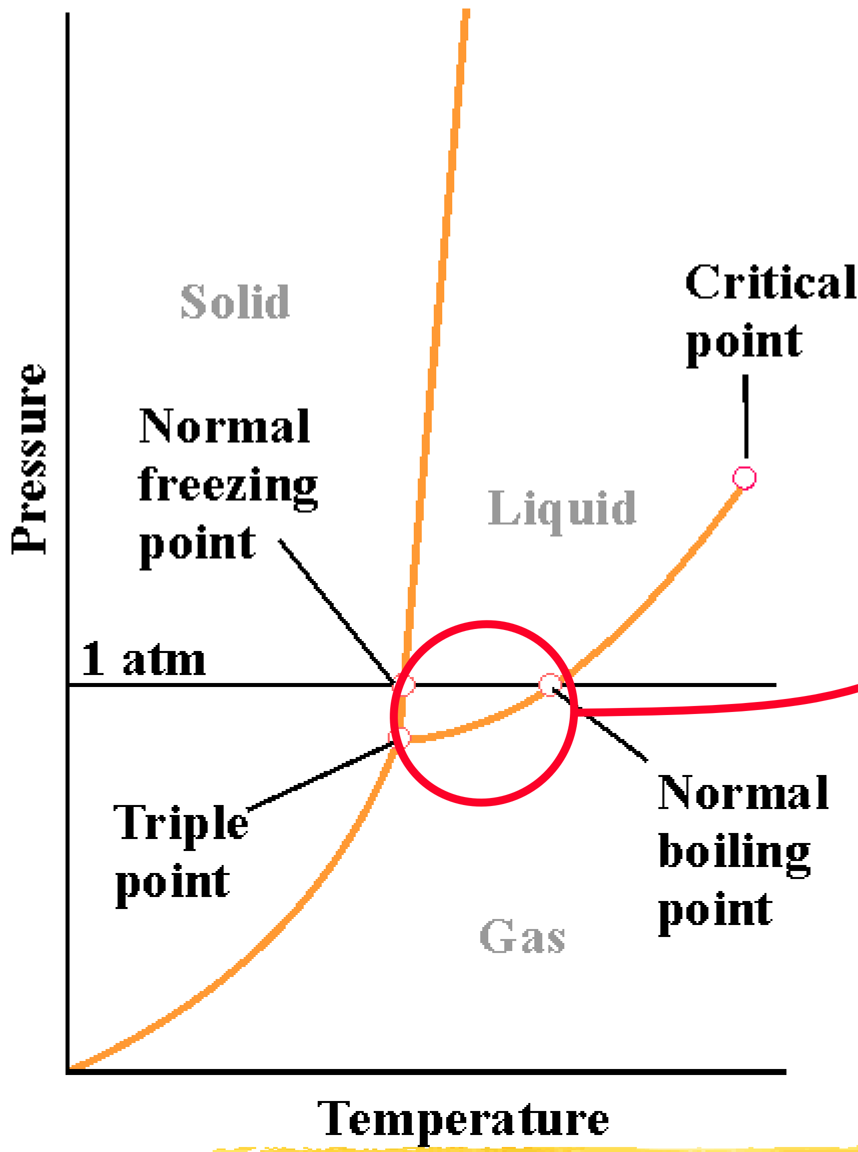
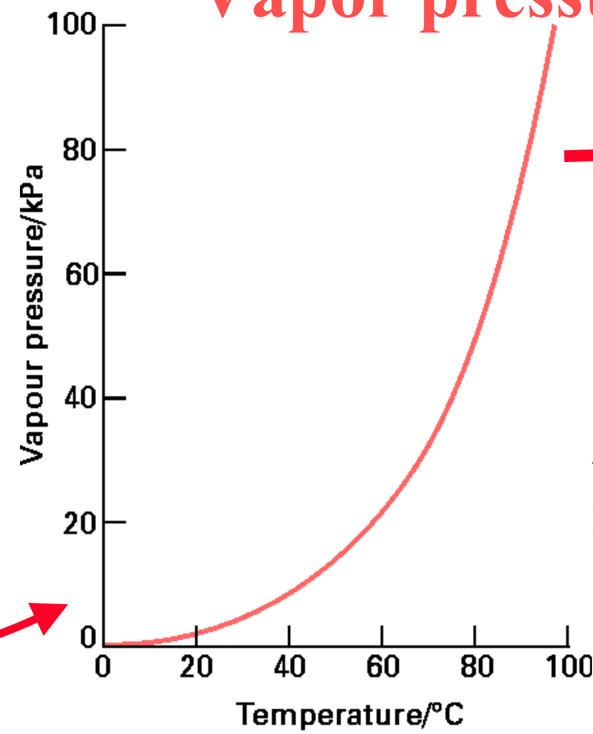
Phase boundaries



