5.111 Principles of Chemical Science
Fall 2008

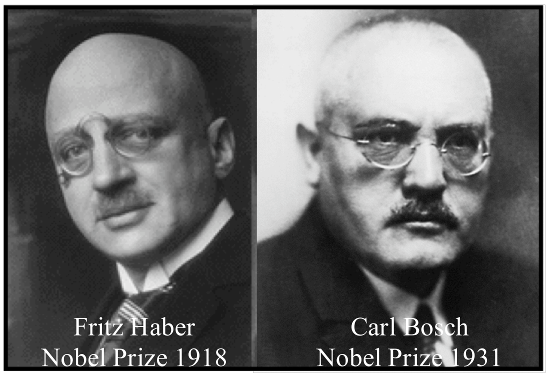
Le Châtelier’s Principle

See lectures 19 and 20 for a discussion of chemical equilibrium.

<u>Principle of Le Châtelier:</u> A system in equilibrium that is subjected to stress will react in a way that tends to minimize the effect of the stress.

Le Châtelier's principle provides a way to predict qualitatively the direction of change of a system under an external perturbation.

Example from pg. 4 of Lecture 20 notes: Maximizing the Yield of Nitrogen Fixation



<u>Haber-Bosch Process</u>
The Haber-Bosch process is a nitrogen fixation reaction in which ammonia (NH_3) is produced from inert nitrogen gas reacting with hydrogen gas.

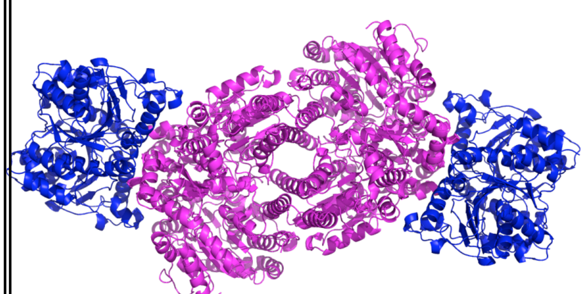
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

exothermic reaction

Over 1.6×10^{10} kg of ammonia are produced by this process per year in the US. Ammonia is used to produce fertilizer, and prior to the Haber-Bosch process, it was extremely difficult to obtain ammonia on an industrial scale.

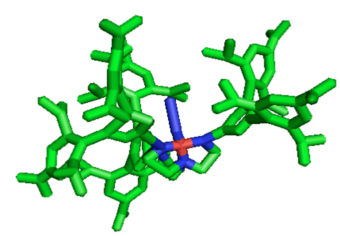
As an **exothermic** reaction, low temperature favors products, *but* low temperature also slows rate. The compromise temperature used is 500°C. What are other ways to drive the reaction toward products?
Answers: *decrease the volume of the container, remove product (NH_3), use an enzyme*

Problems with industrial production of NH_3: high temperature, pressure, and expense. **Bacteria can catalyze the same reaction using an enzyme called nitrogenase!**



Nitrogenase is made up of two proteins that use metal centers to catalyze nitrogen fixation. The molybdenum-iron (MoFe) protein is depicted in magenta, and the iron (Fe) protein is shown in blue.

Inspired by Nature’s approach, the Schrock lab at MIT has reported the first catalytic reduction of molecular nitrogen to ammonia at a well-defined molybdenum (Mo) metal center.



Schrock catalyst with a Mo center (red)

Nitrogenase figure from PDB: 1N2C.
For more information on nitrogenase, see
http://www.rcsb.org/pdb/static.do?p=education_discussion/molecule_of_the_month/pdb26_1.html

Example from page 4 of Lecture 20 notes: Le Châtelier's Principle and Application to Blood-Oxygen Levels

Hemoglobin (Hb) is an oxygen transport protein, and there are approximately 300 million hemoglobin molecules per red blood cell. The combination of oxygen with hemoglobin, can be represented by

$$\mathrm{Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)}$$

where HbO_2 is oxyhemoglobin (oxygen bound to hemoglobin)

At an altitude of 3 km the partial pressure of oxygen is only about 0.14 atm, compared to 0.2 atm at sea level. According to Le Châtelier's principle, the equilibrium would be shifted to the left. This change causes hypoxia (oxygen deprivation). How can the body compensate?

Image courtesy of Olaf Rieck on Wikipedia.

Answer: The body produces more hemoglobin (Hb), which pushes the reaction toward products, resulting in more highly oxygenated blood.

$$\mathrm{Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)}$$

shift to product

body makes more

The structure of Hb. Hb is made up of four polypeptide subunits: two alpha subunits colored in magenta and two beta subunits colored in blue. Each subunit has one iron-containing heme group, which binds oxygen for transport. The heme groups (two are visible) are shown in black. PDB file 1GZX.