ChE curriculum

Chemical Reaction Equilibrium Calculation Task For ChE Undergraduates –

SIMULATING FRITZ HABER'S AMMONIA SYNTHESIS WITH THERMODYNAMIC SOFTWARE

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In 1909, Fritz Haber succeeded in synthesizing ammonia from hydrogen and atmospheric nitrogen. He was awarded the Nobel Prize in Chemistry in 1918. He presented the original experimental results in his Nobel lecture in 1920. This paper demonstrates how to simulate Haber's experimental results with the thermodynamic software HSC Chemistry and how to calculate the equilibrium composition from basic thermodynamic data and equations.

The industrial synthesis of ammonia from its elements, nitrogen and hydrogen, the so-called Haber-Bosch process (named after the inventors Fritz Haber and Carl Bosch) is perhaps the most significant invention of the 20th century, since fertilizers made from ammonia are estimated to be responsible for sustaining almost half of the world's population today.[1] The negative effects of the innovation are enormous. Industrial fertilizers and nitrates pollute oceans and atmosphere. The Haber-Bosch process has enabled the population explosion and the political and environmental problems overpopulation has brought. The first Haber-Bosch process went on-stream in September 1913 in Oppau, Germany.

Fritz Haber was awarded the Nobel Prize in chemistry in 1918, with Carl Bosch receiving one in 1931, for their work on overcoming the chemical and engineering problems posed by ammonia production. Haber's original experimental results at various temperatures and pressures were given in his Nobel lecture June 2, 1920.[2] A snapshot of the results is given in Figure 1 (page 116).

Ammonia synthesis is an exothermic equilibrium reaction.

$$N_2(g)+3H_2(g) \rightleftarrows 2NH_3(g) \quad \Delta H=-91.88\,kJ\cdot mol^{-1}\,(298.15\,K) \tag{1}$$

Le Chatelier's principle suggests that increasing the pressure on the system favors the formation of ammonia and increasing the temperature shifts the equilibrium to the left. Haber's experimental results are in accordance with Le Chatelier's principle.

From the basic thermodynamic data for the compounds: enthalpy (H), entropy (S), heat capacity (C), the students calculate one data point in Figure 1 by hand. All the data points are calculated using the thermodynamic software HSC Chemistry.[3]

THERMODYNAMIC SOFTWARE

The thermodynamic software HSC Chemistry was developed by the Finnish state-owned mining and metallurgical company Outokumpu in 1974. The program is in use at a number of companies, universities, and schools around the world.

HSC Chemistry is designed for many different kinds of chemical reactions and equilibrium calculations. The name of the program is based on the feature that calculation modules automatically utilize the same extensive thermochemical database, which contains enthalpy (H), entropy (S), and heat capacity (C) data for more than 25,000 chemical compounds. The Solgasmix routine based on Gibbs energy minimization is used in calculating equilibrium composition.[3]

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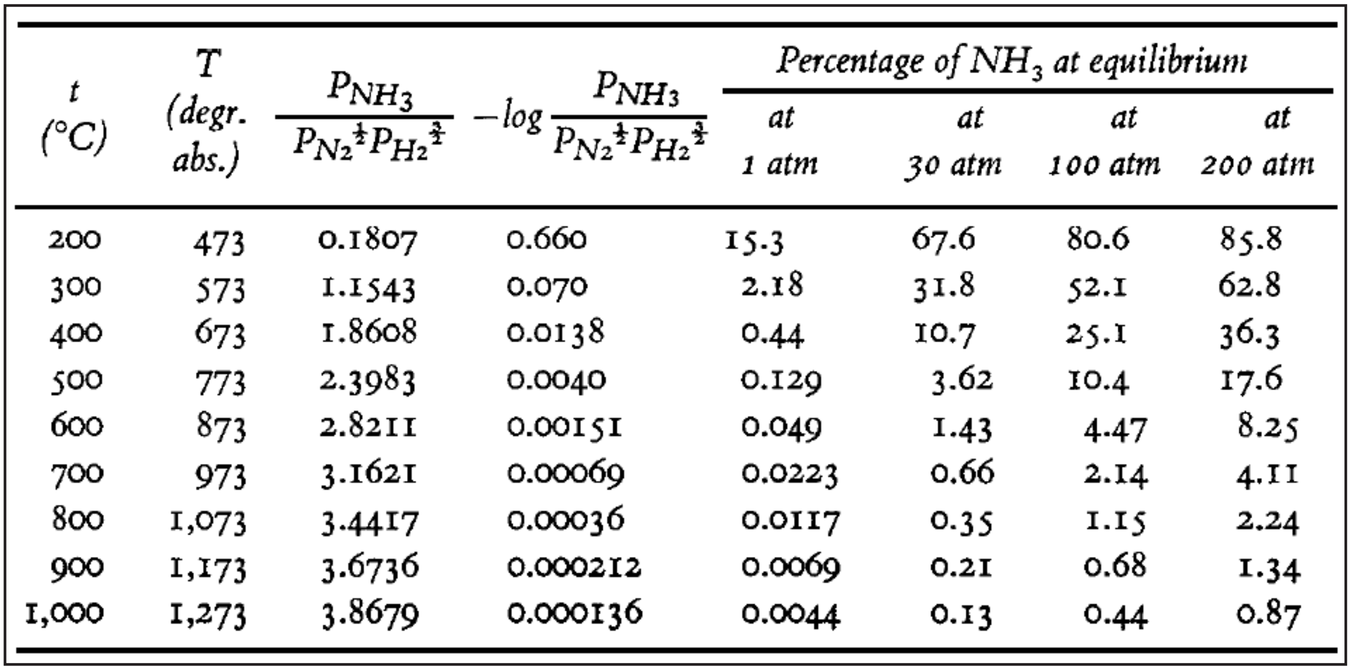