Vapor pressure



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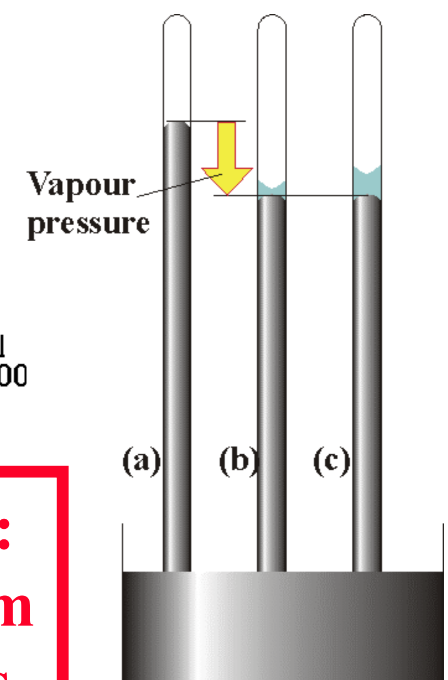


At phase boundary:
Dynamic equilibrium between two phases
$\Delta G = 0$

Phase boundaries: Where are they?

Phase 1: $dG_m(1) = V_m(1)dp - S_m(1)dT$
Phase 2: $dG_m(2) = V_m(2)dp - S_m(2)dT$

$\Big\}$ **in equilibrium**

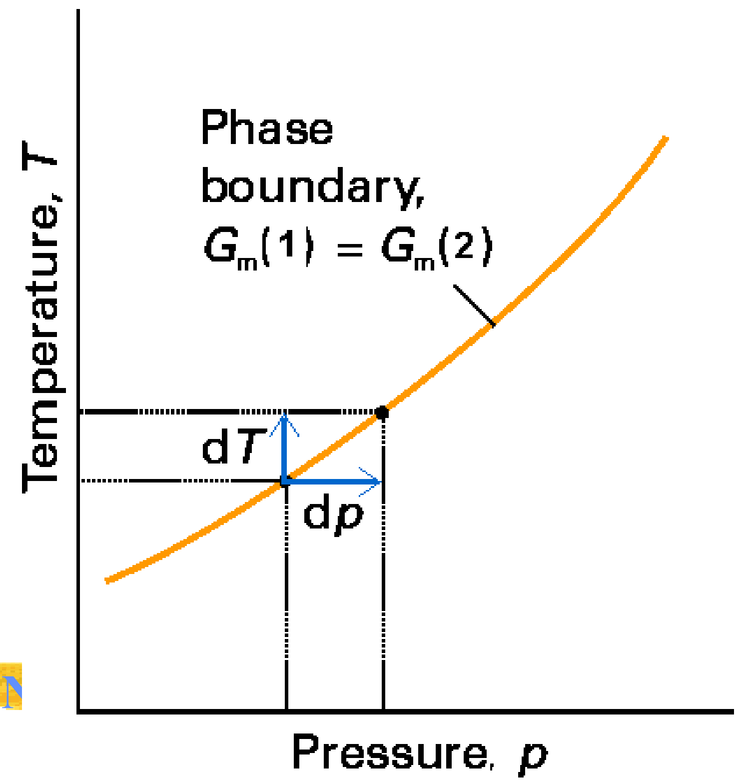
Along the phase boundary, the molar Gibbs energies stay equal
$\Rightarrow$ the changes in their molar Gibbs energies must be equal

$$V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT$$

$$\Rightarrow \underbrace{[S_m(2) - S_m(1)]}_{\Delta_{trs}S}dT = \underbrace{[V_m(2) - V_m(1)]}_{\Delta_{trs}V}dp$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

