Equilibrium & Free Energy

if N, V, T of system constant

$$0 \leq dS_{tot} = dS_{sys} + dS_R$$

$$= -\frac{1}{T} dF_{sys}$$

if $dS_{tot} \geq 0$ $\quad dF_{sys} \leq 0$

F tends to decrease as system approaches equilibrium, when system is in contact with a thermal reservoir at constant N & V.

at constant N, P, & T,

$$dS_{tot} = -\frac{1}{T} dG_{sys}$$

& G tends to decrease. . . .

e.g. Diamond & Graphite → both carbon

at STP, 1 mol diamond has $G = 2900\ J$

1 mol graphite has $G = 0\ J$

graphite is more stable than diamond at STP because it has lower G — more common

at higher pressures, G change

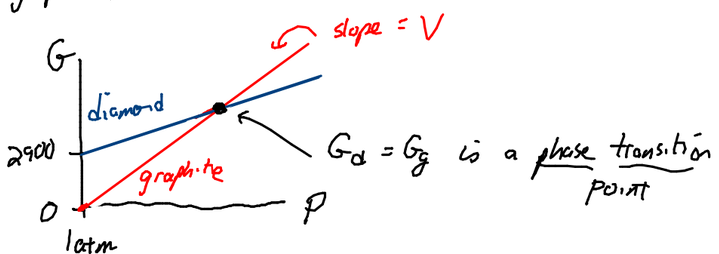
$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$= V\,dP \quad \text{at } T, N \text{ constant}$$

if V constant, $\Delta G = V\,\Delta P$

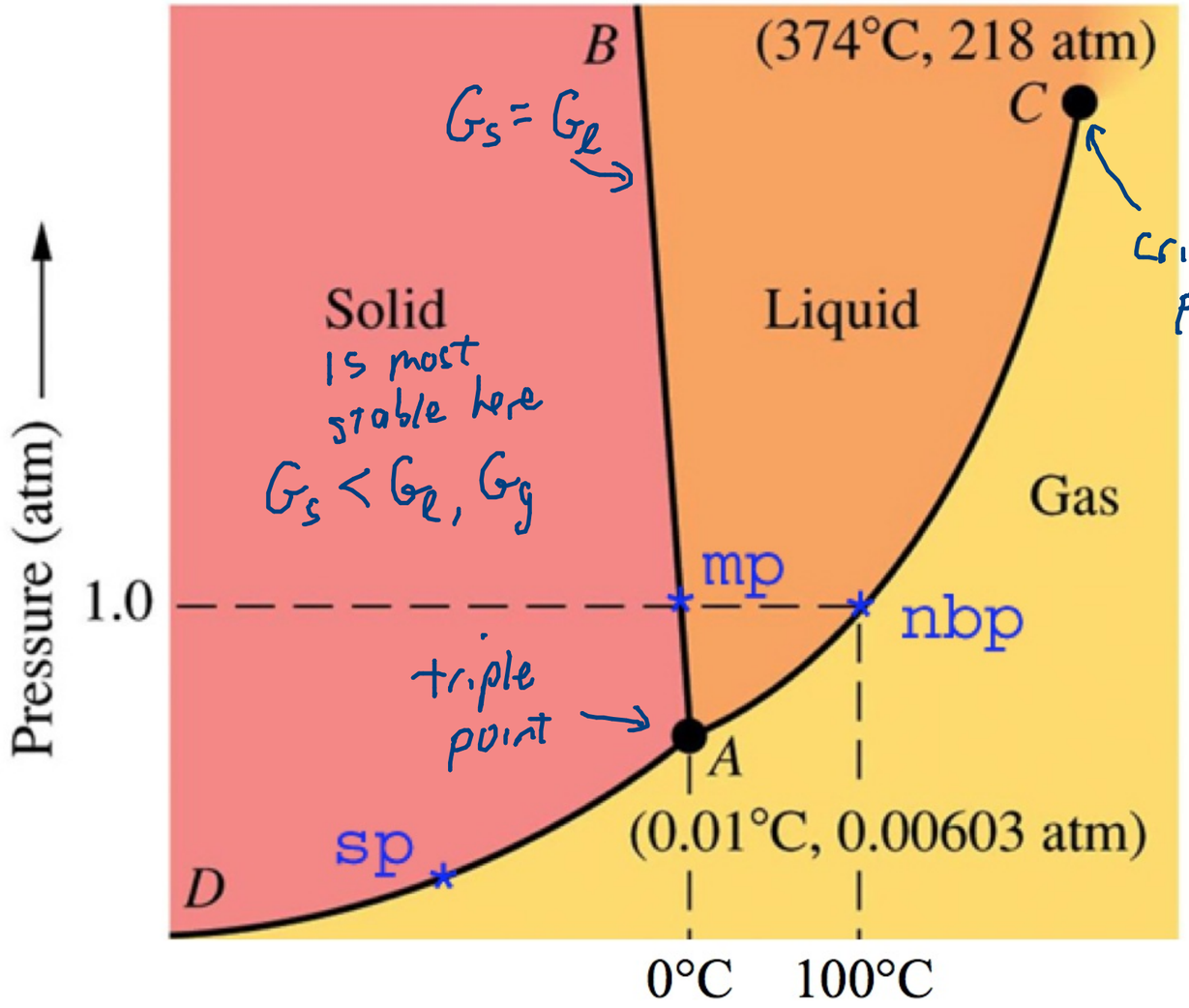
1 mol diamond, $V = 3.42\ cm^3$ pg 404 Schroeder

