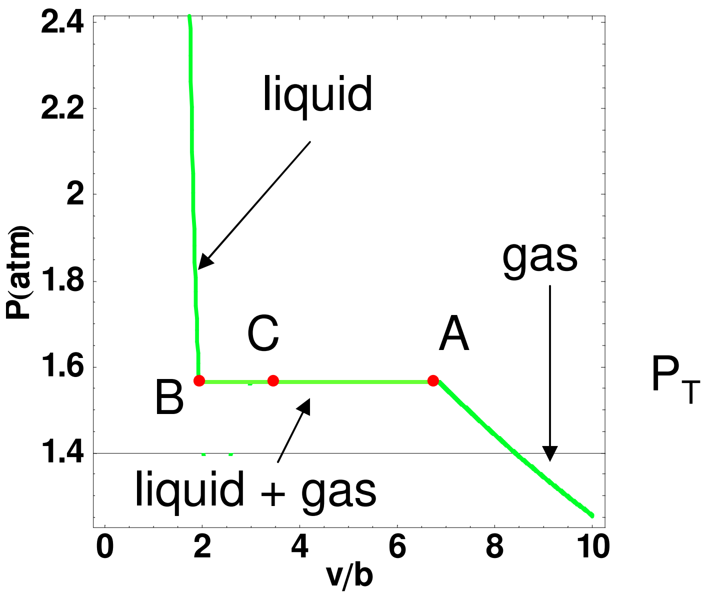
Isotherms of liquid-gas phase transition



From the stable isotherm shape it is clear that there is a continuous change of average 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:

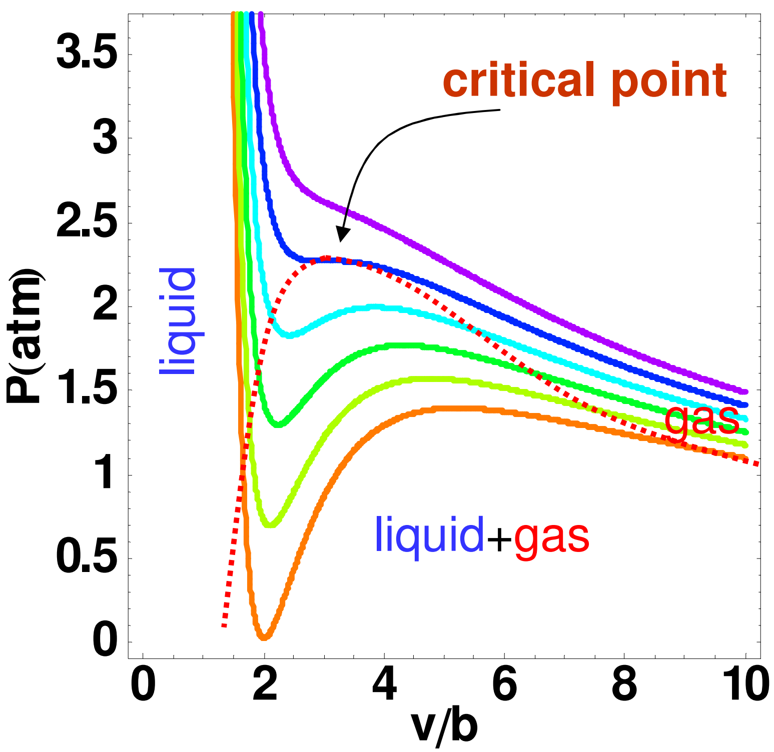
$$x_L = \frac{v_G - v}{v_G - v_L} \qquad x_G = \frac{v - v_L}{v_G - v_L} \qquad x_L = \frac{CA}{BA} \qquad x_G = \frac{BC}{BA}$$

- “lever rule”

