1. Time allowed = 2 hours
2. Total number of questions = 4
3. Total number of marks = 50
4. All questions are NOT of equal value. Marks available for each question are shown in the examination paper.
5. Answer all questions.
6. Please answer each question in a separate booklet.
7. All answers must be in ink. Except where they are expressly required, pencils may only be used for drawing, sketching or graphical work.
8. The use of UNSW-approved calculators is allowed.
9. This paper may be retained by the candidate.
The following information is supplied as an aid to memory.

Boltzmann’s constant \(k_B = 1.38 \times 10^{-23} \text{ J/K}\)
Avogadro’s number \(N_A = 6.022 \times 10^{23} \text{ mol}^{-1}\)
Real gas constant \(R = 8.314 \text{ J/K.mol}\)

Specific heat of liquid \(H_2O = 4.18 \text{ J/gK}\)
Latent heat of the liquid-solid transition for \(H_2O = 333 \text{ J/g}\)
Adiabatic constant for \(N_2 \gamma = 1.4\)
Molar mass of air = 29 g/mol

Ideal gas equation \(PV = nRT = Nk_BT\)

Maxwell’s velocity distribution
\[
D(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)
\]

Thermodynamic Potentials
\[
\begin{align*}
F &= U - TS \\
G &= U - TS + PV
\end{align*}
\]
\[
\begin{align*}
dF &= dU - TdS - SdT \\
dG &= dU - TdS - SdT + PdV + VdP \\
dU &= TdS - PdV
\end{align*}
\]

Clausius-Clapeyron Equation
\[
\frac{dP}{dT} = \frac{L}{TAV}
\]
Question 1 [10 Marks]

A chamber with a movable, heat-conducting, dividing wall is filled with two different gases, as in the diagram. The gas on the left is helium, while the gas on the right is neon. The two gasses initially have different temperatures and pressures. The wall is allowed to move until the system is at equilibrium.

\[ n_1 \text{ atoms/volume} \quad n_2 \text{ atoms/volume} \]

(a) Briefly define temperature in terms of the motions of the particles in a gas for (i) a monotomic gas, and (ii) a diatomic gas.

(b) Define the concepts of thermal equilibrium and pressure equilibrium.

(c) Using the system above as an example, explain the processes by which the system reaches both equilibria after the two chambers are first filled, and the order in which they occur.

(d) The two-gas system is closed and isolated. Chamber 1 (left) initially contains 0.2 mol of a monotomic ideal gas at a temperature of 25°C, while chamber 2 contains 0.5 mol of a different monotomic ideal gas at a temperature of 15°C. The volume of the both chambers together is \(16 \times 10^{-3}\) m\(^3\), and initially the gasses occupy equal volumes.

(i) Find the initial pressures on both sides, before the partition moves.

(ii) Find the final volume that each chamber occupies, after pressure and thermal equilibrium have been reached.
Question 2 [8 Marks]

(a) Give a statement of the first law of thermodynamics. What is the basic underlying principal of this law?

(b) Given that

\[ W = -\int P\,dv, \]

Derive an expression for the work done in

(i) a constant volume process,

(ii) a constant pressure process, and

(iii) an isothermal process (in this case as a function of the number of moles of a gas and the temperature of the gas).

(c) In the course of pumping up a motorcycle tyre, 14 litres of air at atmospheric pressure is compressed adiabatically to a pressure of 200 kPa (air has \( \gamma = 1.4 \))

(i) What is the final volume of the air after the compression?

(ii) If the temperature of the air is initially 300 K, what is the temperature after compression?
Question 3 [20 Marks]

The Carnot cycle is the most efficient cycle possible for a heat engine working between $T_{\text{hot}}$ and $T_{\text{cold}}$.

(a) Draw an energy flow diagram for a general heat engine showing the hot reservoir, the cold reservoir and the various energy flows involved. Define the efficiency of the heat engine.

