

Thermodynamics: Phenomenology

- Work and other forms of energy
 - Transfer and dissipation
 - 1. & 2. Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
 - Technological applications, cyclic engines
- Real gases equation of state
 - Technological applications
- Phase equilibria
- Free energy in chemical reactions

Reading Assignments

Weeks 13&14

LN V-VI:

Kondepudi Ch. 7 & 9
Additional Material

McQuarrie & Simon
Ch. 7 & 8

Condensed-Phase TD (Pure Liquids & Solids)



EoS of solids and liquids: limited response of volume to pressure and temperature $\rightarrow V = V(p, T)$

Isothermal compressibility

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$

Volume expansion coefficient

$$\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

$$dV = \alpha \cdot V \cdot dT - \kappa_T \cdot V \cdot dp$$

Constant coefficients \rightarrow

$$V(p, T) = V(p_0, T_0) \cdot e^{\alpha(T-T_0)} \cdot e^{-\kappa_T(p-p_0)}$$

$$V(p, T) \approx V(p_0, T_0) [1 + \alpha(T - T_0) - \kappa_T(p - p_0)]$$

Per mol entropy $s(p, T) \approx s_0 + \int_0^T \frac{c_V(T')}{T'} dT'$

Solids: $C_V = 3 \cdot R \cdot F_{Debye}(T) \xrightarrow{T} 3R$

Kondepudi
Ch. 6

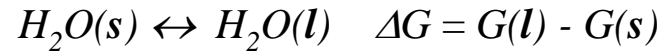
coefficient of thermal expansion α and isothermal compressibility κ_T for some liquids and solids.

Compound	α (10^{-4} K^{-1})	κ_T (10^{-6} atm^{-1})
Water	2.1	49.6
Benzene	12.4	92.1
Mercury	1.8	38.7
Ethanol	11.2	76.8
Carbon tetrachloride	12.4	90.5
Copper	0.501	0.735
Diamond	0.030	0.187
Iron	0.354	0.597
Lead	0.861	2.21

Weak dependence of coefficients on temperature

Phase Domains

Gibbs Free Energy for a Pure Substance



$$G(p, T) = H - TS \quad \text{app. linear in } T$$

$$dG = V \cdot dp - S \cdot dT$$

slope of line: *negative of*

$$|S(\text{gas})| > |S(\text{liquid})| > |S(\text{solid})|$$

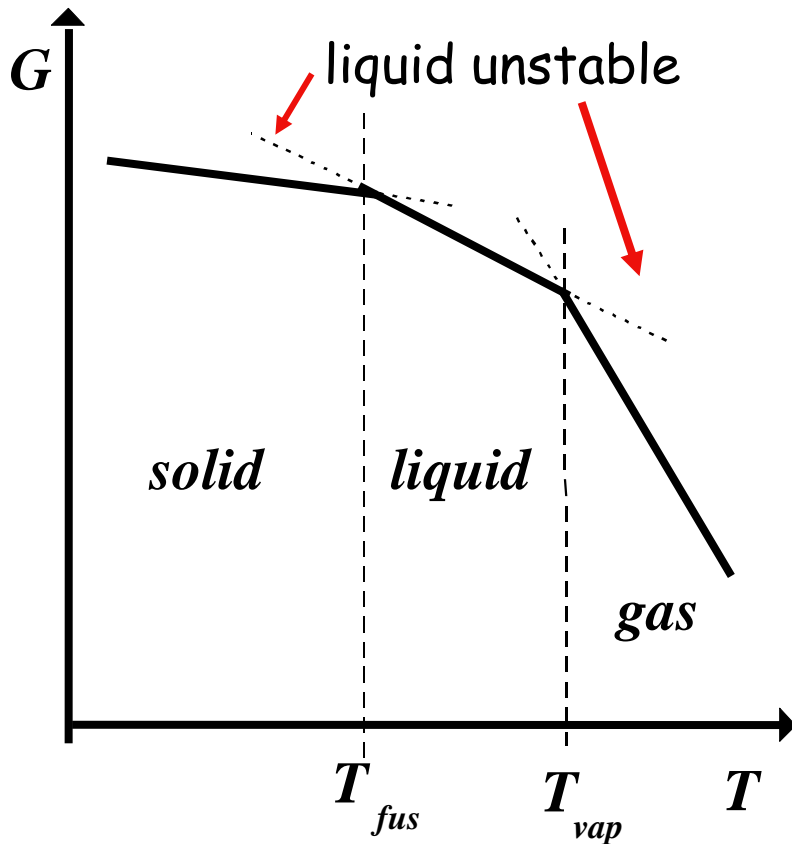
The phase with the lowest free energy is the most stable.

