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

Problem Set 2

Due: 3 October 2020 (Saturday); "T+2" = 5 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 2 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 1st Law of Thermodynamics and Classical Ideal Gas.

2.0 **Reading Assignment.** This is a guide to our progress. **No need to hand in anything**. By the end of Week 3, we finished the discussion of a large part of the basic principles of thermodynamics, including the first and second laws. It is hope that for those who need to apply thermodynamics to different systems in the future, you now have the necessary foundation to read into your specialized subject and focus on the applications. The first law is a statement of energy conservation including heat and work. The change in the internal energy, which is a state function, can be realized by a combination of heat (from some external source into the system) and work (from the surrounding). Both heat and work depend on the path that the system changes from the initial to the final state (and that path can be reversible or irreversible). They, sometimes, are called path functions in order to make this point clear. Therefore, for a system at equilibrium, we can say there is a value of the internal energy U for that state, but we cannot tell what heat and work there are in that state. Work and heat are related to the processes that lead to the change in the state. We discussed the forms of the work done term, using the gas-cylinder-piston system as the major example but also including the results of other systems. For general work done, it is the surrounding, e.g. a force F_{ext}, that is doing the work. For reversible processes, the work done term can be expressed in terms of the system's variables. As we already discussed in Week 3, this is crucial in formulating the central equation of thermodynamics. The second law is necessary because there are so many phenomena in nature that are irreversible, i.e., going one way but not the reversed way. The Clausius statement, as well as the Kelvin-Planck statement, of the 2nd law serves to ban those phenomena that are not observed naturally. The appreciation should be that of a single statement (whichever) is sufficient. Through the analysis of the Carnot cycle, which is a reversible cycle, we can develop the idea of entropy. The entropy change in a reversible process is the ratio of the heat exchange and the temperature at which heat is exchanged. The fact that the Carnot cycle is the most efficient leads to an inequality, i.e. irreversible cycles are necessarily less efficient. This inequality has its root in the 2nd law and propagates to become other inequalities in thermodynamics, e.g. $dS > 0$ for possible irreversible processes that we observe in a thermally isolated system. Putting 1st and 2nd laws together, we have the central equation or fundamental equation of thermodynamics: $dU = TdS - pdV$ or $dS = \frac{1}{T}dU + \frac{p}{T}dV$. This is *an identity* and it is generally true (for any processes). Results that follow from the central equation are, therefore, also general. This summarizes the framework of thermodynamics.

Books: Finn's *Thermal Physics*, C.J. Adkins' *Equilibrium Thermodynamics*, and Pippard's *The Elements of Classical Thermodynamics* are equally good. *Concepts in Thermal Physics* by Blundell and Blundell is exceptionally clear. The chemistry books of McQuarrie and Simon's *Physical Chemistry: A Molecular Approach* and Levine's *Physical Chemistry* give a longer and friendlier discussions, but they are just as clear.

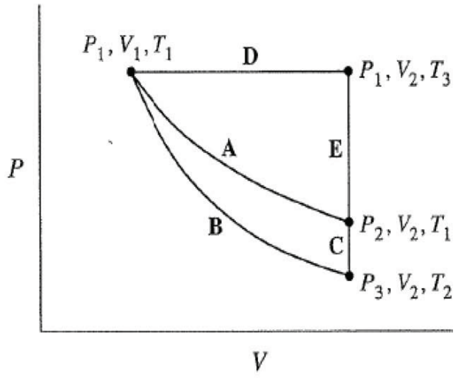

Figure 1: This goes with Problem 2.1. Path A is an isotherm that goes from state 1 to state 2. The second path goes through B+C. The third path goes through D+E.

2.1 (20 points) U **is a state function, but** W **and** Q **are not**

Figure 1 shows three different paths for an expansion of an ideal gas from a state 1 with (P_1, V_1, T_1) to a state 2 with (P_2, V_2, T_1). The Path A is the isotherm at T_1. A second path is to go through B+C to arrive at state 2, where B is an adiabatic curve. A third path is to go through D+E to arrive at state 2.

(a) For the first path along the isotherm A, **obtain** ΔU (the change in internal energy), W (work done **by** the system), and Q (heat into the system).

(b) Repeat part (a) for the second path that goes through B+C to arrive at state 2.

(c) Repeat part (a) for the third path that goes through D+E to arrive at state 2.

2.2 (12 points) **Work in reversible isothermal process in van der Waals gas**

In Problem Set 1, we saw the van der Waals equation of state

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

where n is the number of moles and R is the gas constant. **Obtain an expression** for the work done by a van der Waals gas when it expands isothermally and reversibly from V_1 to V_2 at a temperature T. **Indicate how** the result can be reduced to the ideal gas result (see you just did in 2.1(a)).

2.3 (12 points) **Isothermal curve and adiabatic curve**

(a) In a Carnot cycle, there is an isotherm that goes from a state A to a state B and there is an adiabatic curve that goes from a state B to a state C. Therefore, the two curves meet at the state B. **What are the slopes** of the two curves at the meeting point.

