Isotherms of liquid-gas phase transition

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

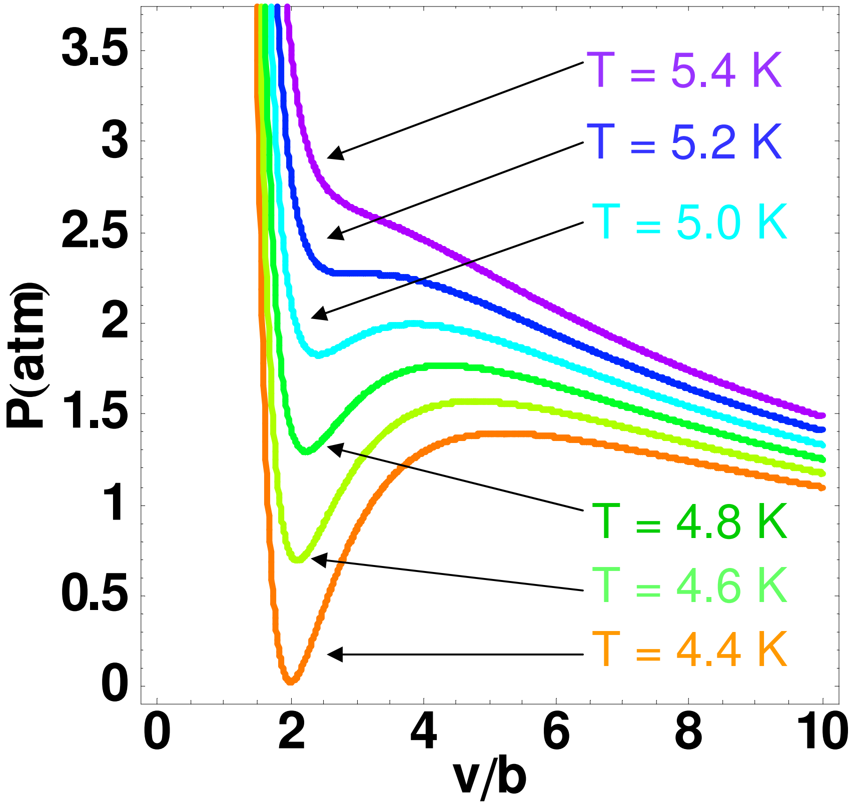
Let us plot P vs v at fixed T for vdW fluid:

For concreteness, we will use a vdW fluid approximating He.

Note that the isotherms with T < 5 K do not satisfy a stability criterion:

$$\kappa_T > 0$$

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T > 0 \quad \Rightarrow \quad \left(\frac{\partial P}{\partial v}\right)_T < 0$$



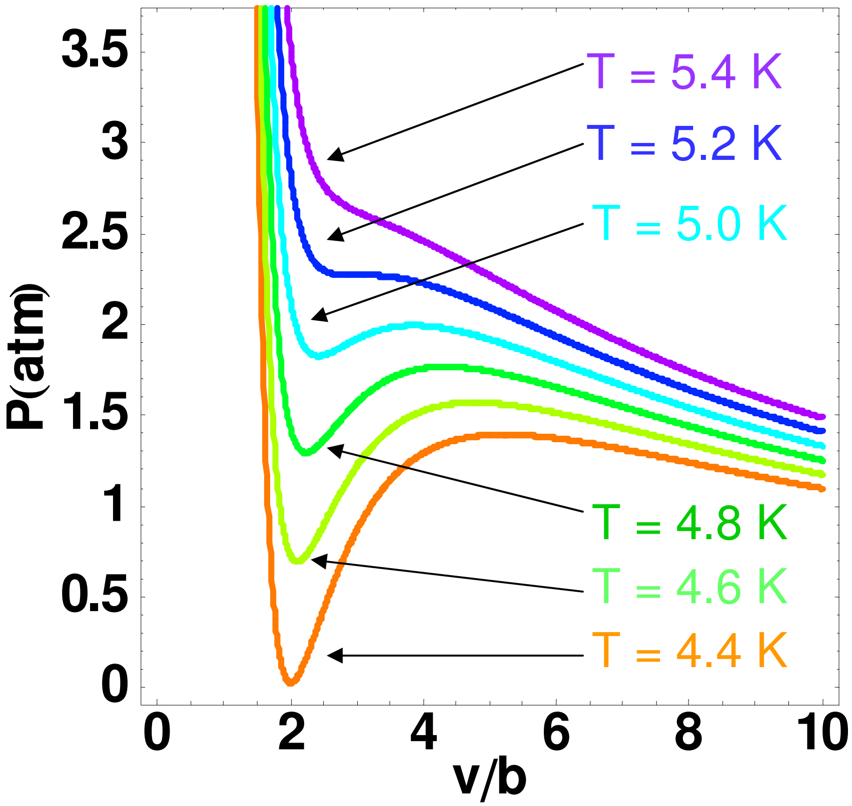
Notes

Isotherms of liquid-gas phase transition

The unstable portion of the isotherm is unphysical and thus the isotherm has to be modified to describe the equilibrium state of the system.

