King's College London (KQC) University of London

SCIENCE SIMULATIONS LABORATORY

AMMONIA SYNTHESIS

STUDENTS' MANUALS (Version 1.02.2003)

Authors R. Edens and K. Shaw
Programmer: J. Bright (1982 GW Basic Version)
D. Terry (2003 Visual Basic Version)
Editors: D.L. Want, (1982 Version), C. Michelsen M.A. Ph.D. (2003 Version)

STUDENTS' MANUAL A – INTRODUCTION

The production of ammonia from nitrogen and hydrogen by the Haber process is one of the most important processes in the chemical Industry.

All modern agriculture relies on the use of nitrogenous fertilizers – those containing compounds of nitrogen – and virtually all the explosives used for mining, quarrying or for military purposes are based on nitrogenous compounds. The list of uses of nitrogenous compounds is very long and includes synthetic fibres, drugs, dyes, pesticides, paints, plastics and (even) cosmetics. The Haber process is almost the only large scale source of these nitrogen compounds.

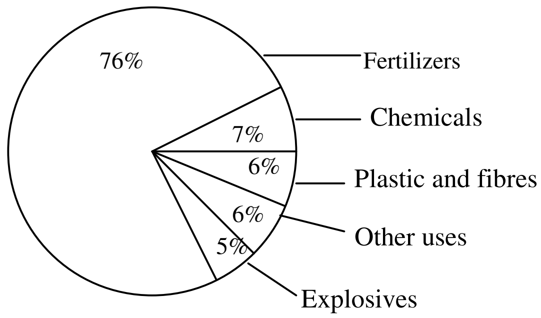


Figure A1 Uses of ammonia

The purpose of this unit is to allow you to investigate some of the factors which influence the production of ammonia from the elements nitrogen and hydrogen. The equation for the reaction is

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(9) \quad \Delta H = 46KJmol^{-1}$$

For reasons which will become apparent it is not possible to carry out laboratory investigations to study this reaction, which is a very interesting one from the points of view of both chemical equilibrium and kinetics. This computer simulation uses a mathematical model of the Haber process designed to enable you to discover for yourself how the various conditions (temperature, pressure, catalyst and reactant concentration ratios) influence the course of the reaction (i.e. the time required to reach equilibrium and the equilibrium yield of ammonia).

Mathematical models are important tools of the research scientist, especially the chemical engineer, as they enable the effects of changes in conditions to be predicted and a set of "best" conditions derived before investing in a pilot scale production plant. However, all models have their limitations: the system under investigation may not be thoroughly understood; simplifications are made to facilitate the calculations and assumptions are made which are valid only within certain prescribed limits. The model used in this unit is no exception and full details of the models and assumptions are given in the Teachers' Guide. However the model used gives a good approximation for most of the allowable conditions and it should fulfill its primary purpose of giving a "feel" for what happens as the conditions are changed.

It is good practice to decide, as far as possible, <u>before</u> using the computer what values you wish to select for the various parameters (temperature, pressure etc).

The computer will calculate the results predicted by the model for your chosen conditions. You will then have to interpret the results you get. The methods you choose will be influenced by the questions associated with each investigation but will be similar to those you would use if you were performing a real experiment in the laboratory.

STUDENTS' MANUAL B – HOW TO USE THIS UNIT

This simulation of the Haber process is divided into two programs: *Ammonia Synthesis 1* and *Ammonia Synthesis 2*. *Ammonia Synthesis 1* allows you to investigate the effect of varying temperature, pressure and molar ratio of hydrogen to nitrogen on the percentage yield of ammonia.

Ammonia Synthesis 2 allows you to investigate the effect of varying temperature, pressure and the catalyst on the rates of both forward and reverse reactions (i.e. on the rate of attaining equilibrium).

Before using either of the programs you should be familiar with the background knowledge described in Manuals C and D. Manuals E and F give suggestions on how to use the computer programs themselves.

Initially the program will request you to select between *Ammonia Synthesis 1* (Equilibrium Position) or *Ammonia Synthesis 2* (Rate Aspects).

In *Ammonia Synthesis 1* you will need to select what is to be varied: Temperature, Pressure or Ratio of Hydrogen to Nitrogen, and then enter the values asked. Finally click on the *Process* button to get the results.

In *Ammonia Synthesis 2* you will need to select the catalyst to be used: Osmium, Tugsten, Molybdenum, Iron, Manganese dioxide, or none. Then enter the values asked and click on the *Process* button to get the results.

The following table gives the minimum and maximum allowable values of the variables.