Phase equilibrium at $\Delta G = 0$

At melting and boiling points:

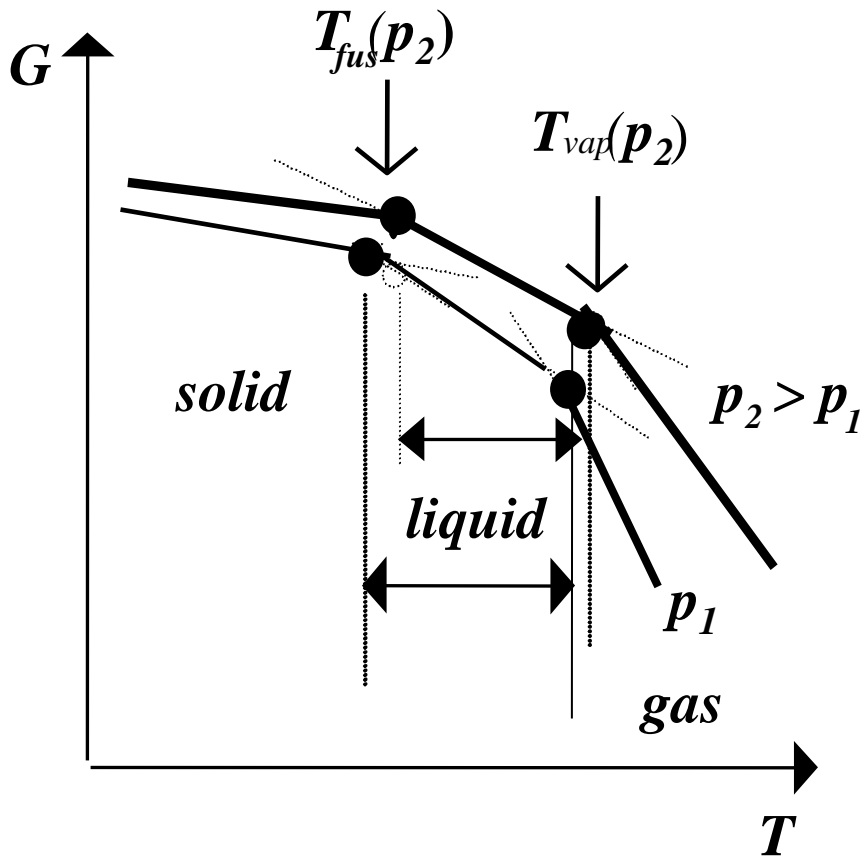
$$\Delta S_{fus} = (\Delta H/T)_{fus} > 0 \quad \Delta G < 0$$

$$\Delta S_{vap} = (\Delta H/T)_{vap} > 0 \quad \Delta G < 0$$



p-Dependence of Phase Domains

p-T Dependence of Gibbs Free Energy



p -dependence of $\Delta G \rightarrow V \cdot dp$
determines sign (increase or decrease)

