

This homework is based on some general principles of the thermodynamics of ideal gases. You will require an understanding of the ideas covered in Chapters 19 and 20 of Mazur.

## SHORT PROBLEMS

### Problem S1: Isentropic Work (numbers can be randomized)

1 mol of a diatomic ideal gas undergoes an isentropic process that takes it from a state  $(P_A, V_A, T_A)$  to a state  $(P_B, V_B, T_B)$ . If  $P_A = 1$  Pa,  $V_A = 1$  L and  $V_B = 2$  L, then find the initial temperature  $T_A$ , the final temperature  $T_B$ , and the work done by the gas  $\Delta W_{A \rightarrow B}$ .

#### Solution:

$$\gamma = \frac{7}{5}, PV^\gamma = C.$$

$$\text{First, one has } T_A = \frac{P_A V_A}{R}, P_B = P_A \left( \frac{V_A}{V_B} \right)^\gamma \implies T_B = \frac{P_B V_B}{R} = \frac{P_A V_A^\gamma}{R V_B^{\gamma-1}}.$$

$$\text{Next, } PV^\gamma = C \implies P = C V^{-\gamma} \implies \Delta W_{A \rightarrow B} = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} C V^{-\gamma} dV = (P_A V_A^\gamma) \left( \frac{V_B^{1-\gamma} - V_A^{1-\gamma}}{1-\gamma} \right)$$

### Problem S2: Triatomic Gas

The value of  $\gamma$  for a triatomic gas is equal to (a) — at low temperatures and (b) — at high temperatures.

$$\text{Solution: } \gamma = 1 + \frac{2}{d}. \text{ (a) } d = 6, \gamma = \frac{4}{3} \text{ (b) } d = 9, \gamma = \frac{11}{9}.$$

### Problem S3: Isothermal Expansion (numbers can be randomized)

Two identical thermally insulated spherical tanks, A and B, are connected by a closed valve. Initially tank A contains 10 mol of an ideal diatomic gas, tank B is evacuated. If the valve is then opened and the gas expands isothermally from A to B, what is the change in the entropy of the gas?

#### Solution:

$$[\Delta S]_{T,N} = N \log \left[ \frac{V_f}{V_i} \right] = N k_B \log 2$$

$$\text{For } N = 10 \cdot N_A = 6.022 \times 10^{24} \text{ this gives } [\Delta S]_{T,N} = 4.17 \times 10^{24} k_B.$$

### Problem S4: Temperature-dependent Specific Heat (numbers can be randomized)

A cryogenic substance is found to have a specific heat capacity (at constant volume)  $c_V$  that varies with temperature according to  $c_V = AT^2$ , where  $A$  is an empirically derived constant with units  $\frac{J}{K^3 kg}$ . If 231 J of energy must be transferred thermally (at constant volume) to an 8000 mg sample of this substance to raise the temperature of the sample from 1.00 to 6.00 K, what is the value of  $A$ ?

#### Solution

$$\text{Let } M = 0.008 \text{ kg be the total mass of the substance. Then } \Delta Q = \int_{T_1}^{T_2} M A T^2 dT = \frac{M A (T_2^3 - T_1^3)}{3} \implies \\ \implies A = \frac{3 \Delta Q}{M (T_2^3 - T_1^3)} = 402.91 \left[ \frac{J}{K^3 kg} \right]$$

## LONG PROBLEMS:

### Problem L1: Extensivity

You are told that  $S(N, V, T)$  (Eq 20.39 in Mazur) is supposed to be an extensive function of  $N$  and  $V$ , i.e.,  $S(\lambda N, \lambda V, T) = \lambda S(N, V, T)$ , for any  $\lambda$ . Based on this information, what term (that depends only on  $N$  and is independent of  $V$  and  $T$ ) *must* the “constant” in Eq 20.39 in Mazur contain? What other kinds of terms *can* it contain?

Be sure to check that the previously known result:  $(S, N) = \text{constants} \implies T^{\frac{d}{2}}V = \text{constant}$  is still valid.

Once you have written these terms down, you will be (almost) fully equipped to deal with problems where  $N$  itself can change during a process. You can calculate changes in entropy due to changes in number of particles at fixed volume and temperature, say.

### Solution

$S(N, V, T)$  is given by:

$$\begin{aligned} S(N, V, T) &= N \log V + \frac{d}{2} N \log T + C(N) \\ \implies S(\lambda N, \lambda V, T) &= [\lambda N] \log [\lambda V] + \frac{d}{2} [\lambda N] \log T + C(\lambda N) \end{aligned}$$

The  $\log V$  term makes this function non-extensive, unless the “constant” term ( $C(N)$ ) contains  $-N \log N$ . In addition it may contain any term linear in  $N$ . In short:

$$\begin{aligned} C(N) &= -N \log N + \alpha N \\ \implies S(N, V, T) &= N \log \left( \frac{V}{N} \right) + \frac{d}{2} N \log T + \alpha N \end{aligned}$$

for some numerical constant  $\alpha$ . This correction can be thought of as coming in part from a Stirling approximation for  $\frac{1}{N!}$  which is crucial in order to avoid situations like the “Gibbs’ Paradox” (look it up). Notice how there is no arbitrary constant offset. This is a consequence of the third law of thermodynamics (Nernst’s theorem) which you will encounter later on.

Also

$$\begin{aligned} (dS)_N &= 0 \\ \implies 0 &= N \left( \frac{dV}{V} + \frac{d}{2} \frac{dT}{T} \right) \implies T^{\frac{d}{2}}V = \text{constant} \end{aligned}$$

as expected.

**Problem L2: Compressibility**

One usually defines the isothermal and adiabatic compressibilities of a thermodynamic system as:

$$\text{Isothermal Compressibility} = \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N}$$

$$\text{Adiabatic Compressibility} = \kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S,N}$$

For a monoatomic ideal gas, show that:

$$\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V}$$

This explains, quantitatively, the discrepancy in the speed of sound in air that you explored in an earlier assignment. As it turns out, this is a universal theorem that holds for arbitrary systems, although proving it requires some gymnastics involving the mathematics of partial derivatives that have not been introduced to you yet.

**Notation:** If you are given a function  $A(X, Y, Z)$ , then  $\left(\frac{\partial A}{\partial Y}\right)_{X,Z}$  means “take the derivative of  $A$  with respect to  $Y$  while holding  $X$  and  $Z$  fixed (i.e., pretend as though  $X$  and  $Z$  are constants)”.

**Solution:**

We have (with  $\gamma = \frac{5}{3}$ ), for the case when  $(S, N)$  are constant:  $PV^\gamma = C \implies V = C'P^{-\frac{1}{\gamma}}$ , and when  $(T, N)$  are constant:  $PV = C'' \implies V = C'''P^{-1}$ . Hence  $\kappa_S = \frac{1}{\gamma}$  and  $\kappa_T = 1$ . Thus  $\frac{\kappa_T}{\kappa_S} = \gamma = \frac{5}{3}$ . Using  $C_V = \frac{3}{2}Nk_B$ ,  $C_P = C_V + Nk_B = \frac{5}{2}Nk_B$ , the equality of the ratios follows.