

5. Phase Diagrams

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A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state. (various solid phases, liquid, gas)

~~Order~~

Landau: Phases can be distinguished by their degree of order
 \Rightarrow ~~order~~ introduces concept of order parameter

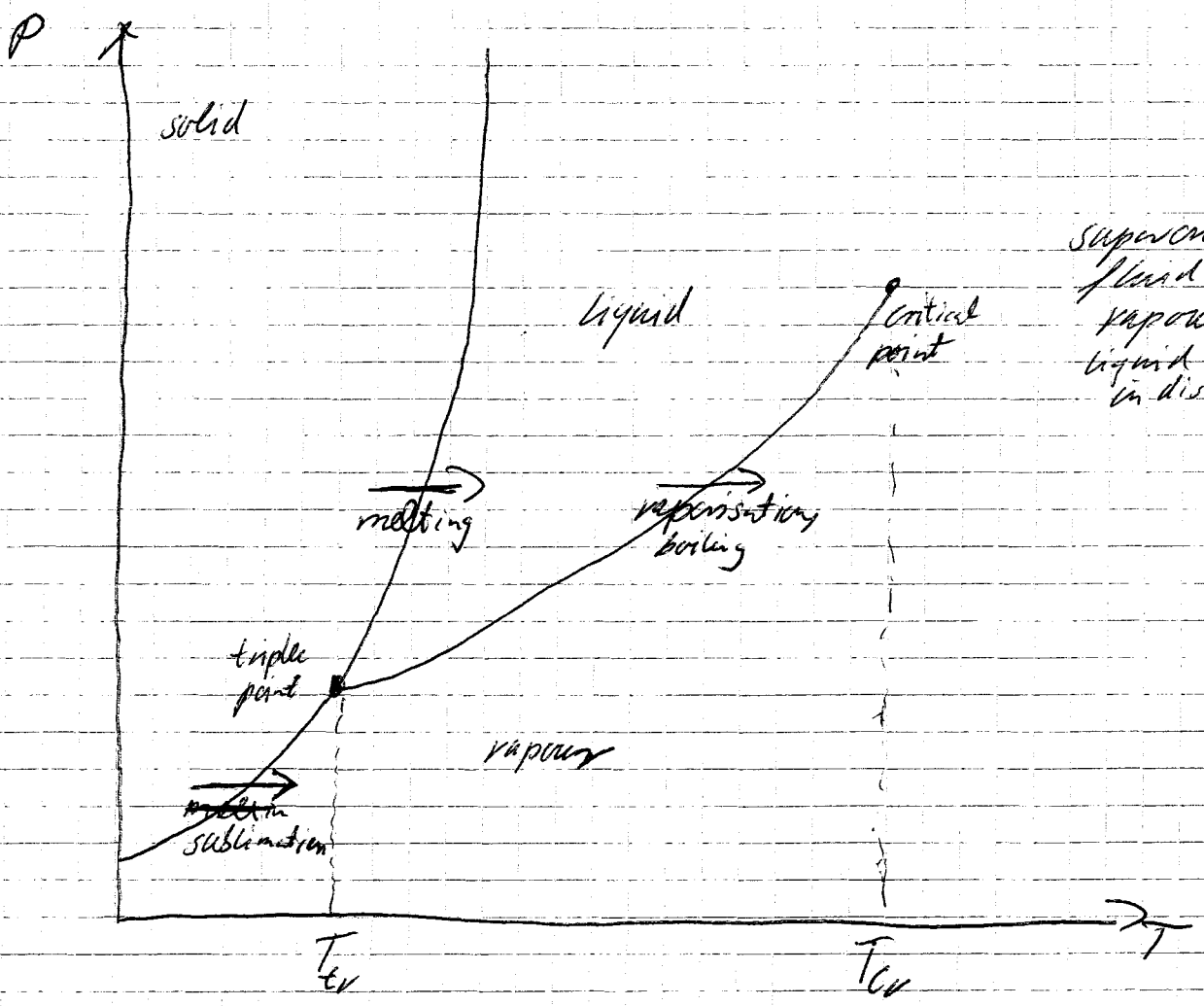
A phase transition is the spontaneous conversion of one phase into another phase.

Note: transition can be impossibly slow
 \Rightarrow metastable states

e.g. diamonds are not forever!

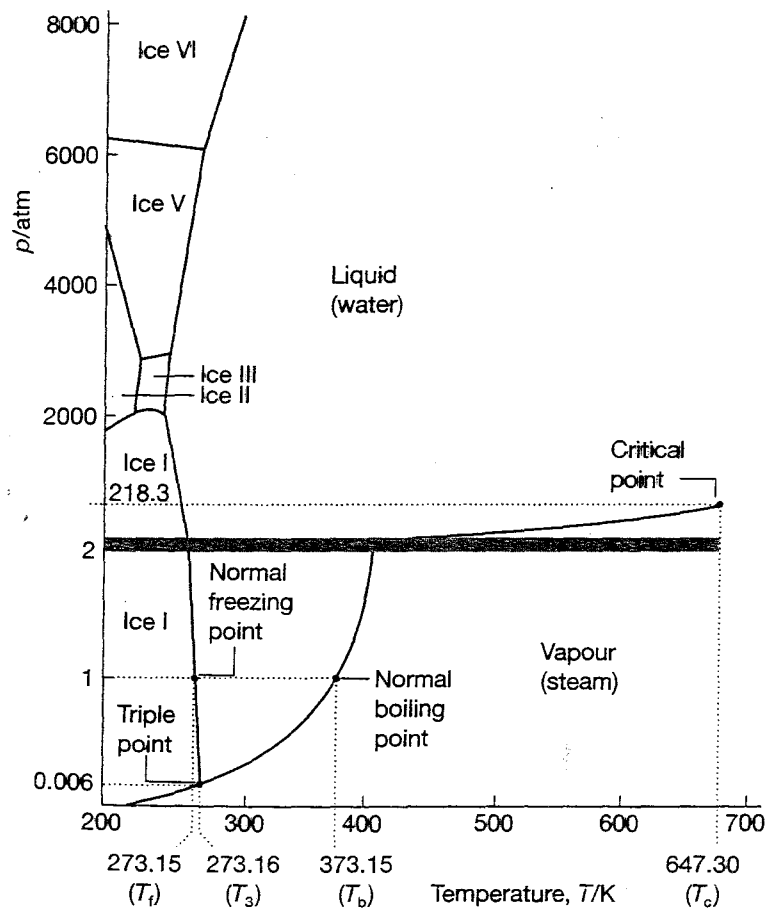
diamond \rightarrow graphite
 \uparrow metastable