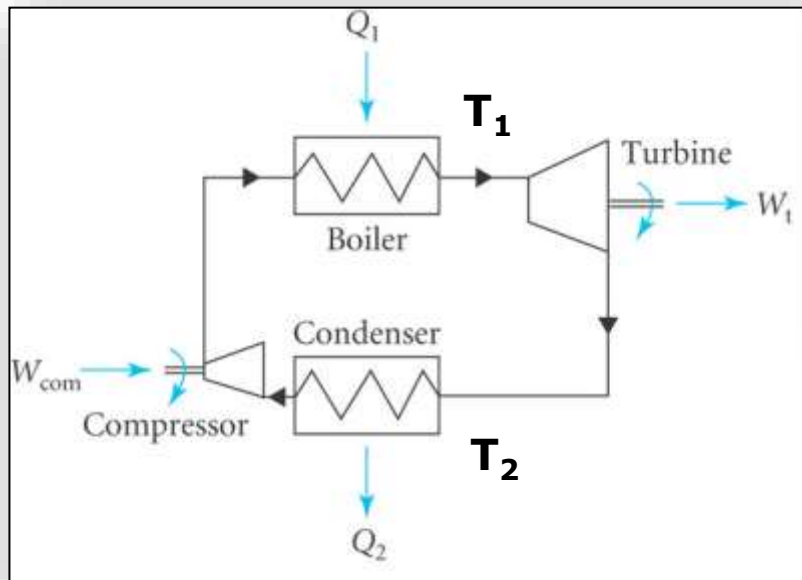
$$V = (\Delta G / \Delta p)_{T=\text{const}}$$

p -dependence strongest for gas phase (largest V).

Increased pressure \rightarrow boiling point T increases, freezing point T increases.

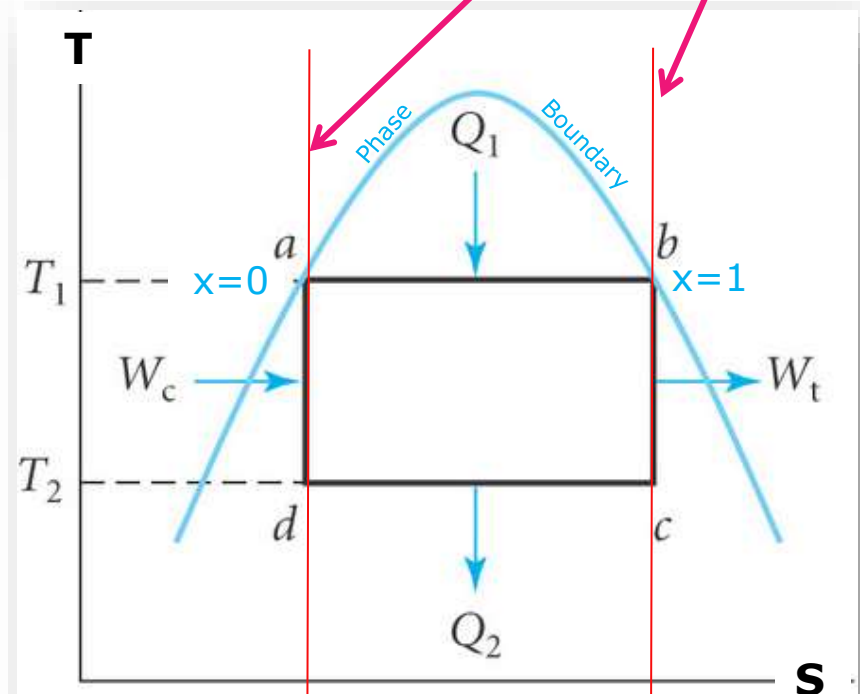
Width of liquid domain shrinks with increasing pressure, vanishes at critical point
 \rightarrow only vapor phase for $T > T_c$.

S-T Diagrams for Steam Carnot Processes



$T(K)$	p (bar)	h (kJ kg ⁻¹)		s (kJ kg ⁻¹ K ⁻¹)	
		h_{fl}	h_{gas}	s_{fl}	s_{gas}
303	0.04	126	2556	0.436	8.452
625	170	1690	2548	3.808	5.181

After Andrews & Jolley



Enthalpy, entropy are extensive.

