

LECTURE

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CY11001
Spring 2018

Clapeyron & Clausius Clapeyron Equations

Variation of Chemical Potential with T and p



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(ii) Liquid to Vapor Phase Boundary $\frac{dp}{dT} = \frac{\Delta S_{\text{trs}}}{\Delta V_{\text{trs}}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}} \Delta V_{\text{vap}}}$

$$\Delta V_{\text{vap}} = V_m(\text{g}) - V_m(\text{l}) \cong V_m(\text{g}) = RT/p \quad (\text{for ideal gas})$$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{TV_m} = \frac{\Delta H_{\text{vap}}}{T(RT)/p} \quad (\text{for ideal gas})$$

$$\frac{dp}{p} \frac{1}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

$$\boxed{\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}}$$

Clausius -Clapeyron Equation

$$\int_{\ln p_1}^{\ln p_2} d \ln p = \frac{\Delta H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\boxed{\ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$p_2 = p_1 \exp(-\xi), \xi = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

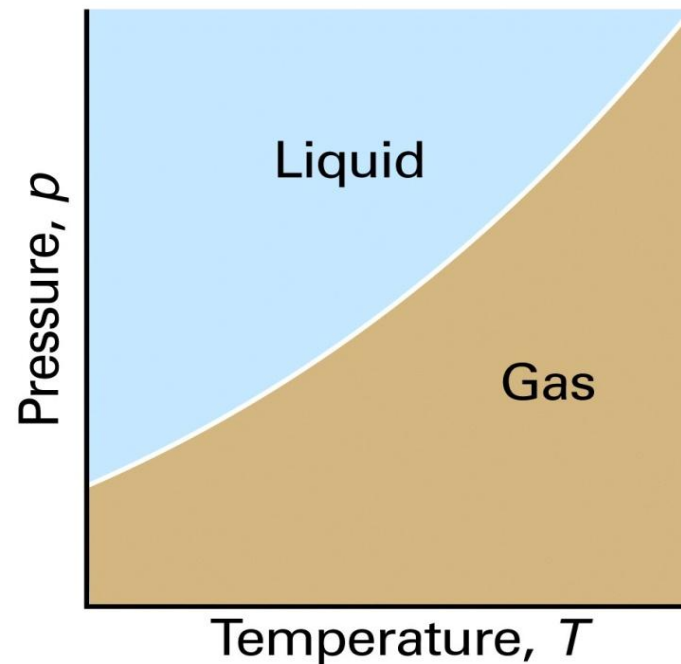


Figure 4-14
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(iii) Solid to Vapor Phase Boundary $\frac{dp}{dT} = \frac{\Delta S_{\text{trs}}}{\Delta V_{\text{trs}}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}} \Delta V_{\text{sub}}}$

$$\Delta V_{\text{sub}} = V_m(\text{g}) - V_m(\text{s}) \cong V_m(\text{g}) = RT/p \quad (\text{for ideal gas})$$

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2}$$

$$\ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$p_2 = p_1 \exp(-\xi),$$

$$\begin{aligned} \xi &= \frac{\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= \frac{\Delta H_{\text{fus}} + \Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

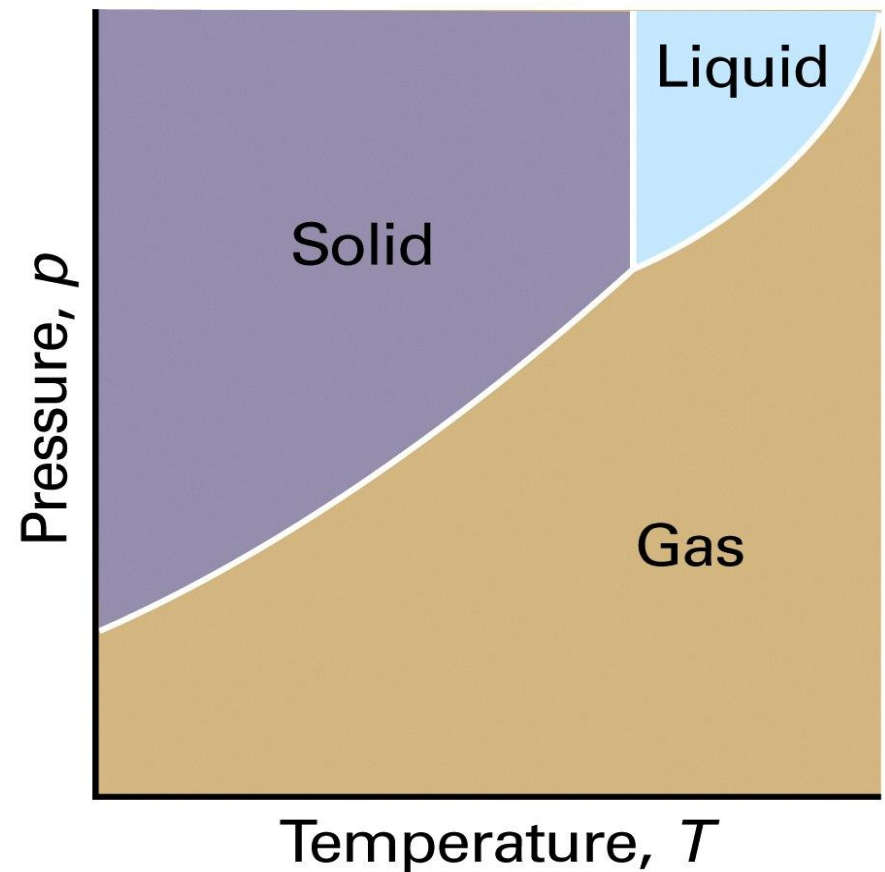


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Location and shape of phase boundary

