

Physics 415 - Lecture 14: Thermodynamic Applications

February 21, 2025

Summary

- Fundamental Relation: $dE = TdS - pdV$.
- Maxwell Relations (derived from exactness of dE, dF, dH, dG):

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V & \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V & \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

- Heat Capacity: $dQ|_x = C_x dT$, and $C_x = T(\partial S/\partial T)_x$.
- Relation between heat capacities: $C_p - C_V = TV\alpha_p^2/K_T$, where
 - Thermal expansion coefficient: $\alpha_p = \frac{1}{V}(\partial V/\partial T)_p$
 - Isothermal compressibility: $K_T = -\frac{1}{V}(\partial V/\partial p)_T$

Check for Ideal Gas: $pV = \nu RT$.

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V} \left(\frac{\partial(\nu RT/p)}{\partial T}\right)_p = \frac{1}{V} \frac{\nu R}{p} = \frac{\nu R}{pV} = \frac{1}{T}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V} \left(\frac{\partial(\nu RT/p)}{\partial p}\right)_T = -\frac{1}{V} \left(-\frac{\nu RT}{p^2}\right) = \frac{\nu RT}{Vp^2} = \frac{pV}{Vp^2} = \frac{1}{p}$$

Substitute into the general relation:

$$C_p - C_V = TV \frac{(1/T)^2}{(1/p)} = \frac{Vp}{T} = \frac{\nu RT}{T} = \nu R$$

In molar terms: $c_p - c_v = R$. ✓

Third Law Implications for Response Functions

The Third Law ($S \rightarrow S_0$ as $T \rightarrow 0$, where S_0 is constant) has interesting implications for specific heats and other response functions at low temperatures.

- **Heat Capacities:** $C_V = T(\partial S/\partial T)_V$. Since S approaches a constant S_0 as $T \rightarrow 0$, the derivative $(\partial S/\partial T)_V$ must remain finite (or go to zero) for S to be well-behaved near $T = 0$. Therefore, $C_V \rightarrow 0$ as $T \rightarrow 0$. Alternatively, $S(T) - S(0) = \int_0^T (C_V(T')/T') dT'$. For this integral to converge at the lower limit $T' = 0$, we must have $C_V(T') \rightarrow 0$ as $T' \rightarrow 0$. Similarly, it follows that $C_p = T(\partial S/\partial T)_p \rightarrow 0$ as $T \rightarrow 0$.

- **Thermal Expansivity:** $\alpha_p = \frac{1}{V}(\partial V/\partial T)_p$. Using Maxwell Relation (4), $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$. As $T \rightarrow 0$, $S \rightarrow S_0$, where S_0 is independent of external parameters like p . Thus, $(\partial S/\partial p)_T \rightarrow (\partial S_0/\partial p)_T = 0$. Therefore, $\alpha_p \rightarrow 0$ as $T \rightarrow 0$.
- **Isothermal Compressibility:** $K_T = -\frac{1}{V}(\partial V/\partial p)_T$. This involves purely mechanical quantities and does not necessarily go to zero as $T \rightarrow 0$. It typically approaches a finite positive value.
- **Relation $C_p - C_V$:** $C_p - C_V = TV\alpha_p^2/K_T$. Assume typical low-temperature behavior based on QM models (e.g., for solids/fermions) $S \sim T^n$ for some $n > 0$. Then $C_V = T(\partial S/\partial T)_V \sim T^n$. Also, $(\partial S/\partial p)_T$. If $S(T, p) \approx S_0(p) + A(p)T^n$, then $(\partial S/\partial p)_T = S'_0(p) + A'(p)T^n$. For $S \rightarrow S_0$ (const), maybe $S'_0(p) = 0$ and $A'(p)$ finite? Let's assume $(\partial S/\partial p)_T \sim T^n$ as suggested by the source notes based on power counting. Then $\alpha_p = -(1/V)(\partial S/\partial p)_T \sim T^n$. $C_p - C_V \sim TV(T^n)^2/K_T \sim T^{2n+1}$ (assuming V, K_T finite at $T = 0$). The ratio $\frac{C_p - C_V}{C_V} \sim \frac{T^{2n+1}}{T^n} = T^{n+1}$. Since $n > 0$, this ratio $\rightarrow 0$ as $T \rightarrow 0$. The difference $C_p - C_V$ goes to zero faster than the specific heats themselves.

