Thermodynamics
SCQF Level 9, U01359, PHY-3-Thermo
Thursday 21st May, 2009
2.30 – 4.30 p.m.

Chairman of Examiners
Professor R D Kenway

External Examiner
Professor M Green

Answer ALL of the questions in Section A
and TWO questions from Section B.

The bracketed numbers give an indication of the value assigned
to each portion of a question.

Only the supplied Electronic Calculators may be used during this examination.

ANONYMITY OF THE CANDIDATE WILL BE MAINTAINED DURING THE MARKING OF
THIS EXAMINATION.
Section A: Answer ALL of the questions in this Section

A.1. What is the definition of ‘heat’ in classical thermodynamics? Give three processes by which heat can be transferred between bodies. [5]

A.2. Carnot’s theorem states that no closed cycle heat engine working between two fixed temperature reservoirs can be more efficient than a Carnot engine. Show that if such a heat engine could be constructed it would violate the Clausius or Kelvin-Planck statement of the second law of thermodynamics. [5]

A.3. State the 3rd law of thermodynamics and explain how it implies that the thermal expansion coefficient

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]

must ultimately tend to zero as temperature is decreased towards 0 K. [5]

A.4. A working substance is taken once around a closed cycle that involves performing some external work. It absorbs heat, \( Q_1 = 1000 \) J, from a reservoir at \( T_1 = 1000 \) K and heat \( Q_2 = 2000 \) J from a reservoir at \( T_2 = 2000 \) K. The only other exchange of heat is with a reservoir at \( T_3 = 300 \) K.

What is the minimum heat that must have been transferred from the substance to the reservoir at \( T_3 \) (explain your reasoning)? [5]
Section B: Answer TWO of the questions in this Section

B.1. This question examines Joule-Kelvin (throttling) expansion.

In a Joule-Kelvin expansion a gas at initial temperature $T_1$ is pushed through a porous plug from a high pressure chamber maintained at a constant pressure $P_1$ into a low pressure chamber maintained at constant pressure $P_2$, both chambers being thermally isolated.

a. Explain why the enthalpy of the gas is unchanged in such a process. | 4 |

![Diagram of isenthalps](image)

Figure 1: 4 isenthalps labelled $H_1$ to $H_4$ (solid lines) for a fluid as a function of temperature and pressure. The inversion line is shown dashed.

b. Figure 1 shows different lines of constant enthalpy (isenthalps) for a fixed mass of gas. Explain the significance of the curve labelled ‘inversion line’. | 2 |

c. Show that the gradient of the isenthalps in figure 1 is

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p} \left( T \left(\frac{\partial V}{\partial T}\right)_p - V \right).$$

$C_p$ is the isobaric heat capacity and $V$ is the volume of gas. | 6 |

d. Show that at any point on the inversion line

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}.$$ | 2 |

e. For helium gas the maximum inversion temperature is 45 K. What consequence does this have for liquifying helium with Joule-Kelvin expansion starting with helium gas at room temperature. | 2 |

f. For the Van der Waals equation of state $(p + a/V^2)(V - b) = RT$ the maximum inversion temperature can be shown to be $RT_{\text{inv max}} = 2a/9b$. From this result and your knowledge of the origin of the constants $a$ and $b$ comment on how the maximum inversion temperature might be expected to change going down the series of noble gases (He, Ne, Ar, Kr, Xe). | 4 |
B.2. This question investigates a material that undergoes a discontinuous change of volume with temperature.

a. Starting from the statement that total entropy ($S_{\text{system}} + S_{\text{surroundings}}$) can only increase show that $G = U - T S + p V$ will attain its minimum value for a system in equilibrium with a fixed pressure and temperature reservoir. [7]

b. At atmospheric pressure a particular substance is found to undergo a discontinuous change between two states at temperature $T_C$ when heated. Its volume increases by $\Delta V$ and it absorbs latent heat $L$ as its temperature is changed from just below $T_C$ to just above $T_C$. Explain why at $T_C$ the value of $G$ is the same for the two states with different volumes. [4]

c. Derive the following equation relating how $T_C$ changes with pressure.

$$\frac{dT_C}{dP} = \frac{\Delta VT_C}{L}. \quad [6]$$

d. Explain briefly why $L$ must be positive and comment on whether $T_C$ is expected to increase or decrease with pressure. [3]
B.3. The speed of sound in a gas $c$ is given in terms of pressure $P$ and mass density $\rho$ by

$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_s.$$ 

a. Show that

$$\left( \frac{\partial P}{\partial \rho} \right)_s = -\frac{V^2}{M} \left( \frac{\partial P}{\partial V} \right)_s$$

with $V$ the molar volume and $\tilde{M}$ the molar mass. \[3\]

b. Derive the following relation

$$\left( \frac{\partial P}{\partial V} \right)_s = -\frac{c_p}{c_v} K_T V.$$

c. Show that for an ideal gas

$$K_T = \frac{\rho RT}{\tilde{M}}.$$ \[3\]

d. Show that for an ideal gas $c_p - c_v = R$. \[5\]

e. Hence estimate the speed of sound in air at 300 K assuming air to be an ideal diatomic gas (for a diatomic gas $c_v = (5/2)R$) and $\tilde{M} = 0.029$ Kg. \[4\]