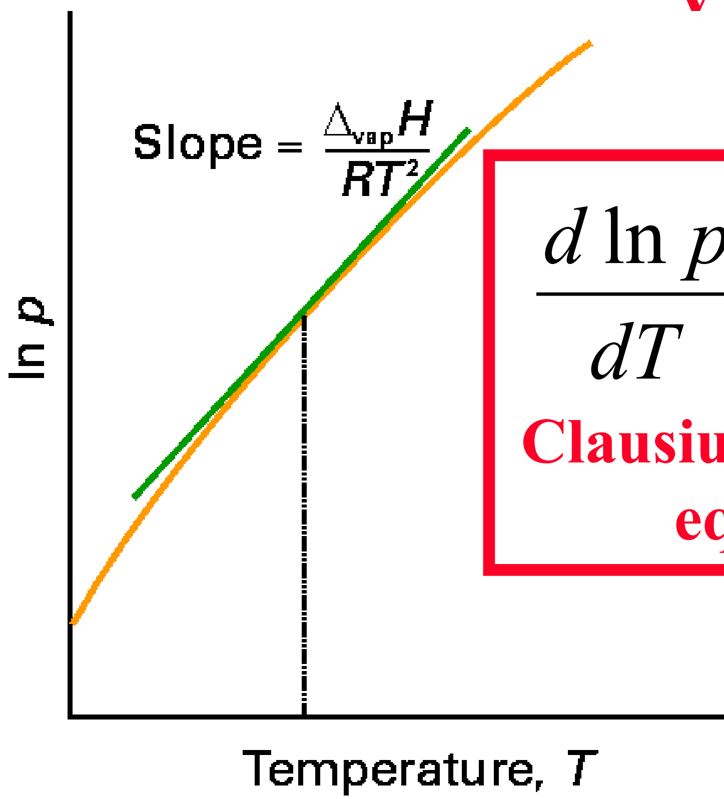
Clapeyron equation



Special case: The liquid-vapor boundary

$$\frac{dp}{dT} \underset{\uparrow}{=} \frac{\Delta_{vap}S}{\Delta_{vap}V} \underset{\uparrow}{=} \frac{\Delta_{vap}H}{T\Delta_{vap}V} \underset{\uparrow}{=} \frac{\Delta_{vap}H}{TV_m(g)} \underset{\uparrow}{=} \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$$

trs → vap | **$\Delta_{vap}S = \Delta_{vap}H/T$** | **$\Delta_{vap}V \approx V_m(g)$; $V_m(l)$ small** | **perfect gas approximation**



$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

Clausius-Clapeyron equation

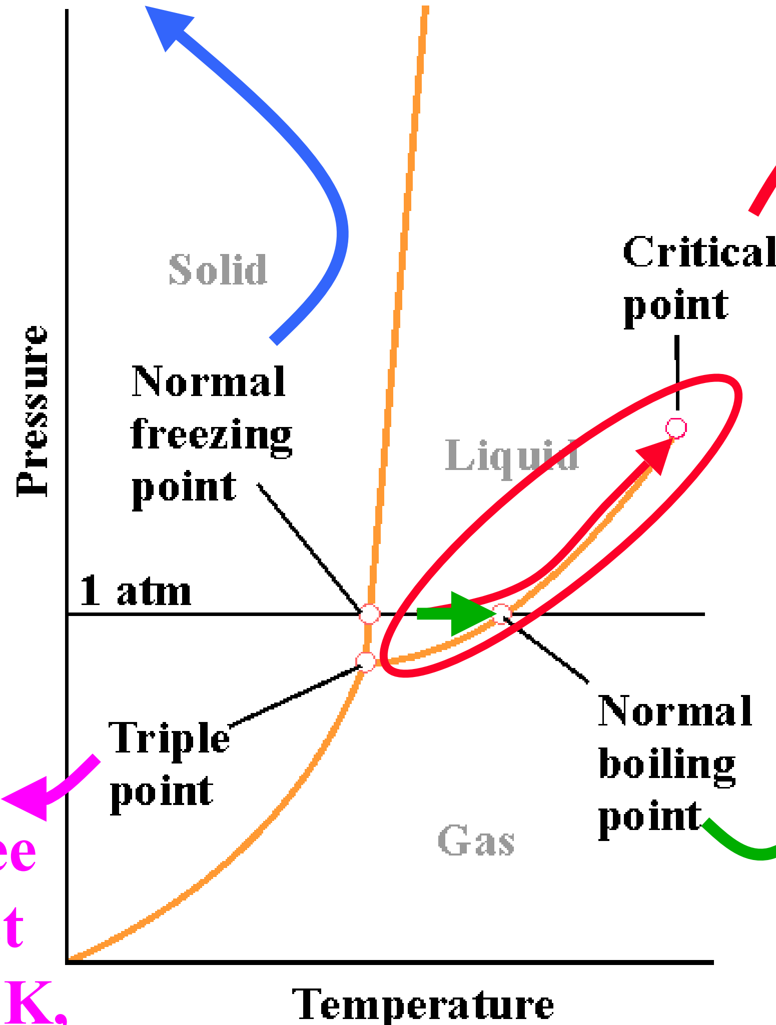
$$\int_p^{p'} d\ln p = \int_T^{T'} \frac{\Delta_{vap}H}{RT^2}\,dT$$