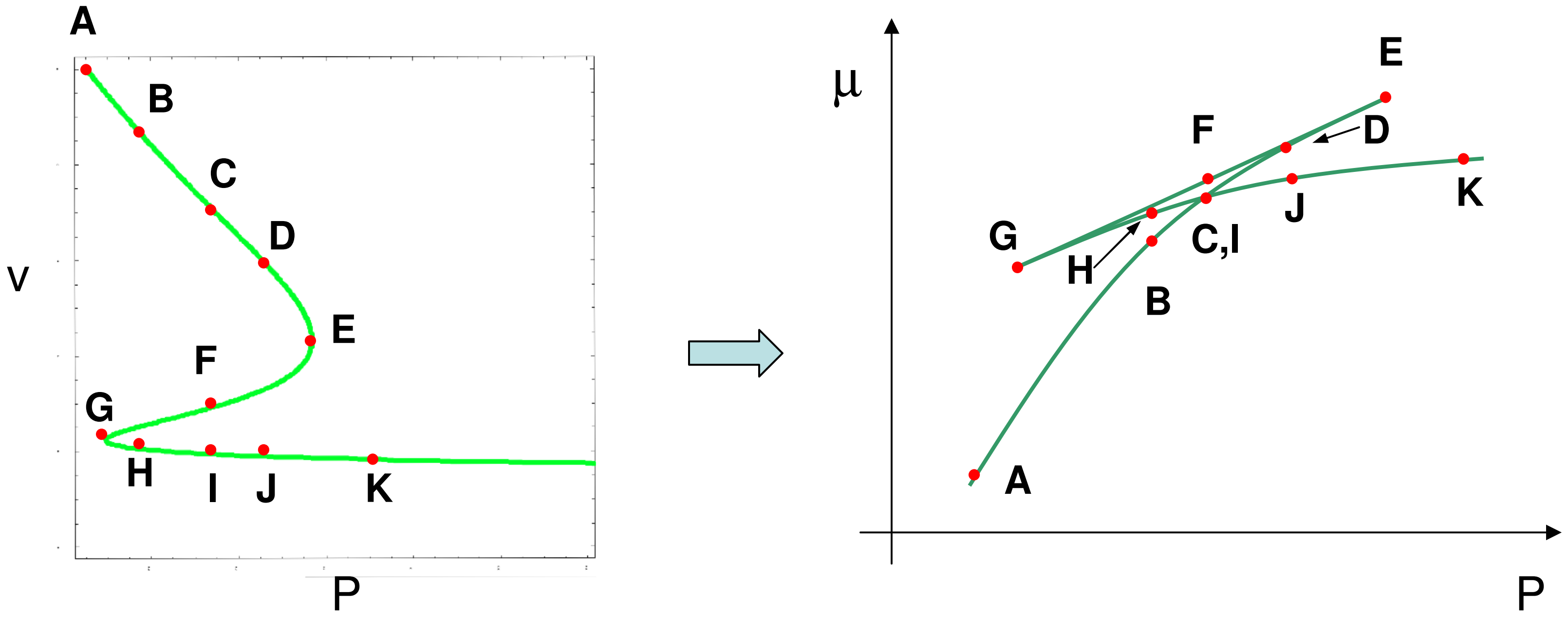
Let us calculate the molar Gibbs potential (chemical potential) using the unstable isotherm and the Gibbs-Duhem relation:

