Thermodynamics & Statistical Physics

Chapter 3. Phase transition of single-component system

Yuan-Chuan Zou
zouyc@hust.edu.cn

School of Physics, Huazhong University of Science and Technology

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- Total change of the entropy: $\Delta \tilde{S} = \Delta S + \Delta S_0$.
- Condition for equilibrium: $\Delta \tilde{S} < 0$, i.e., $\Delta S + \Delta S_0 < 0$, or $\delta \tilde{S} = 0, \delta^2 \tilde{S} < 0$.

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  $\Rightarrow \delta^2 S_0 \ll \delta^2 S$

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- $\delta^2\tilde{S} \simeq \delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V + \frac{\partial^2 S}{\partial V^2}(\delta V)^2$.

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- $\delta U = \left(\frac{\partial U}{\partial T}\right)_V \delta T + \left(\frac{\partial U}{\partial V}\right)_T \delta V$

Condition for the isolated uniform thermal equilibrium state and the stability criterion. (Continuing...)

- $$\delta^2\tilde{S} \simeq \delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V + \frac{\partial^2 S}{\partial V^2}(\delta V)^2.$$
$$= \left[\frac{\partial}{\partial U}\frac{\partial S}{\partial U}\delta U + \frac{\partial}{\partial V}\frac{\partial S}{\partial U}\delta V\right]\delta U + \left[\frac{\partial}{\partial U}\frac{\partial S}{\partial V}\delta U + \frac{\partial}{\partial V}\frac{\partial S}{\partial V}\delta V\right]\delta V,$$
$$\left(\mathrm{d}S = \frac{\mathrm{d}U + p\mathrm{d}V}{T} \Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}.\right)$$
- $$\delta^2 S = \left[\frac{\partial}{\partial U}\left(\frac{1}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{1}{T}\right)\delta V\right]\delta U + \left[\frac{\partial}{\partial U}\left(\frac{p}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{p}{T}\right)\delta V\right]\delta V = \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V.$$
- Convert to (T, V):
- $$\delta U = \left(\frac{\partial U}{\partial T}\right)_V \delta T + \left(\frac{\partial U}{\partial V}\right)_T \delta V = C_V \delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V.$$

Condition for the isolated uniform thermal equilibrium state and the stability criterion. (Continuing...)

$\boxed{\delta^2 S = \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V}$,

$\boxed{\delta U = C_V \delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V}$

- $\delta\frac{1}{T} = \left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V \delta T + \left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T \delta V$

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- $\delta\frac{1}{T} = \left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V \delta T + \left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T \delta V = -\frac{1}{T^2}\delta T.$

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$$= \left[p\left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V\right]\delta T$$

$$+ \left[p\left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\right]\delta V$$

Condition for the isolated uniform thermal equilibrium state and the stability criterion. (Continuing...)

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- $$\begin{aligned}\delta\frac{p}{T} &= \left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V \delta T + \left(\frac{\partial}{\partial V}\frac{p}{T}\right)_T \delta V \\ &= \left[p\left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V\right]\delta T \\ &\quad + \left[p\left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\right]\delta V \\ &= \left[-\frac{p}{T^2} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T \delta V\end{aligned}$$

Condition for the isolated uniform thermal equilibrium state and the stability criterion. (Continuing...)

$$\boxed{\delta^2 S = \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V},$$

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The stability criterion. (Continuing...)

- $$\delta^2\tilde{S} \simeq \delta^2 S = -\frac{1}{T^2}\delta T\left\{C_V\delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V\right\} + \left\{\frac{1}{T^2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\delta V\right\}\delta V$$

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- $$\delta^2\tilde{S} \simeq \delta^2 S = -\frac{1}{T^2}\delta T\left\{C_V\delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V\right\} + \left\{\frac{1}{T^2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\delta V\right\}\delta V = -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T(\delta V)^2 < 0.$$
- δT and δV is independent, and $(\delta T)^2 > 0$, $(\delta V)^2 > 0$.

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- δT and δV is independent, and $(\delta T)^2 > 0$, $(\delta V)^2 > 0$.
- $\therefore C_V > 0, \left(\frac{\partial p}{\partial V}\right)_T < 0.$

The stability criterion. (Continuing...)

- $\delta^2 \tilde{S} \simeq \delta^2 S = -\frac{1}{T^2}\delta T \left\{ C_V \delta T + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] \delta V \right\}$
  $+ \left\{ \frac{1}{T^2} \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] \delta T + \frac{1}{T} \left(\frac{\partial p}{\partial V} \right)_T \delta V \right\} \delta V$
  $= -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T} \left(\frac{\partial p}{\partial V} \right)_T (\delta V)^2 < 0.$
- δT and δV is independent, and $(\delta T)^2 > 0$, $(\delta V)^2 > 0$.
- $\therefore C_V > 0$, $\left(\frac{\partial p}{\partial V} \right)_T < 0$.
- Meaning of $C_V > 0$: suppose $T \gtrsim T_0$, small part loses heat, as $C_V > 0$, temperature decreases, system goes back to the equilibrium.

