LECTURE

10

CY11001
Spring 2018

Phase Diagrams

Department of Chemistry
Indian Institute of Technology
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Chemical Potential and Phase Equilibrium

Chemical potential for a component in a mixture: $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j}$

μ (Chemical Potential) for pure substance = $G_m = G/n$

Chemical potential for substance in the phases that are in equilibrium

$$\mu_i^{\alpha}(p, T) = \mu_i^{\beta}(p, T)$$

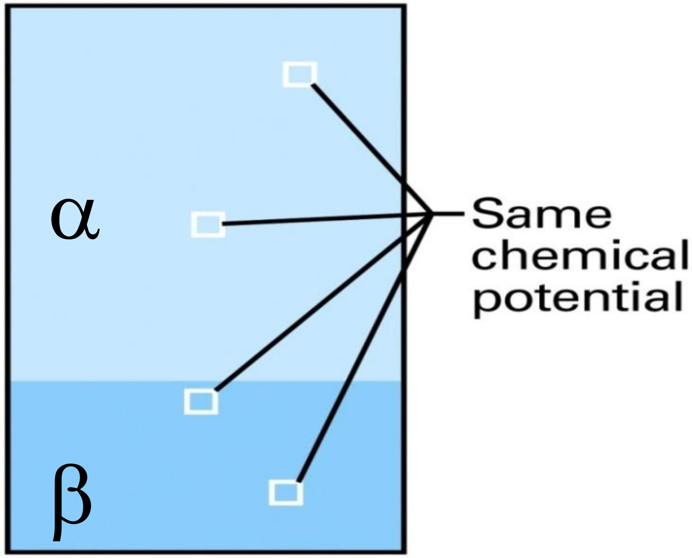

Figure 4-8
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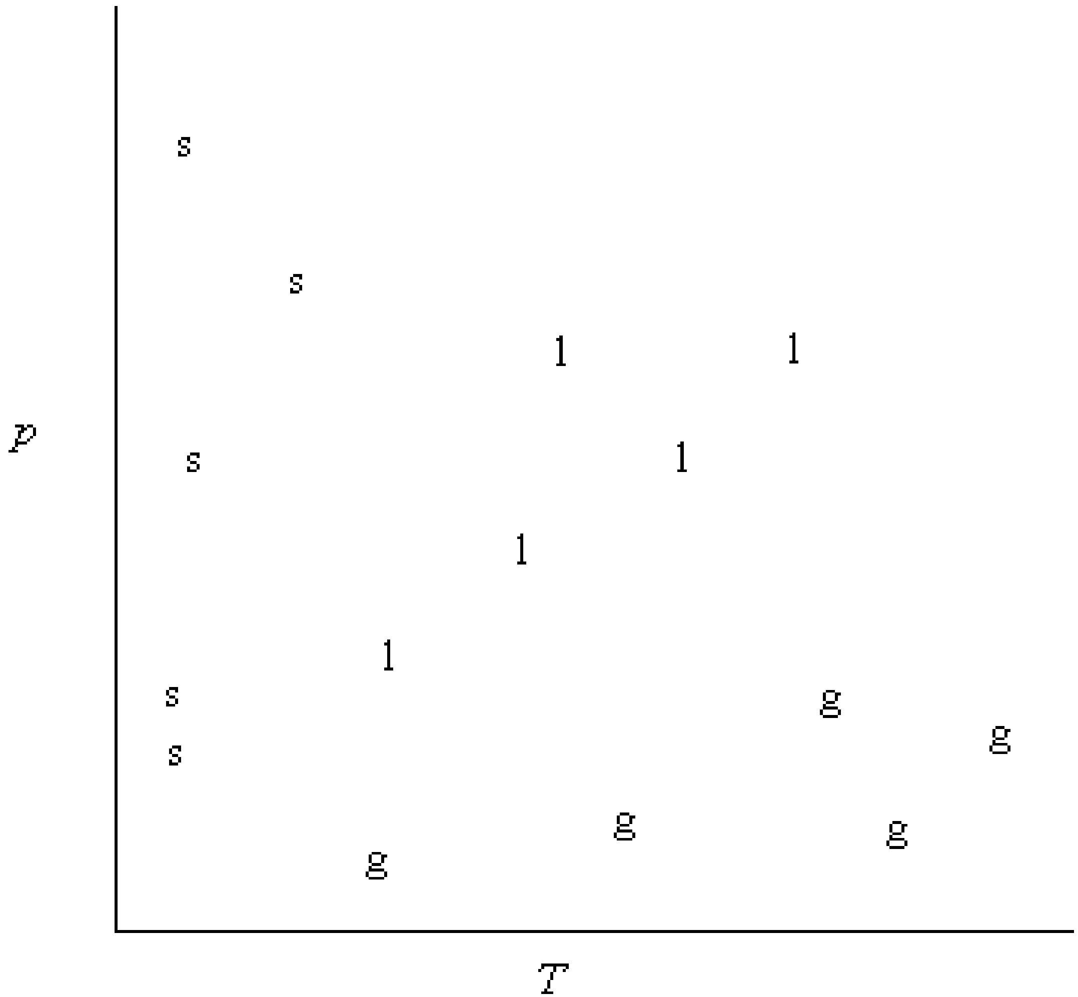
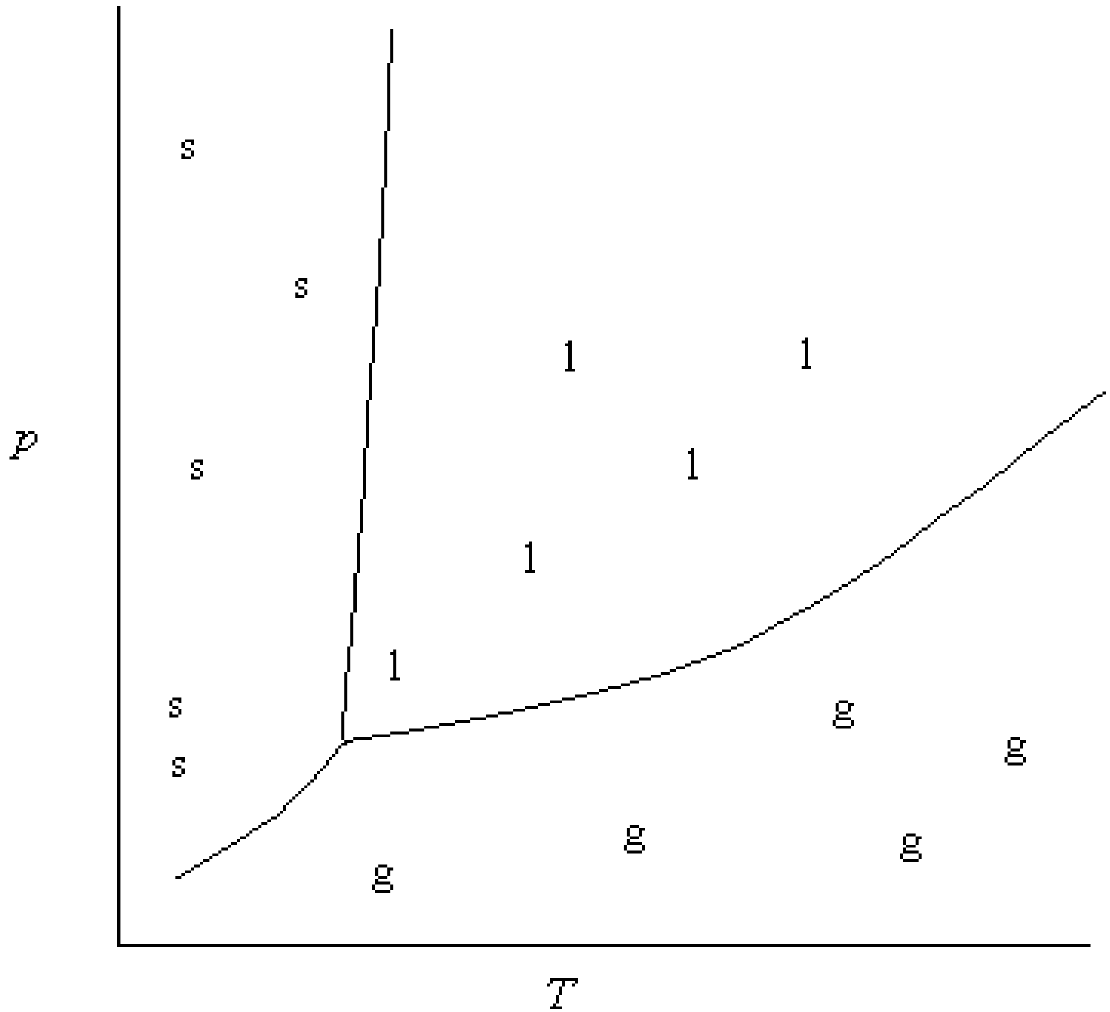
At equilibrium, the chemical potential of a substance in the same throughout a sample, regardless of how many phases are present.

