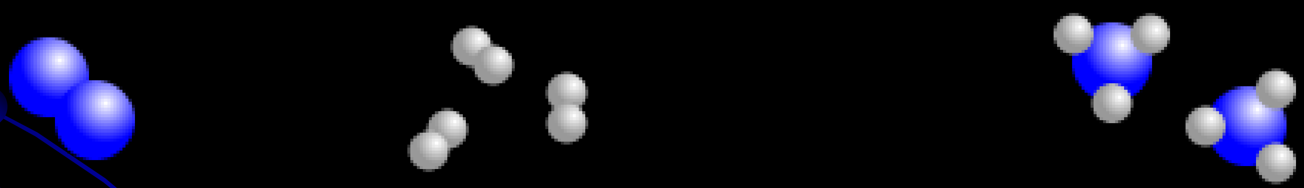
The Industrial Manufacture of Ammonia – $NH_{3(g)}$

Fritz Haber was awarded the Nobel Prize in Chemistry in 1918 for discovering the conditions that are necessary to synthesise ammonia directly from the elements nitrogen and hydrogen. *Carl Bosch* was awarded the Nobel Prize in Chemistry in 1931 for developing the industrial process that is required for the large scale manufacture of ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

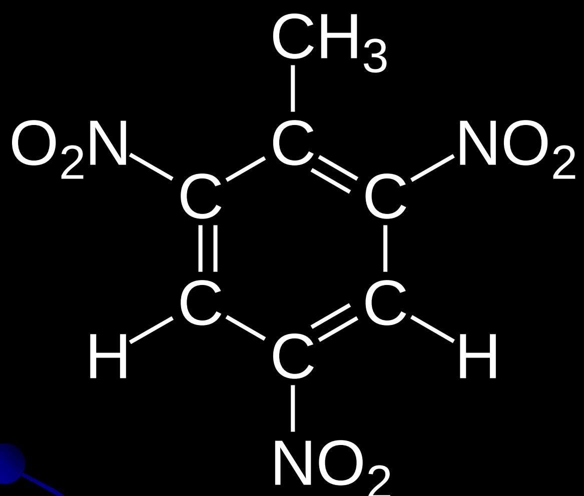


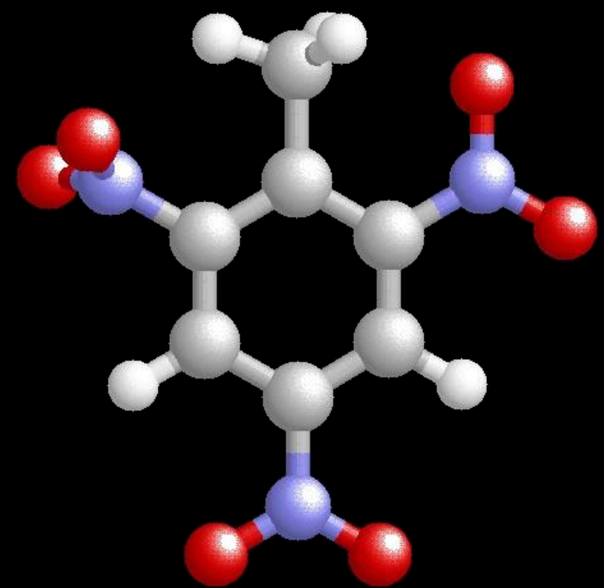
Fritz Haber

Carl Bosch

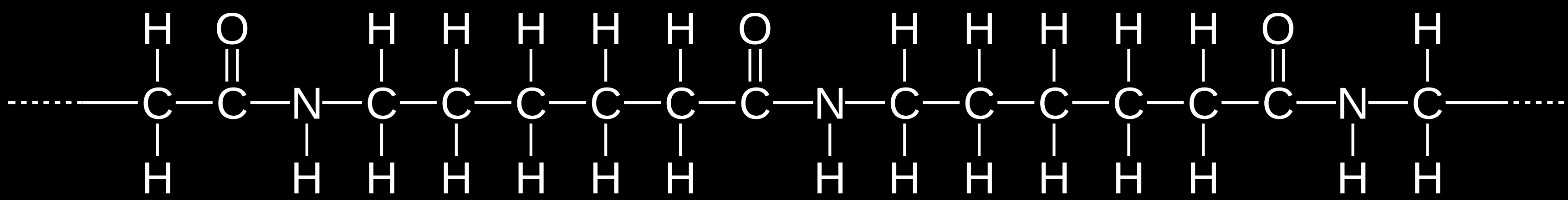
In addition to being an essential raw material for the industrial manufacture of *fertilisers* (such as potassium nitrate, KNO_3) ammonia is also used in the industrial manufacture of…

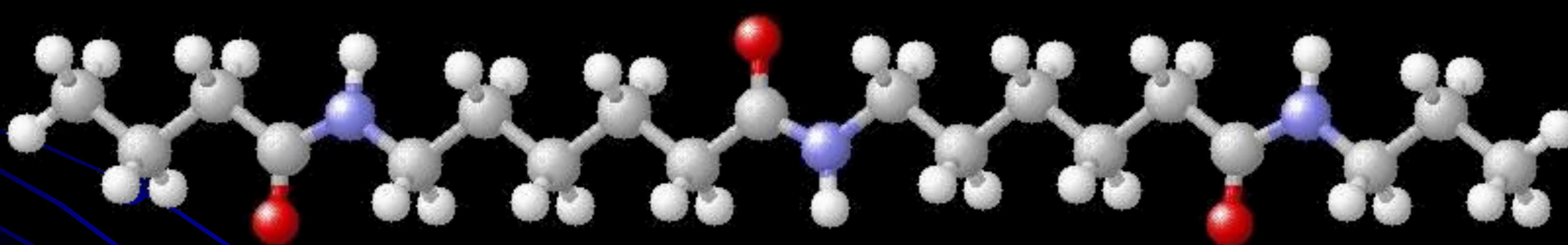
…*explosives* such as 2,4,6-trinitrotoluene (TNT)…



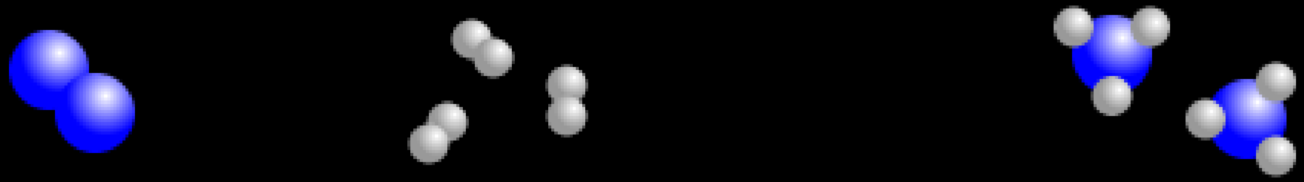


…and *plastics* such as nylon.





