**Phase Equilibrium**

Important criteria for phase equilibrium, α and β represent different phases (at constant T and P):

 

The slope of any coexistence curves, dP/dT gives **Clapeyron equation,**



Application of Clapeyron eqn. to the vaporization curve-the change of Pvap with temperature, **Clausius-Clapeyron** **equation**,



Integrated form of Clausius-Clapeyron eqn.



Indefinite integration of Clausius-Clapeyron eqn. gives,





More commonly, **Antoine equation** used to relate temperature to vapor pressures, ranging from 1 to 200 kPa



**Stability Criteria**

Derivation of the stability criteria for thermodynamic systems is important to understand if we are dealing with stable, neutral, metastable or unstable systems.

Below are the various equilibrium states that differ according to the stability.



According to the first figure, for a system at a *stable equilibrium*, its energy would be minimum. As it moves away from equilibrium, its energy increases. First and second derivatives can be defined as follows,

$$\frac{∂E}{∂z}=0 \frac{∂^{2}E}{∂z^{2}}>0 at z=z^{\*}$$

For a system at neutral equilibrium,

$$\frac{∂E}{∂z}=0 for all z$$

For a system at metastable equilibrium, the ball would can change its initial position in case of a large disturbance into a state of lower energy,

$$\frac{∂E}{∂z}=0 \frac{∂^{2}E}{∂z^{2}}>0 $$

For a system at unstable equilibrium, a small disturbance can change the initial position of the ball into a state of lower energy,

$$\frac{∂E}{∂z}=0 \frac{∂^{2}E}{∂z^{2}} <0 $$

**Mathematical Criteria for Stability of Thermodynamic systems**

|  |  |
| --- | --- |
| Variable | Stability |
| $$\hat{U}$$ | $$δ^{2}\hat{U}\geq 0$$ |
| $$\hat{S}$$ | $$δ^{2}\hat{S}\leq 0$$ |
| $$\hat{H}$$ | $$δ^{2}\hat{H}\geq 0$$ |
| $$\hat{A}$$ | $$δ^{2}\hat{A}\geq 0$$ |
| $$\hat{G}$$ | $$δ^{2}\hat{G}\geq 0$$ |

**Example**

We have liquid ethane at 1 bar pressure. What is the maximum temperature the liquid ethane can be heated to before it reaches the limit of stability? Use the van der Waals equation of state with the following data;

Tc= 305.4 K ; Pc= 48.8 bar ; Tb= 184.5 K (at 1.013 bar)

**References:**

Jefferson W. Tester and Michael Modell, “Thermodynamics and Its Applications”, 1996, Prentice Hall.

Ismail Tosun, “The Thermodynamics of Phase and Reaction Equilibria”, 2012, Elsevier.