1 mol graphite, $V = 5.30\ cm^3$



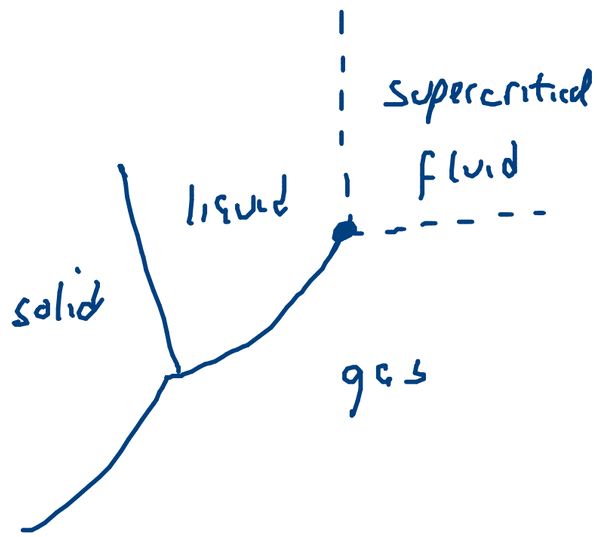
$G_d = G_g$ is a phase transition point

Phase Diagram of Water



Supercritical Fluid

- can dissolve materials like a liquid
- can effuse through solids like a gas
- no surface tension
- excellent solvents
- gas giant atmospheres & Venus



How can water evaporate at $T < 100^\circ C$?

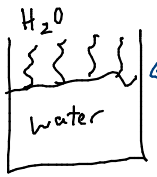
Gases exert pressure on solids & liquids
but <u>not</u> on other gases

Each type of gas has its own <u>partial pressure</u>

P_{N_2}, P_{O_2}, P_{H_2O}, P_{CO_2}, ...

$$P_{atm} = \sum P_i$$

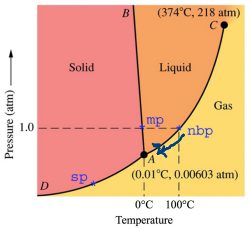
$P_i \sim$ density of gas



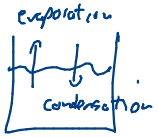
← pressure of water vapor $<<$ 1 atm
Bond at low pressures
$T_{boiling\ point} < 100^\circ C$

If $T_{boiling\ point} <$ room temperature,

then water will evaporate



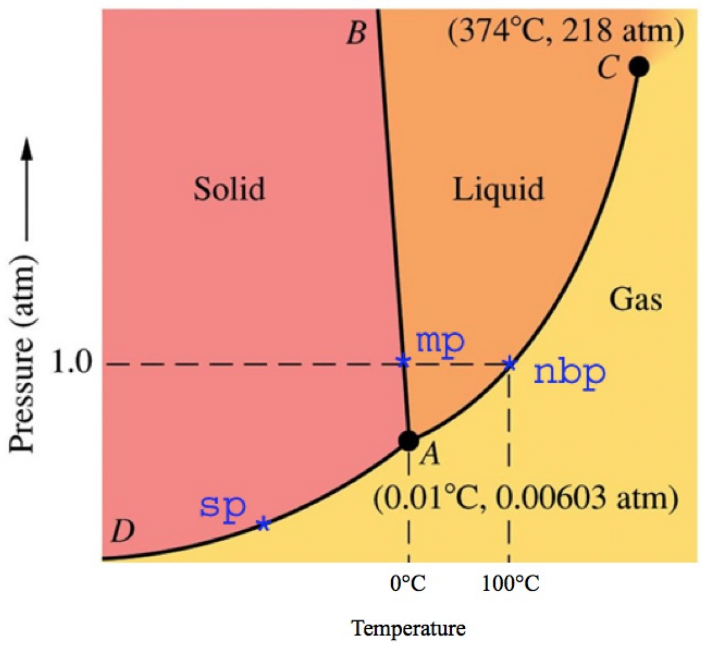
If container is closed,
water vapor will build up & P_{H_2O} will increase
& $T_{b.p.}$ will rise
once it reaches room T, evaporation "ceases"



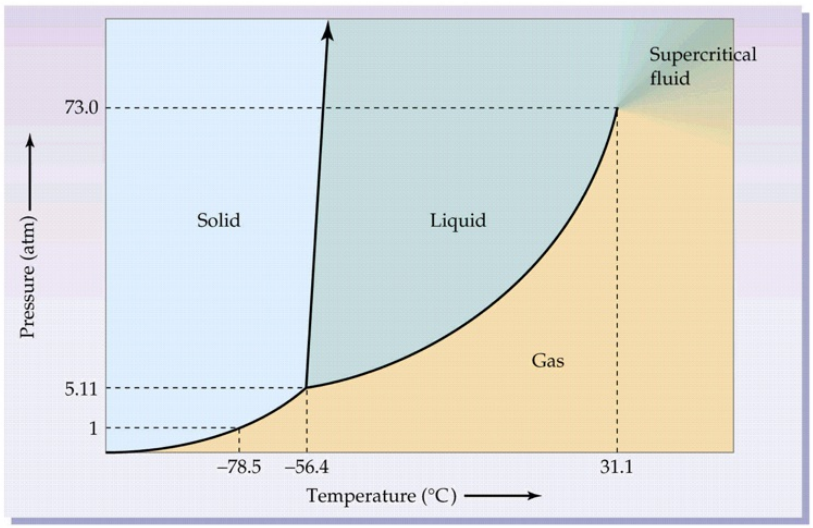
What's special about 100°C?

at 100°C the liquid in the bulk is unstable & turns into bubbles of water vapor.

H_2O


B
(374°C, 218 atm)
C
Solid
Liquid
Gas
mp
nbp
1.0
A
sp
(0.01°C, 0.00603 atm)
D
0°C
100°C
Temperature
Pressure (atm)

CO_2


Supercritical fluid
73.0
Solid
Liquid
Pressure (atm)
Gas
5.11
1
–78.5
–56.4
31.1
Temperature (°C)