t (°C)	T (degr. abs.)	$\frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} p_{H_2}^{\frac{3}{2}}}$	$-\log \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} p_{H_2}^{\frac{3}{2}}}$	Percentage of NH_3 at equilibrium			
				at 1 atm	at 30 atm	at 100 atm	at 200 atm
200	473	0.1807	0.660	15.3	67.6	80.6	85.8
300	573	1.1543	0.070	2.18	31.8	52.1	62.8
400	673	1.8608	0.0138	0.44	10.7	25.1	36.3
500	773	2.3983	0.0040	0.129	3.62	10.4	17.6
600	873	2.8211	0.00151	0.049	1.43	4.47	8.25
700	973	3.1621	0.00069	0.0223	0.66	2.14	4.11
800	1,073	3.4417	0.00036	0.0117	0.35	1.15	2.24
900	1,173	3.6736	0.000212	0.0069	0.21	0.68	1.34
1,000	1,273	3.8679	0.000136	0.0044	0.13	0.44	0.87

Figure 1. *Fritz Haber presented his original ammonia synthesis results in his Nobel lecture in 1920. Reprinted with permission from The Nobel Foundation. ®©*[2]

PROBLEM STATEMENT

Fritz Haber's ammonia synthesis innovation in 1909 was about process conditions and catalyst (originally osmium, later in industrial scale iron). Haber succeeded in building a high-pressure reactor, in which experiments could be carried out at pressures up to 200 atm.

a) *Use the HSC Chemistry program's Equilibrium Compositions module to compute the theoretical equilibrium composition for ammonia reaction in each of Haber's experimental points (Figure 1). The feed to the batch was stoichiometric,* i.e., *1 mol N_2 and 3 mol H_2.*

b) *Compute the following using the HSC Chemistry program's Reaction Equations module:*

ΔH_r (300 °C)

ΔS_r (300 °C)

ΔG_r (300 °C)

K_a (300 °C)

c) *Calculate the above values (b) at 300 °C by hand. Also calculate the ammonia equilibrium composition at 300 °C and 200 atm by hand. Thermodynamic properties of the components in gas phase are given in Table 1. The ideal gas law is assumed to be valid.*

THERMODYNAMIC EQUATIONS FOR THE CALCULATION OF REACTION EQUILIBRIUM

Thermodynamic equations for the calculation of reaction equilibrium are given in Table 2.

PROBLEM SOLUTION

a) *Solution using HSC Chemistry*

The feed input and parameter options of the HSC Chemistry program's Equilibrium Compositions module are given in Figures 2 and 3 (page 119).

