King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/2470 PRINCIPLES OF THERMAL PHYSICS

Summer 1997

Time allowed: THREE Hours

Candidates should answer SIX parts of SECTION A, and TWO questions from SECTION B.

Separate answer books must be used for each Section of the paper.

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.

TURN OVER WHEN INSTRUCTED

Values of physical constants and conversion factors

Universal gas constant	R	$= 8.31\ \mathrm{JK^{-1}mol^{-1}}$
Atmospheric pressure	1 atmosphere	$= 1.01 \times 10^5\ \mathrm{Nm^{-2}}$
Triple point of water	T_{TP}	$= 273.16\ \mathrm{K}$

Throughout this paper, P denotes the pressure, T the thermodynamic temperature, V the volume and v the molar volume.

SECTION A – Answer SIX parts of this section

1.1) State the law of thermodynamics that provides the scientific basis for our concept of temperature.

When the bulb of a mercury-in-glass thermometer is immersed in water at its triple point, the length of the mercury column is 40.0 mm. What is the temperature on the mercury-in-glass scale when the length of the mercury column is 60.0 mm?

[7 marks]

1.2) How many moles are there in 2 kg of hydrogen?

Calculate the work done by the same number of moles of an ideal gas at a temperature of 300 K as it expands quasi-statically and isothermally until its initial pressure is halved.

[7 marks]

1.3) The *energy equation* for any system with the state variables P, V and T is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P\,,$$

where U is the internal energy. Using this equation, prove that the internal energy of an ideal gas is a function of T only. Hence, show that there is no temperature change accompanying the free expansion of an ideal gas.

[7 marks]

1.4) State the theorem of equipartition of energy and use it to estimate the molar heat capacity c_v of oxygen at room temperature and atmospheric pressure.

[7 marks]

1.5) Give the Kelvin-Planck statement and the Clausius statement of the second law of thermodynamics.

[7 marks]

1.6) A reversible Carnot engine operates between reservoirs at 500 K and 300 K. Calculate the efficiency of the engine. During an integral number of complete cycles, the engine absorbs 1500 J of heat from the hotter reservoir. How much work is done by the engine and how much heat is exchanged with the reservoir at 300 K?

[7 marks]

1.7) Calculate the change in entropy when 1 kg of water at 15 °C is heated at atmospheric pressure and converted into steam at 100 °C . The specific heat capacity c_P of water at constant pressure is 4.18 $\text{kJ kg}^{-1}\text{K}^{-1}$ and the latent heat of vaporisation of water is 2.26 kJ g^{-1}.

[7 marks]

1.8) Sketch the $P-T$ phase diagram for water and describe its main features.

[7 marks]

SECTION B – Answer TWO questions

2) Suppose that the state variables of a gas are related by Dieterici's equation of state

$$P(v-b) = RT\exp(-a/RTv)\,,$$

where a and b are constants. Prove that the value of the critical coefficient $RT_c/P_c v_c$ is approximately 3.69.

[20 marks]

For CO_2, $P_c = 73\,\text{atm}$ and $v_c = 94\,\text{cm}^3\text{mol}^{-1}$. Calculate the value of a in $\text{Nm}^4\text{mol}^{-2}$ and b in $\text{m}^3\text{mol}^{-1}$ and hence estimate the critical temperature T_c for CO_2 in degrees Celsius.

[10 marks]

SEE NEXT PAGE

3) The Carnot cycle $\mathcal{C}$ for one mole of an ideal gas consists of two isothermal portions PQ and RS corresponding to temperatures T_1 and $T_2(< T_1)$, respectively, and two adiabatic portions QR and SP. Show that

$$\oint_{\mathcal{C}} \mathrm{d}Q_{\mathrm{R}} = RT_1\,\ell\mathrm{n}\left(\frac{V_{\mathrm{Q}}}{V_{\mathrm{P}}}\right) - RT_2\,\ell\mathrm{n}\left(\frac{V_{\mathrm{R}}}{V_{\mathrm{S}}}\right)\,,$$

where $\mathrm{d}Q_{\mathrm{R}}$ is the infinitesimal heat entering the system reversibly and V_{X} is the volume at the point X in the indicator diagram.

[10 marks]

Prove, by explicit calculation of the contribution from each of the four portions of the cycle, that

$$\oint_{\mathcal{C}} \frac{\mathrm{d}Q_{\mathrm{R}}}{T} = 0\,.$$

[16 marks]

Explain the significance of the last result.

[4 marks]

4) The Joule-Kelvin coefficient μ_{JK} is defined by

$$\mu_{\mathrm{JK}} = \left(\frac{\partial T}{\partial P}\right)_H$$

where H is the enthalpy of the system. Describe briefly how the Joule-Kelvin effect is used to cool a gas.

[10 marks]Show how μ_{JK} is used to calculate the temperature change in the Joule-Kelvin effect.

[5 marks]

Prove that μ_{JK} may be written as

$$\mu_{\mathrm{JK}} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\,,$$

where C_P is the heat capacity at constant pressure.

[10 marks]Hence, show that there is no temperature change when an ideal gas undergoes a throttling process.

[5 marks]

5) The *energy equation* for any system with the state variables P, V and T is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P,$$

where U is the internal energy. Using this equation, show that the energy density $u\,(=U/V)$ of cavity radiation is given by

$$u = A\,T^4,$$

where A is a constant. State any assumptions that you make concerning u and its relationship to the radiation pressure.

[10 marks]

State the *fundamental equation of thermodynamics* and use it to prove that the entropy associated with cavity radiation is given by

$$S = \frac{4}{3}AT^3V + S_0,$$

where S_0 is a constant.

[15 marks]

State the Planck version of the third law of thermodynamics and use it to suggest a value for S_0.

[5 marks]