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- Meaning of $C_V > 0$: suppose $T \gtrsim T_0$, small part loses heat, as $C_V > 0$, temperature decreases, system goes back to the equilibrium.
- $\left(\frac{\partial p}{\partial V}\right)_T < 0$: imaging the small part shrinks, $\Delta V < 0$, as $(\frac{\partial p}{\partial V})_T < 0$, $\Delta p > 0$, $p > p_0$, small part expands.

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§3.2 Basic equations of open system

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- $\mathrm{d}\mu = V_m \mathrm{d}p - S_m \mathrm{d}T$ or $v\mathrm{d}p - s\mathrm{d}T$.

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- State parameter $(U^\alpha, V^\alpha, n^\alpha, T^\alpha)$, $(U^\beta, V^\beta, n^\beta, T^\beta)$
- Constraints:

$$\begin{cases} U^\alpha + U^\beta = \text{Const.} \\ V^\alpha + V^\beta = \text{Const.} \\ n^\alpha + n^\beta = \text{Const.} \end{cases}$$

§3.3 Equilibrium of single-component multi-phase system

- Considering isolated two-phase system, α, β.
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$\delta U^\alpha (\frac{1}{T^\alpha} - \frac{1}{T^\beta}) + \delta V^\alpha (\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}) - \delta n^\alpha (\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta})$

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- $\delta S = \delta S^\alpha + \delta S^\beta =$
$\delta U^\alpha(\frac{1}{T^\alpha} - \frac{1}{T^\beta}) + \delta V^\alpha(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}) - \delta n^\alpha(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}) = 0.$
- Equilibrium condition: $T^\alpha = T^\beta$ (thermodynamics), $p^\alpha = p^\beta$ (mechanics), $\mu^\alpha = \mu^\beta$ (phase).

Equilibrium of single-component multi-phase system

$$\delta S = \delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) + \delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) = 0.$$

- If the equilibrium condition is not satisfied, system proceeds in the direction of increasing the entropy.

Equilibrium of single-component multi-phase system

$$\delta S = \delta U^\alpha(\frac{1}{T^\alpha} - \frac{1}{T^\beta}) + \delta V^\alpha(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}) - \delta n^\alpha(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}) = 0.$$

- If the equilibrium condition is not satisfied, system proceeds in the direction of increasing the entropy.
- 1° $T^\alpha \neq T^\beta$, direction: $\delta U^\alpha(\frac{1}{T^\alpha} - \frac{1}{T^\beta}) > 0$. If $T^\alpha > T^\beta$, direction: $\delta U^\alpha < 0$. Energy $\alpha \to \beta$, from high T to low T.

Equilibrium of single-component multi-phase system

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- 2° If $p^\alpha > p^\beta$ ($T^\alpha = T^\beta$), direction: $\delta V^\alpha \frac{p^\alpha - p^\beta}{T} > 0$, i.e., $\delta V^\alpha > 0$, phase α (high pressure) expands.

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- 2° If $p^\alpha > p^\beta$ $(T^\alpha = T^\beta)$, direction: $\delta V^\alpha \frac{p^\alpha - p^\beta}{T} > 0$, i.e., $\delta V^\alpha > 0$, phase α (high pressure) expands.
- 3° If $\mu^\alpha > \mu^\beta$ $(T^\alpha = T^\beta)$, direction: $-\delta n^\alpha \frac{\mu^\alpha - \mu^\beta}{T}$, i.e., $\delta n^\alpha < 0$, matter changes phase from α (high μ, chemical potential) to β.

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§3.4 Properties of equilibrium of single-component multi-phase system – Phase diagram of water

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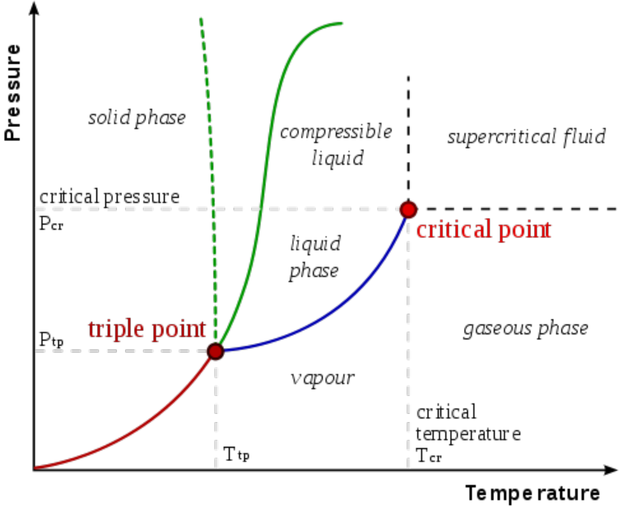

