University of Rhode Island
DigitalCommons@URI

Equilibrium Statistical Physics Physics Open Educational Resources

12-16-2015

05. Thermodynamics of Phase Transitions I

Gerhard Müller
University of Rhode Island, gmuller@uri.edu

Follow this and additional works at: https://digitalcommons.uri.edu/equilibrium_statistical_physics

Abstract

Part five of course materials for Statistical Physics I: PHY525, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.

Recommended Citation

Müller, Gerhard, "05. Thermodynamics of Phase Transitions I" (2015). *Equilibrium Statistical Physics.* Paper 10.
https://digitalcommons.uri.edu/equilibrium_statistical_physics/10

This Course Material is brought to you by the University of Rhode Island. It has been accepted for inclusion in Equilibrium Statistical Physics by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons-group@uri.edu. For permission to reuse copyrighted content, contact the author directly.

Contents of this Document [ttc5]

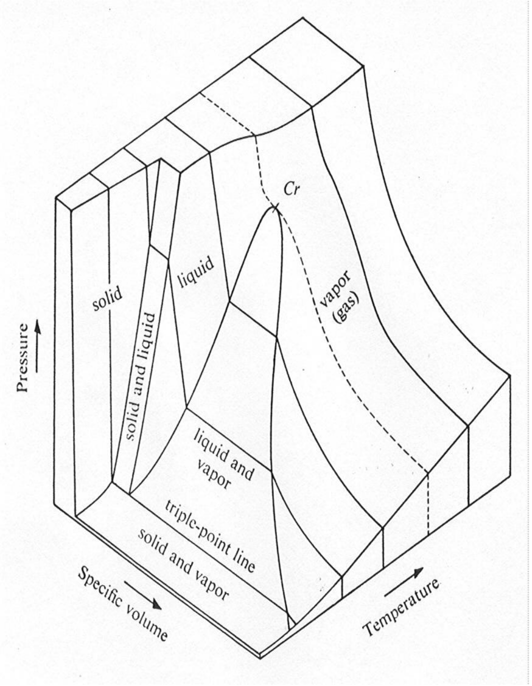
Phase diagram of a “normal” substance [tsl3]

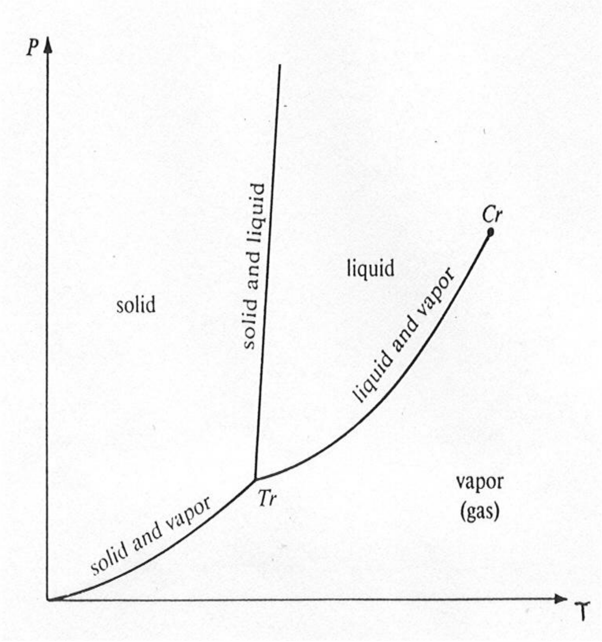
(a) pressure versus volume versus temperature

- 1-phase regions: solid, liquid, gas (vapor)
- 2-phase coexistence regions
- 3-phase coexistence line

(b) projection onto (T, p) plane (intensive variables)

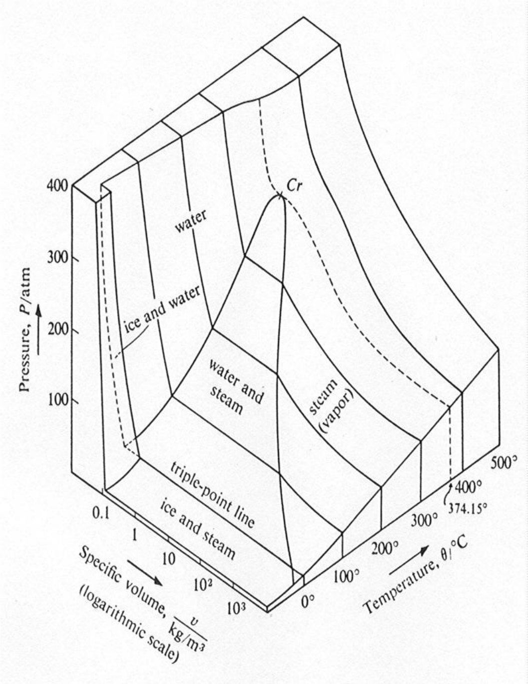
- 2-phase coexistence lines
  - vapor-pressure curve
  - fusion curve
  - sublimation curve
- 3-phase coexistence point
  - triple point

