

# Determining the $K_p$ for the Ammonia Synthesis as a Function of Temperature

This paper describes a short physical chemistry experiment which has been used successfully for several years in our laboratories. The experiment enables an undergraduate student to determine the equilibrium constant for the "classic" ammonia-synthesis reaction as a function of temperature and to calculate the corresponding heat of reaction and entropy change. The equilibrium is studied using a dynamic method which involves a titration of  $\text{NH}_3$  and elementary measurements of flow rates, time, temperature, and pressure. The experiments are performed at atmospheric pressure between 820 and 1020°K in the presence of a commercially available catalyst.

## Theory<sup>1</sup>

The reaction is



Assuming ideal gas behavior for the reaction mixture, its equilibrium constant in terms of pressures is given by

$$K_p = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \quad (2)$$

The variation of an equilibrium constant  $K_p$  with temperature is given by the van 't Hoff equation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (3)$$

where  $\Delta H^\circ$  is the standard heat of reaction. Equation (3) can also be written

$$\frac{d \log_{10} K_p}{d(1/T)} = \frac{-\Delta H^\circ}{2.303R} \quad (4)$$

Hence, the value of  $\Delta H^\circ$  for reaction (1) may be evaluated from a plot of  $\log_{10} K_p$  versus  $1/T$ . Let  $\Delta H_{T^\circ}$  and  $K_{pT}$  be the values at temperature  $T$  of  $\Delta H^\circ$  and  $K_p$ , respectively. The value of the standard entropy change at this temperature may then be calculated from

$$\Delta S_{T^\circ} = \frac{\Delta H_{T^\circ}}{T} + 2.303R \log_{10} K_{pT} \quad (5)$$

When an equilibrium is studied using a flow method, the presence of a catalyst in the reactor is very useful. Indeed a catalyst speeds the attainment of equilibrium without affecting its position. Further it minimizes the importance of the back reaction occurring after the equilibrium reaction mixture leaves the reactor. If this back reaction is negligible, the composition of the ammonia-synthesis equilibrium mixture can be obtained as follows. Let  $n_{\text{NH}_3}$  be the number of moles of  $\text{NH}_3$  leaving the reactor in a given time  $t$ . The number of moles of nitrogen ( $n_{\text{N}_2}$ ) and of hydrogen ( $n_{\text{H}_2}$ ) leaving the reactor in the same time are then equal to the differences between the number of moles  $n_{\text{N}_2}^\circ$  and  $n_{\text{H}_2}^\circ$  entering the reactor during the time  $t$  and what has been consumed to form  $\text{NH}_3$ , that is

$$n_{\text{N}_2} = n_{\text{N}_2}^\circ - \frac{1}{2} n_{\text{NH}_3} \quad (6)$$

$$n_{\text{H}_2} = n_{\text{H}_2}^\circ - \frac{3}{2} n_{\text{NH}_3} \quad (7)$$

The total number of moles leaving the reactor in a given time  $t$  is

$$n = n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3} = n_{\text{N}_2}^\circ + n_{\text{H}_2}^\circ - n_{\text{NH}_3} \quad (8)$$

Under the experimental conditions used,  $n_{\text{NH}_3}$  is at least

Equilibrium Constant  $K_p$  for the Ammonia-Synthesis Reaction as a Function of Temperature.

$T$ (°K)	$P$ (torr)	$10^3 d_{\text{N}_2}$ (l/s)	$10^3 d_{\text{H}_2}$ (l/s)	$10^3 \cdot (d_{\text{N}_2} + d_{\text{H}_2})$ (l/s)	$10^5 \cdot n_{\text{NH}_3}$ (mole)	$t$ (s)	$\log_{10} K_p$
820.0	761	5.15	2.75	7.90	1.83	149	-2.64
820.1	761	5.10	10.5	15.6	1.83	41	-2.66
820.2	761	1.20	10.8	12.0	1.83	63	-2.66
820.3	761	5.00	10.45	15.45	1.83	41.5	-2.66
821.1	761	1.30	2.90	4.20	1.83	149	-2.65
1016.1	761	5.00	10.0	15.0	1.83	188	-3.30
1016.3	761	1.25	10.4	11.65	1.83	280	-3.31
1017.0	761	1.15	10.3	11.45	1.83	286	-3.30
1017.6	761	1.25	2.75	4.00	1.83	724	-3.32
1018.0	761	5.05	2.70	7.75	1.83	718	-3.32