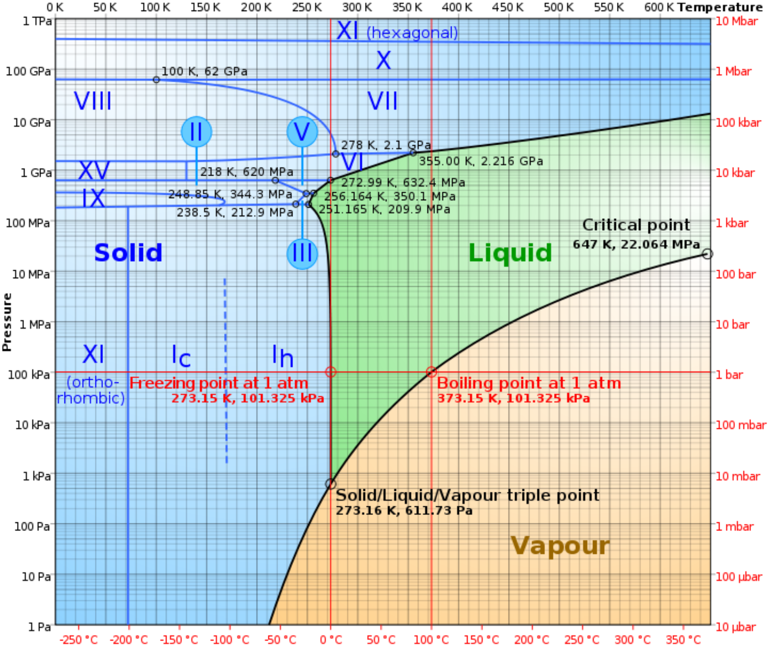

0 K
50 K
100 K
150 K
200 K
250 K
300 K
350 K
400 K
450 K
500 K
550 K
600 K
Temperature
1 TPa
100 GPa
10 GPa
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
100 Pa
10 Pa
1 Pa
Pressure
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
100 mbar
10 mbar
1 mbar
100 µbar
10 µbar
-250 °C
-200 °C
-150 °C
-100 °C
-50 °C
0 °C
50 °C
100 °C
150 °C
200 °C
250 °C
300 °C
350 °C
XI (hexagonal)
X
100 K, 62 GPa
VIII
VII
II
V
278 K, 2.1 GPa
355.00 K, 2.216 GPa
XV
VI
218 K, 620 MPa
272.99 K, 632.4 MPa
IX
248.85 K, 344.3 MPa
256.164 K, 350.1 MPa
238.5 K, 212.9 MPa
251.165 K, 209.9 MPa
Critical point
647 K, 22.064 MPa
Solid
III
Liquid
XI
(ortho-
rhombic)
Ic
Ih
Freezing point at 1 atm
273.15 K, 101.325 kPa
Boiling point at 1 atm
373.15 K, 101.325 kPa
Solid/Liquid/Vapour triple point
273.16 K, 611.73 Pa
Vapour

Properties of equilibrium of s-c multi-phase system

- For three phases coexistence:

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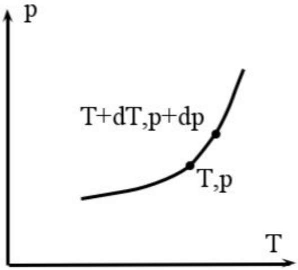

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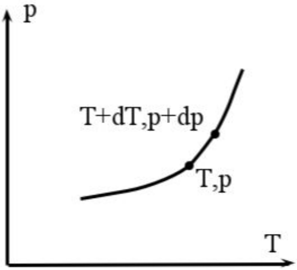
- For two phases coexistence curve:
  - $\mu^\alpha(T,p) = \mu^\beta(T,p)$,



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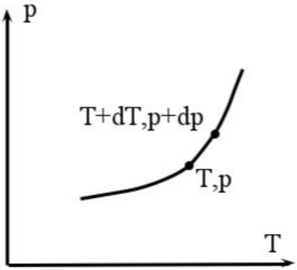

- $\mu^\alpha(T,p) = \mu^\beta(T,p)$,
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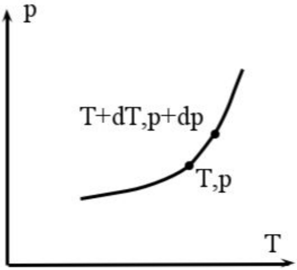
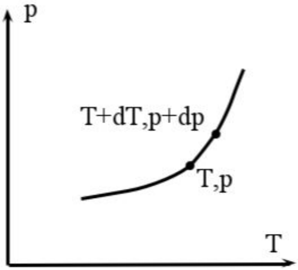