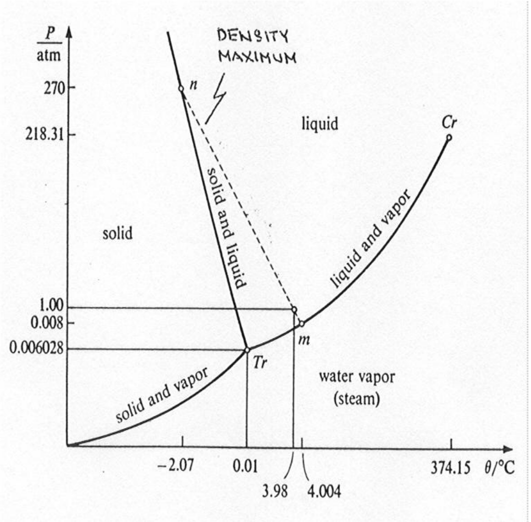




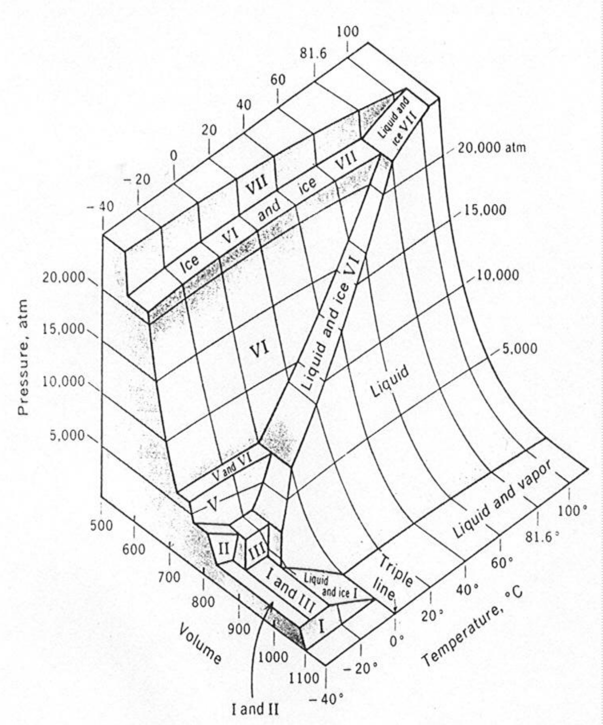
Phase diagram of H_2O [tsl4]

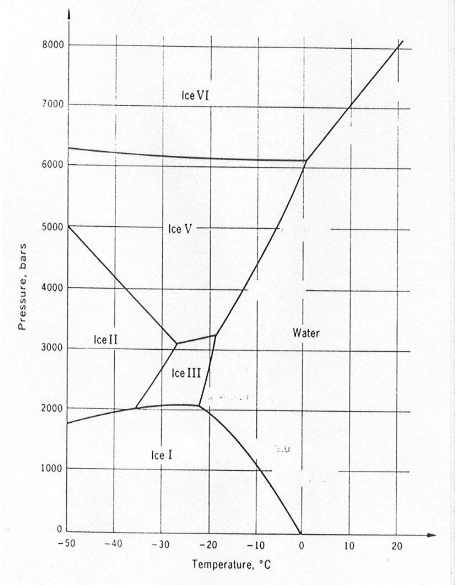
(a) solid – liquid – vapor





(b) solid phases





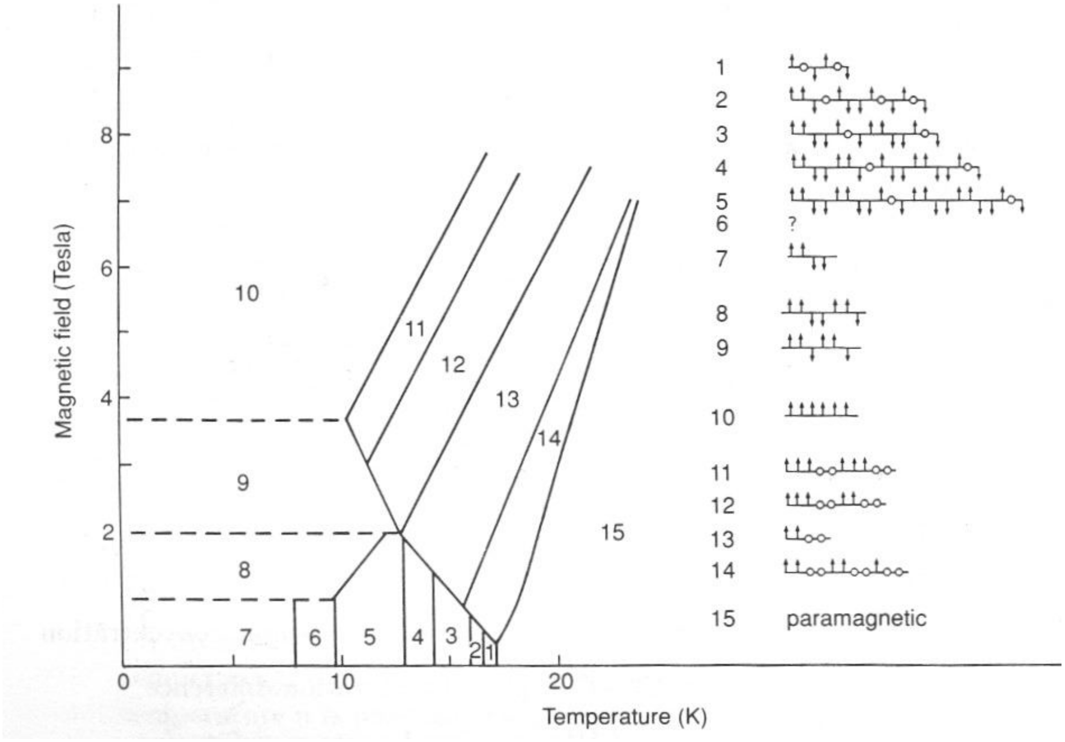
Ferrimagnetic phases of cerium antimonide [tsl49]

