

**CBE 450 Chemical Reactor Fundamentals**  
**Fall, 2009**  
**Homework Assignment #1**

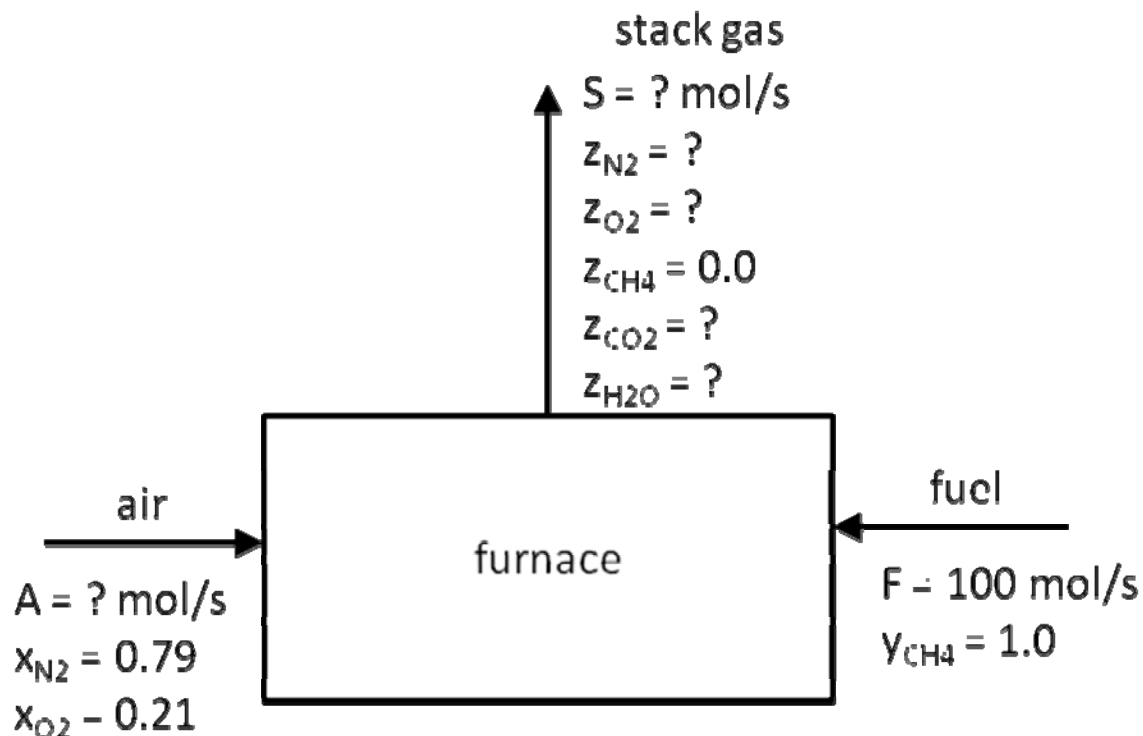
**1. Review of Mass Balances of Reacting Systems**

Natural gas (assume pure methane) is being burned in air (assume 0.79 mol% N<sub>2</sub> and 0.21 mol% O<sub>2</sub>). Assume complete combustion, which means that all of the natural gas is burned and is converted into carbon dioxide and water. Assume that the oxygen is provided in 100% excess. The flow rate of natural gas is 100 mol/s. The furnace operates at steady state.

- (a) Draw a diagram with all input and output streams. Indicate known and unknown flowrates. Indicate known and unknown compositions.
- (b) Determine the flowrate of air.
- (c) Determine the flowrate and composition of the output gas using atomic balances.
- (d) Determine the flowrate and composition of the output gas using molecular balances.

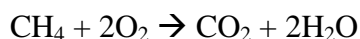
**Solution**

- (a) Draw a diagram with all input and output streams. Indicate known and unknown flowrates. Indicate known and unknown compositions.



- (b) Determine the flowrate of air.

The balanced reaction is



The stoichiometrically required amount of  $O_2$  is two moles of  $O_2$  for every mole of  $CH_4$ . Since the oxygen is provided in 100% excess, you actually need twice as much, or four moles of  $O_2$  for every mole of  $CH_4$ . Since you have 100 mol/s of  $CH_4$ , you need 400 mol/s of  $O_2$ . To determine the total air flowrate,

$$Ax_{O_2} = A(0.21) = 400 \text{ mol/s}$$

$$A = \frac{400}{0.21} \text{ mol/s} = 1905 \text{ mol/s}$$

(c) Determine the flowrate and composition of the output gas using atomic balances.