$x = \text{steam quality (fraction gas)}$

$$h = (1-x) \cdot h_{fl} + x \cdot h_{gas} \quad h = H/\text{unit mass}$$

$$s = (1-x) \cdot s_{fl} + x \cdot s_{gas} \quad s = S/\text{unit mass}$$

$$\text{Example: } s(d) = s(a) = 3.808 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

$$s(d) = (1-x_d) \cdot s_{fl} + x_d \cdot s_{gas} = 3.808$$

$$\quad \quad \quad 0.436 \quad \quad 8.452$$

Solve for $x_d = 0.42$, \rightarrow calculate h_d ,

Phase Equilibria

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Mixture of gas (*vapor*) and liquid

$$\Delta G = G(v) - G(l) \approx 0 \quad \text{Phase difference}$$

Equil: all components have same G .

Different p, T : $p, p = p + dp$ $T, T = T + dT$

$$\begin{aligned} dG(v) &= V(v)dp - S(v)dT = \\ &= V(l)dp - S(l)dT = dG(l) \end{aligned}$$

Clapeyron Equation

$$\frac{dp(T)}{dT} = \frac{S(v) - S(l)}{V(v) - V(l)} = \frac{\Delta S}{\Delta V}$$

$$\frac{dp(T)}{dT} = \frac{\Delta H_{vap}}{T \cdot \Delta V}$$

Boiling point increase:

$$dT(p)/dp = 0.28 \text{ K/kPa} > 0$$

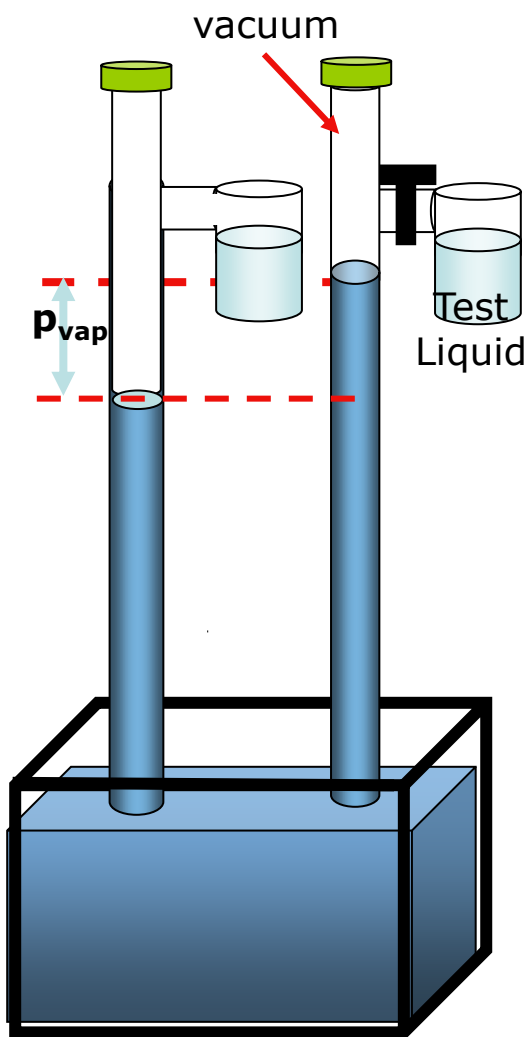
Clapeyron Equation defines p, T dependence of phase equilibrium.
Water:

$$\Delta V_{l \rightarrow v} = [V(v) - V(l)] \approx V(v)$$

$$V(v) = 30.2 \text{ l/mol}$$

$$T_b = 373.1 \text{ K} \quad \Delta H_{vap} = 40.6 \text{ kJ/mol}$$

Measuring and Predicting Vapor Pressures



$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T \cdot \Delta V} \quad \text{with} \quad \Delta V \approx V(v) = \frac{nRT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T \cdot \frac{nRT}{p}} = p \frac{\Delta H_{vap}}{nRT^2} \rightarrow \frac{dp}{pdT} = \frac{\Delta H_{vap}}{nRT^2}$$

Clausius – Clapeyron

$$\frac{d \ln(p)}{d(1/T)} = -\frac{\Delta H_{vap}}{n \cdot R}$$

$$\ln(p(T)) = -\frac{\Delta H_{vap}}{nR} \cdot \frac{1}{T}$$

$$\ln\left(\frac{p(T_2)}{p(T_1)}\right) = -\frac{\Delta H_{vap}}{nR} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example

Normal boiling point of a liquid (T_b): vapor $p = 1 \text{ atm (760 Torr)}$.

