Engineering Tripos Part IIA **THIRD YEAR**

Module 3A5 : Thermodynamics and Power Generation

THERMODYNAMICS

Examples Paper 2

1. *In Lectures, the requirement for phase equilibrium* $\mu_\alpha = \mu_\beta$ *was derived from the condition that the Gibbs function of a system held at constant T and p is a minimum at equilibrium. This question shows that the same result can be obtained by minimising the Helmholtz function of a system held at constant T and V.*

   A mass m of a pure substance is held at constant volume V and temperature T by being placed in a rigid container of volume V which is in intimate contact with a heat reservoir at temperature T. When equilibrium is established, it is observed that two phases α and β are present. The boundary between the phases is flat and there are no semi-permeable membranes affecting the equilibrium so the pressure p is uniform throughout the system.

   (a) Let $f_i = u_i - Ts_i$ be the specific Helmholtz function of phase-*i*. For a change at constant T, prove that,

   $$df_i = -p\,dv_i$$

   where v_i is the specific volume of the phase.

   (b) The Helmholtz function F of the total system is given by,

   $$F = m_\alpha f_\alpha + m_\beta f_\beta$$

   By considering variations of F at constant temperature T, constant total volume $V = m_\alpha v_\alpha + m_\beta v_\beta$ and constant total mass $m = m_\alpha + m_\beta$ show that the chemical potentials (*i.e.*, the specific Gibbs functions) of the two phases are equal at equilibrium.

2. Using the Clausius-Clapeyron equation, derive an approximate equation for the saturated vapour pressure p_S as a function of temperature T, assuming T is well below the critical temperature. Assume that the specific enthalpy of evaporation h_{fg} is constant over the range of interest and make other approximations as you see fit. Using your expression, estimate the saturated vapour pressure ratio (p_{S2}/p_{S1}) for water for T_1 = 40 ^{o}C and T_2 = 100 ^{o}C. Compare your result to the value obtained from the *Steam Tables* in the Data Book.

3. *In Lecture 6, using a Gibbs function formulation $g = g(T, p)$, it was shown how the ideal gas law, $pv = RT$, implies that $h = h(T)$ and $c_p = c_p(T)$. This question develops the parallel analysis using the Helmholtz function formulation $f = f(T, v)$ to show that $u = u(T)$ and $c_v = c_v(T)$.*

(a) Use the Helmholtz function to prove the Maxwell relation,

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

(b) Using $Tds = du + pdv$ and the above Maxwell relation, prove that, for an ideal gas obeying $pv = RT$, u and c_v are functions only of T.

4. *Characteristic equations of state are useful because they assemble all the thermodynamic information about a substance in one equation.*

The characteristic equation of state of a pure substance is expressed in Helmholtz function form $f = f\,(T, v)$ as follows :

$$f \;=\; c(T-T_0) \;-\; cT\ln\left(\frac{T}{T_0}\right) \;-\; RT\ln\left(\frac{v-b}{v_0-b}\right) \;-\; a\left(\frac{1}{v}-\frac{1}{v_0}\right)$$

where T is temperature, v is specific volume, R is the specific gas constant and a, b, c, T_0 and v_0 are constants.

(a) Find the p-v-T equation of state for the substance.

(b) Derive expressions for s, u and c_v all as functions of T and v. What do T_0 and v_0 represent physically?

(c) Show that,

$$(c_p - c_v) \;=\; \left(\frac{RT}{v-b}\right)\left(\frac{\partial v}{\partial T}\right)_p$$

$(\partial v/\partial T)_p$ can now be obtained from the p-v-T equation of state but the algebra is rather messy and the result not very informative.

5. *The van der Waals equation of state is of limited practical use but it occupies such a classical position that all well-educated thermodynamicists ought to be conversant with the basic concepts required for this question.*

The equation of state of a van der Waals fluid can be written,

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$$

where p is pressure, T is temperature, $\bar{v}$ is the molar volume, $\bar{R}$ is the molar gas constant, and a and b are constants. Using the critical point conditions,

$$\left(\frac{\partial p}{\partial \bar{v}}\right)_T = \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = 0$$

express a and b in terms of the temperature T_C and molar volume $\bar{v}_C$ at the critical point. Explain the physical significance of b and show that the value of the *compressibility factor* ($Z = p\bar{v}/\bar{R}T$) at the critical point is 3/8. Finally, derive the *reduced* van der Waals equation,

$$\left(p_R + \frac{3}{V_R^2}\right)(3V_R - 1) = 8T_R$$

where the *reduced* pressure, temperature and volume are defined by,

$$p_R = \frac{p}{p_C}, \qquad T_R = \frac{T}{T_C}, \qquad V_R = \frac{\bar{v}}{\bar{v}_C}.$$

6. Air at low temperature may be assumed to be a mixture of 79% N_2 and 21% O_2 by volume, no other species being present. Suppose that a quantity of air at low temperature is heated to 2000 K, the pressure remaining constant at 1 bar. At this temperature, the species present at equilibrium may be assumed to be N_2, O_2 and NO.

