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 \( PV = nRT = Nk_B T \)

Specific heat \( C = dQ/dT \)

Fick’s law \( J_x = -DA \frac{dn}{dx} \)

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

Thermodynamic Potentials
\[
F = U - TS \\
G = U - TS + PV \\
H = U + PV
\]
\[
dF = dU - TdS - SdT \\
dG = dU - TdS - SdT + PdV + VdP \\
dH = dU + PdV + VdP \\
dU = TdS - PdV = dQ + dW
\]
Question 1 [10 Marks]

(a) Briefly describe the process of diffusion. How does it occur and why?

(b) The typical distance that a particle of diameter \(d\) can travel before it collides with another particle in a gas is known as the mean-free path \(\ell\). By considering that a particle has an ‘effective diameter’ \(2d\) and is moving in a gas of point particles, show that the mean free path is given by:

\[
\ell = \frac{1}{\pi d^2 n}
\]

where \(n\) is the number of particles per volume in the gas.

(c) In a tank full of oxygen, how many molecular diameters \(d\) on average does an oxygen molecule travel (at 1 atm and 20°C) before colliding with another \(O_2\) molecule? The diameter of the \(O_2\) molecule is 3.6Å.

(d) Oxygen diffuses from the surface of an insect to its interior through tiny holes called tracheae. An average trachea is about 2 mm long and has a cross-sectional area \(A\) of \(2 \times 10^{-9}\) m². Assume the diffusion constant \(D\) for oxygen is \(1 \times 10^{-5}\) m²/s.

(i) What is the concentration of oxygen in the air (assume 21% is oxygen) at a temperature of 20°C, in mol/m³?

(ii) Assuming the concentration of oxygen at the interior end of the trachea is half what it is outside in the atmosphere. Calculate the diffusion rate \(J\).

(iii) Estimate the average time \(t\) for a molecule to diffuse in through the trachea.

Question 2 [10 Marks]

(a) Is it possible for the temperature of a system to remain constant even though heat flows into or out of it? If so, give two examples.

(b) On the PV diagram for an ideal gas, one isothermal curve and one adiabatic curve pass through each point. Prove that the slope of the adiabat is steeper than the slope of the isotherm by the factor \(\gamma\).

(c) An ideal gas is carried through a thermodynamic cycle consisting of two isobaric and two isothermal processes as shown in the PV-diagram below. Show that the net work done on the gas in the entire cycle is given by \(W_{\text{net}} = -P_1(V_2 - V_1)\ln(P_2/P_1)\).

\[\begin{array}{c}
\text{P} \\
\text{A} \\
\text{B} \\
\text{C} \\
\text{D} \\
\text{P}_1 \\
\text{P}_2 \\
\end{array} \quad \begin{array}{c}
\text{V}_1 \\
\text{V}_2 \\
\end{array} \]

Question 3 [12 Marks]

(a) A classmate tells you that it is just as likely for all the air molecules in the room you are both in to be concentrated in one corner (with the rest of the
room being a vacuum) as it is for the air molecules to be distributed uniformly about the room in their current state. Is this a true statement? Why doesn’t the situation he describes actually happen? How is this related to the second law of thermodynamics?

(b) Suppose you flip four fair coins (fair meaning equal chances of coming up heads or tails).

(i) Make a list of all the different possible macrostates for these four coins (you shouldn’t need to list all the microstates in doing this).

(ii) Calculate the multiplicity for each macrostate.

(iii) Calculate the probability of achieving each macrostate if all four coins are flipped at the same time.

(iv) How is the entropy related to the multiplicity of a particular macrostate? What is this relationship called?

(v) Considering the relation in (iv), and based on the second law, if you started with all four coins as heads and allowed them to evolve over time in such a way that every $n$ seconds one coin is chosen at random and flipped, which macrostate would the system most likely be found in? Does this result agree with what you’d expect from the probabilities in (iii)? Briefly discuss.

(c) A 30g piece of ice at 0°C is allowed to melt on a bench in a room at room temperature (i.e., 25°C). Assume that the latent heat of ice is 333J/g and specific heat of water is 4.186 J/gK.

(i) Calculate the change in entropy of the ice cube as it melts into water at 0°C.

(ii) Calculate the change in the entropy of the water (from the melted ice) as its temperature rises from 0°C to 25°C.

(iii) Calculate the change of entropy of the room as it gives up heat to the melting ice/water.

(iv) Calculate the net change in the entropy of the universe during this process. Is the net change positive, negative or zero? Is this what you would expect based on the second law of thermodynamics?

**Question 4 [10 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 $e_C = 1 - T_c/T_h$. 
(c) Under what conditions would an ideal heat engine be 100% efficient? Briefly discuss whether such conditions are possible/impossible and why?

(d) Which will give the greater improvement in efficiency of a Carnot engine, a 10°C increase in the high-temperature reservoir or a 10°C decrease in the cold reservoir? Justify your answer.

(e) Prove that if you had a heat engine whose efficiency was better than the ideal value, you could connect it to an ordinary Carnot refrigerator to make a refrigerator that requires no work input. Which statement of the second law of thermodynamics does this combination violate?

Question 5 [8 Marks]

(a) Can you warm a kitchen in winter by leaving the oven door open? Can you cool a kitchen in summer by leaving the refrigerator door open? Briefly explain.

(b) Using the definition of specific heat, the first law of thermodynamics and the ideal gas law, show that:
   (i) \( dQ = C_V dT + P dV \), where \( C_V \) is the specific heat at constant volume,
   (ii) \( C_P = C_V + nR \), where \( C_P \) is the specific heat at constant pressure and \( R \) is the ideal gas constant.

(c) A ferromagnetic system can exist in two distinct phases – all spins up and all spins down – as shown in the phase diagram below. Each phase has a Gibbs free energy \( G \), which obeys the thermodynamic identity \( dG = -S dT - \mu_0 M dH \), where \( S \) is the entropy, \( T \) is the temperature, \( \mu_0 \) is the Bohr magneton, \( M \) is the magnetization of the spins (i.e., how aligned they are) and \( \mu_0 H \) is the externally applied magnetic field.

(i) How are the Gibbs free energies of phases 1 and 2 related at the phase boundary? As you move along the phase boundary, how are the changes in the Gibbs free energies of the two phases related?

(ii) Show that an analogue of the Clausius-Clapeyron equation can be obtained for this system as:
\[
\frac{dH}{dT} = \frac{S_2 - S_1}{\mu_0 (M_2 - M_1)}
\]

(iii) Comment on the application of the equation in (ii) to the ferromagnetic phase diagram above? What does it say about the entropy of the two phases? Explain briefly why this makes sense.