$$d\mu = -sdT + vdP$$



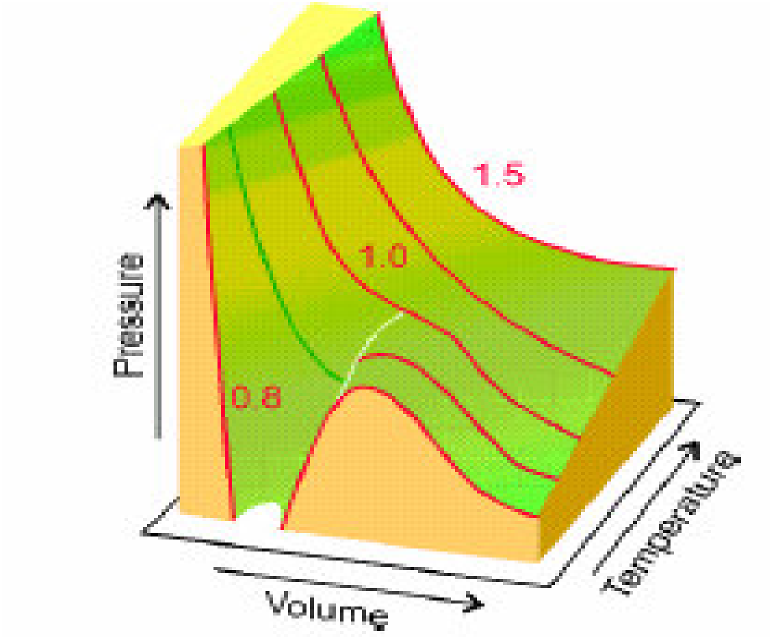
Notes

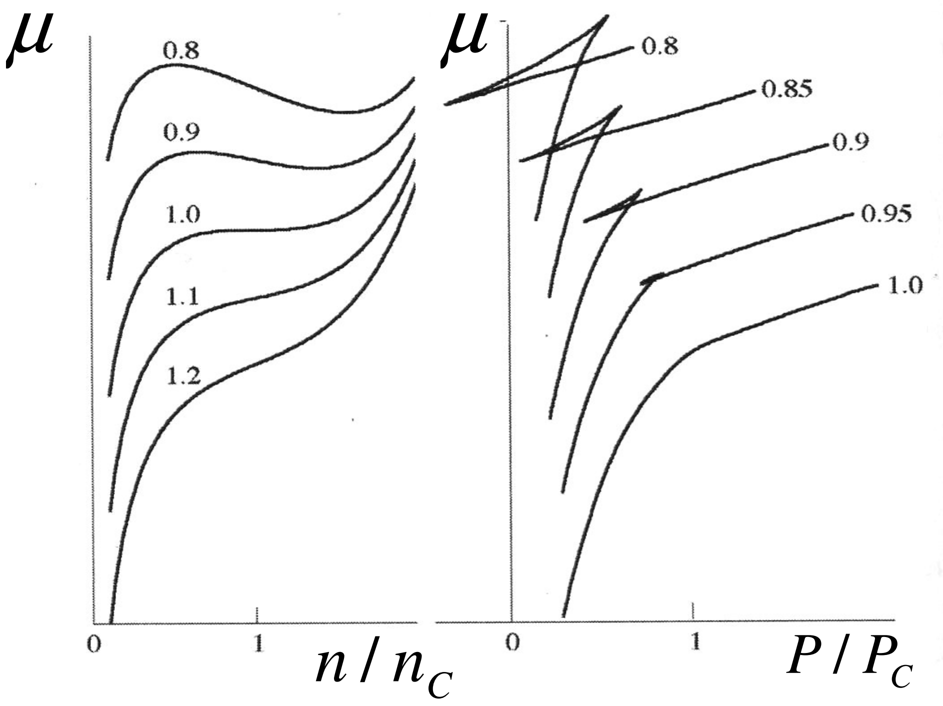
Isotherms of liquid-gas phase transition



Since the Gibbs energy should be at minimum in equilibrium, all equilibrium states should lie on the curve A-B-(C,I)-J-K. Also note that transition between the points C and I should take place at constant pressure and chemical potential!

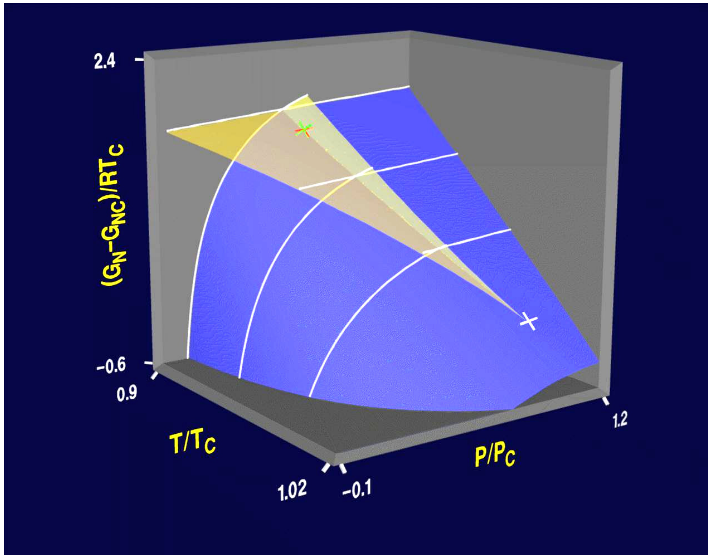
Isotherms of liquid-gas phase transition