We have five unknowns, the flowrate and four compositions of the stack gas. Therefore, we need five equations. The first four equations are atom balances of the form:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

The accumulation term is zero because the furnace is operating at steady state. The generation term is zero because atoms are neither created or destroyed in this furnace. Therefore, the atom balance is

$$\text{in} = \text{out}$$

$$\text{N: } 2Ax_{N_2} = 2Sz_{N_2}$$

$$\text{C: } Fy_{CH_4} = Sz_{CO_2}$$

$$\text{H: } 4Fy_{CH_4} = 2Sz_{H_2O}$$

$$\text{O: } 2Ax_{O_2} = 2Sz_{O_2} + 2Sz_{CO_2} + Sz_{H_2O}$$

The fifth equation is the sum of the mole fractions is unity

$$\text{sum of the mole fractions is unity: } 1 = z_{O_2} + z_{CO_2} + z_{H_2O} + z_{N_2}$$

Now solve.

$$\text{in} = \text{out}$$

$$\text{N: } Sz_{N_2} = Ax_{N_2} = 1505$$

$$\text{C: } Sz_{CO_2} = Fy_{CH_4} = 100$$

$$\text{H: } Sz_{H_2O} = 2Fy_{CH_4} = 200$$

$$\text{O: } Sz_{O_2} = Ax_{O_2} - Sz_{CO_2} - \frac{1}{2}Sz_{H_2O} = 400 - 100 - \frac{1}{2}200 = 200$$

We can multiply the mole fractions sum by S and write

$$S = Sz_{O_2} + Sz_{CO_2} + Sz_{H_2O} + Sz_{N_2} = 200 + 100 + 200 + 1505 = 2005 \text{ mol/s}$$

The compositions are thus

$$\text{N: } z_{N_2} = \frac{1505}{S} = \frac{1505}{2005} = 0.7505$$

$$\text{C: } z_{CO_2} = \frac{100}{S} = \frac{100}{2005} = 0.0499$$

$$\text{H: } z_{H_2O} = \frac{200}{S} = \frac{200}{2005} = 0.0998$$

$$\text{O: } z_{O_2} = \frac{200}{S} = \frac{200}{2005} = 0.0998$$

(d) Determine the flowrate and composition of the output gas using molecular balances.

We again have five unknowns, the flowrate and four compositions of the stack gas. Therefore, we need five equations. The first four equations are molar balances of the form:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

The accumulation term is zero because the furnace is operating at steady state. The generation term is not zero because molecules are created or destroyed in this furnace. Therefore, the molar balances are

$$0 = \text{in} - \text{out} + \text{generation}$$

The generation term is the number of moles created or destroyed. Since the stoichiometric coefficient of methane in the reaction is one, we can use that as our basis.

$$CH_4 \text{ generation} = -100 \text{ mol/s}$$

The generation is negative since  $CH_4$  is consumed in the reaction. The other generation terms are reached by taking the magnitude of the  $CH_4$  generation term and multiplying it by the stoichiometric coefficient for each component.

$$\text{N}_2: 0 = Ax_{\text{N}_2} - Sz_{\text{N}_2}$$

$$\text{CO}_2: 0 = 0 - Sz_{\text{CO}_2} + (1)100$$

$$\text{H}_2\text{O}: 0 = 0 - Sz_{\text{H}_2\text{O}} + (2)100$$

$$\text{O}_2: 0 = Ax_{\text{O}_2} - Sz_{\text{O}_2} + (-2)100$$

$$\text{CH}_4: 0 = Fy_{\text{CH}_4} - 0 + (-1)100$$

We see that the methane balance was actually used to determine the generation term.

The fifth equation is the sum of the mole fractions is unity

$$\text{sum of the mole fractions is unity: } 1 = z_{\text{O}_2} + z_{\text{CO}_2} + z_{\text{H}_2\text{O}} + z_{\text{N}_2}$$

Now solve.

$$\text{N}_2: Sz_{\text{N}_2} = Ax_{\text{N}_2} = 1505$$

$$\text{CO}_2: Sz_{\text{CO}_2} = 100$$

$$\text{H}_2\text{O}: Sz_{\text{H}_2\text{O}} = 200$$

$$\text{O}_2: Sz_{\text{O}_2} = Ax_{\text{O}_2} - 200 = 200$$

We can multiply the mole fractions sum by S and write

$$S = Sz_{\text{O}_2} + Sz_{\text{CO}_2} + Sz_{\text{H}_2\text{O}} + Sz_{\text{N}_2} = 200 + 100 + 200 + 1505 = 2005 \text{ mol/s}$$