$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$



The nitrogen that is required for the reaction is obtained from the fractional distillation of liquefied air:

b.p. O_2 = -183°C   b.p. N_2 = -196°C

Hydrogen is produced from the reaction between methane and steam, using a nickel catalyst at 30 atmospheres pressure and 750°C:

methane + steam → carbon monoxide + hydrogen

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$$

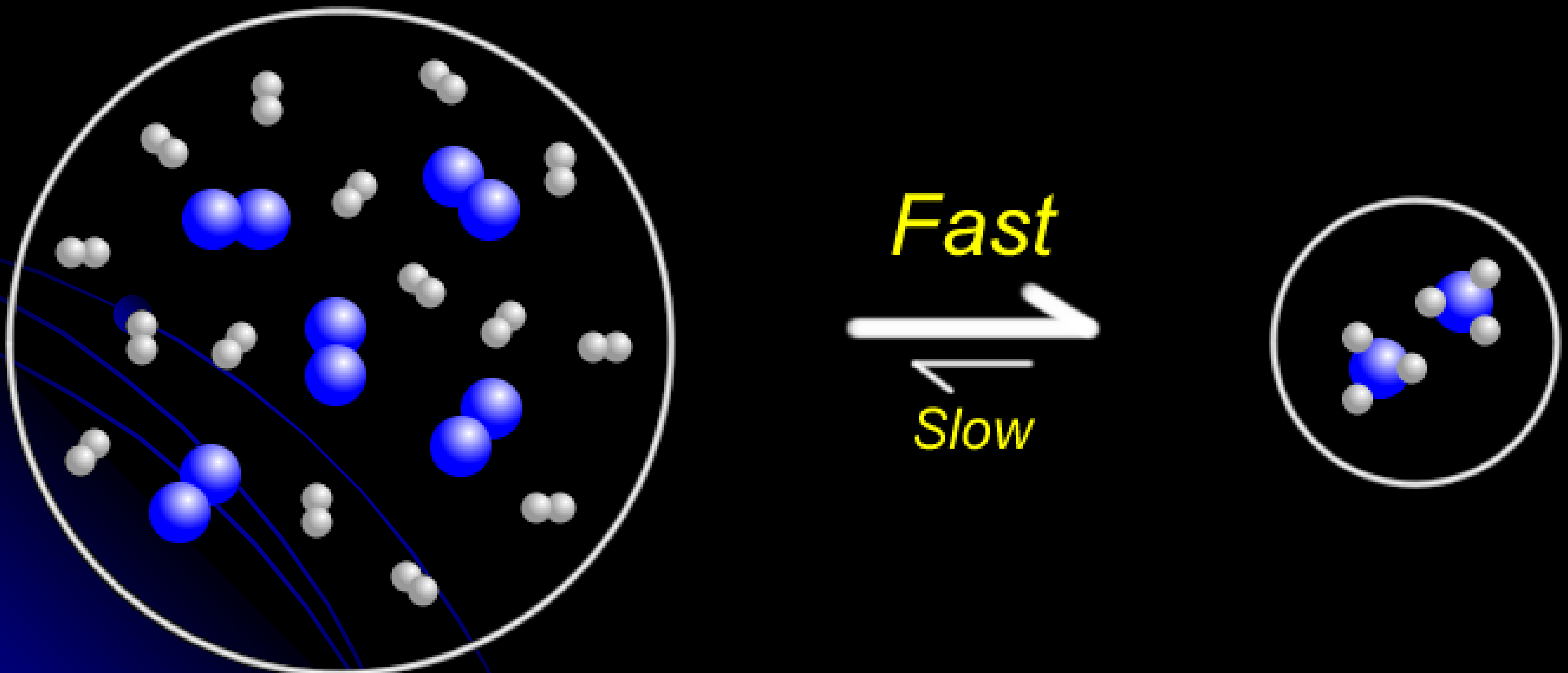
Fritz Haber

Carl Bosch

So, what conditions did Fritz Haber and Karl Bosch discover were best suited for the industrial manufacture of ammonia from nitrogen and hydrogen?

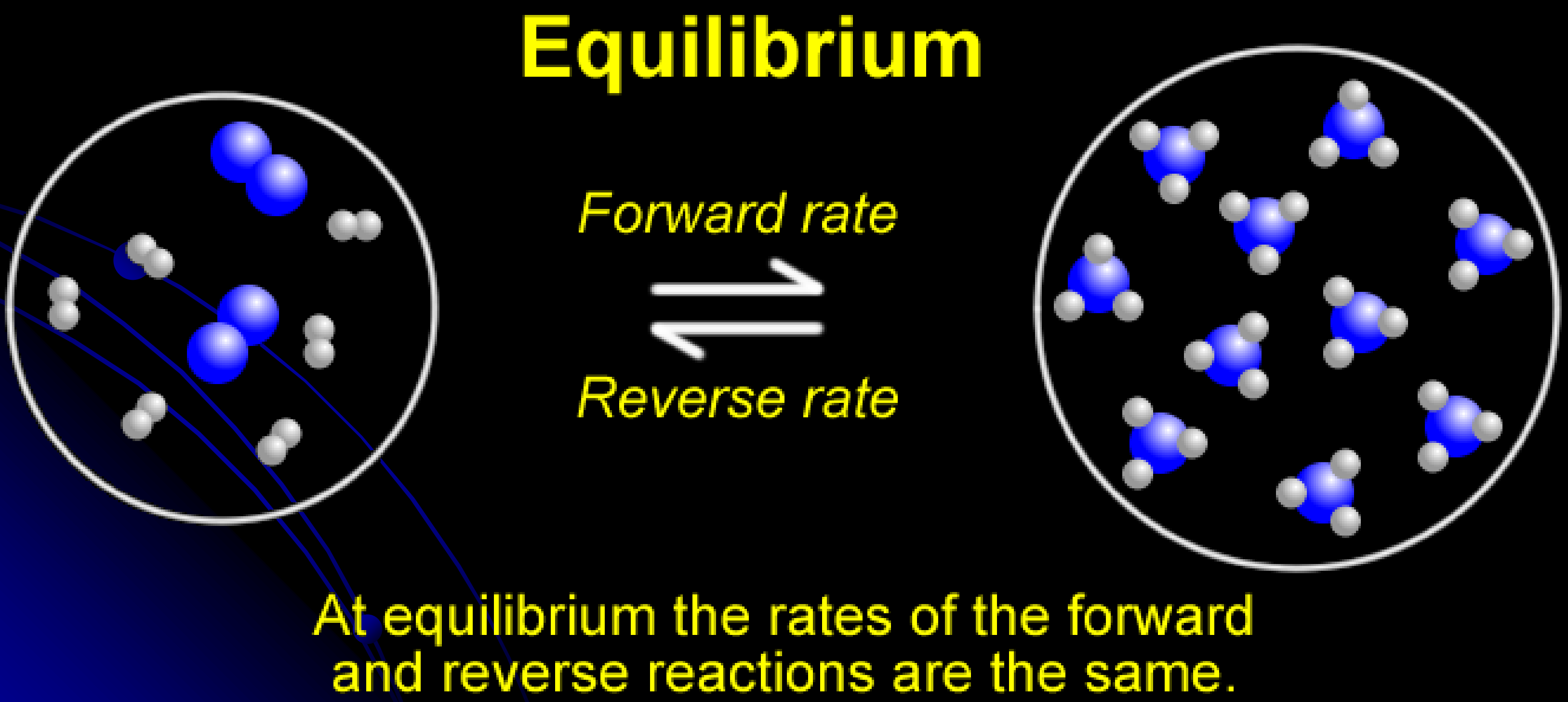
Let’s do some chemistry and find out ☺

When the synthesis of ammonia begins, the concentration of nitrogen and hydrogen will be high, but the concentration of ammonia will be relatively low. This means that the rate of the *forward reaction* will be *high*, but the rate of the *reverse reaction* will be *low*:

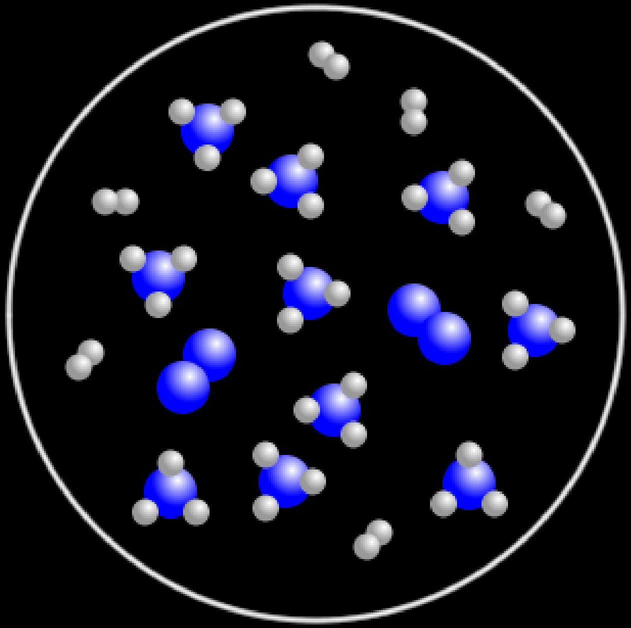


As the reaction continues, the concentration on nitrogen and hydrogen will decrease as they react to form ammonia. Consequently, the concentration of ammonia will increase. This means that the rate of the *forward reaction* will *decrease* while the rate of the *reverse reaction* will *increase*:

Eventually, a point is reached where the *rate of the forward reaction equals the rate of the reverse reaction*. The reaction has reached *equilibrium*. At this point, the concentrations of nitrogen, hydrogen and ammonia remain constant. Note: equilibrium is *not* necessarily reached when there is a 50:50 mixture of reactants and products.



Equilibrium is only reached if both reactants and products are prevented from leaving the reaction vessel. This is called a *closed system*.



How much product there is in the reaction mixture at equilibrium depends upon the *particular reaction* and the *reaction conditions* (e.g. temperature and pressure).

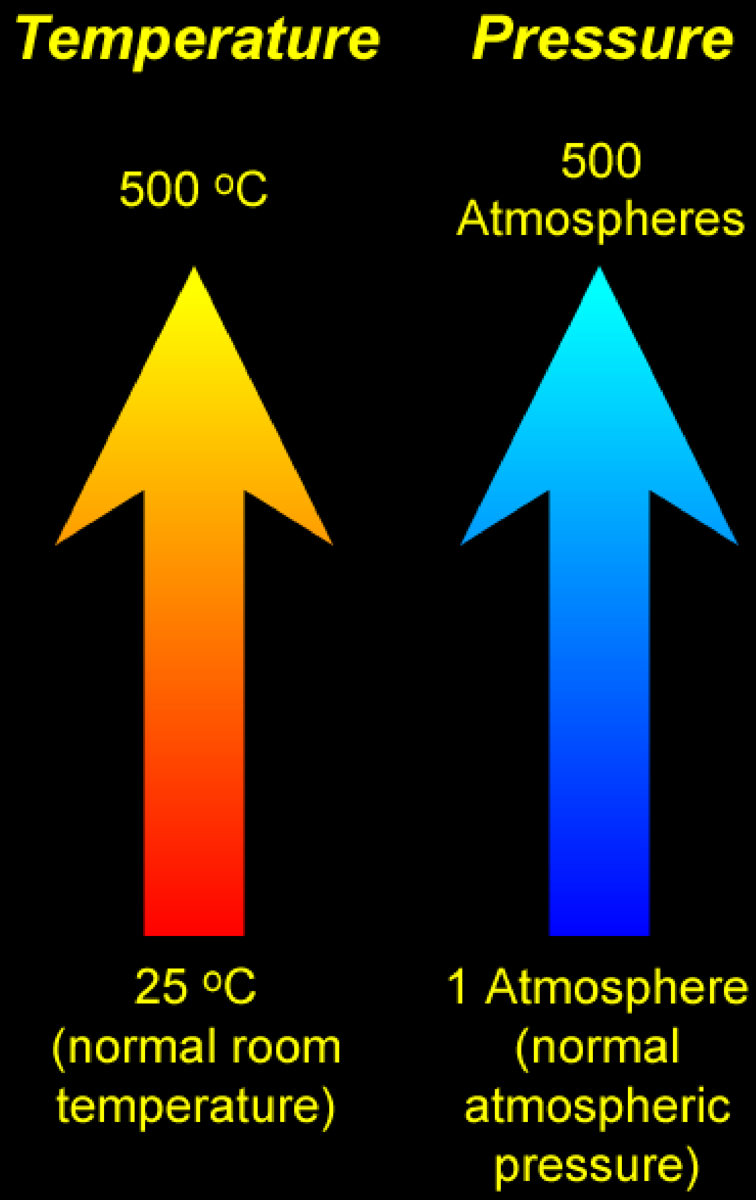
At room temperature and pressure, the yield of ammonia is *only 1%*.

Chemists can use *Le Chatelier's* theory to predict the conditions that will shift the equilibrium position of the reaction from the left-hand-side to the right-hand-side and therefore *increase the yield of ammonia*.

Le Chatelier's theory states that whatever chemical or physical change is imposed upon a chemical system, the equilibrium position of the chemical system shifts to oppose or minimise the change.

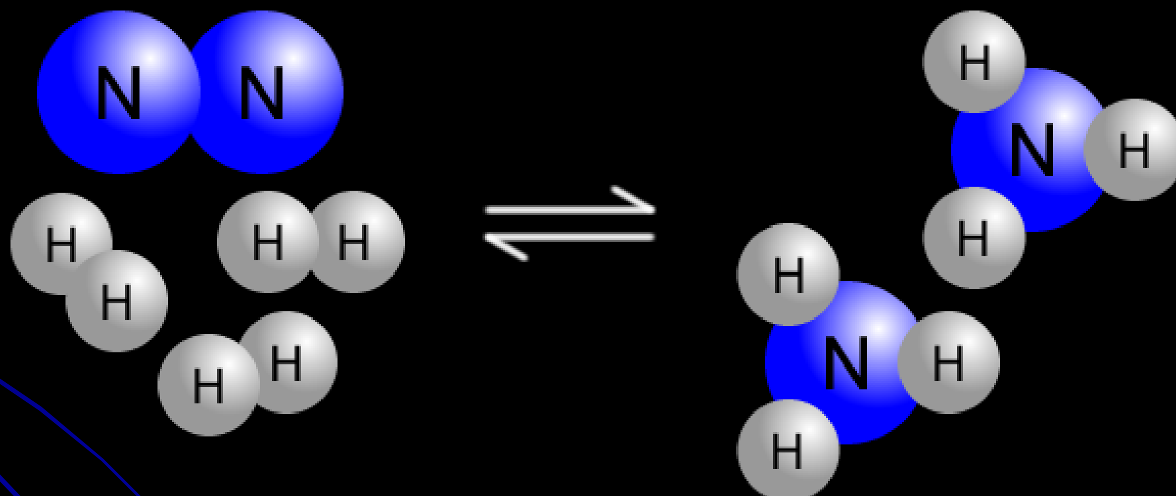
Two conditions can be varied during the industrial manufacture of ammonia:

- The *temperature* of the reaction.
- The *pressure* of the reaction (because the reactants and products are all gases).