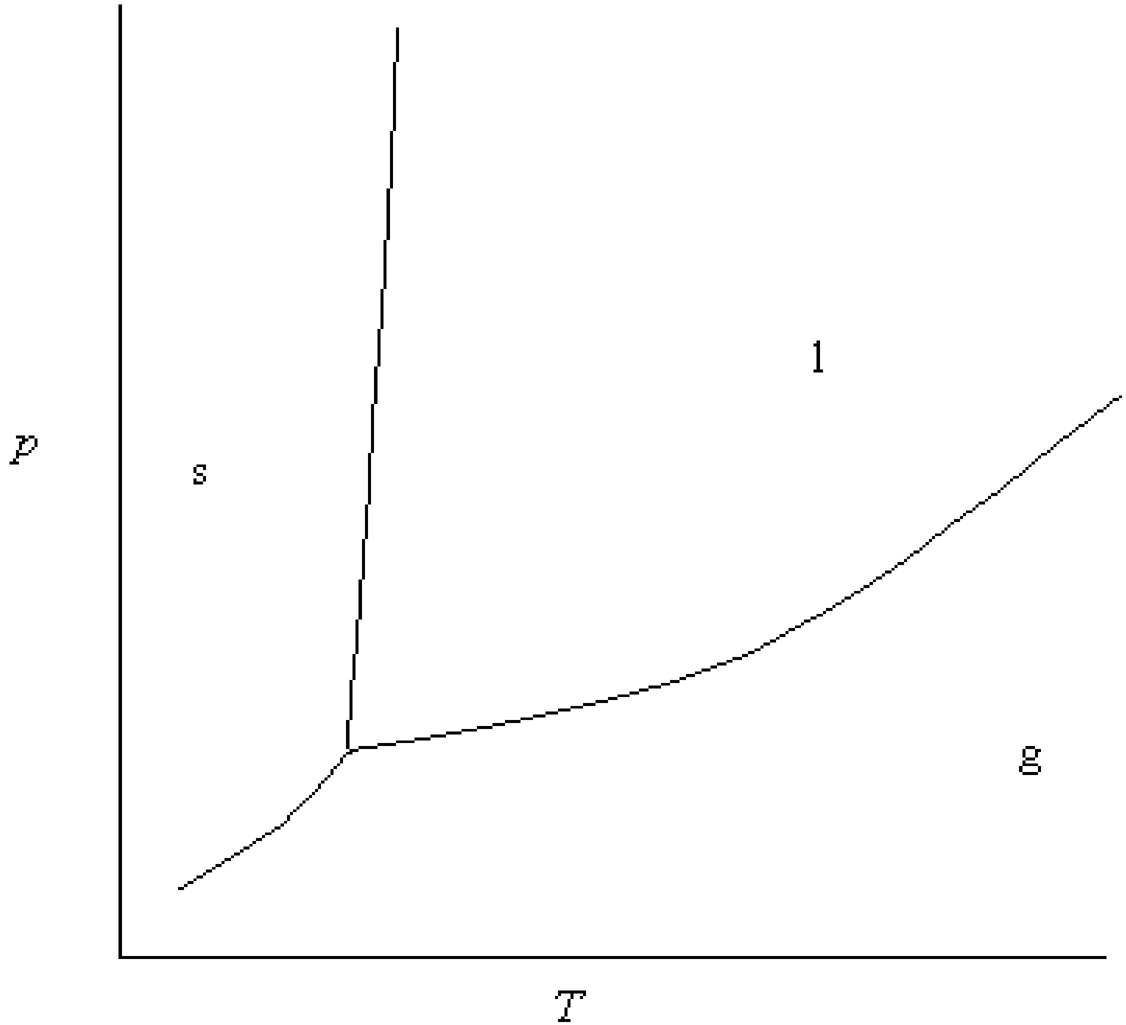
How to construct one-component phase diagrams