Magnetic ordering in phases 1-5, 7-14 is long-ranged and has
- uniform magnetization (↑, ↓),
- no magnetization (∘),

in successive crystalline planes.

Magnetic ordering is short-ranged (paramagnetic) in phase 15.

Magnetic ordering in phase 6 has been unknown at the time.

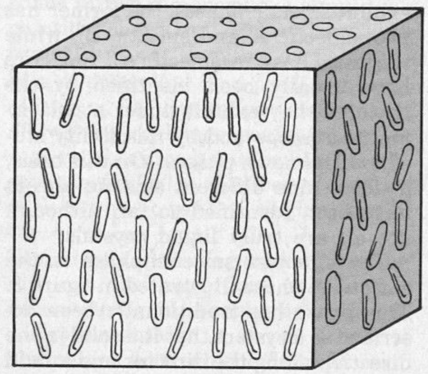


[from Yeomans 1992]

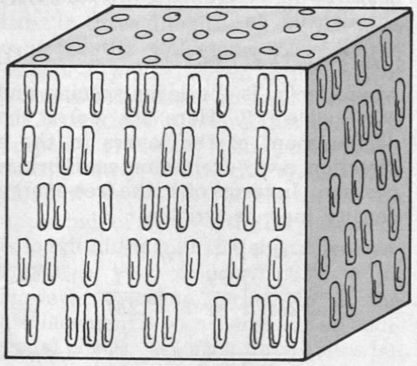
Liquid crystal phases [tsl51]

Most common liquid crystal phases.

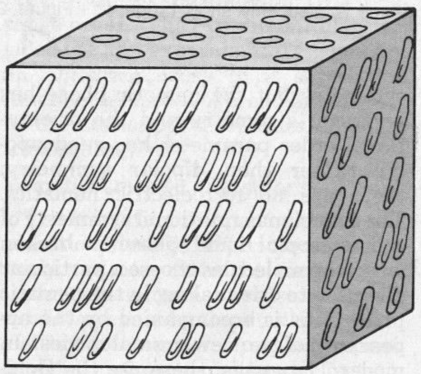
- **Nematic**: Molecular orientational ordering. Continuous rotational symmetry about *director*.
- **Smectic A**: Nematic ordering plus density wave along symmetry axis (director).
- **Smectic C**: Smectic A ordering with broken rotational symmetry. Density wave not perpendicular to director.
- **Smectic B**: Smectic A ordering plus density wave perpendicular to director.



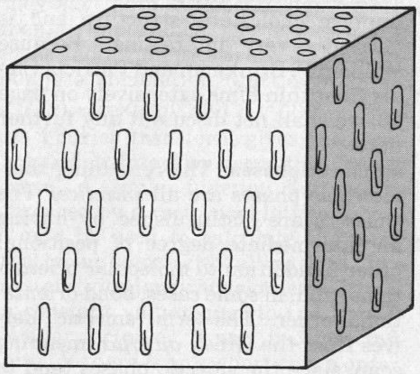
Nematic



Smectic A



Smectic C



Smectic B

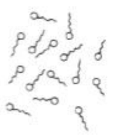
[Physics Today, May 1982]

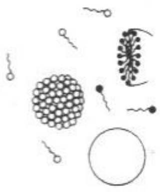
Ordering of surfactant molecules [tsl50]

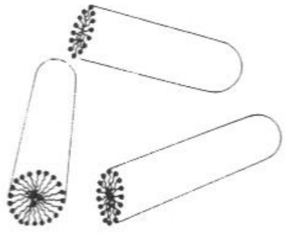
Surfactant molecules have highly soluble polar heads and barely soluble hydrocarbon tails.

