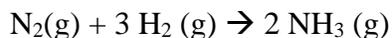


Practice problem #7

The Haber process utilizes the following reaction at high temperatures (to increase the rate of reaction) and high pressures (to increase the yield of an otherwise reactant favored reaction).



Given:

	ΔH°_f (in KJ/mol K) (at 298.15 K)	S°_f (in J/mol) at 298.15 K	ΔG°_f (in KJ/mol K) (at 298.15 K)
$\text{N}_2(\text{g})$	0.0	191.61	0.0
$\text{H}_2(\text{g})$	0.0	130.684	0.0
$\text{NH}_3(\text{g})$	-46.11	192.45	-16.45

a) Is the sign of ΔG° temperature-dependent? Draw the ΔG vs T graph and determine the temperature at which spontaneity changes.

b) What is the value of K_p at an operating temperature of 450.00°C (assuming that ΔH° and ΔS° are constants of temperature)?

Please note change in value (from 1000 bar to 1.000 bar)

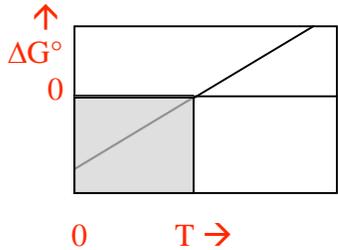
c) Write the expression for K_p . What are the partial pressures at equilibrium if we start off with a total pressure of 1.000 bar of 1.00 part N_2 , 3.00 parts H_2 gas and no NH_3 ?

Solution:

$$a) \Delta H^\circ = 2(-46.11) \text{ kJ/mol} - (3)(0) \text{ kJ/mol} - (1)(0) \text{ kJ/mol} = -92.22 \text{ kJ/mol} = -92,220 \text{ J/mol};$$

$$\Delta S^\circ = (2)(192.45 \text{ J/molK}) - (191.61 \text{ J/molK}) - (3)(130.684 \text{ J/molK}) = -198.762 \text{ J/molK}$$

We note that the signs of both ΔH° and ΔS° are the same, therefore the sign of ΔG° will be temperature – dependent. It has a negative y-intercept and a positive slope:



the temperature at which $\Delta G^\circ = 0$ is the temperature at which it changes its spontaneity:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ \Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92,220 \text{ J/mol}}{-198.762 \text{ J/molK}} = 463.9 \text{ K} (\approx 191^\circ \text{C}).$$

At this temperature the reaction is too slow, so temperature must be increased. But that makes it reactant-favored. It's a price to pay to increase the rate so that the whole process is feasible.

b) You can use the calculated values of ΔH° and ΔS° to calculate ΔG° at 450.00°C (i.e. $450.00 + 273.15 = 723.15 \text{ K}$) – on the assumption that both ΔH° and ΔS° are “constants” of temperature. You can't use the value of ΔG° determined from the above table since ΔG° is definitely a function of temperature. OK

$$\text{So we get: } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92,220 \text{ J/mol} - (723.15 \text{ K})(-198.762 \text{ J/molK}) \\ = -92,220 \text{ J/mol} - (-143,734 \text{ J/mol}) = +51,510 \text{ J/mol} = +51.51 \text{ kJ/mol}$$

This is reactant-favored.

$$K_p = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(\frac{-51,510 \text{ J/mol}}{(8.314 \text{ J/molK})(723.15 \text{ K})}\right) = e^{-8.567} = 1.90 \times 10^{-4}$$

c) Solution:

From Dalton's Law of partial pressures: $P_{\text{tot}} = P_{\text{N}_2} + P_{\text{H}_2}$; Combining this with the ideal

gas equation, we can derive $\frac{P_{\text{N}_2, \text{initial}}}{P_{\text{total}}} = \frac{n_{\text{N}_2, \text{initial}}}{n_{\text{total, initial}}} = X_{\text{N}_2}$

$$P_{\text{N}_2, \text{init}} = X_{\text{N}_2}(P_{\text{tot}}) = \frac{1.00}{1.00 + 3.00}(1.000 \text{ bar}) = 0.250 \text{ bar} \text{ and}$$

$$P_{\text{H}_2, \text{init}} = X_{\text{H}_2}(P_{\text{tot}}) = \frac{3.00}{1.00 + 3.00}(1.000 \text{ bar}) = 0.750 \text{ bar}$$

	$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$		
initial	0.250	0.750	0
change	x	-3x	+2x

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(2x)^2}{(0.250 - x)(0.750 - 3x)^3} \approx \frac{(2x)^2}{(0.250)(0.750)^3} = 1.90 \times 10^{-4} \text{ (see previous question)}$$

$$\text{So: } x \approx \sqrt{\frac{(0.250)(0.750)^3(1.90 \times 10^{-4})}{4}} = 2.24 \times 10^{-3} \text{ bar}$$

(note, that by 5% rule this is an acceptable estimate).

$$P_{\text{NH}_3} = 2x = 2(2.24 \times 10^{-3} \text{ bar}) = 4.48 \times 10^{-3} \text{ bar}$$

$$P_{\text{N}_2} = 0.250 - 2.24 \times 10^{-3} \text{ bar} = 0.248 \text{ bar}$$

$$P_{\text{H}_2} = 0.750 - 3(2.24 \times 10^{-3}) = 0.743 \text{ bar}$$