Department of Energy

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Exercises of "*Fundamentals of Chemical Processes*"

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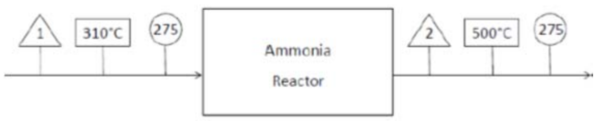
EXERCISE 10

Estimation of the composition at the outlet of a reactor for the production of NH_3

Ammonia is produced by reacting H_2 and N_2 in a catalytic reactor:

$$3/2\ H_2 + 1/2\ N_2 \leftrightarrow NH_3$$

The reactor is maintained at 275 atm. At the exit of the reactor, the gas stream is at 500°C. Determine the composition of the outlet stream assuming that the thermodynamic equilibrium is reached. Assume an ideal mixture of real gases.



Data:

Stream 2: P = 275 atm T_{out} = 500°C

Hypothesis: The thermodynamic equilibrium is reached

Ideal mixture of real gases

Species	Molar fraction (%)
NH_3	3.53
H_2	62.60
N_2	20.87
CH_4	9.78
Ar	3.22

$\Delta G_R^0(T) = -12972 + 27.84 \cdot T$ 600 < T < 1500 K $\Delta G^0_R(T)$ = [cal/mol]

Solution

The composition of the gas stream at the outlet of the reactor is unknown. In order to determine the composition, the material balance is written by application of the extent of reaction approach. The extent of reaction λ is introduced and 100 mol/s inlet gas is assumed as the basis. The following balances are obtained:

Species	**n^{IN} (mol/s)**	**n^{OUT} (mol/s)**
NH_3	3.53	3.53 + λ
H_2	62.60	62.60 – 1.5*λ
N_2	20.87	20.87 – 0.5*λ
CH_4	9.78	9.78
Ar	3.22	3.22

The thermodynamic condition assumed at the outlet requires that:

$$\Delta G_R^0(T) = RT \cdot \ln \prod_{i=1}^{NC} \left(a_i(T,P,\vec{y})^{\nu_i} \right)$$

The activities of the species depend on the composition of the outlet gas stream. Thus, one equation in the unknown λ is this obtained. Considering the definition of the activity, one can write:

$$a_i(T,P,\vec{y}) = \frac{\hat{f}_i^G(T,P,\vec{y})}{\hat{f}_i^0}$$

The reference is the ideal gas, at reference pressure of 1 bar, and at the temperature of the outlet current. Assuming ideal mixture, for each specie the activity is given by:

$$a_i(T,P,\vec{y}) = \frac{\phi_i(T,P) \cdot P \cdot y_i}{1} = \phi_i(T,P) \cdot P \cdot y_i$$

By substitution of the activities, the following equation is obtained:

$$k_{eq}=\frac{P_{NH_3}}{P_{H_2}^{3/2}\cdot P_{N_2}^{1/2}}\cdot\frac{\phi_{NH_3}}{\phi_{H_2}^{3/2}\cdot\phi_{N_2}^{1/2}}=\frac{n_{tot}^{out}}{P}\cdot\frac{\left(n_{NH_3}^{in}+\lambda\right)}{\left(n_{H_2}^{in}-1.5\lambda\right)^{1.5}\cdot\left(n_{N_2}^{in}-0.5\lambda\right)^{0.5}}\cdot k_{\phi}\left(P,T_{out}\right)=k_P\left(P,\lambda\right)\cdot k_{\phi}\left(P,T_{out}\right)$$

$$k_{eq}=\exp\left(-\frac{\Delta G_R^0\left(T_{out}\right)}{R\cdot T_{out}}\right)=k_P\left(P,\lambda\right)\cdot k_{\phi}\left(P,T_{out}\right)$$

The value of the ΔG^0_R at the outlet temperature is obtained from the linearized equation.

$$\Delta G_R^0\left(T\right)=-12972+27.84\cdot T=8552.496\,cal/mol$$
$$k_{eq}=3.811\cdot 10^{-3}$$

In the equilibrium equation, it is noted that the contribution given by the fugacity coefficients (named $k_ø$) depends exclusively on the temperature and the pressure, under the assumption of ideal mixtures. It is therefore possible to calculate this contribution with an appropriate equation of state. The RKS is chosen in the exercise. The reduced parameters and the coefficients for the solution of the cubic equation at P = 278.64 bar (275 atm) and T = 500°C are reported below:

Species	**T_C [K]**	**P_C [bar]**	**ω**	**$\alpha_{RKS}(T_R)$**	**$a_{RKS}(T_C)$**	**b_{RKS} (T_C)**	**A**	**B**
NH_3	405.5	113.5	0.250	0.4509	0.1930	2.573E-05	1.302E-01	1.115E-01
H_2	33.0	12.9	-0.216	0.2438	0.0061	1.843E-05	4.102E-03	7.989E-02
N_2	126.2	33.9	0.039	0.0407	0.0056	2.682E-05	3.811E-03	1.162E-01

The solution of the cubic equation associated to each of the species gives the following results:

Species	**p**	**q**	**D**	**Z**	**Z_1**	**Z_2**	**Z_3**	**Φ^V**
NH_3	-3.271E-01	-8.654E-02	5.753E-04	1.0082				0.9948
H_2	-4.155E-01	-1.018E-01	-6.639E-05		1.0766	-0.0724	-0.0042	1.0792
N_2	-4.593E-01	-1.165E-01	-1.951E-04		1.1135	-0.1098	-0.0036	1.1196

Under the operating conditions of the reactor, all the species are supercritical. In the case of NH_3, the positive determinant D guarantees that only one positive root is present. In the case of N_2 and H_2, the negative determinant indicates that three real solutions are present: given that the species are in the gas phase, the highest value of the compressibility factor must be chosen. This solution is coherent with the absence of a liquid phase at the equilibrium with the gas phase, given that the species are supercritical. From the fugacity coefficients, the value of $k_ø$ is calculated:

$$k_\phi = 0.8386$$

It is then possible to solve the equilibrium equation for λ. The value found for λ is 12.519 mol/s. The composition of the outlet gas stream is:

Species	**n^{OUT} (mol/s)**	**x out (%)**
NH_3	16.05	18.35
H_2	43.82	50.09
N_2	14.61	16.70
Ar	3.22	3.68
CH_4	9.78	11.18
total	87.48	100.00