How does *pressure* affect the equilibrium position of the reaction? Consider the following information:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

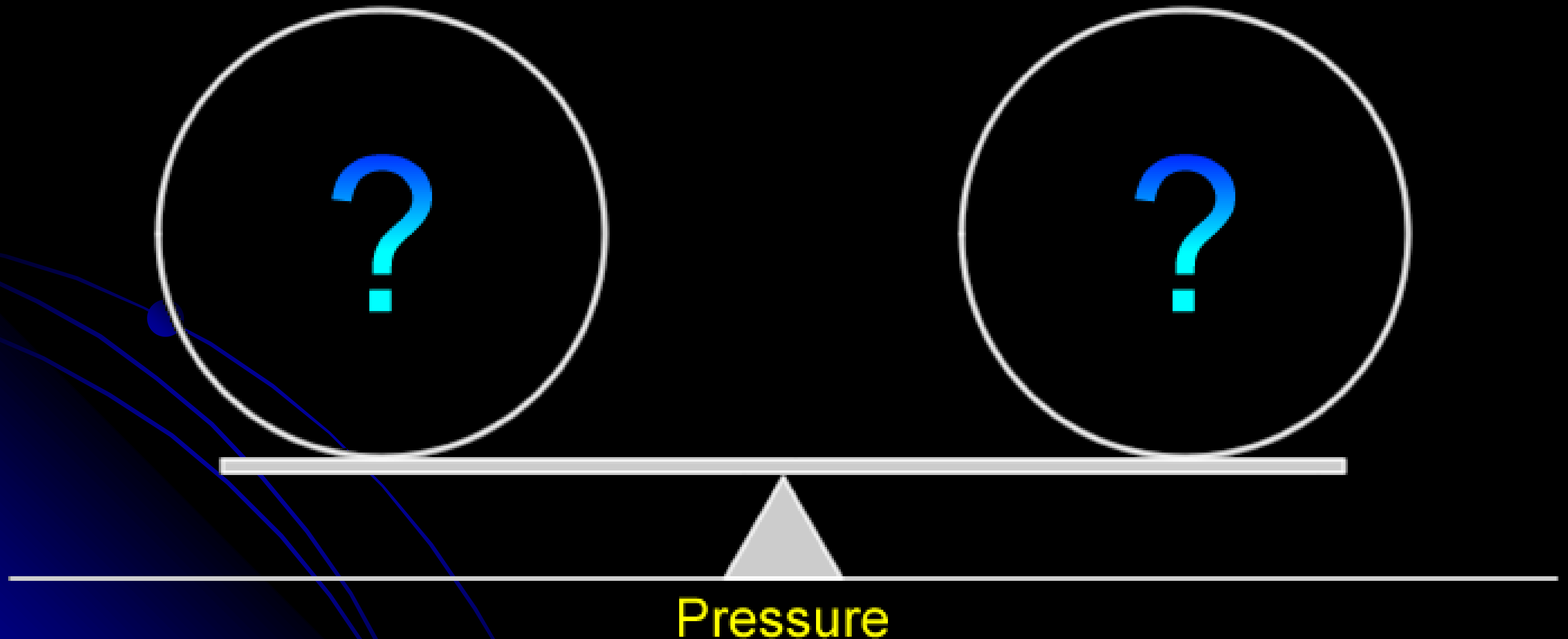


4 moles of gas
4 x 24 = 96 dm^3
(*high pressure*)

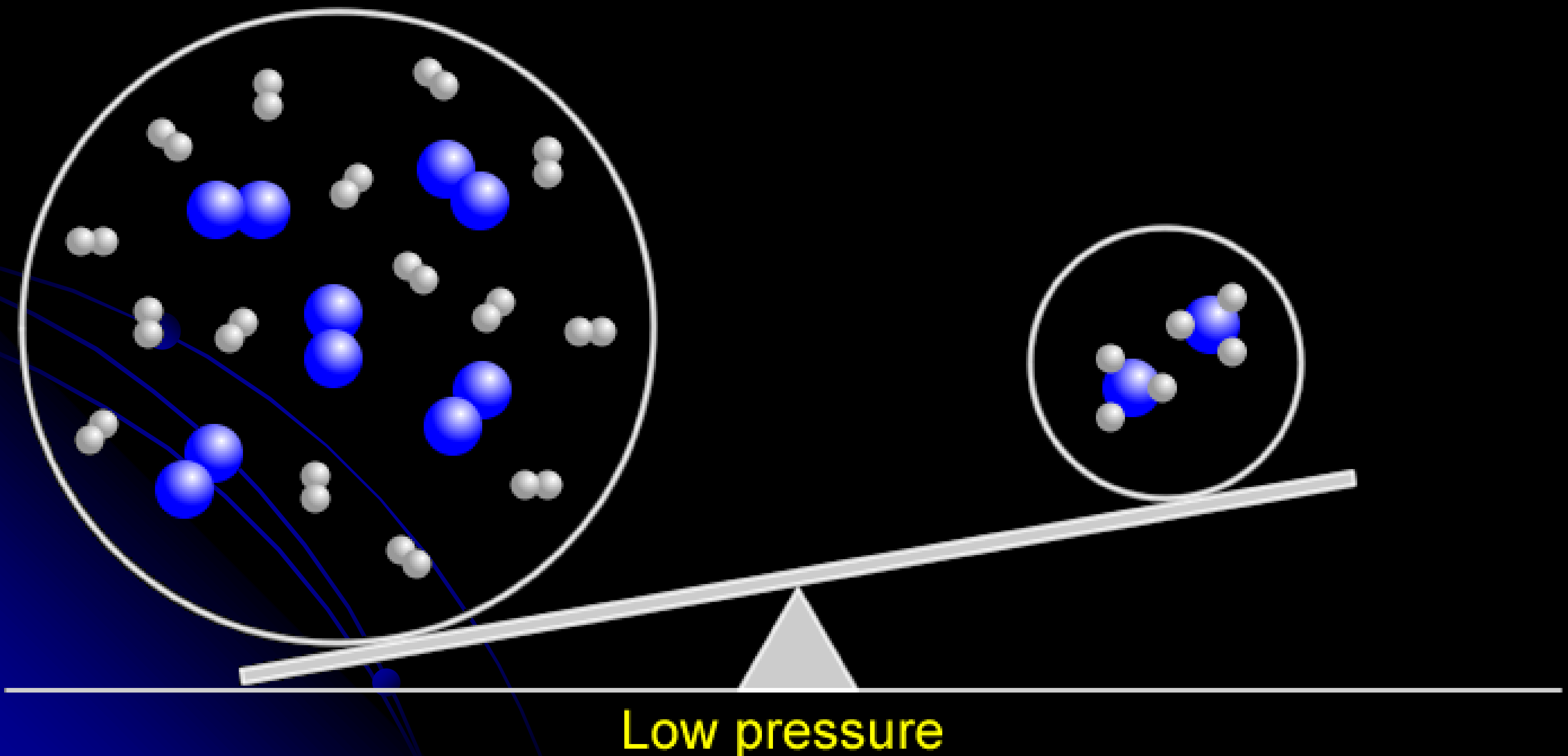
2 moles of gas
2 x 24 = 48 dm^3
(*low pressure*)

Use *Le Chatelier's theory* to predict what effect a *low pressure* will have on the equilibrium position of the reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$



If a *low pressure* is used, Le Chatelier's theory predicts that the equilibrium position of the reaction will shift in the direction that opposes/minimises this change, i.e. it will shift in the direction that *increases the pressure* which is from the right-hand-side to the left-hand-side, *reducing the yield of ammonia*.