$$\Rightarrow \ln\frac{p'}{p} = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

Characteristic points

Same as melting point;
"normal" = at 1 atm

Highest T for liquid



Lowest T for liquid

Only set of conditions where all three phases coexist (water: 273.16 K, 611 Pa)

<u>Closed vessel:</u>
Pressure increases until critical point is reached (T_c, p_c); <u>phase boundary is lost</u>

<u>Open vessel:</u>
Vapor pressure equals external pressure
$\Rightarrow$ vapor drives back atmosphere: <u>Boiling</u>

How many phases can coexist in equilibrium?

Four phases: $G_m(1) = G_m(2)$; $G_m(2) = G_m(3)$; $G_m(3) = G_m(4)$

BUT: Only two unknown parameters (p, T) in a phase diagram

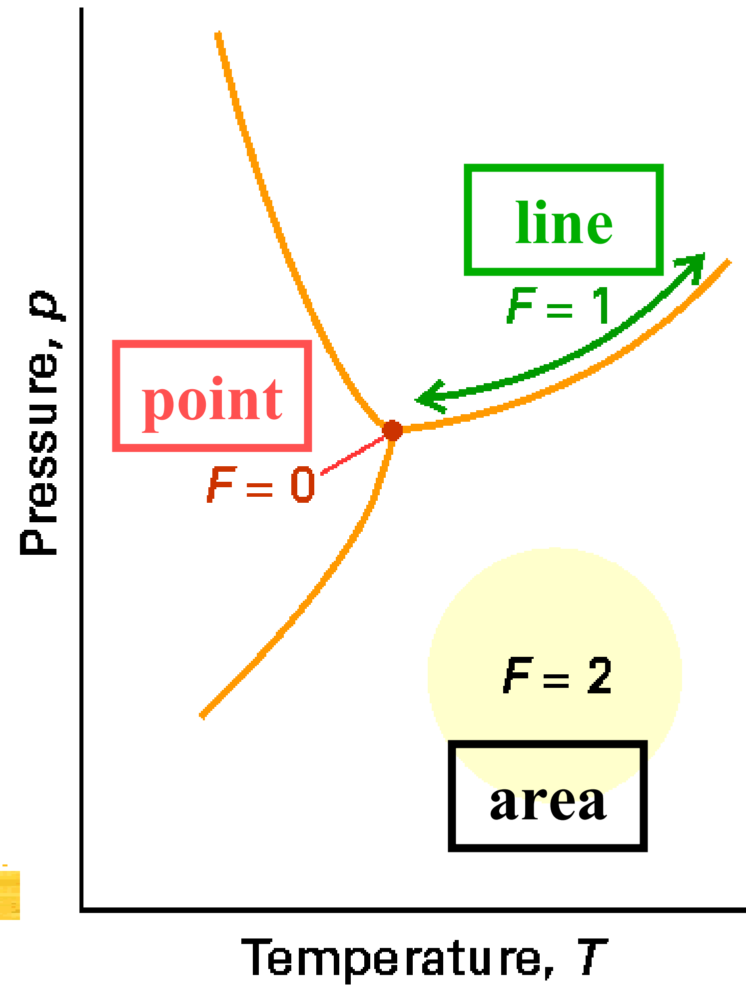
$\Rightarrow$ **Four phases cannot coexist in equilibrium!**