HSC Chemistry uses the thermodynamic data bank (H, S, and C) and the thermodynamic equations (2–11) for the calculation of the equilibrium composition at various temperatures and constant pressure. The HSC Chemistry results (solid lines) and Fritz Haber's original experimental results (points) are given in Figure 4 (page 120).

b) *The HSC Chemistry program's Reaction Equations module gives for ammonia reaction:*

ΔH_r (300 °C) = -101.863 $kJ \cdot mol^{-1}$

ΔS_r (300 °C) = -222.383 $J \cdot mol^{-1} \cdot K^{-1}$

ΔG_r (300 °C) = 25.596 $kJ \cdot mol^{-1}$

K_a (300 °C) = 0.004646

c) *The principle for calculating the equilibrium composition is shown in Figure 5 (page 120).*

Calculations by hand follow, in accordance with the "map" given in Figure 5.

Eq. (8) gives:

$$\Delta H_r^o = 2*(-45.940) - 0 - 3*0 = -91.88 \text{ kJ} \cdot \text{mol}^{-1} \quad (12)$$

TABLE 1

Thermodynamic properties of the components (N_2[4], H_2[4,5], NH_3[6]) in gas phase. The superscript ° indicates reference state (298.15 K, 1.013×10⁵ Pa).

$N_2(g)$	ΔH_f^o	0.000 $kJ \cdot mol^{-1}$
	S^o	191.610 $J \cdot mol^{-1} \cdot K^{-1}$
	C_p	$(29.192 - 1.121 \times 10^{-3}\ T + 3.092 \times 10^{-6}\ T^2)\ J \cdot mol^{-1} \cdot K^{-1}$
$H_2(g)$	ΔH_f^o	0.000 $kJ \cdot mol^{-1}$
	S^o	130.679 $J \cdot mol^{-1} \cdot K^{-1}$
	C_p	$(25.855 + 4.837 \times 10^{-3}\ T + 1.584 \times 10^{5}\ T^{-2} - 0.372 \times 10^{-6}\ T^2)\ J \cdot mol^{-1} \cdot K^{-1}$
$NH_3(g)$	ΔH_f^o	-45.940 $kJ \cdot mol^{-1}$
	S^o	192.778 $J \cdot mol^{-1} \cdot K^{-1}$
	C_p	$(25.794 + 31.623 \times 10^{-3}\ T + 0.351 \times 10^{5}\ T^{-2})\ J \cdot mol^{-1} \cdot K^{-1}$

TABLE 2

Thermodynamic equations for the calculation of reaction equilibrium. The superscript ° indicates reference state (298.15 K, 1.013×10⁵ Pa). All Gibbs energies, reaction entropies, and reaction enthalpies are molar.

The thermodynamic equilibrium constant K_a (liquid phase)	$K_a = \prod_{i=1}^{n} a_i^{\upsilon_i} = K_\gamma K_x = \prod_{i=1}^{n} \gamma_i^{\upsilon_i} \prod_{i=1}^{n} x_i^{\upsilon_i} \qquad (2a)$
The thermodynamic equilibrium constant K_a (gas phase)	$K_a = \prod_{i=1}^{n} f_i^{\upsilon_i} = K_\phi K_p = \prod_{i=1}^{n} \Phi_i^{\upsilon_i} \prod_{i=1}^{n} \left(\frac{p_i}{p^o} \right)^{\upsilon_i} \qquad (2b)$
The van´t Hoff equation	$K_a(T) = \exp\left(-\frac{\Delta G_r(T)}{RT} \right) \qquad (3)$
The temperature dependence of the equilibrium constant K_a	$\frac{d(\ln K_a)}{dT} = \frac{\Delta H_r(T)}{RT^2} \qquad (4)$
When ΔH_r is constant in the temperature range T_1–T_2	$\ln K_a(T_1) = \ln K_a(T_2) - \frac{\Delta H_r}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (5)$
The reaction Gibbs energy in the reference state	$\Delta G_r^o = \sum_{i=1}^{n} \upsilon_i \Delta G_{fi}^o \qquad (6)$
The reaction entropy in the reference state	$\Delta S_r^o = \sum_{i=1}^{n} \upsilon_i S_i^o \qquad (7)$
The reaction enthalpy in the reference state	$\Delta H_r^o = \sum_{i=1}^{n} \upsilon_i \Delta H_{fi}^o \qquad (8)$
The temperature dependence of the reaction Gibbs energy	$\Delta G_r(T) = \Delta H_r(T) - T \Delta S_r(T) \qquad (9)$
The temperature dependence of the reaction entropy	$\Delta S_r(T) = \Delta S_r^o + \int_{298.15\,K}^{T} \left(\frac{\sum \upsilon_i C_{pi}}{T} \right) dT \qquad (10)$
The temperature dependence of the reaction enthalpy	$\Delta H_r(T) = \Delta H_r^o + \int_{298.15\,K}^{T} \left(\sum \upsilon_i C_{pi} \right) dT \qquad (11)$

Fritz Haber's ammonia synthesis innovation in 1909 was about process conditions and catalyst (originally osmium, later in industrial scale iron). Haber succeeded in building a high-pressure reactor, in which experiments could be carried out at pressures up to 200 atm.

