UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION - DECEMBER 2001

Third Year - Program 6

CHE331H1 - THERMODYNAMICS II

Examiner - C.E. Chaffey

Examination type: C, one aid sheet prepared by the student.
A non-programmable calculator may be used.
Answer all five questions, which have values as indicated; total = 100.

MARKS

1. A liquid mixture contains 10.0 mol of *n*-octane (N) and 20.0 mol of 2,2-diethylpentane (D). Its temperature is the normal boiling point of pure N.

20 a *[15 MARKS]* What is the bubble-point pressure of this mixture (the total pressure of the vapor in equilibrium with the liquid)?
b *[5 MARKS]* Find the K-factors (K-values), K_N and K_D.
Data: The normal boiling points are 125.7°C for N and 146.2°C for D. The molar enthalpies of vaporization are 36.7 kJ mol^{-1} for N and 37.3 kJ mol^{-1} for D. A mixture having mole fractions x_N of N and x_D of D has molar excess Gibbs energy $856x_Nx_D$ J mol^{-1} at 125.7°C and at all pressures less than 2 bar.

2. In a gaseous reacting mixture containing oxygen and some nitrogen oxides, the following reactions might occur: $4NO_2 = 2N_2O_3 + O_2$;
$N_2O_3 + O_2 = N_2O_5$; $N_2O_3 + 2NO_2 = 2N_2O_5$;
$N_2O_3 + N_2O_5 = 2N_2O_4$; $N_2O_5 = 2NO_2 + \frac{1}{2}O_2$.

20 a *[5 MARKS]* Find a set of independent chemical reactions.
b *[10 MARKS]* At 300 K, the gas-phase reaction $2NO_2 = N_2O_4$ is exothermic, with standard enthalpy of reaction −57.2 kJ mol^{-1}, and its equilibrium constant is 5.78. What is its equilibrium constant at 400 K? The molar heat capacities at constant pressure, in J K^{-1} mol^{-1}, are $32.5 + 5.0 \times 10^{-5}T^2$ for NO_2, and $65.0 + 1.5 \times 10^{-4}T^2$ for N_2O_4, both as ideal gases (with T in K).

3. The behavior of real gases may be approximated roughly by the Clausius equation of state (EoS), $P = RT/(\underline{V} - b)$. This is like the van der Waals (or Peng-Robinson) EoS with $a = 0$. For nitrogen, $b = 0.020$ L mol^{-1} at the temperature 600 K.

15 **a** *[5 MARKS]* Find the molar residual enthalpy of nitrogen at a pressure of 200 bar and at a temperature of 600 K using the Clausius EoS.
b *[10 MARKS]* Nitrogen flows steadily without heat transfer (adiabatically) through a pressure-reducing valve (the nitrogen undergoes a Joule-Thomson expansion). The inlet stream is at a pressure of 200 bar and at a temperature of 600 K (the conditions of part **a**). The outlet stream is at a pressure of 1.00 bar. What is its temperature?
As an ideal gas (in the limit of zero pressure) nitrogen has molar heat capacity at constant pressure 30.0 J K^{-1} mol^{-1} at the temperature 600 K.

4. A cool stream of air at a pressure of 100 kPa and at a temperature of −10°C, needed to cool a gas chromatograph, flows with a volumetric flow rate of 2.50 L s^{-1}. This cool air stream is produced as one outlet stream of a Hilsch-Ranque vortex tube, a device which operates without heat transfer (adiabatically) and with no shaft work. The single input to the vortex tube is a stream of air at a pressure of 350 kPa and at a temperature of 25°C, with a volumetric flow rate of 1.50 L s^{-1}. Also from the vortex tube, a second outlet stream flows out at a pressure of 100 kPa. Under these conditions, air is an ideal gas with heat capacity at constant volume equal to $2.5R$.

25 **a** *[10 MARKS]* What is the temperature of the second outlet stream?
b *[5 MARKS]* What is its volumetric flow rate?
c *[10 MARKS]* At what rate does the vortex tube generate entropy?

5. In liquid mixtures of sulfuric acid (S) and water (W), the partial molar excess enthalpy of S is $30x_W^2 - 115x_W^3$ kJ mol^{-1}, and the partial molar excess enthalpy of W is $-140x_S^2 + 115x_S^3$ kJ mol^{-1}, at a pressure of 1 bar and at a temperature of 340 K. Here x_S and x_W are the mole fractions of S and W, respectively. At a pressure of 1 bar, 15.00 mol of a mixture of S and W having $x_S = 0.800$ is diluted with 5.00 mol of water.

20 To keep the temperature constant at 340 K, how much heat must be transferred? State whether the heat is added or taken away.