The compositions are thus

$$\text{N: } z_{\text{N}_2} = \frac{1505}{S} = \frac{1505}{2005} = 0.7505$$

$$\text{C: } z_{\text{CO}_2} = \frac{100}{S} = \frac{100}{2005} = 0.0499$$

$$\text{H: } z_{H_2O} = \frac{200}{S} = \frac{200}{2005} = 0.0998$$

$$\text{O: } z_{O_2} = \frac{200}{S} = \frac{200}{2005} = 0.0998$$

This is the same result as was obtained from the atomic balances, as it must be.

## 2. Molecular Description of Reaction Equilibrium

Consider the distribution of para-xylene, meta-xylene and ortho-xylene.

- For an ideal gas at a given temperature, what factors at the molecular level determine the equilibrium distribution of components?
- At a given temperature, will the mole fraction of the component with the lowest enthalpy be greater or less than the mole fraction of the other components (all other things being equal)? Why?
- At a given temperature, will the mole fraction of the component with the lowest entropy be greater or less than the mole fraction of the other components (all other things being equal)? Why?
- At a given temperature, will the mole fraction of the component with the lowest free energy be greater or less than the mole fraction of the other components (all other things being equal)? Why?
- As the temperature is increased, will the mole fraction of the component with the lowest enthalpy increase or decrease (all other things being equal)? Why?
- As the temperature is increased, will the mole fraction of the component with the lowest entropy increase or decrease (all other things being equal)? Why?

### Solution:

- For an ideal gas at a given temperature, what factors at the molecular level determine the equilibrium distribution of components?

At the molecular level, the enthalpy and the entropy can be broken into contributions from

- translation of the center of the mass of the molecule
- rotation about the center of mass of the molecule
- vibration of bonds within the molecule
- internal rotation of internal rotors like the methyl groups in xylene

The total enthalpy and entropy (and thus the free energy) are related to these contribution. Thus the equilibrium distribution is based on these contributions.

- At a given temperature, will the mole fraction of the component with the lowest enthalpy be greater or less than the mole fraction of the other components (all other things being equal)? Why?

$$\frac{N_1}{N_2} = K_{eq,1-2} = \exp\left(-\frac{\Delta G_{1-2}}{RT}\right) = \exp\left(-\frac{\Delta H_{1-2} - T\Delta S_{1-2}}{RT}\right) = \exp\left(\frac{\Delta S_{1-2}}{R}\right) \exp\left(-\frac{\Delta H_{1-2}}{RT}\right)$$

The enthalpy difference between state 1 and 2 is

$$\Delta H_{1-2} = H_{f,1} - H_{f,2}$$

If state one has the lowest enthalpy, then  $\Delta H_{1-2} < 0$

If all other things are equal (meaning  $\Delta S_{1-2} = 0$ ), then

$$-\frac{\Delta H_{1-2}}{RT} > 0 \text{ and } \exp\left(-\frac{\Delta H_{1-2}}{RT}\right) > 1 \text{ so } N_1 > N_2$$

A low enthalpy state is favored at equilibrium.

(c) At a given temperature, will the mole fraction of the component with the lowest entropy be greater or less than the mole fraction of the other components (all other things being equal)? Why?

The entropy difference between state 1 and 2 is

$$\Delta S_{1-2} = S_{f,1} - S_{f,2}$$

If state one has the lowest entropy, then  $\Delta S_{1-2} < 0$

If all other things are equal (meaning  $\Delta H_{1-2} = 0$ ), then

$$\frac{\Delta S_{1-2}}{R} < 0 \text{ and } \exp\left(\frac{\Delta S_{1-2}}{R}\right) < 1 \text{ so } N_1 < N_2$$

A high entropy state is favored at equilibrium.

(d) At a given temperature, will the mole fraction of the component with the lowest free energy be greater or less than the mole fraction of the other components (all other things being equal)? Why?

The free energy difference between state 1 and 2 is

$$\Delta G_{1-2} = G_{f,1} - G_{f,2}$$

If state one has the lowest free energy, then  $\Delta G_{1-2} < 0$  then

$$-\frac{\Delta G_{1-2}}{RT} > 0 \text{ and } \exp\left(-\frac{\Delta G_{1-2}}{RT}\right) > 1 \text{ so } N_1 > N_2$$

A low free energy state is favored at equilibrium.