Isotherms of liquid-gas phase transition

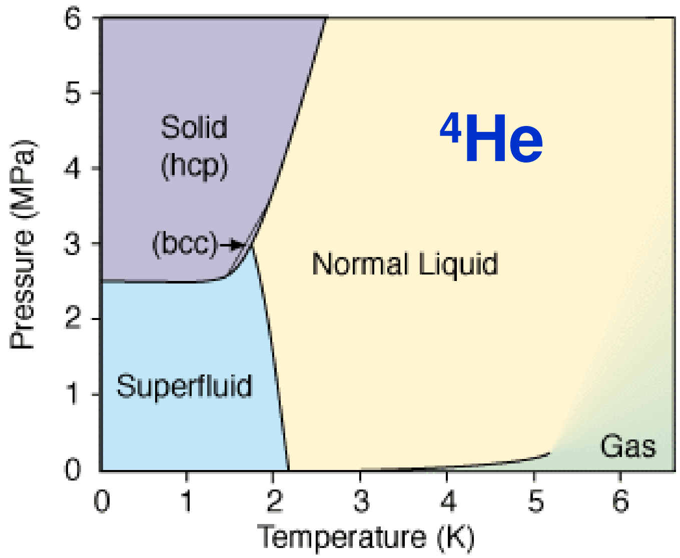
Transformation from liquid to gas without a phase transition requires a process with pressures above the critical pressure.

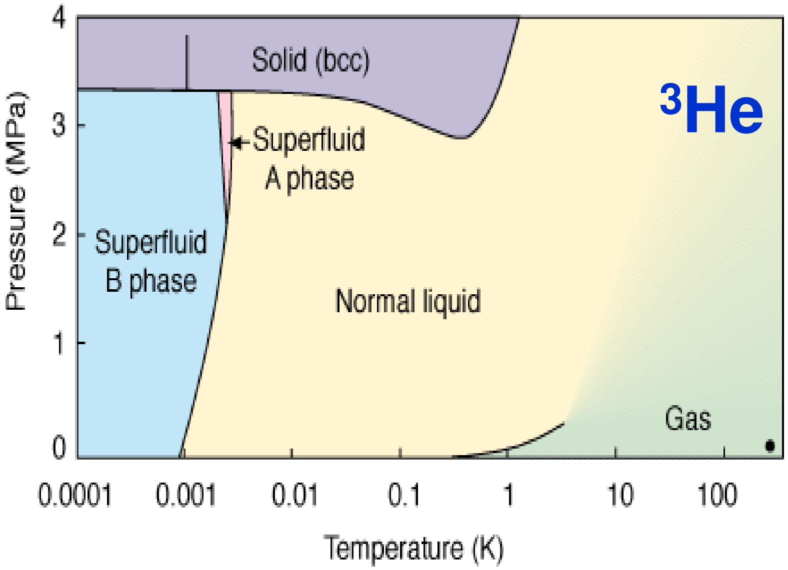
There is only one phase of fluid above the critical pressure.



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)