For the heat capacity:

$$\begin{aligned}\Delta C_p = \sum_{i=1}^{n} \upsilon_i C_{p,i} &= (2*25.794-29.192-3*25.855)\\ &+(2*31.623+1.121-3*4.837)\cdot 10^{-3}\,T+\\ &(2*0.351-0.000-3*1.584)\cdot 10^{5}\,T^{-2}+\\ &(2*0.000-3.092+3*0.372)\cdot 10^{-6}\,T^{2}\\ &=-55.169+49.856\times10^{-3}\,T-4.05\times10^{5}\,T^{-2}-1.976\times10^{-6}\,T^{2}\end{aligned} \qquad (13)$$

Eq. (11) gives:

$$\Delta H_r(573.15\,K)=\Delta H_r^o+\int_{298.15\,K}^{573.15\,K}\Delta C_p\,dT=-101.837\,kJ\cdot mol^{-1} \qquad (14)$$

The integral was calculated numerically using Simpson's numerical integrator (or analytically). Eq. (7) gives:

$$\Delta S_r^o=2*192.778-191.610-3*130.679=-198.091\,J\cdot mol^{-1}\cdot K^{-1} \qquad (15)$$

Eq. (10) gives:

$$\Delta S_r=(573.15\,K)=\Delta S_r^o+\int_{298.15\,K}^{573.15\,K}\frac{\Delta C_p}{T}dT=-222.335\,J\cdot mol^{-1}\cdot K^{-1} \qquad (16)$$

The integral was calculated numerically using Simpson's numerical integrator (or analytically). Eq. (9) gives:

$$\Delta G_r=(573.15\,K)=-101.837\,kJ\cdot mol^{-1}-573.15\,K*(-222.335)\,J\cdot mol^{-1}\cdot K^{-1}=25.594\,kJ\cdot mol^{-1} \qquad (17)$$

Eq. (3) gives:

$$K_a(573.15\,K)=\exp\left(\frac{-25594\,J\cdot mol^{-1}}{8.314\,J\cdot mol^{-1}\cdot K^{-1}*573.15\,K}\right)=4.649\times10^{-3} \qquad (18)$$

A summary of HSC Chemistry results and hand calculation results:

	HSC	Hand calculation
ΔH_r (300 ºC) kJ·mol^{-1}	101.863	101.837
ΔS_r (300 ºC) J·mol^{-1}·K^{-1}	-222.383	-222.335
ΔG_r (300 ºC) kJ·mol^{-1}	25.596	25.594
K_a (300 ºC)	4.646E-3	4.649E-3

Eq. (2b) with ideal gas assumption:

$$K_a=K_p=\prod_{i=1}\left(\frac{p^i}{p^o}\right)^{\upsilon_i}=\left(\frac{p_{NH_3}}{p^o}\right)^2\left(\frac{p_{N_2}}{p^o}\right)^{-1}\left(\frac{p_{H_2}}{p^o}\right)^{-3}=\frac{p_{NH_3}{}^2(p^o)^2}{p_{N_2}p_{H_2}{}^3} \qquad (19)$$

Total pressure is 200 atm and

$$x_i=\frac{p_i}{p_{iot}}\Rightarrow p_i=x_ip_{tot} \qquad (20)$$

We solve the mole amount of each component. Initially we have 1 mole of N_2, of which y moles have reacted at equilibrium.