- For two phases coexistence curve:
  - $\mu^\alpha(T,p) = \mu^\beta(T,p)$,
    $\Rightarrow \mathrm{d}\mu^\alpha = \mathrm{d}\mu^\beta$.
  - $\because \mathrm{d}\mu = \frac{V}{n}\mathrm{d}p - \frac{S}{n}\mathrm{d}T = V_m\mathrm{d}p - S_m\mathrm{d}T$,

Properties of equilibrium of s-c multi-phase system



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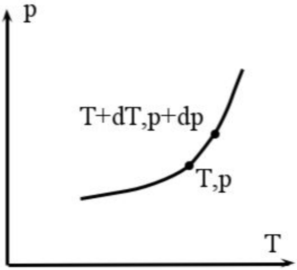

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  - $\therefore V_m^\alpha\mathrm{d}p - S_m^\alpha\mathrm{d}T = V_m^\beta\mathrm{d}p - S_m^\beta\mathrm{d}T \Rightarrow \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha}.$

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- Define L: Latent heat of phase change of 1 mol matter, then $L = T(S_m^\beta - S_m^\alpha)$.

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- $\therefore \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_m^\beta - V_m^\alpha)}$ called Clapeyron's equation.
- The slope of phase-boundary curve is available in theory then (phase-boundary curve comes from experiment).

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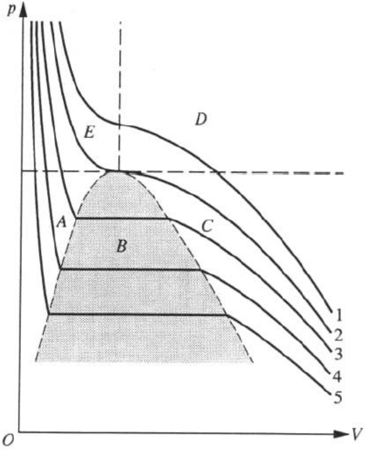

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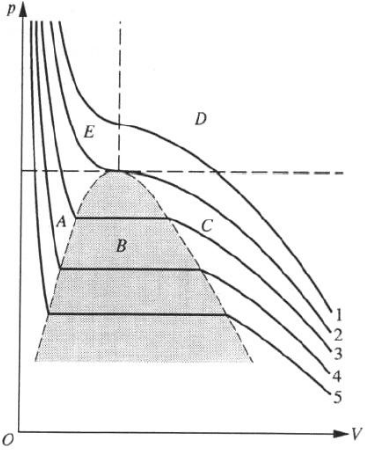

Stability condition: $\left(\frac{\partial p}{\partial V_m}\right)_T = 0, \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = 0, \left(\frac{\partial^3 p}{\partial V_m^3}\right)_T < 0.$

Provement of $\left(\frac{\partial p}{\partial V_m}\right)_T = 0, \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = 0, \left(\frac{\partial^3 p}{\partial V_m^3}\right)_T < 0.$

- Consider two-phase coexistence, but very close to the critical point.

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- $\Rightarrow \left(\frac{\partial p}{\partial V_m}\right)_T + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T \delta V_m = 0.$
- When $T \to T_c$, $\delta V_m \to 0$,

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- Consider two-phase coexistence, but very close to the critical point.
- Volume of liquid V_m, gas $V_m + \delta V_m$ (close to each other).
- Pressure: $p(V_m + \delta V_m, T) = p(V_m, T)$, while $p(V_m + \delta V_m, T) =$ $p(V_m, T) + \left(\frac{\partial p}{\partial V_m}\right)_T \delta V_m + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T (\delta V_m)^2$,
- $\Rightarrow \left(\frac{\partial p}{\partial V_m}\right)_T + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T \delta V_m = 0.$
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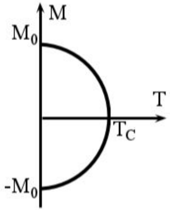

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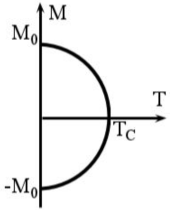

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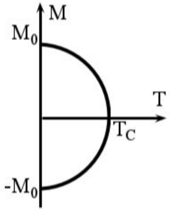

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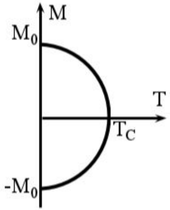

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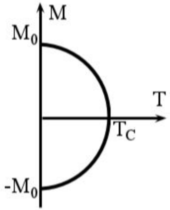

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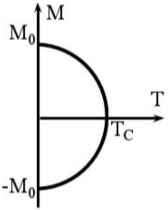

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- For isothermal and isochoric process, criterion for stable equilibrium: $\delta F = 0$, $\delta^2 F > 0$:

$$\frac{\partial F}{\partial M} = M(a + bM^2) = 0,$$

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