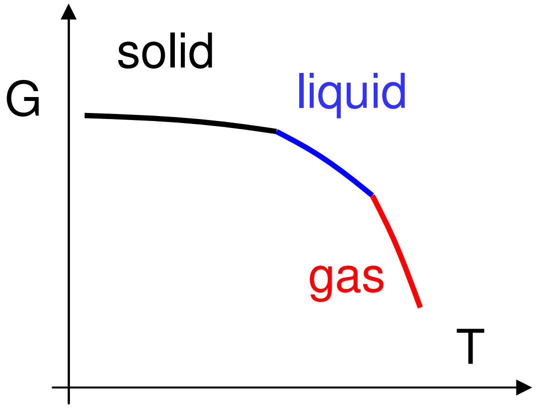
Notes

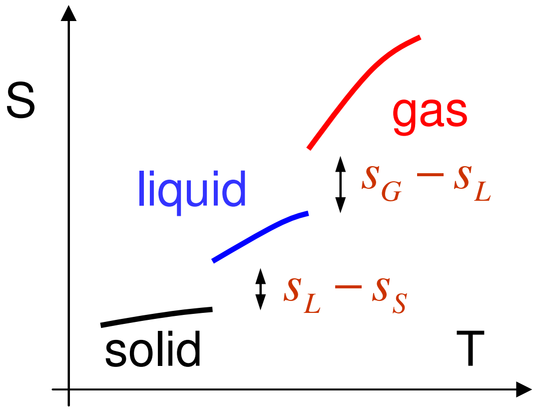
Summary of phase transitions so far

- 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

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





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

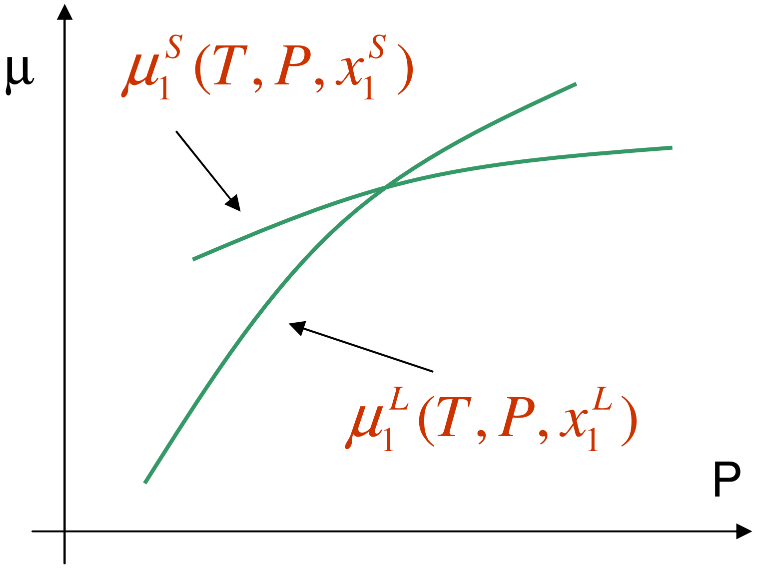
x_1^L - molar fraction of the first component in the liquid phase $\quad x_1^L + x_2^L = 1$

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

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:

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

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

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

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

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

Phase diagrams of binary systems

Behavior of mixtures of two types of substances is described by thermodynamics. The process is different from chemical reactions as no chemical transformations take place, but heat may be released and molar volumes may change upon mixing.

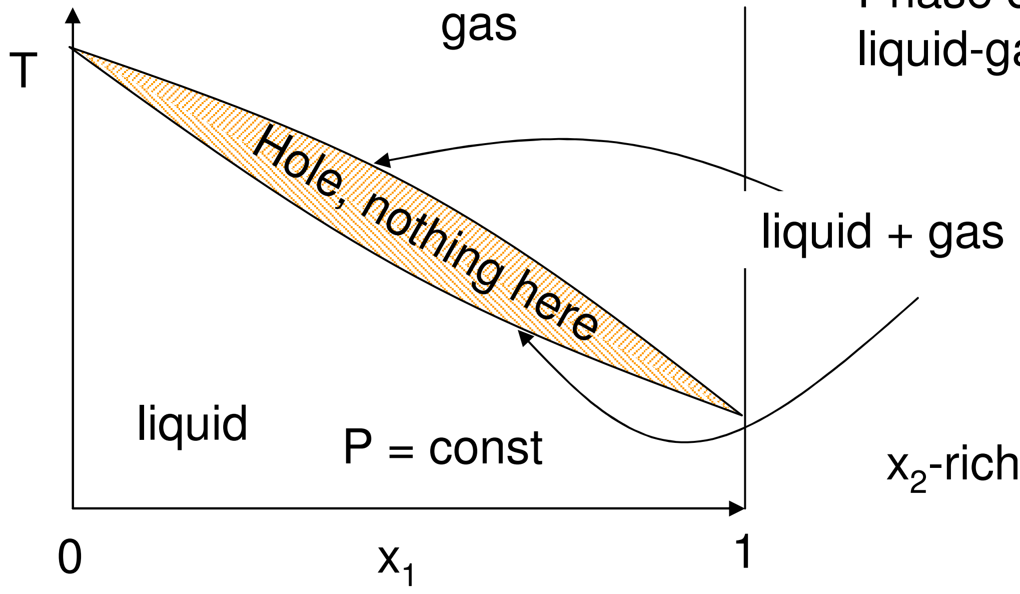
The molar Gibbs potential (chemical potential) for a binary system is a function of T, P and x_1 – the mole fraction of the chemical component 1 of the system.

It is convenient to represent the phase diagram of such a system on the T-x_1 plane at a fixed pressure.

