

$$\alpha_J = \left(\frac{\partial T}{\partial V} \right)_U$$

For $U = U(T, V)$, chain rule for partial derivatives (see PHY1116):

$$\begin{aligned} \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_U \left(\frac{\partial V}{\partial U} \right)_T &= -1 \\ \therefore \left(\frac{\partial T}{\partial V} \right)_U &= - \frac{(\partial U / \partial V)_T}{(\partial U / \partial T)_V} \end{aligned}$$

In general $(\partial U / \partial T)_V = C_V$ (see PHY1002)

In general $dU = TdS - pdV$ hence (divide by dV treating T as a constant) :

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p$$

$$\therefore \alpha_J = \left(\frac{\partial T}{\partial V} \right)_U = - \frac{1}{C_V} \left(T \left(\frac{\partial S}{\partial V} \right)_T - p \right)$$

3rd Maxwell relation : $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$ hence

$$\boxed{\alpha_J = - \frac{1}{C_V} \left(T \left(\frac{\partial p}{\partial T} \right)_V - p \right)}$$

$$\text{Similarly } \alpha_{JT} = \left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_p - V \right)$$

Hence calculate α_J and α_{JT} from the equation of state $p = p(V, T)$

e.g. n moles of ideal gas: $pV = nRT$ hence

$(\partial p / \partial T)_V = nR/V = p/T$ and $(\partial V / \partial T)_p = nR/p = V/T$ hence

$\alpha_J = \alpha_{JT} = \text{zero}$.

Real gas virial equation of state (see PHY1002):

$$\frac{pV}{nRT} = \left(1 + B(T) \left(\frac{n}{V} \right) + C(T) \left(\frac{n}{V} \right)^2 + D(T) \left(\frac{n}{V} \right)^3 + \dots \right)$$

Usually only first 2 terms are needed for good accuracy, hence

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V} \frac{d}{dT} \left(T + \left(\frac{n}{V} \right) B(T) T \right) = \frac{nR}{V} \left(1 + \left(\frac{n}{V} \right) \left(T \frac{dB(T)}{dT} + B(T) \right) \right)$$

$$\begin{aligned} \therefore T \left(\frac{\partial p}{\partial T} \right)_V - p &= \frac{nRT}{V} \left(1 + \left(\frac{n}{V} \right) (T + B(T)) \right) - \frac{nRT}{V} \left(1 + \left(\frac{n}{V} \right) B(T) \right) \\ &= R \left(\frac{nT}{V} \right)^2 \frac{dB(T)}{dT} \end{aligned}$$

$$\therefore \alpha_J = - \frac{R}{C_V} \left(\frac{nT}{V} \right)^2 \frac{dB(T)}{dT}$$

For all real gases $\frac{dB(T)}{dT} > 0$ (Mandl sec 5.5) hence $\alpha_J < 0$ i.e.

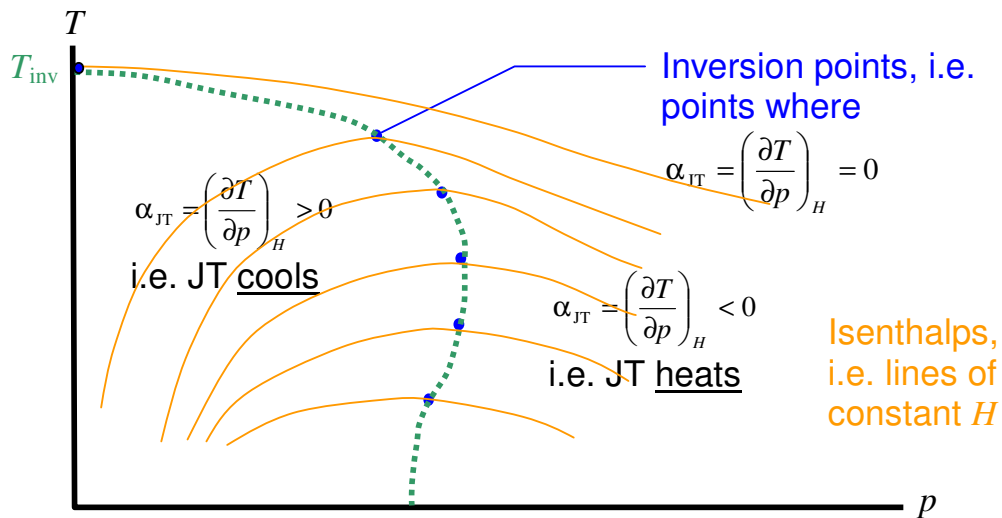
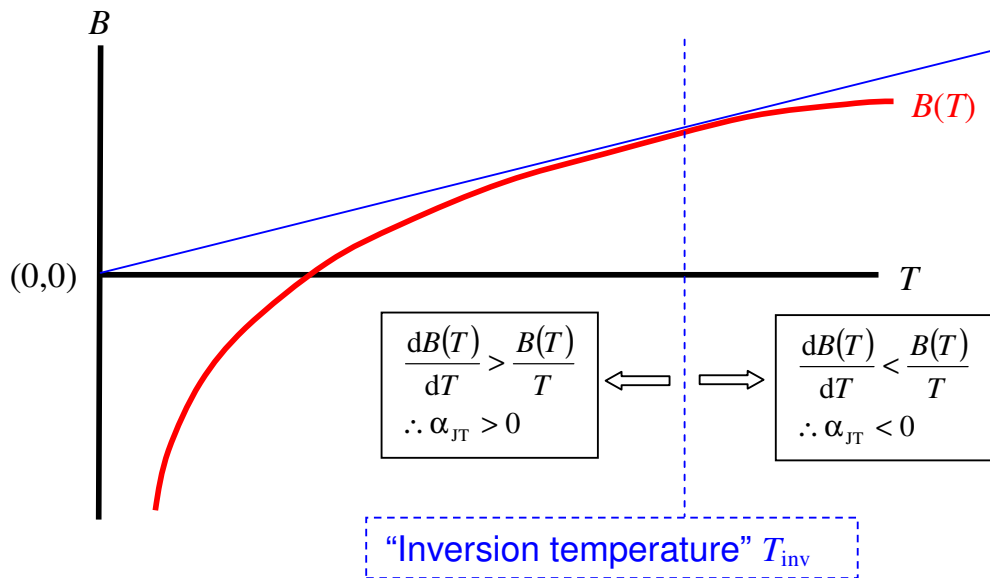
Joule expansion always cools.

In the limit of low pressure (i.e. $p \rightarrow 0$) (problem sheet 3 question 5)

$$\alpha_{JT} = \frac{n}{C_p} \left(T \frac{dB(T)}{dT} - B(T) \right)$$

Hence $\alpha_{JT} > 0$ (i.e. JT expansion cools) if $dB(T)/dT > B(T)/T$ but

$\alpha_{JT} < 0$ (i.e. JT expansion heats) if $dB(T)/dT < B(T)/T$.



T_{inv} (inversion temperature) is maximum temperature a gas can have and still be cooled by J-T expansion.

	O ₂	H ₂	N ₂	He ⁴
T_{inv} (K)	893	205	621	50

JT can cool (ultimately liquefy) O₂ and N₂ directly. Must pre-cool H₂ and He⁴ e.g. by heat exchange with liquefied N₂.

JT expansion is a step in the “Linde Liquefaction Cycle”. Very widely used to manufacture cryogenics, rocket fuel etc.