Phase rule: F = C - P + 2

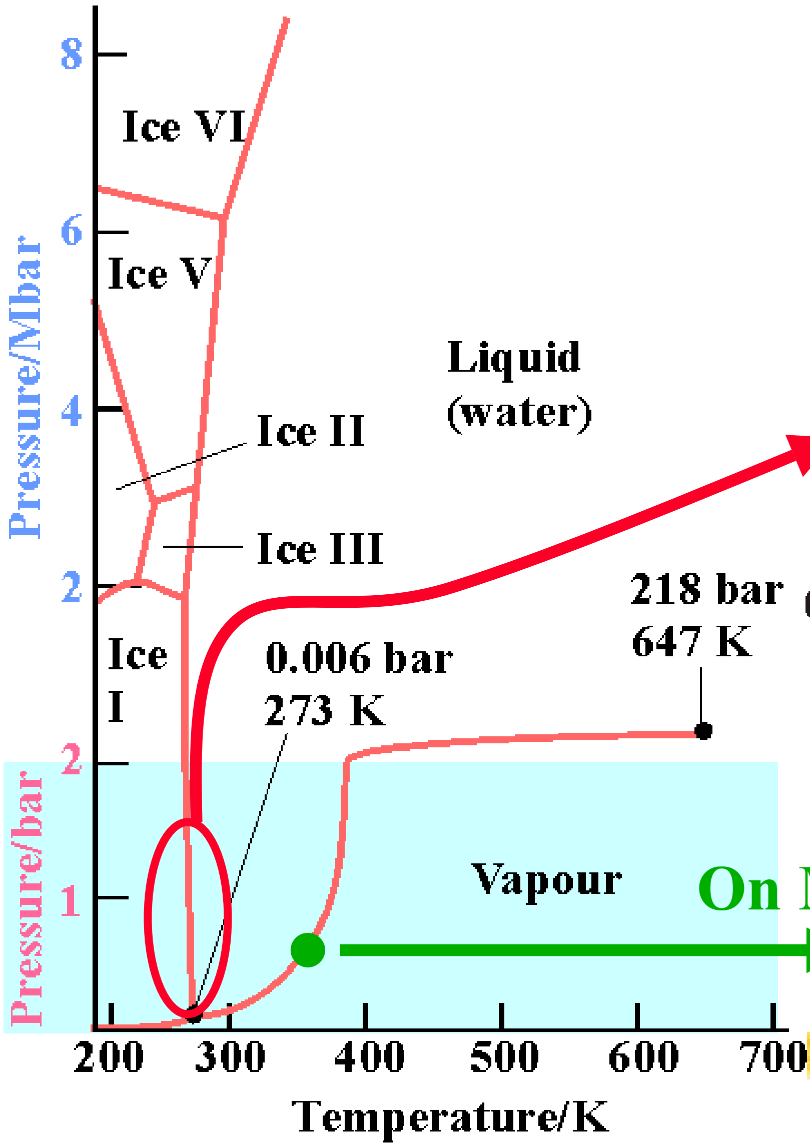
F = Number of degrees of freedom

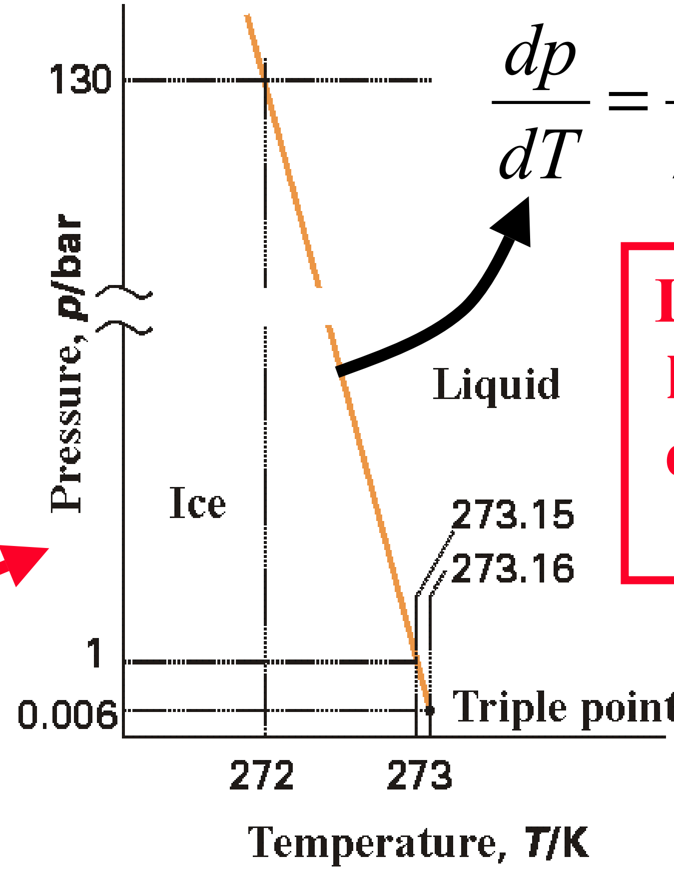
C = number of components (pure: 1)

P = number of phases



Phase diagrams: Water





$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

Liquid water has a higher density than water ice

