

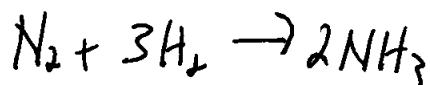
CH353 – Physical Chemistry I
Spring 2015, Unique 51170

Quiz 5, 24 April 2015

The synthesis of ammonia gas from hydrogen and nitrogen gases is one of the most important modern industrial reactions. 500 million tons of ammonia are synthesized every year; the energy required to run the reactors in which this is done accounts for approximately 2% of the world's total annual energy use. It is therefore extremely important that this reaction go as far as completion as possible.

Explain in as much quantitative detail as possible, ideal reaction conditions for the synthesis of ammonia from hydrogen and nitrogen gases. The following information may be useful.

	ΔH_f° (kJ mol ⁻¹)	S_m° (J K ⁻¹ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)
N ₂ (g)	0	191.6	0
H ₂ (g)	0	130.7	0
NH ₃ (g)	-46.1	192.5	-16.5



$$\Delta G_{\text{rxn}}^\circ = \sum_{\text{prod.}} \Delta G_f^\circ - \sum_{\text{react}} \Delta G_f^\circ = 2 \Delta G_f^\circ(\text{NH}_3) - \Delta G_f^\circ(\text{N}_2) - 3 \Delta G_f^\circ(\text{H}_2)$$

$$\Delta G_{\text{rxn}}^\circ = 2(-16.5 \text{ kJ/mol}) = -33 \text{ kJ/mol}$$

$$K_p = \exp\left[\frac{-\Delta G_{\text{rxn}}^\circ}{RT}\right] = \exp\left[\frac{-(-33 \text{ kJ/mol})}{(8.31 \text{ J/(mol}\cdot\text{K)})(298 \text{ K})}\right] = \underline{6.2 \times 10^5 = K_p}$$

K_p is already large, so rxn will proceed far to products. However, given the energy of production considerations, we need to think about how to get the maximum amount of products possible. There are 3 things we can change easily: rxn. pressure, rxn temperature, and rxn. amounts.

Rxn pressure. Changing pressure will not change K_p , but it will alter rxn. yield to keep K_p constant. The easiest way to assess this is

$$K_p = K_x P_{\text{tot}}^{\sum \nu_i} = K_x P_{\text{tot}}^{2-1-3} = K_x P_{\text{tot}}^{-2}$$

$$K_p = \frac{K_x}{P_{\text{tot}}^2}$$

Every increase of P_{tot} by 10 increases the denominator in this expression by 100, so the numerator must increase by 100x as well.

$$K_x = \frac{x(\text{NH}_3)^2}{x(\text{N}_2) x^3(\text{H}_2)} = \frac{x^2(\text{products})}{x^4(\text{reactants})}, \text{ so increasing}$$

the numerator increases products.

Rxn temperature. $\ln\left(\frac{K_p(T_2)}{K_p(T_1)}\right) = \frac{-\Delta H_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\Delta H_{\text{rxn}}^\circ = 2\Delta H_f^\circ(\text{NH}_3) - \Delta H_f^\circ(\text{N}_2) - 3\Delta H_f^\circ(\text{H}_2) = -92.2 \text{ kJ/mol} \text{ (very exothermic)}$$

Increasing $\ln\left(\frac{K_p(T_2)}{K_p(T_1)}\right)$ by 10x means decreasing T_2 by approximately 3000x ($T_2 \sim 0.1 \text{ K}$).

Rxn amount $Q = \frac{P(\text{NH}_3)}{P(\text{N}_2) P(\text{H}_2)^3}$ everywhere but equilibrium

If $Q < K_p$, rxn will go towards products, so we should add

$\text{N}_2 + \text{H}_2$ in stoichiometrically balanced ratio. The other thing

we can do is remove NH_3 (i.e. reduce the numerator instead of

increase the denominator). The analysis of rxn pressure has

already told us we should increase $P(\text{N}_2) + P(\text{H}_2)$. Removing

NH_3 after it is formed is an additional tool to make the

rxn. generate as much NH_3 as possible.