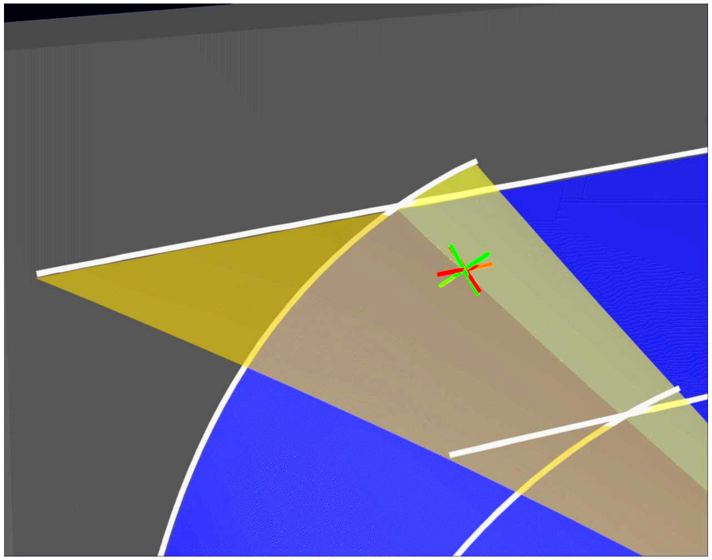


Notes

3D view of the chemical potential as a function of P and T



Plot of the molar Gibbs potential (the chemical potential) as a function of pressure and temperature (normalized to the pressure and temperature at the critical point marked by white cross).



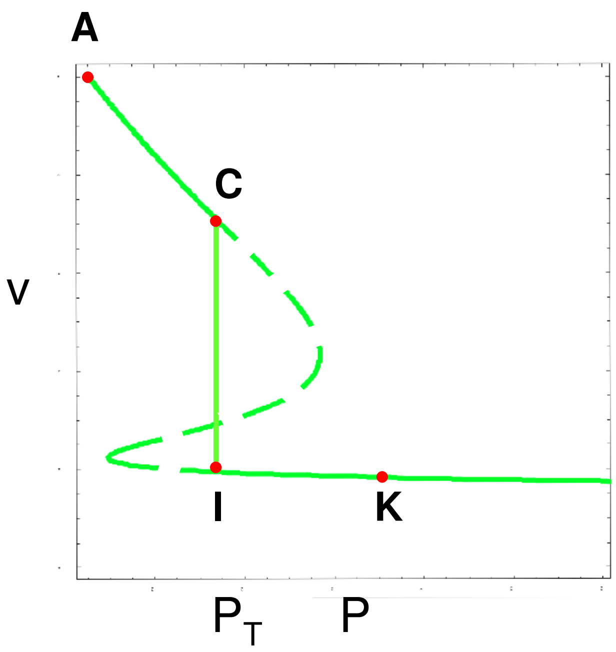
Blowup of a region of the plot on the left. The chemical potential surface intersects itself along the coexistence curve. Blue surfaces are equilibrium liquid and gas phases. Yellow surfaces are meta-stable states.

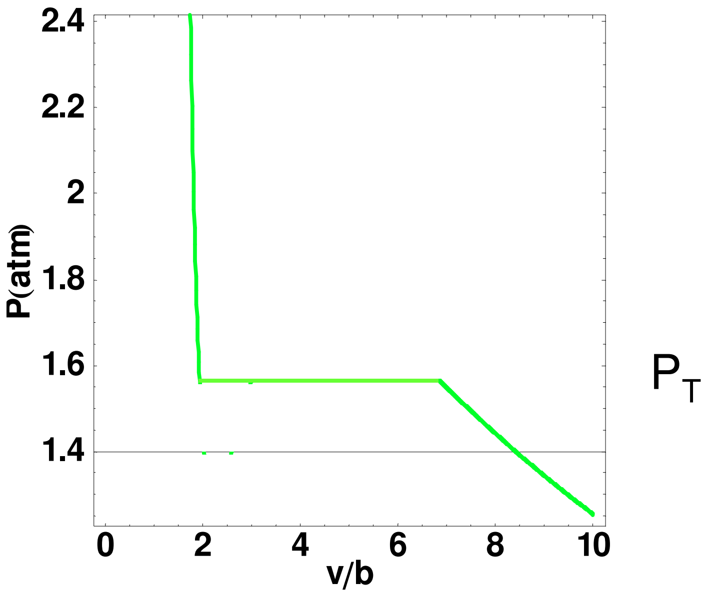
Notes

Source: www.public.iastate.edu/ ~jolls/dedication.html

Isotherms of liquid-gas phase transition

Since transition between points C and I has to take place at a constant pressure, it is represented by a straight line of P=const on the P-v diagram.





