

Physics 415 - Lecture 15: Free Expansion and Throttling

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Summary

- Adiabatic Free Expansion: Gas expands into vacuum in isolated container ($V_1 \rightarrow V_2$).
 - $Q = 0, W = 0 \implies \Delta E = 0$. Energy is conserved: $E(T_1, V_1) = E(T_2, V_2)$.
 - For Ideal Gas: $E = E(T) \implies T_1 = T_2$.
 - In general: $(\partial T / \partial V)_E = (1/C_V)[p - T(\partial p / \partial T)_V]$. Sign depends on gas.
 - Entropy change: $\Delta S = \int_{V_1}^{V_2} (\partial S / \partial V)_E dV = \int_{V_1}^{V_2} (p/T) dV > 0$. Irreversible.

Example: van der Waals (vdW) Gas Free Expansion

The van der Waals equation of state (empirical) is:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where $v = V/\nu$ is the molar volume.

- a : correction to pressure due to attractive interactions between particles.
- b : reduction in available volume due to finite size of particles.

We need $(\partial T / \partial v)_E$ for molar quantities ($E = \nu \epsilon, V = \nu v, C_V = \nu c_v$).

$$\left(\frac{\partial T}{\partial v}\right)_E = \frac{1}{c_v} \left[p - T \left(\frac{\partial p}{\partial T}\right)_v \right]$$

From vdW eqn: $p = \frac{RT}{v-b} - \frac{a}{v^2}$.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

Substitute into the expression for $(\partial T / \partial v)_E$:

$$\left(\frac{\partial T}{\partial v}\right)_E = \frac{1}{c_v} \left[\left(\frac{RT}{v-b} - \frac{a}{v^2}\right) - T \left(\frac{R}{v-b}\right) \right] = \frac{1}{c_v} \left[-\frac{a}{v^2} \right] = -\frac{a}{c_v v^2}$$

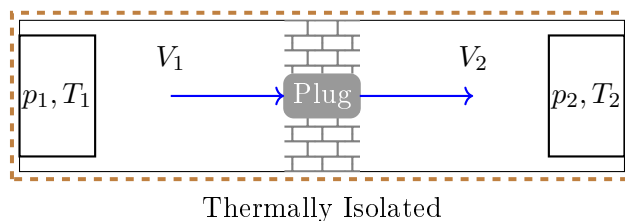
It can be shown (see Appendix) that c_v for a vdW gas is the same as for an ideal gas, $c_v = c_v(T)$ only (e.g., $\frac{3}{2}R$ for monatomic). Assuming c_v is constant over the temperature range:

$$\begin{aligned} \Delta T = T_2 - T_1 &= \int_{v_1}^{v_2} \left(\frac{\partial T}{\partial v}\right)_E dv = \int_{v_1}^{v_2} \left(-\frac{a}{c_v v^2}\right) dv \\ \Delta T &= -\frac{a}{c_v} \left[-\frac{1}{v} \right]_{v_1}^{v_2} = \frac{a}{c_v} \left(\frac{1}{v_2} - \frac{1}{v_1} \right) \end{aligned}$$

Since $V_2 > V_1 \implies v_2 > v_1$, the term $(1/v_2 - 1/v_1)$ is negative. Since $a > 0$ and $c_v > 0$, we have $\Delta T < 0$. Conclusion: A van der Waals gas cools upon free expansion ($T_2 < T_1$). This is due to the attractive interactions (term a); work must be done against these forces as the gas expands, using internal energy, thus lowering T .

Joule-Thomson Process (Throttling)

Consider gas flowing steadily from a region of constant pressure p_1 and temperature T_1 , through a porous plug (or other constriction), to a region of constant (lower) pressure p_2 . The entire system is thermally isolated.



Question: What is the final temperature T_2 ?

Analyze the process by considering a fixed amount (e.g., one mole) of gas passing through the plug. Initial state: Gas occupies volume V_1 at (p_1, T_1) with energy E_1 . Final state: Gas occupies volume V_2 at (p_2, T_2) with energy E_2 .

Work done during the process:

- Work done *on* the gas on the left side to push it through the plug: $W_{on,1} = p_1 V_1$.
- Work done *by* the gas on the right side as it expands into volume V_2 : $W_{by,2} = p_2 V_2$.
- Net work done *by* the gas: $W = W_{by,2} - W_{on,1} = p_2 V_2 - p_1 V_1$.

System is thermally isolated $\implies Q = 0$. First Law: $\Delta E = E_2 - E_1 = Q - W = 0 - (p_2 V_2 - p_1 V_1) = p_1 V_1 - p_2 V_2$. Rearranging:

$$E_1 + p_1 V_1 = E_2 + p_2 V_2$$

Since Enthalpy is $H = E + pV$, this means:

$$H_1 = H_2$$

The Joule-Thomson process occurs at constant enthalpy. The final state (T_2, p_2) is determined by $H(T_2, p_2) = H(T_1, p_1)$. (Compare with $E(T_2, V_2) = E(T_1, V_1)$ for free expansion).

Ideal Gas Case: Enthalpy $H = E + pV$. For ideal gas, $E = E(T)$ and $pV = \nu RT$. So $H = E(T) + \nu RT = H(T)$ only. The condition $H(T_1) = H(T_2)$ implies $T_1 = T_2$ (assuming H is monotonic with T). There is no temperature change for an ideal gas in a Joule-Thomson process.