Variable	Units	Minimum	Maximum
Temperature	K	350	1750
Pressure	atm	1	1500
Ratio of H:N	-	1:1	10:1
Time	hours	0	10^9
	minutes	0	10^9
	seconds	0	10^9

The choice of catalysts available in this unit is

1	None	
2	Osmium	0
3	Tungsten	W^S
4	Molybdenum	Mo
5	Iron	Fe
6	Manganese dioxide	$Mn\ 0_2$

STUDENTS' MANUAL C – PRIOR KNOWLEDGE FOR AMMONIA SYNTHESIS 1

In order to appreciate the significance of the results produced in *Ammonia Synthesis 1*, you should understand the following:

CHEMICAL EQUILIBRIUM

1 For any system in equilibrium, there is a simple relationship between the concentrations of the substances present. If this system is represented by the equation

$$mA + nB \rightleftharpoons pC + qD$$

the relationship is

$$\frac{[C]^p_{eqm} \cdot [D]^q_{eqm}}{[A]^m_{eqm} \cdot [B]^n_{eqm}} = K_c$$

and is known as the equilibrium law for this reaction. K_C is called the equilibrium constant.

When dealing with gases it is often more convenient to use an equilibrium constant K expressed in terms of pressures since the concentration of a gas is proportional to its partial pressure.

Thus for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \cdot P^3_{H_2}} \qquad \text{............................(1)}$$

where P_{NH_3} stands for the partial pressure of NH_3 at equilibrium, etc.

2 The partial pressure of a gas may be written as

partial pressure = mole fraction x total pressure

For example the partial pressure of ammonia is given by

$$P_{NH_3} = X_{NH_3} \cdot P$$

Where is the mole fraction of ammonia

i.e. $$X_{NH_3} = \frac{\text{moles of ammonia}}{\text{total number of moles}}$$

and P is the total pressure
Similarly for nitrogen and hydrogen

$$P_{N_2} = X_{N_2} \cdot P \quad \text{and} \quad P_{H_2} = X_{H_2} \cdot P$$

Substituting for the partial pressures in equation (1) we get:

$$K_p = \frac{\left(X_{NH_3} \cdot P\right)^2}{\left(X_{N_2} \cdot P\right) \cdot \left(X_{H_2} \cdot P\right)^3}$$

$$= \frac{\left(X_{NH_3}\right)^2}{X_{N_2}\left(X_{H_2}\right)^3} \cdot \frac{P^2}{P \cdot P^3}$$

Thus $$K_p = \frac{\left(X_{NH_3}\right)^2}{X_{N_2} \cdot \left(X_{H_2}\right)^3} \cdot \frac{1}{P^2}$$

As K_P is a constant for a given temperature any change in the pressure, P, must be cancelled exactly by changes in the partial pressures: i.e. the amount of ammonia present at equilibrium is dependent on the pressure.

3 Chemical equilibrium is a dynamic state in which opposing changes on the molecular level are continually taking place. The next result of these molecular changes is that the macroscopic properties of the system in equilibrium do not change. This is an example of the more general and very important mechanism known as a self-regulatory system which is sensitive and adaptable to conditions imposed on it.

This dynamic aspect of equilibrium means that the system is stable under fixed conditions but sensitive to variations in these conditions.

The way in which a particular system at equilibrium will respond can be predicted qualitatively by applying Le Chatelier's Principle of Equilibrium, which may be stated as follows:

> "If a system in equilibrium is subjected to a change, the processes which take place are such as to attempt to counteract the effect of that change".

STUDENTS' MANUAL D – PRIOR KNOWLEDGE FOR AMMONIA SYNTHESIS 2

In order to appreciate the significance of the results produced in *Ammonia Synthesis 2*, you should understand the following.

CHEMICAL KINETICS

1 Introduction

For many chemical reactions it is found experimentally that the way in which the concentrations of the reactants affect the rate of the reaction can be expressed in the form of a simple law. If a certain reaction is represented by the equation

$$A \rightarrow B + C,$$

the rate law may be expressed as

$$\text{rate} \propto [A]^x \cdot [B]^Y \cdot [C]^z$$

where x, y, and z are experimentally determined numbers.

The order of the reaction is defined as the sum of the exponents of the concentration terms. In the above case the order = x + y + z.

For example, the reaction

$$2N_2O\ (g) \rightarrow 2N_2\ (g) + O_2\ (g)$$

is found to follow the rate law

$\text{rate} \propto [N_2O]$ and is independent of $[N_2]$ and $[O_2]$

This is therefore a First Order reaction. The rate law can be written as

$$\text{rate} = -k\ [N_2O]$$

where the rate referred to is the rate of change in the concentration of N_2O and where k is the rate constant. (We write -k $[N_2O]$ because the concentration of N_20 is decreasing.)

