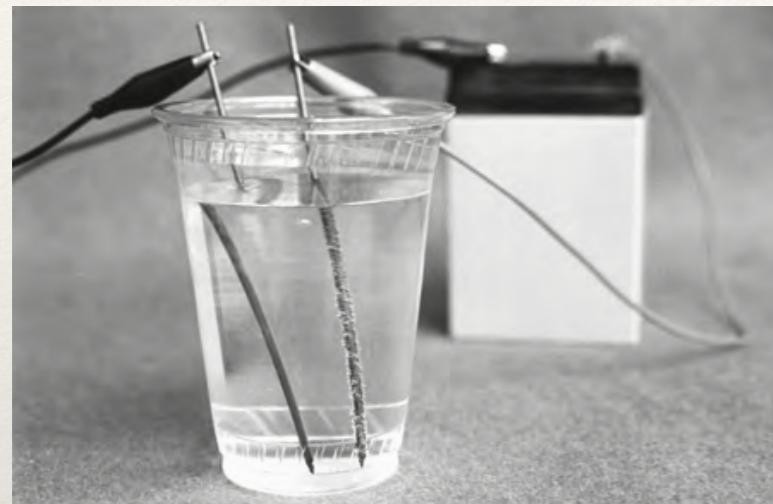
constant T and p: $dG = dQ + dW - TdS + pdV$

similarly, $dQ - TdS \leq 0$

$$dG \leq dW - pdV = dW_{\text{other}} \longrightarrow \text{Does not include expansion work}$$

- Remarks:
- 1) $\Delta G = \Delta H - T\Delta S \longrightarrow$ calculated from heat capacity data
→ measured at constant p
 - 2) U , therefore H, F and G are defined with respect to a convenient but arbitrary reference point. We are interested in *changes* in them anyway

Classroom Exercise: Electrolysis



$p = 1\text{ atm}$, $T = 298\text{ K}$

$$\Delta H = 286\text{ kJ}$$

$$\Delta H = -286\text{ kJ}$$

(data: burning hydrogen)

$$S_{H_2O} = 70\text{ J/K}, \quad S_{H_2} = 131\text{ J/K} \quad S_{O_2} = 205\text{ J/K}$$

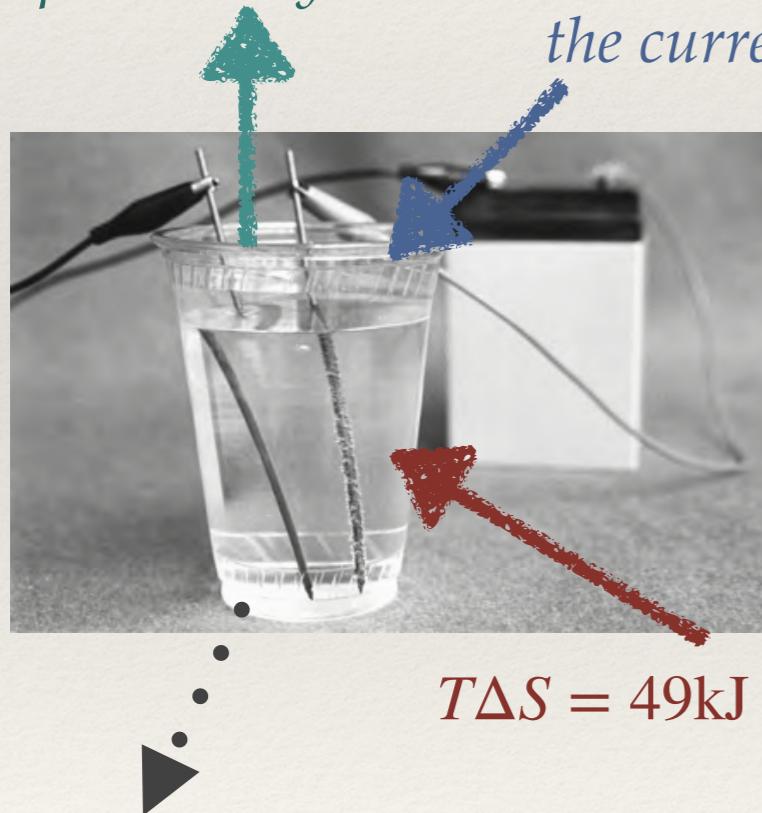
*How much work do we have to provide to
realize this reaction?*

*all quantities are per mole

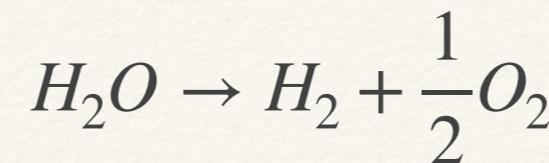
Electrolysis

$$p\Delta V = 4 \text{ kJ}$$

Of the 286 kJ of energy, 4 kJ is used for pushing the atmosphere away



$$\Delta U = \Delta G + T\Delta S - p\Delta V = 282 \text{ kJ}$$



$$p = 1 \text{ atm}, T = 298 \text{ K}$$

$$\Delta H = 286 \text{ kJ}$$

(data: burning hydrogen)

$$S_{H_2O} = 70 \text{ J/K}, \quad S_{H_2} = 131 \text{ J/K} \quad S_{O_2} = 205 \text{ J/K}$$

subsidy (heat from the environment):

$$T\Delta S = T \times (S_{H_2} + S_{O_2}/2 - S_{H_2O}) = 49 \text{ kJ}$$

Work we need to provide:

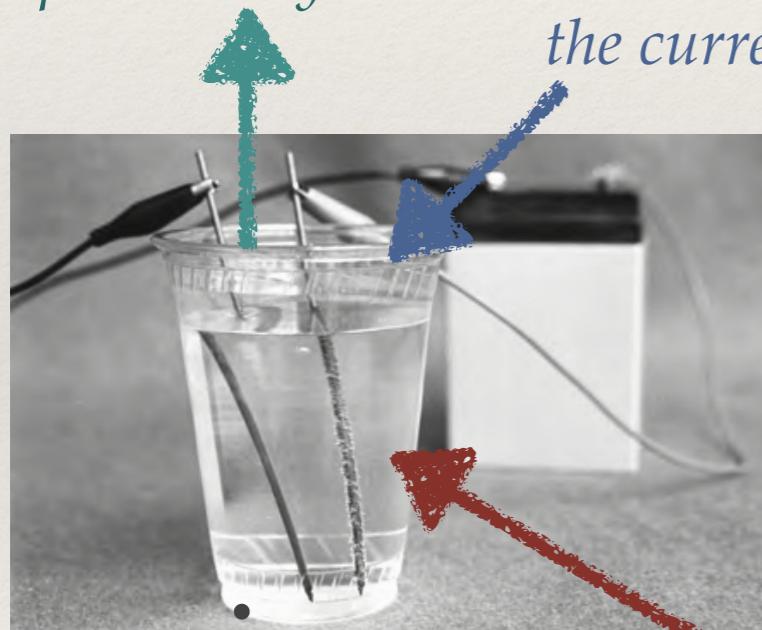
$$\Delta G = \Delta H - T\Delta S = 286 \text{ kJ} - 49 \text{ kJ} = 237 \text{ kJ}$$

cost subsidy

Electrolysis

$$p\Delta V = 4 \text{ kJ}$$

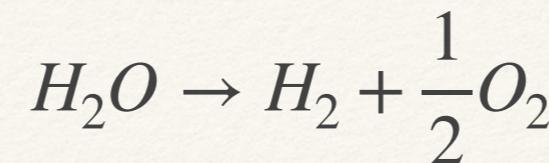
Of the 286 kJ of energy, 4 kJ is used for pushing the atmosphere away



$\Delta G = 237 \text{ kJ}$
electrical work by
the current

• $\Delta U = \Delta G + T\Delta S - p\Delta V = 282 \text{ kJ}$

• $T\Delta S = 49 \text{ kJ} \quad \text{heat}$



$$p = 1 \text{ atm}, T = 298 \text{ K}$$

$$\Delta H = 286 \text{ kJ}$$

$\Delta H = -286 \text{ kJ}$
(data: burning hydrogen)

$$S_{H_2O} = 70 \text{ J/K}, \quad S_{H_2} = 131 \text{ J/K} \quad S_{O_2} = 205 \text{ J/K}$$

$$T\Delta S = T \times (S_{H_2} + S_{O_2}/2 - S_{H_2O}) = 49 \text{ kJ}$$

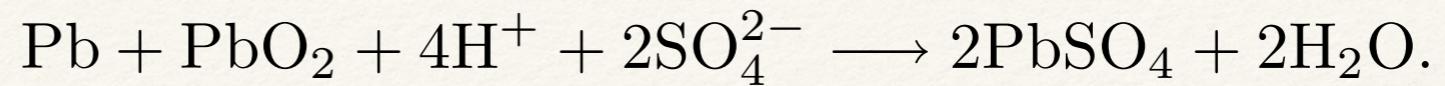
Run the process in reverse:
we *gain* 237 kJ of electrical
work

``fuel cell''
efficiency of
a heat engine: $e = \frac{\Delta G}{\Delta G + T\Delta S} = 83\%$

Classroom Exercise: Battery



lead-acid car battery



data: $\Delta G = -394 \text{ kJ}$ $\Delta H = -316 \text{ kJ}$

How much work does the battery provide?

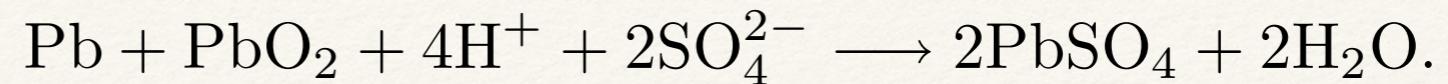
Does the battery dump heat to the environment or use heat from the environment?

How much heat does it dump to / take from the environment?

Classroom Exercise: Battery



lead-acid car battery



data: $\Delta G = -394 \text{ kJ}$ $\Delta H = -316 \text{ kJ}$

$$W = \Delta G = -394 \text{ kJ}$$

The battery provides 394 kJ of energy per mole
(recall - sign: work done by the system)

Energy that comes out of the chemicals: $\Delta H = 316 \text{ kJ}$



$\Delta H < 0$: the wizard gains energy!

W provided by the battery is *more* than the energy comes out the chemicals by the amount 78 kJ = heat *absorbed* from the environment

Thermodynamic Identities

recall Energy: $U(S,V,N)$

$$dU = TdS - pdV + \mu dN$$

Enthalpy: $H=U+pV$

$$dH = dU + pdV + Vdp = TdS + Vdp + \mu dN$$

- $H(S,p,N)$  Note different argument

$$V = \left(\frac{\partial H}{\partial p} \right)_{S,N}$$

Helmholtz free energy: $F=U-TS$

$$dF = -SdT - pdV + \mu dN$$

- $F(T,V,N)$ $S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}$ $p = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$ $\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$

Gibbs free energy: $G=U+pV-TS$

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

- $G(T,p,N)$ $S = - \left(\frac{\partial G}{\partial T} \right)_{p,N}$ $V = \left(\frac{\partial G}{\partial p} \right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N} \right)_{T,p}$

Maxwell Relations

Enthalpy: $H=U+pV$ (let N be always fixed for simplicity)

$$dH = TdS + Vdp$$

• $H(S,p)$

$$V = \left(\frac{\partial H}{\partial p} \right)_S \quad \left(\frac{\partial V}{\partial S} \right)_p = ?$$

↓

$$\left(\frac{\partial V}{\partial S} \right)_p = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right)_S = \frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right)_p = \left(\frac{\partial T}{\partial p} \right)_S \quad \left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial T}{\partial p} \right)_S$$

↑

*partial derivatives
commute*

``Maxwell Relation''

Classroom exercise: Maxwell Relations

Helmholtz free energy: $F=U-TS$ (let N be always fixed for simplicity)

$$dF = -SdT - pdV$$

- $F(T, V)$ $p = - \left(\frac{\partial F}{\partial V} \right)_T$ $\left(\frac{\partial p}{\partial T} \right)_V = ?$

Classroom exercise: Maxwell Relations

Helmholtz free energy: $F=U-TS$ (let N be always fixed for simplicity)

$$dF = -SdT - pdV$$

• $F(T, V)$

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad \left(\frac{\partial p}{\partial T} \right)_V = ?$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(- \left(\frac{\partial F}{\partial V} \right)_T \right) = \frac{\partial}{\partial V} \left(- \left(\frac{\partial F}{\partial T} \right)_V \right) = \left(\frac{\partial S}{\partial V} \right)_T$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

*partial derivatives
commute*

“Maxwell Relation”

Similar relation from G...

Legendre Transformation

(keep $N & V$ fixed for simplicity)

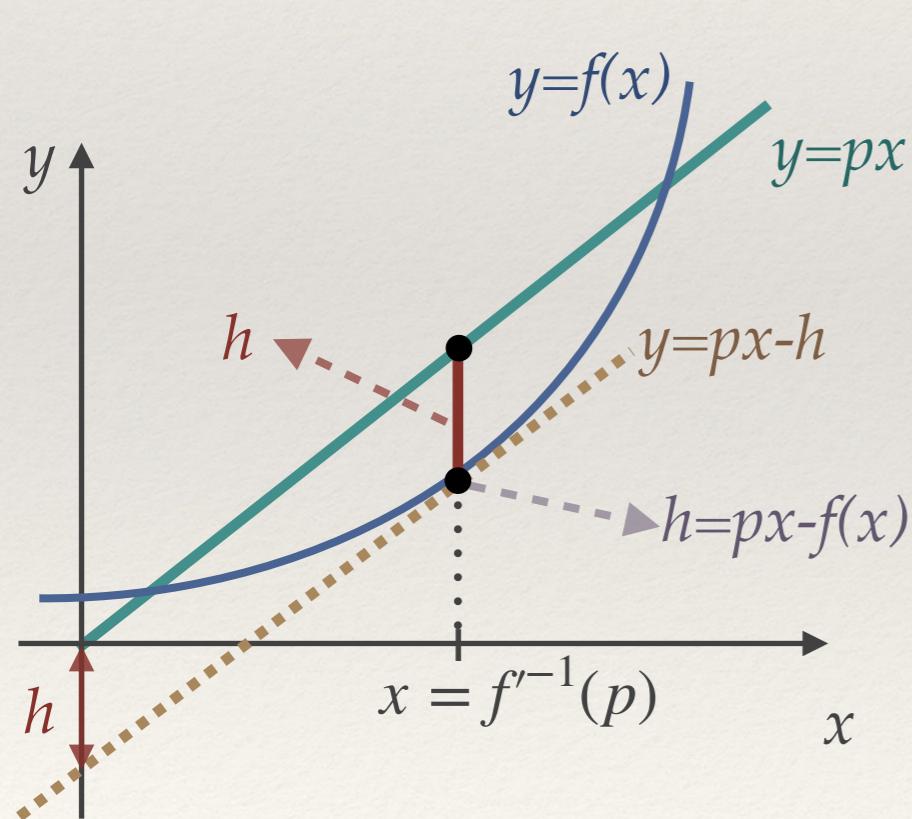
$$dU = TdS \quad U(S) \longrightarrow F = U - TS \quad F(T) \quad dF = -SdT$$

Notice: 1) the change in argument: S to T

$$2) \quad T = \frac{\partial U}{\partial S}$$

Looks a lot like

$$H(\mathbf{p}, \mathbf{q}) = \dot{\mathbf{q}} \cdot \mathbf{p} - L(\dot{\mathbf{q}}, \mathbf{q}), \quad \mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{q}}}$$



Given $f(x)$ express it in terms of its slope

At which point x the $f(x)$ has slope p ?

$h(x,p) = px - f(x)$: *distance between $y=f(x)$ and $y=px$*

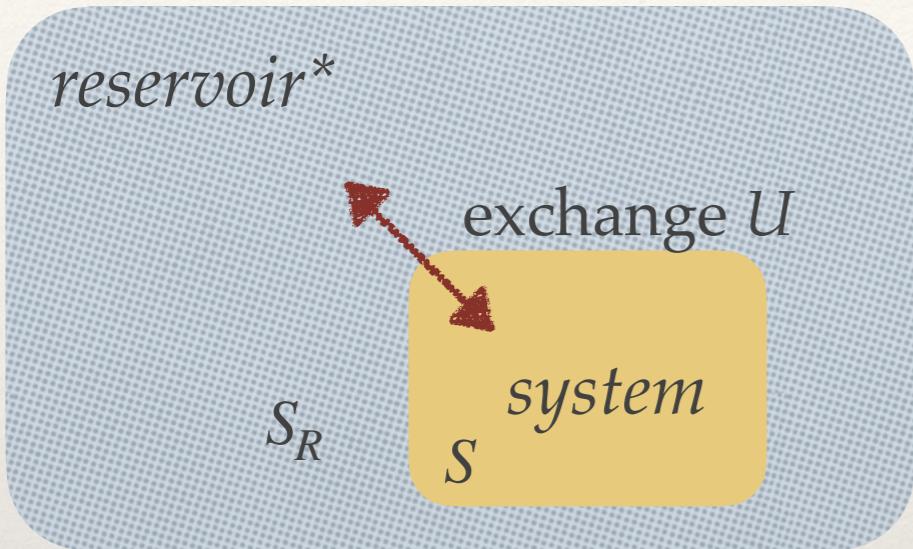
$$\frac{\partial h}{\partial x} = 0 \Leftrightarrow p = \frac{\partial f}{\partial x}$$

h : maximum $\Leftrightarrow p$ = slope of f

$h(p) = px - f(x)$ such that $p = f'(x)$

Legendre transform of f

Free Energy as a Force Towards Equilibrium



$$\Delta S_{tot} \geq 0$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \quad V, N: \text{constant}$$

constant temperature
 $T_R = T$

conservation of energy
 $dU = -dU_R$

$$dS_{tot} = dS_R + dS = \frac{1}{T_R} dU_R + dS = -\frac{1}{T} dU + dS = -\frac{1}{T} dF$$

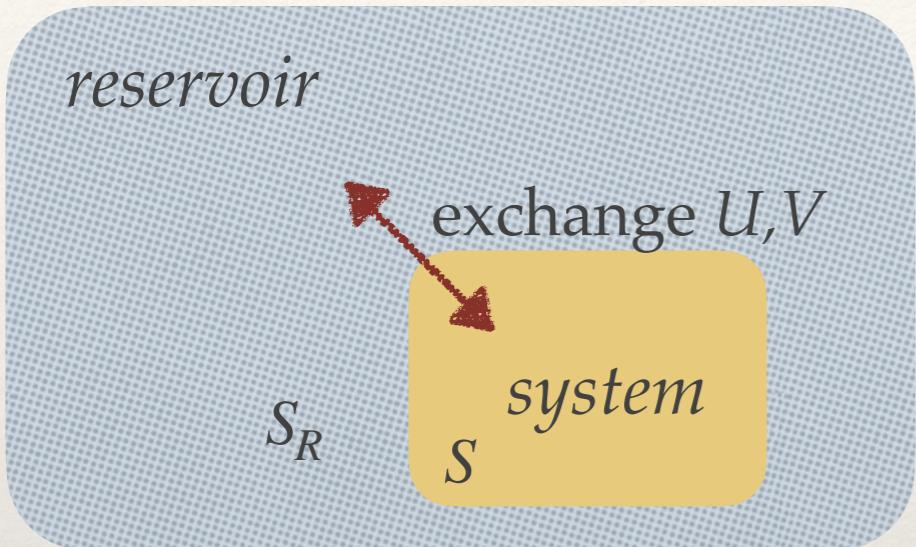
constant T, V, N

Total entropy of the universe increases

= Helmholtz free energy of the system decreases

*a large enough environment that can absorb a lot of energy without changing its temperature

Free Energy as a Force Towards Equilibrium



$$\Delta S_{tot} \geq 0$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN \quad N: \text{constant}$$

constant temperature and pressure

$$T_R = T, p_R = p$$

$$dV = -dV_R$$

$$dU = -dU_R$$

$$dS_{tot} = \frac{1}{T_R} dU_R - \frac{p_R}{T_R} dV_R + dS = -\frac{1}{T} dU + \frac{p}{T} dV + dS = -\frac{1}{T} dG$$

constant T, p, N

Total entropy of the universe increases

=

Gibbs free energy of the system decreases

Free Energy as a Force Towards Equilibrium

constant E, V
fixed N

Total entropy of the universe increases = Entropy of the system increases

constant T, V
fixed N

Total entropy of the universe increases = Helmholtz free energy of the system decreases

U : decreases (S_R increases)
(more important at low T)

$$F = U - TS \longrightarrow S: \text{increases}$$

(more important at high T)

constant T, p
fixed N

Total entropy of the universe increases = Gibbs free energy of the system decreases

U : decreases, S_R increases

$$G = U + pV - TS \longrightarrow S: \text{increases}$$

(more important at high T)

V : decreases, S_R increases

Intensive vs Extensive Quantities

We have seen a plethora of thermodynamic variables / potentials:

$$U, T, S, p, V, \mu, N, H, F, G$$



V, U, S, P, T



Extensive (double):
 $U, N, V, S, H, F, G, \text{mass}$

Intensive (do not double):
 $T, p, \mu, \text{density}$

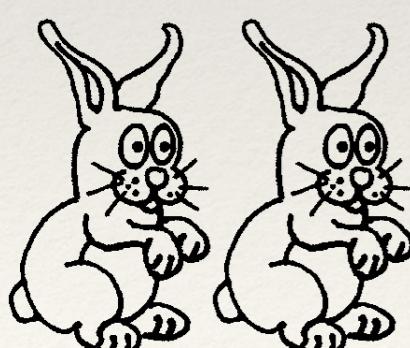
intensive \times extensive = extensive

cannot add together intensive and extensive quantities



More generally: $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$ (extensive)

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad p = T \frac{\partial S}{\partial V} \quad \mu = T \frac{\partial S}{\partial N} \quad (\text{intensive})$$



$2V, 2U, 2S, P, T$

ratio of extensive quantities

Intensive vs Extensive Quantities

- e.g.
- Helmholtz free energy

$$F = U - TS$$

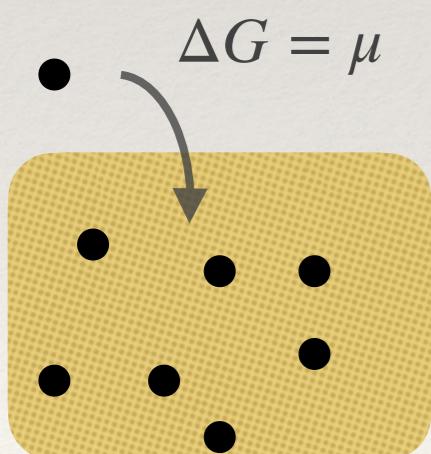
↑
T: intensive
↓
F, U, S, TS: extensive

- Gibbs free energy

$$G = U - TS + pV$$

↑
G: extensive
↓
G(T, p, N)
T, p: intensive
↓
N: extensive

$G(T, p, N) = \text{extensive} \propto N$ (the only extensive argument)



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

multiple types of particles
 $G = N_1 \mu_1 + N_2 \mu_2 + \dots$

Chemical potential = Gibbs Free energy per particle

Note: same argument does not hold for $F(T, V, N)$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V}$$

\downarrow
N & V: extensive

Intensive vs Extensive Quantities

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

e.g. fixed amount of gas at constant T

$$\left(\frac{\partial \mu}{\partial p} \right)_T = \frac{1}{N} \left(\frac{\partial G}{\partial p} \right)_T = \frac{V}{N}$$

for ideal gas: $\frac{\partial \mu}{\partial p} = \frac{V}{N} = \frac{kT}{p}$ $\mu(T, p) = \mu(T, p_0) + kT \log(p/p_0)$

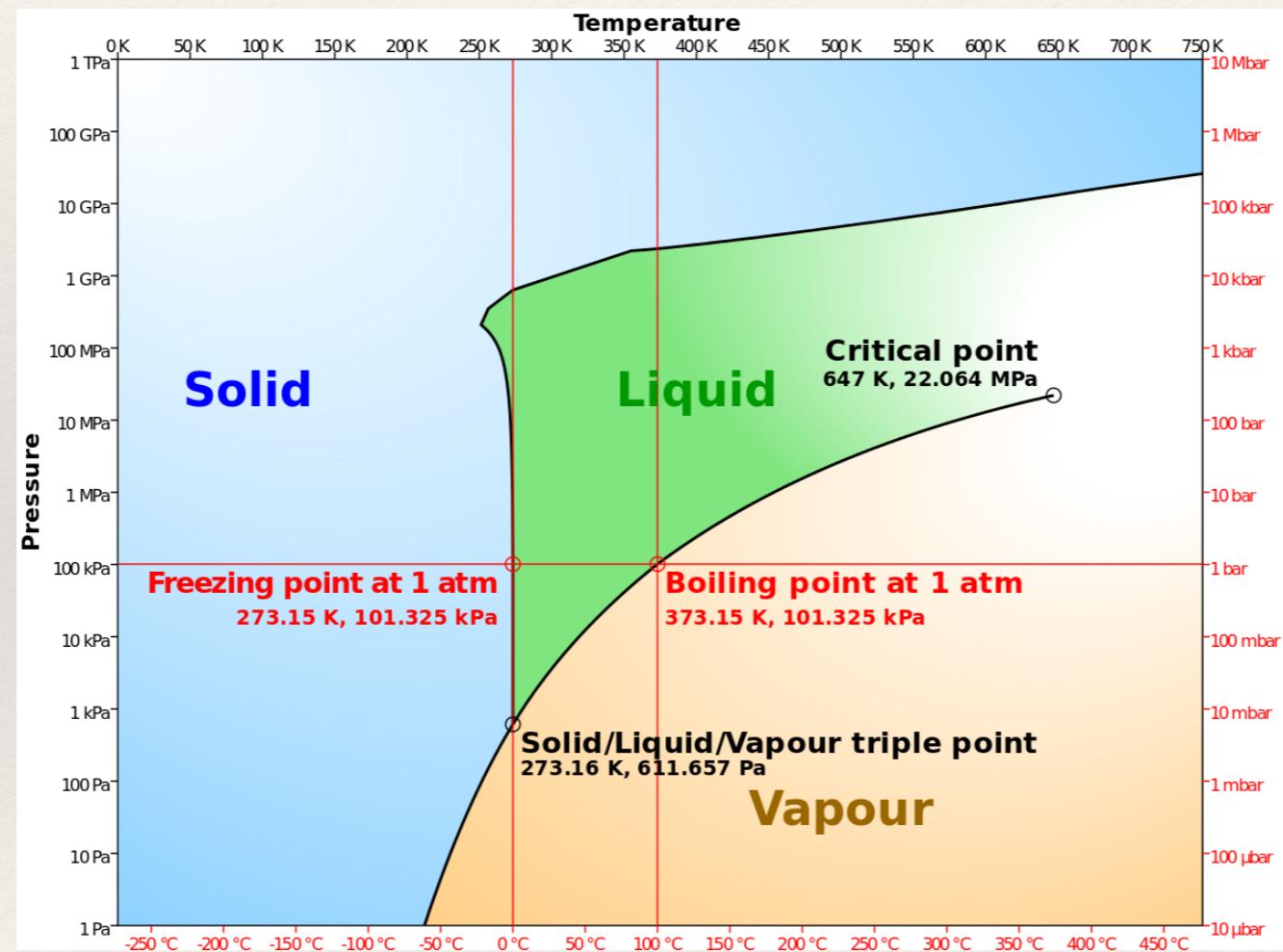
can set $p_0=1$ atm

$\mu(T, p_0) = \mu^\circ(T)$: read from Gibbs free energy tables

Phase Transitions

Abrupt, discontinuous change in the properties of the system

e.g.: melting of ice, boiling of water, condensation, ...