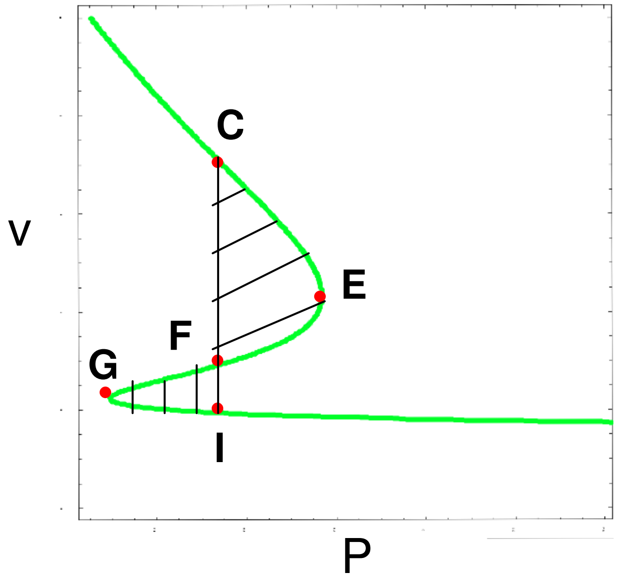
Stable isotherm for a vdW fluid

Notes

Isotherms of liquid-gas phase transition

The value of the pressure P_T at which the transition from C to I takes place can be determined from the condition $\mu_C = \mu_I$.

$$\mu_I - \mu_C = \int_C^I v(P)\,dP = 0$$



Notes

Isotherms of liquid-gas phase transition

$$\mu_I - \mu_C = \int_C^I v(P)\,dP = 0$$

$$\Downarrow$$

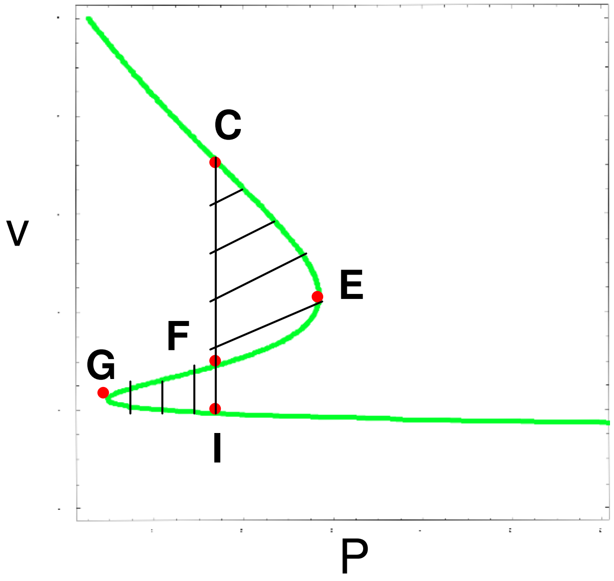
$$\mu_I - \mu_C = \int_C^E v\,dP + \int_E^F v\,dP + \int_F^G v\,dP + \int_G^I v\,dP = 0$$

