1. Time allowed – 2 hours
2. Reading time – 10 minutes
3. This examination paper has 5 pages.
4. Total number of questions – 5
5. Total number of marks – 50
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 \( \text{H}_2\text{O} = 333 \text{ J/g} \)
Adiabatic constant for \( \text{N}_2 \gamma = 1.4 \)
Molar mass of air = 29 g/mol

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

Maxwell’s velocity distribution
\[
D(v) = \left( \frac{m}{2\pi k_BT} \right)^{\frac{3}{2}} 4\pi v^2 \exp \left( -\frac{mv^2}{2k_BT} \right)
\]

Thermodynamic Potentials
\[
F = U - TS \quad \quad \quad dF = dU - TdS - SdT
\]
\[
G = U - TS + PV \quad \quad \quad dG = dU - TdS - SdT + PdV + VdP
\]
\[
dU = TdS - PdV
\]

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

The concepts of thermal equilibrium and the zeroth law of thermodynamics form an essential foundation of thermodynamics.

(a) In one or two sentences, define and briefly explain the concept of thermal equilibrium from a macroscopic viewpoint (i.e., without resorting to the kinetic theory result).

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

(c) From the kinetic theory of gases we find that when two gases are at thermal equilibrium, the mean kinetic energy of their center of mass motions are equal. Using this result, and the principle of equipartition of energy, briefly discuss the definition of the Kelvin scale of temperature.

(d) A vessel contains 1 L of Nitrogen gas (molar mass = 28 g) at 25°C, using your results from (c), calculate the root mean square velocity \(v_{\text{rms}} = \langle v^2 \rangle^{1/2}\) for the N\(_2\) molecules in the gas.

(e) What is the probability of a randomly chosen molecule having a particular velocity between \(v\) and \(v + dv\)? Briefly discuss with one or two paragraphs and a sketched graph of the probability density \(D(v)\) versus velocity \(v\). Indicate on your graph how the probability density varies with \(v\) in the limit of \(v \rightarrow 0\) and \(v \rightarrow \infty\), and the locations of the most-probable velocity \(v_{\text{m.p.}}\) and the root-mean-square velocity \(v_{\text{rms}}\).

(f) Derive an expression for the most probable velocity \(v_{\text{m.p.}}\), and calculate \(v_{\text{m.p.}}\) for the gas in (d). Show that \(v_{\text{rms}}\) is 22.5% greater than \(v_{\text{m.p.}}\)?

Question 2 [10 Marks]

The first law of thermodynamics relates the change in internal energy of a system \(dU\) to the work done on/by the system \(W\) and the heat \(Q\) flowing into or out of the system, giving \(dU = Q + W\).

(a) What key concept of physics does the first law relate to?

(b) In a few sentences, clearly distinguish between temperature, heat and internal energy (Hint: be careful that your discussion doesn’t only relate to gases – your answer should be universal for all systems).

There are two idealised ways of compressing a gas. The first is isothermal compression, which is so slow that the temperature of the gas doesn’t rise at all. The second is adiabatic, which is so fast that no heat escapes from the gas during the process. For a monatomic ideal gas, the internal energy \(U = 3/2 \, Nk_B T\).

(c) For an isothermal compression, show that \(Q = Nk_B T \ln (V_f/V_i)\). Given that \(V_f < V_i\), what is the sign of \(Q\)? Does heat enter or leave the system in an isothermal compression?
(d) Using the first law, the expression for $U$ given above and $dW = -PdV$, show that for the adiabatic compression of an ideal gas:

$$\frac{3}{2} \frac{dT}{T} = -\frac{dV}{V}$$

(Hint: Do not use $PV^{\gamma} = \text{const}$, you’ll show that in part (e) and don’t integrate $dW$ to get $W$ like in (c)).

(e) Integrating both sides of your result in (d) from the initial values ($V_i$ and $T_i$) to the final values ($V_f$ and $T_f$), and using the ideal gas law to eliminate $T$, show that you can obtain the relationship $PV^{\gamma} = \text{constant}$ for an adiabatic process, where $\gamma = 5/3$.

**Question 3 [12 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. Define the efficiency of the heat engine.

(b) Using the first law, show that the efficiency $e$ can be written $e = 1 - Q_c/Q_h$, 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.

A diesel engine operates similarly to an Otto cycle engine, with the exception that combustion occurs due to auto-ignition of the fuel by the temperature generated in the adiabatic compression, and so this engine doesn’t require a spark plug. The diesel cycle is shown in the $PV$-diagram below, and differs from the Otto cycle because the combustion process B-C occurs at constant pressure and not constant volume.

Consider a 4-cylinder diesel engine where each cylinder has a volume $V_A = 0.5 \text{ L}$, a compression ratio $r = V_d/V_B = 22$, and a cut-off ratio $r_c = V_C/V_B = 2.0$. If the engine starts its cycle at A and has initial pressure $P_A = 100 \text{ kPa}$, temperature $T_A = 300 \text{ K}$, and the fuel-air mixture is mostly air (i.e., $\gamma = 1.4$ and the molar mass is 29 g/mol):

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

(d) Given the process $A \rightarrow B$ is adiabatic, calculate $P_B$ and $T_B$. 

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(e) Given the process $B \rightarrow C$ is at constant pressure, calculate $T_C$.

(f) Given the process $C \rightarrow D$ is adiabatic, calculate $P_D$ and $T_D$.

(g) If the specific heat at constant pressure and constant volume are $c_p = 1005$ J/kgK and $c_v = 718$ J/kgK, respectively, calculate the heat input $Q_h$, heat output $Q_c$ and work done by the engine $W$.

(h) What is the engine’s efficiency $e$?

**Question 4 [9 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.

(a) Draw the $PV$-diagram for the Carnot cycle indicating the key features of the cycle.

(b) In one or two sentences, briefly explain the significance of the Carnot cycle in thermodynamics.

(c) 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 $e_C = 1 - T_c/T_h$.

(d) Following on from your analysis in (c), obtain the entropy $S$. Comment briefly on the behaviour of the entropy in a reversible cycle like the Carnot cycle. How does this result change for an irreversible cycle?

**Question 5 [9 Marks]**

Dihydrogen Oxide (H₂O) can exist in three phases – as a vapour called steam, as a liquid called water, and as a solid called ice.

(a) Given that the triple point occurs at $P = 0.006$ bar and $T = 0.01 \degree C$, and the critical point occurs at $P = 221$ bar and $T = 374 \degree C$, draw the $P$ vs. $T$ phase diagram for H₂O, and indicate on it the three phases, the triple and critical points, and any other important features that aren’t obvious in your drawing.

(b) 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.

(c) The density of water at 1000 kg/m³, is slightly higher than that of ice at 917 kg/m³. Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

(d) How much pressure would you have to put on a 1 gram ice cube to make it melt at $-1 \degree C$.

(e) Use the third law of thermodynamics to argue that the slope of the solid-liquid phase boundary of H₂O must go to zero in the limit of $T \rightarrow 0$. 