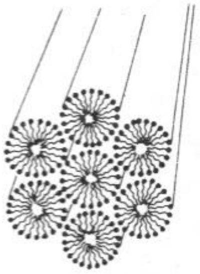
Increasing the surfactant concentration produces a succession of structures.

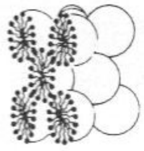
Some structures exhibit short-range order, others exhibit long-range order.

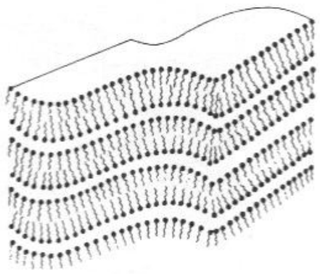

Molecules


Spherical micelles


Cylindrical micelles


Hexagonal phase


Cubic phase


Lamellar phase

[from Yeomans 1992]

Phase coexistence: Gibbs phase rule [tln27]

Consider a K-component fluid system in a state that allows P coexisting phases (a pure pVT system has $K = 1$).

Internal energy: $dU^{(i)} = T^{(i)}dS^{(i)} - p^{(i)}dV^{(i)} + \sum_{\ell=1}^{K} \mu_\ell^{(i)} dN_\ell^{(i)}, \quad i = 1, \ldots, P.$

Each $U^{(i)}$ depends on $K + 2$ extensive variables for a total of $P(K + 2)$.

Conditions of phase coexistence: $[(P - 1)(K + 2)$ relations$]$

- thermal equilibrium: $T^{(1)} = T^{(2)} = \cdots = T^{(P)}$,
- mechanical equilibrium: $p^{(1)} = p^{(2)} = \cdots = p^{(P)}$,
- chemical equilibrium: $\mu_\ell^{(1)} = \mu_\ell^{(2)} = \cdots = \mu_\ell^{(P)}, \ \ell = 1, \ldots, K$.

The number of independent *extensive* variables is independent of P:

$$P(K + 2) - (P - 1)(K + 2) = K + 2.$$

Of this set, P extensive variables, e.g. $V_1, \ldots, V_P$, are necessary to specify the size of all coexisting phases. The remaining independent state variables can be chosen to be *intensive*.

The number of independent intensive state variables required to describe the thermodynamic state of P coexisting phases in a K-component system is

$$F = K + 2 - P \qquad \text{(Gibbs phase rule)}.$$

The maximum number of coexisting phases is $K + 2$, which is realized for $F = 0$. In this case, no intensive variables need to be specified. All are determined by the conditions of phase coexistence.

Example: 1-component fluid ($K = 1$)

- $P = 1$ (one phase): $F = 2$ means that both p and T must be specified to locate the thermodynamic state in the (p, T)-plane.
- $P = 2$ (two phases): $F = 1$ means that only p or T must be specified to locate the thermodynamic state in the (p, T)-plane. The state lies on a coexistence line.
- $P = 3$ (three phases): $F = 0$ means that the coexistence condition determines the values of p and T. The state is located at the triple point in the (p, T)-plane.

Classification of phase transitions [tln28]

Consider a 1-component fluid system with phases I and II.

The Gibbs free energy has a different functional dependence on its natural variables in the two phases:

$$G^I(T,p,n) = \mu^I(T,p)n, \quad G^{II}(T,p,n) = \mu^{II}(T,p)n.$$

For given values of T and p, the equilibrium state is the one with the lowest Gibbs free energy, i.e the state with the lower chemical potential.

At the transition: $G^I = G^{II}$, i.e. $G^* = \mu^*(n^I + n^{II})$ with $n^I + n^{II} = n$.

Discontinuous transition:

The volume and the entropy change discontinuously:

1. $\left(\dfrac{\partial G}{\partial n}\right)^I_{T,p} = \left(\dfrac{\partial G}{\partial n}\right)^{II}_{T,p} \;\Rightarrow\; \mu^I = \mu^{II} = \mu^*.$
2. $\left(\dfrac{\partial G}{\partial p}\right)^I_{T,n} \neq \left(\dfrac{\partial G}{\partial p}\right)^{II}_{T,n} \;\Rightarrow\; V^I \neq V^{II}.$
3. $\left(\dfrac{\partial G}{\partial T}\right)^I_{n,p} \neq \left(\dfrac{\partial G}{\partial T}\right)^{II}_{n,p} \;\Rightarrow\; S^I \neq S^{II}.$