One component (pure) system

Clapeyron Equation

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

Solid to Liquid Phase Boundary

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

Liquid to Vapor Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{TV_m} = \frac{\Delta H_{\text{vap}}}{T(RT)/p}$$

Clausius -Clapeyron Equation

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

For Solid to Vapor

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2} = \frac{\Delta H_{\text{fus}} + \Delta H_{\text{vap}}}{RT^2}$$

Temperature Dependence of Chemical Potential:

$$dG = Vdp - SdT$$

$$d\mu = V_m dP - S_m dT$$

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -S_m$$

$$S_m(\text{solid}) < S_m(\text{liquid}) \ll S_m(\text{gas})$$

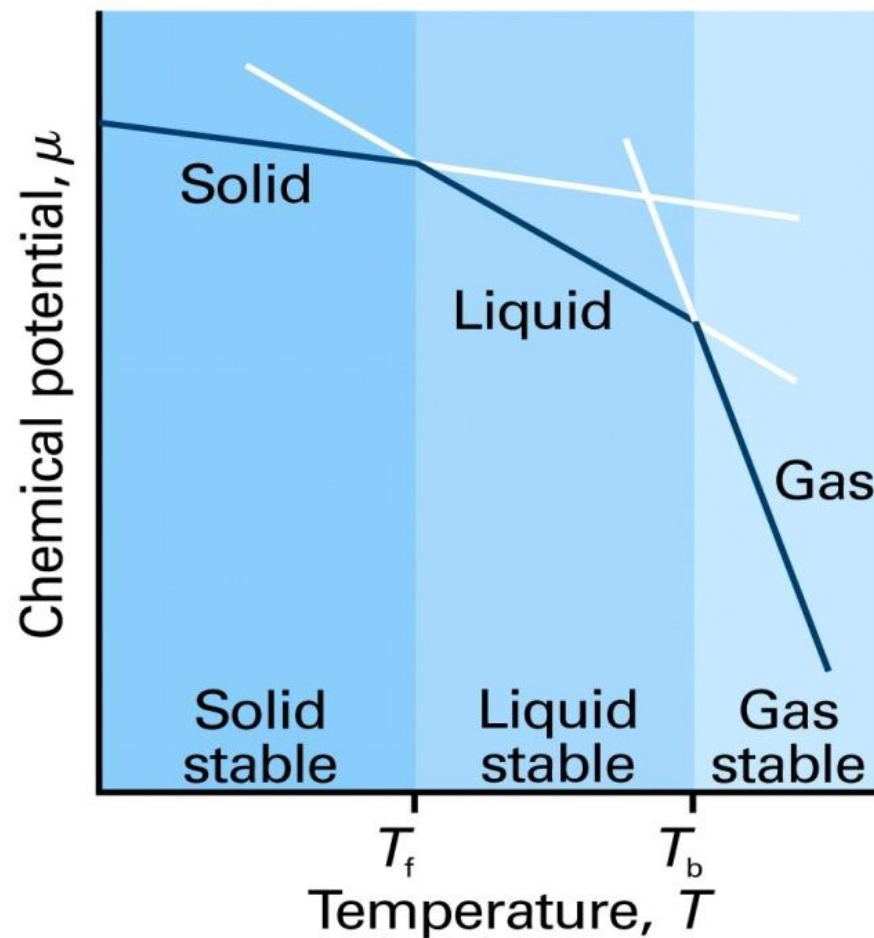


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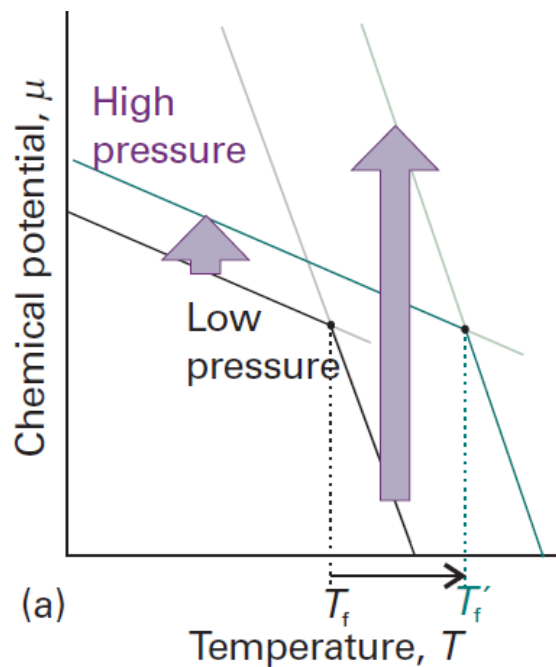
Effect of pressure on Melting/Boiling Point