	N_2	H_2	NH_3	Σ	
t = 0	1	3	0	4	moles
t = ∞	1-y	3-3y	2y	4-2y	moles

At equilibrium,

$$x_{N_2}=\frac{1-y}{4-2y}\quad x_{H_2}=\frac{3-3y}{4-2y}\quad x_{NH_3}=\frac{2y}{4-2y} \qquad (21)$$

Now we have:

$$p_{N_2}=\frac{1-y}{4-2y}p_{tot},\,p_{H_2}=\frac{3-3y}{4-2y}p_{tot},\,p_{NH_3}=\frac{2y}{4-2y}p_{tot} \qquad (22)$$

We obtain:

$$K_a=\frac{\left(\frac{2y}{4-2y}\right)^2 p_{tot}{}^2}{\frac{1-y}{4-2y}p_{tot}\left(\frac{3-3y}{4-2y}\right)^3 p_{tot}{}^3}p^{o^2} \qquad (23)$$

$$K_a=\frac{(2y)^2(4-2y)^2p^{o^2}}{(1-y)(3-3y)^3p_{tot}{}^2}=4.649\times10^{-3} \qquad (24)$$

The reference pressure p^o is 1 atm and the total pressure is 200 atm. The final equation is easily solved numerically. The value for y was found to be 0.7688417. We get the following equilibrium composition.

N_2	0.23116 mol	9.39%
H_2	0.69348 mol	28.16%
NH_3	1.53768 mol	62.45% (Haber's measurement 62.8%, HSC 62.3%)

Nonideality was not taken into account. However, the fugacity coefficients can be calculated and included in the HSC Chemistry calculations (Figure 2) and in the hand calculations [Eq. (2b) in Table 2]. Binous and Nasri[7] state that ammonia processes are operated at very high pressures to get a reasonably high conversion of reactants and that high gas-phase pressures imply significant deviation from ideality. They used the Peng–Robinson equation of state to calculate the K_Φ term [Eq. (2b)] at constant temperature 800 K and at pressures up to 1500 bar. At 200 bar, the K_Φ value was found to be 0.93. Taking this nonideality into account, the equilibrium ammonia composition at 800 K and 200 bar was calculated to be 14.86 mol %. With an ideal gas assumption, the equilibrium ammonia composition was calculated to be 14.46 mol %. At lower pressures the deviation is smaller.

DISCUSSION AND CONCLUSIONS

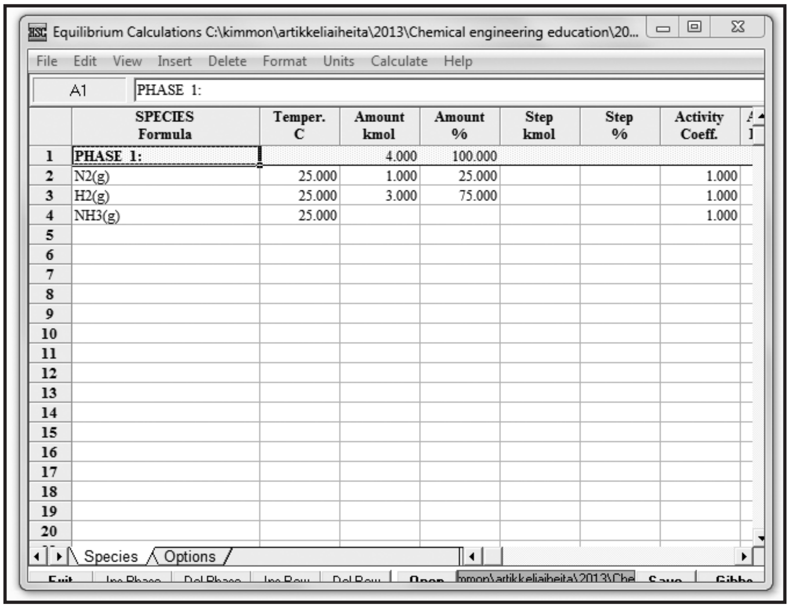
The ammonia task has been deployed for a couple of years as an individual homework assignment in the Chemical Reaction Engineering course. The students have been chemical engineering undergraduates (89%), environmental engineering undergraduates (7%), and industrial management undergraduates (4%). Most of them have been third-year students.

The HSC Chemistry program is quite user friendly. Before the students were given the ammonia task, a similar kind of exercise (methanol synthesis) was done in a computer classroom and the students were given a printed step-by-step guide to HSC Chemistry concerning this exercise. So the students were familiar with the program when they started doing the ammonia simulation.

The students did not have too many difficulties with the HSC Chemistry simulations. Some of the students need the HSC Chemistry program later in their studies. For them it is an asset to be familiar with the program. The hand calculation of ammonia composition is so complicated that most of the students had to redo the calculation because of some error or errors, for example in the calculation of the integral values (enthalpy and entropy).