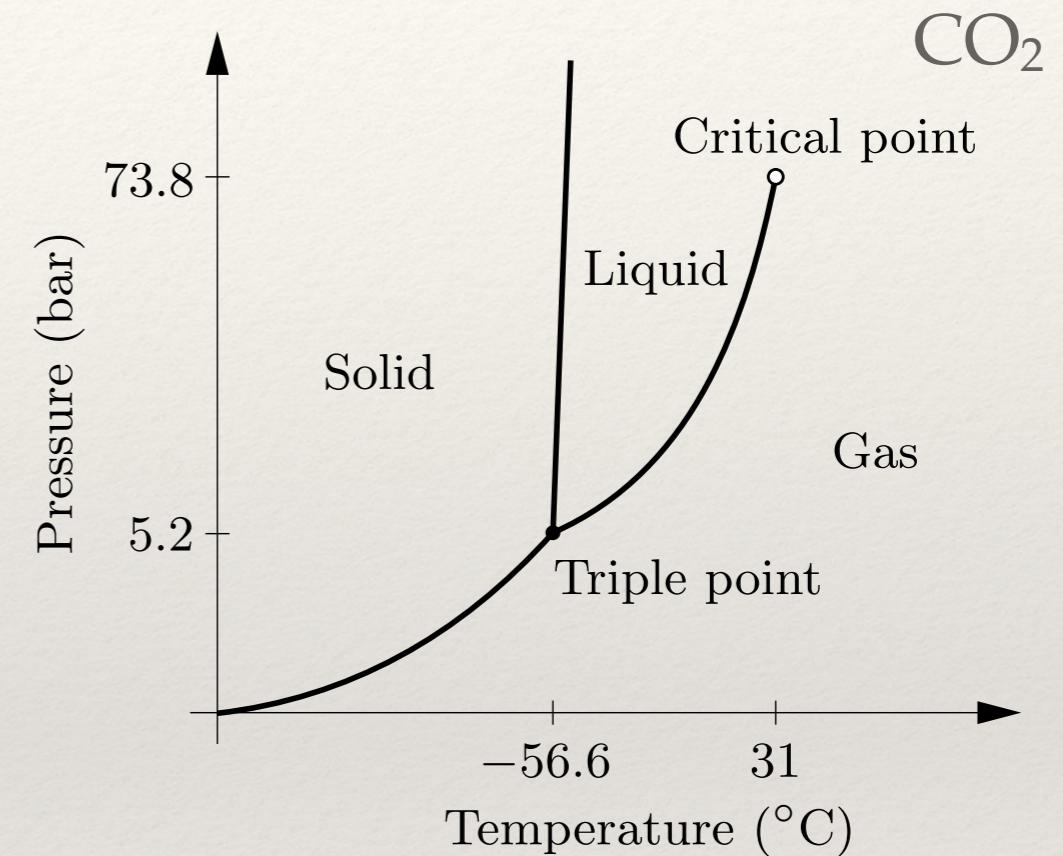
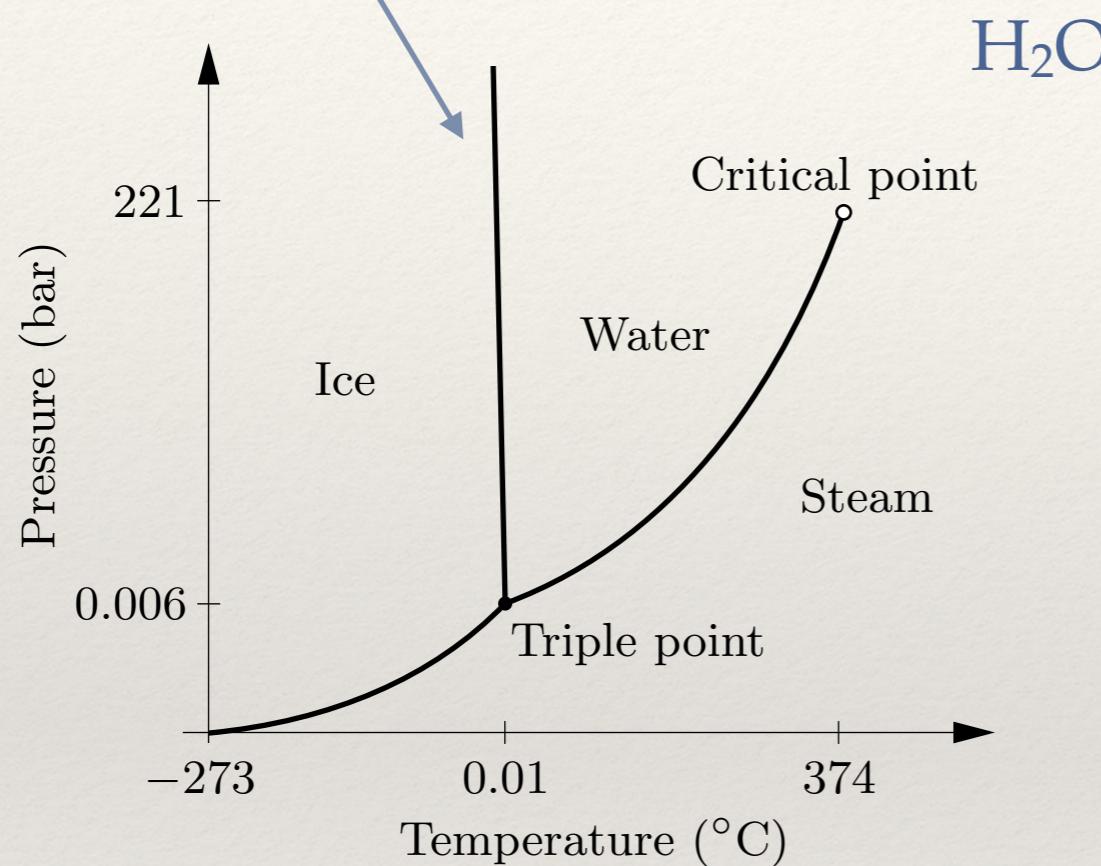


solid, liquid, vapor:
phases

phase diagram: Most stable phases for given parameters (here p, T)

Phase Transitions

Negative slope: *unusual*



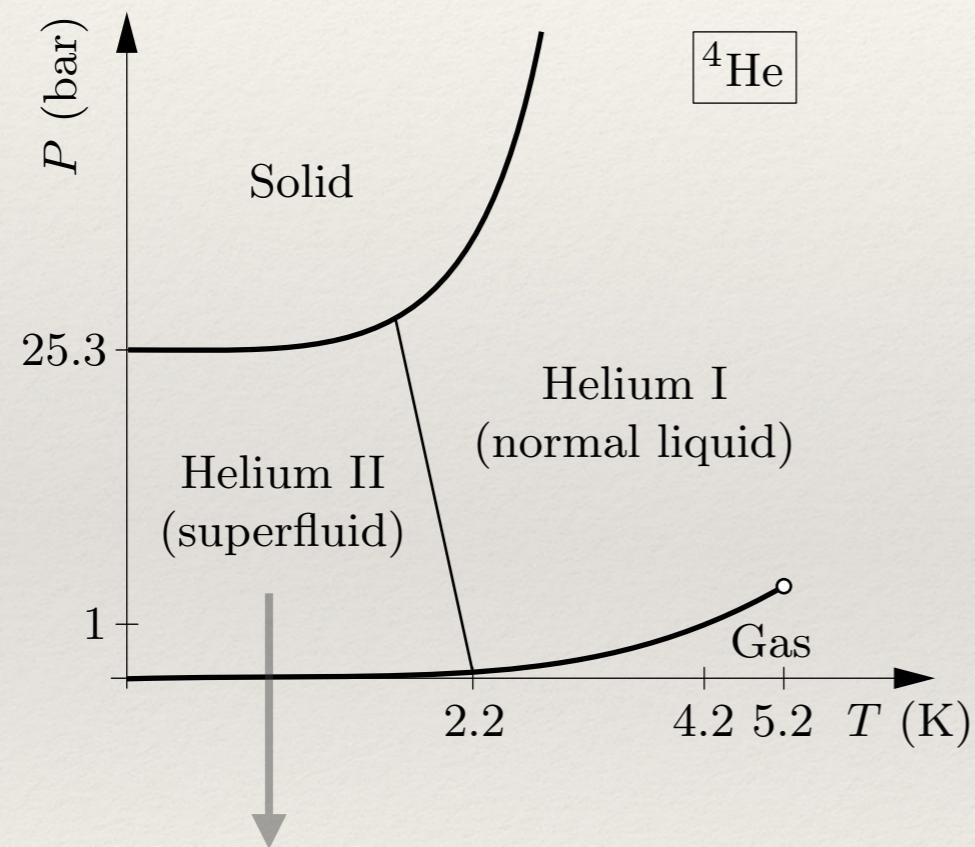
liquid-gas slope: always positive (need higher p to keep liquid phase for higher T)

Liquid-gas transition *ends at critical point*: no distinction between the two phases beyond it.

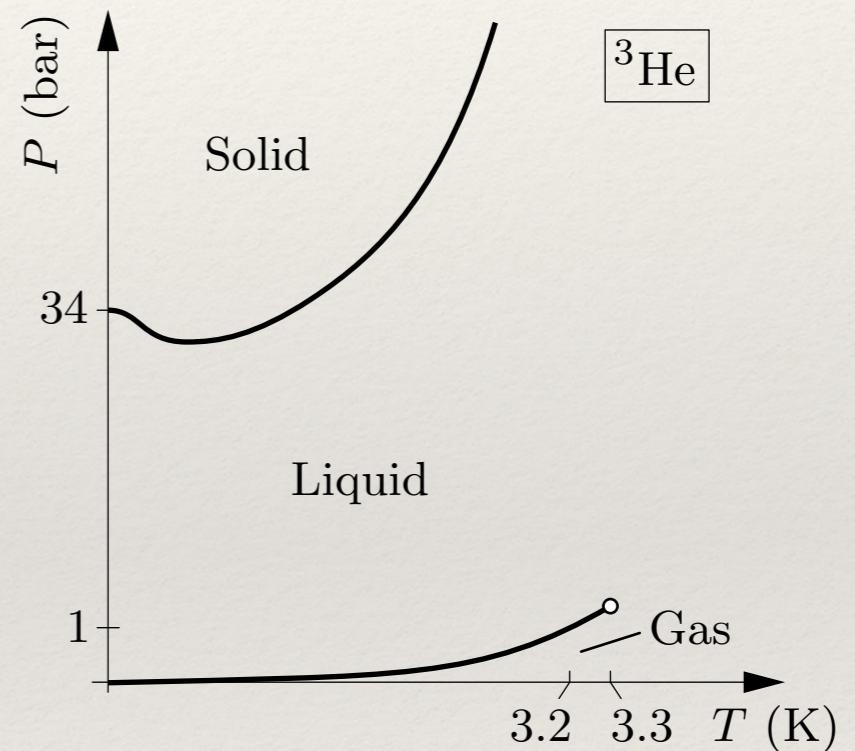
Solid-liquid phases are qualitatively distinct (crystal vs random), no critical point

Phase Transitions

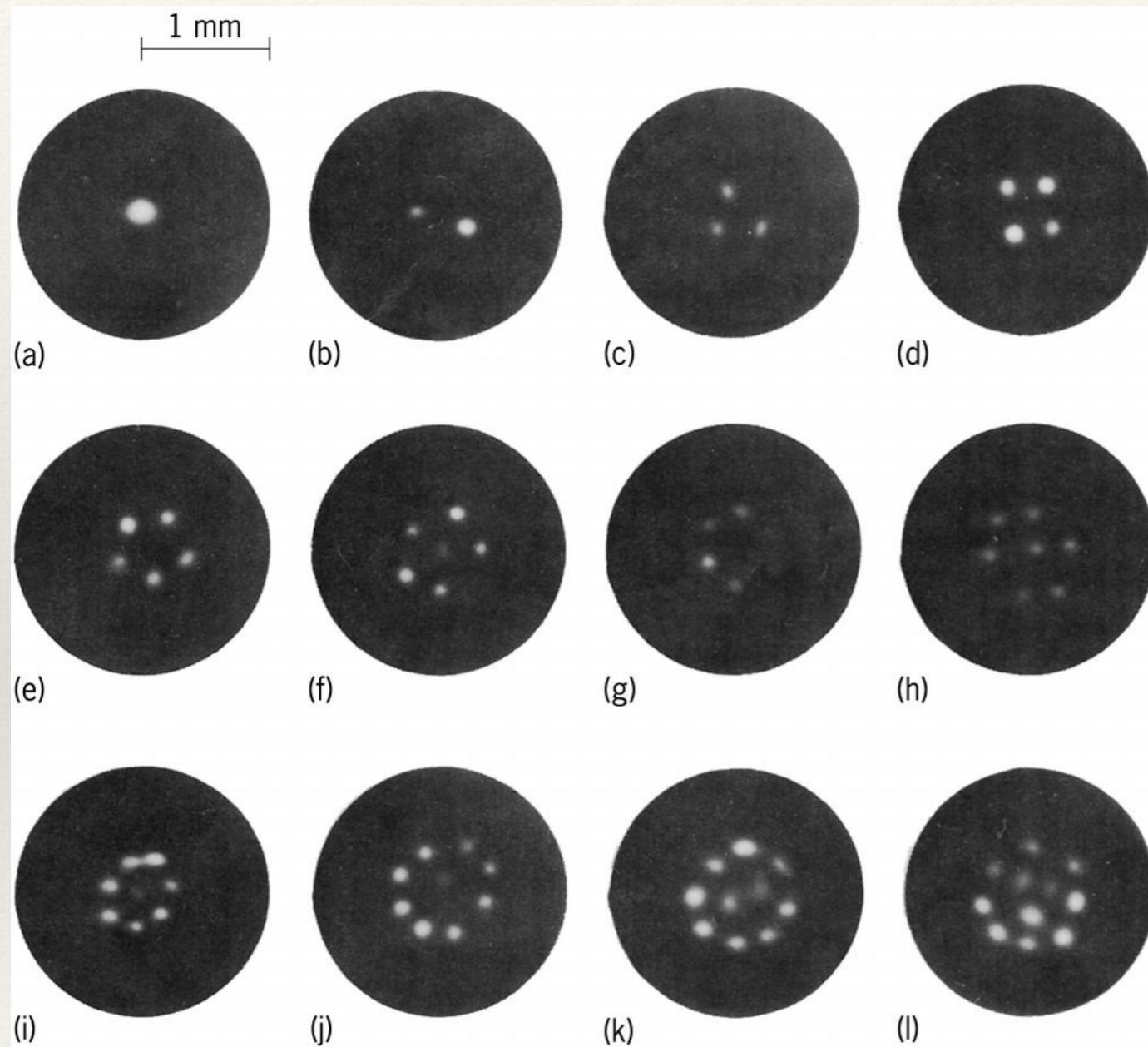
Helium: Liquid at 0 K!



No viscosity,
high conductivity,
Quantum mechanical



Phase Transitions



*Superfluid:
Large-scale quantum mechanical
wave function*

Vortices in superfluid He₄

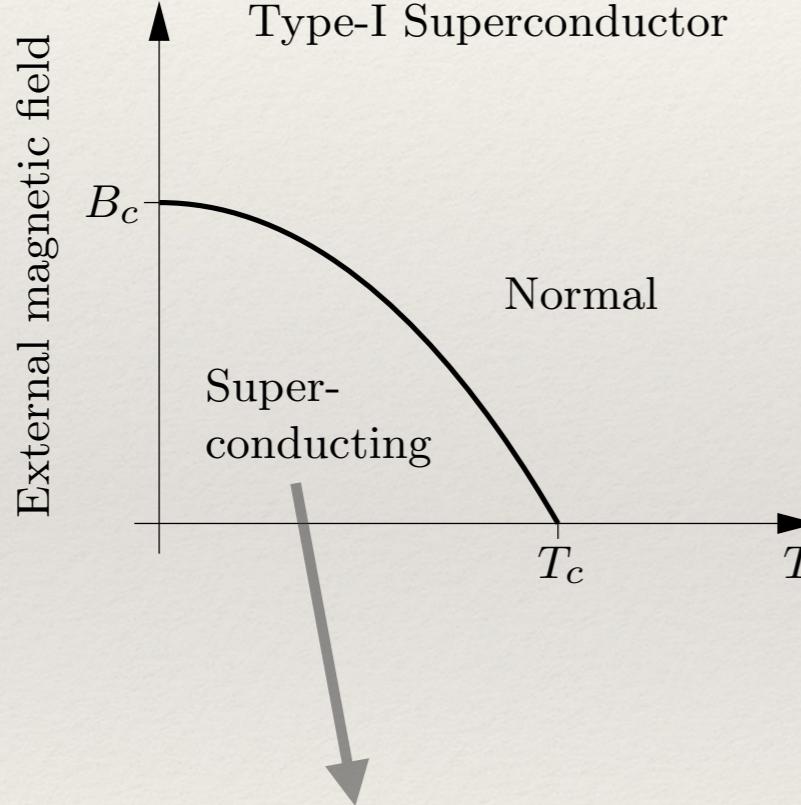
*Rotational energy levels are
quantized:*

Number of vortices
↔
Level number

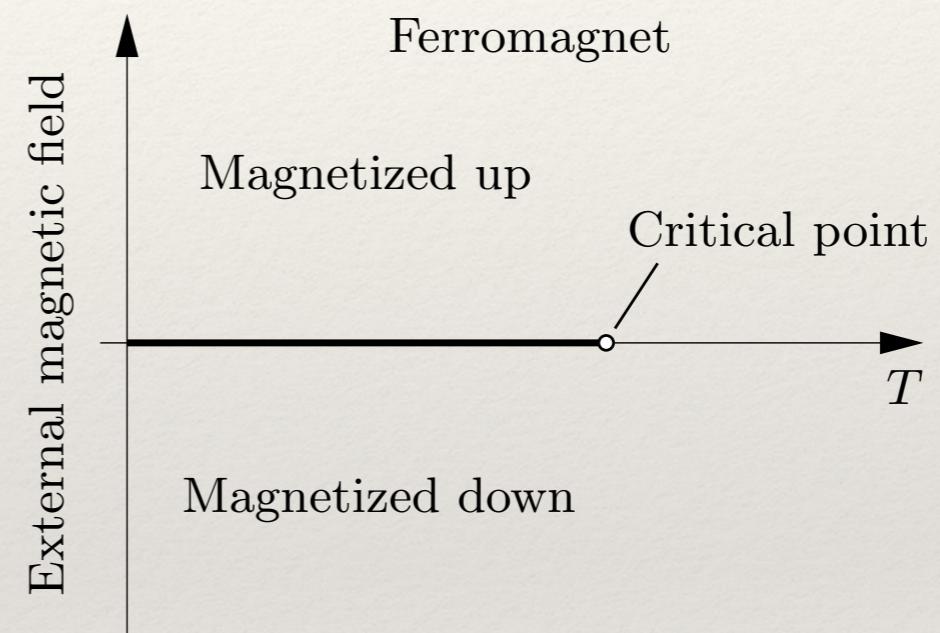
[E. J. Yarmchuk, M. J. V. Gordon, and R. E. Packard, PRL 3:214–217, 1979]

Phase Transitions

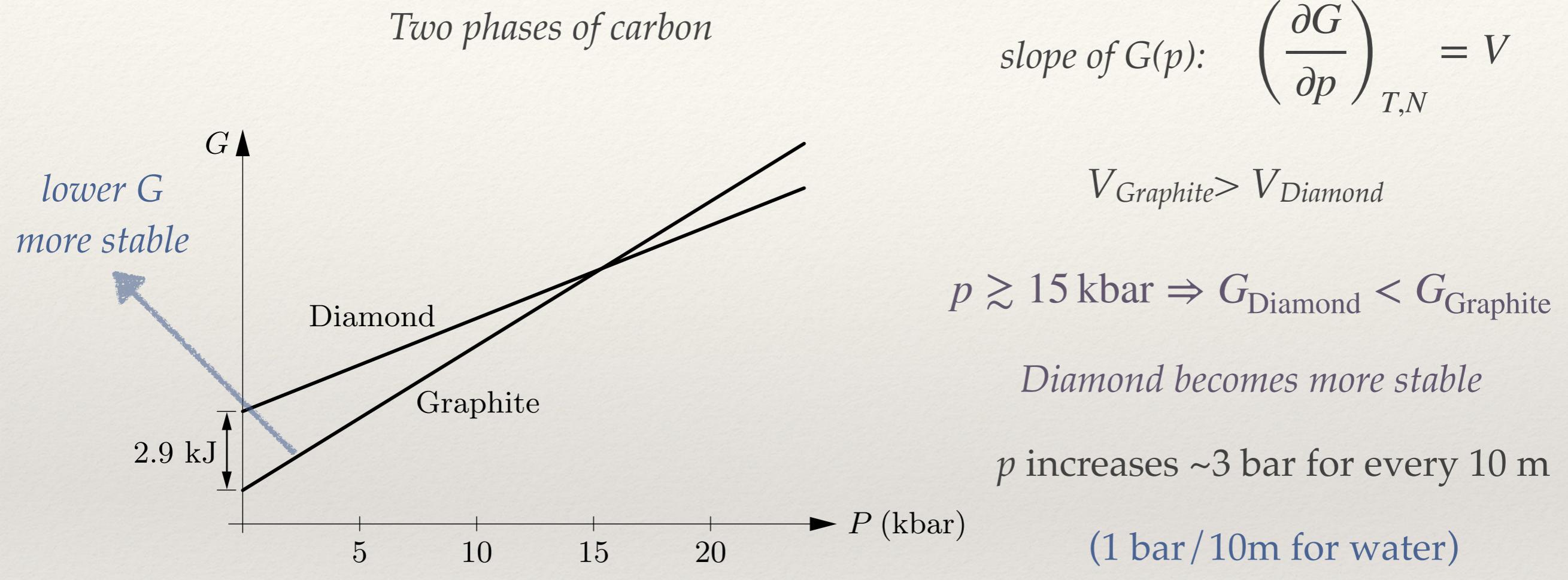
There are other variables that lead to phase transitions in certain materials



Zero electrical resistance



Graphite and Diamond



At a depth of $\sim 50\text{km}$ underground, diamond is more stable.
(taking into account the change in T , diamond is mostly formed at $\sim 100\text{-}200$ km depth)

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S$$

$$S_{\text{Graphite}} > S_{\text{Diamond}}$$

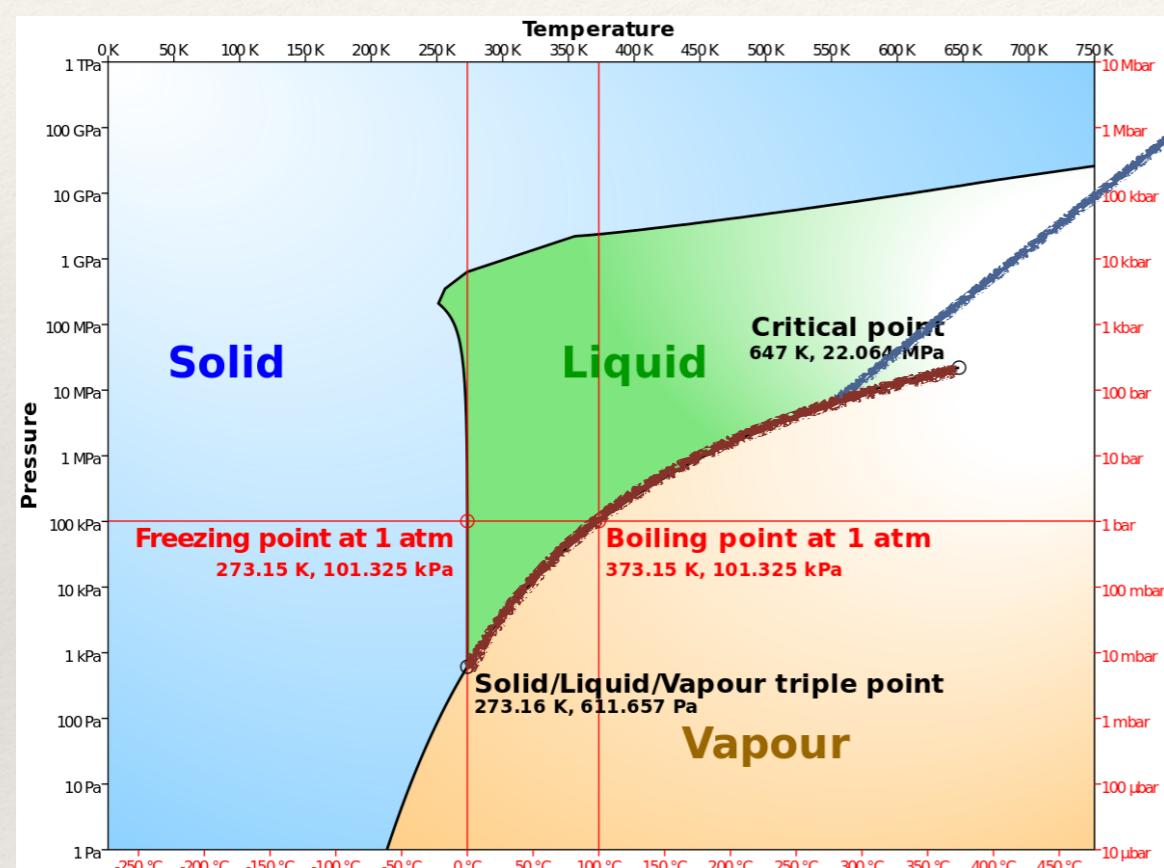
Diamond is *less stable at higher T*

Graphite and Diamond



Phase Boundaries

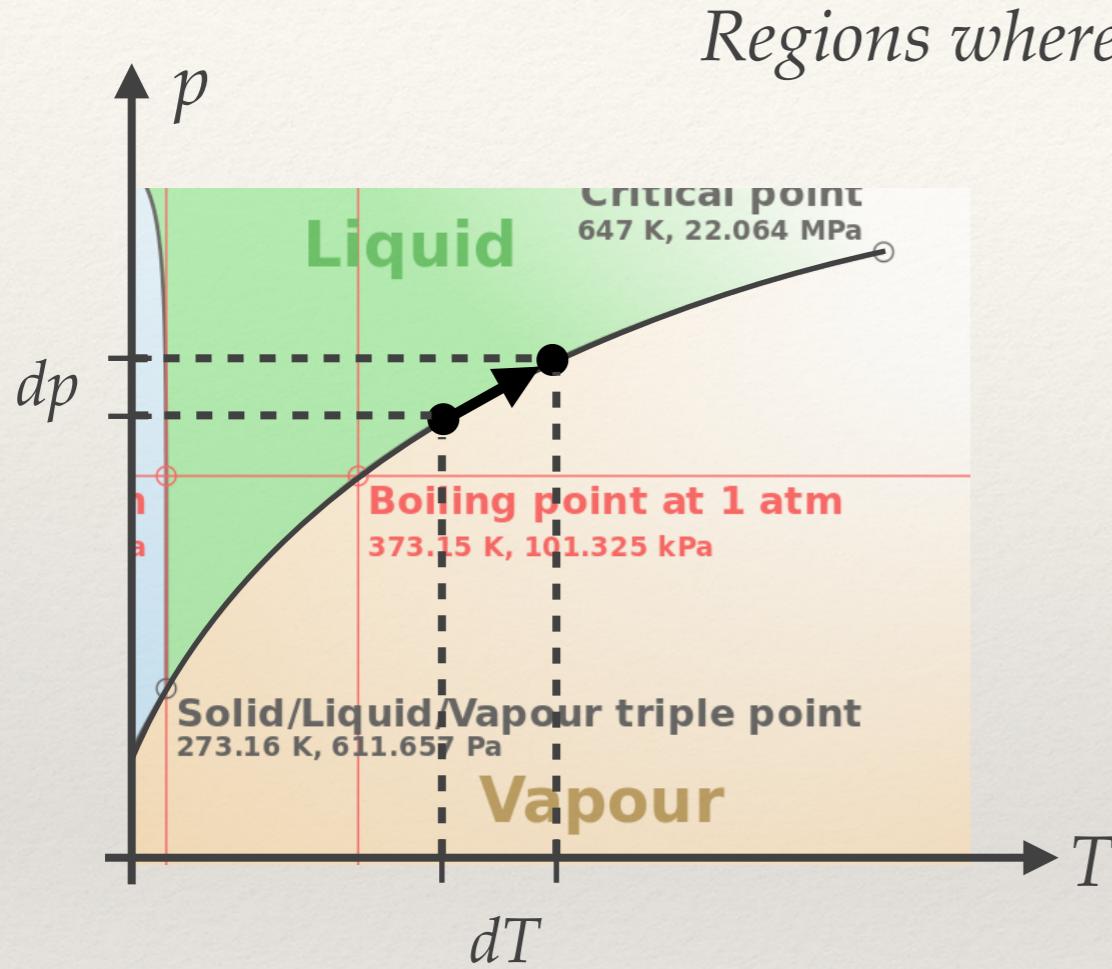
Regions where two phases are equally stable



e.g. liquid-gas boundary

curve defined by $G_l(T,p)=G_g(T,p)$
(assume N=fixed)