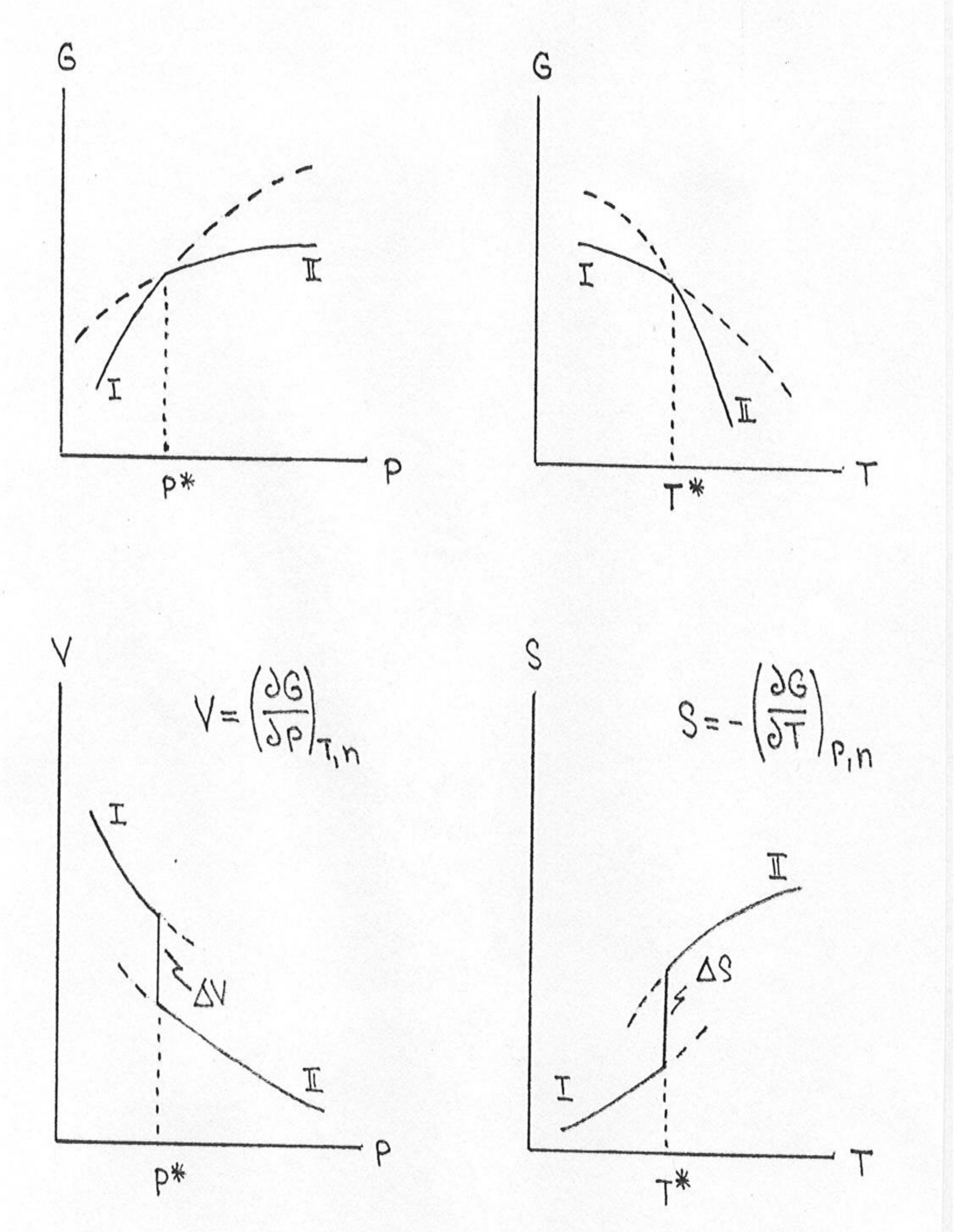
Latent heat (change in enthalpy): $\Delta E = \Delta(G + TS) = T\Delta S$

Continuous transition:

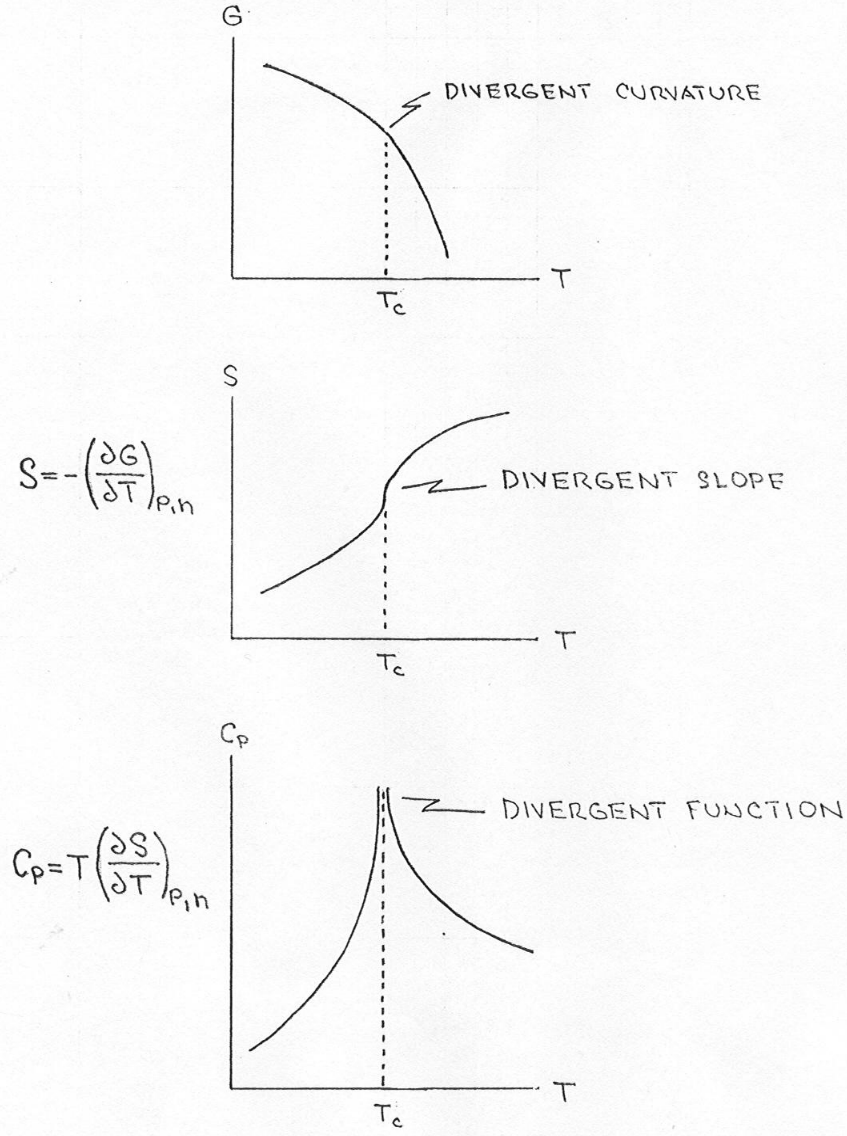
The volume and the entropy change continuously. Discontinuities or divergences occur in higher-order derivatives.

1. $\left(\dfrac{\partial G}{\partial n}\right)^I_{T,p} = \left(\dfrac{\partial G}{\partial n}\right)^{II}_{T,p} \;\Rightarrow\; \mu^I = \mu^{II} = \mu^*.$
2. $\left(\dfrac{\partial G}{\partial p}\right)^I_{T,n} = \left(\dfrac{\partial G}{\partial p}\right)^{II}_{T,n} \;\Rightarrow\; V^I = V^{II}.$
3. $\left(\dfrac{\partial G}{\partial T}\right)^I_{n,p} = \left(\dfrac{\partial G}{\partial T}\right)^{II}_{n,p} \;\Rightarrow\; S^I = S^{II}.$

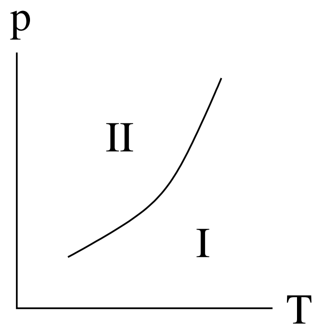
Gibbs free energy and derivatives at discontinuous transition [tsl7]



Gibbs free energy and derivatives at continuous transition [tsl8]



Clausius-Clapeyron equation [tln29]



Consider the variation of the free energy in the two phases I and II along their coexistence line: $dG^I = dG^{II}$.

$$\Rightarrow \; V^I dp - S^I dT = V^{II} dp - S^{II} dT.$$

Slope of the coexistence line:

$$\left(\frac{dp}{dT}\right)_{coex} = \frac{S^I - S^{II}}{V^I - V^{II}} = \frac{\Delta S}{\Delta V} = \frac{\Delta E}{T\Delta V} \quad \text{(Clausius-Clapeyron equation).}$$

Latent heat (change in enthalpy): $\Delta E = T\Delta S$

Fact: $\Delta S > 0$ if $dT > 0$.
Consequence: $(dp/dT)_{coex} > 0$ if $\Delta V > 0$.

The case of H_2O: The substance contracts upon melting. Therefore, the fusion curve has negative slope. The highest melting temperature occurs at the triple point. The density maximum at pressures $0.008\text{atm} \lesssim p \lesssim 270\text{atm}$ occurs inside the liquid phase. Ice under pressure tends to melt, which makes skating possible.

