Answer on Question #75605, Physics / Molecular Physics | Thermodynamics

Define first order phase transition. Derive the Clausius-Clapeyron equation. Plot
(a) entropy, and (b) Gibbs function as a function of temperature for a first order
phase transition.

Solution

1. Definition

First-order phase transition is a transition in which the molar Gibbs energies or molar Helmholtz energies of the two phases (or chemical potentials of all components in the two phases) are equal at the transition temperature ($G_1=G_2$ or $A_1=A_2$), but their first derivatives with respect to temperature and pressure (for example, specific enthalpy of transition and specific volume) are discontinuous at the transition point, as for two dissimilar phases that coexist and that can be transformed into one another by a change in a field variable such as pressure, temperature, magnetic or electric field. Examples: melting of ice, boiling of water, sublimation, transition from one crystal modification to another.

2. Clausius-Clapeyron equation

We have two phases (phase 1 and phase 2) that are at equilibrium. Full differentials of molar Gibbs energies are equal $dG_1 = dG_2$

$dG_1= -S_1dT + V_1dP$, where S_1 and V_1 – molar entropy and molar volume of phase 1;

$dG_2= -S_2dT + V_2dP$, where S_2 and V_2 – molar entropy and molar volume of phase 2.

$dG_1 = dG_2$;

$-S_1dT + V_1dP =-S_2dT + V_2dP$

or $$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \qquad (1)$$

Considering that phases are at equilibrium and the temperature is constant we have:

$S_2-S_1 = \Delta_{tr}S = \Delta_{tr}H/T_{tr}$

Where $\Delta_{tr}H$ –heat of phase transition, absorbed (or released) when 1 mole of a substance from phase 1 transferes in phase 2 at temperature T.

Volume change when 1 mole of a substance from phase 1 transferes in phase 2 at temperature T is :

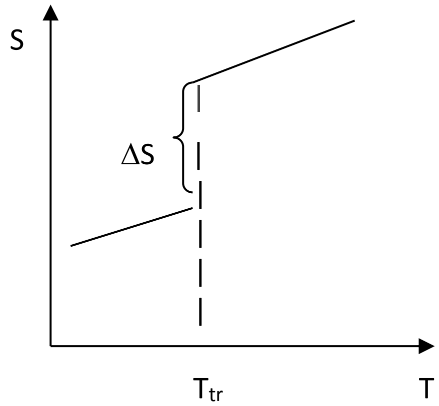
$V_2-V_1 = \Delta_{tr}V$

Then the equation (1) can be written as:

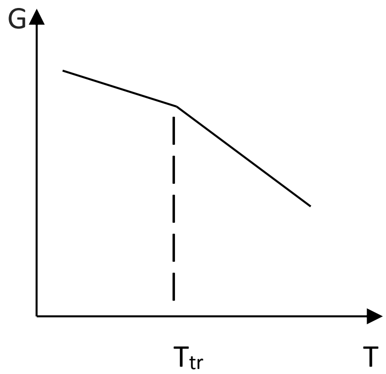
$$\frac{dP}{dT} = \frac{\Delta_{tr}H}{T_{tr}\cdot\Delta_{tr}V} \quad \text{or} \quad \frac{dP}{dT} = \frac{L}{T_{tr}\cdot\Delta_{tr}V}, \text{ where } L = \Delta_{tr}H \qquad (2)$$

Equation (2) is the Clausius-Clapeyron equation.

3. (a) entropy function as a function of temperature for a first order phase transition



(b) Gibbs function as a function of temperature for a first order phase transition.



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