Note: Specific heats of the classical ideal gas ($C_V = \frac{3}{2}\nu R$, $C_p = \frac{5}{2}\nu R$) are constant and fail to satisfy $C_V \rightarrow 0$, $C_p \rightarrow 0$ as $T \rightarrow 0$. This is because classical theory breaks down at low T, where QM effects become important.

Reconstruction of Entropy and Energy

Take (T, V) as independent variables describing the macroscopic system. Question: What information do we need to reconstruct $S(T, V)$ and $E(T, V)$?

Entropy $S(T, V)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Using $C_V = T(\partial S/\partial T)_V$ and Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$:

$$dS = \frac{C_V(T, V)}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

To integrate this to find $S(T, V)$ relative to a reference state (T_0, V_0) , we need to know $C_V(T, V)$ and the equation of state $p = p(T, V)$ (to find the partial derivative $(\partial p/\partial T)_V$).

In fact, the dependence of C_V on V is determined by the equation of state:

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \frac{\partial}{\partial V} \left[T \left(\frac{\partial S}{\partial T}\right)_V \right]_T = T \frac{\partial}{\partial V} \left[\frac{\partial S}{\partial T} \right]_T = T \frac{\partial}{\partial V} \left[\frac{\partial S}{\partial T} \right]_T \\ &= T \frac{\partial}{\partial T} \left[\left(\frac{\partial S}{\partial V}\right)_T \right]_V \end{aligned}$$

Using Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial}{\partial T} \left[p T^2 \right]_V\right)$$

So, if $C_V(T, V_0)$ is known at a single volume V_0 (e.g., from experiment or theory), we can find $C_V(T, V)$ at any other volume using the equation of state $p(T, V)$:

$$C_V(T, V) = C_V(T, V_0) + \int_{V_0}^V \left(\frac{\partial C_V}{\partial V'}\right)_T dV' = C_V(T, V_0) + \int_{V_0}^V T \left(\frac{\partial}{\partial T} \left[p(T, V') T^2 \right]_V\right) dV'$$

Therefore, $S(T, V)$ can be reconstructed from knowledge of the equation of state $p(T, V)$ and the heat capacity $C_V(T)$ at a single volume (or density). Explicitly, integrating dS :

$$S(T, V) - S(T_0, V_0) = \int_{(T_0, V_0)}^{(T, V)} \left[\frac{C_V(T', V')}{T'} dT' + \left(\frac{\partial p(T', V')}{\partial T'} \right)_V dV' \right]$$

A convenient integration path is $(T_0, V_0) \rightarrow (T_0, V) \rightarrow (T, V)$:

$$S(T, V) - S(T_0, V_0) = \int_{V_0}^V \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V dV' + \int_{T_0}^T \frac{C_V(T', V)}{T'} dT'$$

Internal Energy $E(T, V)$: From $dE = TdS - pdV$, substitute $dS = (C_V/T)dT + (\partial p/\partial T)_V dV$:

$$dE = T \left[\frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV \right] - pdV$$

$$dE = C_V dT + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV$$

Comparing with $dE = (\partial E/\partial T)_V dT + (\partial E/\partial V)_T dV$:

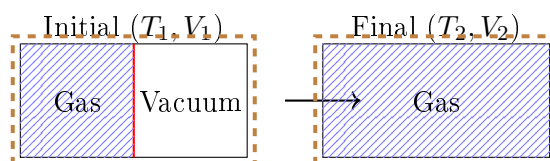
$$\left(\frac{\partial E}{\partial T} \right)_V = C_V(T, V)$$

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

(This confirms the relation $(\partial E/\partial V)_T = T^2(\partial(p/T)/\partial T)_V$ derived earlier). $E(T, V)$ can again be obtained by integration from a reference state (T_0, V_0) using knowledge of $C_V(T)$ (at some reference volume) and the equation of state $p(T, V)$.

Free Expansion (Joule Expansion)

This example illustrates some general methods in macro thermodynamics. Consider a gas initially in equilibrium at temperature T_1 and volume V_1 in one side of an insulated container. The other side is evacuated. The partition is removed, and the gas expands freely into the total volume V_2 . The system is thermally isolated throughout.