Use *Le Chatelier's theory* to predict what effect a *high pressure* will have on the equilibrium position of the reaction:

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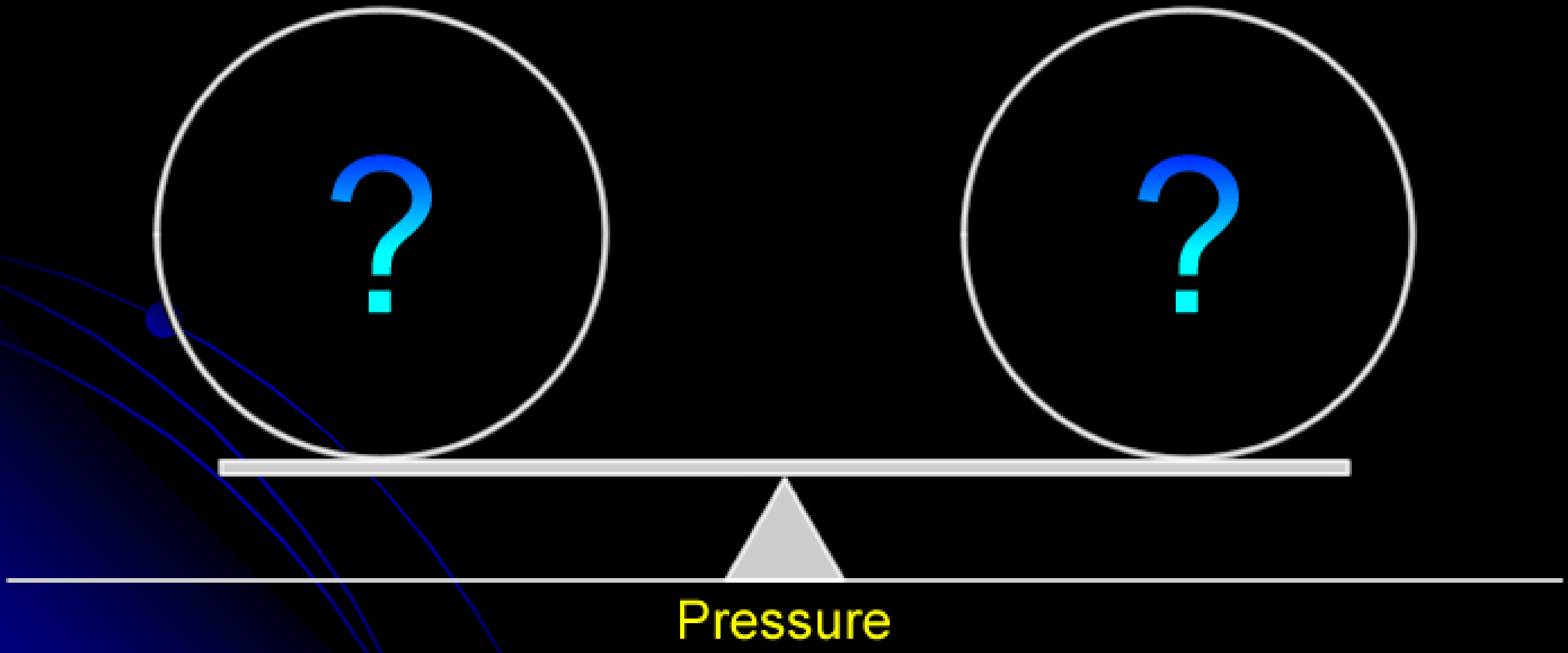
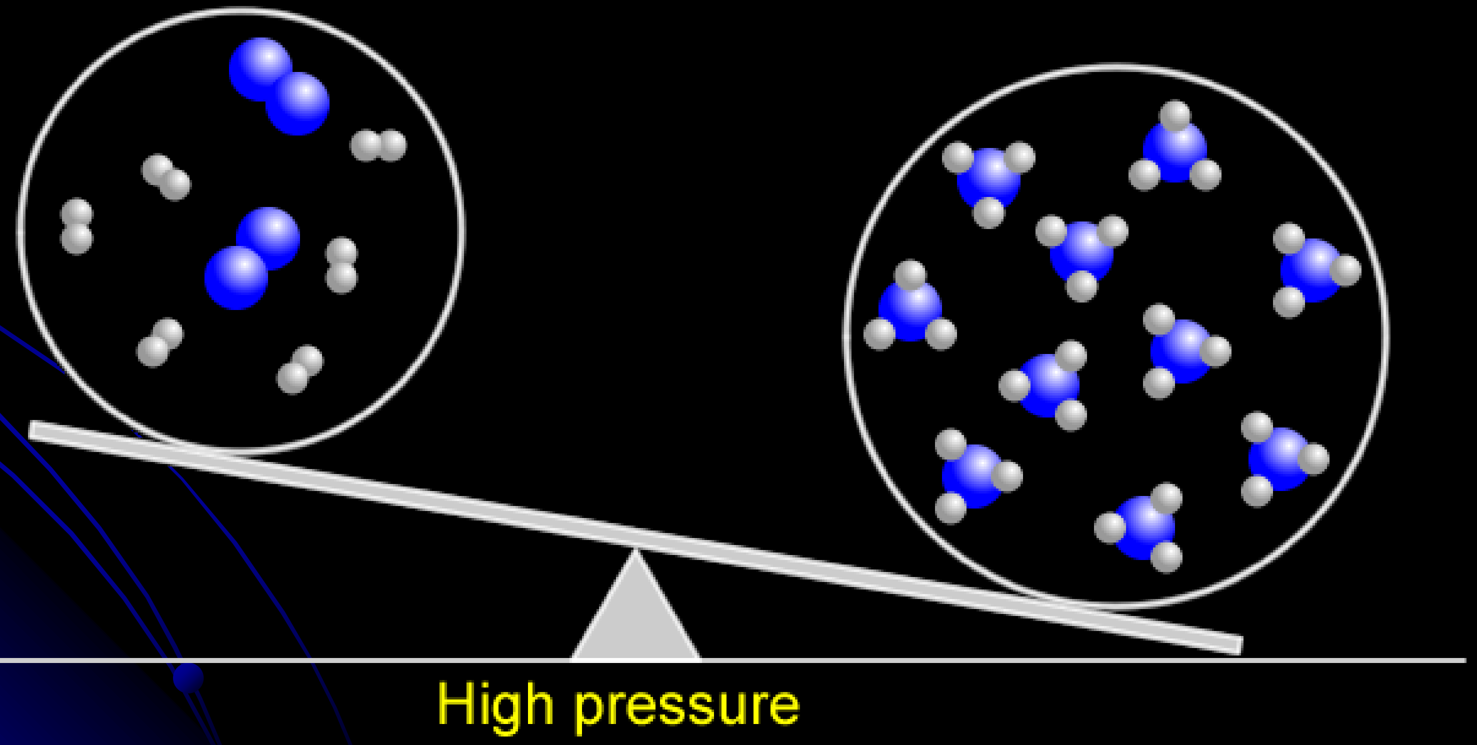


If a *high pressure* is used, Le Chatelier's theory predicts that the equilibrium position of the reaction will shift in the direction that opposes/minimises this change, i.e. it will shift in the direction that *reduces the pressure* which is from the left-hand-side to the right-hand-side, *increasing the yield of ammonia*.



