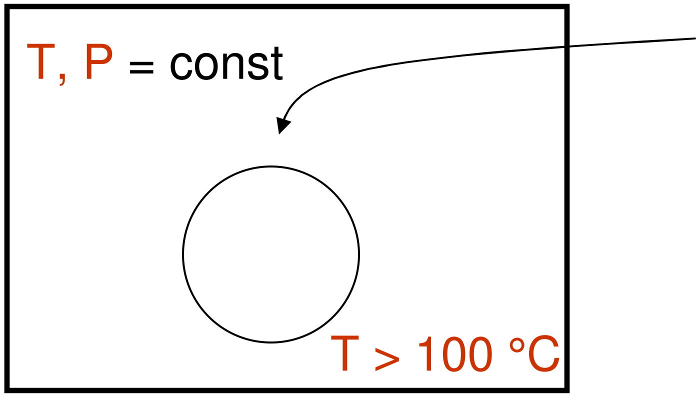
Example: vessel with water vapor

A typical setting for observation of a phase transition is the situation of constant pressure and externally settable temperature. This situation is best described by the Gibbs thermodynamic potential.

Let us consider an example of water vapor just above the boiling temperature of water



Vessel with water vapor

T, P = const

T > 100 °C

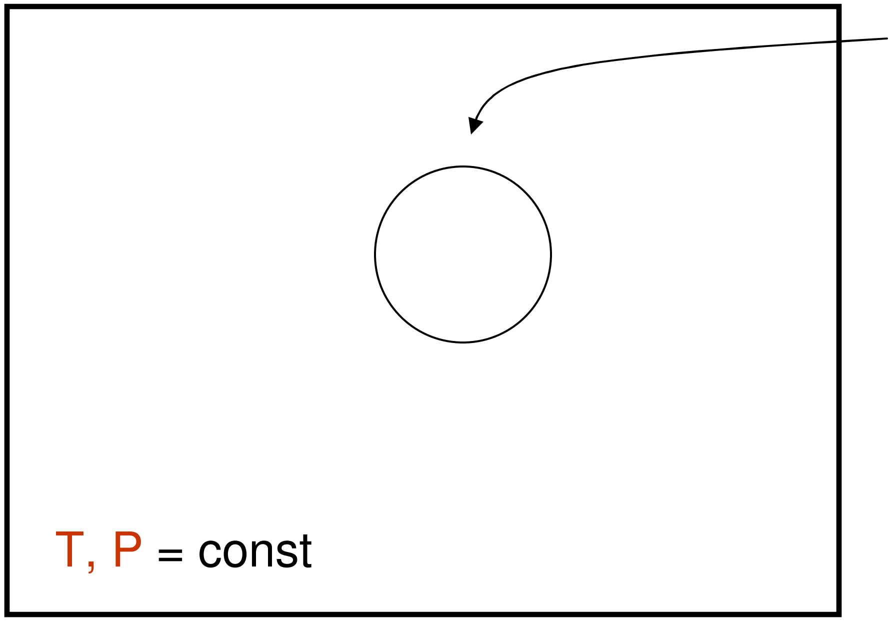
Region that contains fixed number of particles (its volume and energy fluctuate)

Both volume and entropy of this region can fluctuate (are unconstrained)

