Example 17.9 Adiabatic reaction in an ammonia reactor

Estimate the outlet temperature and equilibrium mole fraction of ammonia synthesized from a stoichiometric ratio of N_2 and H_2 fed at 400 K and reacted at 100 bar. How would these change if the pressure was 200 bar?

$$1/2\ N_{2(g)} + 3/2\ H_{2(g)} \rightleftarrows NH_{3(g)}$$

Solution: For a rough estimate we will use the shortcut approximation of temperature effects. Furthermore, we will assume $K_\varphi \approx 1$. (Is this a good approximation or not?[a]) Therefore we obtain,

$$P\,K_a = y_{NH3} / [(y_{N2})\,(y_{H2})^3]^{½}$$

Basis: Stoichiometric ratio in feed.

$$\dot{n}_{N_2}^{out} = \frac{1}{2} - \frac{1}{2}\dot{\xi} = \frac{1}{2}(1-\dot{\xi})\,;\ \dot{n}_{H_2}^{out} = \frac{3}{2} - \frac{3}{2}\dot{\xi} = \frac{3}{2}(1-\dot{\xi})\,;\ \dot{n}_{NH_3}^{out} = \dot{\xi};\ \dot{n}_T^{out} = 2-\dot{\xi} \qquad 17.46$$

For the purposes of the example, the shortcut van't Hoff equation will be used to iterate on the adiabatic reactor temperature. However, the full van't Hoff method will be used to obtain $\Delta G^\circ_{T\text{near}}$ and $\Delta H^\circ_{T\text{near}}$ at an estimated nearby temperature T_{near} = 600K as suggested in Section 17.8. Then the shortcut van't Hoff equation will be used over a limited temperature range for less error. The energy balance will also use $\Delta H^\circ_{T\text{near}}$; we will create an energy balance path through T_{near} = 600K rather than 298.15K. We will compare the approximate answer with the full van't Hoff method at the end of the example.

For ammonia, $\Delta G^\circ_{f,\,298.15}$ = –16,401.3 J/mol, $\Delta H^\circ_{f,\,298.15}$ = –45,940 J/mol. Since the reactants are in the pure state, the respective reactant formation values are zero, and therefore the formation values for ammonia represent the standard state values for the reaction. Inserting the formation values along with the heat capacities into the detailed van't Hoff equation—one of the K_a calculators highlighted in the margin note to Example 17.4 on page 645 is used—at an assumed temperature of 600 K, the values obtained are ΔH°_{600} = – 51,413 J/mol and $K_{a,600}$ = 0.0417659. Then the shortcut van't Hoff in the vicinity will be

$$\ln\left(\frac{K_{a,\,T}}{0.0417659}\right) = \frac{51,413}{8.314}\left(\frac{1}{T} - \frac{1}{600}\right) \qquad 17.47$$

From an assumed value of T, this equation will provide the equilibrium constant. Some manipulation is necessary to obtain the material balance from $K_{a,T}$. Plugging the mole fraction expressions into Eqn. 17.17, and collecting the fractions 1/2 and 3/2,

$$PK_{a,\,T}\left(\frac{3^3}{2^4}\right)^{1/2} = \frac{\dot{\xi}(2-\dot{\xi})}{(1-\dot{\xi})^2} \Rightarrow 2\dot{\xi} - \dot{\xi}^2 = \frac{\sqrt{27}}{4}PK_{a,\,T}(1-\dot{\xi})^2$$

$$\text{defining } M = \frac{\sqrt{27}}{4}PK_{a,\,T} \Rightarrow (M+1)\dot{\xi}^2 - 2(M+1)\dot{\xi} + M = 0 \Rightarrow \dot{\xi}^2 - 2\dot{\xi} + \left(\frac{M}{M+1}\right) = 0$$

Example 17.9 Adiabatic reaction in an ammonia reactor (Continued)

Applying the quadratic formula,

$$\dot{\xi} = \frac{2 \pm \sqrt{4 - 4M/(1+M)}}{2} = 1 - \sqrt{1 - M/(1+M)} \qquad 17.48$$

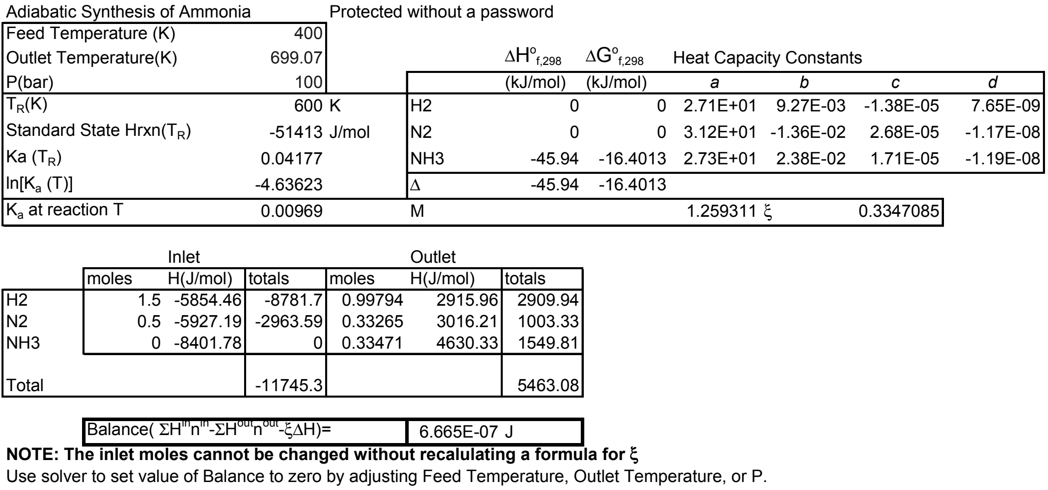
The strategy will be to guess T, and calculate $K_{a,T}$, M, and $\dot{\xi}$. $\dot{\xi}$ will be used in Eqn. 17.46 to perform the material balance. The material balance will be combined with the energy balance using the Heat of Reaction method (*cf.* Example 3.6), until the energy balance closes as represented by:

$$F(T) = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,i} dT - \dot{\xi} \Delta H_R^o = 0 \qquad 17.49$$

Workbook Rxns.xlsx, worksheet RxnAdia-shortcut or MATLAB Ex17_09.m.

Heat capacity integrals and the energy balance have been entered in the workbook Rxns.xlsx. At the initial guess of 600 K, the $F(T)$ of Eqn. 17.49 is 19.4 kJ. A converged result is found at 699 K shown in Fig. 17.4 and the $\dot{\xi} = 0.33$, conversion of feed is 33%. At 200 bar, the answer is 739 K, and conversion is 38%.

The detailed van't Hoff is available in the same workbook and results in 698 K and 33% conversion at 100 bar, and 737 K and 37% conversion at 200 bar.



Adiabatic Synthesis of Ammonia   Protected without a password

Feed Temperature (K)	400	
Outlet Temperature(K)	699.07	
P(bar)	100	
T_R(K)	600	K
Standard State Hrxn(T_R)	-51413	J/mol
Ka (T_R)	0.04177	
ln[K_a (T)]	-4.63623	
K_a at reaction T	0.00969	

	$\Delta H^o_{f,298}$ (kJ/mol)	$\Delta G^o_{f,298}$ (kJ/mol)	Heat Capacity Constants *a*	*b*	*c*	*d*
H2	0	0	2.71E+01	9.27E-03	-1.38E-05	7.65E-09
N2	0	0	3.12E+01	-1.36E-02	2.68E-05	-1.17E-08
NH3	-45.94	-16.4013	2.73E+01	2.38E-02	1.71E-05	-1.19E-08
Δ	-45.94	-16.4013				
M			1.259311	ξ	0.3347085	

	Inlet moles	H(J/mol)	totals	Outlet moles	H(J/mol)	totals
H2	1.5	-5854.46	-8781.7	0.99794	2915.96	2909.94
N2	0.5	-5927.19	-2963.59	0.33265	3016.21	1003.33
NH3	0	-8401.78	0	0.33471	4630.33	1549.81
Total			-11745.3			5463.08

Balance($\Sigma H^{in} n^{in} - \Sigma H^{out} n^{out} - \xi \Delta H$)= 6.665E-07 J

NOTE: The inlet moles cannot be changed without recalulating a formula for ξ

Use solver to set value of Balance to zero by adjusting Feed Temperature, Outlet Temperature, or P.

Figure 17.4 *Display from Rxns.xlsx showing a converged answer.*

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[a] We can evaluate this assumption by calculating the reduced temperatures at the end of our calculation and estimating the virial coefficients, then fugacity coefficients.

Graphical Visualization of the Energy Balance

The energy balance is presented in Fig. 3.6 on page 117. The difference here is that the appropriate curve from Fig. 3.6 is superimposed on the plot and the outlet conversion and outlet temperature are determined by the intersection of the energy balance line and the equilibrium line. Fig. 17.5 illustrates an exothermic reaction. In the event that the reaction does not reach equilibrium because