What are the potential problems of using a very high pressure, especially on an industrial scale?

- Operating at a very high pressure increases the risk of a gas leak, or even an explosion.

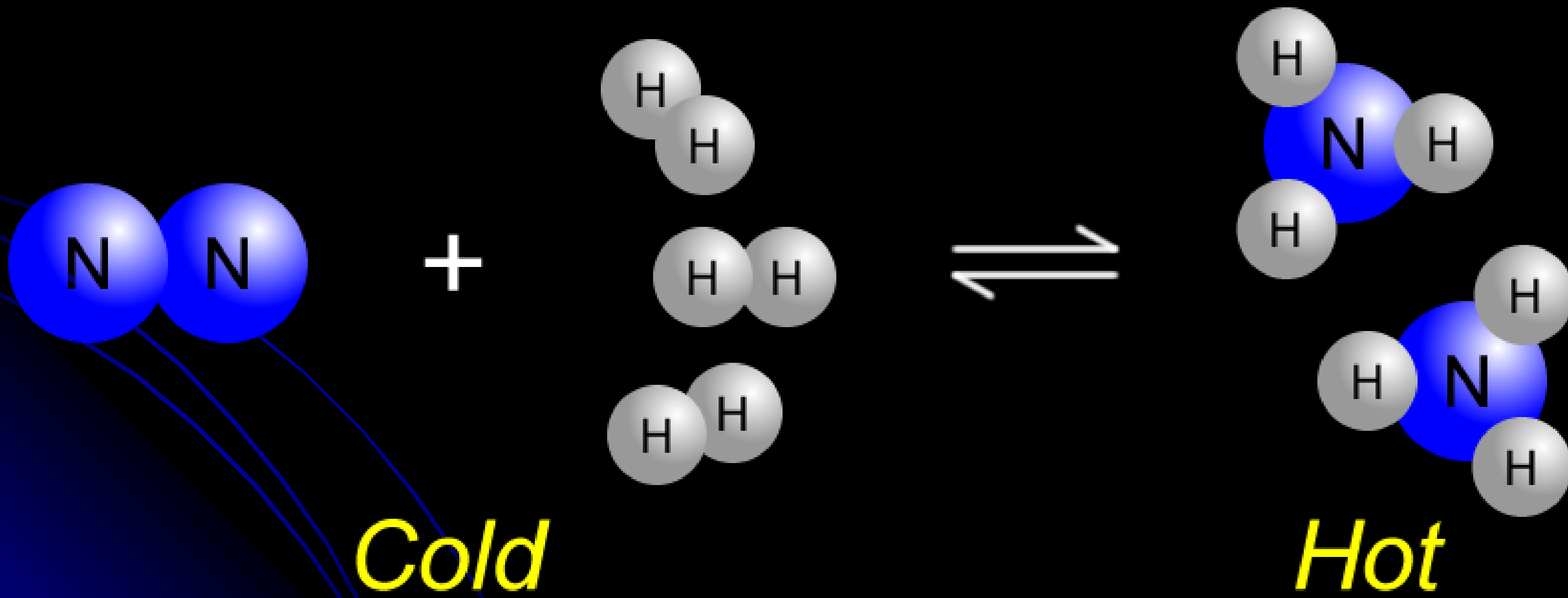
- Generating a very high pressure requires a great deal of energy, and so the process is expensive.

- The walls of the reaction chamber and pipes will have to be much thicker to withstand the very high pressure, and so the chemical plant will be very expensive to build.

How does *temperature* affect the equilibrium position of the reaction? Consider the following information:

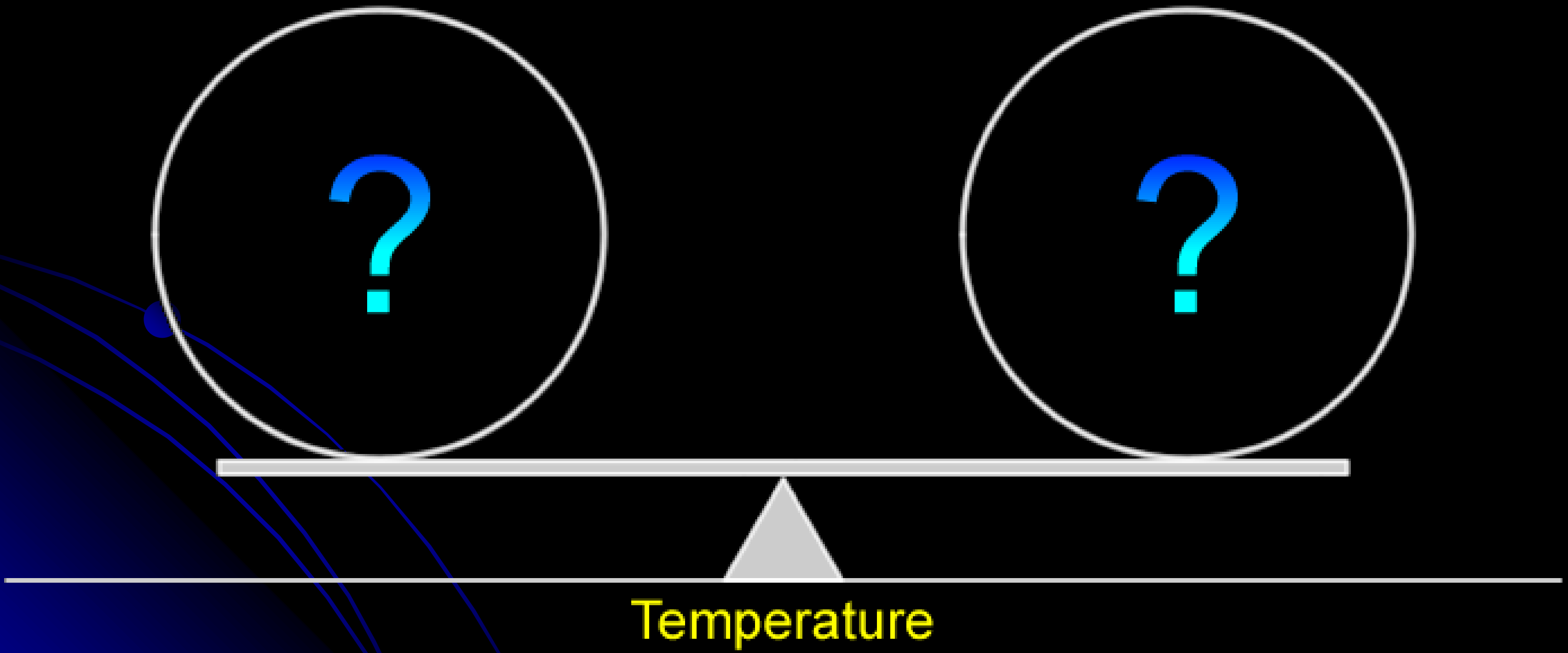
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$(\Delta H = -93 \text{ kJ mol}^{-1})$$