Notes

Example: vessel with water vapor

T > 100 °C

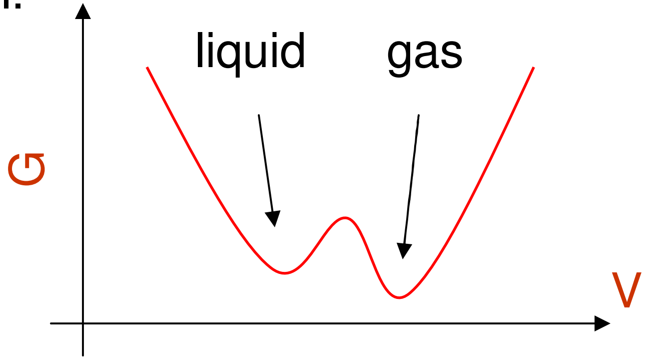


T, P = const

Vessel with water vapor

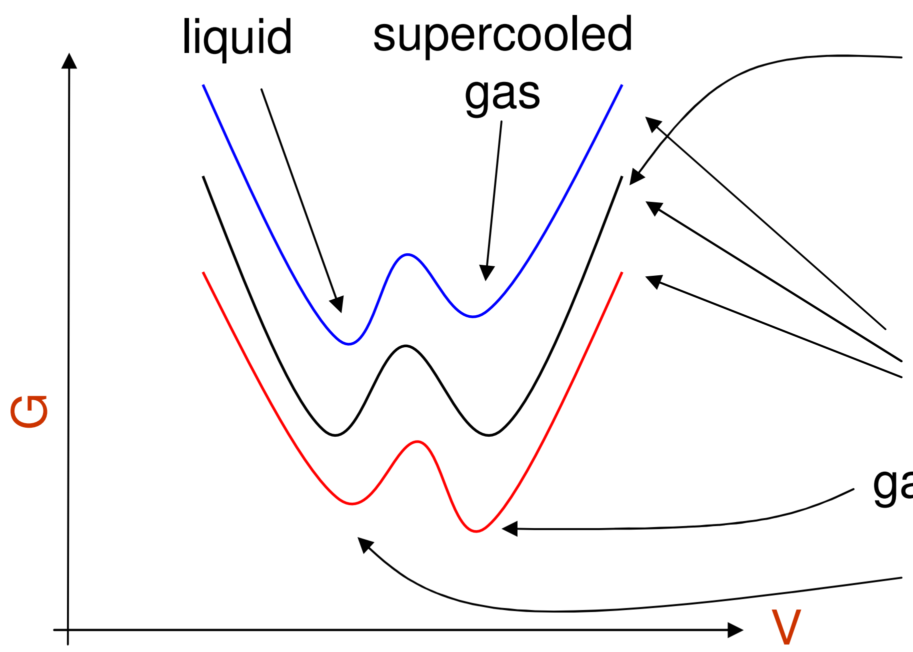
Region that contains fixed number of particles (its volume and energy fluctuate)

The region is in contact with pressure and temperature reservoirs, so its equilibrium state is conveniently described by Gibbs potential.



Example: vessel with water vapor

If we lower the temperature of the vessel, the Gibbs potential energy shifts from the minimum with higher molar volume to that with lower molar volume (condensation).



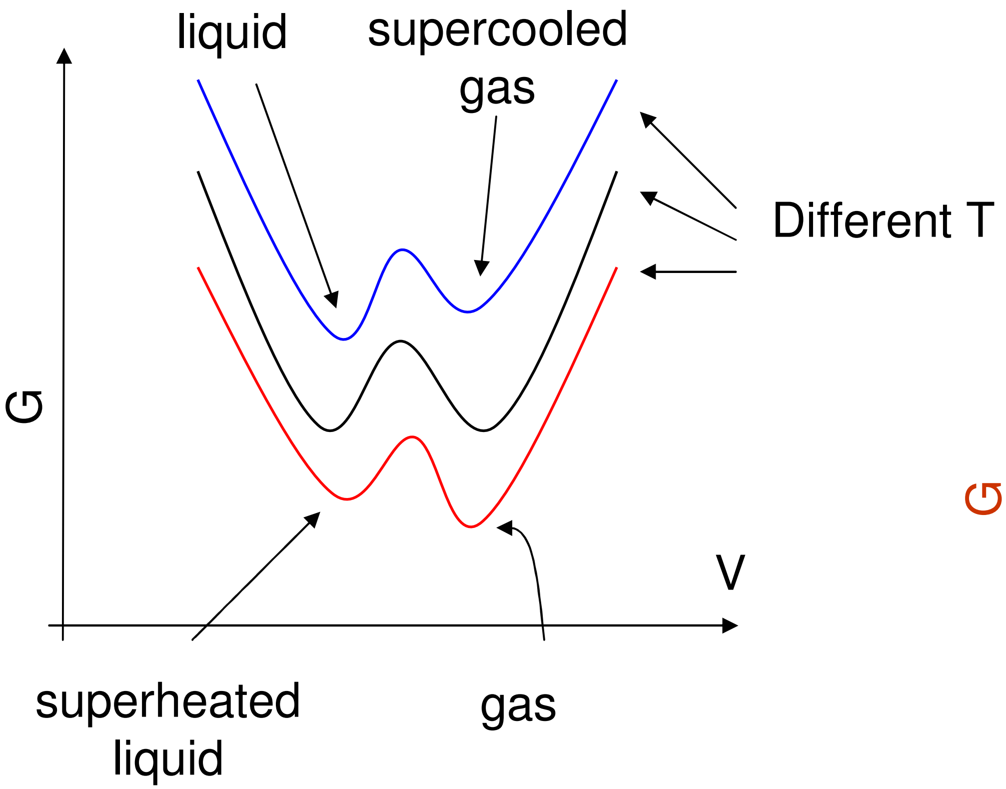
At this temperature G for both gas and liquid are the same, so they can coexist at this temperature ($g_L = g_G$).