Phase Boundaries



e.g. liquid-gas boundary

curve defined by $G_l(T,p)=G_g(T,p)$
(assume $N=\text{fixed}$)

infinitesimal change: $dG_l = dG_g$

$$\frac{\partial G_l}{\partial T}dT + \frac{\partial G_l}{\partial p}dp = \frac{\partial G_g}{\partial T}dT + \frac{\partial G_g}{\partial p}dp$$

$$-S_l dT + V_l dp = -S_g dT + V_g dp$$

Clausius-Clapeyron relation

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

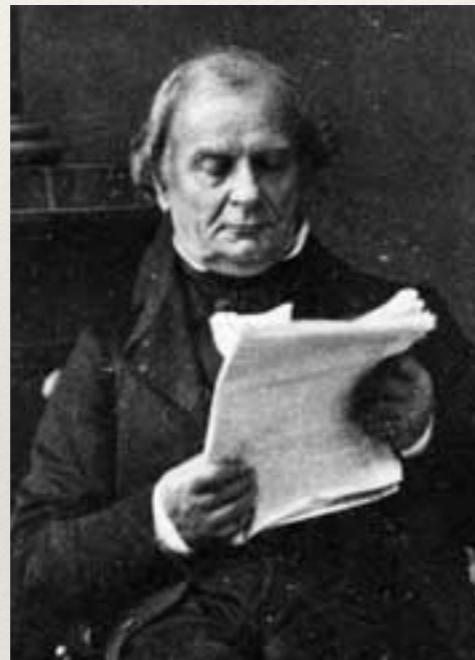
slope: $\frac{dp}{dT} = \frac{S_g - S_l}{V_g - V_l}$

latent heat: $L = T\Delta S$

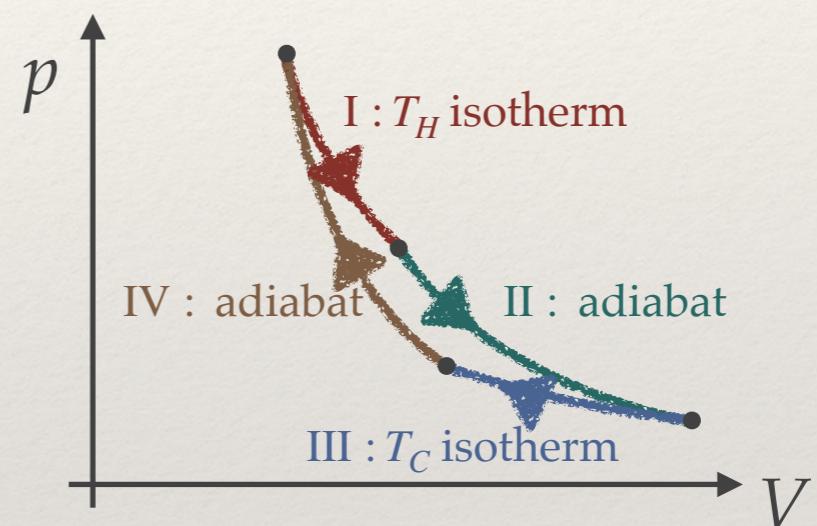
holds for any phase boundary in pT plane

Phase Boundaries

Clausius-Clapeyron relation $\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$ latent heat: $L = T\Delta S$

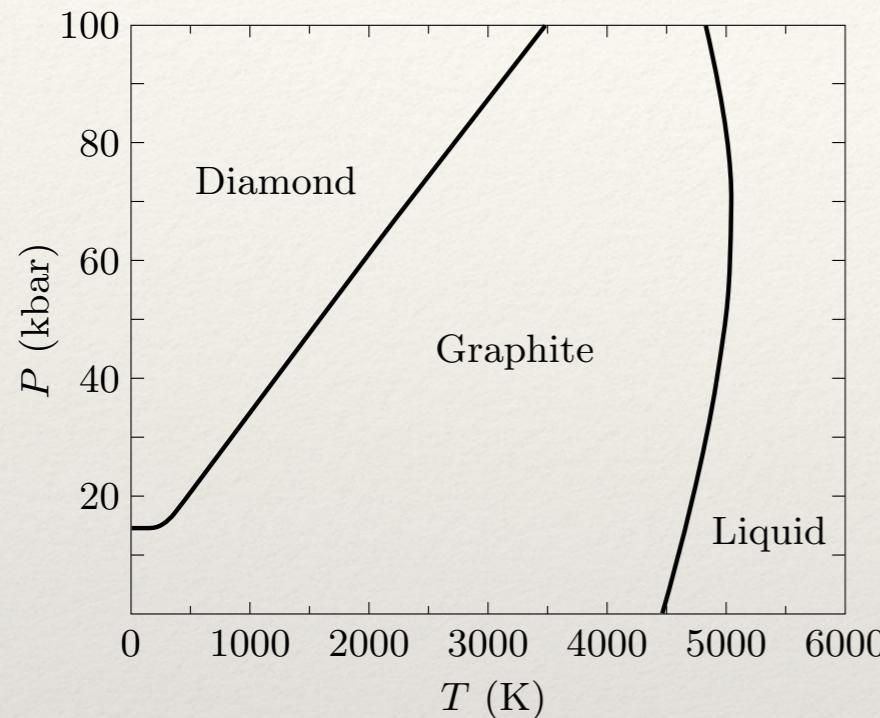


Benoît Paul Émile Clapeyron
[1799-1864]



Classroom Exercise: Graphite-Diamond

e.g. diamond-graphite



at room temperature:

$$S_g - S_d = 3.4 \text{ J/K}$$

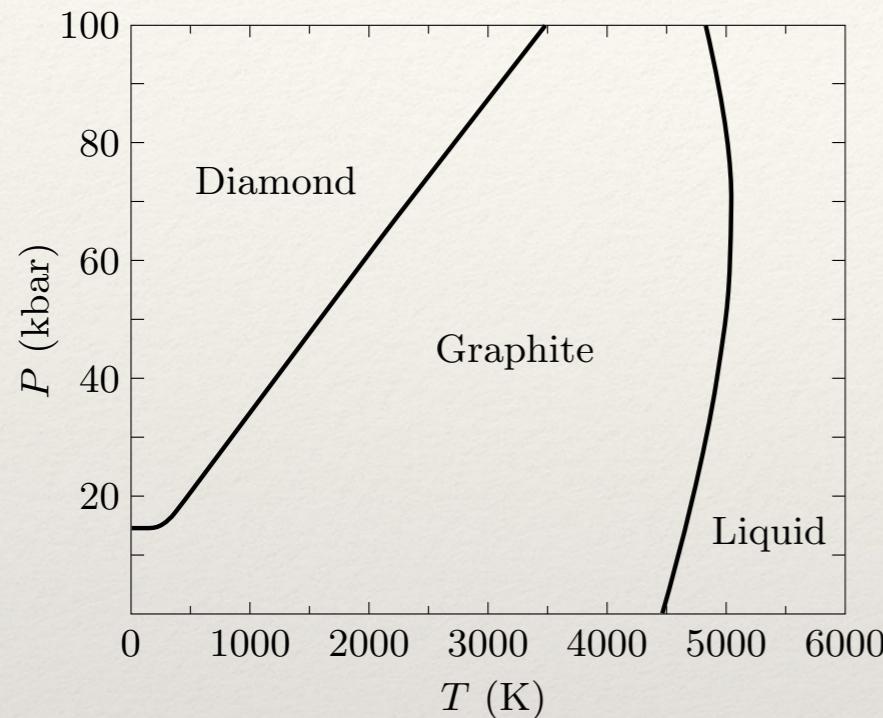
$$V_g - V_d = 1.9 \times 10^{-6} \text{ m}^3$$

Recall that at room temperature ($\sim 300\text{K}$) graphite-diamond phase transition occurs at 15 kbar.

*Using the room temperature values of ΔV and ΔS
estimate what pressure the phase transition occur at 2000K*

Classroom Exercise: Graphite-Diamond

e.g. diamond-graphite



at room temperature:

$$S_g - S_d = 3.4 \text{ J/K}$$

$$V_g - V_d = 1.9 \times 10^{-6} \text{ m}^3$$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = 1.8 \times 10^6 \text{ Pa/K} = 18 \text{ bar/K}$$

For each 1K increase in T , p goes up by 18 bars.

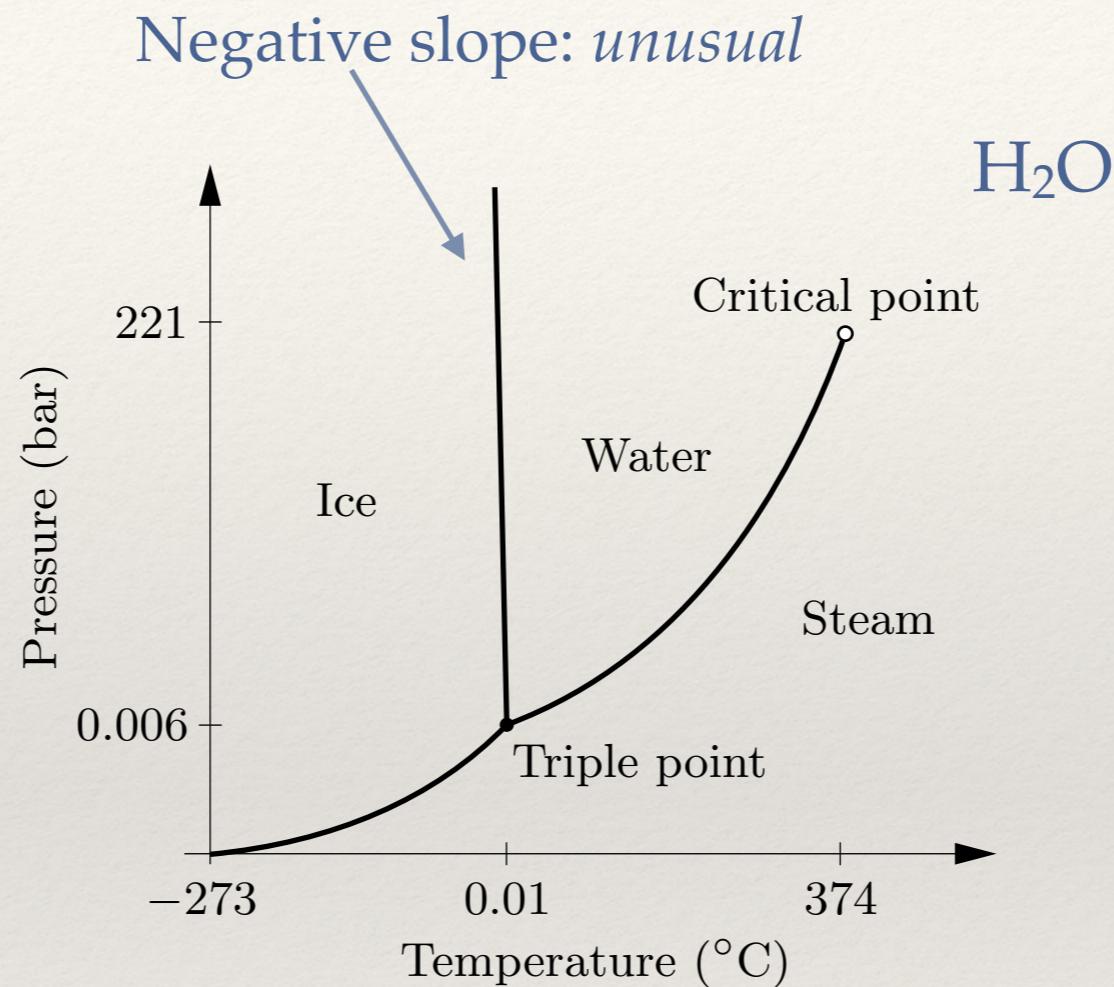
$$\Delta p = (18 \text{ kbar/K}) \times \Delta T = (18 \text{ kbar/K}) \times (2000\text{K} - 300\text{K}) = 30.6 \text{ kbar}$$

$$p(2000 \text{ K}) = p(300\text{K}) + \Delta p = 15 \text{ kbar} + 30.6 \text{ kbar} = 45.6 \text{ kbar}$$

Note: Comparing with the actual phase diagram (figure) this is an underestimate.
 ΔS at higher temperatures is higher than the room temperature value.

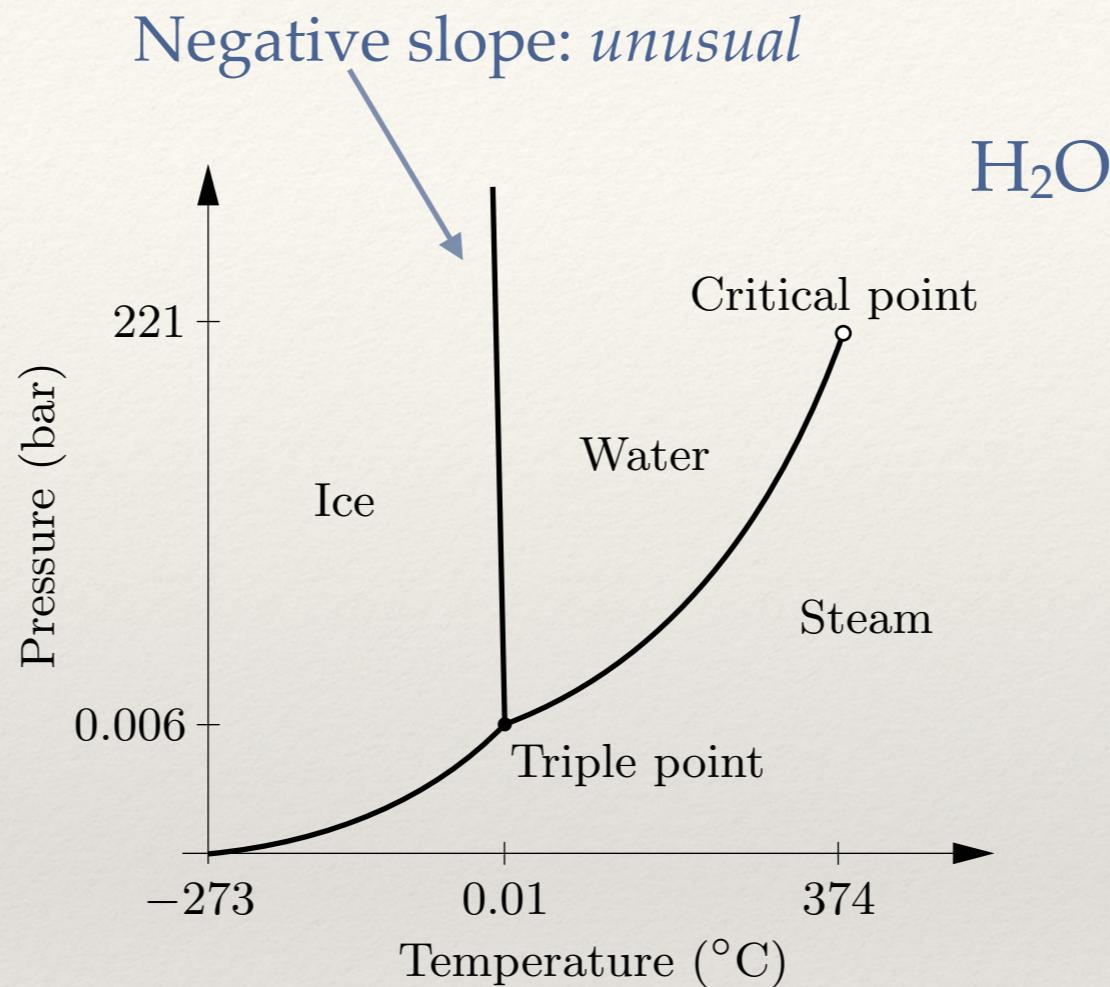
Assuming the pressure increases 3 bar / 10 m, 45-60 kbar occurs at ~150-200 km depth

Classroom Exercise: Water and Ice



Based on the figure above explain why ice floats

Classroom Exercise: Water and Ice

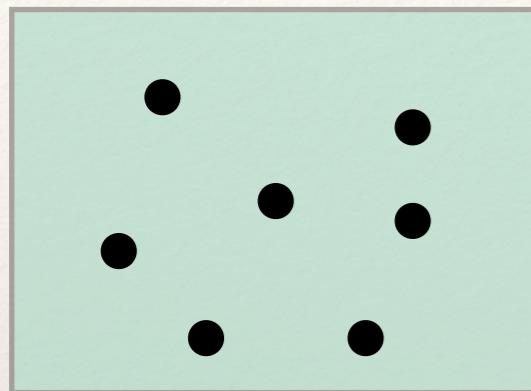


Negative slope
 $\frac{dp}{dT} < 0$

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

$\Delta S > 0$: entropy of water is greater
(latent heat: $L = T\Delta S > 0$)
 $\Delta V < 0$: water occupies *less* volume
than ice, hence larger density

van der Waals Equation of State



Average inter-particle
distance

ideal gas:

$$l = (V/N)^{1/3} \gg \lambda$$

thermal de Broglie
wavelength

Equation of state: $pV=NkT$

no interactions between particles

This is a good approximation for a dilute gas, but cannot describe the phase transition to liquid since it ignores interactions

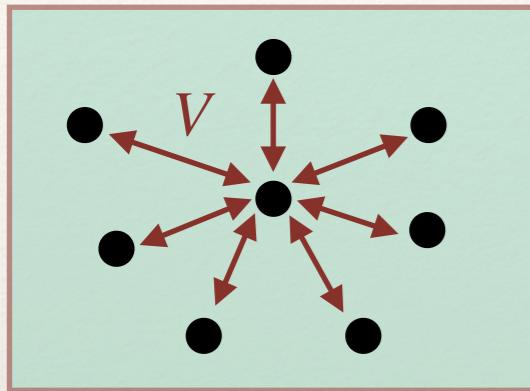
two modifications: 1. There is short-range attractive interaction between particles
2. Each particle has a repulsive core (cannot compress all the way to $V=0$)

$$\left(p + \frac{aN^2}{V^2} \right) (V - Nb) = NkT$$

1. a =strength of
repulsive interaction

2. b ``=“minimum volume occupied
by each particle when compressed

van der Waals Equation of State



Potential energy per particle:

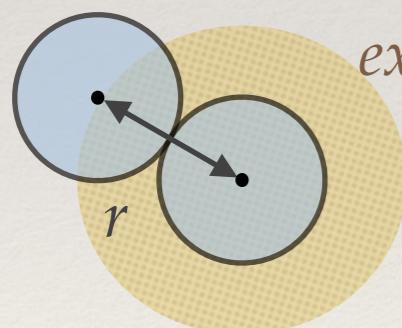
$$V_{int} = -a\rho = -a\frac{N}{V}$$

a = empirical constant
(depends on the type of molecule)

Total potential energy: $V_{int}N = -a\frac{N^2}{V}$

attractive interaction *decreases* the pressure by the amount

$$P_{int} = -\frac{\partial U}{\partial V} = -\frac{d}{dV}\left(-\frac{aN^2}{V}\right) = -\frac{aN^2}{V^2}$$



excluded volume per particle= $2b$

of configurations: $\frac{1}{N!} \prod_{k=0}^{N-1} (V - 2bk) \approx \frac{1}{N!} (V - Nb)^N$

available volume= $V-Nb$

Total pressure: $P = \frac{NkT}{V - Nb} + P_{int} = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$

[van der Waals, 1873 (PhD thesis)]

van der Waals Equation of State

Remarks

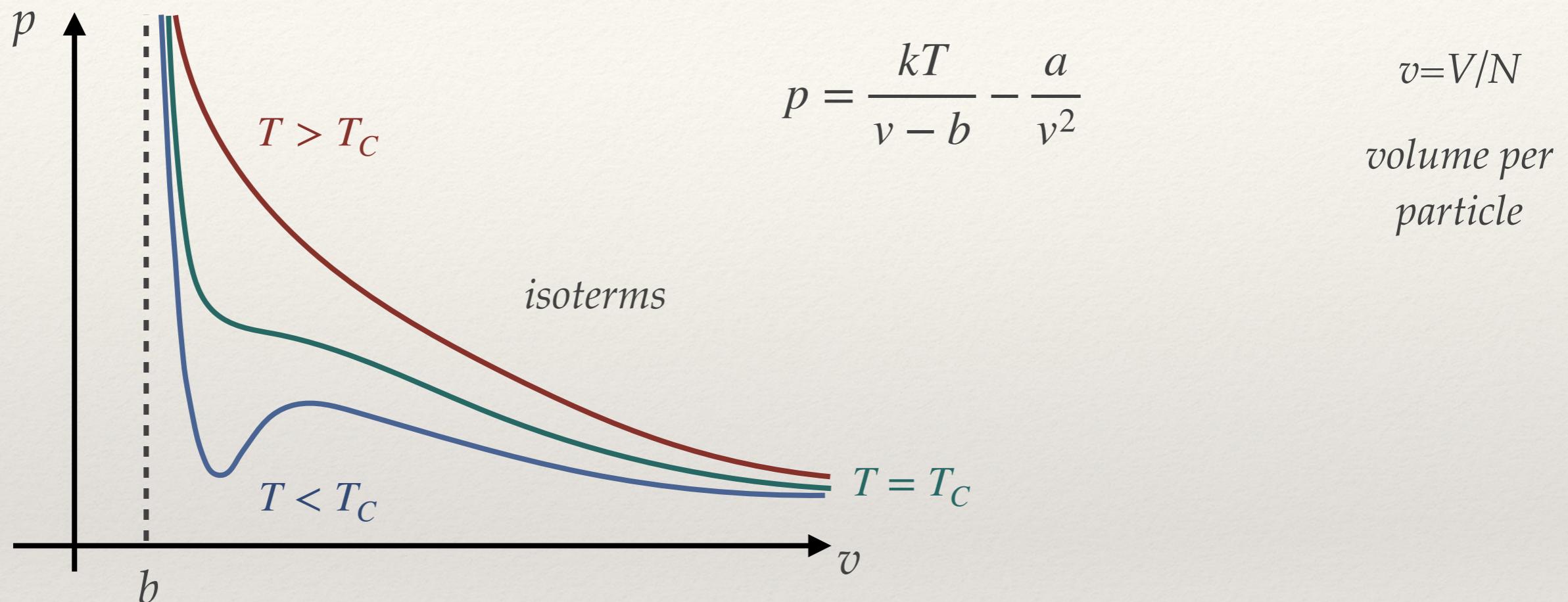
- vdW equation is a model and is not derived from fundamental laws
 - It does a *fantastic job* in qualitatively understanding the liquid-gas phase transition
 - a, b are empirical constants that depend on the kind of molecules

$b \sim$ typical size of the molecule $b \sim (4 \text{ \AA})^3 \sim 10^{-29} \text{ m}^3$ for N₂, H₂O etc...