General Case: How does T change with p at constant H ? We look at the Joule-Thomson coefficient μ_{JT} :

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p} \right)_H$$

From $dH = (\partial H / \partial T)_p dT + (\partial H / \partial p)_T dp$, if $dH = 0$:

$$\left(\frac{\partial T}{\partial p} \right)_H = - \frac{(\partial H / \partial p)_T}{(\partial H / \partial T)_p}$$

We know $(\partial H / \partial T)_p = C_p$. We need $(\partial H / \partial p)_T$. From $dH = TdS + Vdp$: Divide by dp at constant T :

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

Use Maxwell relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$:

$$\left(\frac{\partial H}{\partial p}\right)_T = T \left[-\left(\frac{\partial V}{\partial T}\right)_p \right] + V = V - T \left(\frac{\partial V}{\partial T}\right)_p$$

Substitute back into the expression for μ_{JT} :

$$\mu_{JT} = \left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p} \left[V - T \left(\frac{\partial V}{\partial T}\right)_p \right] = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right]$$

Using the thermal expansion coefficient $\alpha_p = \frac{1}{V}(\partial V/\partial T)_p \implies (\partial V/\partial T)_p = V\alpha_p$.

$$\mu_{JT} = \frac{1}{C_p} [T(V\alpha_p) - V] = \frac{V}{C_p} (T\alpha_p - 1)$$

The sign of μ_{JT} determines whether the gas cools ($\mu_{JT} > 0$) or heats ($\mu_{JT} < 0$) upon throttling (pressure drop, $dp < 0$).

- Cooling ($\Delta T < 0$ for $\Delta p < 0$) occurs if $\mu_{JT} > 0$, i.e., $T\alpha_p > 1$.
- Heating ($\Delta T > 0$ for $\Delta p < 0$) occurs if $\mu_{JT} < 0$, i.e., $T\alpha_p < 1$.
- $\mu_{JT} = 0$ defines the "inversion curve" in the (T, p) plane.

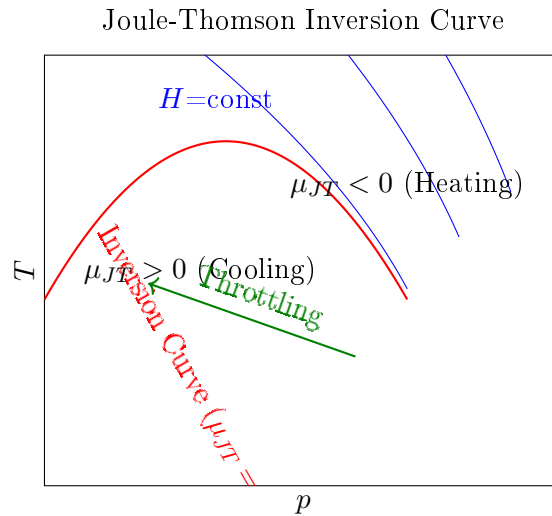
Ideal gas check: $\alpha_p = 1/T \implies T\alpha_p - 1 = 0 \implies \mu_{JT} = 0$.

Entropy Change: From $dH = TdS + Vdp$, at constant H , $TdS = -Vdp \implies dS = -(V/T)dp$.

$$\Delta S = S_2 - S_1 = \int_{p_1}^{p_2} \left(-\frac{V}{T} \right) dp$$

Since $p_2 < p_1$, $\Delta p = p_2 - p_1 < 0$. Also $V/T > 0$. $\Delta S > 0$. The Joule-Thomson process is irreversible.

Inversion Curve Diagram: Curves of constant enthalpy H in the (T, p) plane typically have the following qualitative form:



Inside the inversion curve (hatched region in source), $\mu_{JT} > 0$, and throttling leads to cooling. Outside, $\mu_{JT} < 0$, leading to heating. This process is used industrially to cool and liquefy gases by operating within the appropriate (T, p) region.

Appendix: C_V for van der Waals Gas

From general thermodynamics, we found $(\partial E/\partial V)_T = T(\partial p/\partial T)_V - p$. Using the molar vdW equation $(p + a/v^2)(v - b) = RT$, we calculated $(\partial p/\partial T)_v = R/(v - b)$. So, $(\partial \epsilon/\partial v)_T = T(\partial p/\partial T)_v - p = T(R/(v - b)) - p$. Substituting $p = RT/(v - b) - a/v^2$:

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = \frac{RT}{v - b} - \left(\frac{RT}{v - b} - \frac{a}{v^2}\right) = \frac{a}{v^2}$$

where $\epsilon = E/\nu$ is the molar internal energy. Integrating with respect to v :

$$\epsilon(T, v) = \int \frac{a}{v^2} dv = -\frac{a}{v} + f(T)$$

The molar energy is $\epsilon(T, v) = f(T) - a/v$. The total energy is $E(T, V) = \nu\epsilon = \nu f(T) - \nu^2 a/V$. The molar heat capacity is:

$$c_v = \left(\frac{\partial \epsilon}{\partial T}\right)_v = \frac{\partial}{\partial T}(f(T) - a/v) = f'(T)$$

So c_v depends only on T . To find $f(T)$, consider the dilute limit $v \rightarrow \infty$. In this limit, the vdW gas behaves like an ideal gas. $\epsilon(T, v \rightarrow \infty) = f(T)$. This must equal the molar energy of the corresponding ideal gas, $\epsilon^{ideal}(T)$. Let $c_v^{ideal}(T)$ be the molar specific heat of the ideal gas. Then $\epsilon^{ideal}(T) = \int c_v^{ideal}(T) dT + \text{const}$. So $f(T) = \epsilon^{ideal}(T)$. Then $c_v^{vdW}(T) = f'(T) = \frac{d\epsilon^{ideal}}{dT} = c_v^{ideal}(T)$. Conclusion: The molar heat capacity c_v for a van der Waals gas is the same function of T as for the corresponding ideal gas (e.g., $\frac{3}{2}R$ for monatomic). It does not depend on volume v .