Heat Capacities

The heat capacity C_X is the rate heat must be added to a system to increase its temperature when X is held fixed:

$$C_X = T \left(\frac{\partial S}{\partial T} \right)_X .$$

The fundamental thermodynamic relation for a gas with a fixed number of particles is

$$dU = TdS - PdV.$$

A. Express C_V as a partial derivative of U.

constant $V \implies dU = TdS$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The thermodynamic potential that determines the equilibrium state of a system whose pressure P is held fixed is the enthalpy: $H = U + PV$.
B. Determine the thermodynamic relation for H.

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= (TdS - PdV) + PdV + VdP \\ &= TdS + VdP \end{aligned}$$

C. Express C_P as a partial derivative of H.

constant $P \implies dH = TdS$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

The thermodynamic variables for a monatomic ideal gas in equilibrium satisfy

$$PV = NkT, \qquad U = \tfrac{3}{2}NkT.$$

D. Determine the enthalpy H as a function of N, T, and V.

$$H = U + PV = \tfrac{3}{2}NkT + NkT = \tfrac{5}{2}NkT$$

E. Determine the heat capacities C_V and C_P by evaluating partial derivatives of U and H with respect to T.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{d}{dT}\left(\tfrac{3}{2}NkT\right) = \tfrac{3}{2}Nk$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{d}{dT}\left(\tfrac{5}{2}NkT\right) = \tfrac{5}{2}Nk$$

The entropy for a monatomic ideal gas in the microcanonical ensemble is

$$S(E,V,N) = Nk\left[\log\frac{(V/N)(4\pi mE/3N)^{3/2}}{(2\pi\hbar)^3} + \frac{5}{2}\right].$$

F. Express S as a function of N, V, and P.

$$E = U = \tfrac{3}{2}NkT = \tfrac{3}{2}PV$$

$$S = Nk\left[\log\frac{(V/N)(4\pi m\cdot PV/N)^{3/2}}{(2\pi\hbar)^3} + \frac{5}{2}\right]$$

An adiabatic process is one in which no heat flows so the entropy is constant. There is a number γ such that PV^γ is constant for an adiabatic process.
G. Use the expression for S in part F to determine the adiabatic constant γ for a monatomic ideal gas. Verify that $\gamma = C_P/C_V$.

$$\text{constant } S \implies \text{constant } V(PV)^{3/2}$$

$$\implies \text{constant } \left[V(PV)^{3/2}\right]^{2/3} = PV^{5/3}$$

$$\implies \gamma = \tfrac{5}{3}$$

$$C_P/C_V = \left(\tfrac{5}{2}NkT\right)/\left(\tfrac{3}{2}NkT\right) = \tfrac{5}{3}$$