(a) Write down the chemical equation relating the (metastable) low temperature situation to the equilibrium high temperature situation in terms of the unknown mole numbers of N_2, O_2 and NO.

(b) By considering the equilibrium requirement for the reaction,

$$-2\,NO + O_2 + N_2 = 0$$

calculate the mole fractions of N_2, O_2 and NO present at 2000 K and 1 bar.
Note that the set of equations can be solved analytically in this particular case.

(c) How would the mixture composition change if the pressure were raised to 5 bar, the temperature remaining at 2000 K?

7. A gas mixture consisting of CO and H_2 in molar proportions 3 : 1 (CO : H_2) is ignited with stoichiometric O_2 (not air) in an experiment in a <u>constant volume</u> combustion chamber. The initial temperature and pressure of the mixture are 400 K and 2 bar. The final temperature is 2600 K and the products are in chemical equilibrium. Assume all species behave as ideal gases.

(a) Assuming that the only species present are H_2O, CO_2, CO and O_2 (*i.e.*, neglecting any dissociation of the H_2O) find the mole fractions of these species and the final pressure. *Note that an iterative solution is required.*

(b) Assuming that the dissociation of H_2O into H_2 is very slight, estimate the mole fraction of H_2 present in the mixture.

8. A gas A_1 dissociates according to the reaction,

$$-A_1 + \tfrac{1}{2}A_2 + \tfrac{1}{2}A_3 = 0$$

All species behave as ideal gases and the equilibrium constant of the reaction is $K(T)$.

(a) Show that the mole fractions of an equilibrium mixture originating from 1 mole of A_1 are given by,

$$X_1 = \frac{1}{1+2K}, \qquad X_2 = \frac{K}{1+2K}, \qquad X_3 = \frac{K}{1+2K},$$

and hence that the molar enthalpy of the mixture is given by,

$$\bar{h}(T) = \frac{\bar{h}_1 + K\bar{h}_2 + K\bar{h}_3}{(1+2K)}$$

(b) Using van't Hoff's equation, show that the isobaric molar heat capacity of the mixture is given by,

$$\bar{c}_p(T) = \left(\frac{\partial \bar{h}}{\partial T}\right)_p = \frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{(2K+1)} + \frac{2K\bar{R}}{(2K+1)^2}\left(\frac{\Delta \bar{H}_{\mathrm{T}}}{\bar{R}T}\right)^2$$

where $\bar{c}_{pi}(T)$ is the molar heat capacity of species-i and $\Delta \bar{H}_{\mathrm{T}}$ is the molar enthalpy change of reaction at temperature T (*i.e.*, the enthalpy change when one mole of A_1 dissociates completely).

Provide a physical interpretation for the two terms on the right hand side of the equation and explain why dissociation always has a tendency to reduce the temperature.

Tripos questions for revision :

2007 (3A5)	Q1, Q2
2006 (3A5)	Q1 (b), Q2
2005 (3A5 Sample Paper)	Q2
2005 (3A5 Old style)	Q1 (a), Q6
2002 (G10)	Q2 (b & c only)
2000 (G10)	Q3, Q6 (c only)
1999 (G10)	Q1
1996 (G10)	Q2 (b, c & d only), Q3

ANSWERS

2. 13.37, 13.73 (from Steam Tables)

4. van der Waals fluid

5. $a = \dfrac{9\bar{v}_C \bar{R} T_C}{8}$, $b = \dfrac{\bar{v}_C}{3}$

6. (b) $X_{NO} = 0.0080$, $X_{O2} = 0.2060$, $X_{N2} = 0.7860$

7. (a) $X_{H2O} = 0.2412$, $X_{CO2} = 0.6530$, $X_{CO} = 0.0705$, $X_{O2} = 0.0353$, 8.984 bar
   (b) $X_{H2} \cong 0.0041$

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