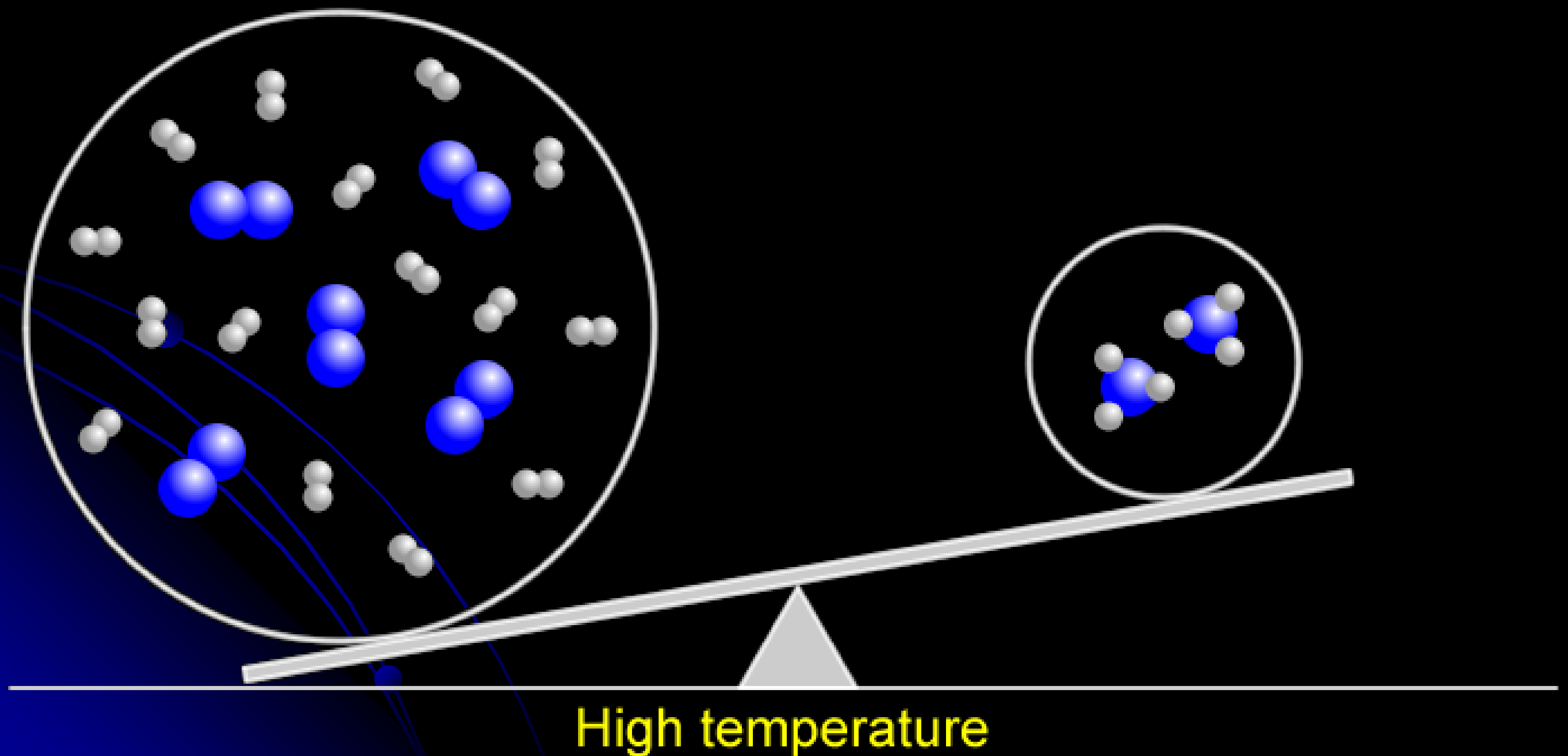


Use *Le Chatelier's theory* to predict what effect a *high temperature* will have on the equilibrium position of the reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

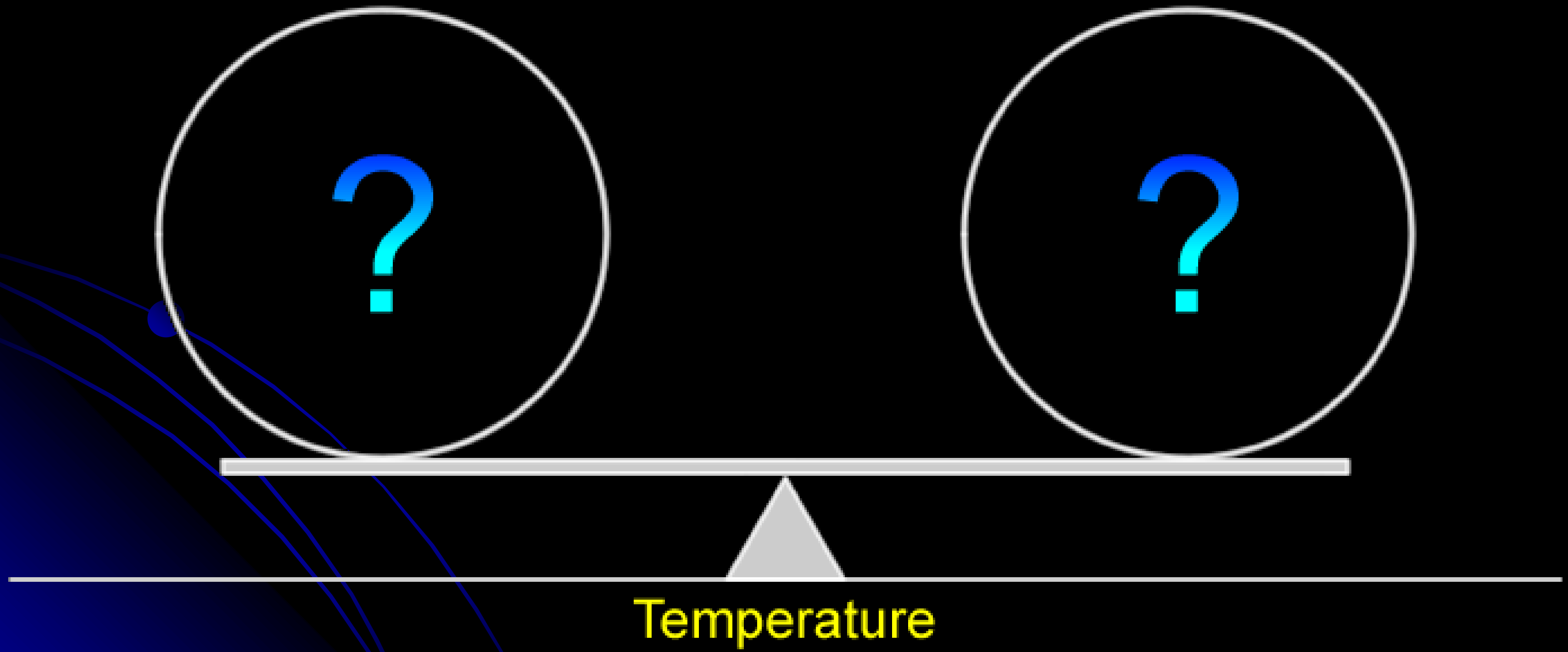


If a *high temperature* is used, Le Chatelier's theory predicts that the equilibrium position of the reaction will shift in the direction that opposes/minimises this change, i.e. it will shift in the direction that *reduces the temperature* which is from the right-hand-side to the left-hand-side, *reducing the yield of ammonia*.