(b) Considering conservation of energy, show that the efficiency $e$ can be written $e = 1 - \frac{Q_d}{Q_h}$, where $Q_h$ and $Q_c$ are the energy flows from the hot reservoir to the engine and from the engine to the cold reservoir respectively.

(c) An engine operates in a Carnot cycle. The engine starts its cycle at point A, where the cylinder has a maximum volume of $V_A = 0.7 \, \text{L}$, and an initial pressure $P_A = 100 \, \text{kPa}$, temperature $T_A = 290 \, \text{K}$. The cylinder contains pure nitrogen with $\gamma = 1.4$ and a molar mass of 28 g/mol:

(i) Calculate the mass of nitrogen in the cylinder at A. Assume this mass will remain constant for the rest of the question.

(ii) Sketch a diagram of the Carnot cycle. Use the point A as the maximum volume (parameters given above) then label the start of the next legs (processes) of the cycle B, C, D. Draw isotherms clearly on your diagram, and show the relationship of the cycle to these. Label the type of expansion or contraction (isothermal / adiabatic) on each process/leg of the cycle.

(iii) Give a brief description of each process, referring to your diagram.

(iv) For the process $A \rightarrow B$, $V_B = 1/5 \, V_A$. Hence calculate $P_B$ and $T_B$.

(v) For the process $B \rightarrow C$, $V_C = 1/2 \, V_B$. Hence calculate $P_C$ and $T_C$.

(d) Prove directly, by calculating the heat taken in and the heat expelled, that a Carnot engine using an ideal gas as the working substance has an efficiency of $1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$. Start by considering the heat entering and leaving the engine during the isothermal legs of the cycle. You will find the result

$$\ln\left(\frac{V_A}{V_B}\right) = \ln\left(\frac{V_B}{V_C}\right)$$

useful to reach the final result for efficiency.

(e) You can also manipulate your results from part (d) to show that for the Carnot engine

$$\frac{Q_c}{T_c} = \frac{Q_H}{T_H}.$$ Use this expression to define entropy.
Question 4 [12 Marks]

An inventor proposes to make a heat engine using water/ice as the working substance inside a cylindrical piston and taking advantage of the fact that water expands as it freezes and can therefore lift a piston supporting some mass $m$. The engine process consists of four steps, as shown in the schematic:

(i) The weight to be lifted is placed on top of a piston over a cylinder of water held at a temperature of $1^\circ C$. The piston sits at height $z = 0$.

(ii) The system is then placed in thermal contact with a low temperature reservoir at $-1^\circ C$ until the water freezes into ice, lifting the weight to a height $z > 0$.

(iii) The weight is then removed and the ice is melted by putting it back in contact with the high-temperature reservoir at $1^\circ C$, returning the piston to $z = 0$.

(iv) Another mass is added to the piston and the process is repeated.
The inventor is pleased with this device because it can seemingly perform an unlimited amount of work (by lifting an unlimited mass \( m \)) while absorbing only a finite amount of heat each cycle.

(a) At a phase boundary, a material is equally stable in either of the two phases and hence the Gibbs free energy \( G = U + PV - TS \) is equal in the two phases. Starting from this fact, derive the Clausius-Clapeyron relation:

\[
\frac{dP}{dT} = \frac{L}{T \Delta V}
\]

where \( L \) is the latent heat of the transition and \( \Delta V \) is the change in volume during the transition.

(b) Referring to the Clausius-Clapeyron equation, explain why will this engine not lift an unlimited mass \( m \) as the inventor suggests.

(c) Assuming that the piston has a cross-sectional area of 10 cm\(^2\) and contains 50 cm\(^3\) of H\(_2\)O, calculate:

(i) The work done by the piston in raising a mass of 10 g. Assume the density of ice is 917 kg cm\(^{-3}\).

(ii) The mass required to stop the engine working (i.e., reduce the freezing point of the water to \(-1^\circ C\)).

(d) Use the Clausius-Clapeyron equation to prove that the maximum efficiency of this engine is still given by the Carnot formula \( \eta = 1 - \frac{T_c}{T_h} \).