Answer on Question #50674-Physics-Molecular Physics-Thermodynamics

What do you understand by first order phase transition? Derive Clausius-Clapeyron equation to explain variation of temperature with pressure in such a transition. Can we use this equation for transitions of order higher than one? Explain.

Answer

First-order transition is a transition in which one or more first derivatives of the relevant thermodynamic potentials change discontinuously as a function of their variables.

Consider four points on the phase coexistence curve two on either side but infinitesimally separated along the coexistence curve. If points A1 and A2 are across from each other in the two phases 1 and 2 we have

$\mu_{A1} = \mu_{A2}$. Points B1 and B2 are across from each other separated by infinitesimal Δp and ΔT we also have $\mu_{B1} = \mu_{B2}$. Therefore, we find

$$\mu_{B1} - \mu_{A1} = \mu_{B2} - \mu_{A2}.$$

From the fundamental thermodynamic identity we have the Gibbs-Duhem relation $\mu_{B1} - \mu_{A1} = -s_1\, dT + v_1\, dP$ since we are in phase 1 and similarly we also have $\mu_{B2} - \mu_{A2} = -s_2\, dT + v_2\, dP$. Therefore, we obtain the slope of the coexistence

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta S}{\Delta V}.$$

ΔS and ΔV the jumps of the entropy and volume at the transition line.

We cannot use Clausius-Clapeyron equation for transitions of order higher than one, because we have there the jumps of second and higher derivatives of the relevant thermodynamic potentials (the entropy and volume are continuous).