

# Chemistry 201

Pressure  
dependence of  $K$

**NC State University**

# Pressure dependence of species

We can see from the gas phase form of the equilibrium constant that pressure of species depend on pressure. For the general gas phase reaction,



we can write the equilibrium constant as

$$K = \frac{P_Z^z}{P_C^c P_D^d}$$

And the free energy is

$$\Delta G^o = -RT \ln \frac{P_Z^z}{P_C^c P_D^d}$$

From Dalton's law

$$P_C = x_C P_{tot}, P_D = x_D P_{tot}, P_Z = x_Z P_{tot}$$

# Pressure dependence of species

If we substitute these mole fractions and total pressure into the equilibrium constant we have

$$\Delta G^{\circ} = -RT \ln \frac{x_Z^z}{x_C^c x_D^d} P_{tot}^{z-c-d}$$

Which depends on the total pressure unless  $z - c - d = 0$ .

This expression shows that, in general, the free energy depends on the total pressure. This means that for the fixed pressure may affect the proportion of products to reactants.

# Equilibrium of smog formation

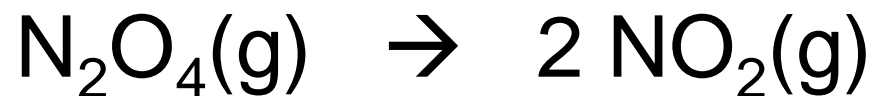


Why is the dissociation greater at low pressure?



Can the trend be explained in simple terms?

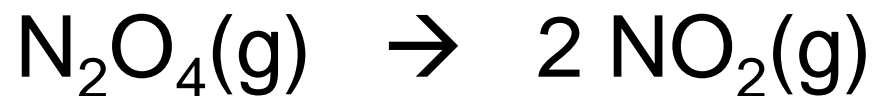
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Yes, this is an example of Le Chatelier's principle.

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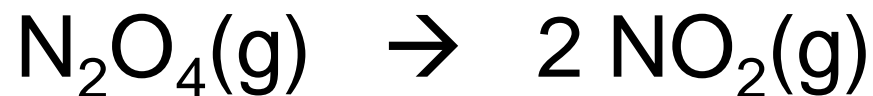


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Can the trend be explained quantitatively?

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Can the trend be explained in simple terms?

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Can the trend be explained quantitatively?

$$\Delta G^{\circ} = -RT \ln \left( \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} P_{\text{tot}} \right)$$



Another way that we can examine the effect of Changing the total pressure is to examine the ratio Of mole fractions as a function of the total pressure:

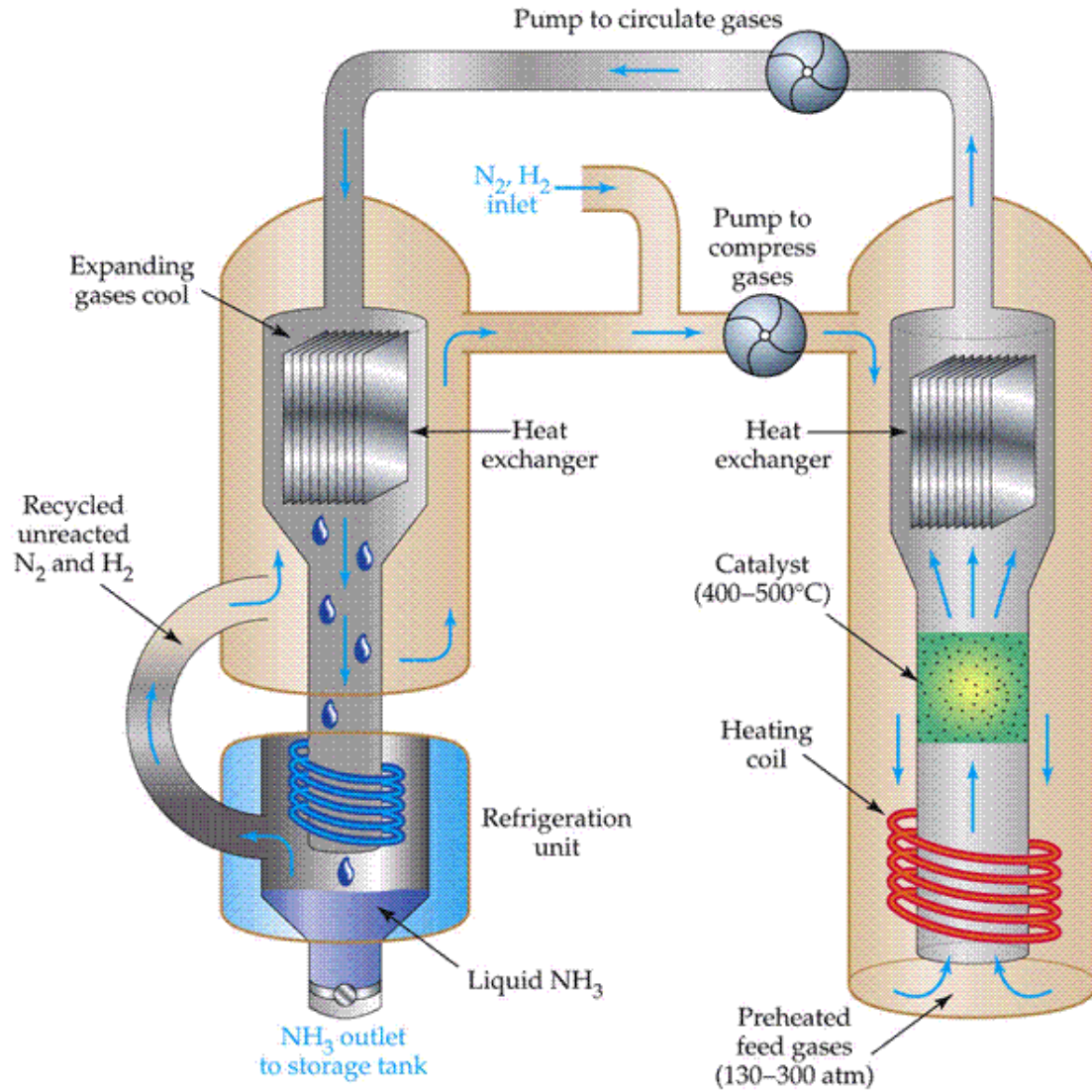
$$K = \frac{x_{NO_2}^2}{x_{N_2O_4}} P_{tot}$$

