

Department of Physics, The Chinese University of Hong Kong  
PHYS 5130 Principles of Thermal and Statistical Physics (M.Sc. in Physics)

**Problem Set 3**

**Due: 17 October 2020 (Saturday); “T+2” = 19 October 2020 (Monday) (20% discount)**

You should **submit your work in one PDF file via Blackboard** to the appropriate folder no later than 23:59 on the due date. Late submission before the T+2 due date will be marked with a 20% discount on the score. Follow Blackboard → Course Contents → Problem Set → **Problem Set 3 Submission Folder**.

*Please work out the steps of the calculations in detail. Discussions among students are highly encouraged, yet it is expected that we do your homework independently.*

**This Problem Set is related to the 2nd Law of Thermodynamics, the thermodynamic potentials, and other selected topics. Total 110 Points.**

**3.0 Reading Assignment.** This is a guide to our progress. **No need to hand in anything.** By the end of Week 5, we finished our coverage on the basic principles of thermodynamics, including the laws of thermodynamics, the central equation and its many consequences, thermodynamic potentials (useful under different conditions), Maxwell relations (to relate “strange derivatives” to measurable quantities) and some general relationships. Our purpose is to acquire sufficient thermodynamics to learn and appreciate statistical mechanics efficiently and effectively. For example, we can focus on the meaning of what Boltzmann said in his formula  $S = k \ln W$  and once we obtain  $S(U, V, N)$  following Boltzmann recipe, we could obtain  $T$ ,  $P$ , and  $\mu$  by taking appropriate derivatives because we learned from thermodynamics that  $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$  (central equation). We need not spend time on finding the equations (what to “d”). This is the strategy in our course. We don’t pretend that we don’t know thermodynamics (I hope that we DO). We will make use of general relations, e.g. once  $C_V$  is obtained by statistical mechanics,  $C_P$  follows.

We certainly cannot cover every topic in thermodynamics. It is a subject with a few basic laws that can be applied to systems of macroscopic scale (it means the system consists of many particles in the microscopic scale, say atoms and molecules, but thermodynamics needs not know the microscopic physics). The wide range of applications make it hard to cover anything in one (even two) courses. References (a list of books) are given to direct you to books of different focuses - the classics, physical chemistry, engineers, and materials science. It is hoped that with the essential background, one can cut into an application without any problem.

**3.1 (12 points) Engine operating between two baths**

An engine works between a bath at a higher temperature of 300 K and a bath at a lower temperature of 150 K. Its efficiency is 0.25. It rejects 750 J to the colder bath.

- (a) **How much heat** does the engine take from the hotter bath?
- (b) **Demonstrate** the Clausius inequality for this engine using explicit numbers.

**3.2 (22 points) Calculate  $\Delta S$  in separate steps across phases**

Consider one kilogram of  $H_2O$ . Let’s start from 200 K at which it is in the ice form. It is heated up to a temperature of 400 K at which it is in the superheated steam form. Therefore, this kilogram of  $H_2O$  goes through the heating up of ice, the melting of ice into water at 273 K, heating up the water, boiling at 373 K, and heating up the steam. **Calculate the total entropy change** in the whole process.

The following data are given:  $c_P^{(ice)} = 2.108 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (kilojoule per kilogram per Kelvin),  $c_P^{(water)} = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ , and  $c_P^{(steam)} = 1.996 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . The latent heat of fusion of ice  $\ell_{SL} = 334 \text{ kJ kg}^{-1}$  (kilojoule per kilogram) at 273 K. The latent heat of vaporization of water  $\ell_{LV} = 2260 \text{ kJ kg}^{-1}$  at 373 K. If you find some numbers doubtful, check them out in google.

- 3.3 (25 points) Consider a system consisting of 1,000 moles of a monatomic ideal gas. In a state A, it has a pressure of  $10^6 \text{ Nm}^{-2}$  (newton per meter squared) and a volume of  $2 \text{ m}^3$ . The system is taken through a cycle as shown in Figure 1. The curve AB is a reversible adiabatic expansion, BC is a isobaric (constant pressure) compression, and CA is an isochoric (constant volume) increase of pressure. There are unknowns marked in the Figure. Recall that  $c_V = 3R/2$  and  $c_P = 5R/2$  for one mode of ideal gas.