$$\Downarrow$$

$$\int_C^E v\,dP - \int_F^E v\,dP - \int_G^F v\,dP + \int_G^I v\,dP = 0$$

$$\Downarrow$$

$$\int_C^E v\,dP - \int_F^E v\,dP = \int_G^F v\,dP - \int_G^I v\,dP$$

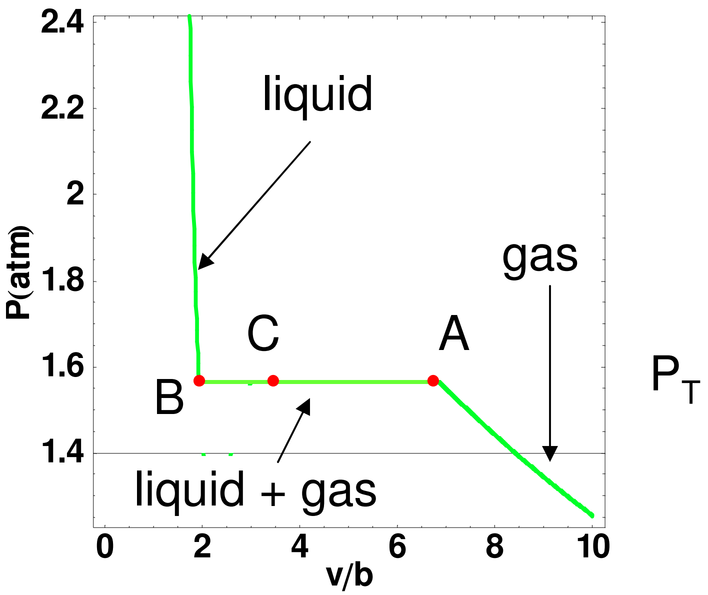


⇒ This condition means that the are enclosed by CEF should be equal to the are enclosed by FGI.

Notes

Isotherms of liquid-gas phase transition

From the stable isotherm shape it is clear that there is a continuous change of molar volume across the phase transition. Molar entropy and internal energy also change across the phase transition.



$$v = x_L v_L + x_G v_G \qquad x_L + x_G = 1$$

where v_L and v_G are molar volumes of liquid and gas and x_L and x_G are molar fractions of liquid and gas in the liquid/gas mixture. Solving for x_L:

$$x_L = \frac{v_G - v}{v_G - v_L} \qquad x_G = \frac{v - v_L}{v_G - v_L} \qquad x_L = \frac{CA}{BA} \qquad x_G = \frac{BC}{BA}$$

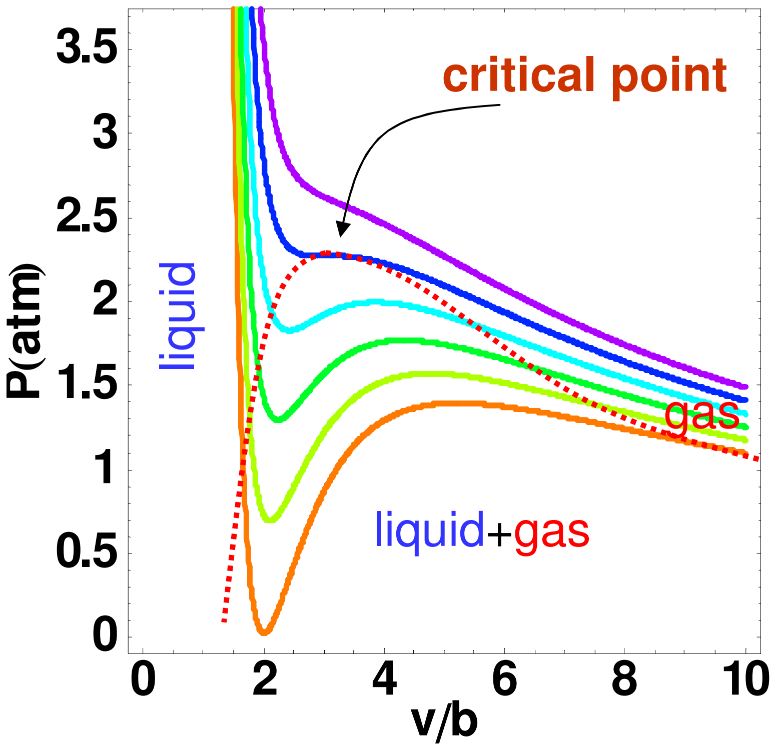
- "lever rule"

Notes

Isotherms of liquid-gas phase transition

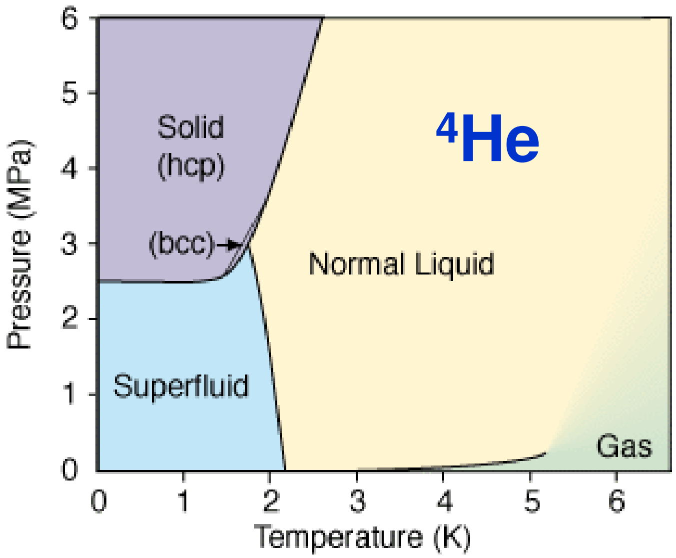
Transformation from liquid to gas without a phase transition requires a process with pressures above the critical pressure.

