# King's College London 

## University of London

This paper is part of an examination of the College counting towards the award of a degree. Examinations are governed by the College Regulations under the authority of the Academic Board.

B.Sc. EXAMINATION

CP/2470 Principles of Thermal Physics

January 2005

## Time allowed: THREE Hours

Candidates should answer ALL parts of SECTION A, and no more than TWO questions from SECTION B. No credit will be given for answering further questions.

The approximate mark for each part of a question is indicated in square brackets.

You must not use your own calculator for this paper. Where necessary, a College calculator will have been supplied.

## Physical Constants

Permittivity of free space
Permeability of free space
Speed of light in free space
Gravitational constant
Elementary charge
Electron rest mass
Unified atomic mass unit
Proton rest mass
Neutron rest mass
Planck constant
Boltzmann constant
Stefan-Boltzmann constant
Gas constant
Avogadro constant
Molar volume of ideal gas at STP
One standard atmosphere
$\epsilon_{0}=8.854 \times 10^{-12} \quad \mathrm{Fm}^{-1}$
$\mu_{0}=4 \pi \times 10^{-7} \quad \mathrm{Hm}^{-1}$
$c=2.998 \times 10^{8} \quad \mathrm{~m} \mathrm{~s}^{-1}$
$G=6.673 \times 10^{-11} \quad \mathrm{~N} \mathrm{~m}^{2} \mathrm{~kg}^{-2}$
$e=1.602 \times 10^{-19} \quad \mathrm{C}$
$m_{\mathrm{e}}=9.109 \times 10^{-31} \quad \mathrm{~kg}$
$m_{\mathrm{u}}=1.661 \times 10^{-27} \mathrm{~kg}$
$m_{\mathrm{p}}=1.673 \times 10^{-27} \mathrm{~kg}$
$m_{\mathrm{n}}=1.675 \times 10^{-27} \mathrm{~kg}$
$h=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$k_{\mathrm{B}}=1.381 \times 10^{-23} \quad \mathrm{~J} \mathrm{~K}^{-1}$
$\sigma=5.670 \times 10^{-8} \quad \mathrm{Wm}^{-2} \mathrm{~K}^{-4}$
$R=8.314 \quad \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
$N_{\mathrm{A}}=6.022 \times 10^{23} \quad \mathrm{~mol}^{-1}$
$=2.241 \times 10^{-2} \mathrm{~m}^{3}$
$P_{0}=1.013 \times 10^{5} \quad \mathrm{~N} \mathrm{~m}^{-2}$

Throughout this paper, $T$ denotes the temperature, $V$ the volume and $P$ the pressure. $C_{P}$ and $C_{V}$ respectively denote the heat capacity at constant pressure and the heat capacity at constant volume. $\gamma=C_{P} / C_{V}$ and $n$ is the number of moles.

## SECTION A - Answer ALL parts of this section

1.1) Boiling water, at the pressure $P=1 \mathrm{~atm}$, is poured into twice the same quantity of liquid water at $0{ }^{\circ} \mathrm{C}$. Explain how to obtain the temperature of the mixture and give its value in degrees Celsius (the heat capacity of water may be supposed independent of the temperature)
[7 marks]
1.2) Describe the different phases of a 4-stroke engine and explain in which one work is given to the surroundings.
[7 marks]
1.3) Define the Gibbs free energy $G$ and derive an expression for its differential $d G$ in terms of $T, P, V$ and the entropy $S$. Hence deduce the associated Maxwell relation.
[7 marks]
1.4) An engine $A$ operates in a reversible cycle and is successively in contact with two heat sources $\Sigma_{1}$ and $\Sigma_{2}$ at the temperatures $T_{1}$ and $T_{2}$ such that $T_{1}>T_{2}$. The global system $\left(A, \Sigma_{1}, \Sigma_{2}\right)$ is isolated. Define the efficiency $\eta$ of the engine and, using the second law, show that $\eta=1-T_{2} / T_{1}$.
[7 marks]
1.5) A gas has entropy $S$ and exchanges the heat $\delta Q$ with the surroundings during an infinitesimal process at temperature $T$. Explain why and in which circumstances the change in entropy is given by $d S=\delta Q / T$.
[7 marks]
1.6) Sketch the phase diagram $(P, T)$ of a pure substance, showing the three phases (solid, liquid, vapour), and explain how it is possible to go from the liquid state to the vapour state without experiencing any phase transition.
[7 marks]