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V_m$$

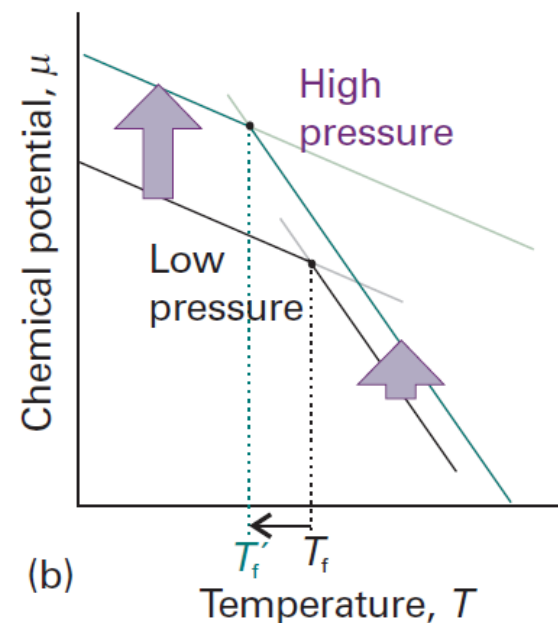
$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$

$$dG = Vdp - SdT$$

$$d\mu = V_m dP - S_m dT$$



Melting point increases
with pressure when
 $V_m(l) > V_m(s)$



Melting point decreases
with pressure when
 $V_m(l) < V_m(s)$

(isothermal) Pressure dependence of Chemical Potential

$$\left(\frac{\partial G}{\partial p} \right)_T = V \qquad \int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp \qquad G_2 = G_1 + \int_{p_1}^{p_2} V dp$$

for one component system, $\mu_2(T) = \mu_1(T) + \int_{p_1}^{p_2} V_m dp$

Case 1: liquid or solid; V weakly dependent on p

$$\mu_2(T) = \mu_1(T) + V_m(p_2 - p_1) \qquad \text{for one component system}$$

Case 2: ideal gas; V is dependent on p ,

$$\mu_2(T) = \mu_1(T) + RT \ln \frac{p_2}{p_1}$$

$$\mu(T) = \mu^\circ(T) + RT \ln \frac{p}{p^\circ}$$

$$\mu(T) = \mu^\circ(T) + RT \ln p$$

μ° = standard chemical potential, the chemical potential of the pure gas at 1 bar at temp T .

p expressed in bar.

The Gibbs Energy of Mixing of Ideal Gases

$$\mu_i(T) = \mu_i^o(T) + RT \ln p_i \quad p_i = \text{partial pressure of } i^{\text{th}} \text{ gas in bar.}$$

Before mixing:

$$G_{\text{before mixing}} = \sum_i n_i \left(\mu_i^o(T) + RT \ln p \right)$$

After mixing:

$$\begin{aligned} G_{\text{mixture}} &= \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^o(T) + RT \ln p_i \right) \\ &= \sum_i n_i \left(\mu_i^o(T) + RT \ln \chi_i p \right) \end{aligned}$$

Dalton's law of partial pressure, $p_i = \chi_i p$

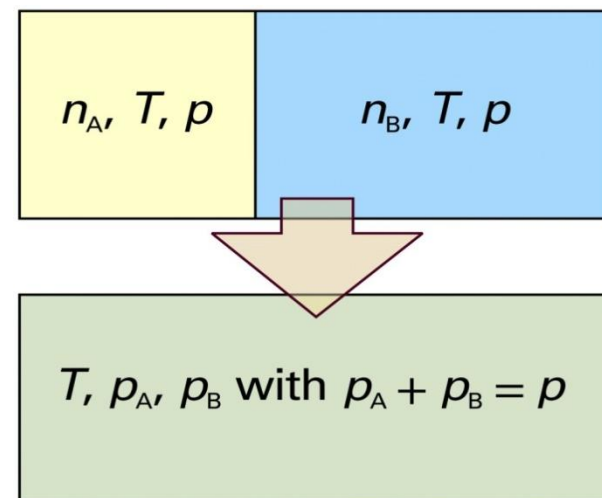


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$$\Delta G_{\text{mix}} = nRT \sum_i \chi_i \ln \chi_i$$

Gibbs free energy of mixing of ideal gases is always negative, and hence spontaneous

The Enthalpy of Mixing of Ideal Gases

$$\Delta G_{mix} = nRT \sum_i \chi_i \ln \chi_i$$

$$\Delta S_{mix} = - \left(\frac{\partial(\Delta G_{mix})}{\partial T} \right)_{p,n} = -nR \sum_i \chi_i \ln \chi_i$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$

Ideal gases show no intermolecular interactions and hence change in enthalpy is zero