(e) As the temperature is increased, will the mole fraction of the component with the lowest enthalpy increase or decrease (all other things being equal)? Why?

If state one has the lowest enthalpy, then  $\Delta H_{1-2} < 0$  and  $\Delta S_{1-2} = 0$ , then the derivative of this distribution with respect to temperature is

$$\frac{\partial}{\partial T} \left( \frac{N_1}{N_2} \right) = \exp\left(\frac{\Delta S_{1-2}}{R}\right) \exp\left(-\frac{\Delta H_{1-2}}{RT}\right) \left(\frac{\Delta H_{1-2}}{RT^2}\right) < 0$$

where we neglected the temperature dependence of the enthalpies of formation. So as the temperature increases the relative amount of  $N_1$  decreases. In other words, the low energy state is more favored at low temperature.

(f) As the temperature is increased, will the mole fraction of the component with the lowest entropy increase or decrease (all other things being equal)? Why?

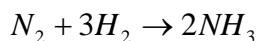
If state one has the lowest entropy, then  $\Delta S_{1-2} < 0$  and  $\Delta H_{1-2} = 0$ , then the derivative of this distribution with respect to temperature is

$$\frac{\partial}{\partial T} \left( \frac{N_1}{N_2} \right) = \exp\left(\frac{\Delta S_{1-2}}{R}\right) \exp\left(-\frac{\Delta H_{1-2}}{RT}\right) \left(\frac{\Delta H_{1-2}}{RT^2}\right) = 0$$

where we neglected the temperature dependence of the enthalpies of formation. So as the temperature increases the relative amount of  $N_1$  remains unchanged. In other words, the entropic contribution to the distribution of components does not have a temperature dependence.

### 3. Review Continuum Description of Reaction Equilibrium

Consider a batch reactor initially containing nitrogen and hydrogen gases. The volume of the batch reactor is  $1 \text{ m}^3$ . The initial pressure is 1 atm. The temperature is kept constant at 500 K. The initial mole fractions are 0.25  $N_2$  and 0.75  $H_2$ . The relevant reaction is



The reference enthalpies of formation are at a reference temperature of 298.15 K

$$H_{f,N_2} = 0 \text{ kcal/mol}$$

$$H_{f,H_2} = 0 \text{ kcal/mol}$$

$$H_{f,NH_3} = -10.96 \text{ kcal/mol}$$

The reference Gibbs free energies of formation are at a reference temperature of 298.15 K

$$G_{f,N_2} = 0 \text{ kcal / mol}$$

$$G_{f,H_2} = 0 \text{ kcal / mol}$$

$$G_{f,NH_3} = -3.903 \text{ kcal / mol}$$

In this project, you may assume that the heat capacities are constant, given by

$$C_{p,N_2} = 7.03 \text{ cal / mol / K}$$

$$C_{p,H_2} = 6.92 \text{ cal / mol / K}$$

$$C_{p,NH_3} = 9.31 \text{ cal / mol / K}$$

(a) What are the heats of formation at 500 K for each component?

$$H_{f,i}(T) = H_{f,i}(T_{ref}) + \int_{T_{ref}}^T C_{p,i} dT$$

For constant heat capacities

$$H_{f,i}(T) = H_{f,i}(T_{ref}) + C_{p,i}(T - T_{ref})$$

$$H_{f,N_2}(T = 500 \text{ K}) = 0.0 + \frac{7.03}{1000}(500 - 298) = 1.42 \text{ kcal / mol}$$

$$H_{f,H_2}(T = 500 \text{ K}) = 0.0 + \frac{6.92}{1000}(500 - 298) = 1.40 \text{ kcal / mol}$$

$$H_{f,N_2}(T = 500 \text{ K}) = -10.96 + \frac{9.31}{1000}(500 - 298) = -9.08 \text{ kcal / mol}$$

(b) What are the free energies of formation at 500 K for each component. (You may assume that the heat of formation is constant in this part (b) calculation only.)

$$G_{f,i}(T) = \frac{T}{T_{ref}} G_{f,i}(T_{ref}) - T \int_{T_{ref}}^T \frac{H_{f,i}}{T^2} dT$$