Vapor pressure of benzene: $p = 75 \text{ Torr at } T=20^\circ\text{C}$.

Q: What is boiling point of benzene?

Hint: Use Clausius-Clapeyron. Tables: $\Delta H_{\text{vap}} = 30.8 \text{ kJ/mol}$

A: Calculate T_b for benzene, when $p_1 = 75 \text{ Torr at } T_1 = 293^\circ\text{C}$ is known.

$$\begin{aligned}\frac{1}{T_2} &= \frac{1}{T_1} - \ln\left(\frac{p(T_2)}{p(T_1)}\right) \frac{nR}{\Delta H_{\text{vap}}} \\ &= \frac{1}{293\text{K}} - \ln\left(\frac{760\text{Torr}}{75\text{Torr}}\right) \frac{8.3145\text{J / Kmol}}{30.8\text{kJ / mol}} = \frac{1}{359\text{K}}\end{aligned}$$

$$T_2 = 359\text{K (86}^\circ\text{C)}$$

Solutions

Mixture of pure substances, each with different phases,

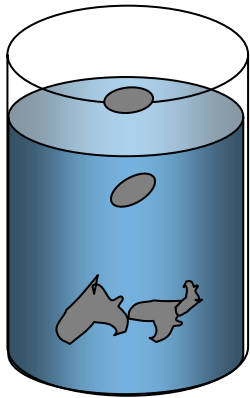
$i = 1, 2, \dots, A$ counts substances and phases, n_i moles

e.g., $i = 1$ (liquid water), $i = 2$ (water vapor),

$i = 3$ (solid NaCl), $i = 4$ (Na^+ aqu), $i = 5$ (Cl^- aqu)

Chemical potential (for substance in a given phase) $p, T = \text{const.}$: $\mu_i = G_i/n_i$

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Total free energy

$$G = n_1 \cdot \mu_1 + \dots + n_A \cdot \mu_A = \sum_{i=1}^A n_i \cdot \mu_i$$

Equilibrium: $G = \text{minimum}$, $\Delta G = 0$

$$\sum_{i=1}^A \mu_i \Delta n_i = \mu_1 \Delta n_1 + \dots + \mu_A \Delta n_A = 0$$

Multi-Component Solution

Free energy of individual component i

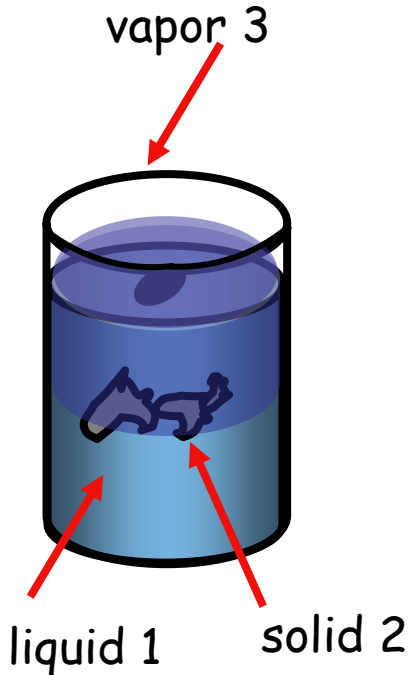
$$\mu_i = \mu_i^0(v) + RT \ln(p_i) \quad i = 1, 2, \dots, A$$

in equilibrium with its own pure liquid i :