The students think that the ammonia task is laborious, but they are happy to realize that the basic thermodynamics are closely related to an important chemical process. At Lappeenranta University of Technology, before the students are given the task, a lecture is given on Fritz Haber's innovation, the development of the industrial ammonia process, and the importance of the innovation.

Simplified versions of the ammonia task have been examination questions in the past. On average, these question have given 6.43 points of maximum 10 points (the average for all questions is 5.07 points). For the ammonia question, the maximum 10 points have been given to 24% of the answers.



A1 PHASE 1:

	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
1	PHASE 1:		4.000	100.000			
2	N2(g)	25.000	1.000	25.000			1.000
3	H2(g)	25.000	3.000	75.000			1.000
4	NH3(g)	25.000					1.000
5							
6							
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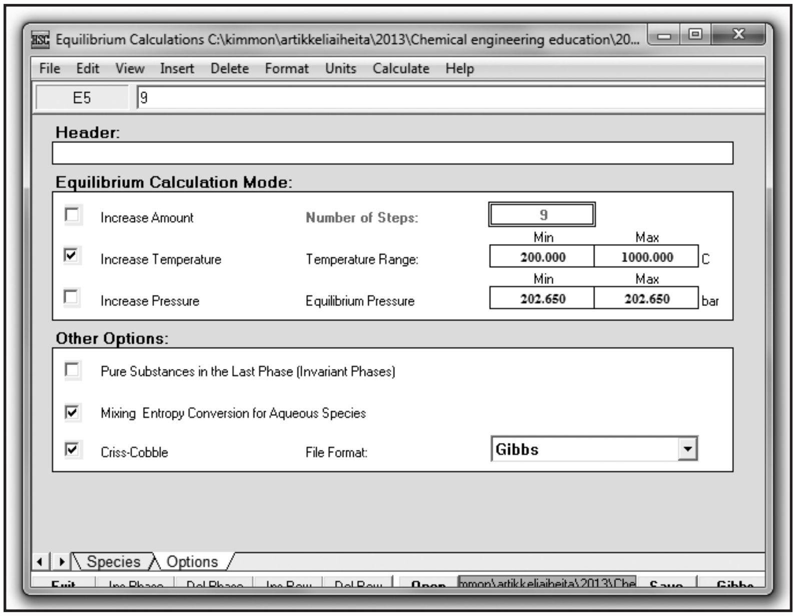
Figure 2. *Feed Input of the HSC Chemistry program's Equilibrium Compositions module.*



E5 9

Header:

Equilibrium Calculation Mode:

☐ Increase Amount — Number of Steps: 9

☑ Increase Temperature — Temperature Range: Min 200.000 Max 1000.000 C

☐ Increase Pressure — Equilibrium Pressure Min 202.650 Max 202.650 bar

Other Options:

☐ Pure Substances in the Last Phase (Invariant Phases)

☑ Mixing Entropy Conversion for Aqueous Species

☑ Criss-Cobble — File Format: Gibbs

Figure 3. *Parameter options of the HSC Chemistry program's Equilibrium Compositions module.*

For all the questions, the maximum 10 points have been given to 19% of the answers.