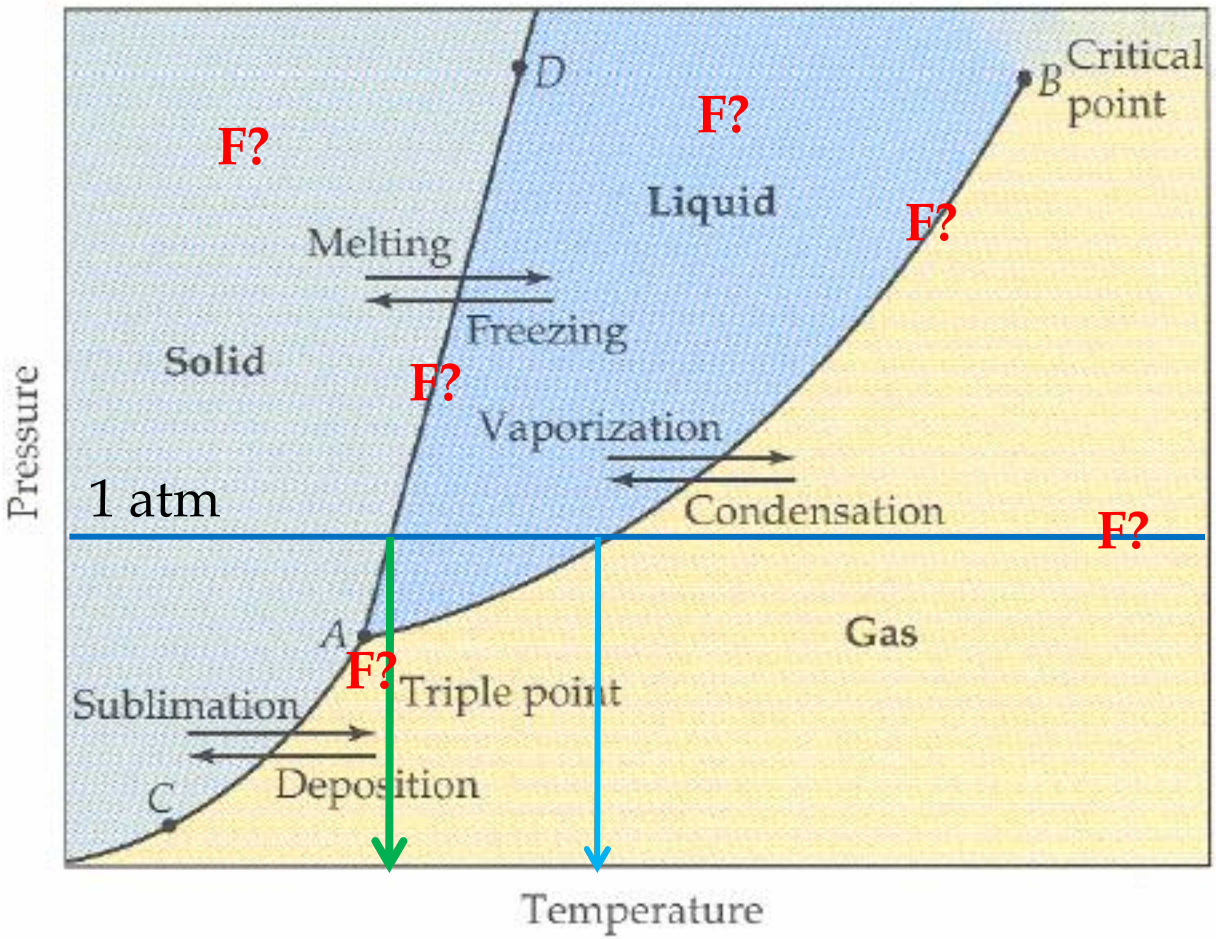
How to construct one-component phase diagrams



