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A hundred years of chemical equilibrium calculations – The case of ammonia synthesis

Mordechai Shacham[a,*], Neima Brauner[b]

[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
[b] School of Mechanical Engineering, Tel-Aviv University, Tel-Aviv 69978, Israel

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ABSTRACT

An exercise that involves a process of great historical importance – that of synthesizing ammonia from its elements – is presented. In the exercise, the students are required to calculate the equilibrium conversion to ammonia using three mathematical models: a regression model which is based on experimental equilibrium data obtained by Haber and le Rossignol over a hundred years ago; a model based on the Gibbs energy and ideal gas conditions; and the Gibbs energy model with gas phase non-ideality included. The use of state-of-the-art problem-solving tools, including mathematical software packages and process simulation programs, combined with reliable physical property databases for the equilibrium computations, is emphasized. On one hand, the exercise gives students an opportunity to become familiar with and to appreciate the precision of the experimental work and the manual calculations that were carried out more than a hundred years ago, and on the other hand, it gives them an opportunity to practice the use of the modern numerical problem-solving tools. It also helps them master the complex issues involved in phase and chemical equilibrium in reacting systems.

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1. Introduction

The introduction of the personal computer in the early nineteen-eighties, and the emergence of commercial Internet providers a few years later, leads to revolutionary changes in chemical engineering problem-solving. As a result of these changes, numerical calculations are carried out nowadays mostly by mathematical software packages such as Excel®, MAPLE™, MATHCAD®, MATLAB®, Mathematica® and POLYMATH™ (Shacham and Cutlip, 1999; Mahecha-Botero et al., 2011). More complex calculations are carried out by computational fluid dynamics (CFD) packages (Morscheidt et al., 2013) and process simulation programs (such as Aspen, ChemCAD and UniSim; see, for example, Shacham et al., 2009). Physical and thermodynamic property data needed for the computation are routinely retrieved from property databases, such as DIPPR or NIST. It is very important for chemical engineering students to learn, and practice the use of, these modern computational tools. In this paper we present an exercise where the use of these tools can be practiced together with the modeling of chemical equilibrium at various levels of rigor with respect to the ammonia synthesis process.

The industrial synthesis of ammonia from its elements is considered by many as the most important technical invention of the twentieth century (Smil, 2001). This is because large scale production of ammonia enabled production of fertilizers that leads to huge increase in crop yields, which in turn enabled the expansion of the world's population from 1.6 billion people in 1900 to 6 billion at the end of the century. The breakthrough in ammonia synthesis was brought about by Fritz Haber (Haber, 1920) and coworkers, who carried out many experiments to determine the equilibrium constant of the ammonia synthesis reaction at various temperatures and pressures. The objective was to prove that under certain

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* *Corresponding author*. Tel.: +972 8 6461481; fax: +972 8 6472916.
E-mail address: shacham@exchange.bgu.ac.il (M. Shacham).

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conditions, high enough conversion of the elements H_2 and N_2 to ammonia can be reached, which would justify development of a commercially viable large scale process. Haber and le Rossignol (see p. 277 in Smil, 2001) carried out experiments at atmospheric and at 30 atm pressures at various temperatures in 1907. The results of the equilibrium constants at various conditions were reported by Haber (who received the Nobel Prize in Chemistry in 1918 for proving the feasibility of this process) in his Nobel lecture (Haber, 1920). Haber and le Rossignol (HR) used the experimental data they collected to develop a correlation for the equilibrium constant of the ammonia synthesis reaction as a function of temperature and pressure. At that time the physical and thermodynamic data were less accurate than today, and the calculations were carried out manually, usually with two or at most three decimal digits accuracy. For example, the heat capacity correlation for gaseous ammonia used by HR contains three constants with two or three decimal digits, while the same correlation provided by the NIST database contains five constants with seven decimal digits. Prior to the introduction of mathematical software packages, it was necessary to neglect the impact of some of the less influential factors (such as gas phase non-ideality) on the equilibrium conversion, because of the long time and the great effort involved in the calculations.

The exercises included here can be best given as homework assignments in thermodynamics, reaction engineering and process simulation courses. Solution of the exercises requires the use of physical and thermodynamic databases, such as DIPPR (dippr.byu.edu) or NIST (webbook.nist.gov), where up-to-date, evaluated (thus more reliable) property data are available. The use of mathematical software packages (e.g., POLYMATH (www.polymath-software.com), MATLAB (www.mathworks.com)) and process simulation programs (e.g., Aspen (www.aspentech.com), UniSim (www.honeywellprocess.com) ChemCAD (www.chemstations.com)) is also essential. Useful references for the ammonia synthesis equilibrium can be found in the textbook of Sandler (1999) and in the recent journal articles of Nasri and Binous (2009) and Klemola (2014).

2. Problem background – equilibrium composition in the ammonia synthesis reaction

Nitrogen and hydrogen react in an exothermic, equilibrium reaction to form ammonia,

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3 \tag{1}$$

The reaction is carried in the gas phase in the presence of a solid catalyst. The chemical equilibrium coefficient for the reaction can be expressed as:

$$K_a = \frac{a_{NH_3}}{a_{N_2}^{1/2}a_{H_2}^{3/2}} = \frac{\tilde{P}_{NH_3}}{\tilde{P}_{N_2}^{1/2}\tilde{P}_{H_2}^{3/2}}\,\frac{\bar{\phi}_{NH_3}}{\bar{\phi}_{N_2}^{1/2}\bar{\phi}_{H_2}^{3/2}} \tag{2}$$

where a_i is the activity of species i, $\tilde{P}_i$ is the dimensionless partial pressure, $\tilde{P}_i = P_i/P_0$, P_i is the partial pressure, P_0 is a reference (standard state) pressure and $\bar{\phi}_i$ is the fugacity coefficient of species i in the mixture. Assuming ideal gas phase (low pressure) all $\bar{\phi}_i = 1$ and Eq. (2) is reduced to

$$K_a = \frac{\tilde{P}_{NH_3}}{\tilde{P}_{N_2}^{1/2}\tilde{P}_{H_2}^{3/2}} \tag{3}$$

Using Eq. (3) for a specified value of K_a, the molar extent of the reaction (X) and the mole fractions and the partial pressures of the various components at equilibrium conditions can be calculated using the initial mole numbers. With inlet mole number of 1/2 for N_2 and 3/2 for H_2, the outlet mole fractions are the following: $X/(2-X)$ for NH_3, $(1-X)/[2\times(2-X)]$ for N_2, and $3\times(1-X)/[2\times(2-X)]$ for H_2 (where X is number of NH_3 moles produced). Substituting these expressions and the total pressure (P_{tot}) into Eq. (3) yields:

$$K_a = \frac{X(2-X)}{[(1-X)/2]^{1/2}[3(1-X)/2]^{3/2}(P_{tot}/P_0)} \tag{4}$$

Haber and le Rossignol (see p. 277 in Smil, 2001) carried out ammonia synthesis experiments at atmospheric and at 30 atm. pressures at various temperatures in 1907. Based on these experiments they developed the following correlation (the HR correlation) for the equilibrium constant[1]:

$$\log_{10}\frac{\tilde{P}_{NH_3}}{\tilde{P}_{N_2}^{1/2}\tilde{P}_{H_2}^{3/2}} = 2.10 + \frac{1}{4.571}\left(\frac{9591}{T} - 0.00046T + 0.85\times10^{-6}T^2\right) - \frac{4.98}{1.985}\log_{10}T \tag{5}$$

where T is the temperature in K. Using this correlation implies that ideal gas phase is assumed as all $\bar{\phi}_i$ values are set to 1 (as in Eq. (3)).

Using this equation, Haber and Rossignol calculated the percentage of ammonia at equilibrium for nine temperatures ($T = 473, 573, \ldots, 1273$ K) and four pressures ($P = 1$, 30, 100 and 200 atm, $P_0 = 1$ atm, units of atm are used for pressure to be consistent with the published version of the HR correlation).

Based on thermodynamic considerations, the equilibrium constant and its temperature dependence can be expressed as function of the Gibbs energy of the reaction, $\Delta G_r(T)$.

$$K_a(T) = \exp\left[-\frac{\Delta G_r(T)}{RT}\right] \tag{6}$$

The Gibbs energy of the reaction (at temperature T) can be calculated from the enthalpy (ΔH_r) and the entropy (ΔS_r) of the reaction at the same temperature.

$$\Delta G_r(T) = \Delta H_r(T) - T\Delta S_r(T) \tag{7}$$

The enthalpy of the reaction is a sum of the enthalpy of formation of the various species at standard state ($T_0 = 298.15$ K, $P_0 = 1$ bar) and a sum of the heat required to bring the reactants and the products to the temperature of the reaction

$$\Delta H_r(T) = \sum \nu_i \Delta H_{f,i}^0 + \int_{T_0}^{T} \sum \nu_i Cp_i dT \tag{8}$$

where ν_i is the stoichiometric coefficient (positive for products, negative for reactants), $\Delta H_{f,i}^0$ is the heat of formation at standard state and Cp_i is the ideal gas heat capacity (at constant pressure) of species i. The entropy of the reaction is given by

$$\Delta S_r(T) = \sum \nu_i \Delta S_{f,i}^0 + \int_{T_0}^{T} \sum \frac{\nu_i Cp_i}{T} dT \tag{9}$$

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[1] In the original publication (Haber, 1920) one of the parameters is misprinted (498 instead of 4.98).

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