(b) To obtain the isothermal curve, we only need to know the equation of state, e.g. $pV = NkT$ for an ideal gas fixes the p-V curve for fixed T. However, we need some additional information in order to obtain the adiabatic curve. Study the derivation of the ideal gas adiabatic curve as discussed in the class notes and **point out** what the additional piece of information is.

2.4 (10 points) **Change in internal energy in isobaric expansion of an ideal gas**

An isobaric expansion has the pressure being kept constant. **Find the change in the internal energy** of one mode of monatomic ideal gas in an isobaric expansion at 1 atm from a volume of 5 m^3 to a volume of 10 m^3. [Hint: The parameter γ for a monatomic ideal gas is 5/3.]

2.5 (16 points) **Slight deviation from classical ideal gas**

Let's make our third encounter of the van der Waals equation of state. It is meant to describe real gases better. For classical ideal gas, we have $pV = NkT$ and so

$$\frac{p}{kT} = \frac{N}{V} \equiv \tilde{n}\,, \tag{2}$$

where $\tilde{n} = N/V$ is the number density of particles in the gas, i.e., number of gas particles per volume. When you learned the ideal gas once upon a time, you knew that gases must be dilute for them to behave as an ideal gas. It means that the number density is expected to be small.

It is therefore reasonable to ask if the equation of state of a gas that deviates only slightly from an ideal gas would have an equation of state that looks like

$$\frac{p}{kT} = \frac{N}{V} + B_2\left(\frac{N}{V}\right)^2 + \cdots = \frac{N}{V}\left(1 + B_2\left(\frac{N}{V}\right) + \cdots\right) = \tilde{n} + B_2\,\tilde{n}^2 + \cdots \tag{3}$$

where we stop after the first **correction term**.

Consider the van der Waals equation of state

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT = NkT \tag{4}$$

where $n = N/N_A$ is the number of moles and $R = N_A k$ is the gas constant. Here, N is the number of particles in the gas that has a volume V and pressure P. **Obtain an expression** for B_2 from the van der Waals equation. [Hint: There are $\cdots$ that you can ignore.]

Look up (you should have learned it in the past from either physics or chemistry) what the physics is behind the terms related to the parameter a and b in the van der Waals equation. Hence, **write no more than 50 words on the physics related to** a **and** b. Finally, observe your answer on B_2 and **comment** on the difference in the contributions of a and b terms to B_2.

2.6 (20 points) **Enthalpy**

From the 1st law $\Delta U = Q + W$, with $W = -\int_{V_1}^{V_2} PdV$ for the P-V type of work, it is easy to see that $\Delta U = Q_v$ under the condition of **constant volume**. It says that ΔU is the energy transfer as heat in a constant-volume process Q_v (as the subscript emphasized). You are asked to make a similar argument for the enthalpy H below. We discussed in class that H comes from U via a Legendre transform so that a picture of $U(V)$ can be seen as $H(P)$. Here, you will see that H is actually useful.

(a) With the enthalpy $H = U + PV$, **show that** the enthalpy change ΔH is the energy transfer as heat Q_P in a **constant-pressure** process.

(b) Constant-pressure processes are ordinary. Take for example the melting of ice at 0^{o}C at 1 atm (1 atmosphere). Data tables say that $Q_P = 6.01$ kJ·mol^{-1} (kilo-Joule per mole). It is given that the difference between the volumes of ice and water is small. Specifically, the molar volume of ice $v_s = 0.0196$ L·mol^{-1} (liter per mole) and the molar volume of water

$v_\ell = 0.0180$ L·mol^{-1}. Here the subscripts "s" and "ℓ" refer to solid (ice) and liquid (water), respectively. **Calculate** the change in internal energy ΔU from ΔH and $P\Delta V$.

[Hint: You need to be careful with units. It is a fact of life of doing science! Data books will be turn everything to make your calculations convenient. Here you see data in Q_P that are cited in liter-per-mole and pressure in atmosphere. You need to look up what 1 atm means and you will find that it is slightly more than 1 bar. But what is 1 bar? Then you find something called Pascal. What is a Pascal?...]

(c) Let's do the same thing for water turning into vapour at 100 ^{o}C at 1 atm. Data say $Q_P = 40.7$ kJ·mol^{-1}, $v_\ell = 0.0180$ L·mol^{-1}, and $v_g = 30.60$ L·mol^{-1}. The molar volume of vapor (gas) is much bigger, as expected. **Calculate** ΔU from ΔH and $P\Delta V$.

(d) A common sense is that roughly in a gas (vapour), the kinetic energy of the particles (water molecules) is much bigger than the potential energy (water molecules are too far apart to be interacting in the gas phase). In the liquid phase, the kinetic energy is about the same order as the potential energy. [Q: How about a solid? No bonus point.] From your answer in part (c), **identify the energy** used to overcome the inter-molecular interaction in vaporization and the energy corresponding to **work done against the atmosphere**.