100 times smaller than  $n_{\text{N}_2}^\circ$  and  $n_{\text{H}_2}^\circ$  so that the flow rates of  $\text{N}_2$  and  $\text{H}_2$  are practically not altered by the reaction. Hence eqns. (6)–(8) may be written to a good approximation

$$n_{\text{N}_2} = n_{\text{N}_2}^\circ = d_{\text{N}_2} P_0 t / RT_0 \quad (9)$$

$$n_{\text{H}_2} = n_{\text{H}_2}^\circ = d_{\text{H}_2} P_0 t / RT_0 \quad (10)$$

$$n = n_{\text{N}_2}^\circ + n_{\text{H}_2}^\circ = (d_{\text{N}_2} + d_{\text{H}_2}) P_0 t / RT_0 \quad (11)$$

where  $d_{\text{N}_2}$  and  $d_{\text{H}_2}$  are  $NTP$  flow rates in l/s ( $P_0 = 1$  atm,  $T_0 = 298.2^\circ\text{K}$ ) measured in the absence of reaction,  $R = 0.0821$  l atm/mole °K and  $t$  is expressed in s. It follows that the partial pressures of eqn. (2) may be calculated from

$$p_{\text{N}_2} = \frac{n_{\text{N}_2} P}{n} = \frac{d_{\text{N}_2} P}{(d_{\text{N}_2} + d_{\text{H}_2})} \quad (12)$$

$$p_{\text{H}_2} = \frac{n_{\text{H}_2} P}{n} = \frac{d_{\text{H}_2} P}{(d_{\text{N}_2} + d_{\text{H}_2})} \quad (13)$$

$$p_{\text{NH}_3} = \frac{n_{\text{NH}_3} P}{n} = \frac{n_{\text{NH}_3} R T_0 P}{(d_{\text{N}_2} + d_{\text{H}_2}) P_0 t} = \frac{24.48 n_{\text{NH}_3} P}{(d_{\text{N}_2} + d_{\text{H}_2}) t} \quad (14)$$

where  $P$  is the total pressure at the outlet of the reactor. Substitution of eqns. (12)–(14) into eqn. (2) yields

$$K_p = \frac{24.48 n_{\text{NH}_3} (d_{\text{N}_2} + d_{\text{H}_2})}{d_{\text{N}_2}^{1/2} d_{\text{H}_2}^{3/2} t P} \quad (15)$$

which shows the experimental parameters to be measured for determining  $K_p$ .

## The Experiment

### Apparatus<sup>2</sup> and Materials

The experiments are performed in the apparatus represented in Figure 1. Pure tank hydrogen (1' Oxhydrique Internationale S.A., type B, 99.999% purity,  $\leq 5$  ppm  $\text{O}_2$ ,  $\leq 5$  ppm  $\text{N}_2$  and  $\leq 5$  mg  $\text{H}_2\text{O}/\text{m}^3$ ) and nitrogen (1' Oxhydrique Internationale S.A., type E, 99.9974% purity,  $\leq 1$  ppm  $\text{O}_2$ ,  $\leq 25$  ppm A and  $\leq 5$  mg  $\text{H}_2\text{O}/\text{m}^3$ ) are allowed to flow through rotameters<sup>3</sup> into the reactor. The flow rates are regulated by valves and their ranges of variation are 2.7–10.8 and 1.1–5.3  $\text{cm}^3/\text{s}$  for  $\text{H}_2$  and  $\text{N}_2$ , respectively. The reactor is a quartz tube, 60 cm long and 1.3 cm i. d., provided with ground joints at both ends. The catalyst is the pre-reduced ICI catalyst

<sup>1</sup>See, e.g., Moore, W. J., "Physical Chemistry," Longman Group Ltd, London, 1972.

