

HW #1 solutions (2025)

①. $S = k (NVE)^{1/3}$, yielding

$$\left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{k}{3} \left(\frac{NV}{E^2} \right)^{1/3}.$$

at equilibrium,

$$\frac{N^A V^A}{(E^A)^2} = \frac{N^B V^B}{(E^B)^2}, \text{ where}$$

$$E^A + E^B = E = \text{const.}$$

Thus, $(E - E^A)^2 N^A V^A = (E^A)^2 N^B V^B,$

$$\left(\frac{E^A}{E - E^A} \right)^2 = \frac{N^A V^A}{N^B V^B}, \text{ or}$$

$$\left\{ \begin{array}{l} E^A = \frac{E_0}{1 + \sqrt{\frac{N^B V^B}{N^A V^A}}}, \\ E^B = \frac{E_0}{1 + \sqrt{\frac{N^A V^A}{N^B V^B}}}. \end{array} \right.$$

②.

(a) at $p = \text{const}$,

$$ds = C_p \frac{dT}{T}$$

Then $dE = \underbrace{C_p dT}_{TdS} - p dV = (C_p - Nk_B) dT$

$p dV = Nk_B dT$
for ideal gas @ $p = \text{const}$

On the other hand, $E = E(T)$ for an ideal gas:

$$dE = C_v dT \quad \left(\frac{\partial E}{\partial T} \right)_v$$

$\leftarrow dE = dQ$ since $V = \text{const}$,
no mechanical work
is done on the
system

can also show
formally that
 $\left(\frac{\partial E}{\partial V} \right)_T = 0$

Thus, $C_v = C_p - Nk_B \Rightarrow C_p - C_v = \underline{\underline{Nk_B}}$

(b) Now we consider the
adiabatic process: $ds = 0$.

We have $dE = C_v dT = -p dV$.

The equation of state now gives

$$dT = \frac{1}{Nk_B} d(pV) = \frac{1}{C_p - C_v} (p dV + V dp), \text{ or}$$

$$p dV + V dp = - \frac{C_p - C_v}{C_v} p dV,$$

$$V dp = - \frac{C_p}{C_v} p dV.$$

Finally, $\left(\frac{\partial p}{\partial V} \right)_S = - \frac{C_p}{C_v} \frac{p}{V} = - \gamma \frac{p}{V}$, as desired

(c) Use the equation of state again:

$$V = \frac{Nk_B T}{P} \text{ gives}$$

$$dV = Nk_B \left(\frac{dT}{P} - \frac{T}{P^2} dP \right).$$

Using $VdP = -\gamma P dV$, we obtain:

$$\gamma Nk_B T \frac{dP}{P} = \cancel{\gamma Nk_B T \frac{dT}{P} - \gamma Nk_B T \frac{T}{P^2} dP}, \text{ or}$$
$$\gamma Nk_B dT + \frac{Nk_B T}{P} dP$$

$$\frac{dP}{P}(1-\gamma) + \gamma \frac{dT}{T} = 0.$$

Since $\gamma = \text{const}$,

$$d \log (P T^{\gamma/(1-\gamma)}) = 0, \text{ or}$$

$$P T^{\frac{\gamma}{1-\gamma}} = \text{const for an adiabatic process}$$

③. $\gamma = \frac{C_p}{C_v}$, where

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p, \quad C_v = T \left(\frac{\partial S}{\partial T} \right)_v.$$

Using $\begin{cases} \left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_s \left(\frac{\partial p}{\partial S} \right)_T = -1, \\ \left(\frac{\partial S}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_s \left(\frac{\partial v}{\partial S} \right)_T = -1, \end{cases}$

we obtain:

$$\gamma = \frac{\left(\frac{\partial T}{\partial v} \right)_s \left(\frac{\partial v}{\partial S} \right)_T}{\left(\frac{\partial T}{\partial p} \right)_s \left(\frac{\partial p}{\partial S} \right)_T} \uparrow \frac{\left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial v}{\partial S} \right)_T}{\left(\frac{\partial T}{\partial p} \right)_s \left(\frac{\partial v}{\partial T} \right)_s} \quad \text{④}$$

Maxwell relations

$$\text{④} \quad \frac{\left(\frac{\partial v}{\partial p} \right)_T}{\left(\frac{\partial v}{\partial p} \right)_s} = \frac{\kappa_T}{\kappa_s}, \quad \text{where}$$

$$\begin{cases} \kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T, \\ \kappa_s = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_s. \end{cases}$$

In more detail, recall that

$$dE = TdS - pdV$$

$$\left(\frac{\partial E}{\partial S}\right)_V - \left(\frac{\partial E}{\partial V}\right)_S \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (1)$$

$$dH = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial H}{\partial P}\right)_S \Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad (2)$$

Then

$$\gamma = - \frac{\left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial p}{\partial S}\right)_T} = \frac{\left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial p}{\partial S}\right)_T} \quad (1)$$

$$\left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_S = -1$$

$$\begin{aligned} \textcircled{=} \frac{\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_S} &= \frac{\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial V}{\partial T}\right)_S}, \text{ as desired} \\ &\quad \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial P}\right)_S \underset{\substack{\uparrow \\ (2)}}{=} \left(\frac{\partial V}{\partial T}\right)_S \end{aligned}$$