Chemical Engineering Thermodynamics qualify test (2005)

1. (15%)

   Start from the relation that $dH = TdS + VdP$ and one of the Maxwell's equations $(\frac{\partial V}{\partial T})_P = -(\frac{\partial S}{\partial P})_T$ to derive an expression for dH as a function of T and P in terms of measurable properties. Also evaluate dH for an ideal gas. Making use of the obtained relation above, please show $(\partial C_P / \partial P)_T = -T(\partial^2 V / \partial T^2)_P$.

2. (10%)

   Find the ideal change in free energy G and entropy S when 6 mol of Argon, initially at 1 atm and 298 K, are allowed to mix with 4 mol of Xenon at the same initial conditions.

3. (10%)

   The Trouton rule says that entropy change for a pure fluid changing from liquid to gas at its boiling point ($\Delta S = \lambda / T$, $\lambda =$ evaporation heat, $T =$ boiling point) is near the same at about 85 J/(mol·K) in spite of different fluids. From the microscopic viewpoint of entropy, i.e., $S = k \ln \Omega$, please explain the meaning of the Trouton rule.

4. (15%)

   An air compressor takes in air at 1 atm, 20℃, and discharges into a line with 1 cm inner diameter. The air velocity in the discharge line is 7 m/s at 3.5 atm. Assuming ideal, adiabatic compression, what is the power demand (W)? The velocity of the intake air is negligible. Air is nearly ideal under these conditions with $C_p = \frac{7}{2}R$.

5. (15%)

(a) Show that the rate at which shaft work is obtained or required for a reversible change of state in a closed system at constant internal energy and volume is equal to the negative of the product of the temperature and the rate of change of the entropy for the system.

(b) Show that the rate at which shaft work is obtained or required for a reversible change of state in a closed system at constant entropy and pressure is equal to the rate of change of enthalpy of the system.

6. (15%)

The fugacity coefficient of a binary mixture of gases at 200 °C and 50 bar is given by the equation

$$\ln \phi = (1 + y_2) y_1 y_2$$

where y_1 and y_2 are the mole fractions of components 1 and 2, respectively. Please find expressions for the fugacities $\hat{f}_1$ and $\hat{f}_2$ and determine their values in an equimolar mixture at the given conditions.

Hint: $\ln \hat{\phi}_i = \left[\dfrac{\partial (n \cdot \ln \phi)}{\partial n_i} \right]_{P,T,n_j}$, where *n* is the number of moles.

7. (20%)

Carbon dioxide is assumed to follow the equation of state

$$\left(P + \frac{n}{V^2 T^{\frac{1}{2}}} \right)(V - m) = RT$$

Where *n* and *m* are constants for any gas. Given that the critical pressure and the critical temperature of carbon dioxide are 72.9 *atm* and 304.2 K, respectively, please determine the compressibility factor of the gas at 100°C and at a volume of 6.948 cubic decimeters per kilogram (molecular weight of carbon dioxide = 44 *g/mol*, R = 82.06 cm^3 *atm / mol K*).

Chemical Engineering Thermodynamics, 2006

1. (30%)

As proposed by Arrhenius in 1896, "greenhouse effect" stands for the phenomenon that certain gases such as CO_2, CH_4, and N_2O trap heat in the troposphere. The effect is critical for the birth of life on earth. Without our current heat-trapping blanket of gases, the earth's temperature would be −18 °C instead of its current 15 °C. However, people nowadays are concerned about global warming by the enormous input of greenhouse gases as fossil fuels are burned, and the carbon cycle is disturbed. To understand the forest turnover rate, scientists set up experiments to study how plants grow under high concentration of CO_2. A perfectly insulated pressurized room at 4 bar and 27 °C containing 1 m^3 of 90 %CO_2, and 10 % O_2 (assumed ideal gas) was used. The gases need to be vented down to 1 bar during routine sampling and maintenance once every two month. The gases therefore need to be pumped in afterwards. A 100 W (J/s) electric cooler is switched on when the gas is flowing into the room. A control valve is used to adjust gas flow rate so that the temperature in the room is unchanged.

a) What is the flow rate of gas into the room that you recommend?

b) How long will it take to increase the pressure from 1 bar to 4 bar?

c) Give us some reasons why the electric cooler is used? What are possible consequences if the flow rate varies?

2. (20%)

a) Starting from the 1st law, please derive equations describing an adiabatic reversible expansion or compression of an ideal gas (with heat capacities of C_V^*, C_P^*) from P_1 ,T_1 to P_2 ,T_2.

b) Presently, high-pressure air (N = 8 mol/s, T = 300 K, p = 10 bar) is vented to one atmosphere in the chemical plant that you are working in. You now are considering setting up a turbine to recover waste energy from the air. Starting from defining the system, formulating the mass balance, and energy balance, please estimate the power generated from adiabatic, reversible operations of the turbine.

3. (15%)

Three processes are described below for a single phase fluid whose internal energy depends only on temperature. For each process, use thermodynamics principles (first law and relationship of internal energy to temperature) to explain why the process is possible or impossible.

(a) A fluid contracts as it is pushed by a piston in an adiabatic process and its temperature remains constant.

(b) A fluid contracts as it is pushed by a piston and cooled, and its temperature goes up. ("cooled" means heat transfer out)

(c) A fluid expands pushing a piston as it is heated, and its temperature goes down.

4. (15%)

The entropy of a certain fluid has theoretically been found to be related to its internal energy and volume in the following way

$$\underline{S} = \underline{S}^0 + \alpha \ln \frac{\underline{U}}{\underline{U}^0} + \beta \ln \frac{\underline{V}}{\underline{V}^0} \quad \text{and} \quad Td\underline{S} = d\underline{U} + Pd\underline{V}$$

where $\underline{S}^0, \underline{U}^0, \underline{V}^0$ are, respectively, the molar entropy, internal energy, and volume of the fluid in some appropriately chosen reference state, and α and β are positive constants.

(a) Develop an interrelationship between internal energy, temperature, and specific volume (the thermal equation of state) for this fluid.

(b) Develop an interrelationship between pressure, temperature, and volume (the volumetric equation of state) for this fluid.

5. (20%)

The excess Gibbs energy of a binary liquid mixture at fixed T and P is given by

$$\frac{G^E}{RT} = (-1.2x_1 - 1.5x_2)x_1x_2$$

For the given T and P, please show that the expression satisfies the Gibbs-Duhem equation.