typical phase diagrams (e.g. CO₂)



Supercritical fluid = vapour and liquid indistinguishable

different phase diagram of water due to H-bonds!



6.4 The experimental phase diagram for water showing the different solid phases. Note the change of vertical scale at 2 atm.

varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very open molecular structure of ice: the H_2O molecules are held apart as well as together by the hydrogen bonds between them, but the structure partially collapses on melting, and the liquid is denser than the solid.

At high pressures, different structural forms of ice come into stability as the hydrogen bonds between molecules are modified by the stress. Some of these phases (which are called ice II, III, V, VI, and VII) melt at high temperatures.² Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed.

Phase stability and phase transitions

chemical potential μ_i for a one-component system it is the molar Gibbs energy
 $\mu = G_m$

At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present

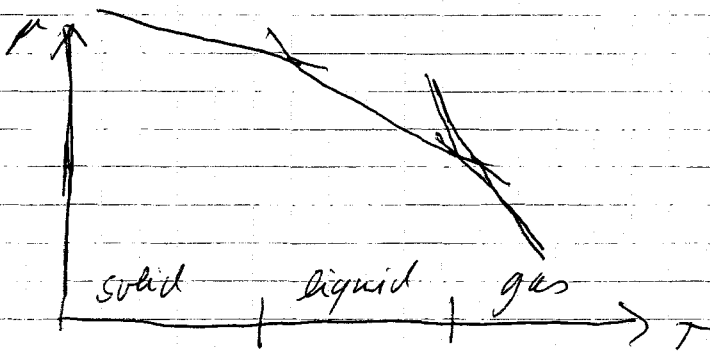
proof $\mu_1 > \mu_2$ amount dn transferred from 1 \rightarrow 2

$$\Rightarrow dG = (\mu_2 - \mu_1) dn < 0 \Rightarrow \text{spontaneous reaction}$$

$$\left. \frac{\partial \mu}{\partial T} \right|_p = -S_m$$

\Rightarrow temperature raised \Leftrightarrow chemical potential of pure substance decreases since $S_m > 0$

$$S_m(g) > S_m(l) > S_m(s)$$



$$\left. \frac{\partial \mu}{\partial p} \right|_T = V_m$$

$$V_m(l) > V_m(s)$$

⇒ pressure increases μ in a liquid more than in a solid

⇒ most substances melt at a higher temperature when subject to pressure

Location of phase boundaries between a phase α and β when in equilibrium:

$$\mu_\alpha(p, T) = \mu_\beta(p, T)$$

⇒ resulting slopes of phase boundaries

$$d\mu = -S_m dT + V_m dp \quad d\mu_\alpha = d\mu_\beta$$

$$-S_{\alpha,m} dT + V_{\alpha,m} dp = -S_{\beta,m} dT + V_{\beta,m} dp$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta_{fus} S}{\Delta_{fus} V}} \quad \text{Clapeyron eqn}$$

solid-liquid: $\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V} > 0$, steep

⇒ phase boundary:

$$\int_{p^*}^p dp = \frac{\Delta_{fus} H}{\Delta_{fus} V} \int_{T^*}^T \frac{dT}{T}$$

↑
melting pressure at T^* T-independent

$$\Rightarrow p \approx p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T}{T^*}$$

$T \approx T^*$ $\ln \frac{T}{T^*} \approx \frac{T-T^*}{T^*} \Rightarrow \boxed{p \approx p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V} (T - T^*)}$

Liquid vapour:

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T \Delta_{\text{vap}}V} > 0, \text{ small}$$

\searrow
 $> 0, \text{ large}$

$$\Delta_{\text{vap}}V \approx V_m(g) \quad \text{perfect: } V_m(g) = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T(RT/p)} \Rightarrow \frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}}H}{RT^2} \quad \text{Clausius - Clapeyron}$$

$$\left(\frac{dx}{x} = d \ln x \right)$$

$\Delta_{\text{vap}}H$ temperature independent

$$p = p^* e^{-x} \quad x = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

\downarrow
vapour pressure at T^*

Phase Transition, Ehrenfest classification

first-order phase transition \Leftrightarrow first derivative of the chemical potential with respect to temperature is discontinuous
 heating required!

second-order phase transition \Leftrightarrow first derivative of μ with respect to T is continuous but its second ~~derivative~~ derivative is discontinuous
 no jump in volume or entropy

λ -transition \Leftrightarrow not first-order but heat capacity becomes infinite at transition temperature