Different temperatures

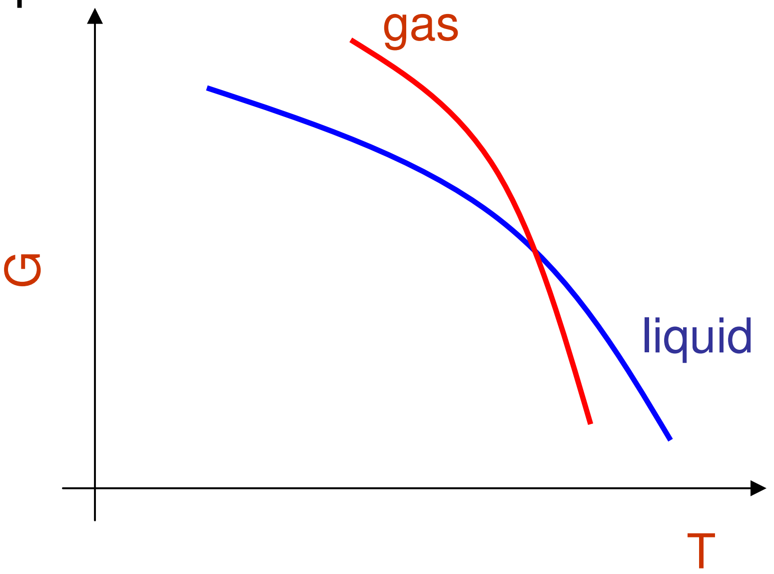
gas

superheated liquid

Example: vessel with water vapor

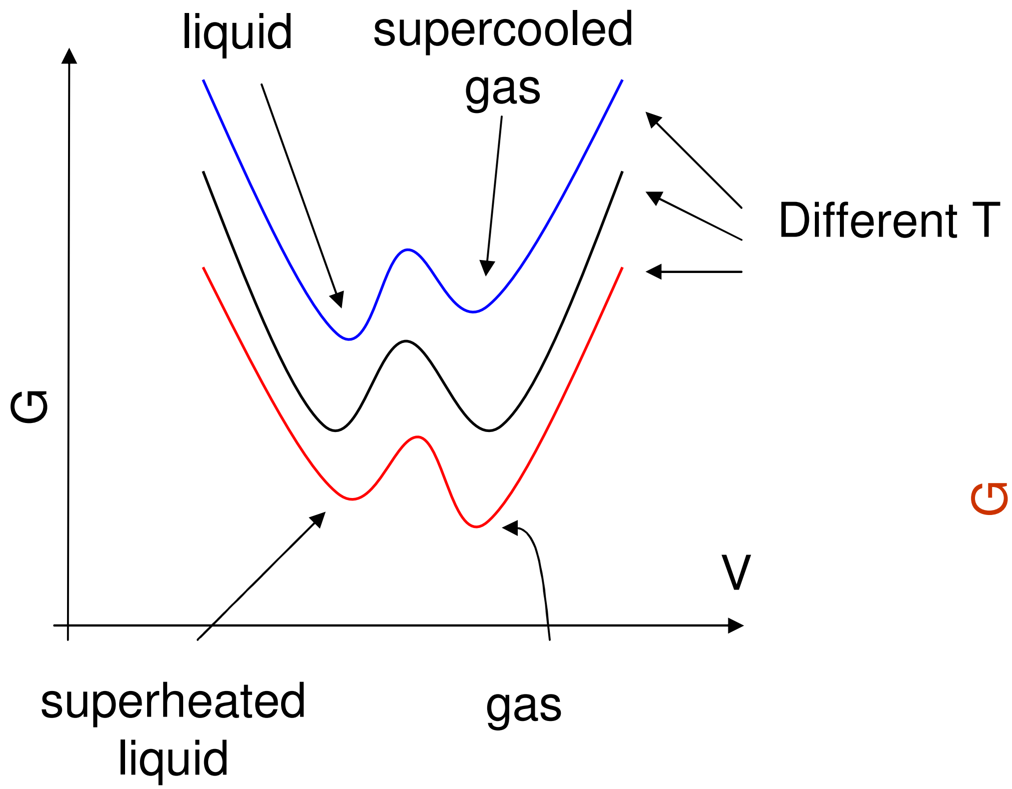


Gibbs potential minima as a function of temperature

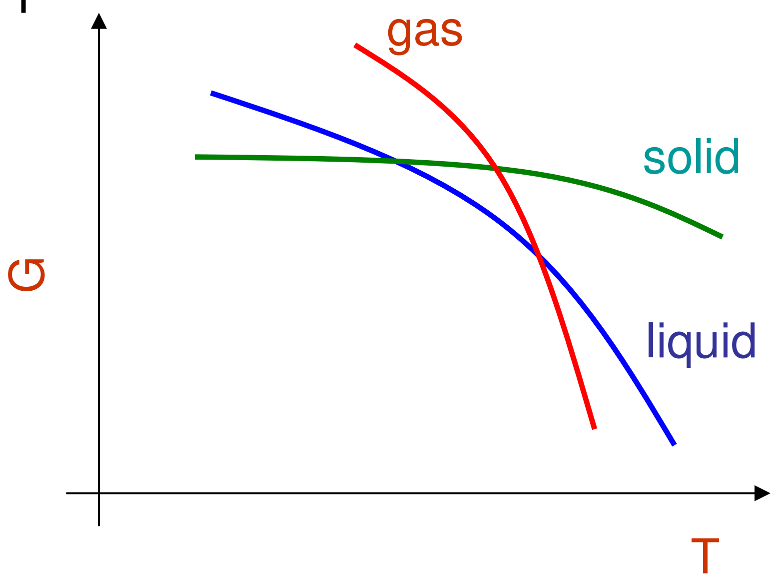


Notes

Example: vessel with water vapor