Can be rearranged to give

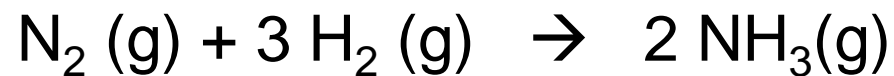
$$\frac{x_{NO_2}^2}{x_{N_2O_4}} = \frac{K}{P_{tot}}$$

In this expression we see that increasing the total pressure has the same effect as decreasing the equilibrium constant and thereby decreasing the number of moles of  $NO_2$ . This quantitative result agrees with Le Chatelier's principle.

# The Haber-Bosch Process

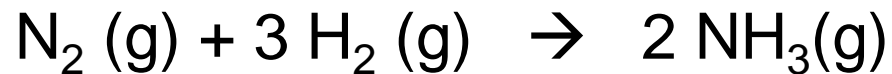


## The Haber-Bosch process



Involves both high temperature and pressure.

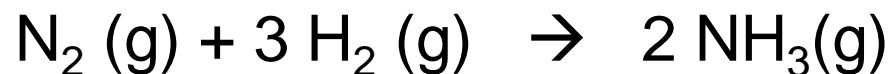
# The Haber-Bosch process



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## The Haber-Bosch process

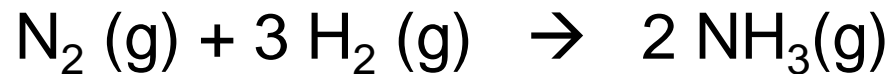


Involves both high temperature and pressure.

Why high pressure?

Forces the equilibrium to the right. This is an example of Le Chatelier's principle.

# The Haber-Bosch process



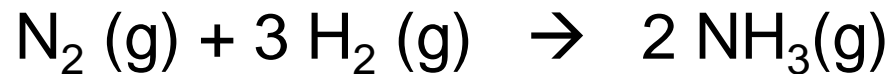
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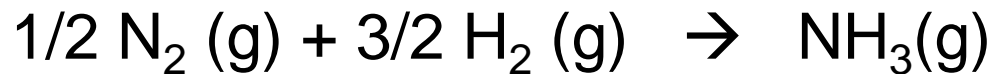
Why high pressure?

Forces the equilibrium to the right. This is an example of Le Chatelier's principle.

Why high temperature?

Although this is an exothermic reaction, it also has a large barrier. The process uses a catalyst. But, what does the temperature do to the equilibrium?

## The Haber-Bosch process



The enthalpy change of the reaction is equal to the enthalpy of formation of  $\text{NH}_3$ .  $\Delta_f H^\circ = -45.9 \text{ kJ/mol}$

The entropy can be calculated from tabulated absolute entropies.

Mol	$S^\circ$
$\text{NH}_3$	192.77
$\text{N}_2$	153.3
$\text{H}_2$	114.7



# The Haber-Bosch Process

Under standard conditions

$$\Delta_{\text{rxn}} S^{\circ} = S^{\circ}(\text{NH}_3) - 1/2 S^{\circ}(\text{N}_2) - 3/2 S^{\circ}(\text{H}_2)$$

$$\Delta_{\text{rxn}} S^{\circ} = 192.77 - 1/2(153.3) - 3/2(114.7)$$

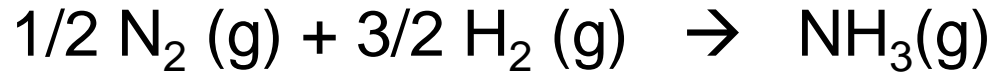
$$\Delta_{\text{rxn}} S^{\circ} = -55.9 \text{ J/molK}$$

$$\Delta_{\text{rxn}} G^{\circ} = \Delta_{\text{rxn}} H^{\circ} - T \Delta_{\text{rxn}} S^{\circ}$$

$$\Delta_{\text{rxn}} G^{\circ} = \left( -45,900 \frac{\text{J}}{\text{mol}} \right) - (298 \text{ K}) \left( -55.9 \frac{\text{J}}{\text{molK}} \right)$$

$$\Delta_{\text{rxn}} G^{\circ} = -30.1 \text{ kJ/mol}$$

# The Haber-Bosch Process



As we did previously for the smog reaction we can express the mole fraction ratio as a function of the total pressure:

$$K = \frac{x_{\text{NH}_3}}{x_{\text{N}_2}^{1/2} x_{\text{H}_2}^{3/2}} \frac{1}{P_{\text{tot}}}$$

$$\frac{x_{\text{NH}_3}}{x_{\text{N}_2}^{1/2} x_{\text{H}_2}^{3/2}} = P_{\text{tot}} K$$

# Hydrogenation: use of pressure