$$\mu_i^{pure}(l) = \mu_i(v) = \mu_i^0(v) + RT \ln(p_i^{vap})$$

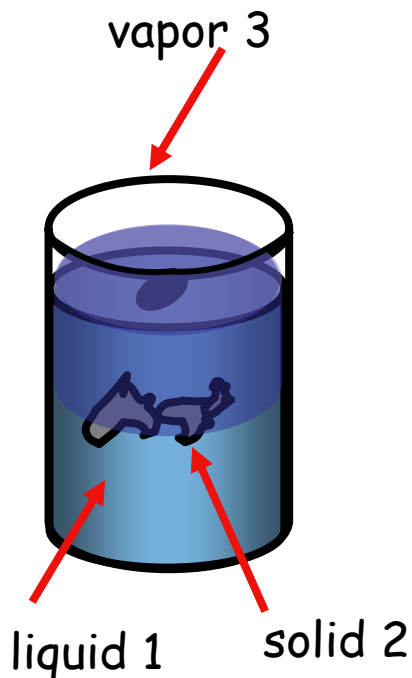
If component i is part of (mix) equil. solution

$$\begin{aligned} \mu_i(sol) &= \mu_i^0(v) + RT \ln(p_i) = \\ &= \left[\mu_i^{pure}(l) - RT \ln(p_i^{vap}) \right] + RT \ln(p_i) \\ &= \mu_i^{pure}(l) + RT \ln\left(p_i / p_i^{vap}\right) \end{aligned}$$



Multi-Component Solution

If substance i ($i = 1, \dots, A$) is part of a solution, then its vapor pressure and chemical potential are different, influenced by other components (they all interact).



$$\mu_i(sol) = \mu_i^{pure}(l) + RT \ln\left(p_i / p_i^{vap}\right)$$

Raoult's Law: vapor pressure of component in solution is reduced by mole fraction:

$$p_i = x_i \cdot p_i^{vap} \quad (\text{plausible})$$

Then:

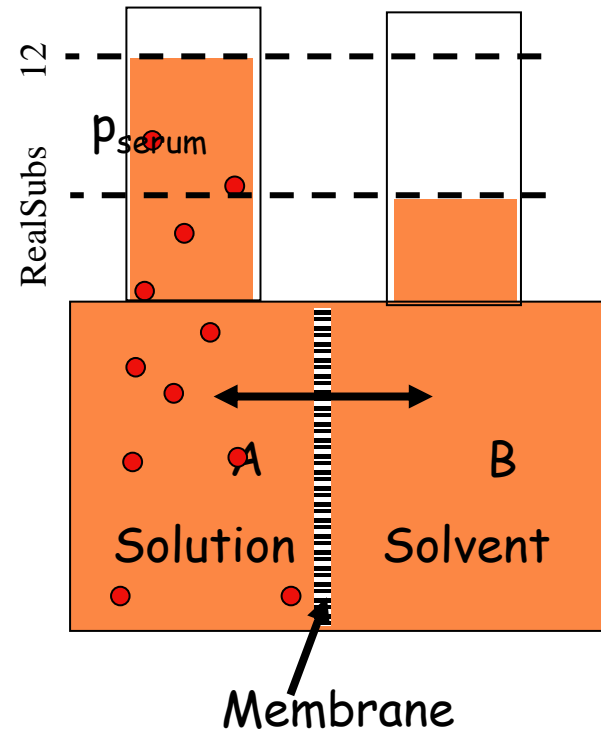
$$\mu_i(sol) = \mu_i^{pure}(l) + RT \ln(x_i)$$

Adding an impurity to a liquid i , lowers x_i and its potential

$$\mu_i(sol) = \mu_i^{pure}(l) + RT \ln(x_i) < \mu_i^{pure}(l)$$

Example: Osmotic Pressure

Volume B containing a pure solvent (e.g. blood serum) is in contact with volume A (cell) containing solvent and solute. Semi-permeable membrane lets solvent pass but not solute.



$$\mu_{serum}(sol) = \mu_{serum}^{pure}(l) + RT \ln(x_{serum})$$

$$\mu_{serum}(sol) < \mu_{serum}^{pure}(l)$$

Since the solution (A) has lower potential, solvent flows spontaneously through the membrane and increases the mole fraction and pressure inside A. Increased pressure/activity prevents such flow:

$$\ln(p_{serum}) = - \left(\frac{\mu_{serum}(sol) - \mu_{serum}^{pure}(l)}{RT} \right)$$