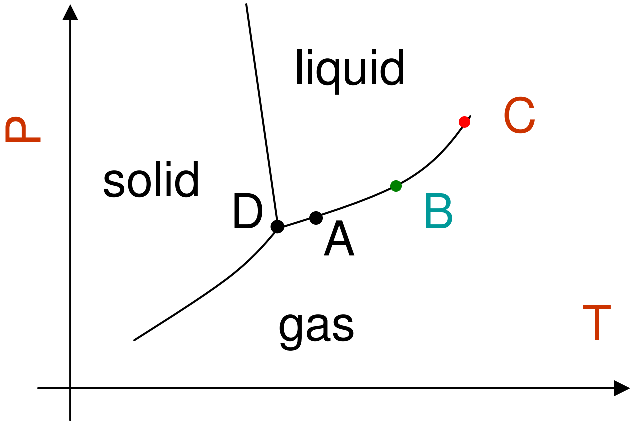


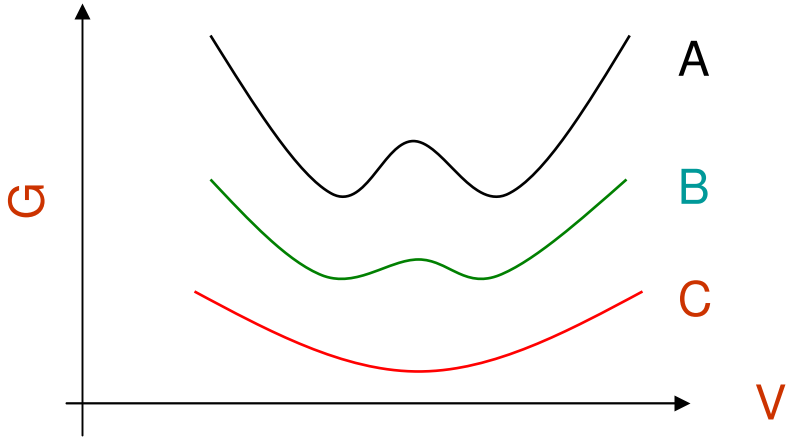
Gibbs potential minima as a function of temperature



Notes

Example: vessel with water vapor





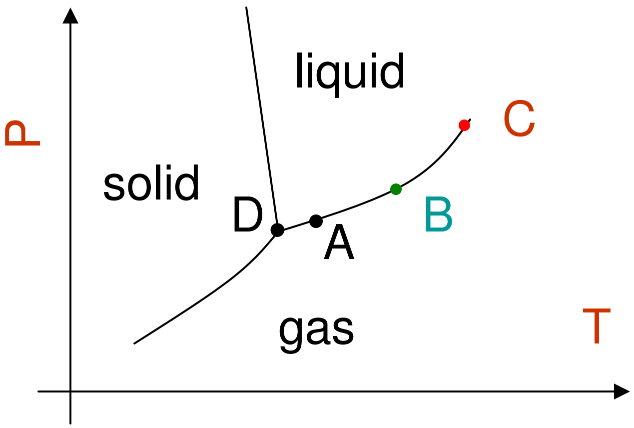
going along the coexistence curve

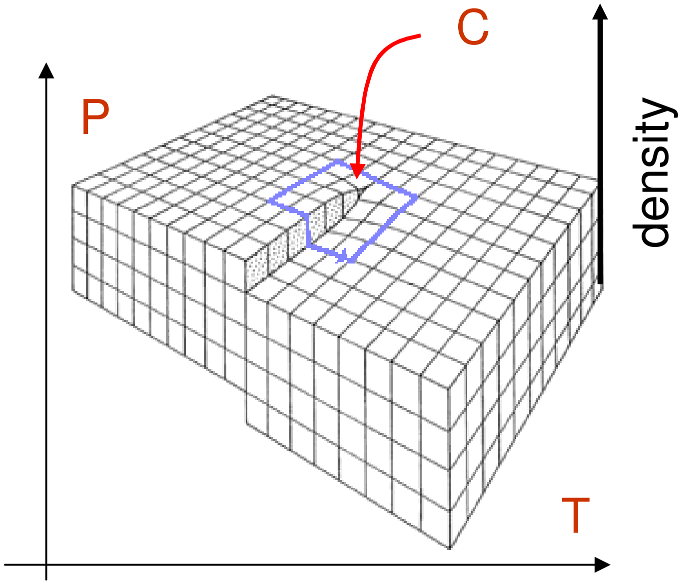
C is the *critical point*   D is the *triple point*

The appearance of two nearby minima of Gibbs potential at the critical point is an example of the *continuous phase transition.*

Thermodynamic potentials other then Gibbs are discontinuous across the first order transition but are continuous across the continuous phase transition