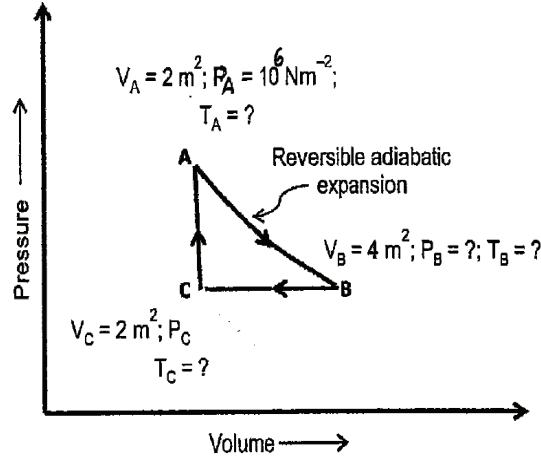


Figure 1: This goes with Problem 3.3. Path AB, BC, and CA form a cycle. You are asked to analyze the heat, work, and change in entropy in each of the paths, and the efficiency of the cycle.

- Calculate**  $T_A$ ,  $P_B$ ,  $T_B$ , and  $T_C$ .
- Calculate** the heat  $Q_{AB}$ , work  $W_{AB}$  and the change in entropy  $\Delta S_{AB}$  for the process AB.
- Calculate** the heat  $Q_{BC}$ , work  $W_{BC}$  and the change in entropy  $\Delta S_{BC}$  for the process BC.
- Calculate** the heat  $Q_{CA}$ , work  $W_{CA}$  and the change in entropy  $\Delta S_{CA}$  for the process CA.
- Hence, **find the efficiency**  $\eta$  of the cycle and **analyze** the difference between heat absorbed and heat rejected **and** the net work performed in a cycle.

### 3.4 (21 points) Applying general relations to van der Waals equation of state

Let's work on the van der Waals equation of state

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (1)$$

again, where  $n$  is the number of moles and  $R$  is the gas constant. This time, we have a better sense as we discussed that  $a$  and  $b$  are related to the inter-particle interaction. For simplicity, let's consider the molar form (1 mole) of the equation

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

where  $v$  is the molar volume.

- (a) We discussed the “energy equation” in Ch.VII. It refers to

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (3)$$

**Evaluate** the right hand side of Eq. (3) for a van der Waals gas. **Point out** how your result depends on the parameters  $a$  and  $b$  in the van der Waals equation, as well as the variables  $T$  and  $v$ . **Contrast** your result with that of an ideal gas.

[Remark: A by-product is that you also have the Joule coefficient.]

- (b) Starting with the total differential of  $u(T, v)$  (or  $U(T, V)$ ), **show** that

$$du = c_V dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dv . \quad (4)$$

Hence, **argue** that the molar internal energy  $u$  for a van der Waals gas depends on both  $T$  and  $v$ . [Remark: This should be contrasted with the simple ideal gas result of  $u(T)$  only. However, the difference in  $u$  between a van der Waals gas and an ideal gas is a term unrelated to the temperature. Thus, the heat capacity  $c_V$  of a van der Waals gas is the same as an ideal gas and is independent of temperature.]

- (c) We also derived a general expression for the difference between the heat capacities  $c_P - c_V$ . [You need to rewrite the result into “per mole”.] **Evaluate**  $c_P - c_V$  for a van der Waals gas. Also, **give the expressions** for the expansivity  $\beta$  and compressibility  $\kappa$ .

### 3.5 (14 points) **General expression for $C_P/C_V$**

We defined the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (5)$$

We can also define an adiabatic compressibility (no heat involved means no entropy change) as

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S \quad (6)$$

**Show that** in general

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \quad (7)$$

As an illustration, **apply** the result to an ideal gas and recover the known result.

[Hint: Give the steps explicitly. The “−1” rule and chain rule of partial derivations will be useful.]

### 3.6 (16 points) **Find thermodynamic variables by taking derivatives for a given $S(U, V, N)$**

The central equation can be written as  $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$ . It is the most important equation in statistical mechanics calculations. A student obtained the following expression of  $S(U, V, N)$  for a system after a lengthy calculation following Boltzmann’s approach. The answer is

$$S(U, V, N) = Nk \ln \left( \frac{V}{N} \left( \frac{mU}{3\pi N \hbar^2} \right)^{3/2} \right) + \frac{5}{2}Nk , \quad (8)$$

for a system consisting of  $N$  particles, each of mass  $m$ , in a volume  $V$ , and an internal energy  $U$ . Here, I included the Boltzmann’s constant  $k$  and the Planck constant  $\hbar$  so as to confuse you.

- (a) As the student's teacher, you want to check quickly whether Eq. (8) is a possible answer for the entropy. **Demonstrate** that the entropy given by Eq. (8) is an extensive quantity as required.
- (b) **Calculate**  $T$  (or  $1/T$  if you prefer) and  $P$  from  $S(U, V, N)$  by taking appropriate derivatives.
- (c) Hence, **find a relation** among  $T$ ,  $P$ ,  $V$ , and  $N$ . **What is the system** that the student has worked on?
- (d) **Calculate**  $\mu$ .