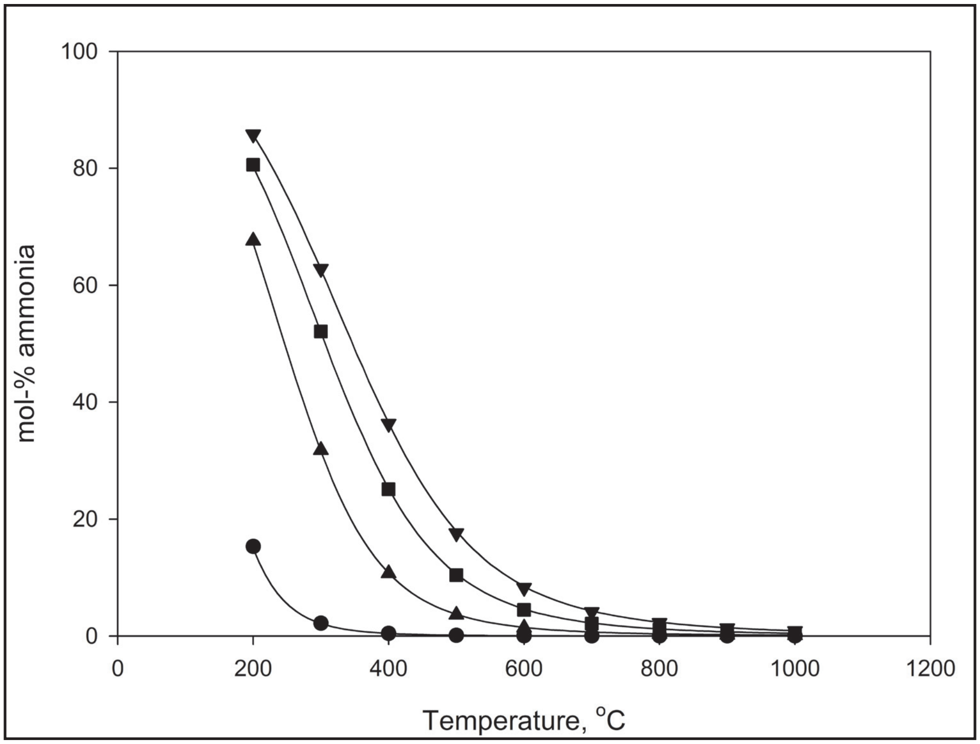


Figure 4. *Ammonia equilibrium compositions calculated with HSC Chemistry (solid lines) and Fritz Haber's experimental results (circle = 1 atm, triangle up = 30 atm, square = 100 atm, triangle down = 200 atm).*

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NOMENCLATURE

a	Activity, -
C_{pi}	Heat capacity in constant pressure (component i), $J \cdot mol^{-1} \cdot K^{-1}$
f	Fugacity, Pa
ΔG^o_{fi}	Gibbs energy of formation (component i), $J \cdot mol^{-1}$
ΔG_r	Free reaction Gibbs energy, $J \cdot mol^{-1}$
ΔH^o_{fi}	Enthalpy of formation (component i), $J \cdot mol^{-1}$
ΔH_r	Reaction enthalpy, $J \cdot mol^{-1}$
n	Number of components in reaction equation (reagents and products), -
p	Partial pressure, Pa
p^o	Reference pressure, $1.013 \cdot 10^5$ Pa
R	Gas constant, 8.314 $J \cdot mol^{-1} \cdot K^{-1}$
ΔS^o_i	Entropy (component i), $J \cdot mol^{-1} \cdot K^{-1}$
ΔS_r	Reaction entropy, $J \cdot mol^{-1} \cdot K^{-1}$
T	Temperature, K
x	Mole fraction, -
γ	Activity coefficient, -
υ	Stoichiometric coefficient (reagents < 0, products > 0), -
Φ_i	Fugacity coefficient of component i, -
i	component i (subscript) ❐

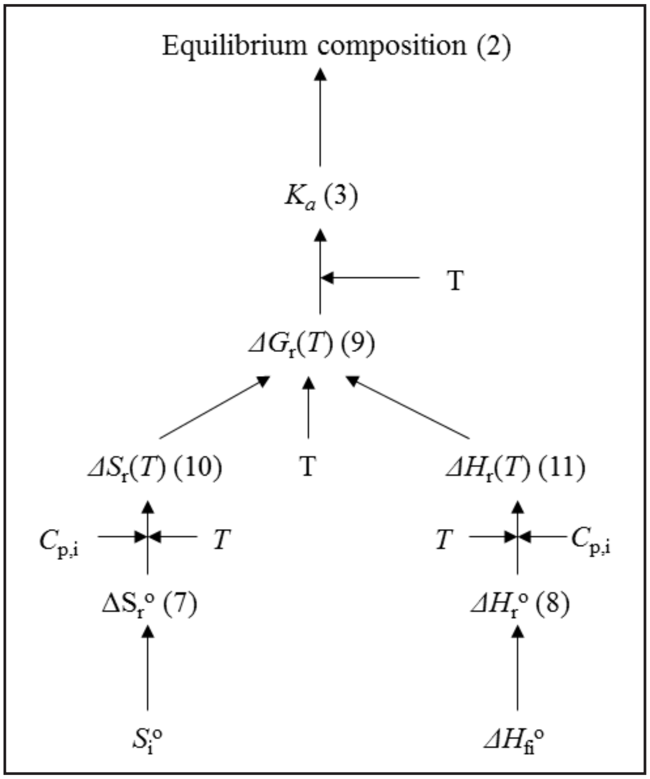

Figure 5. *Principle for calculating equilibrium composition. Eqs. (2)–(11) are given in Table 2.*