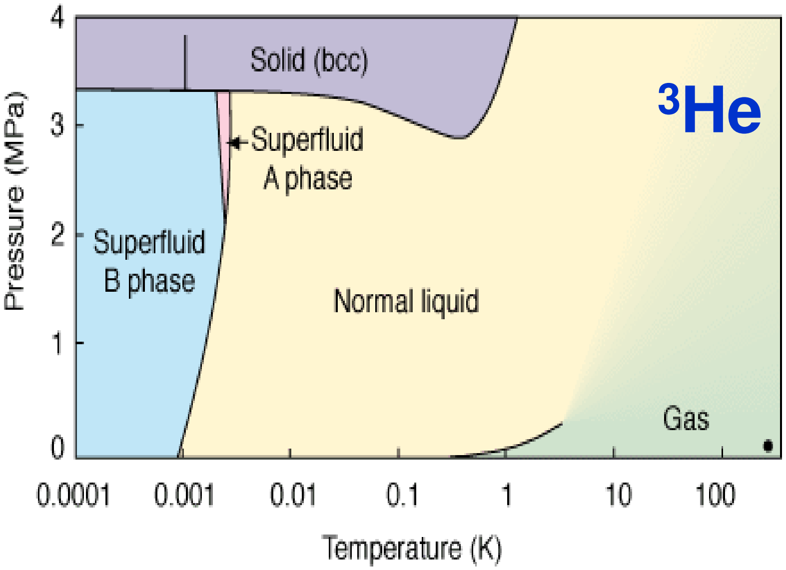
There is only one phase of fluid above the critical pressure.



Notes

Phase Transitions in Helium





The vdW model of a fluid fails at low temperatures where interaction energy between atoms and molecules becomes comparable to temperature.

- Quantum phases such as superfluid phases of He are not described (a fluid with zero viscosity)

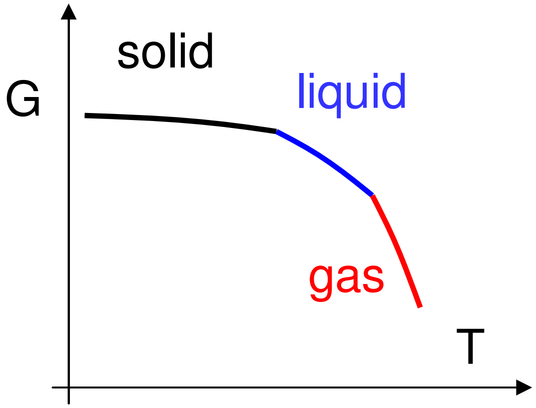
Notes

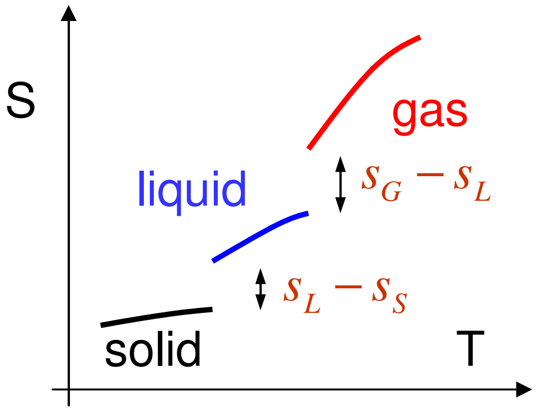
Summary of phase transitions so far

- Entropy is discontinuous across the phase coexistence curve, e. g. molar entropies of liquid and gas phases at the same pressure and temperature are different. This also implies that a system undergoing a first order phase transition absorbs or emits heat at constant temperature (latent heat).

- Thermodynamically stable isotherms can be constructed from the unstable isotherms by using the fact the pressure and chemical potential remain constant across the phase transition

$$dG = -SdT + VdP + \mu dN \quad \Rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$





Notes

First order phase transitions in multi-component systems

A two-component system where each of the components can be either solid or liquid.