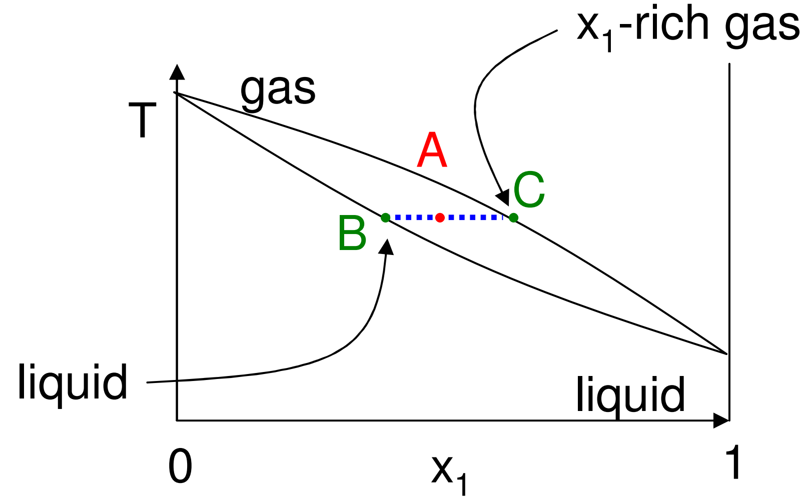
Since the number of components $r = 2$ and the number of phases $M = 2$, liquid and gas phases can coexist in 2D regions of the thermodynamic coordinate space $(2+r-M)=2$

Notes

Phase diagrams of binary systems



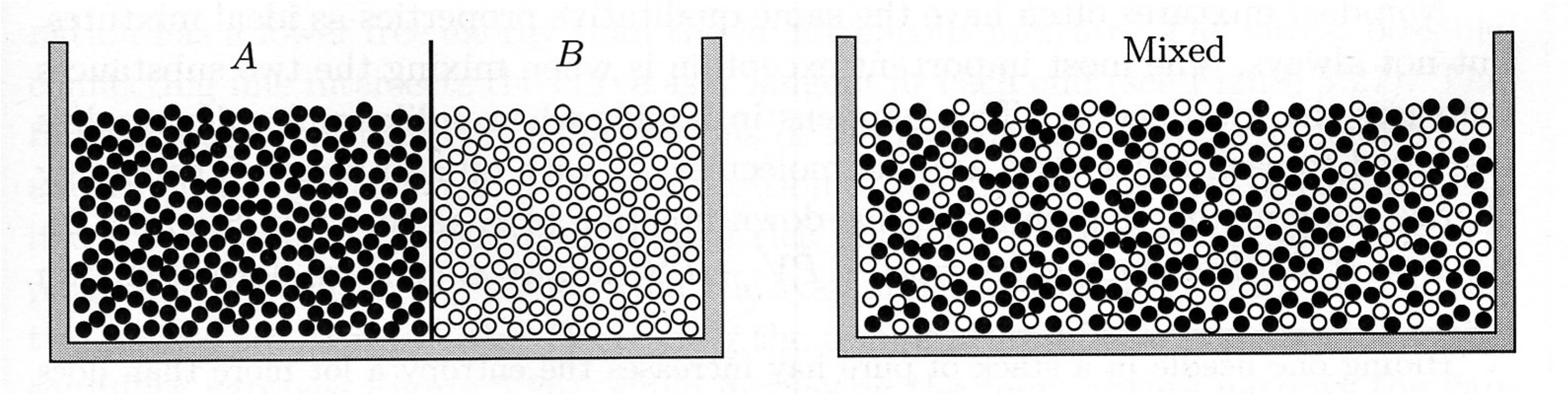
Phase diagram for a simple two-component liquid-gas system at P = const



Notes

Mixtures – the entropy of mixing

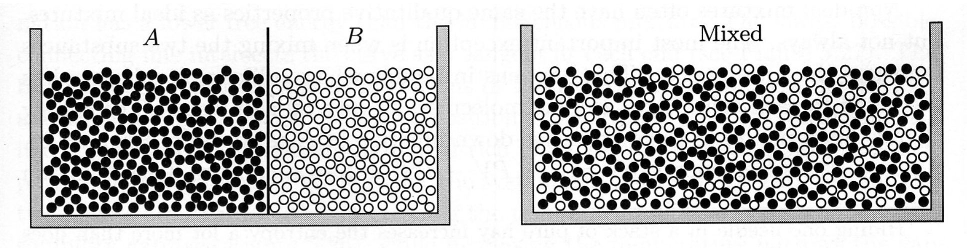
When considering thermodynamics of multi-components, it is important to take into account the entropy of mixing. If you have two types of molecules, then the state of them being intermixed has higher entropy than the state when they are not mixed:



$$S_1 < S_2$$

Notes

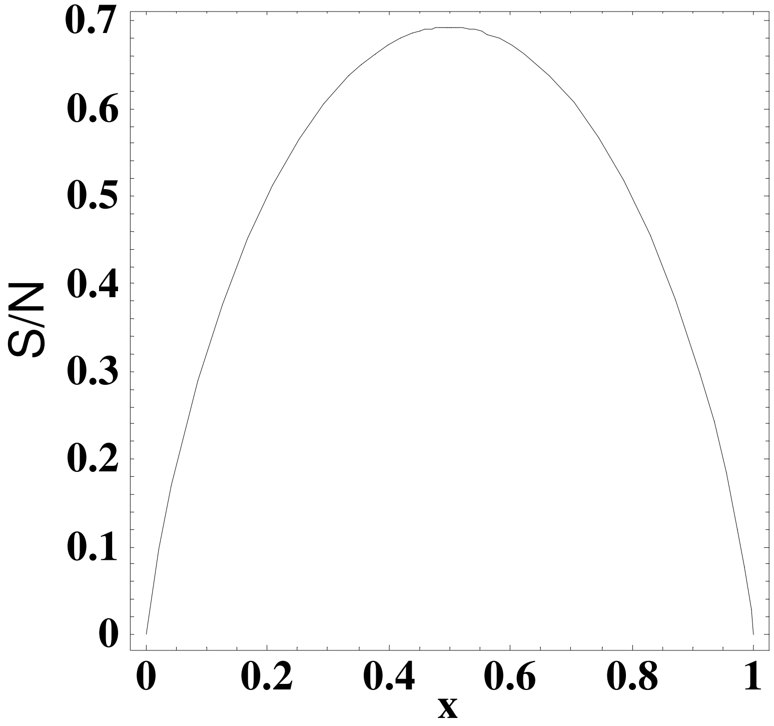
Mixtures – the entropy of mixing



From statistical mechanical considerations (by counting the microstates), one can show that the entropy of mixing is given by:

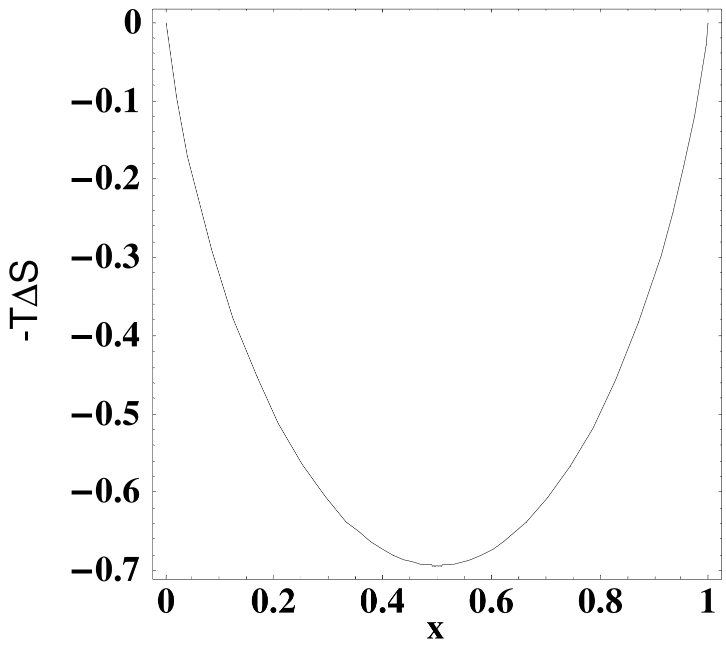
$$\Delta S = -N\left[(1-x)\ln(1-x) + x\ln x\right]$$

Where x is the fraction of the molecules of one type in the binary mixture.