How to construct one-component phase diagrams



A typical phase diagram



<u>Phase Rule</u>: $F = C - P + 2$

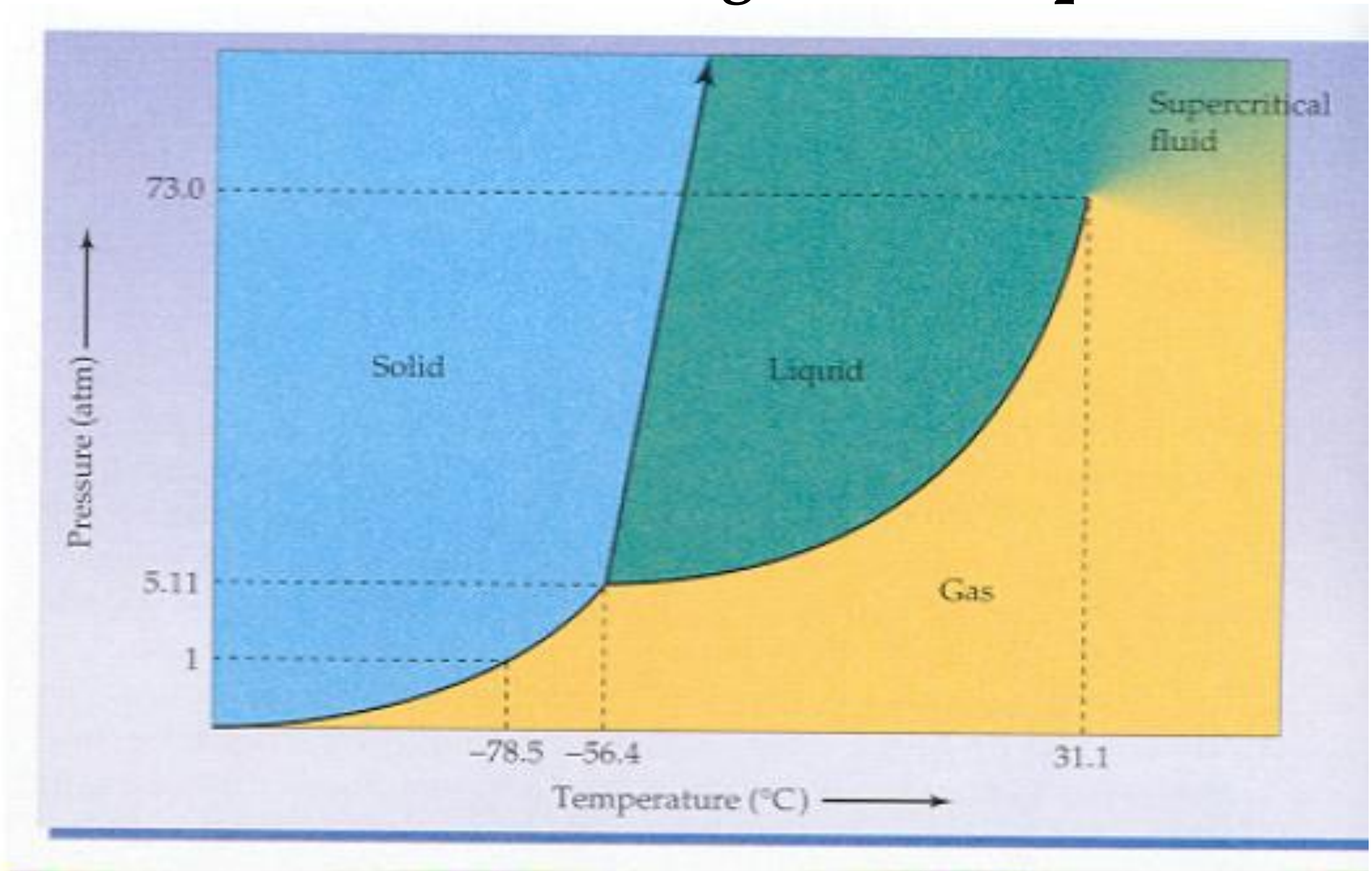
C: # of components

P: # of phases

F: # of parameters that can be varied independently

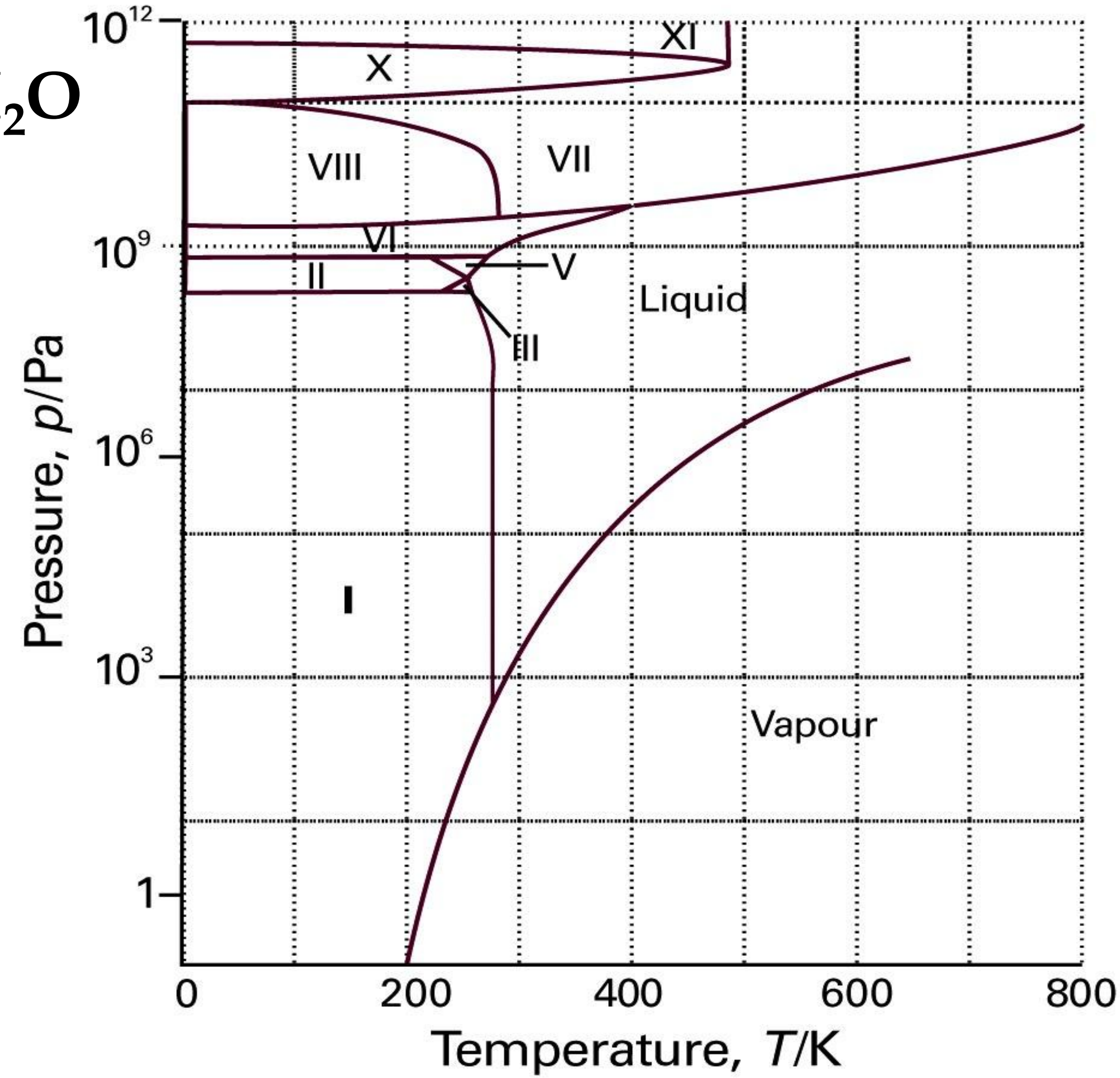
- Thermodynamic stability
- Metastable states
- Phase boundary/Coexistence curves
- Boiling/melting point
- Normal boiling/ normal melting point (1 atm)
- Standard boiling/ standard melting point (1 bar)
- Triple point
- Critical temperature
- Vapor pressure/ Sublimation vapor pressure

Phase Diagram of CO_2



Melting point of solid CO_2 rises with pressure
At normal atmospheric pressure, CO_2 can not be liquefied (dry ice).

Phase Diagram of H_2O



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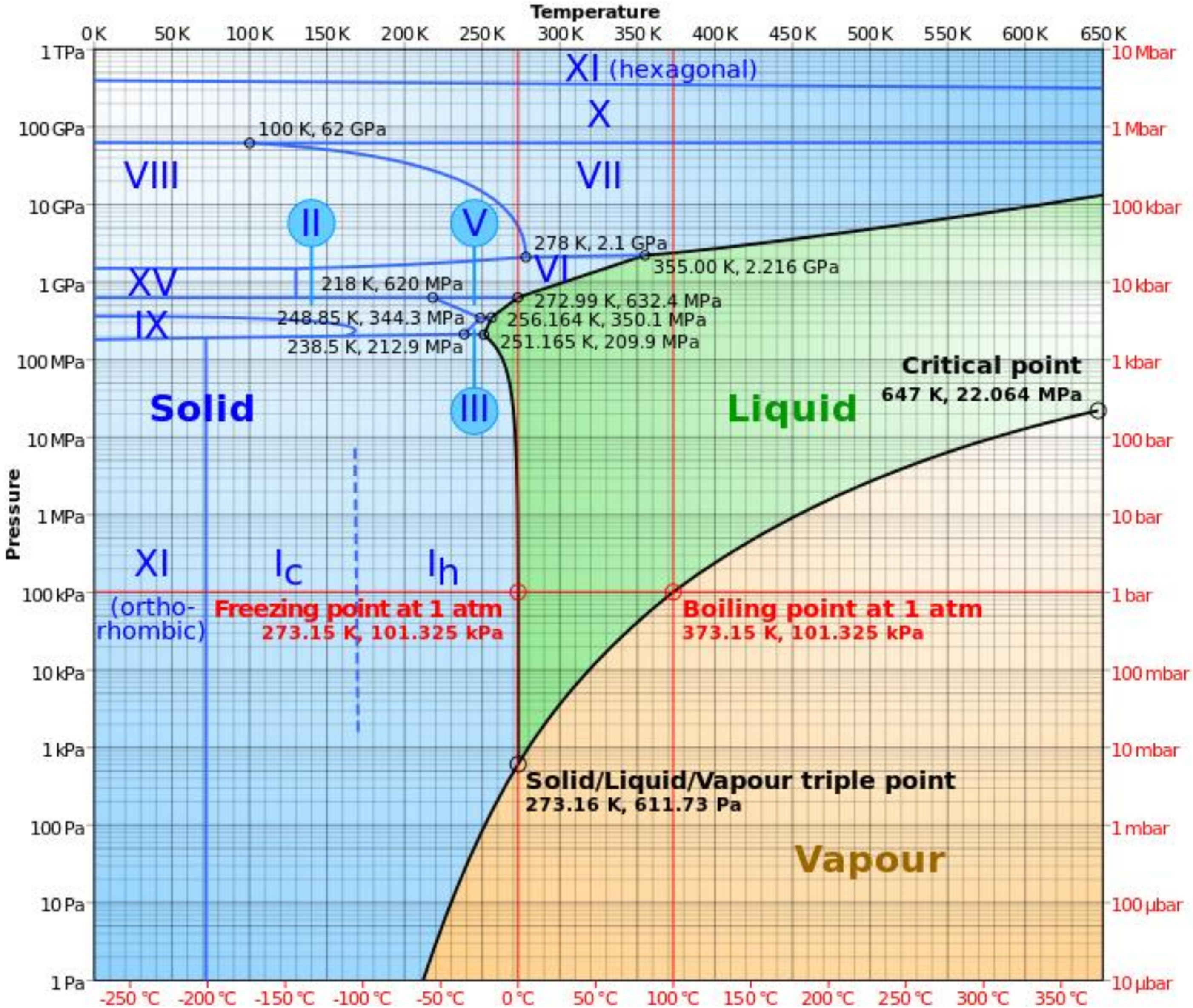
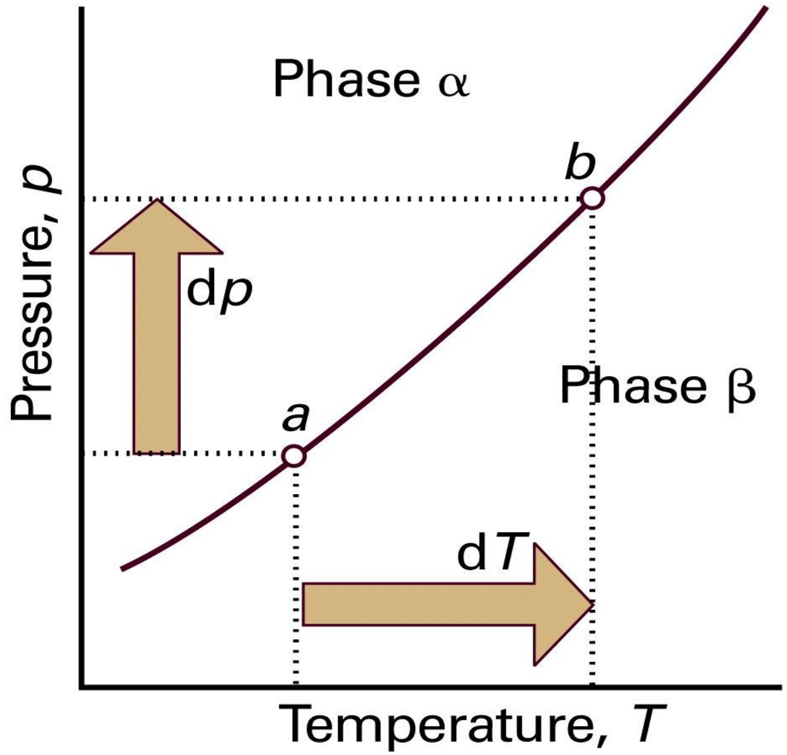
Phase Diagram of H_2O



Location and shape of phase boundary

One component (pure) system



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For point "a"

$$\mu^{\alpha}(p, T) = \mu^{\beta}(p, T)$$

For point "b"

$$\mu^{\alpha}(p+dp, T+dT) = \mu^{\beta}(p+dp, T+dT)$$

$$\mu^{\alpha}(p, T) + d\mu^{\alpha} = \mu^{\beta}(p, T) + d\mu^{\beta}$$

$$d\mu^{\alpha} = d\mu^{\beta}$$

$$\boxed{d\mu = V_m dp - S_m dT}$$

$$V_m^{\alpha} dp - S_m^{\alpha} dT = V_m^{\beta} dp - S_m^{\beta} dT$$

$$dp/dT = (S_m^{\alpha} - S_m^{\beta}) / (V_m^{\alpha} - V_m^{\beta})$$

$$\boxed{dp/dT = \Delta S_{m,\mathrm{trs}} / \Delta V_{m,\mathrm{trs}}}$$

$$\boxed{dp/dT = \Delta S_{\mathrm{trs}} / \Delta V_{\mathrm{trs}}}$$

$$\boxed{\mathbf{dT/dp = \Delta V_{trs} / \Delta S_{trs}}}$$

The Clapeyron Equation
Applies to any phase equilibrium of any pure substance.

(i) Solid to Liquid Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta S_{\mathrm{trs}}}{\Delta V_{\mathrm{trs}}} = \frac{\Delta H_{\mathrm{fus}}}{T_{\mathrm{fus}}\Delta V_{\mathrm{fus}}}$$

If T_1 is melting point at p_1, and T_2 at p_2

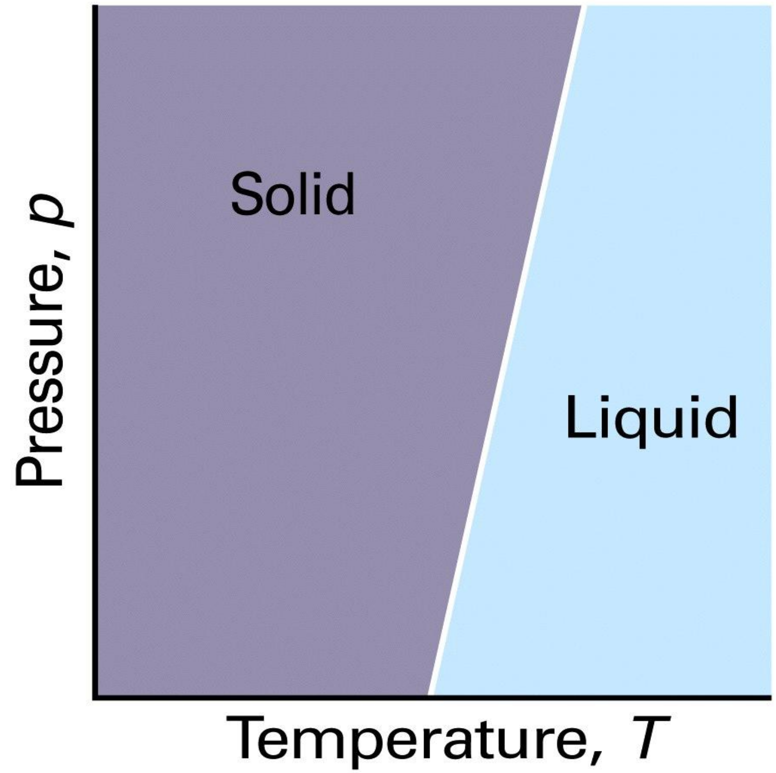
$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{\mathrm{fus}}}{\Delta V_{\mathrm{fus}}} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta p = \frac{\Delta H_{\mathrm{fus}}}{\Delta V_{\mathrm{fus}}} \ln \frac{T_2}{T_1}$$

$$\text{for, } T_2 \approx T_1, \ln\frac{T_2}{T_1} = \ln\left(1 + \frac{T_2 - T_1}{T_1}\right) \approx \frac{T_2 - T_1}{T_1} = \frac{\Delta T}{T_1}$$

$$\Delta p = \frac{\Delta H_{\mathrm{fus}}}{T_1 \Delta V_{\mathrm{fus}}} \Delta T$$

$$\Delta T = \frac{T_1 \Delta V_{\mathrm{fus}}}{\Delta H_{\mathrm{fus}}} \Delta p$$



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Melting point (linearly) rises with pressure