Example: vessel with water vapor

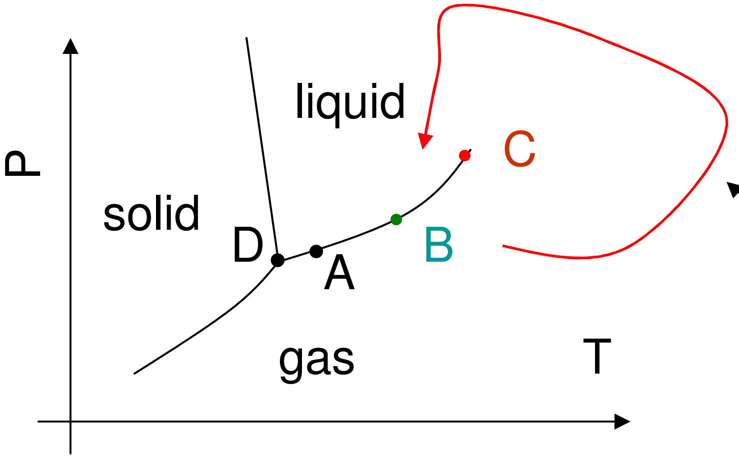




Discontinuities disappear at the critical point (e. g. discontinuity in density). The second order phase transitions are also called continuous phase transitions.

Notes

Coexistence curves



No real qualitative difference between liquid and gas

Points on the coexistence curves do not represent a unique state of the system. Many possible states with different *average* density (or molar volume) correspond to the same point on these lines

The triple point (D) of water exists only at a single value of temperature and pressure, therefore it may serve as a standard of pressure and temperature. The Kelvin scale of temperature is defined by assigning the value of 273.16 K to the temperature of the triple point.

Notes

Discontinuity in the entropy and the latent heat

It is experimentally observed that as a thermodynamic system transforms from one phase to another, it either emits or absorbs heat. This is despite the fact that temperature stays constant during the phase transition!

For example, to transform 1 gram of ice into water at 0 °C and ambient pressure, one needs to transfer 335 Joules of heat to the ice.

Heat transfer is accompanied by entropy transfer to the system ($\delta Q = T\,dS$). Therefore entropy of one gram (or mole) of water is higher than entropy of one gram (or mole) of ice. In general, molar entropy of a liquid is higher than that of the corresponding solid at the same temperature and pressure:

$$s^{(L)} > s^{(S)}$$

Notes

Discontinuity in the entropy and the latent heat

The heat necessary for melting one mole of solid is called the *heat of fusion* or the *latent heat of fusion*:

$$\delta Q_{LS} = \ell_{LS} = T\left(s^{(L)} - s^{(S)}\right)$$

For a general first order phase transition (e. g. liquid-gas etc), the latent heat is:

$$\ell = T\Delta s$$

$$\ell = \Delta h \qquad \mu_L \equiv g_L = \mu_G \equiv g_G \qquad \mu_L = h_L - Ts_L$$

Notes

Discontinuity in the entropy and the latent heat

What is the physical origin of the latent heat? Let us consider an example of the liquid – gas phase transition for a vdW fluid.

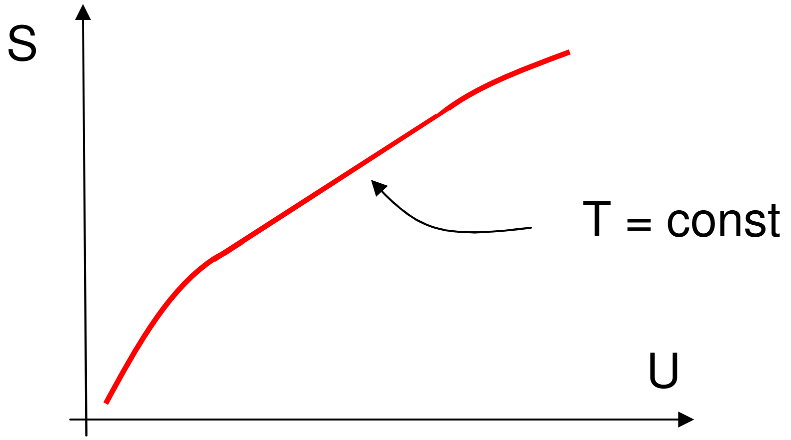
When one particle of the fluid evaporates, the potential energy of this particle increases due to the attractive interactions between the particles of the fluid. If we did not supply heat, that would lead to a decrease of kinetic energy of this evaporated particle and thus to a decrease of temperature of the gas compared to that of the liquid. However, we are in a situation of constant temperature, so the kinetic energy of the evaporated particle has to remain constant (time average). Therefore, conservation of energy requires us to supply energy to the particle in the form of heat transfer to the system.