$\Downarrow$

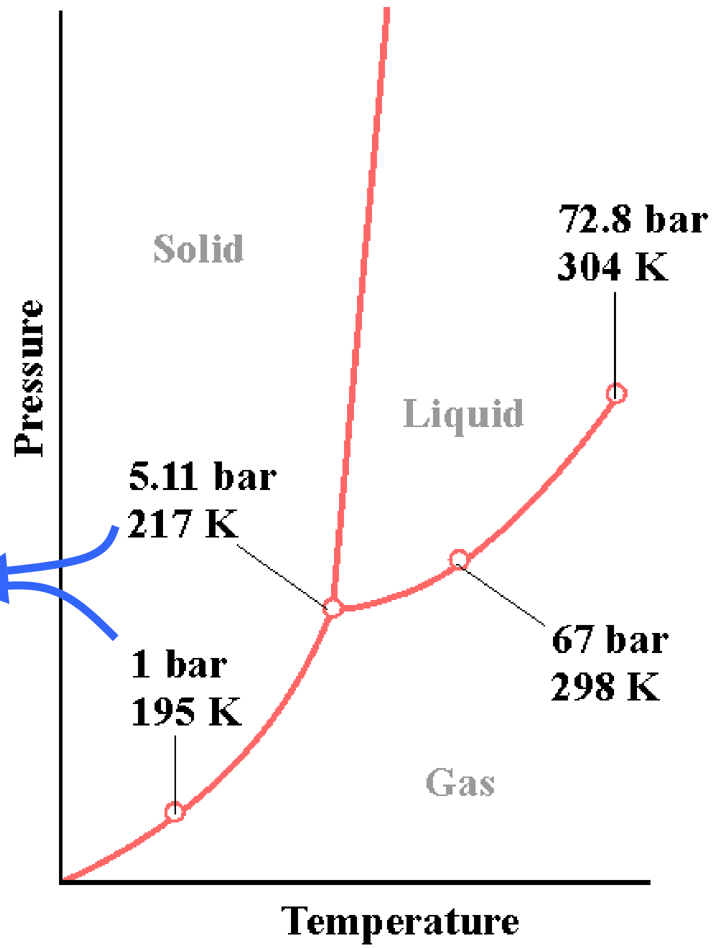
ice skating!

frozen ponds sustain fish!

On Mt. Everest "boiling" eggs becomes easier

Phase diagrams: CO_2 and Helium

CO_2: quite typical



Sublimes at 1 atm; exists as a liquid only under pressure

He: solid and gas are never in equilibrium; He-II is superfluid