<sup>2</sup>Inspired by the Thesis of R. Maudgal, University of Brussels, 1962.

<sup>3</sup>The rotameters (Heinrichs, type DK 2) are preliminarily calibrated against a "soap-bubble" type flowmeter connected to the outlet of the reactor.

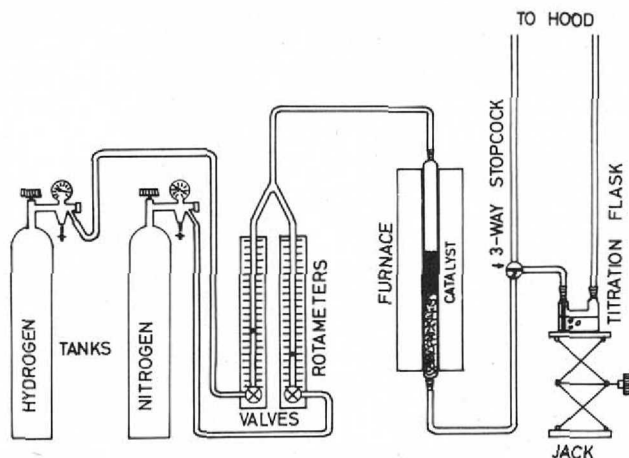


Figure 1. Apparatus. The tubings between the reactor and the titration flask are made of Pyrex.

35-4 based on iron (Imperial Chemical Industries Limited, Catalyst and Licensing Department, Post office box 1, Billingham Teeside, TS 23 1 LB, England). Its composition, poisoning by  $O_2$  and  $H_2O$ , and reduction by  $H_2$  to its active state have been described.<sup>4</sup> Twenty grams of the catalyst (14–28 mesh; 0.59–1.17 mm diameter) are placed on a plug of quartz wool in the middle of the reactor. The pressure at the inlet of the catalyst never exceeds that at the outlet by more than 5%. The reactor is heated by an electric furnace of 500 W. The heater consists of a stainless steel tube of 40 cm length and 2.0 cm i. d., covered with asbestos around which a Nichrome wire is coiled. The wire is insulated by asbestos and quartz wool from the outer cylindrical jacket, 40 cm long and 10 cm diameter. Two chromel-alumel thermocouples are located in the middle of the furnace between the heater and the reactor: one actuates an electronic relay device regulating and selecting the temperature and the other is used to measure the temperature. Preliminary experiments with a thermocouple embedded up to the center of the catalyst bed have shown that the temperature rise due to the exothermicity of the reaction is negligible. The reaction mixture leaving the reactor at almost atmospheric pressure escapes directly into a laboratory hood or bubbles first into a titration flask. This flask contains a known number of moles of dilute sulfuric acid (e.g. 40 ml of  $2.5 \times 10^{-4} M H_2SO_4$ ) and a few drops of a methyl red solution ( $\sim 0.2\%$  by weight in ethyl alcohol).

#### Procedure

The following procedure enables a student to carry out five determinations of  $K_p$  at at least three different temperatures between 820 and 1020°K in a four-hour laboratory period.

- 1) Connect the outlet of the reactor directly to the hood by means of the three-way stopcock.
- 2) Flush the reactor with  $N_2$  alone ( $d_{N_2} \sim 5$  ml/s) for about 2 min. Add afterwards  $H_2$  to  $N_2$  ( $d_{H_2} \sim 10$  ml/s) and switch on the electric furnace (during the warming up of the furnace, one sometimes observes, at the outlet of the reactor, a temporary condensation of water resulting from the reduction of the catalyst by  $H_2$ ). The lowest reaction temperature (820°K) is reached in about 40 min. Use this time to prepare 2 l of 2.5

<sup>4</sup>Bridger, G. W., and Snowden, C. B., "Catalyst Handbook", Wolfe Scientific Books, London, 1970, p. 126.

<sup>5</sup>Actually, due to the bubbling of the reaction mixture through the titration solution,  $P$  oscillates between  $1.002 P_{atm}$  and  $1.000 P_{atm}$ .

