Advance Lecture on Joule-Thompson Experiment and Inversion Temperature

$$Ques:\ For\ VDW\ gas, prove:\ \mu_{JT} = \frac{1}{c_p}\left[\frac{2a}{RT} - b\right]$$

$$dH = T\,dS + V\,dP$$

$$dH = T\,dS + V\,dP \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Step1:

Using Maxwell's relation→ $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

$$\boxed{\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]}$$

Step2:

The Virial Equation of State (Low Density Approximation)

For **real gases**, we often write the equation of state as a **series expansion** in powers of $\frac{1}{V}$:

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots \quad \text{Eq.1}$$

- $B(T)$: **Second virial coefficient** (accounts for pairwise interactions)
- $C(T)$: Third virial coefficient (triplet interactions), etc.

For many practical cases, especially at **low pressures** (large V), we can truncate the series to just:

$$\frac{PV}{RT} \approx 1 + \frac{B(T)}{V} \quad \text{Eq.2}$$

Now take the **Van der Waals equation**:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

We want to expand this in powers of $\frac{1}{V}$ to extract the **virial coefficients.**

Use binomial expansion for $\frac{1}{V-b}$:

$$\frac{1}{V-b} = \frac{1}{V}\left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \cdots\right) \Rightarrow \frac{RT}{V-b} \approx \frac{RT}{V} + \frac{RTb}{V^2} + \cdots$$

So Van der Waals pressure becomes:

$$P = \frac{RT}{V} + \left(\frac{RTb - a}{V^2}\right) + \cdots$$

Multiply both sides by V and divide by RT:

$$\frac{PV}{RT} \approx 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} \quad \text{Eq.3}$$

Identify Second Virial Coefficient $B(T)$

$$\Rightarrow B(T) = b - \frac{a}{RT}$$

From Eq. 2→ $$V \approx \frac{RT}{P}\left(1 - \frac{B(T)P}{RT}\right) = \frac{RT}{P} - B(T) \quad \text{(to first order in } B/V\text{)}$$

Recall→ $$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

Step2:

Now substitute $V \approx \frac{RT}{P} - B(T)$:

Compute each piece:

1. $V \approx \frac{RT}{P} - B(T)$
2. $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} - \frac{dB}{dT}$

Now plug into the formula:

$$\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T\left(\frac{R}{P} - \frac{dB}{dT}\right) - \left(\frac{RT}{P} - B(T)\right)\right]$$

Distribute and simplify:

$$\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[\frac{RT}{P} - T\frac{dB}{dT} - \frac{RT}{P} + B(T)\right]$$

$$\boxed{\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T\left(\frac{\partial B}{\partial T}\right) - B(T)\right]}$$

Step3:

$$\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T\left(\frac{\partial B(T)}{\partial T}\right) - B(T)\right]$$

Let's plug in the expression for $B(T) = b - \frac{a}{RT}$:

First, compute derivative:

$$\frac{\partial B}{\partial T} = \frac{a}{RT^2}$$

Now:

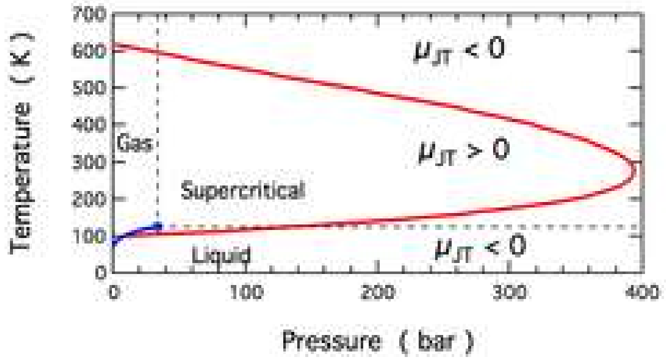
$$\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T \cdot \frac{a}{RT^2} - \left(b - \frac{a}{RT}\right)\right] = \frac{1}{C_P}\left[\frac{a}{RT} - b + \frac{a}{RT}\right] = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$$

$$\mu_{JT} = \frac{1}{c_p}\left[\frac{2a}{RT} - b\right]$$

This form is very handy:

- When $T\left(\frac{dB}{dT}\right) > B(T)$, $\mu_{\mathrm{JT}} > 0$ → **cooling** occurs.
- When $\mu_{\mathrm{JT}} = 0$, that gives the **inversion temperature**.

$$\mu_{\mathrm{JT}} = \frac{1}{C_P}\left[T\left(\frac{dB}{dT}\right) - B(T)\right]$$



Jule Thompson Coefficient for N_2

Set $\mu_{\mathrm{JT}} = 0$ to get the **inversion temperature** T_{inv}:

$$T_{\mathrm{inv}}\left(\frac{dB}{dT}\right) = B(T)$$

For Van der Waals gas:

$$B(T) = b - \frac{a}{RT} \quad \Rightarrow \quad \frac{dB}{dT} = \frac{a}{RT^2}$$

Plug in:

$$T \cdot \left(\frac{a}{RT^2}\right) = b - \frac{a}{RT} \quad \Rightarrow \quad \frac{a}{RT} = b - \frac{a}{RT} \quad \Rightarrow \quad \frac{2a}{RT} = b \quad \Rightarrow \boxed{T_{\mathrm{inv}} = \frac{2a}{Rb}}$$

This gives the **maximum inversion temperature** — again, valid in the **low-pressure limit**. (**Another relevant expression of μ_{JT} you may find here: https://en.wikipedia.org/wiki/Joule-Thomson_effect**