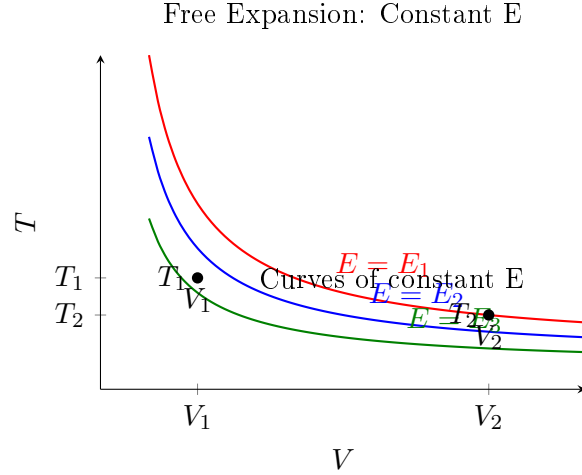
Question: What is the final temperature T_2 , after the system reaches equilibrium in volume V_2 ?

- System is thermally isolated $\implies Q = 0$.
- System does no work on surroundings (expansion into vacuum) $\implies W = 0$.
- First Law: $\Delta E = Q - W = 0$.
- The internal energy of the system does not change: $E(T_1, V_1) = E(T_2, V_2)$.

This is an implicit equation for T_2 .

Ideal Gas Case: For an ideal gas, $E = E(T)$ only (independent of V). The condition $E(T_1) = E(T_2)$ implies $T_1 = T_2$. For an ideal gas, there is no change in temperature in a free expansion.

General Case: We need to know $E(T, V)$ to determine T_2 . The process itself (removing partition) is highly irreversible, not quasi-static. However, the initial and final states are equilibrium states. We can relate them by the condition $E = \text{constant}$.



The initial state (T_1, V_1) and final state (T_2, V_2) lie on the same curve of constant E .

To see how T changes with V at constant E , consider the derivative $(\partial T/\partial V)_E$ (Joule coefficient μ_J). From $dE = (\partial E/\partial T)_V dT + (\partial E/\partial V)_T dV$, if $dE = 0$:

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{1}{C_V} \left(\frac{\partial E}{\partial V}\right)_T$$

We previously showed (from dS exactness) that $(\partial E/\partial V)_T = T(\partial p/\partial T)_V - p$.

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T}\right)_V - p \right] = \frac{1}{C_V} \left[p - T \left(\frac{\partial p}{\partial T}\right)_V \right]$$

Using Maxwell relation $(\partial p/\partial T)_V = (\partial S/\partial V)_T$:

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V} \left[p - T \left(\frac{\partial S}{\partial V}\right)_T \right]$$

We also showed $(\partial p/\partial T)_V = \alpha_p/K_T$.

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V} \left(p - \frac{T\alpha_p}{K_T} \right)$$

For ideal gas, $\alpha_p = 1/T$, $K_T = 1/p$, so $p - T\alpha_p/K_T = p - T(1/T)/(1/p) = p - p = 0$. So $(\partial T/\partial V)_E = 0$. For a finite change, we integrate along a (fictitious) quasi-static path of constant E :

$$T_2 - T_1 = \int_{V_1}^{V_2} \left(\frac{\partial T}{\partial V}\right)_E dV$$

In principle, free expansion could be used to cool (or heat) non-ideal gases, but the effect $(\partial T/\partial V)_E$ is usually very small.

Entropy Change in Free Expansion: The process is irreversible, so $\Delta S_{tot} > 0$. Since the system is isolated, $\Delta S_{tot} = \Delta S_{system}$. We expect $\Delta S > 0$. To calculate $\Delta S = S(T_2, V_2) -$

$S(T_1, V_1)$, we use the fact that S is a state function and devise any reversible path between the initial and final states. Since E is constant, the initial and final states lie on a curve $E(T, V) = E_1$. We can integrate dS along this curve. From $dE = TdS - pdV$, if $dE = 0$, then $TdS = pdV \implies dS = (p/T)dV$ along a path of constant E .

$$\Delta S = S(E_1, V_2) - S(E_1, V_1) = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V} \right)_E dV'$$

We need $(\partial S/\partial V)_E$. From $dS = (1/T)dE + (p/T)dV$, we have $(\partial S/\partial V)_E = p(E, V)/T(E, V)$.

$$\Delta S = \int_{V_1}^{V_2} \frac{p(E_1, V')}{T(E_1, V')} dV'$$

Ideal Gas Case: $E = E(T)$, so constant E implies constant $T = T_1$. $p/T = N/V$.

$$\Delta S = \int_{V_1}^{V_2} \frac{N}{V'} dV' = N[\ln V']_{V_1}^{V_2} = N \ln \left(\frac{V_2}{V_1} \right)$$

Since $V_2 > V_1$ (expansion), $\ln(V_2/V_1) > 0$, so $\Delta S > 0$. The entropy increases, confirming the process is irreversible.