2 Ammonia synthesis

Unfortunately, the mechanism of ammonia synthesis is still not fully understood even though the reaction has been used in industry since about 1910. For the purposes of this simulation it will be assumed that for

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

the reaction is first order with respect to $[N_2]$ and independent of $[H_2]$, while for

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

the reaction is first order with respect to $[NH_3]$.

3 Effect of temperature on the rate constant

The rate of a reaction is usually very sensitive to changes in temperature.

For most reactions the way in which the rate constant changes with temperature is found to fit the Arrhenius equation.

$$k = A\exp\left(\frac{-E}{RT}\right)$$

where

k = rate constant at T kelvins
A = Arrhenius factor (also called the pre-exponential factor)
E = activation energy for the reaction in j mol^{-1}
R = the universal gas constant in J K^{-1} mol^{-1}

CATALYSTS

Catalysts are often used to make a reaction go faster at a given temperature in order to obtain a reasonable reaction rate without having too high a temperature. Catalysts speed up reactions by lowering the energy barrier between reactants and products i.e. by reducing the value of E. The following energy diagram for an exothermic reaction illustrates this.

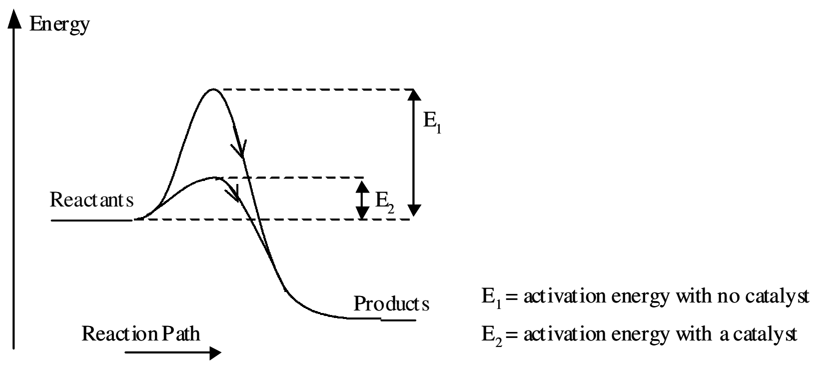


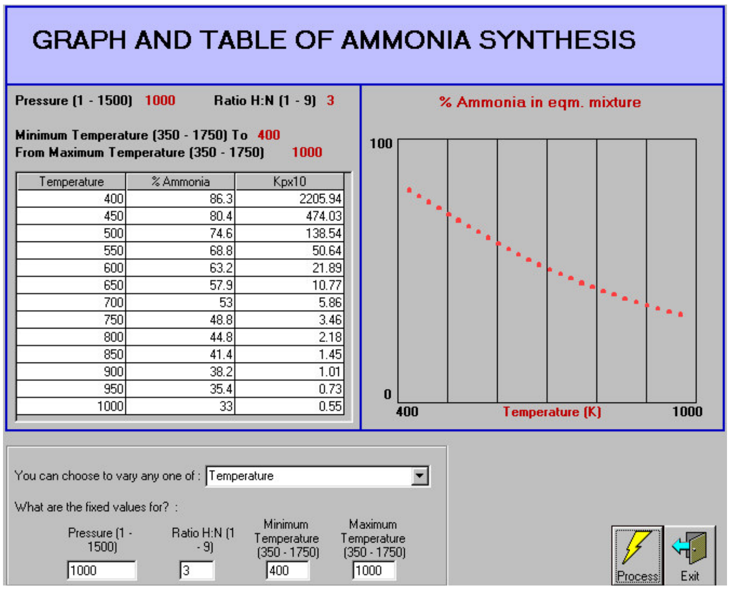
Figure D1 The effect of a catalyst on a reaction.

STUDENTS' MANUAL E – USING AMMONIA SYNTHESIS 1

This leaflet describes a typical use of the program *Ammonia Synthesis 1*. It also includes some questions which you may try to answer through use of the program. Firstly, however, you should have read Students Manual B.

You will first be asked to choose which one of temperature, pressure or ratio of hydrogen to nitrogen is to be varied. For example, if temperature is chosen as the variable you will then be asked to give a value for the other parameters (pressure and ratio in this example) and to give a minimum and maximum figure for the variable. As acceptable figures are entered the following information will be displayed. (The values in this example are: Pressure = 1000; Ratio H:N = 3; Minimum Temperature = 400; Maximum Temperature = 1000).

You may change any of the values and click on the *Process* button to see the new results.



Temperature	% Ammonia	Kpx10
400	86.3	2205.94
450	80.4	474.03
500	74.6	138.54
550	68.8	50.64
600	63.2	21.89
650	57.9	10.77
700	53	5.86
750	48.8	3.46
800	44.8	2.18
850	41.4	1.45
900	38.2	1.01
950	35.4	0.73
1000	33	0.55

Figure E1 Shows the results after clicking on the *Process* button.