<sup>6</sup>JANAF Interim Thermochemical Tables, (Thermal Laboratory Dow Chemical Company, Midland, Michigan, 1965).

<sup>7</sup>Stull, D. R., Westrum Jr., E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, New York, 1969, p. 231.

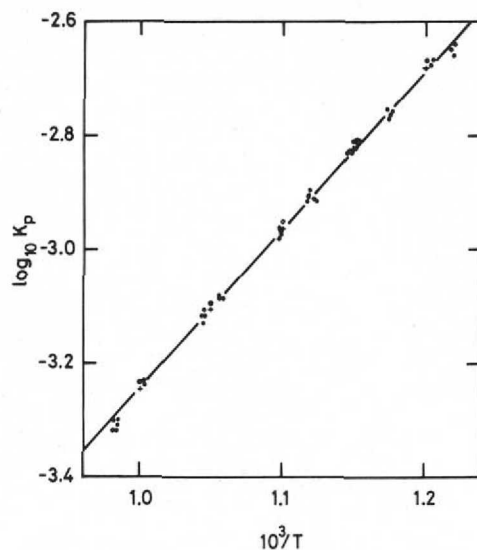


Figure 2. Equilibrium constant  $K_p$  for the ammonia-synthesis reaction as a function of temperature. (●) this work, (+) reference (7), (○) reference (6).

$\times 10^{-4} M$  sulfuric acid. To enable one to study a supplementary temperature, these operations may be performed before the arrival of the students in the laboratory.

- 3) Select a  $N_2$  flow rate between 1.1 and 5.3 ml/s and a  $H_2$  flow rate between 2.7 and 10.8 ml/s.
- 4) Using a pipet or a buret, fill the titration flask with the sulfuric acid solution. Add a few drops of the methyl red solution. Connect the two ground joints of the titration flask to the apparatus.
- 5) Measure the flow rates of  $N_2$  and  $H_2$ , the temperature of the reactor, and the atmospheric pressure.
- 6) Make the reaction mixture bubble through the titrating solution by turning the three-way stopcock and simultaneously start a stopwatch to measure the time  $t$  required for the solution to turn to yellow. If the titration solution contains  $q$  moles of  $H_2SO_4$ , i.e.  $2q$  moles of  $H^+$ , the time  $t$  corresponds to  $n_{NH_3} = 2q$  moles of  $NH_3$  having left the reactor.
- 7) Repeat operation 1. Remove and clean up the titration flask.
- 8) Repeat the experiment for different flow rates of  $N_2$  and  $H_2$ . When a new temperature is selected, make use of the time needed to reach this temperature by calculating the values of  $K_p$  using eqn. (13) with  $P$  set equal to  $P_{atm}$ , the atmospheric pressure in atm.<sup>5</sup>

#### Results and Discussion

Some typical experimental results are given in the table. Varying the total flow rate ( $d_{N_2} + d_{H_2}$ ) (i.e. the reaction time) by a factor 3.7 and the relative flow rate  $d_{N_2}/d_{H_2}$  (i.e. the composition of the reagents) from 0.5–9.0 has no influence on the measured value of  $K_p$ . Furthermore, preliminary experiments have shown that reducing the catalyst volume by a factor of three also has no effect. Both observations prove that reaction (1) has actually reached its equilibrium position in the flow reactor. Figure 2 shows a plot of values of  $\log_{10} K_p$  versus  $1/T$  obtained by students and some literature data<sup>6,7</sup> for comparison. The agreement is very satisfactory. The plot is a straight line indicating that  $\Delta H^\circ$  is constant within the experimental error limits over the temperature range 820–1020°K. The value calculated from the slope is  $\Delta H_{920}^\circ = -(12.68 \pm 0.05)$  kcal/mole and the corresponding  $\Delta S_{920}^\circ = -(27.52 \pm 0.11)$  cal/mole °K, where the limits are standard deviations. This shows that the ammonia-synthesis reaction is exothermic and entropic.

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