(i) **Vaporization curve** (liquid-gas coexistence line):

The equilibrium pressure is then the saturated vapor pressure $p(T)_{coex}$. It can be derived by integrating the Clausius-Clapeyron equation:

$$\left(\frac{dp}{dT}\right)_{coex} = \frac{\Delta E}{T\Delta V} \simeq \frac{\Delta E}{TV_{vap}} \simeq \frac{p}{nRT^2}\Delta E \;\Rightarrow\; \ln\frac{p}{p_0} = -\frac{\Delta E}{nR}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$\Rightarrow \; p(T)_{coex} = p(T_0)_{coex} \exp\left[-\frac{\Delta E}{nR}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right].$$

(ii) **Fusion curve** (solid-liquid coexistence line):

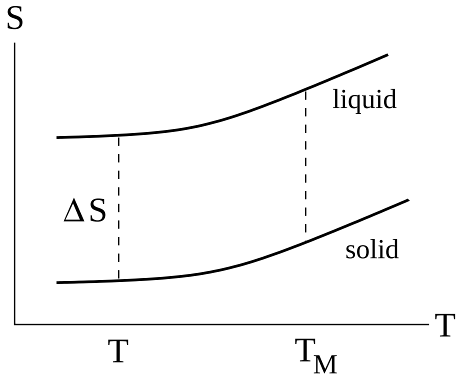
The fusion curve does not terminate in a critical point. The solid and liquid phases have different symmetries.

(iii) **Sublimation curve** (solid-gas coexistence line):

The sublimation curve ends in the triple point.

[tex30] Entropy of supercooled liquid

The heat capacity at constant pressure of a substance is C_{sol} in its solid state and C_{liq} in its liquid state. Both quantities can be treated as constants. When the substance melts (at $T = T_M$) it absorbs the latent heat L. Find the entropy difference $\Delta S = S_{liq} - S_{sol}$ between the supercooled liquid state and the solid state at some temperature $T < T_M$.



Solution:

[tex37] Coexistence line of continuous phase transition

Consider 1 mol of a fluid with two phases 1 and 2 in coexistence. The coexistence line is $p(T)_{coex}$. Suppose that the volume V and the entropy S vary continuously at the transition ($\Delta S = 0$ and $\Delta V = 0$), but the response functions C_p (heat capacity at constant pressure), α_p (thermal expansivity), and κ_T (isothermal compressibility) are discontinuous. Now consider the differentials dS and dV for each phase and for paths in the (T, p)-plane. Then calculate $\Delta S \doteq dS^{(2)} - dS^{(1)}$ and $\Delta V \doteq dV^{(2)} - dV^{(1)}$ between points an infinitesimal distance across the coexistence line
(a) at constant p,
(b) at constant T.
In the limit where the distance between the two points shrinks to zero, the ratio $\Delta S/\Delta V$ stays finite and expresses (via Clausius-Clapeyron) the slope $(dp/dT)_{coex}$ of the coexistence line in terms of the discontinuities, $\Delta C_p, \Delta\alpha_p, \Delta\kappa_T$, in the response functions.
(c) Derive a relation between $\Delta C_p, \Delta\alpha_p, \Delta\kappa_T$ from the consistency condition of the results obtained in parts (a) and (b).

Solution:

[tex124] Latent heat and response functions

Consider a discontinuous transition between phases 1 and 2 of a simple fluid. The latent heat is $L(T)$ and the coexistence curve is $p = p(T)_\text{coex}$.
(a) Show that the rate at which the latent heat changes along the transition curve depends on the heat capacity C_p and the thermal expansivity α_p of the coexisting two phases as follows:

$$\left(\frac{dL}{dT}\right)_\text{coex} = C_p^{(2)} - C_p^{(1)} + L(T)\left[\frac{1}{T} - \frac{V_2\alpha_p^{(2)} - V_1\alpha_p^{(1)}}{V_2 - V_1}\right].$$

(b) Simplify this expression when phase 2 is a classical ideal gas, in which case we have $V_2 \gg V_1$, $\alpha_p^{(2)} \gg \alpha_p^{(1)}$, and an explicit result for the T-dependence of $\alpha_p^{(2)}$.

Solution:

[tex41] Heat capacity of vapor in equilibrium with liquid phase

Consider 1 mol of a simple fluid. Use $V_{gas} \gg V_{liq}$, $pV_{gas} = RT$. The heat capacities in the gas and liquid phases are $C_p^{(gas)}$ and $C_p^{(liq)}$, respectively. The latent heat of vaporization is $L(T)$.
(a) Show that the heat capacity $C_{coex} \doteq T(dS/dT)_{coex}$ of vapor for a process along which the vapor is maintained in equilibrium with the liquid phase can be expressed in the following two alternative ways:

$$C_{coex} = C_p^{(gas)} - \frac{L}{T} = C_p^{(liq)} + T\frac{d}{dT}\left(\frac{L}{T}\right).$$

Use the result of [tex124] to derive the second expression.