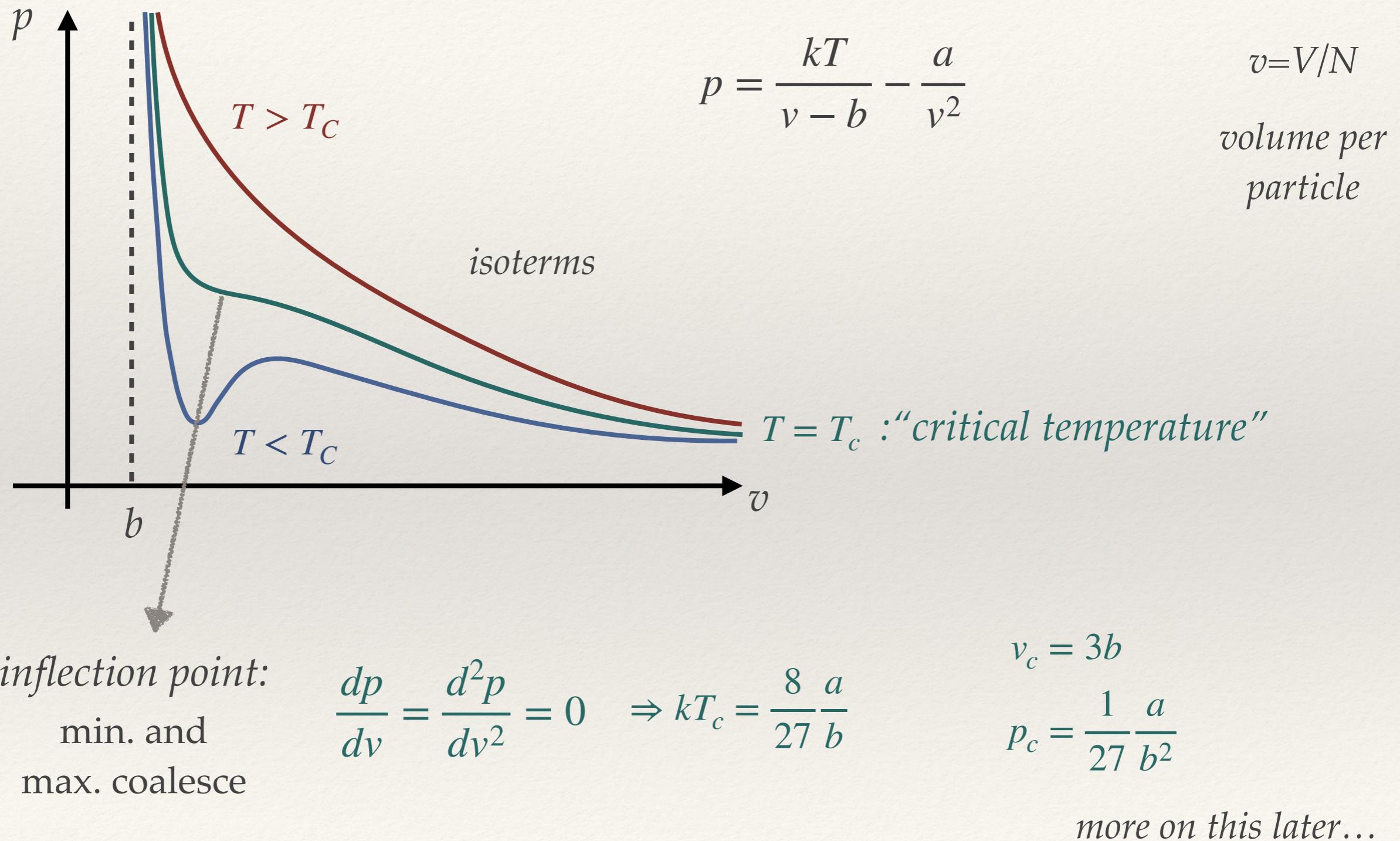
$[a] = J m^3$, $a = (\text{average molecular interaction energy}) \times (\text{volume it acts})$ (more variable than b)

- $\sim 0.04 \text{ eV} (\text{N}_2) \quad (4 \text{ \AA})^3$
- $\sim 0.16 \text{ eV} (\text{H}_2\text{O})$
- $\sim 0.001 \text{ eV} (\text{He})$

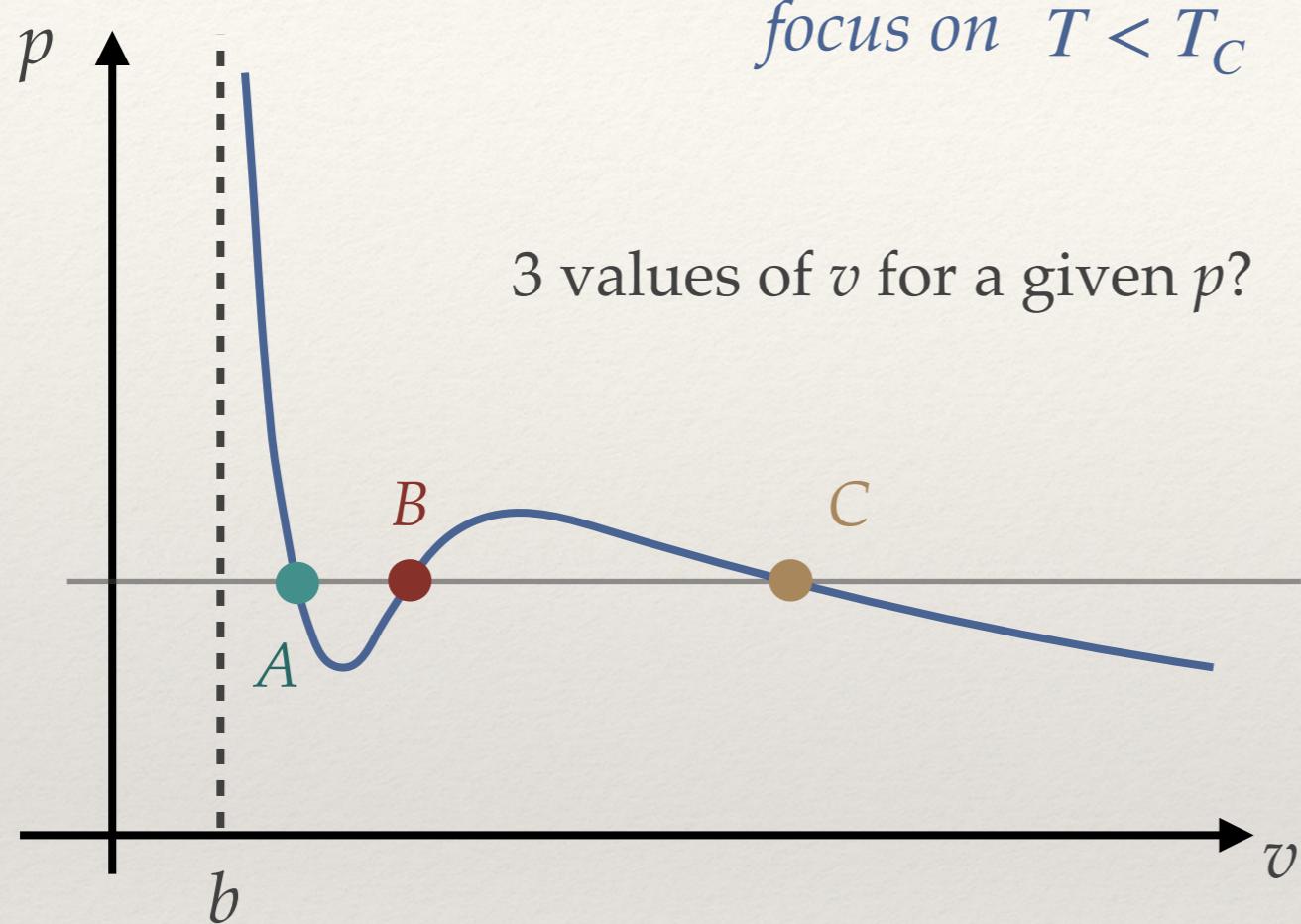
van der Waals Equation of State



van der Waals Equation of State



vdW: Phases



focus on $T < T_C$

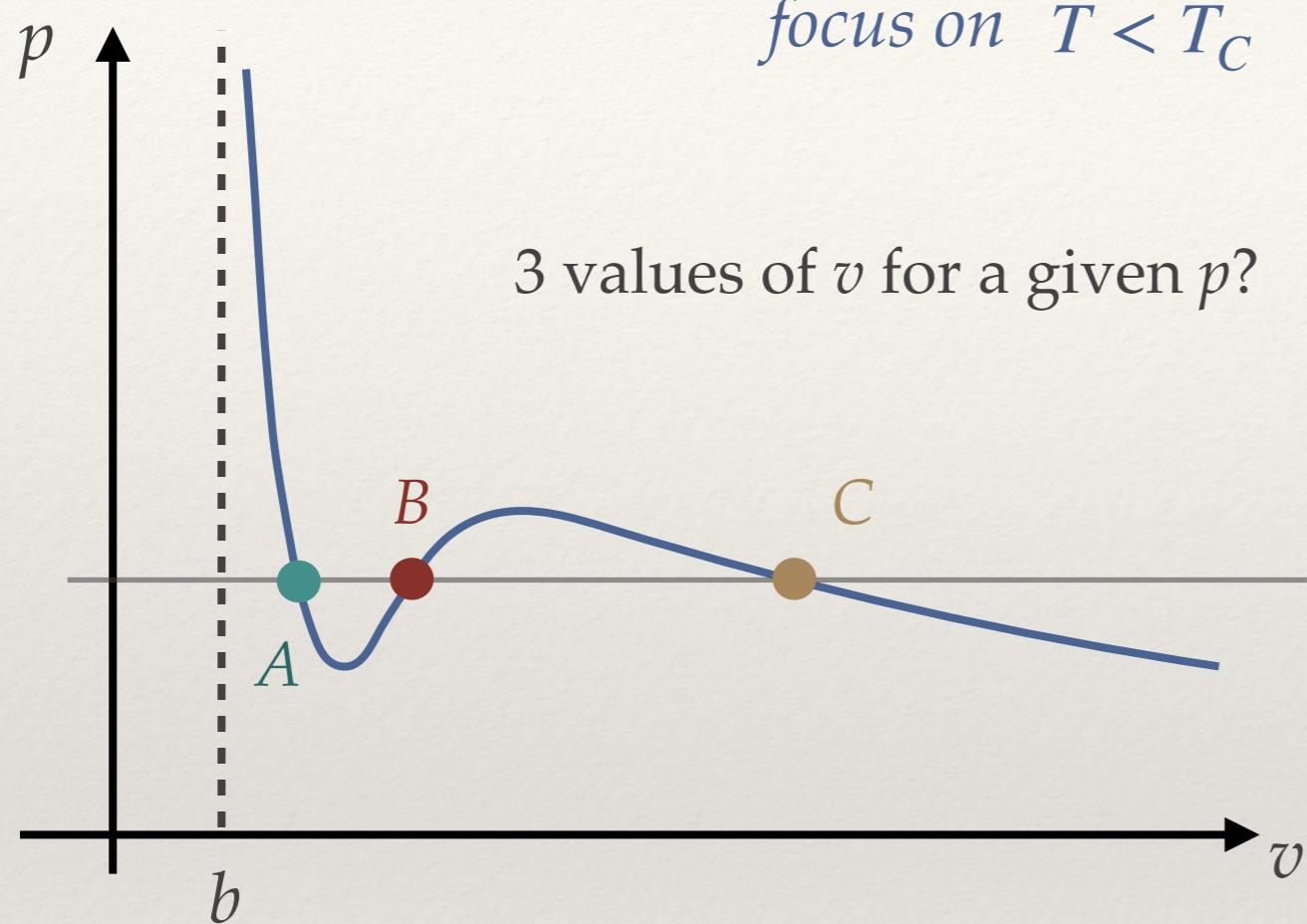
3 values of v for a given p ?

B. $\frac{dp}{dv} < 0$

Pressure *increases* as you make the gas more dilute and *decreases* when compressed

?????

vdW: Phases

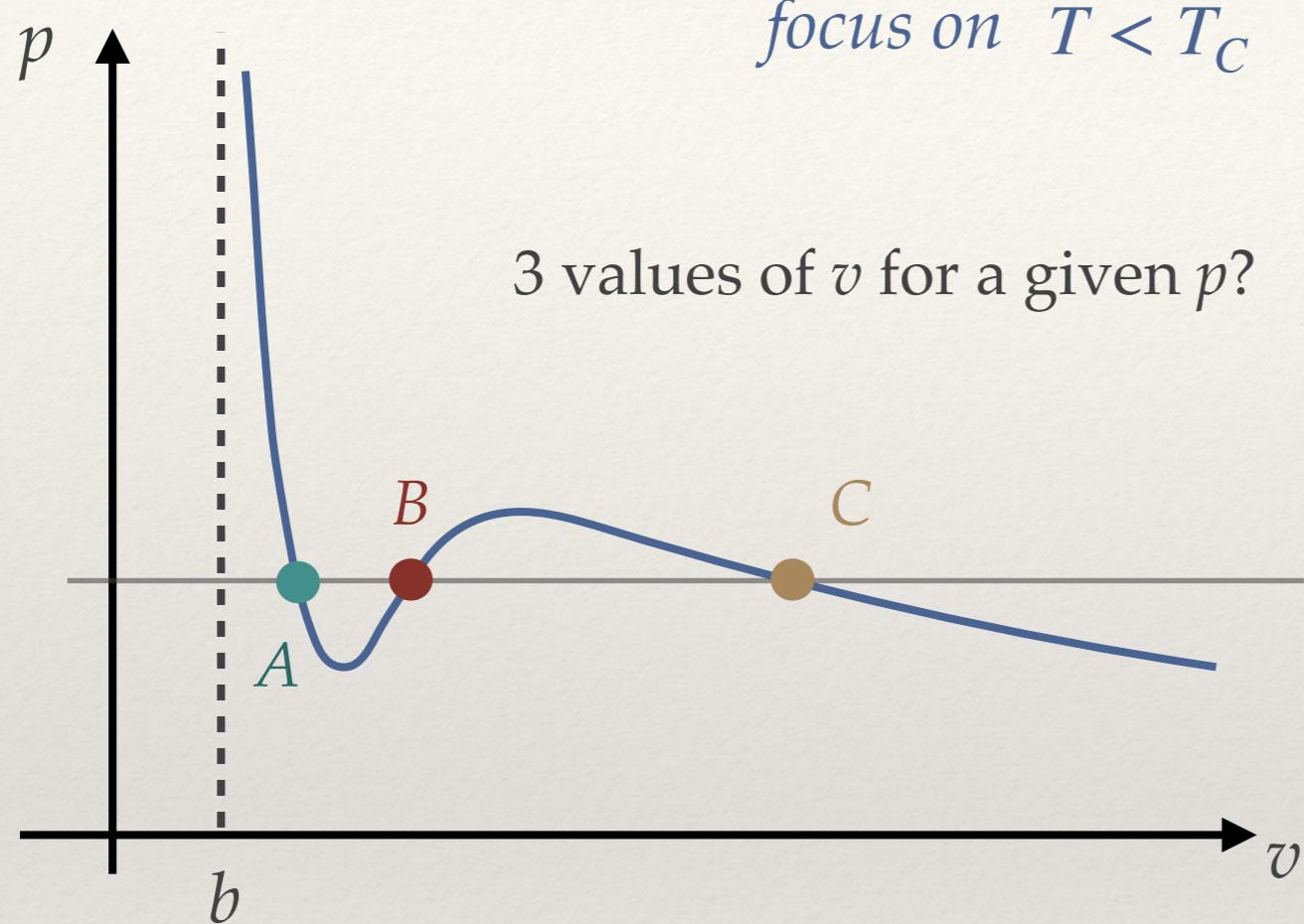


B. $\frac{dp}{dv} < 0$

Pressure *increases* as you make the gas more dilute and *decreases* when compressed

``*unstable state*''
Instability towards small changes in density

vdW: Phases



$$\left| \frac{dp}{dv} \right| : \text{large}$$

Need to apply lots of pressure
to decrease the volume
difficult to compress

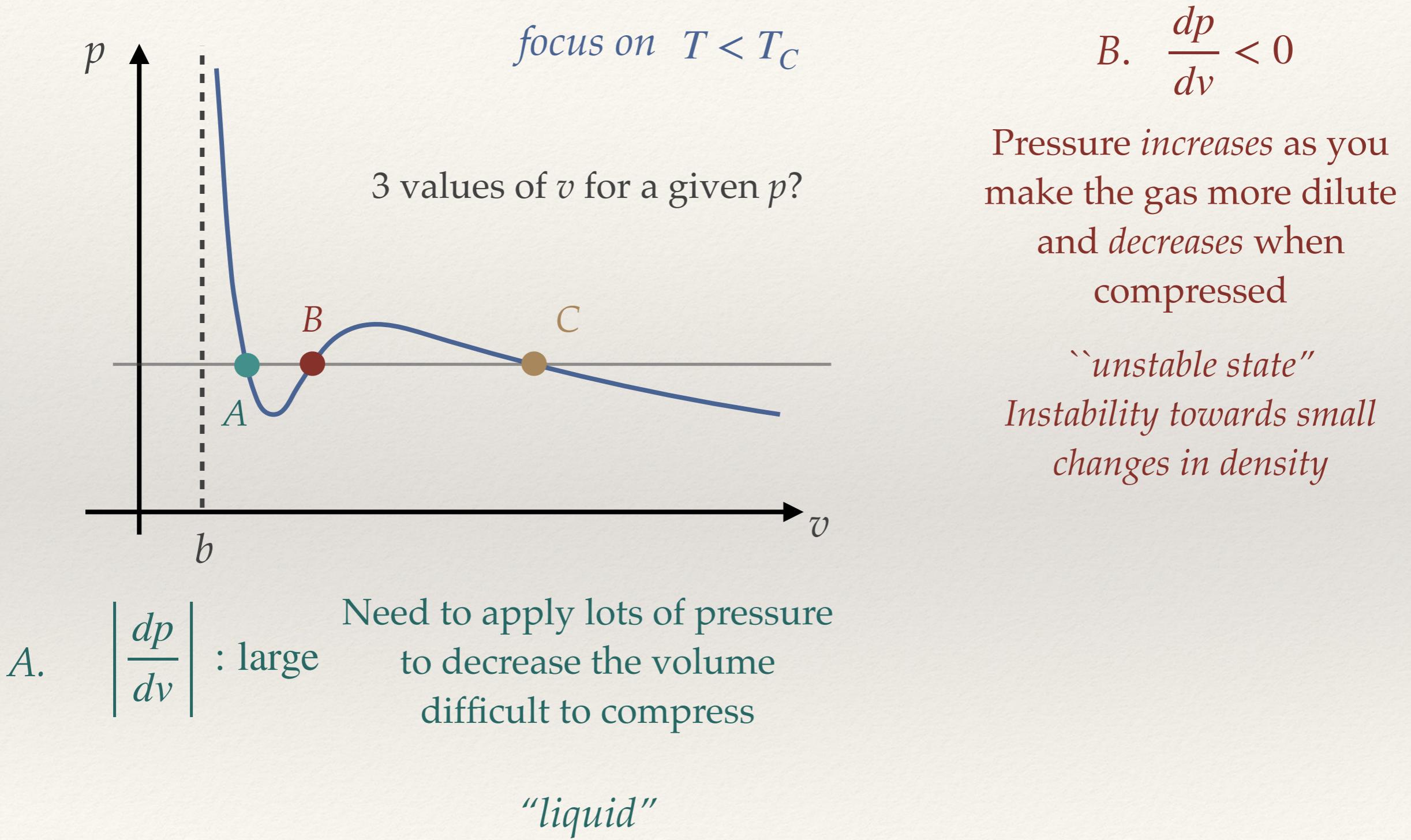
????

B. $\frac{dp}{dv} < 0$

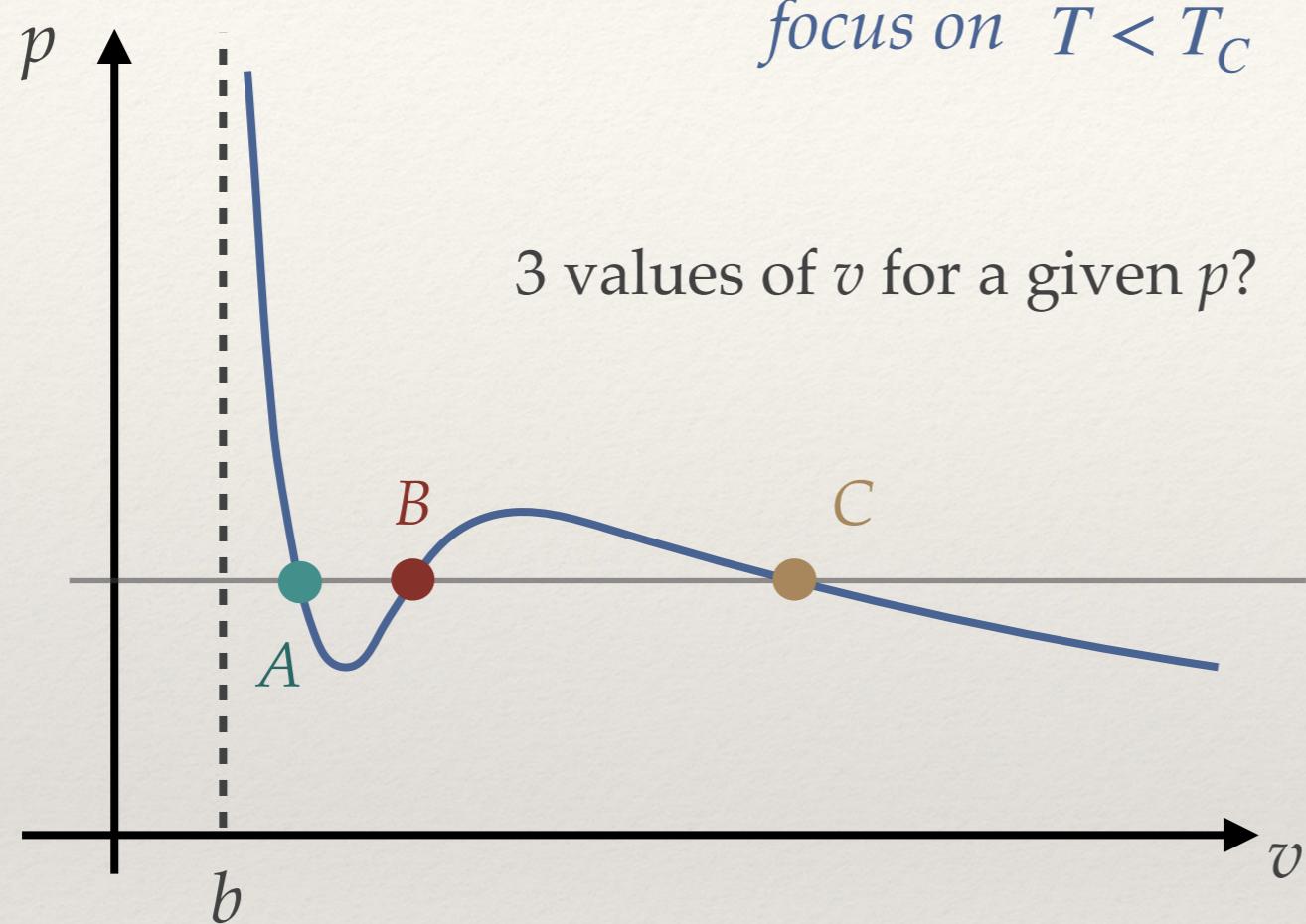
Pressure *increases* as you make the gas more dilute and *decreases* when compressed

``*unstable state*''
Instability towards small changes in density

vdW: Phases



vdW: Phases



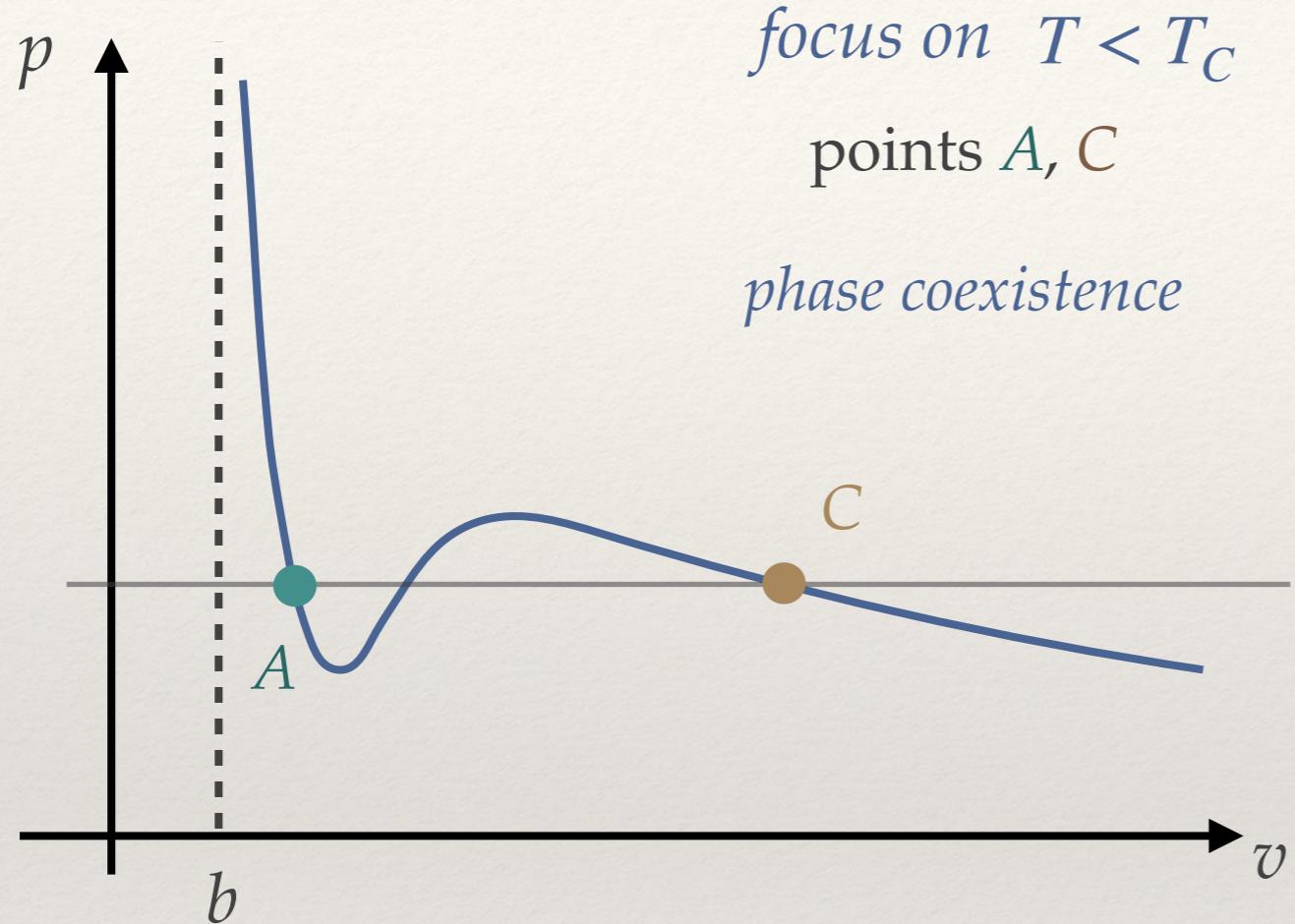
A. $\left| \frac{dp}{dv} \right|$: large
Need to apply lots of pressure
to decrease the volume
difficult to compress
“liquid”

B. $\frac{dp}{dv} > 0$
Pressure *increases* as you
make the gas more dilute
and *decreases* when
compressed

“*unstable state*”
*Instability towards small
changes in density*

C. $\left| \frac{dp}{dv} \right|$: small
easy to compress
“*gas*”

vdW: Phase Equilibrium



focus on $T < T_C$

points A, C

phase coexistence

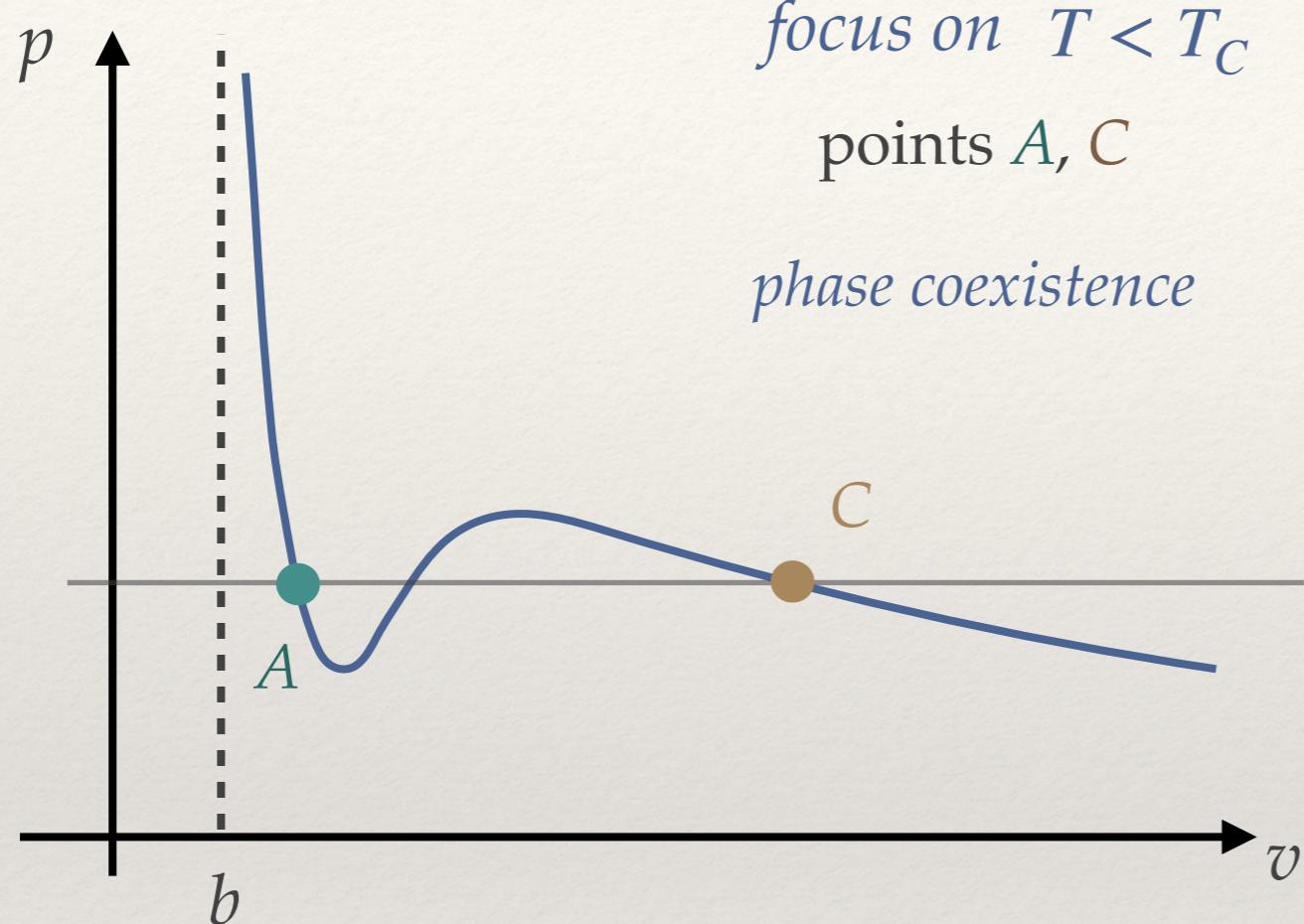
conditions for equilibrium

1. Mechanical $p_A = p_C$ ✓

2. Thermal $T_A = T_C$ ✓

3. ????