For constant heats of formation,

$$G_{f,i}(T) = \frac{T}{T_{ref}} G_{f,i}(T_{ref}) + TH_{f,i} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)$$



$$G_{f,N_2}(T) = \frac{500}{298}(0) + 500(1.42) \left( \frac{1}{500} - \frac{1}{298} \right) = -0.96 \text{ kcal/mol}$$

$$G_{f,H_2}(T) = \frac{500}{298}(0) + 500(1.40) \left( \frac{1}{500} - \frac{1}{298} \right) = -0.95 \text{ kcal/mol}$$

$$G_{f,NH_3}(T) = \frac{500}{298}(-3.903) + 500(-9.08) \left( \frac{1}{500} - \frac{1}{298} \right) = -0.394 \text{ kcal/mol}$$

(c) Compute the heat of reaction and free energy of reaction at 500 K on a per mole basis of  $NH_3$  produced.

$$\Delta H_r = H_{f,NH_3} - \frac{1}{2}H_{f,N_2} - \frac{3}{2}H_{f,H_2} = -11.89 \text{ kcal/mol}$$

$$\Delta G_r = G_{f,NH_3} - \frac{1}{2}G_{f,N_2} - \frac{3}{2}G_{f,H_2} = 1.51 \text{ kcal/mol}$$

(d) Compute the equilibrium coefficient of the reaction at 500 K.

$$K_{eq} = \exp\left(-\frac{\Delta G_r}{RT}\right) = \exp\left(-\frac{1.51}{0.001987(500)}\right) = 0.219$$

(e) Compute the equilibrium mole fractions of each component at 500 K.

For an ideal gas, we can write the equilibrium coefficient in terms of the mole fractions.

$$K_{eq} = \left(\frac{P}{P_{ref}}\right)^{\sum_j \nu_j} \prod_j x_j^{\nu_j}$$

We can write the mole fractions in terms of the initial number of moles  $N_{o,j}$ , the moles reacted,  $\chi$ , and the total number of moles,  $N$ ,

$$x_j = \frac{N_{o,j} - \nu_j \chi}{N}$$

The initial number of moles is

$$N_{o,j} = x_i \frac{pV}{RT} = x_i \frac{(101325)(1)}{(8.314)(500)} = x_i 24.4 \text{ moles}$$

$$N_{o,N_2} = x_i 24.4 \text{ moles} = 6.09$$

$$N_{o,H_2} = x_i 24.4 \text{ moles} = 18.3$$

$$N_{o,NH_3} = x_i 24.4 \text{ moles} = 0$$

The total number of moles is given by

$$N = N_o + \left( \sum_i \nu_i \right) \chi = 24.4 - \chi$$

The number of each species is

$$N_j = N_{o,j} + \nu_j \chi$$

$$N_{N_2} = N_{o,N_2} + \nu_{N_2} \chi = 6.09 - 0.5 \chi$$

$$N_{H_2} = N_{o,H_2} + \nu_{H_2} \chi = 18.3 - 1.5 \chi$$

$$N_{NH_3} = N_{o,NH_3} + \nu_{NH_3} \chi = 0.0 + 1.0 \chi$$

The reference pressure is 101325 Pa.

The final pressure is (using the ideal gas law)

$$p = \frac{NRT}{V} = \frac{N_o + \left( \sum_i \nu_i \right) \chi RT}{V}$$

Substituting these into equations the equilibrium coefficient

$$K_{eq} = \left( \frac{p}{p_{ref}} \right)^{(-1)} \frac{x_{NH_3}}{x_{H_2}^{3/2} x_{N_2}^{1/2}} = \frac{x_{NH_3}}{x_{H_2}^{3/2} x_{N_2}^{1/2}}$$

$$K_{eq} = \left( \frac{p}{p_{ref}} \right)^{(-1)} \frac{\frac{\chi}{24.4 - \chi}}{\left( \frac{18.3 - 1.5 \chi}{24.4 - \chi} \right)^{3/2} \left( \frac{6.09 - 0.5 \chi}{24.4 - \chi} \right)^{1/2}} = \left( \frac{p}{p_{ref}} \right)^{(-1)} \frac{\chi(24.4 - \chi)}{(18.3 - 1.5 \chi)^{3/2} (6.09 - 0.5 \chi)^{1/2}}$$

Solving this single, non-linear algebraic equation, I find

$$\chi = 1.37$$

and mole fractions

$$x_j = \frac{N_{o,j} - \nu_j \chi}{N} =$$

$$x_{N_2} = \frac{6.09 - (0.5)1.37}{24.37 - 1.37} = 0.235$$

$$x_{H_2} = \frac{18.28 - (1.5)1.37}{24.37 - 1.37} = 0.705$$

$$x_{NH_3} = \frac{0 + (1)1.37}{24.37 - 1.37} = 0.059$$