1. Time allowed – 2 hours

2. Reading time – 10 minutes

3. This examination paper has 6 pages.

4. Total number of questions – 5

5. Total number of marks – 55

6. All questions are not of equal value. Marks available for each question are shown in the examination paper.

7. Answer all questions.

8. The following materials will be provided by the Enrolment and Assessment Section: Calculators.

9. All answers must be in ink. Except where they are expressly required, pencils may only be used for drawing, sketching or graphical work.

10. 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 \( \text{H}_2\text{O} = 4.18 \text{ J/gK} \)
Latent heat of the liquid-solid transition for \( \text{H}_2\text{O} = 333 \text{ J/g} \)
Latent heat of the liquid-gas transition for \( \text{H}_2\text{O} = 2270 \text{ J/g} \)
Adiabatic constant for \( \text{N}_2 \) \( \gamma = 1.4 \)
Specific heat at constant pressure for \( \text{N}_2 \) \( C_p = 29.12 \text{ J mol}^{-1} \text{ K}^{-1} \)
Specific heat at constant volume for \( \text{N}_2 \) \( C_v = 20.8 \text{ J mol}^{-1} \text{ K}^{-1} \)
Molar mass of air = 29 g/mol

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

Specific heat \( C = dQ/dT \)

Entropy \( dS = dQ_n/T \)

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
\[
\begin{align*}
F &= U - TS & dF &= dU - TdS - SdT \\
G &= U - TS + PV & dG &= dU - TdS - SdT + PdV + VdP \\
H &= U + PV & dH &= dU + PdV + VdP \\
\end{align*}
\]
\[
\begin{align*}
dU &= TdS - PdV = dQ + dW \\
\end{align*}
\]
Question 1 [10 Marks]

The kinetic theory of gases links the macroscopic properties of a gas such as pressure, temperature and internal energy to the motions of the particles composing that gas. Considering a piston with area $A$ in a cylinder full of gas, the force on the piston will be due to particles colliding with the piston as shown below.

(a) In one or two sentences each, explain why:
   (i) the number of particles hitting the piston in time $t$ is given by $n_c = n v_x t A$, where $n$ is the number of particles per volume and $v_x$ is the $x$-component of the velocity of a particle colliding with the wall, and;
   (ii) the momentum per particle is given by $dp/dn_c = -2mv_x$, where $m$ is the mass.

(b) Using the results in (a), show that the collision of the gas particles with the piston results in a pressure $P = 2mnv_x^2$.

(c) Briefly explain the rationale behind
   (i) replacing $v_x^2$ with $\frac{1}{2}\langle v_x^2 \rangle$ rather than $\frac{1}{2}\langle v_x \rangle^2$ (i.e., why is the root-mean-square used rather than the simple average);
   (ii) replacing $\langle v_x^2 \rangle$ with $1/3\langle v^2 \rangle$, and;
   (iii) show how these two replacements are used to obtain the generalised result for a gas in a box $PV = \frac{2}{3}N\langle \frac{1}{2}mv^2 \rangle = \frac{2}{3}U$.

(d) 1 mole of monatomic He gas occupies a volume of 2 m$^3$ at a pressure of 12 atm. Calculate the average kinetic energy per particle $\langle \frac{1}{2}mv^2 \rangle$.

Question 2 [10 Marks]

(a) State the zeroth law of thermodynamics. Define temperature and briefly explain how the concept of temperature relies on the zeroth law.

(b) Can you tell whether the internal energy of a body was acquired by heat transfer or by performance of work? Briefly discuss.

(c) An ideal gas is taken from an initial temperature $T_i$ to a higher final temperature $T_f$ along two different reversible paths: Path A is at constant pressure and Path B is at constant volume. Which is the correct relation between the entropy changes of the gas for these paths: (a) $\Delta S_A > \Delta S_B$, (b) $\Delta S_A = \Delta S_B$ or (c) $\Delta S_A < \Delta S_B$. Briefly explain your answer. (hint: it may help to sketch the two processes on a $PV$-diagram)
Sketch a qualitatively accurate graph of the entropy of \( \text{H}_2\text{O} \) as a function of temperature at fixed pressure. Indicate where the substance is solid, liquid and gas. Explain each feature of the graph briefly. What will the entropy do in the limit of \( T \to 0 \) and why?

Question 3 [15 Marks]

A heat engine is any device that absorbs heat and converts part of that energy into useful work.

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

(b) Define the efficiency \( e \) of the heat engine.

(c) Using the first law, show that the efficiency \( e \) can be written \( e = 1 - \frac{Q_c}{Q_h} \), 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.

The Ericsson cycle consists of two isothermal (constant temperature) processes and two isobaric (constant pressure) processes. At the beginning of the isothermal compression, the pressure, volume and temperature are 100 kPa, 0.08 m\(^3\) and 20ºC, respectively. In the isothermal compression, the volume is reduced by a factor of 5. After the isothermal compression, the volume is doubled during the constant pressure process. You may assume that the gas used in the cycle is \( \text{N}_2 \), and that it is an ideal gas.

(d) On a \( PV \)-diagram, sketch the cycle described above with appropriate annotation.

(e) Calculate the maximum temperature achieved during the cycle.

(f) Calculate the net work done by the cycle.

(g) Calculate the heat input/output in each stage of the cycle, and thus obtain the efficiency of the cycle.

(h) Suppose that a regenerator is added to this engine such that the heat generated in the isobaric compression is recovered to provide the heat input for the isobaric expansion. Calculate the efficiency of the engine with the regenerator added and show that this efficiency is equal to the efficiency of a Carnot engine between the same two reservoirs.

Question 4 [8 Marks]

In 1824, a French engineer named Sadi Carnot described a theoretical engine, now called the Carnot engine, which is of great importance from both theoretical and practical viewpoints because it represents the most efficient engine cycle allowed by the laws of physics.

(a) Draw the \( PV \)-diagram for the Carnot engine indicating the key features of the cycle. In your diagram, indicate the parts of the cycle where heat is added and removed, and the direction around the cycle needed to get useful work out.

(b) Using the properties of the four processes comprising this cycle (i.e., without resorting to entropy), show that the efficiency of the Carnot cycle can be written as \( e_C = 1 - \frac{T_c}{T_h} \).

(c) An inventor claims to have developed a heat pump that will draw heat from a river a 3ºC and deliver heat to a building at 35ºC at a rate of 20 kW while
consuming only 1.9 kW of electric power. Would you take this claim seriously? Explain referring to the coefficient of performance.

**Question 5 [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 below.

1. **Load**: The weight to be lifted is placed on top of a piston over a cylinder of water held at a temperature of 1°C. The piston sits at height $h_w$.

2. **Lift**: The system is then placed in thermal contact with a low temperature reservoir at $-1°C$ until the water freezes into ice, lifting the weight to a height $h_i$.

3. **Unload**: The weight is then removed at height $h_i$ while the ice remains frozen.

4. **Reset**: The ice is melted by putting it back in contact with the high-temperature reservoir at 1°C, returning the piston $h_w$. Another mass is added to the piston and the cycle is ready to be 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 and in a few sentences, 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 liquid H\(_2\)O (i.e. \( h_w = 5 \) cm), calculate:

   (i) The work done by the piston in raising a mass of 10 g.

   (ii) The mass required to stop the engine working (i.e., reduce the freezing point of the water to −1°C).

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