Solution:

[tex123] Discontinuous transition: change in internal energy

Consider a discontinuous transition in a simple fluid system. The latent heat is $L(T)$ and the coexistence curve is $p = p(T)_{\mathrm{coex}}$. Show that the change in internal energy during the phase transition is

$$\Delta U = L(T)\left[1 - \left(\frac{d\,\ln p(T)_{\mathrm{coex}}}{d\,\ln T}\right)^{-1}\right].$$

Solution:

[tex125] Dry ice

The T-dependence of the vapor pressure of CO_2 below the triple point ($T_t = -56.2°C$) is well represented by the empirical relation

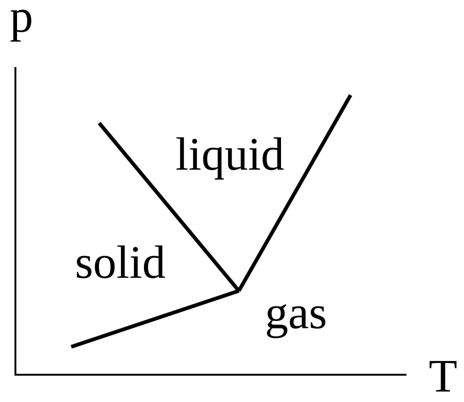
$$\ln\left(\frac{p(T)_{coex}}{1\text{atm}}\right) = 16 - \frac{3116\text{K}}{T}.$$

The molar heat of melting is $L_{sl} = 8330\text{J}$ with negligible T-dependence.
(a) Find the pressure p_t at the triple point.
(b) Find the latent heat of sublimation, L_{sg}, and the latent heat of vaporization, L_{lg}.
(c) Find the vapor pressure $p(T)_{coex}$ at 20°C.

Solution:

[tex54] Abnormal phase behavior

The figure shows the two-phase coexistence lines near the triple point of a hypothetical substance. Under the reasonable assumption that the densities of the liquid and solid phases are similar and much larger than the density of the gas phase, this phase diagram implies a material property that is abnormal under the circumstance described.
Show that in this substance the solid phase near the triple point has a higher entropy than the liquid phase. Melting the substance along a specific path thus releases heat. A somewhat related exotic property is actually observed in ^{3}He (see [tsl14]).



Solution:

[tex51] Melting or freezing?

A vessel with insulating walls of negligible heat capacity contains 7kg of ice at -20°C. Now we pour 2kg of water at $+30^\circ$C into the vessel and seal it.
(a) How much ice (in kg) will remain in the vessel when the system is in thermal equilibrium again?
(b) Find the entropy change that takes place inside the insulated vessel.
Specific heat of ice: $c_s = 2090$J/kgK.
Specific heat of water: $c_l = 4180$J/kgK.
Latent heat of liquid-solid transition: $L = 3.34 \times 10^5$J/kg.

Solution:

[tex52] Triple point phase changes

A vessel with insulating and rigid walls contains 1g of water, 1g of ice, and 1g of H_2O vapor in thermal equilibrium. Now we add the amount $\Delta Q = 251$J of heat to the vessel. Find the amount (in grams) of ice, water, and vapor in the new equilibrium state. The densities of ice and water are taken to be equal and much larger than the density of vapor.
Triple point temperature: $T = 273$K.
Triple point pressure: $p = 611$N/m^2.
Latent heat of fusion: $L_{sl} = 335$J/g.
Latent heat of vaporization: $L_{lg} = 2495$J/g.
Latent heat of sublimation: $L_{sg} = L_{sl} + L_{lg} = 2830$J/g.

Solution:

[tex153] Cooling down? Heating up?

A vessel with insulating walls of negligible heat capacity has two compartments. The first compartment contains 1kg of ice and 1kg of water coexisting at 0°C. The second compartment contains 5kg of ice at -20°C. Now we open the wall between the compartments and wait until thermal equilibrium has been reached. What are the final temperature, the final masses of ice and water, and the change in entropy?
In a modified experiment the first compartment again contains 1kg of ice and 1kg of water coexisting at 0°C but the second compartment contains 5kg of water at $+20^\circ$C. What are the final temperature, the final masses of ice and water, and the change in entropy?
Specific heats of water and ice: $c_w = 4180$J/kgK, $c_i = 2090$J/kgK.
Latent heat of melting: $L_m = 3.34 \times 10^5$J/kg.

Solution:

[tex55] Phase coexistence of ammonia

The vapor pressure curve of solid NH_3 (sublimation curve) is found to satisfy the relation $\ln p = 23.03 - 3754/T$ and the vapor pressure curve of liquid NH_3 the relation $\ln p = 19.49 - 3063/T$, where p is measured in units of mm Hg and T in Kelvin.
Consider $n = 1\text{mol}$ of this substance. Assume that the densities of the solid and liquid phases are much larger than the density of the gas phase. Treat the NH_3 vapor as an ideal gas.
(a) Find the pressure p_0 and the temperature T_0 at the triple point.
(b) Find the latent heat $L_0^{(lg)}$ (in units of Joule) of the liquid-gas transition at the triple point.
(c) If the latent heat of the solid-gas transition (at the triple point) is $L_0^{(sg)} = 3.143 \times 10^4\text{J}$ what is the latent heat $L_0^{(sl)}$ of the solid-liquid transition?

Solution: