

Phase diagram of one component systems

Narayanan Kurur

Department of Chemistry
IIT Delhi

06 and 07 August 2013

Heating of a liquid at constant pressure

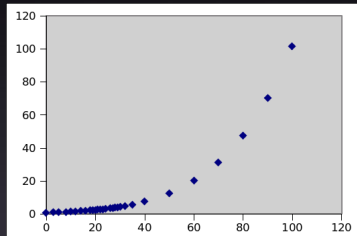
Experimental protocol

- 1 Vessel filled to the brim with a liquid and heated at constant pressure, say P_1 .
- 2 Note temperature as a function of time
- 3 Repeat for different pressure

Observations

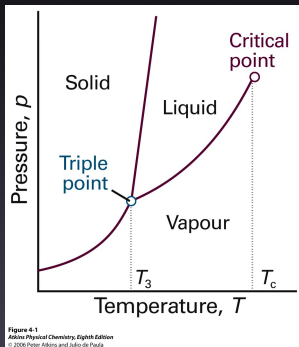
- 1 Temperature rises as heat is provided
- 2 Meniscus forms and T is steady - T_s
- 3 T rises when meniscus disappears
- 4 T_s increases when P increases

Variation of T with P for water



Perform similar experiments for variation of melting point and sublimation temperature with pressure

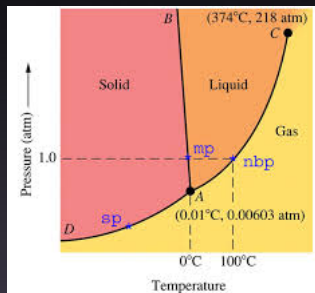
Prototypical Phase diagram



- Regions of stability for s , l , and g - system defined by T and P
- One phase regions separated by a co-existence curve - system defined by either T or P
- l - v coexistence curve ends at the critical point
- Slope of s - l line determined by the densities of s and l
- Triple point when three phases are in equilibrium - invariant pt.

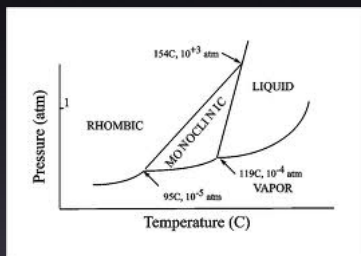
Two examples

Water



Ice is less dense than water so the *s-l* line has a negative slope

Sulfur



More than one solid phase, number of triple points increases

Molar Gibbs energies are equal at equilibrium

- Equilibrium $\alpha \rightleftharpoons \beta$ in a closed system.
- Molar Gibbs energies of the two phases be G_α and G_β .
- $G = n_\alpha G_\alpha + n_\beta G_\beta$, where n_α and n_β are the number of moles of α and β
- $dG = dn_\alpha G_\alpha + dn_\beta G_\beta + n_\alpha dG_\alpha + n_\beta dG_\beta$
- At constant T and P , the condition for equilibrium is $dG = 0$
- For a closed system $dn_\alpha = -dn_\beta$
- $(G_\alpha - G_\beta)dn_\alpha = 0$ or $G_\alpha = G_\beta$

Explaining the coexistence curve

- Phases in equilibrium, $G_\alpha = G_\beta$ at T, P .
- Phases in equilibrium at $T + dT, P + dP$, $G_\alpha + dG_\alpha = G_\beta + dG_\beta$
- $dG_\alpha = V_\alpha dP - S_\alpha dT$ and $dG_\beta = V_\beta dP - S_\beta dT$
- $V_\alpha dP - S_\alpha dT = V_\beta dP - S_\beta dT$
- $\frac{dP}{dT} = \frac{S_\beta - S_\alpha}{V_\beta - V_\alpha} = \frac{\Delta H}{T\Delta V}$

This is called the Clausius equation.

Various approximations to integrate the Clapeyron equation

0th-level approximation: $\frac{\Delta H}{T\Delta V}$ taken to be constant

1st-level approximation: $\frac{\Delta H}{\Delta V}$ taken to be constant

Further improvement: $\int dP = \int \frac{\Delta H(T)}{T\Delta V(T)} dT$

Clapeyron equation for $s \rightarrow g$ or $l \rightarrow g$

For the $s \rightarrow g$ or $l \rightarrow g$, $\Delta V \approx V_g$. Replace $V_g = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta H P}{RT^2}$$

$$\ln \frac{P}{P_i} = \int \frac{\Delta H(T)}{RT^2} dT$$

Often $\Delta H(T)$ taken to have the form $\Delta H_i + C_P T$

What to read?

Sections 4.1, 4.2, 4.3, 4.4, 4.5, and 4.6 of Atkins (section numbers from the 8e)

OR

Sections 23-1, 23-2, 23-3, and 23-4 of McQuarrie and Simon