## SECTION B - Answer TWO questions

2) One mole of an ideal gas is involved in the following two-stage process. The gas is first compressed in a reversible and isothermic way at temperature $T_{0}$, from the pressure $P_{0}$ to $10 P_{0}$. It is then expanded in a reversible and adiabatic way, back to the pressure $P_{0}$.
a) Give an expression for the temperature $T_{1}$ after this two-stage process. Give the numerical value for $T_{1}$, using $\gamma=1.41$ and $T_{0}=273 \mathrm{~K}$.
[5 marks]
b) Show that the temperature $T_{k}$ after $k$ similar two-stage processes done in a row is

$$
T_{k}=T_{0} \times 10^{\frac{k(1-\gamma)}{\gamma}},
$$

and give the numerical value for $T_{5}$.
[5 marks]
c) Using the Mayer relation and the definition of $\gamma$, show that $C_{V}=R /(\gamma-1)$.
[5 marks]
d) Explain why the change in internal energy for the $k$-th two-stage process is $\Delta U_{k}=C_{V}\left(T_{k}-T_{k-1}\right)$.
e) Show that

$$
\Delta U_{k}=\frac{R T_{0}}{\gamma-1} \times 10^{\frac{k(1-\gamma)}{\gamma}}\left[1-10^{\frac{\gamma-1}{\gamma}}\right]
$$

[5 marks]
f) Give an expression for the work exchanged with the surroundings during the $k$-th two-stage process.
3) An ideal gas, initial state $\left(P_{A}, V_{A}\right)$, operates in a reversible cycle that can each be decomposed into three steps. The first step $A \rightarrow B$ is an isochoric process where the pressure reaches $P_{B}>P_{A}$. The second step $B \rightarrow C$ is an adiabatic process which leads to the volume $V_{C}>V_{A}$ and the last step is an isobaric process which leads back to the initial state $A$.
a) Plot the cycle in a Clapeyron diagram ( $P$ versus $V$ ) and give the signs of the heats $Q_{A B}$ and $Q_{C A}$ exchanged with the surroundings.
b) Define the efficiency $\eta$ of the engine and show that it is given by

$$
\eta=1+\frac{Q_{C A}}{Q_{A B}}
$$

[6 marks]
c) Express $Q_{A B}$ and $Q_{C A}$ in terms of the temperatures $T_{A}, T_{B}, T_{C}$ and the heat capacities $C_{V}$ and $C_{P}$.
[6 marks]
d) Show that the efficiency is given by

$$
\eta=1+\gamma \frac{a-1}{a} \frac{P_{A}}{P_{B}-P_{A}}
$$

where $a=V_{A} / V_{C}$.
[6 marks]
e) Using an equation characterizing the adiabatic process $B \rightarrow C$, give an expression for $\eta$ in terms of $\gamma$ and $a$ only.
[6 marks]
4) The liquid and vapour phases of a pure substance are in equilibrium at temperature $T$.
a) Explain the concept of saturated vapour pressure $P_{S}$ and define the quantity $L$ given by the Clausius-Clapeyron equation

$$
L=T\left(v_{g}-v_{l}\right) \frac{d P_{S}}{d T}
$$

where $v_{g}$ and $v_{l}$ are the volumes per unit mass of the vapour and liquid phases respectively.
[5 marks]
b) Experiments show that $L=A-B T$ is a good approximation in the range of temperatures considered here, where $A$ and $B$ are constants. The vapour is supposed to be an ideal gas. Neglecting the volume per unit mole of the liquid compared with that of the vapour, show that

$$
P_{S}=P_{0}\left(\frac{T_{0}}{T}\right)^{\frac{B M}{R}} \exp \left\{\frac{A M}{R}\left(\frac{1}{T_{0}}-\frac{1}{T}\right)\right\}
$$

where $M$ is the mass per unit mole and $\left(T_{0}, P_{0}\right)$ is a reference point.
[8 marks]
c) For water $A=3.34 \times 10^{6} \mathrm{~J} \mathrm{~kg}^{-1}$ and $B=2.93 \times 10^{3} \mathrm{~J} \mathrm{~kg}^{-1} \mathrm{~K}^{-1}$. If boiling water at atmospheric pressure is taken as the reference point, compute $P_{S}$ for $T=433 \mathrm{~K}$.
[5 marks]
d) From the relation found in b), compute the slope $d P_{S} / d T$ at $100{ }^{0} \mathrm{C}$.
[4 marks]
e) At $100{ }^{0} \mathrm{C}$, this slope is actually $0.036 \mathrm{~atm} \mathrm{~K} \mathrm{~K}^{-1}$ and $L=2.256 \times 10^{6} \mathrm{~J} \mathrm{~kg}^{-1}$. Considering that $v_{l} \ll v_{g}$, compute the volume per unit mass of the saturated vapour at this temperature (reminder: $1 \mathrm{~atm} \simeq 10^{5} \mathrm{~Pa}$ ).
[4 marks]
f) The mass per unit volume of liquid water at $100{ }^{0} \mathrm{C}$ is $958 \mathrm{~g} \mathrm{l}^{-1}$. Give an estimate, as a percentage, of the error made in the above calculation of $v_{g}$ by neglecting $v_{l}$.
[4 marks]