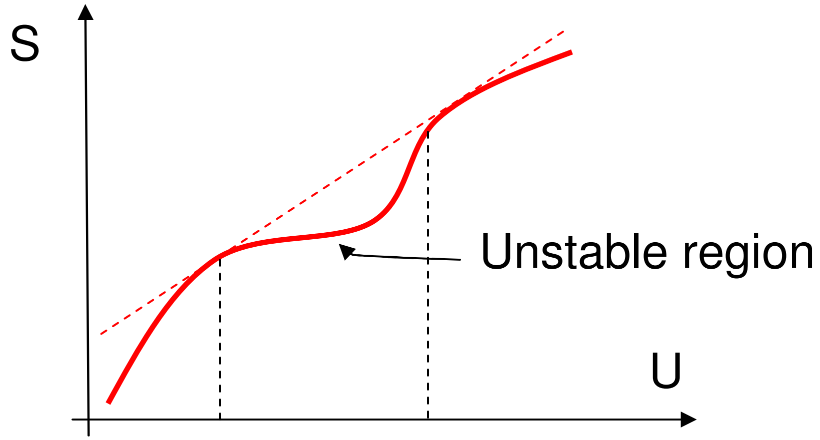
Notes

Form of the fundamental relation in the phase transition

During the phase transition, we transfer both energy and entropy into the system, however it temperature remains constant. These conditions define the shape of the fundamental relation curve of U vs S during the phase transition.

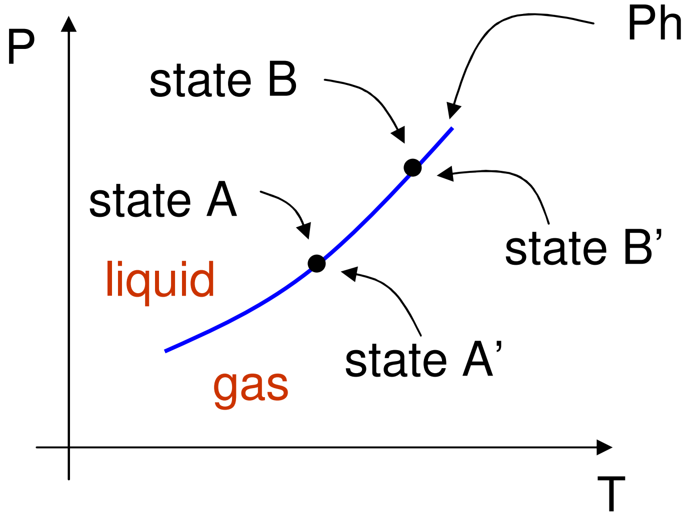
Since $1/T = \partial S/\partial U$, the slope of S vs U has to be constant during the phase transition.





Notes

The Clapeyron Equation



Gibbs potential of liquid in thermal equilibrium with gas at constant pressure and temperature should be equal to the Gibbs potential of gas:

$$\mu_A = \mu_{A'} \qquad \mu_B = \mu_{B'}$$

⇓

$$\mu_B - \mu_A = \mu_{B'} - \mu_{A'}$$

Notes

The Clapeyron Equation

$$\mu_B - \mu_A = \mu_{B'} - \mu_{A'}$$

⇓

$$\mu_B - \mu_A = -s\,dT + v\,dP = \mu_{B'} - \mu_{A'} = -s'\,dT + v'\,dP$$ ⇒

$$(s'-s)\,dT = (v'-v)\,dP$$ ⇒ $$\frac{dP}{dT} = \frac{(s'-s)}{(v'-v)} = \frac{\Delta s}{\Delta v}$$ Since $\ell = T\Delta s$ ⇒

$$\boxed{\frac{dP}{dT} = \frac{\ell}{T\Delta v}}$$

- Clapeyron equation

The Clapeyron equation is general, it is not only applicable to liquid-gas but to solid-liquid and other first order phase transitions.

Notes