Using this program should enable you to answer the following questions.

E1 *What is the best molar ratio of hydrogen to nitrogen to use if you wish to maximise the percentage of ammonia? Why do you think this is the best ratio? Is this what you would have predicted using Le Chatelier's Principle? Explain!*

E2 *What influence does pressure have on the position of equilibrium? Explain this in terms of Le Chatelier's Principle. What appears to be the best pressure for carrying out the Haber process? Say why you think this would be the best pressure. How is K_P affected by changing the pressure?*

Knowing that

$$K_p = \frac{(X_{NH_3})^2}{(X_{N_2}) \cdot (X_{H_2})^3} \cdot \frac{1}{P^2}$$

Can you suggest an explanation for this observation?

E3 *In the chemical industry a pressure of between 200 and 300 atmospheres is used in ammonia production. Why do you think this pressure is chosen?*

E4 *What influence does temperature have on the position of this equilibrium? What appears to be the best temperature at which this reaction would be carried out? Say why you think this would be the best temperature. What can you deduce about the enthalpy change during this reaction? Is the reaction*

a exothermic, or
b endothermic?

Explain your answer in terms of Le Chatelier's Principle.

E5 *How is K_P affected by changing the temperature? What does this tell you about the relationship of K_P to temperature in*

a exothermic reactions? and
b endothermic reactions?

STUDENTS' MANUAL F – USING AMMONIA SYNTHESIS 2

This leaflet describes a typical use of the program *Ammonia Synthesis 2*. It also includes some questions which you may try to answer through use of the program. Firstly, however, you should have read Students' Manual B.

This program allows a study to be made of how the rate of the reaction is influenced by temperature, pressure and catalyst used. The values of the three parameters, temperature, pressure and type of catalyst, must then be chosen. <u>In this program the ratio of hydrogen is fixed at 3:1.</u> The computer will calculate 12 sets of results for time intervals specified by you. Note that it is possible to set the units (hours, minutes or seconds) as well as the interval and that the maximum time shown on the axis is 12 times the chosen interval.

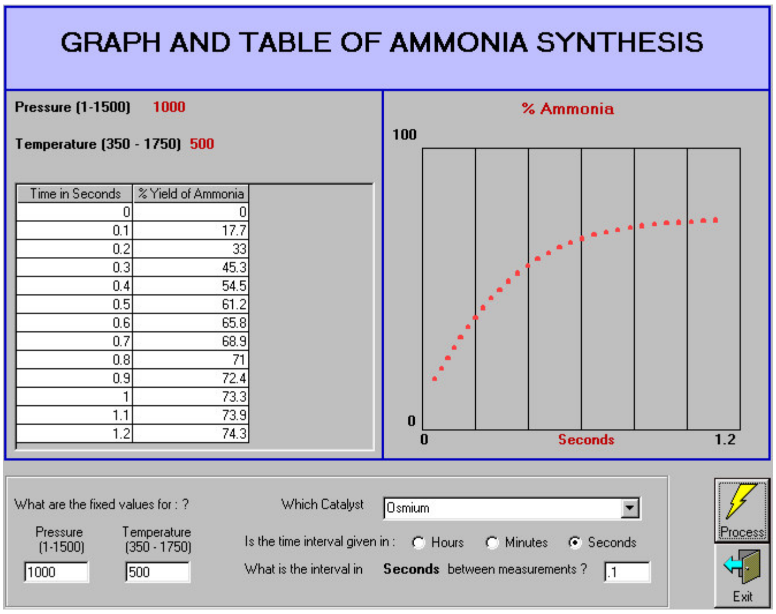


Figure F1

F1 *What effect does the use of a catalyst have on the rate of attaining equilibrium?*

F2 *Does the use of a catalyst affect the percentage of ammonia in the equilibrium mixture? Why? Explain this in terms of the rates of the forward and reverse reactions and hence the position of equilibrium.*

F3 *Which is the most effective of the catalysts listed in this simulation and why?*

F4 *Why do you think iron is the catalyst used in practice?*

F5 *What effect does varying the pressure have on the rate of attaining equilibrium? Can you explain this?*

F6 *What effect does varying the temperature have on the rate of attaining equilibrium? Can you explain this in terms of:*

a the *kinetic theory of gases?*

b *the Arrhenius equation for the rate constant*

$$k = A\exp\left(\frac{-E}{RT}\right) \quad ?$$

Bearing in mind the effect of temperature on the percentage of ammonia at equilibrium can you now see why a temperature of about 7000 K is used in *practice?*

F7 *Why do you think it is difficult to study this reaction in the laboratory?*

STUDENTS' MANUAL G – FLOW SHEET SHOWING STAGES IN THE SYNTHESIS OF AMMONIA