Notes

Gibbs Potential of Mixtures



The Gibbs potential is:

$$G = U + PV - TS$$

Consider a process where we intermix two types of **non-interacting** molecules at constant pressure and volume. Non-interaction means that U does not change, so the change of G will only come from the –TS term:

$$\Delta G = -T\Delta S$$

Note that the resulting shape of the Gibbs potential is stable against phase separation

---

Notes

Gibbs Potential of Mixtures

Now let us consider an interesting case where there is a **repulsive microscopic interaction** between two types of molecules (e.g. water and any hydrophobic substance such as oil)

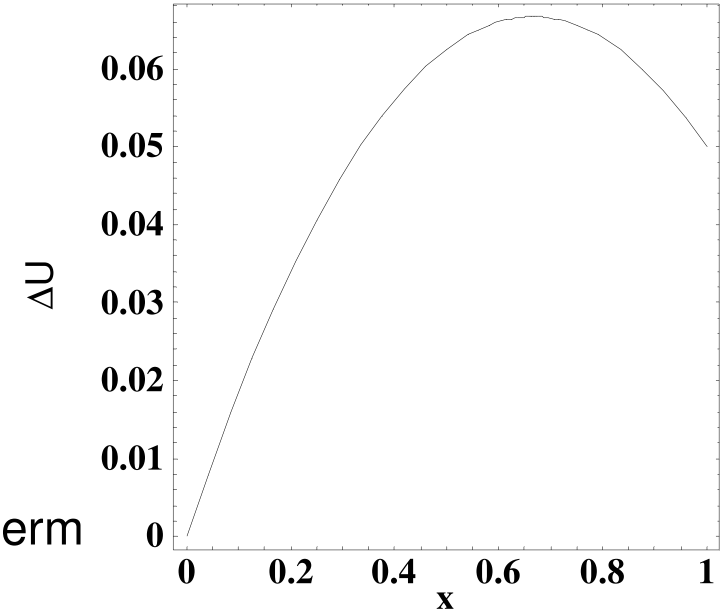
Now as two types of atoms intermix on the microscopic level, the internal energy U increases:

$$\Delta U > 0$$

A typical variation is given by:

$$\Delta U = U_0\left(Ax - Bx^2\right)$$

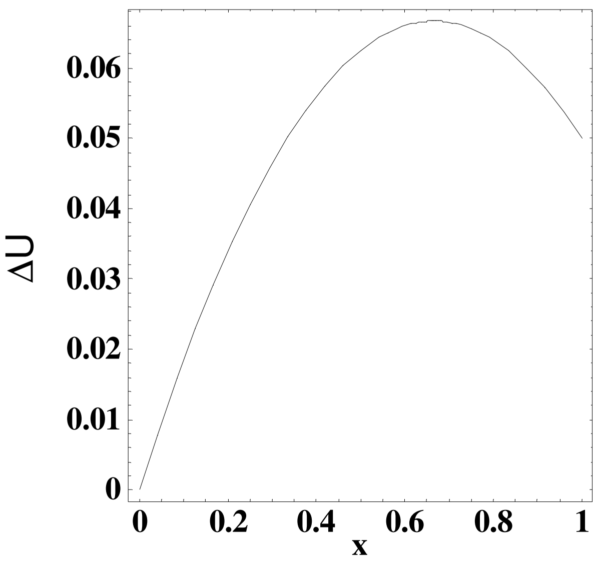
Interaction term



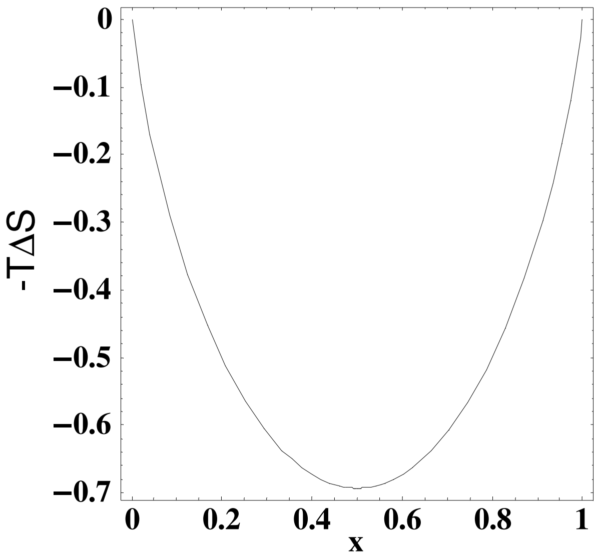
Gibbs Potential of Mixtures

The variation of the Gibbs potential upon mixing is more complex:

$$\Delta G = \Delta U - T\Delta S$$



+

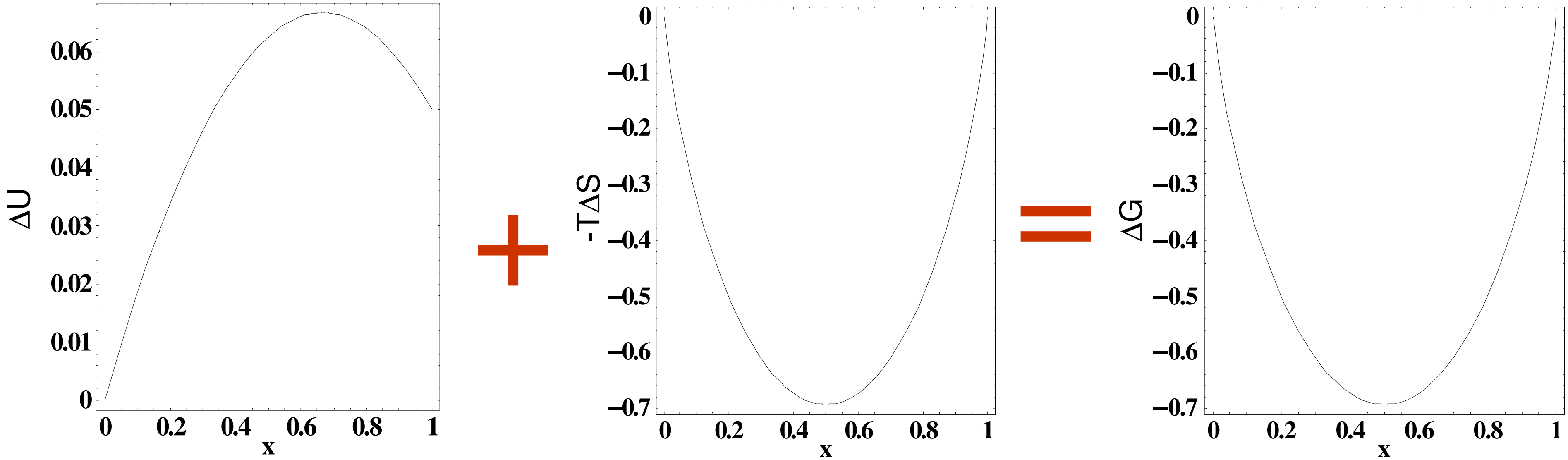


=?

Notes

Gibbs Potential of Mixtures

High temperature limit $\Delta G = \Delta U - T\Delta S \approx -T\Delta S$



The Gibbs potential is stable and mixture at any concentration is stable

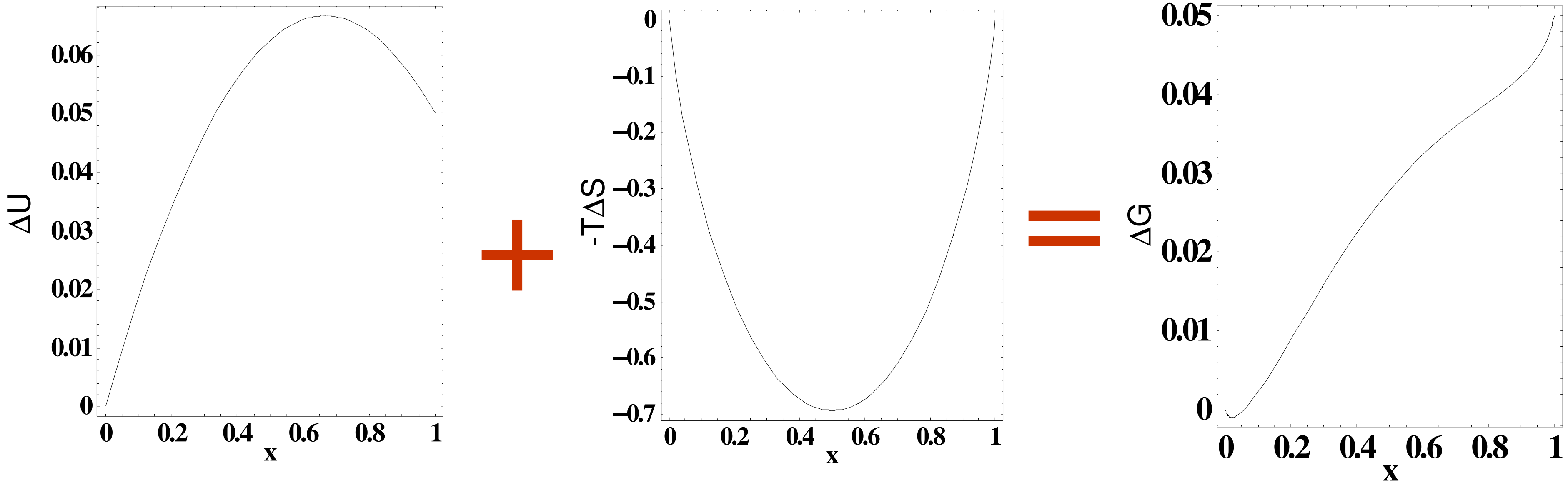
---

Notes

Gibbs Potential of Mixtures

Low temperature limit

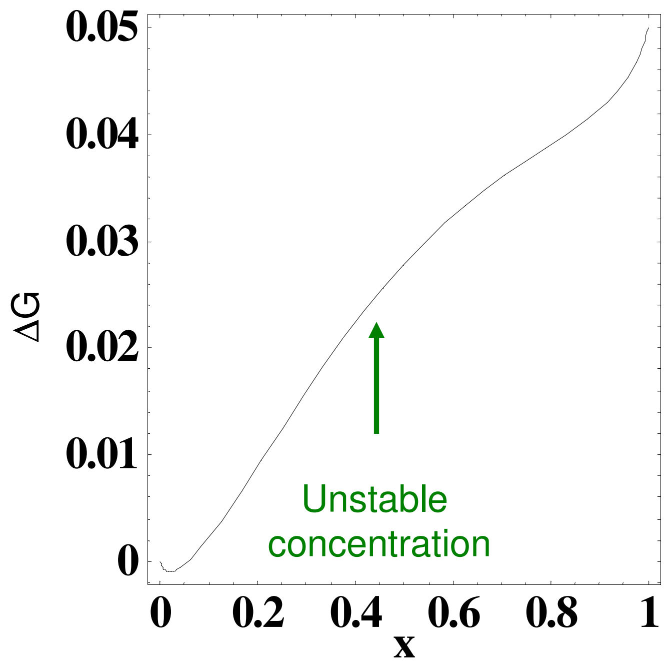
$$\Delta G = \Delta U - T\Delta S$$

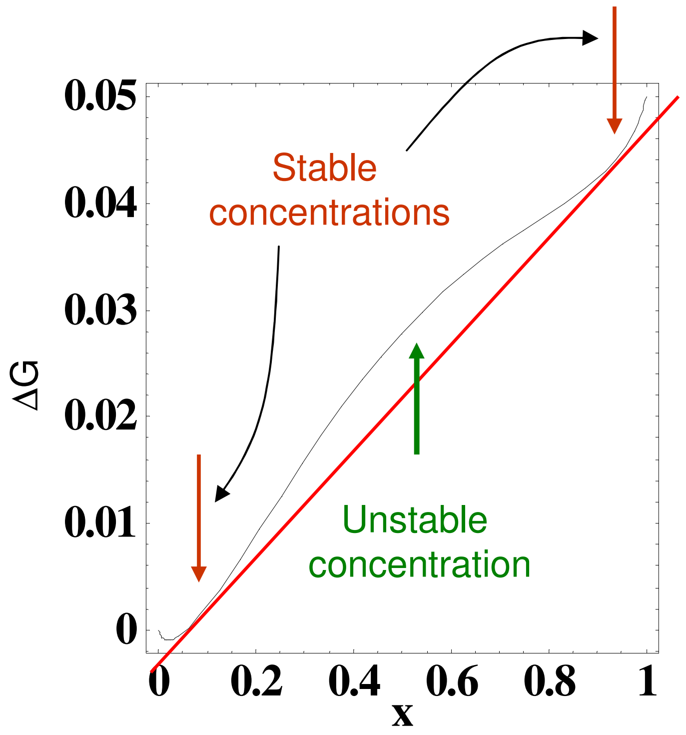


The resulting form of the Gibbs potential is unstable and will phase separate for some values of x

Notes

Phase Separation in Mixtures





Separation onto phases will lower the average Gibbs energy and thus the equilibrium state is phase separated

---

Notes