$\mu_1^L(T, P, x_1^L)$ - chemical potential of the first component in the liquid state

$\mu_1^S(T, P, x_1^S)$ - chemical potential of the first component in the solid state

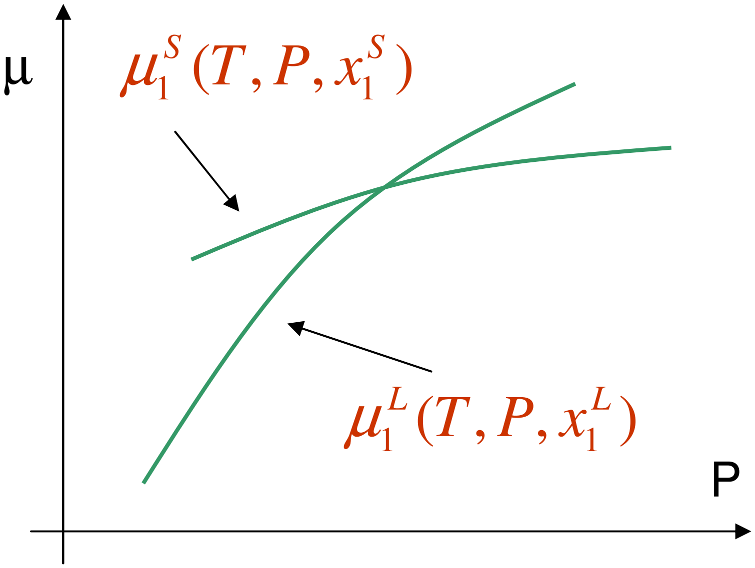
x_1^L - molar fraction of the first component in the liquid phase $x_1^L + x_2^L = 1$

x_1^S - molar fraction of the first component in the solid phase $x_1^S + x_2^S = 1$

Notes

Two-phase, two-component system

For component 1:



The liquid and solid phases do coexist at the point when chemical potentials of the two phases are equal to each other:

$$\boxed{\mu_1^S(T,P,x_1^S)=\mu_1^L(T,P,x_1^L)} \qquad (1)$$

$$\mu_2^S(T,P,x_2^S)=\mu_2^L(T,P,x_2^L)$$

$$\Downarrow$$

$$\boxed{\mu_2^S(T,P,1-x_1^S)=\mu_2^L(T,P,1-x_1^L)} \qquad (2)$$

Solving (1) and (2), we find

$x_1^L(P,T)$ and $x_1^S(P,T)$

A solution exists in a 2D region of the P-T phase diagram.

Three-phase, two-component system

Now assume that both components can exist in three phases: solid, liquid and gas

Gas, liquid and solid for both phases coexist if:

$$\mu_1^S(T,P,x_1^S) = \mu_1^L(T,P,x_1^L) = \mu_1^G(T,P,x_1^G)$$

$$\mu_2^S(T,P,1-x_1^S) = \mu_2^L(T,P,1-x_1^L) = \mu_2^G(T,P,1-x_1^G)$$

Note that these are four equations for three unknowns: x_1^S , x_1^L and x_1^G

Notes

Three-phase, two-component system

These are four equations for three unknowns: x_1^S , x_1^L and x_1^G

These means that three phases cannot coexist at arbitrary values of P and T. For a given value of T, the above 4 equations give P, x_1^S , x_1^L and x_1^G

Similarly, if four phases of a two-component system are possible, they can only coexist at a uniquely defined point (or a few points) with given pressure and temperature.

Five phases cannot generally coexist in a two-component system.

Notes

Gibbs Phase Rule

For an arbitrary system with *r* components and *M* phases.

1-component system:

1 phase: exists at any T and P	2 degrees of freedom
2 phases: coexist on the coexistence curves T(P)	1 degree of freedom
3 phases: coexist at a single point T_t, P_t	0 degrees of freedom

2-component system:

2 phases: coexist in 2D regions of the T-P plane	2 degrees of freedom
3 phases: coexist in 1D regions T(P) of the T-P plane	1 degree of freedom
4 phases: coexist at a finite set of points $\{T_q, P_q\}$	0 degrees of freedom

r-component system:

M phases:	2+r-M degrees of freedom

Notes

Gibbs Phase Rule

Gibbs phase rule: for r-component system, M phases can coexist in 2+r-M dimensional regions of the thermodynamic coordinate space.

$$g = g(T, P, x_1, \ldots x_r) \qquad x_1 + \ldots + x_r = 1$$

: r+1 thermodynamic coordinates

M phases coexist: $\mu_1(T, P, x_1, \ldots x_r) = \ldots = \mu_M(T, P, x_1, \ldots x_r)$

: M-1 equations connecting thermodynamic coordinates

Therefore, there are r+1-(M-1) = 2+r-M independent thermodynamic coordinates in the regions of thermodynamic coordinate space where M phases coexist.

Notes