vdW: Phase Equilibrium



conditions for equilibrium

1. Mechanical $p_A = p_C$ ✓

2. Thermal $T_A = T_C$ ✓

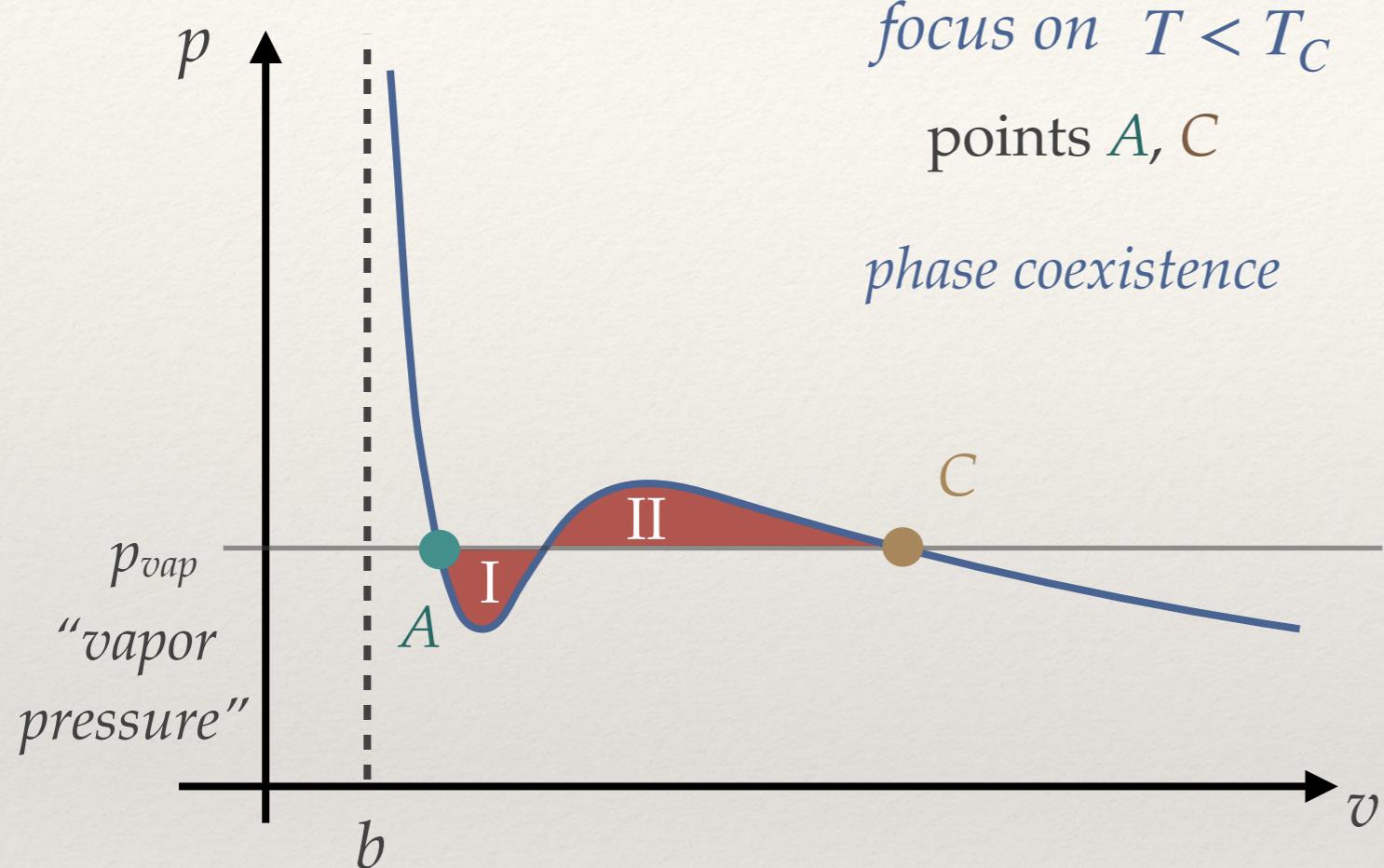
3. Diffusive $\mu_A = \mu_C$

(recall $G = \mu N$) $G_A = G_C$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} \Rightarrow v = \left(\frac{\partial \mu}{\partial p} \right)_{T,N}$$

$$\mu(p, T) = \mu_A(p, T) + \int_{p_A}^p v(p', T) dp'$$

vdW: Maxwell Construction



conditions for equilibrium

1. Mechanical $p_A = p_C$ ✓

2. Thermal $T_A = T_C$ ✓

3. Diffusive $\mu_A = \mu_C$

(recall $G = \mu N$)

$$G_A = G_C$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} \Rightarrow v = \left(\frac{\partial \mu}{\partial p} \right)_{T,N}$$

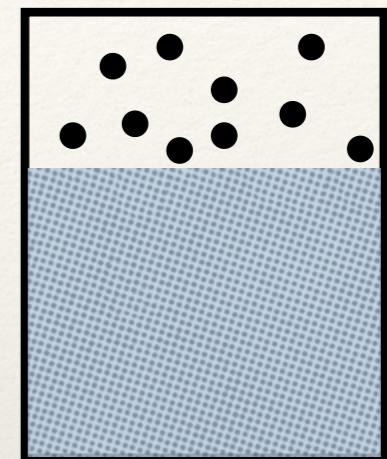
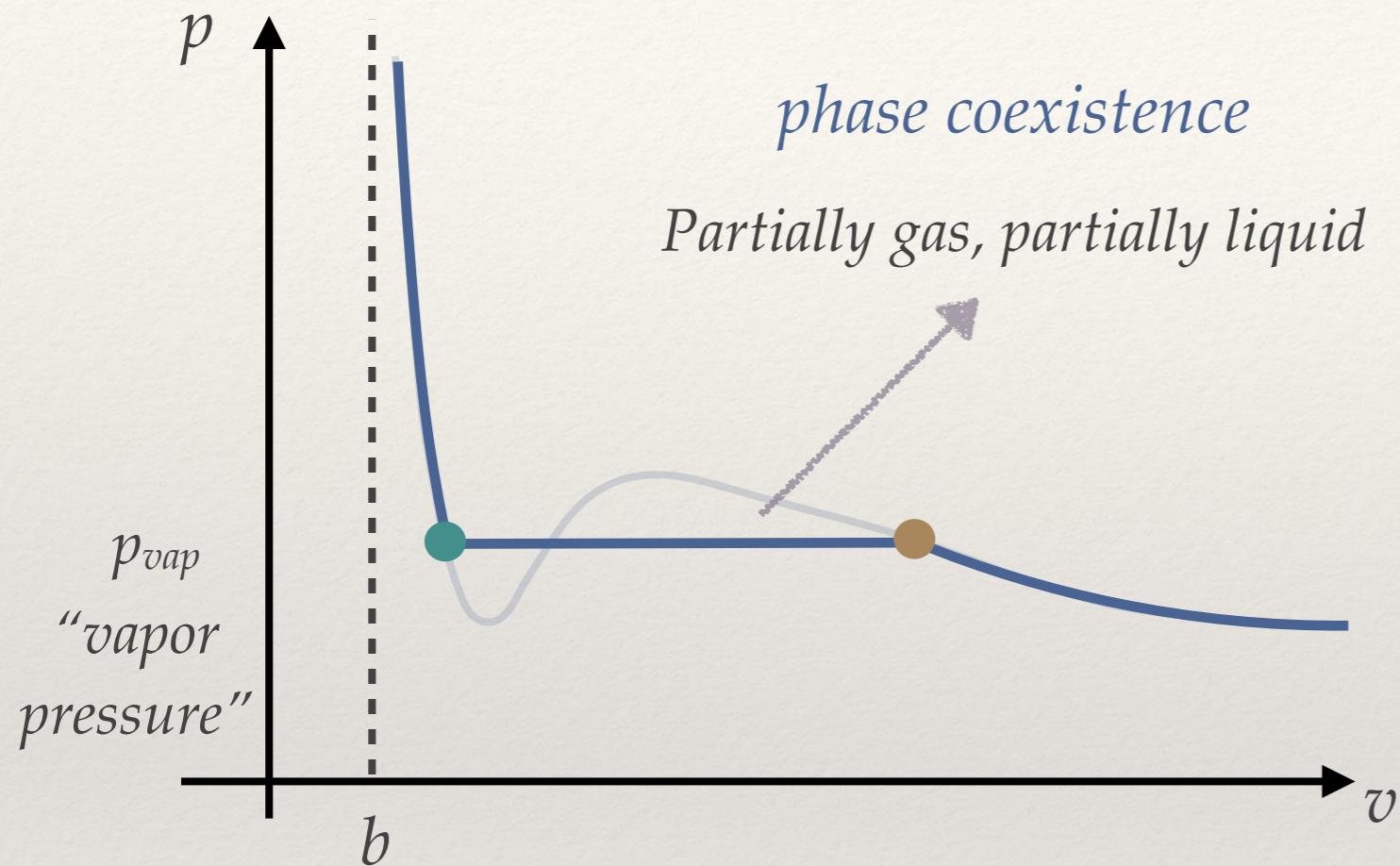
$$\mu(p, T) = \mu_A(p, T) + \int_{p_A}^p v(p', T) dp'$$

$$\mu_C(p, T) - \mu_A(p, T) = \int_{p_A}^{p_C} v(p', T) dp'$$

$\mu_A = \mu_C \Rightarrow$ shaded area=0
 (i.e. area I=area II)

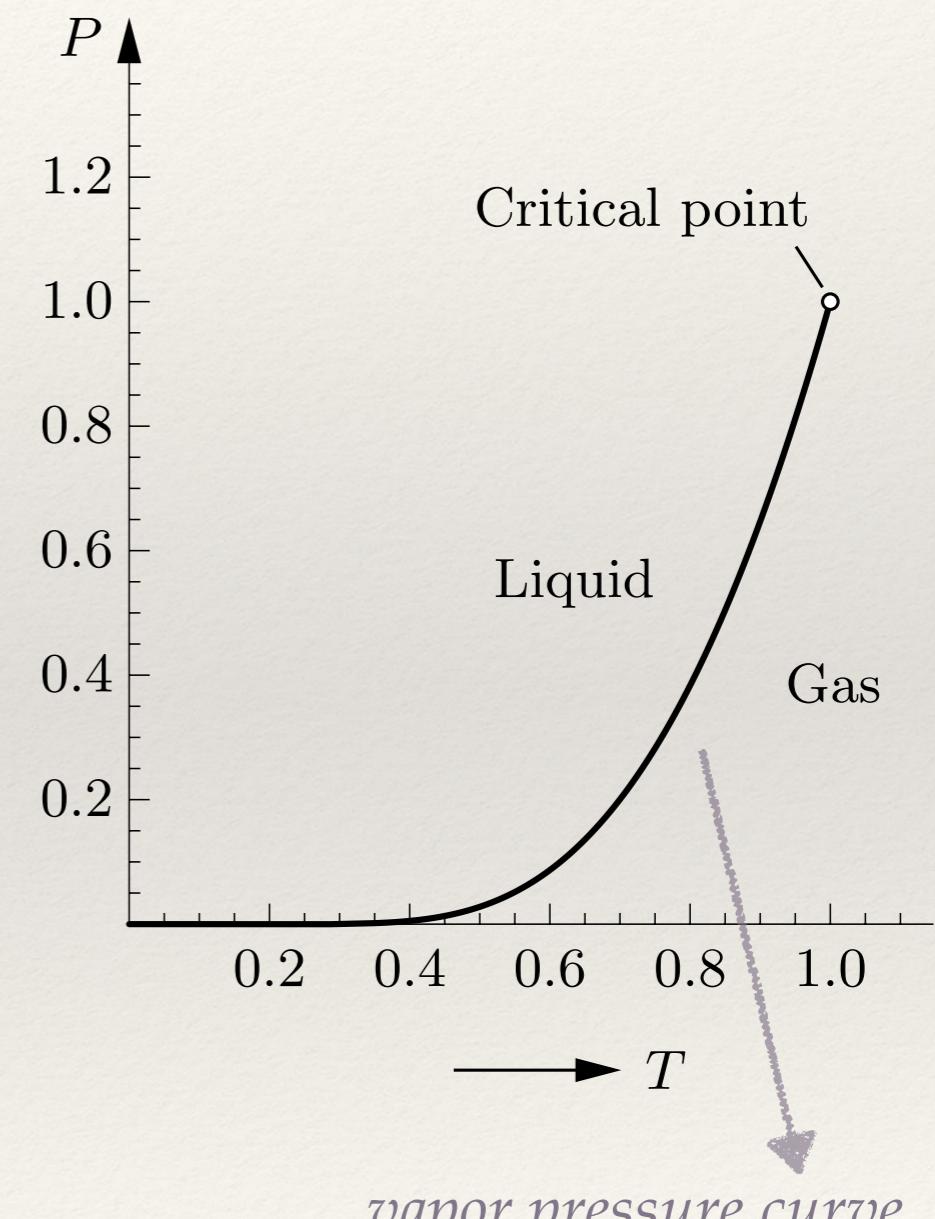
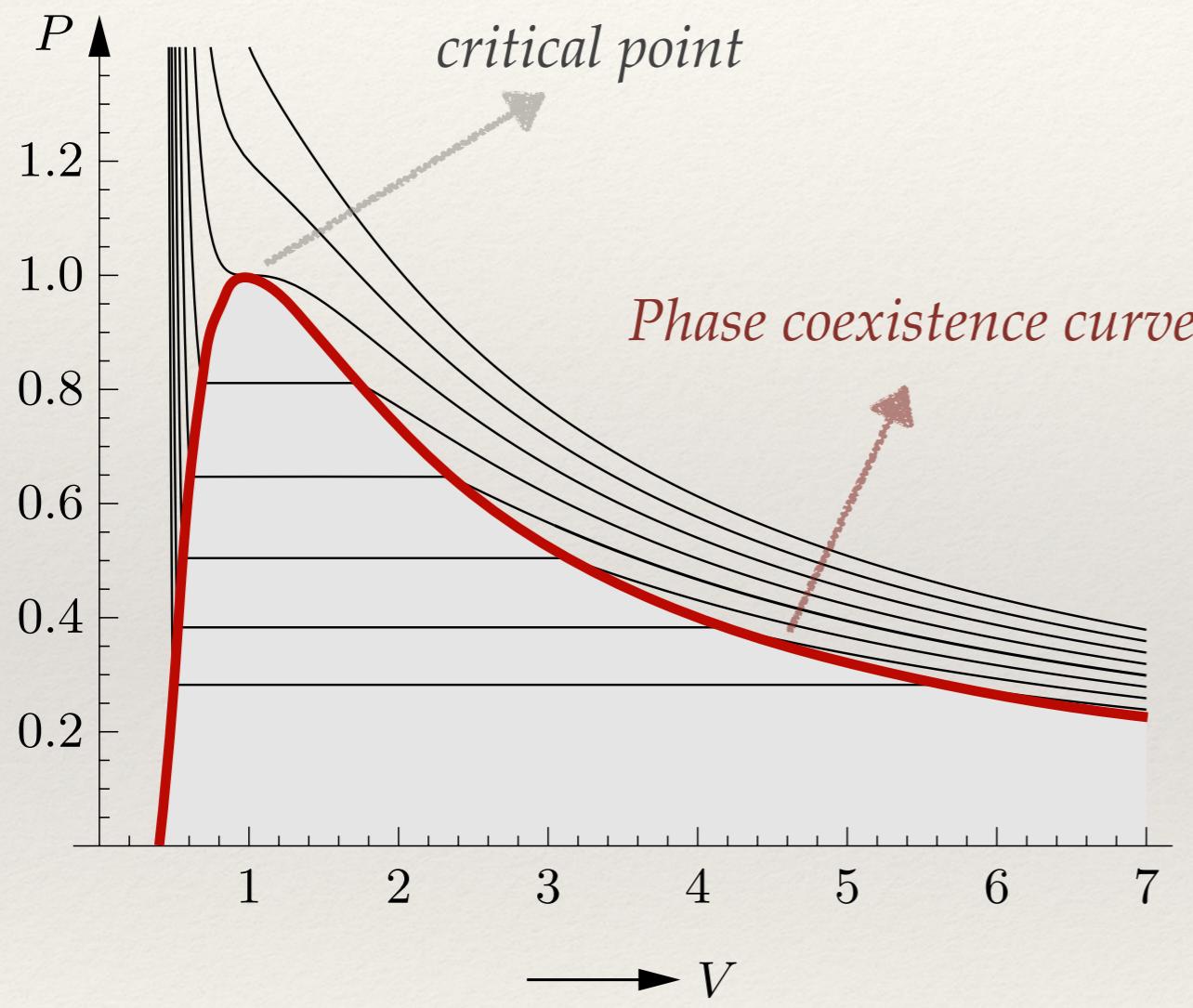
``Maxwell construction''

vdW: Phase Coexistence

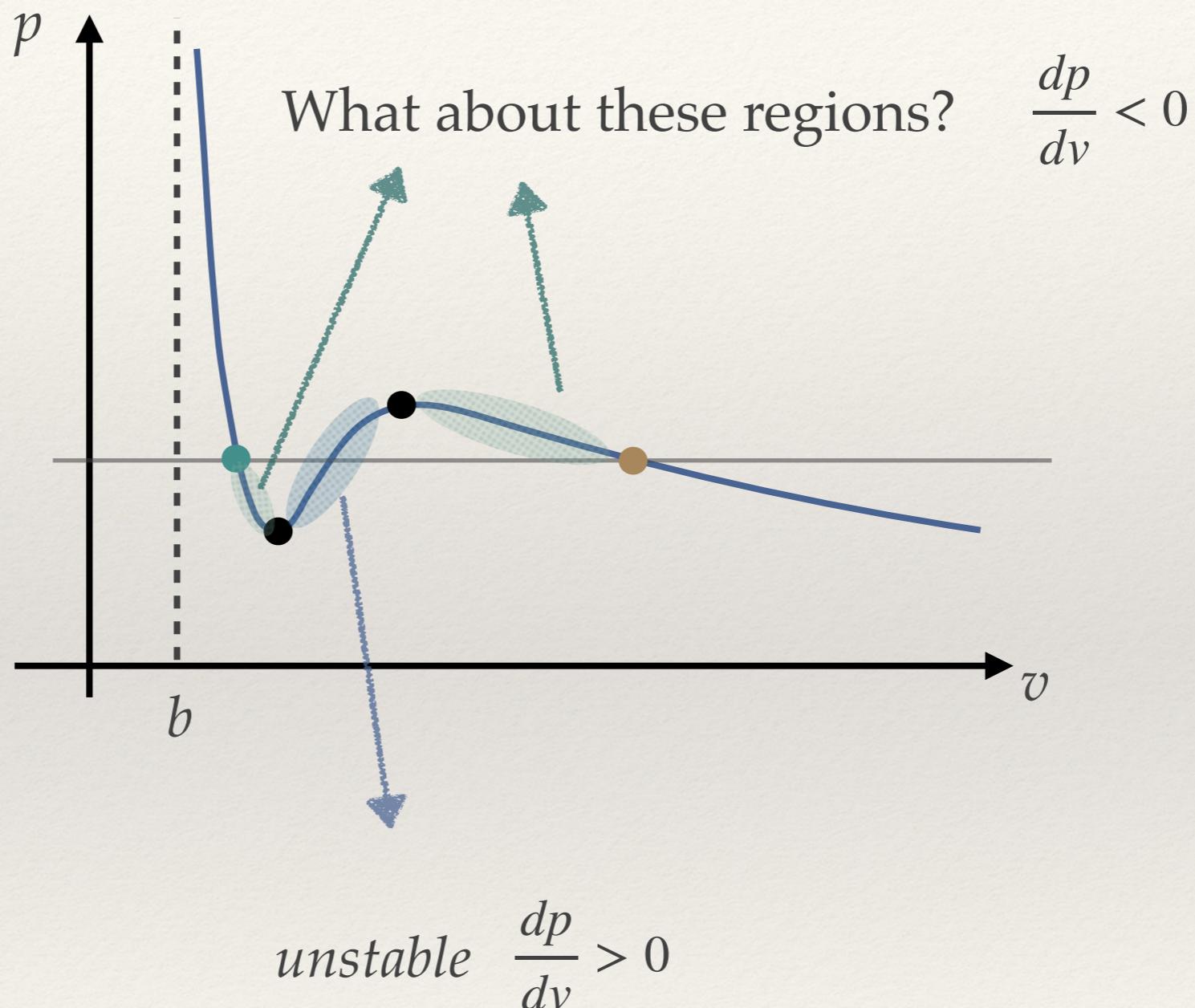


phase separation:
Energetically favorable
configuration,
Interface between phases
costs energy

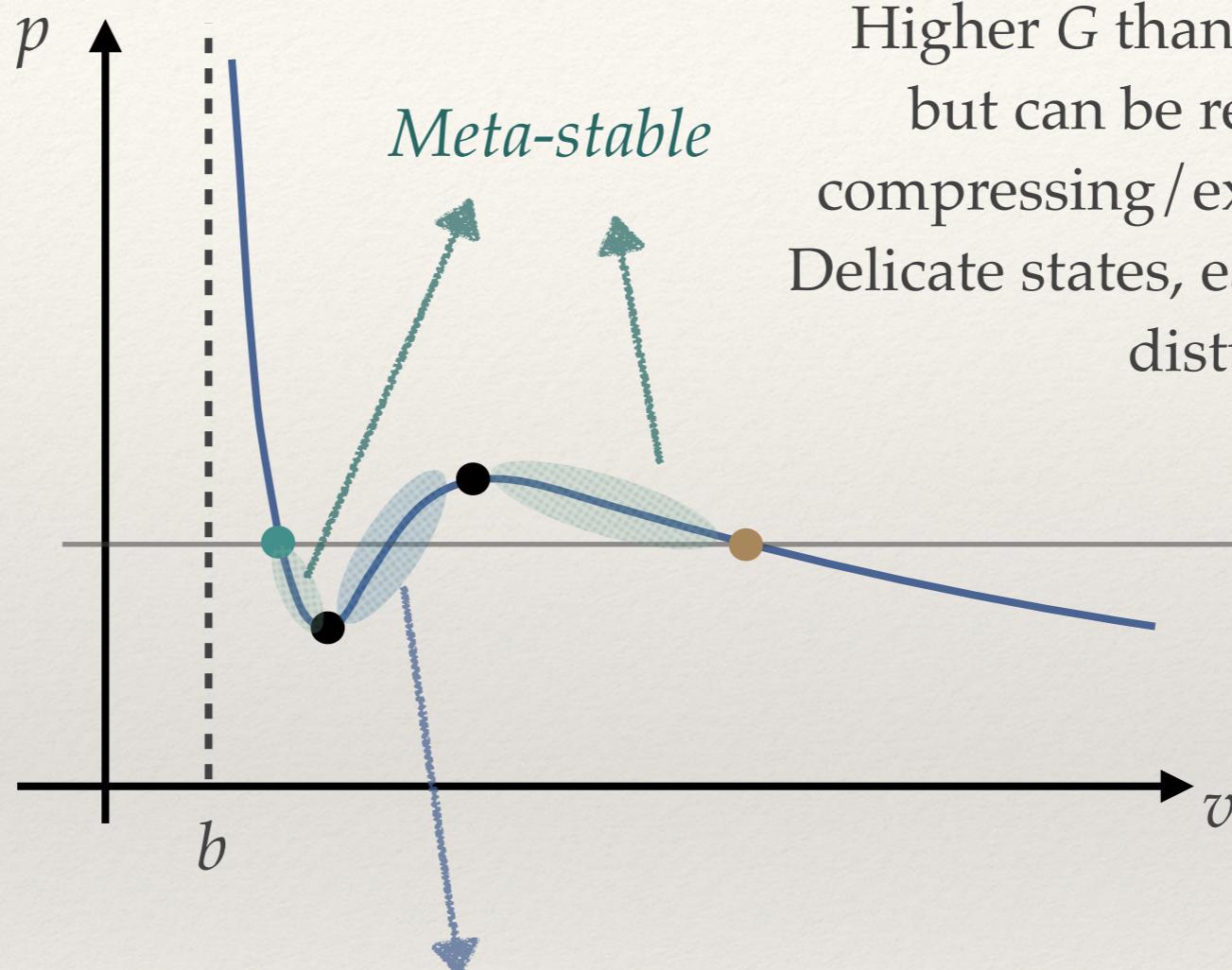
vdW: Phase Coexistence



vdW: Meta-stable states



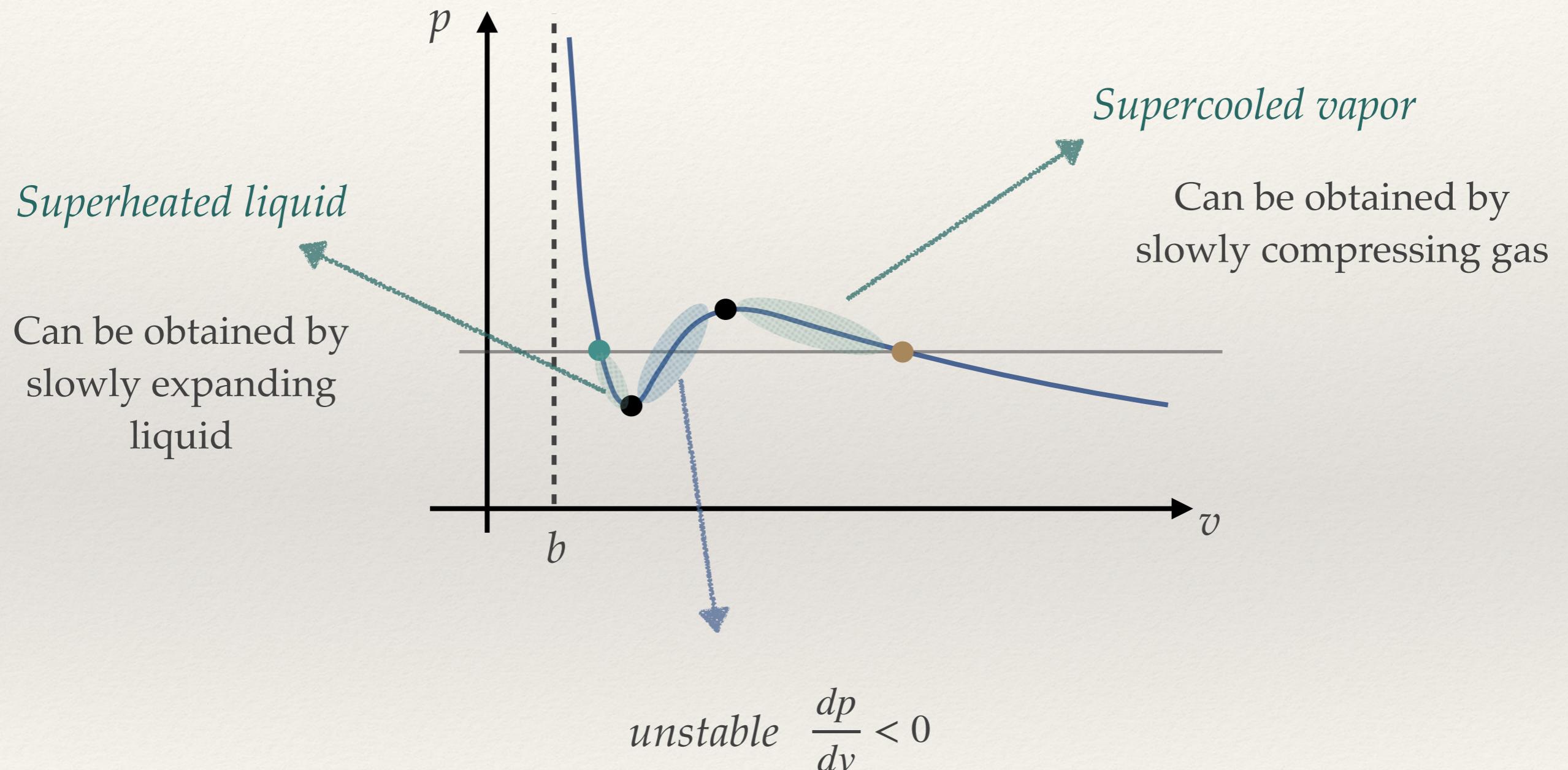
vdW: Meta-stable states



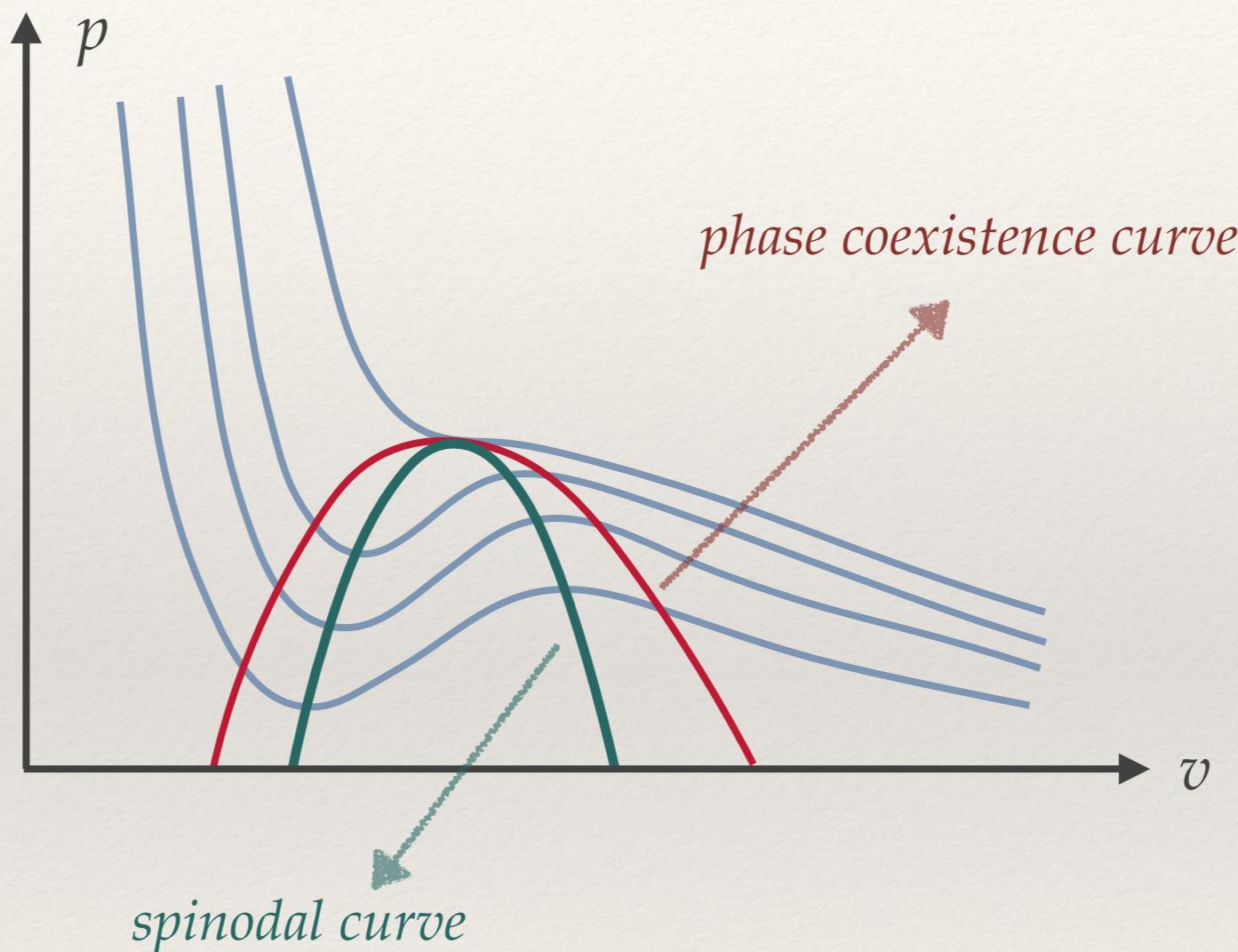
Higher G than liquid-gas mixture
but can be realized by slowly
compressing/expanding the system
Delicate states, easily spoiled by small
disturbances

$$unstable \quad \frac{dp}{dv} < 0$$

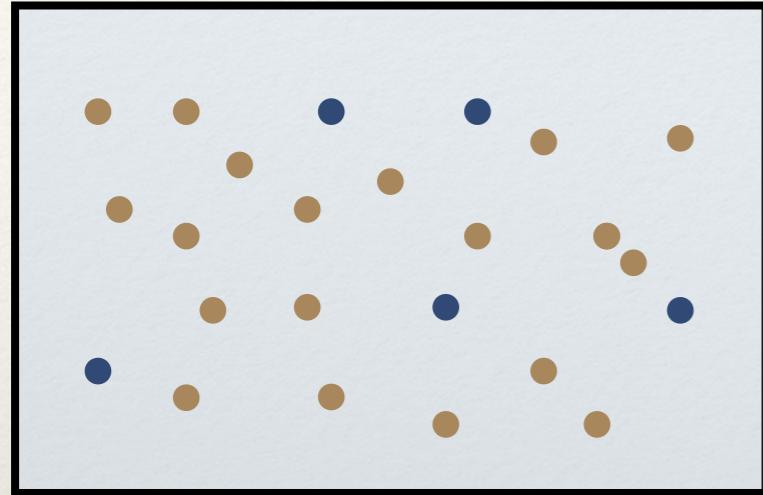
vdW: Meta-stable states



vdW: Meta-stable states



Phase Transitions of Mixtures

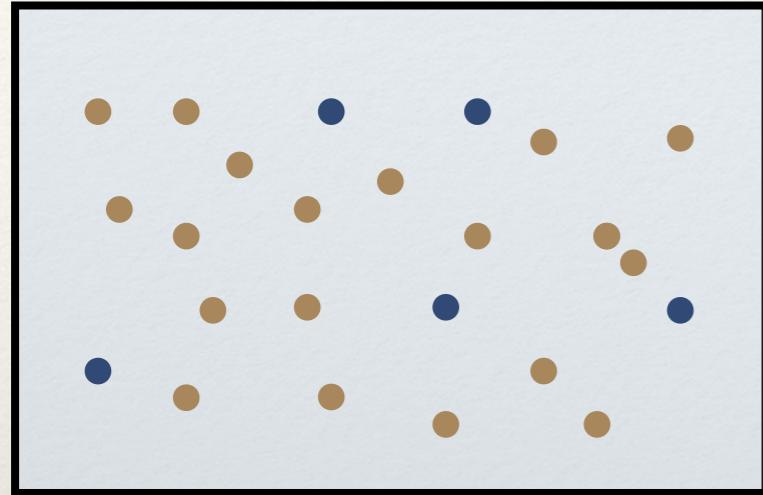


e.g air: 21% O₂, 78% N₂, ~1% other ignore for simplicity

$$T_{O_2} = 90.2 \text{ K}, \quad T_{N_2} = 77.4 \text{ K}$$

What happens when we cool air?

Phase Transitions of Mixtures



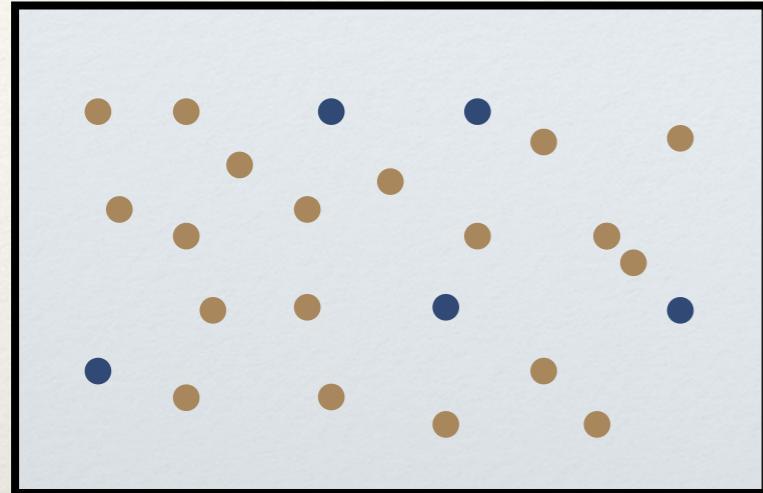
e.g air: 21% O₂, 78% N₂, ~1% other ignore for simplicity

$$T_{O_2} = 90.2 \text{ K}, \quad T_{N_2} = 77.4 \text{ K}$$

What happens when we cool air?

All of O₂ liquifies at T=90.2 K then all of N₂ liquifies at T=77.4K ?

Phase Transitions of Mixtures



e.g air: 21% O₂, 78% N₂, ~1% other ignore for simplicity

$$T_{O_2} = 90.2 \text{ K}, \quad T_{N_2} = 77.4 \text{ K}$$

What happens when we cool air?

All of O₂ liquifies at T=90.2 K then all of N₂ liquifies at T=77.4K ? NO!

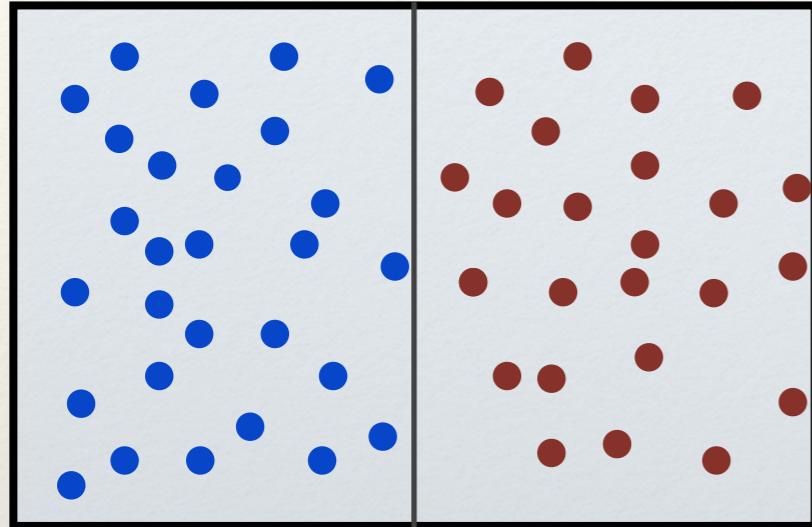
No liquid forms at all until T=81.6 K!

At T=81.6 K, liquid with 48% O₂ begins to condense

At T=79.0 K, the whole system is entirely liquid with 21% O₂ + 78% N₂

Similar for other mixtures, liquid-gas, solid-solid-liquid etc....

Phase Transitions of Mixtures



Two kinds of particles: A & B

1-x: fraction of A, x: fraction of B

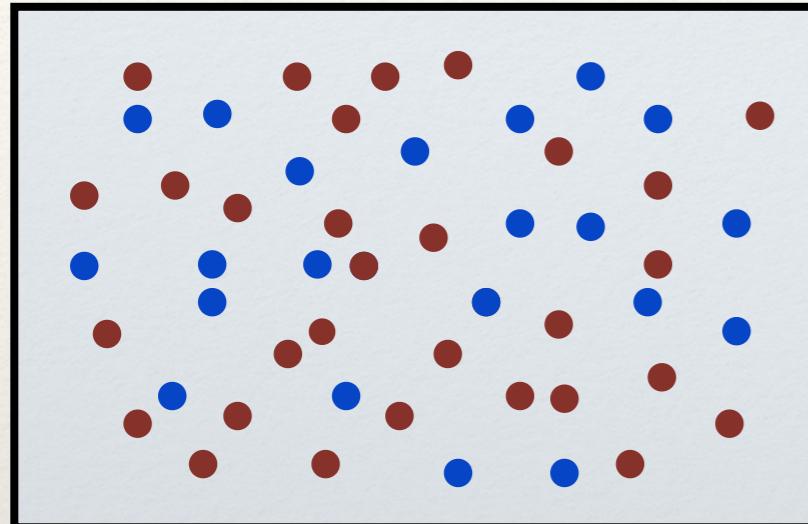
When unmixed:

Gibbs free energy

$$G = (1 - x)G_A^0 + xG_B^0$$

G_A^0, G_B^0 : Gibbs free energy of pure A & B particles

Phase Transitions of Mixtures



Two kinds of particles: A & B

$1-x$: fraction of A , x : fraction of B

When unmixed:

Gibbs free energy

$$G = (1 - x)G_A^0 + xG_B^0$$

G_A^0, G_B^0 : Gibbs free energy of pure A & B particles

When mixed: recall $G=U+PV-TS$

$$S_{mix} = -Nk(x \log x + (1 - x)\log(1 - x))$$

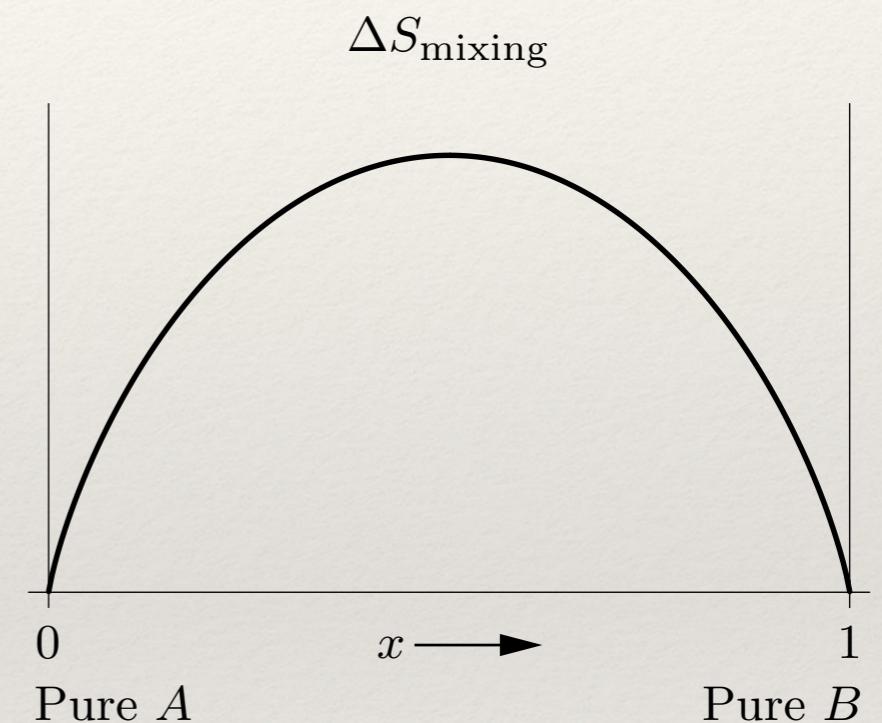
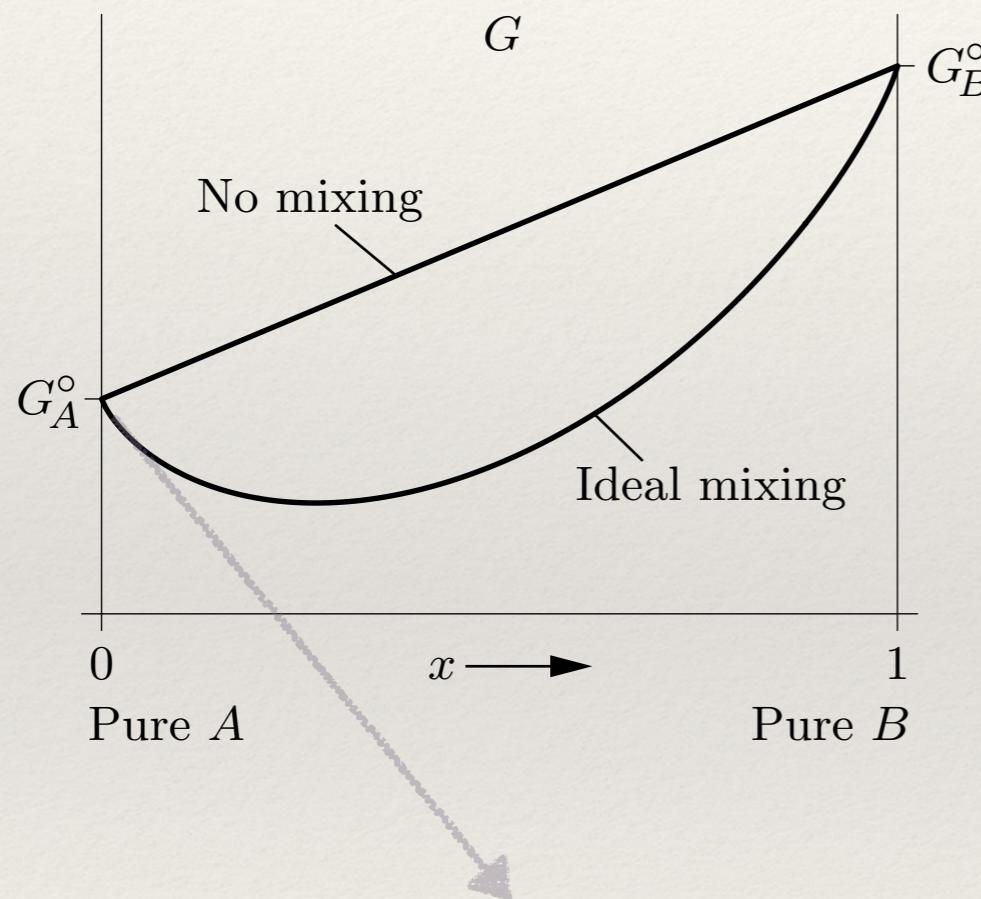
$$G = (1 - x)G_A^0 + xG_B^0 - TS_{mix}$$

(can ignore changes in U and V due to mixing)

$$G = (1 - x)G_A^0 + xG_B^0 + NkT(x \log x + (1 - x)\log(1 - x))$$

Phase Transitions of Mixtures

$$G = (1 - x)G_A^0 + xG_B^0 + NkT(x \log x + (1 - x)\log(1 - x))$$



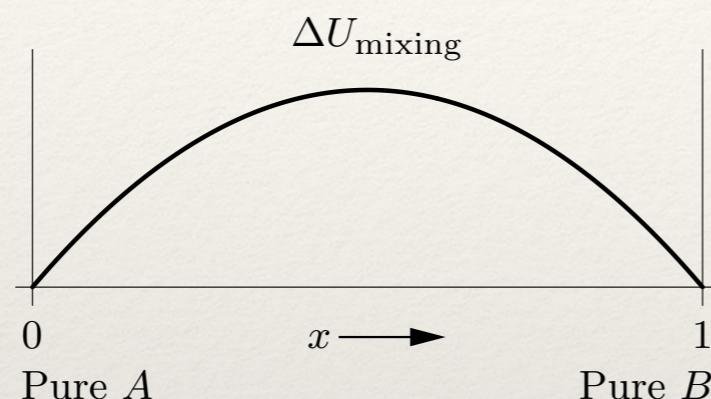
Steep slope: adding a small amount
of B reduces G substantially

Phase Transitions of Mixtures

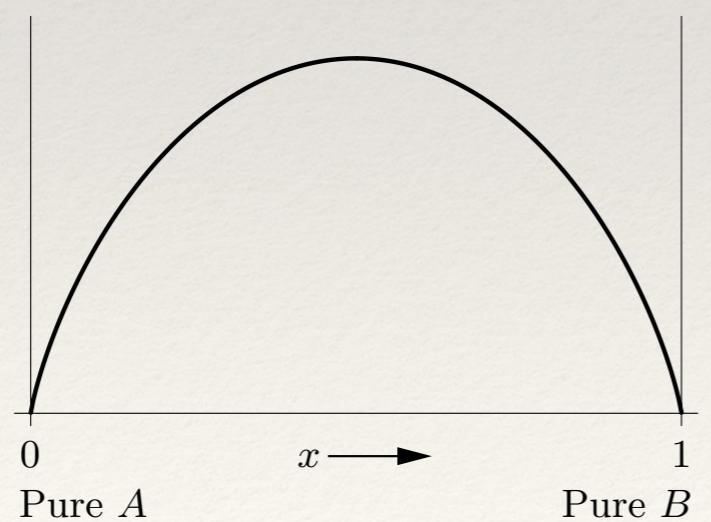
attraction between like particles > attraction between unlike particles



$$G = U + PV - TS$$

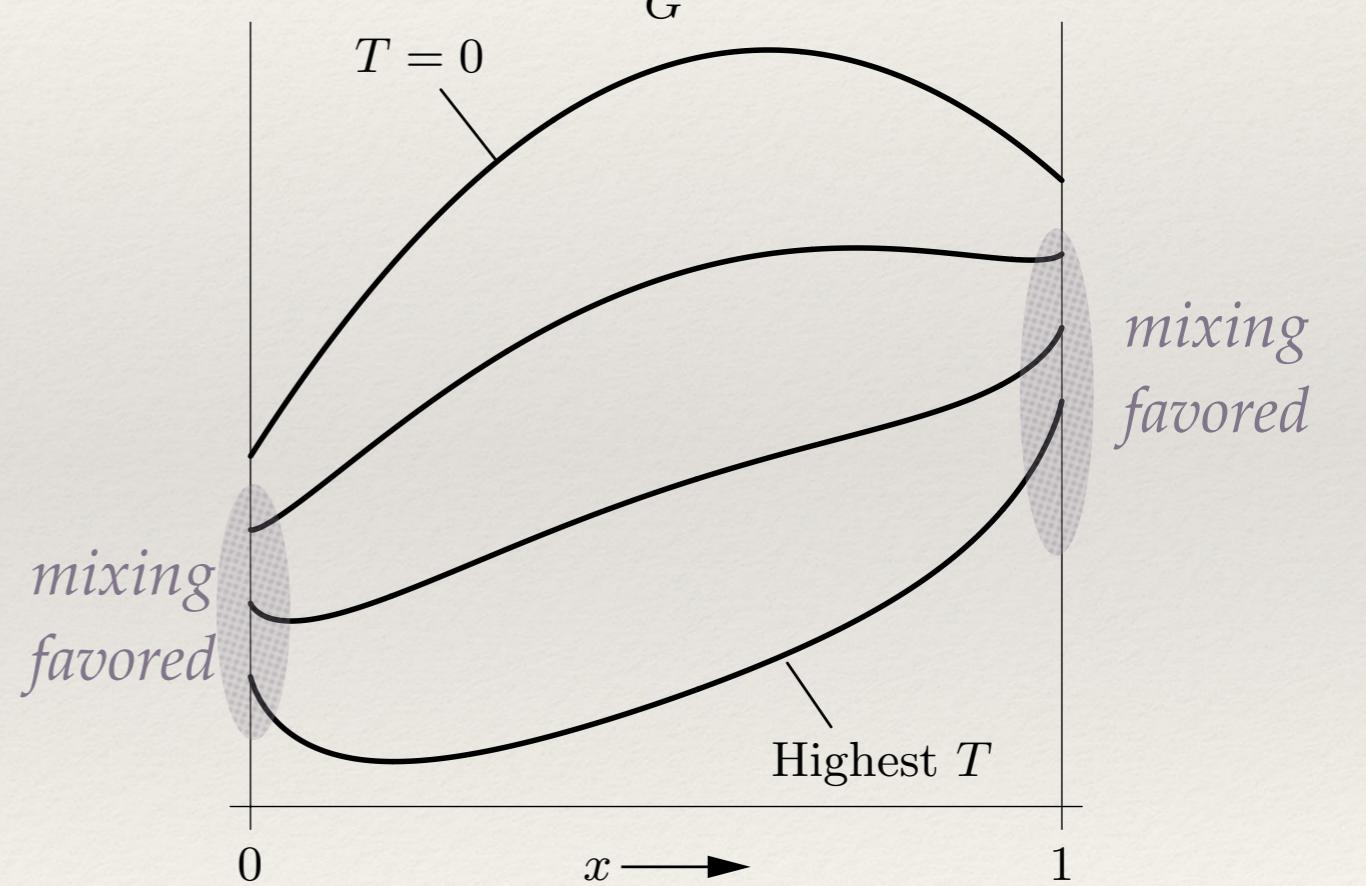


vs



G : concave down = ΔU wins

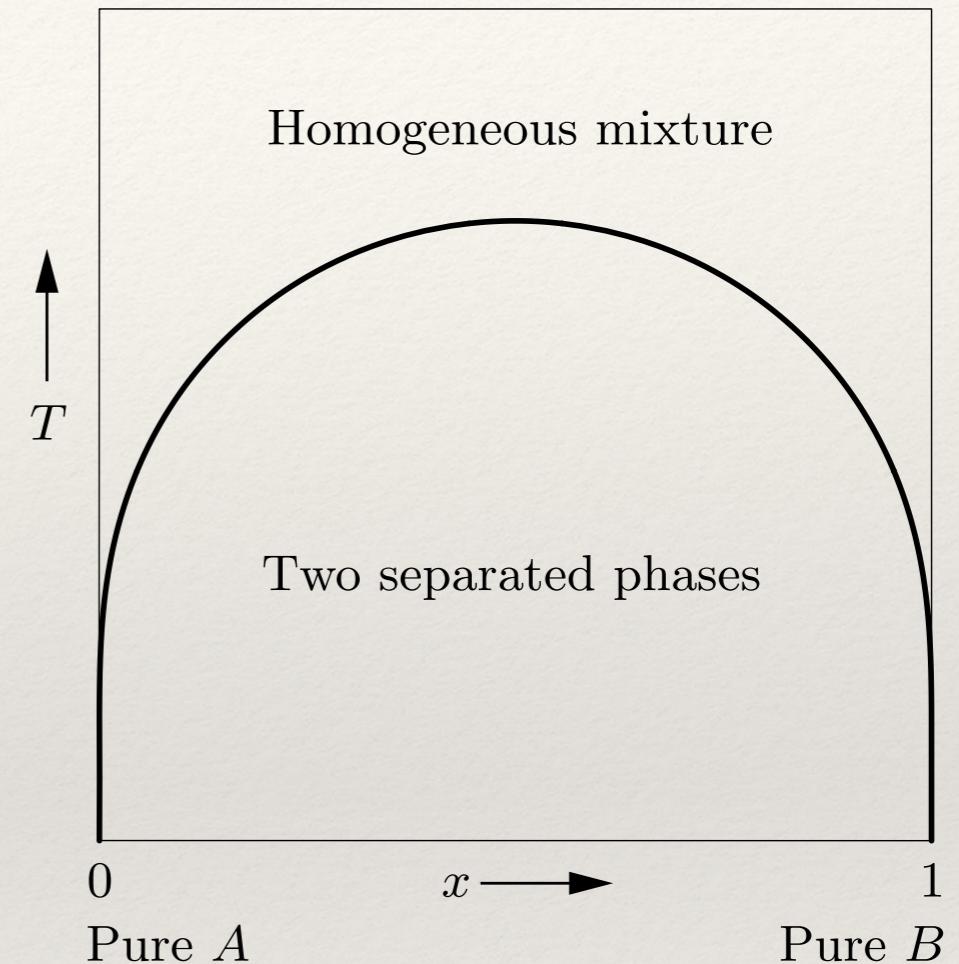
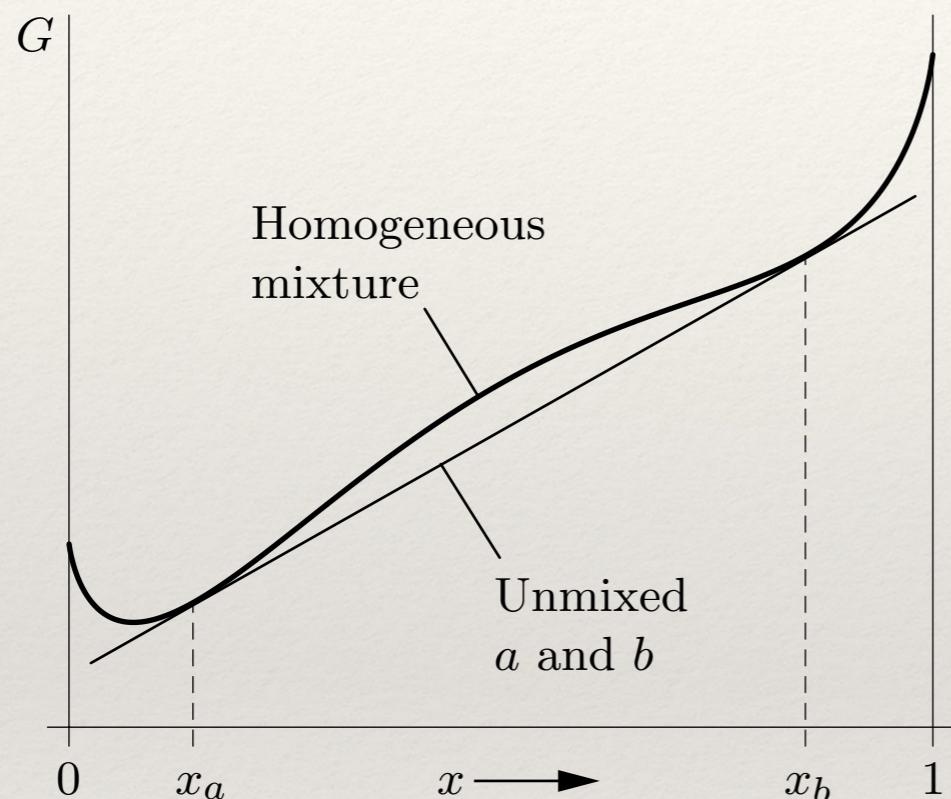
immiscible



G : convex = entropy wins

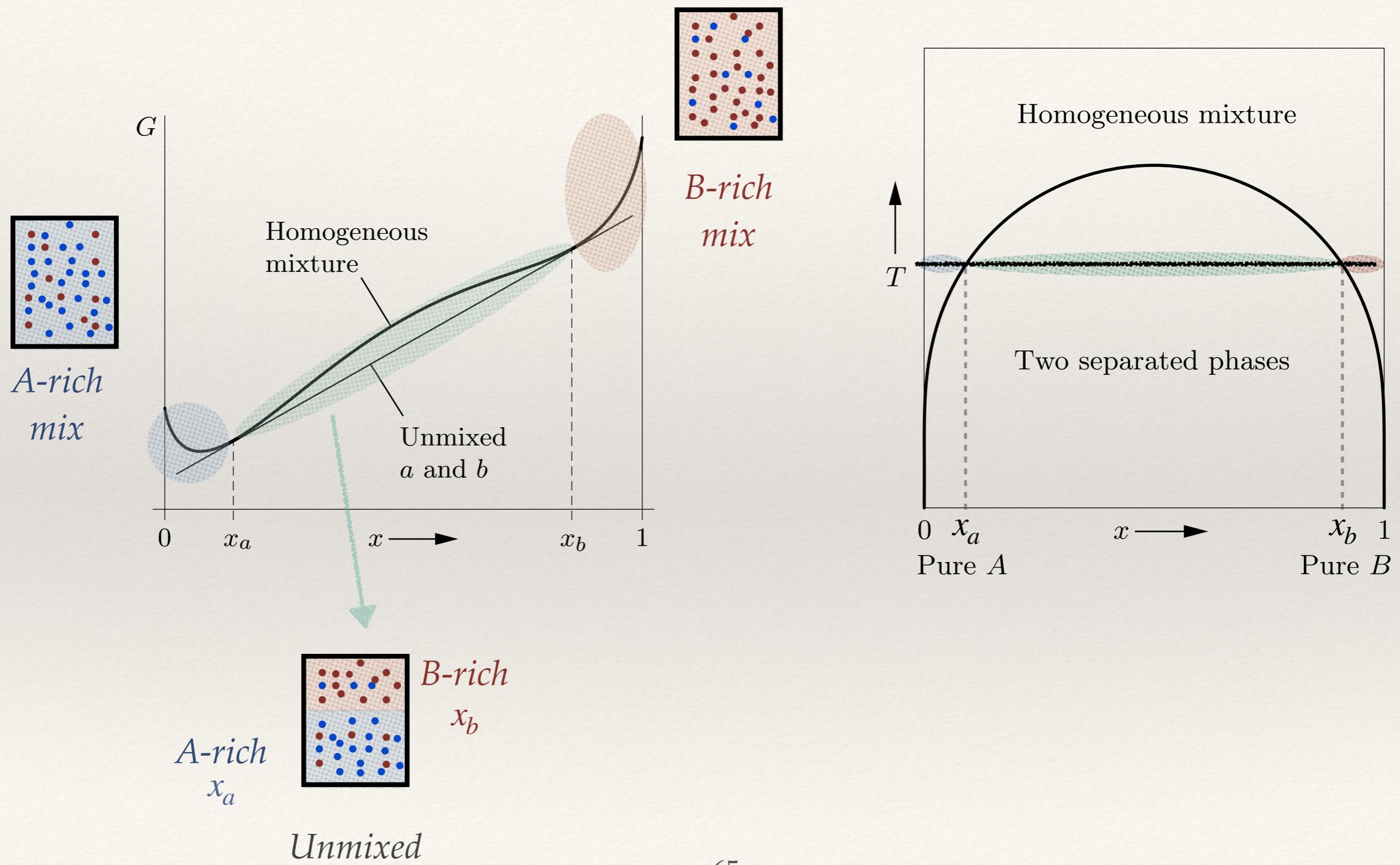
$G_{\text{unmixed}} > G_{\text{mixed}}$
mixing occurs

Phase Transitions of Mixtures



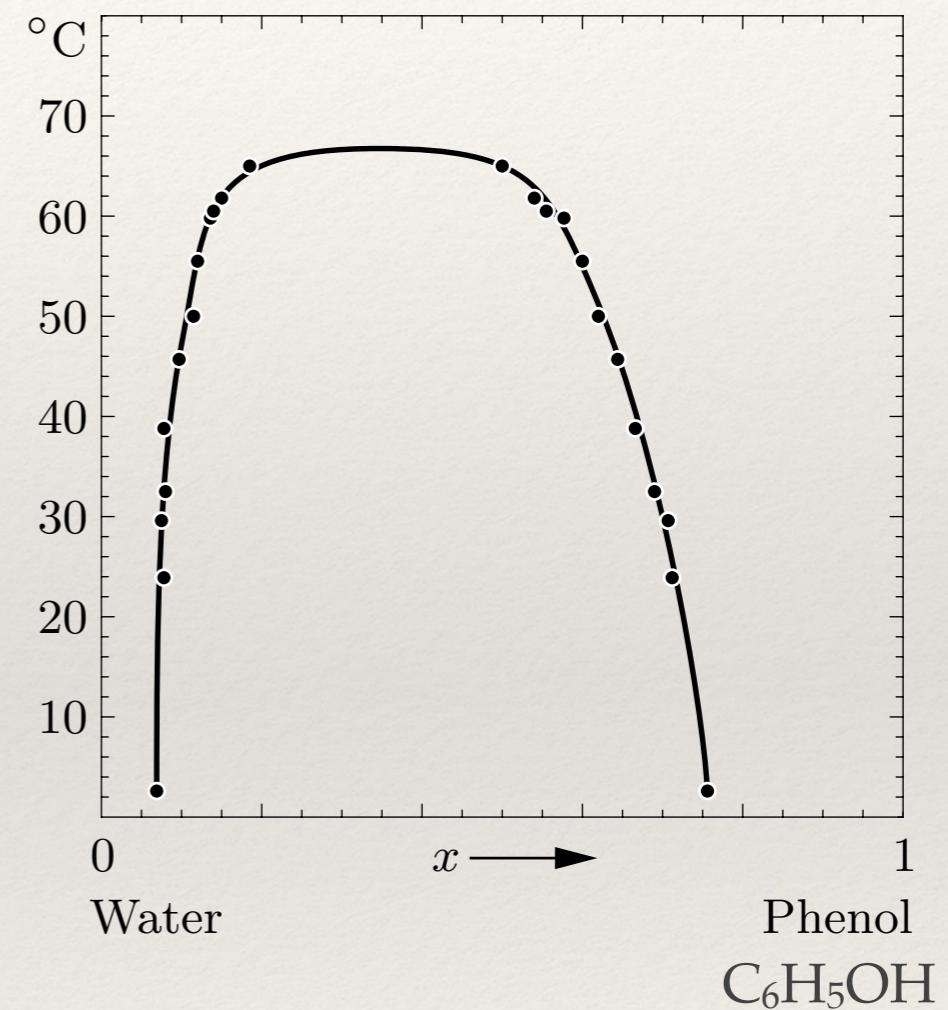
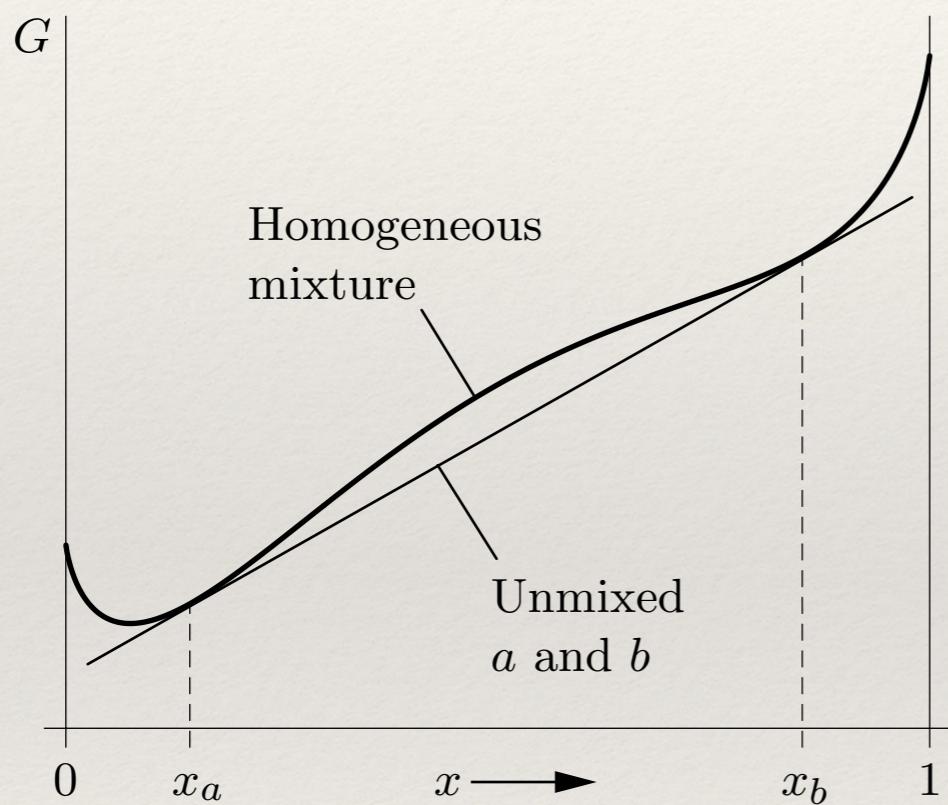
phase diagram

Phase Transitions of Mixtures



Phase Transitions of Mixtures

For oil+water complete mixing occurs $T \gg 100^\circ\text{C}$



real data

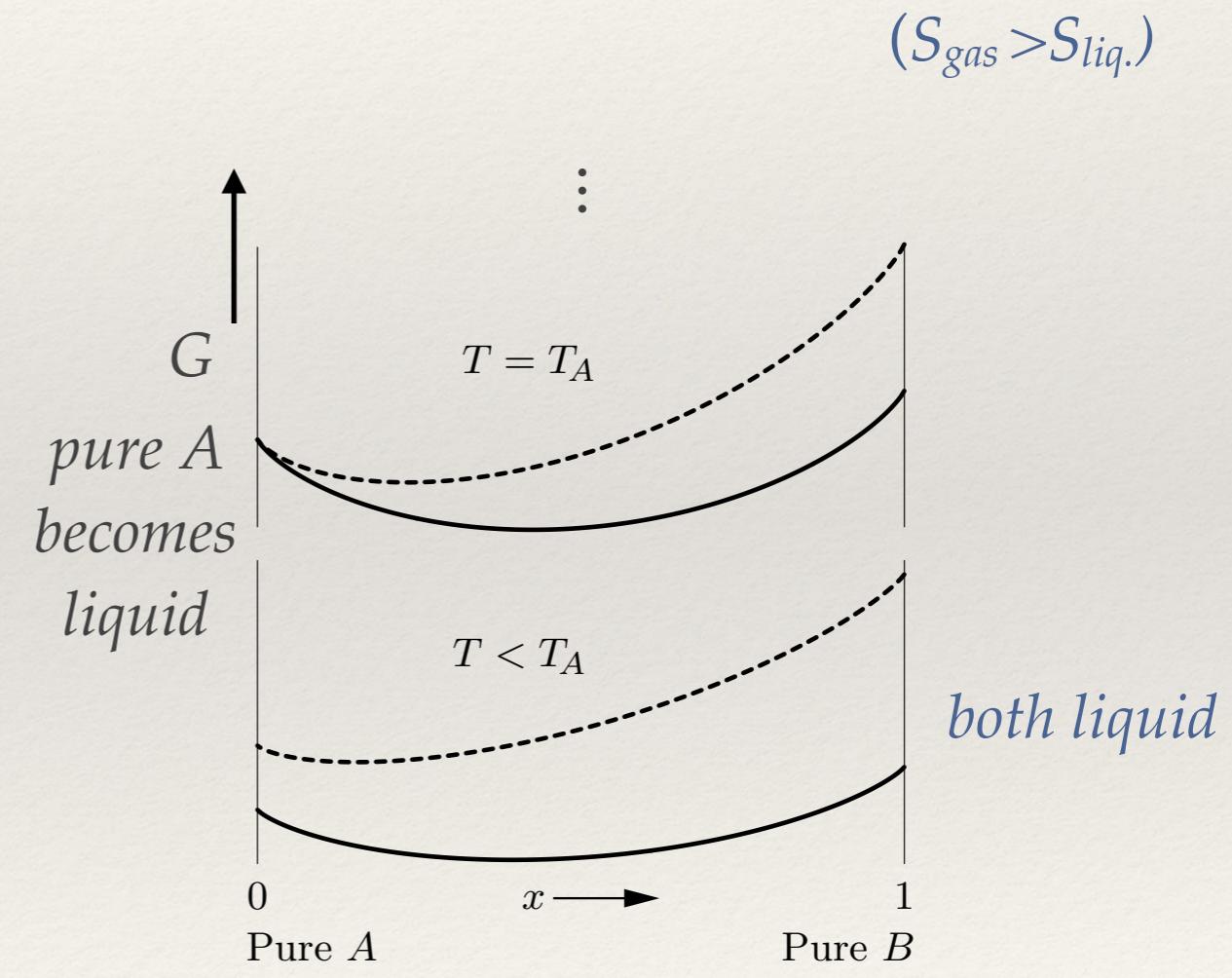
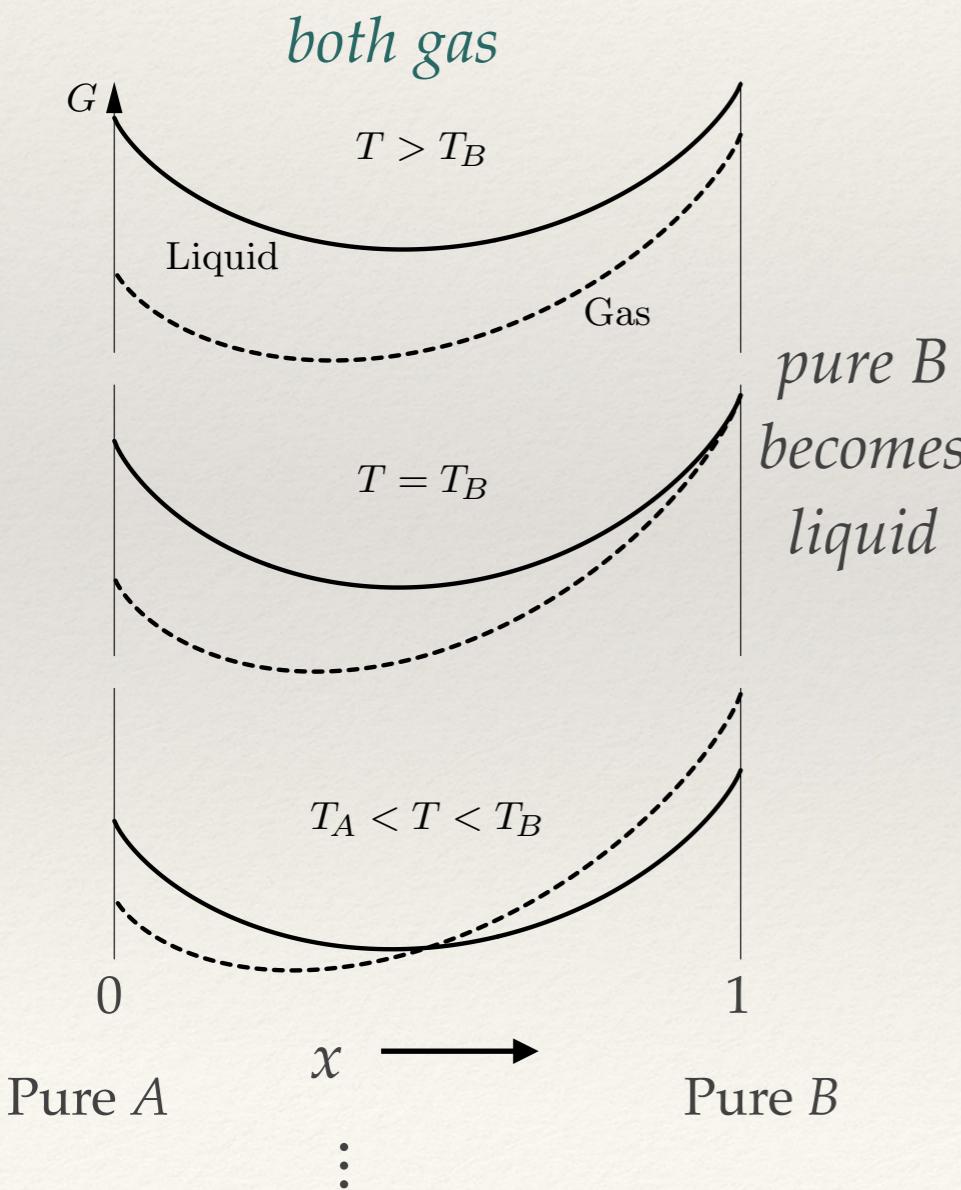
[Campbell, Campbell, Journal of the American Chemical Society, 59, 2481]

Phase Transitions of Miscible Mixtures

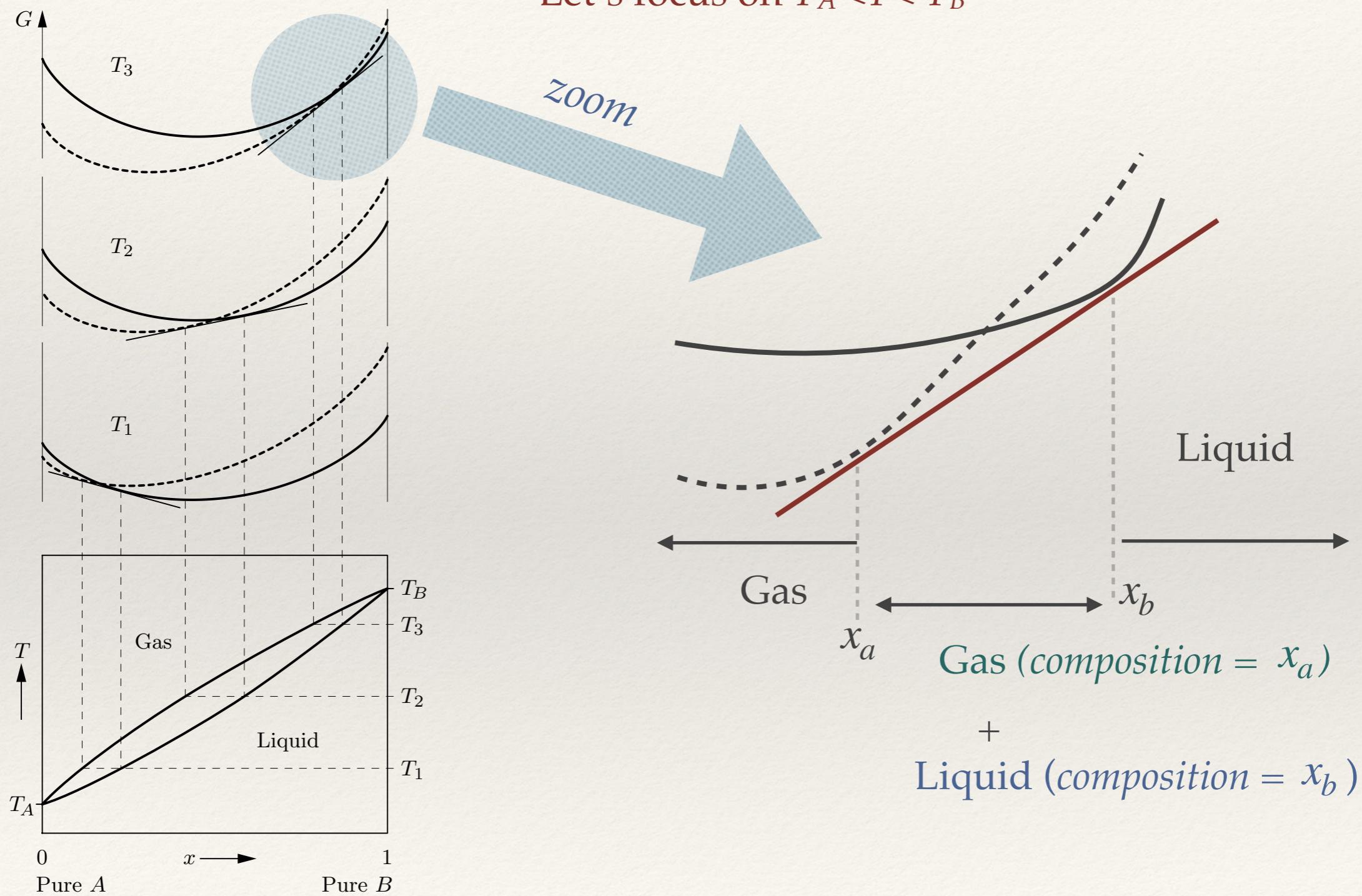
Air: N_2+O_2

G of $N_2 + O_2$ mixture is convex everywhere for both liquid and gas phases

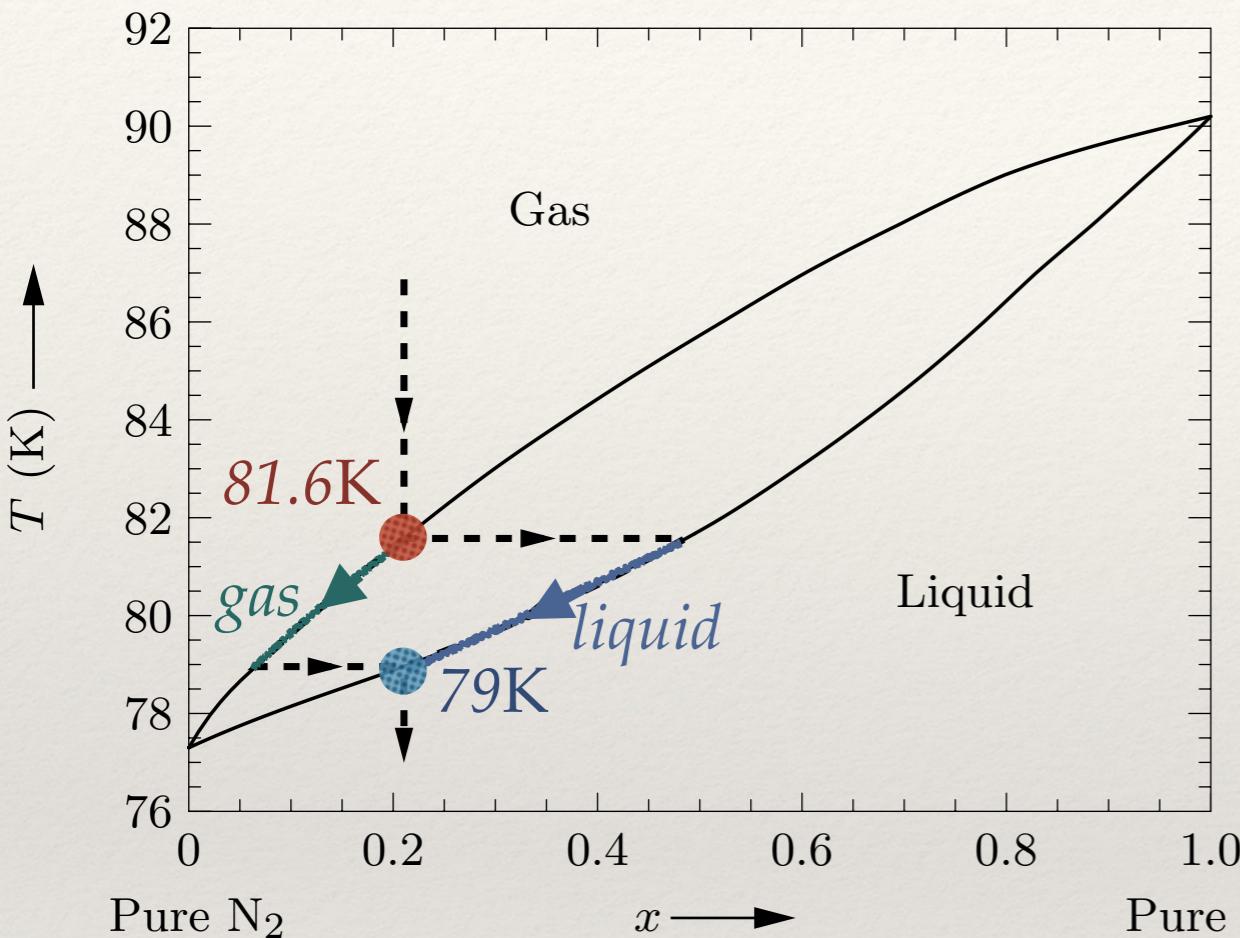
$$\frac{\partial G}{\partial T} = -S : \text{as we decrease } T \text{ } G_{gas} \text{ increases faster than } G_{liq.}$$



Phase Transitions of Miscible Mixtures



Phase Transitions of Miscible Mixtures

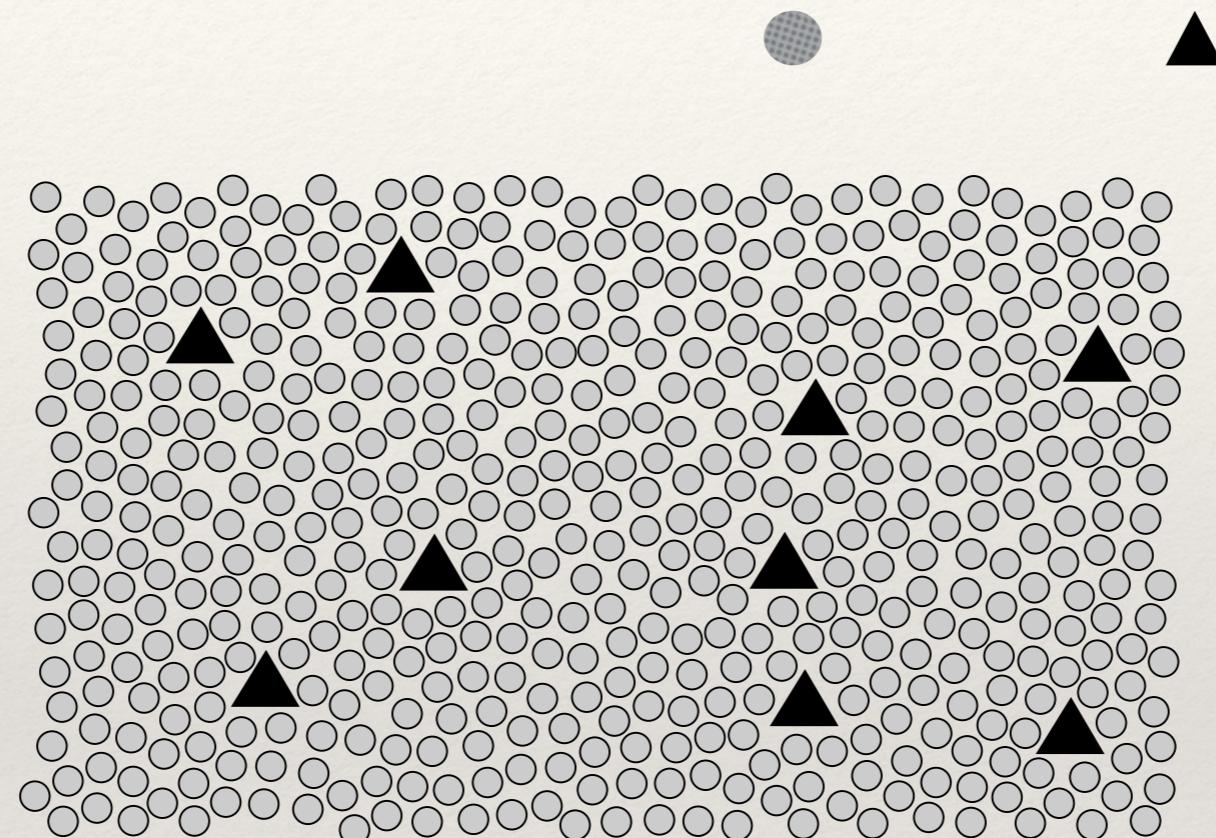


Real data
[International Critical
Tables (volume 3)]

- Air is cooled to 81.6K (below $T_{O_2} = 90.2\text{ K}$)
 - $T=81.6\text{K}$ liquid condenses forming a mixture of
21% O₂ gas
48% O₂ liquid
(not pure O₂ due to entropy of mixing)
 - Further cooling 81.6K to 79 K
Gas mixture: green curve, liquid mixture: blue curve
% O₂ decreases in liquid
% O₂ decreases in gas as well
 - T just above 79.0K
O₂ drops to 7% in gas
approaches 21% in liquid
 - T=79.0K: rest gas condenses
21% O₂ in liquid, no gas left

Dilute Solutions

Solution: mixture with $A = \text{"solvent"}, B = \text{"solute"}$

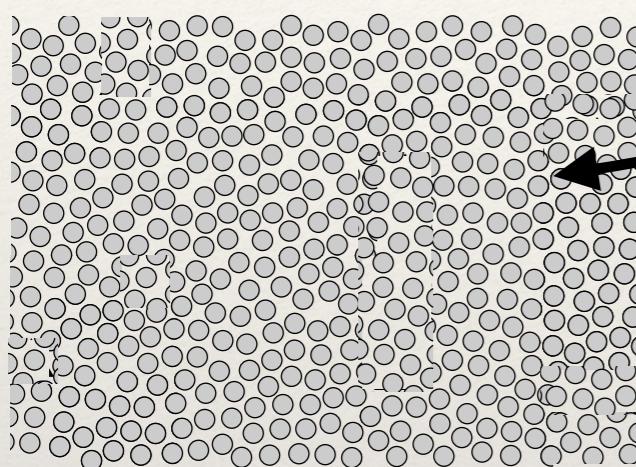


Dilute: $N_{\text{solute}} \ll N_{\text{solvent}}$

Solutes are surrounded by solvents,
do not interact directly with each other
Dilute solution \sim ``ideal gas of solutes''

Dilute Solutions

initially: $G = N_A \mu_0(T, p)$



Add a single solute particle: $\Delta G = \Delta U + p\Delta V - T\Delta S$

$\Delta U, \Delta V$: depend on short-range interactions between the solute and solvent locally, *independent of N_A*

$$\Delta S = k \log N_A + (N_A \text{ independent terms})$$

where to place the solute

$$\Rightarrow \Delta G = f(T, p) - kT \log N_A$$

Add N_B solute particles: $\Delta G = N_B f(T, p) - kT \log \left(\frac{N_A^{N_B}}{N_B!} \right)$

where to place N_B solutes
indistinguishable particles

$$G = N_A \mu_0(T, p) + N_B f(T, p) - N_B kT \left(\log \left(\frac{N_A}{N_B} \right) + 1 \right)$$

Dilute Solutions

$$G = N_A \mu_0(T, p) + N_B f(T, p) - N_B kT \left(\log \left(N_A / N_B \right) + 1 \right)$$

Chemical potentials:

$$\mu_A = \left(\frac{\partial G}{\partial N_A} \right)_{T, p, N_B} = \mu_0(T, p) - \frac{N_B}{N_A} kT$$

- Adding more solute decreases μ_A , increases μ_B
- N_A / N_B : intensive

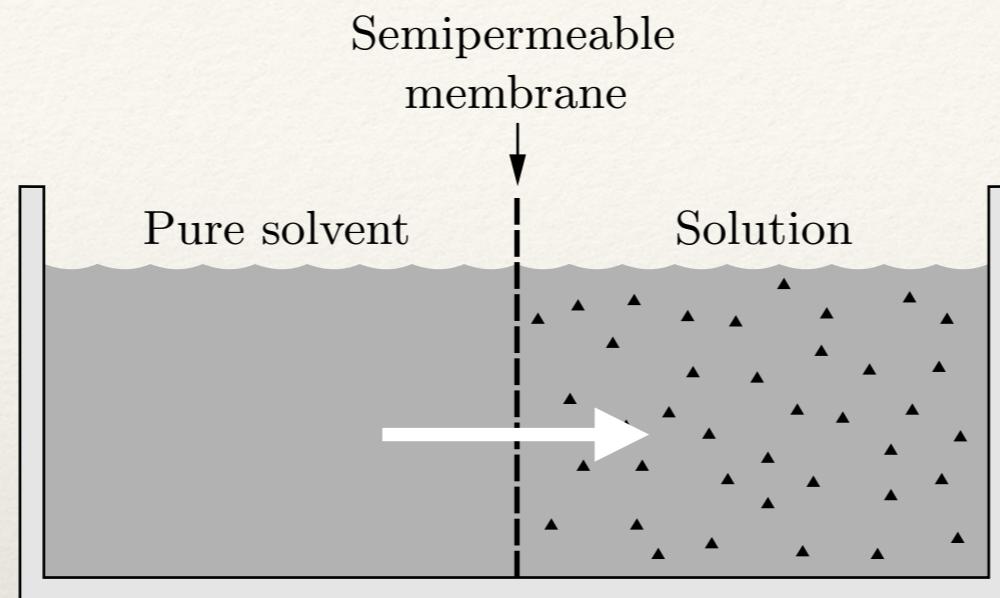
$$\mu_B = \left(\frac{\partial G}{\partial N_A} \right)_{T, p, N_A} = f(T, p) + kT \log \left(\frac{N_B}{N_A} \right)$$

molality:

$$m_B = \frac{\text{number of moles of B}}{\text{kg of moles of A}} \propto \frac{N_B}{N_A}$$

$$\mu_B = \mu^\circ(T, p) + kT \log m_B$$

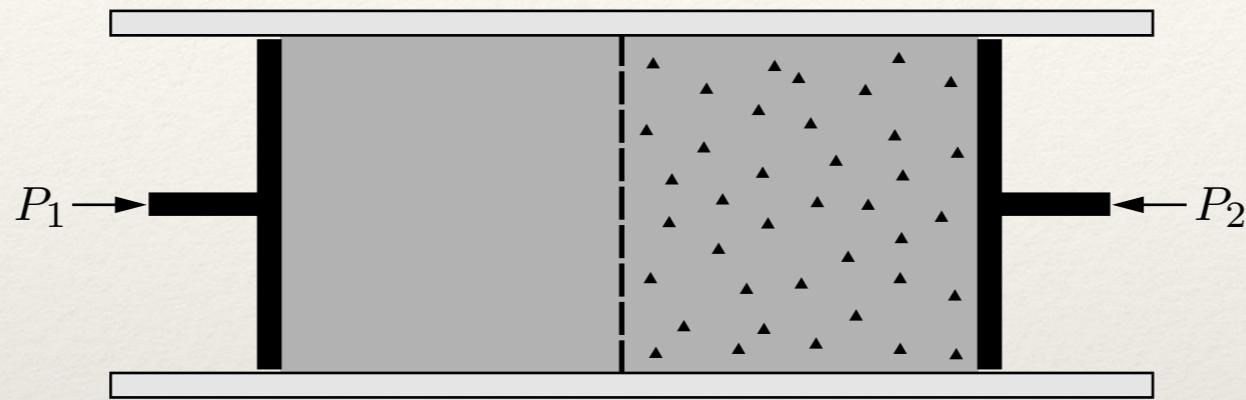
Dilute Solutions: Osmosis



$$\mu_0(T, p) > \mu_0(T, p) - \frac{N_B}{N_A} kT$$

Dilute Solutions: Osmosis

To prevent osmosis:



pressure
difference is
small:
 $p_2 - p_1 \ll p_2, p_1$

$$\mu_0(T, p_1) = \mu_0(T, p_2) - \frac{N_B}{N_A} kT$$

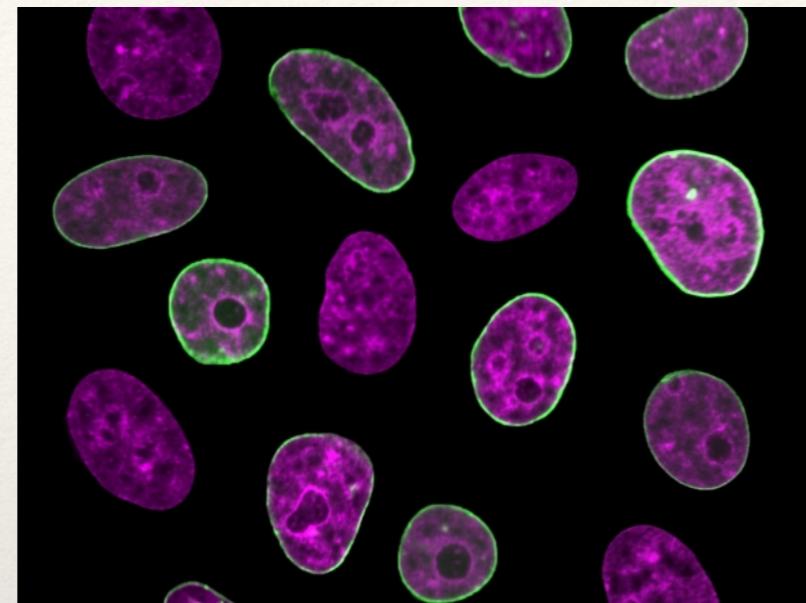
$$\mu_0(T, p_2) \approx \mu_0(T, p_1) + (p_2 - p_1) \frac{\partial \mu_0}{\partial p} = \mu_0(T, p_1) + (p_2 - p_1) \frac{1}{N_A} \frac{\partial G_0}{\partial p} = \mu_0(T, p_1) + (p_2 - p_1) \frac{V}{N_A}$$

$$\Rightarrow \frac{N_B}{N_A} kT = (p_2 - p_1) \frac{V}{N_A} \Rightarrow (p_2 - p_1) = \frac{kT}{N_B V}$$

``osmotic pressure''
van 't Hoff formula

Classroom Example: Osmosis

Human cell nuclei with fluorescently labeled chromatin (purple) and nuclear envelope (green). Credit: Fang-Yi Chu and Alexandra Zidovska, Department of Physics, New York University.
From: <https://www.technologynetworks.com/cell-science/lists/7-stunning-cell-images-from-2017-294838>



``osmotic pressure''
van 't Hoff formula

$$(p_2 - p_1) = \frac{N_B k T}{V}$$

cell: water + sugar+ amino acids etc... $N_{\text{stuff}}/N_{\text{water}} \sim 1/200$

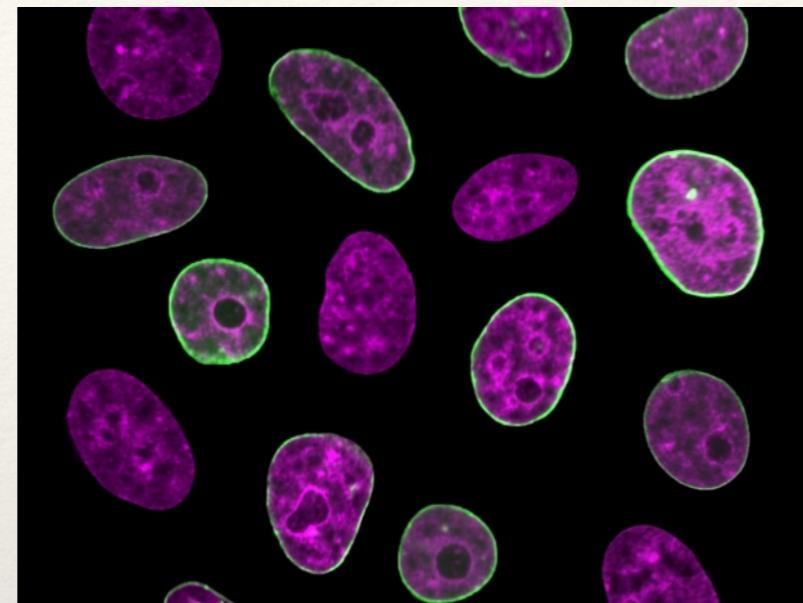
1 mole of water has a volume of 18 cm^3 , $1\text{atm}=10^5 \text{ Pa}$, $T=300\text{K}$

If a cell is put into pure water it will absorb water until the pressure inside equals the osmotic pressure.

Calculate the osmotic pressure for this case.
What will happen to the cell?

Classroom Example: Osmosis

Human cell nuclei with fluorescently labeled chromatin (purple) and nuclear envelope (green). Credit: Fang-Yi Chu and Alexandra Zidovska, Department of Physics, New York University.
From: <https://www.technologynetworks.com/cell-science/lists/7-stunning-cell-images-from-2017-294838>



``osmotic pressure''
van 't Hoff formula

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1 mole of water has a volume of 18 cm^3 , $1\text{atm}=10^5 \text{ Pa}$, $T=300\text{K}$

$$\frac{N_{B,\text{mole}}}{V} = \left(\frac{1}{200}\right) \left(\frac{1\text{mol}}{18\text{cm}^3}\right) \left(\frac{1\text{cm}}{1\text{m}}\right)^3 = 278\text{mol/m}^3$$

$$(p_2 - p_1) = \frac{N_{B,\text{mole}} R T}{V} = 6.9 \times 10^5 \text{ Pa} \approx 7\text{atm}$$

An animal cell will most likely burst, plant cells have rigid walls and can withstand such pressures

Dilute Solutions: Boiling and Freezing



boiling salty water

$$T_{\text{salty}} \text{ ??? } T_{\text{pure}}$$

Dilute Solutions: Boiling and Freezing



boiling salty water

expand around $T_0 = T_{pure}$:

$$T_{salty} \text{ ??? } T_{pure}$$

boiling point: $\mu_{gas}(T, p) = \mu_{liq}(T, p)$

$$\mu_{liq}(T, p) = \mu_{liq,0}(T, p) - \frac{N_B}{N_A} kT$$

\uparrow
pure liquid

$$\mu_{gas}(T, p) = \mu_{gas}(T_0, p) + (T - T_0) \frac{\partial \mu_{gas}}{\partial T}$$

$$\mu_{liq,0}(T, p) = \mu_{liq,0}(T_0, p) + (T - T_0) \frac{\partial \mu_{liq,0}}{\partial T}$$

$$\Rightarrow \mu_{gas}(T_0, p) + (T - T_0) \frac{\partial \mu_{gas}}{\partial T} = \mu_{liq,0}(T_0, p) + (T - T_0) \frac{\partial \mu_{liq,0}}{\partial T} - \frac{N_B kT}{N_A}$$

notice that $\mu_{gas}(T_0, p) = \mu_{liq,0}(T_0, p)$, $\partial \mu / \partial T = -S/N$

Dilute Solutions: Boiling and Freezing



$$T_{\text{salty}} > T_{\text{pure}}$$

$$-(T - T_0) \left(\frac{S}{N_A} \right)_{\text{gas}} = -(T - T_0) \left(\frac{S}{N_A} \right)_{\text{liq}} - \frac{N_B k T}{N_A}$$

boiling salty water

$$S_{\text{gas}} - S_{\text{liq}} = \frac{L}{T_0}$$

L =latent heat of vaporization: (2260 kJ for 1 kg water)

$$\Rightarrow T = T_0 + \frac{N_B k T_0^2}{L}$$

e.g. seawater: 35g of NaCl/ 1kg water

average atomic mass of Na & Cl: 29

$$n_{B,\text{mole}} = 35/29 = 1.2$$

$$T - T_0 = \frac{N_{B,\text{mole}} R T_0^2}{L} = 0.6\text{K}$$

Dilute Solutions: Boiling and Freezing



boiling salty water



freezing salty water

If we instead vary the *pressure*

$$\frac{P}{P_0} = 1 - \frac{N_B}{N_A}$$

e.g. seawater:
 $\frac{\Delta P}{P_0} = -0.022$

vapor pressure *decreases*

``Raoult's Law''

why the - sign?

freezing temp

$$T = T_0 - \frac{N_B k T_0^2}{L}$$

Latent heat of melting
(water: 334 kJ/kg)

e.g. seawater

$$T = -2.2^\circ\text{C}$$

e.g. ~10% salt

$$T \approx -10^\circ\text{C}$$

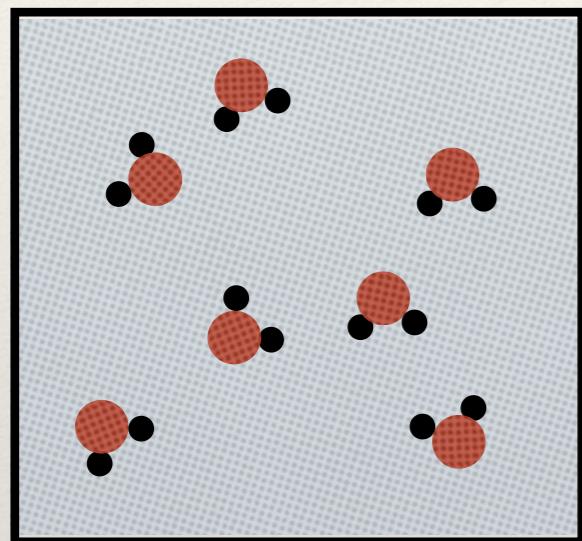
note: The roads have to be pre-treated with the liquid+salt mixture!

Chemical Equilibrium

more stable



less stable



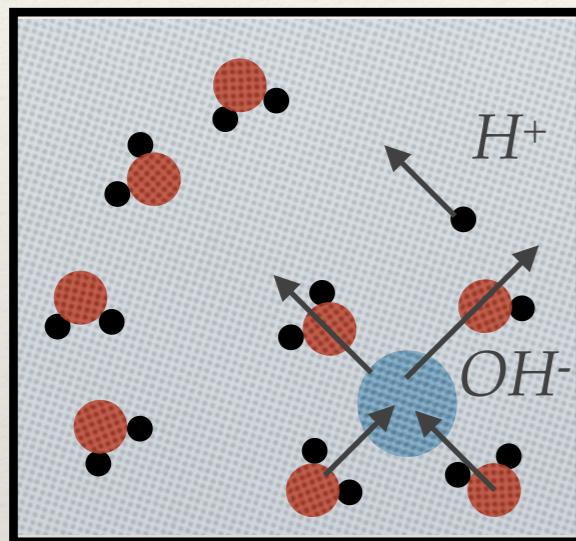
Equilibrium: all H_2O no ions ??

Chemical Equilibrium

more stable



less stable



Equilibrium: all H₂O no ions ?? *NO!*

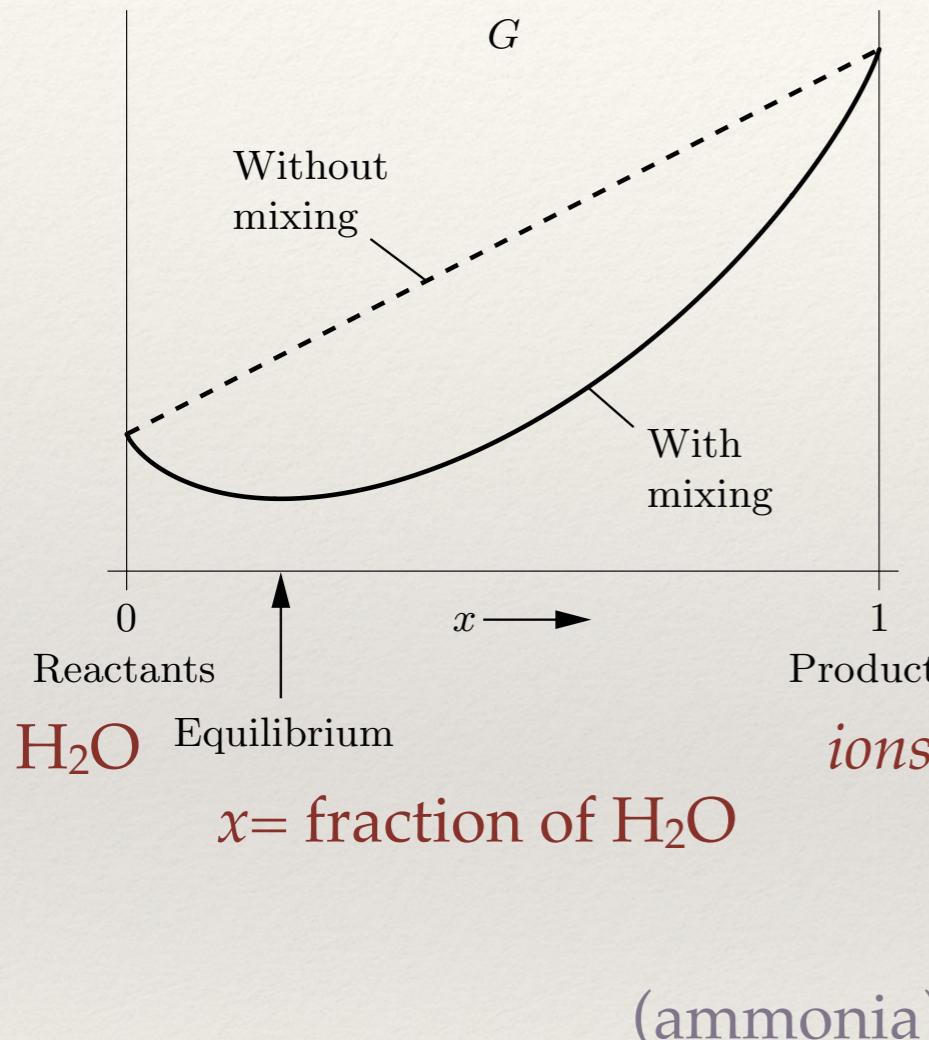
In a cup of water there *are* ions (~1 pair / 5x10⁸ H₂O molecules)
Collisions between molecules produce ions once in a while
Ions recombine

Equilibrium: dynamical state where ions form and recombine

Water + ions : dilute solution

Recall: a having little bit of impurity (i.e. ions) is energetically favored compared to pure substance (i.e. water) due to increase in entropy

Chemical Equilibrium



$$\mu_{\text{N}_2} + 3\mu_{\text{H}_2} = 2\mu_{\text{NH}_3}$$

Equilibrium: minimum of G

$$dG = \sum_i \mu_i dN_i = 0 \quad (\text{constant } T, p)$$

$$\mu_{\text{H}_2\text{O}} dN_{\text{H}_2\text{O}} + \mu_{\text{H}^+} dN_{\text{H}^+} + \mu_{\text{OH}^-} dN_{\text{OH}^-} = 0$$

$$dN_{\text{H}_2\text{O}} = -1, \quad dN_{\text{H}^+} = 1, \quad dN_{\text{OH}^-} = 1 \quad (\text{not independent})$$

Equilibrium: $\mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-}$

In general:



$$\nu_1 \mu_1 + \nu_2 \mu_2 + \dots = \nu_3 \mu_3 + \nu_4 \mu_4 + \dots$$

Chemical Equilibrium

reaction:



equilibrium:



4 examples

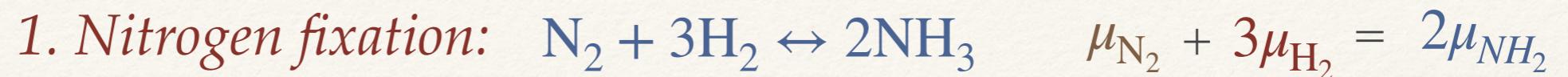
1. *Nitrogen fixation:* $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$

2. *Dissociation of water:* $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$

3. *Oxygen dissolving in water:* $\text{O}_2(\text{gas}) \leftrightarrow \text{O}_2(\text{in water})$

4. *Ionization of hydrogen:* $\text{H} \leftrightarrow \text{p}^+ + \text{e}^-$

Chemical Equilibrium



Recall $\mu(T, p) = \mu^\circ(T) + kT \log(p/p_0)$ set $p^\circ=1$ bar

$$\mu_{\text{N}_2}^\circ + kT \log(p_{\text{N}_2}/p^\circ) + 3\mu_{\text{H}_2}^\circ + 3kT \log(p_{\text{H}_2}/p^\circ) = 2\mu_{\text{NH}_2}^\circ + 2kT \log(p_{\text{NH}_2}/p^\circ)$$

$$\Rightarrow kT \log \left(\frac{p_{\text{N}_2} p_{\text{H}_2}^3}{p_{\text{NH}_2}^2 p^\circ 2} \right) = 2\mu_{\text{NH}_2}^\circ - \mu_{\text{N}_2}^\circ - 3\mu_{\text{H}_2}^\circ = \Delta G^\circ \xrightarrow{\Delta G \text{ of the reaction. Can be found in tables}}$$

Equilibrium: $\frac{p_{\text{NH}_3}^2 p^\circ 2}{p_{\text{N}_2} p_{\text{H}_2}^3} = e^{-\frac{\Delta G^\circ}{kT}} = K: \text{Equilibrium constant}$

$K = 5.9 \times 10^5$ (@ room temp.)

Le Chatelier's principle:

If you disturb equilibrium the system will respond in a way that opposes the change

Thank you!