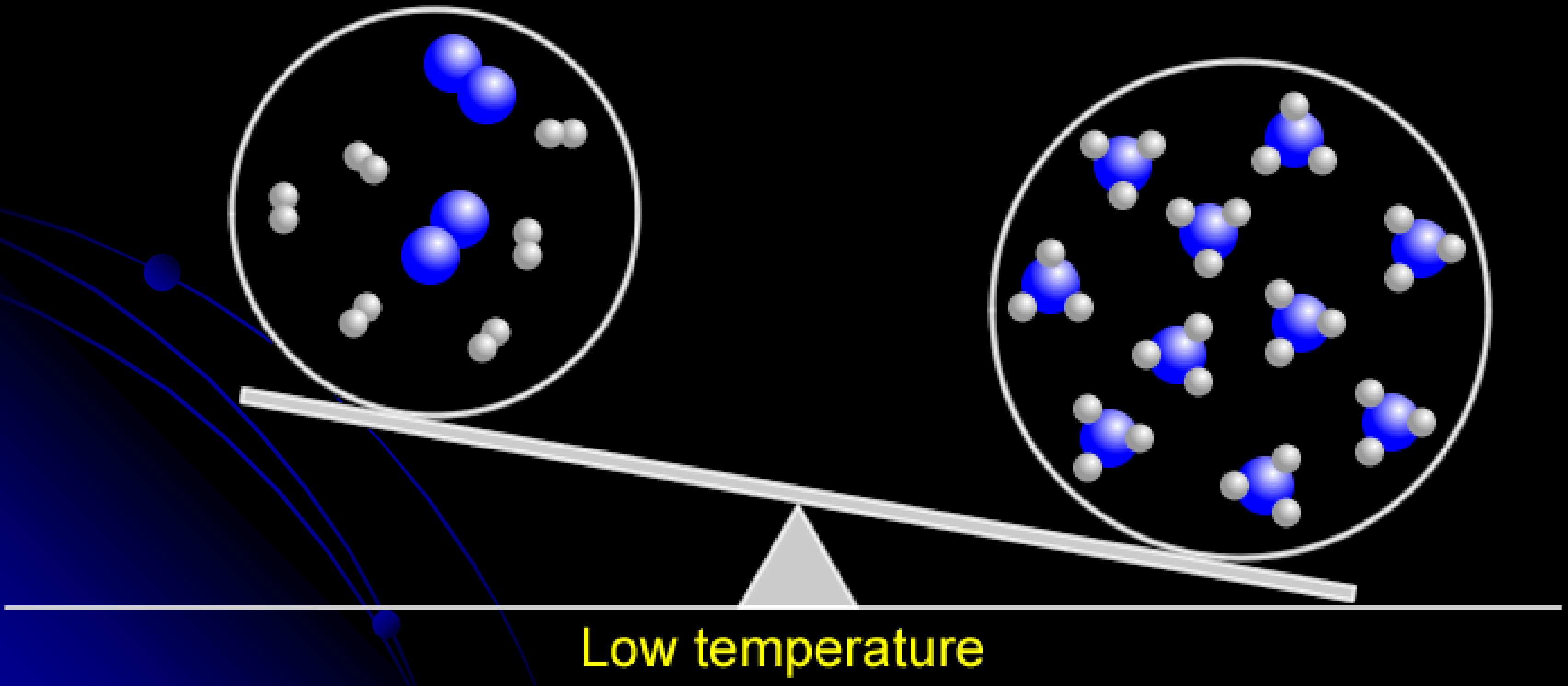


Use *Le Chatelier's theory* to predict what effect a *low temperature* will have on the equilibrium position of the reaction:

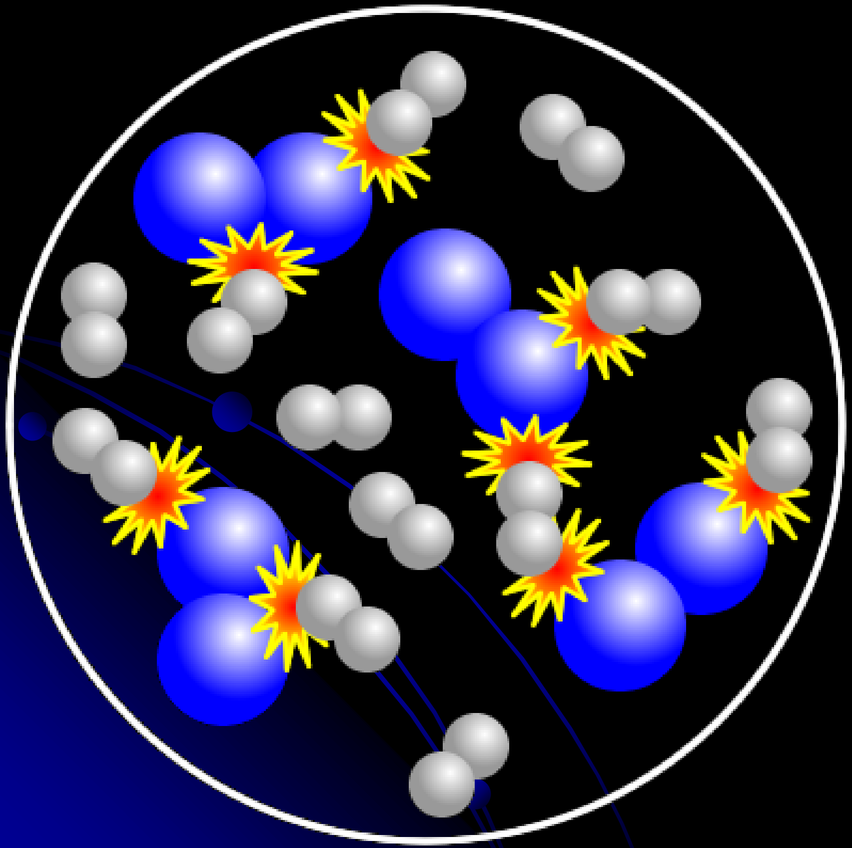
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$



If a *low temperature* is used, Le Chatelier's theory predicts that the equilibrium position of the reaction will shift in the direction that opposes/minimises this change, i.e. it will shift in the direction that *increases the temperature* which is from the left-hand-side to the right-hand-side, *increasing the yield of ammonia*.

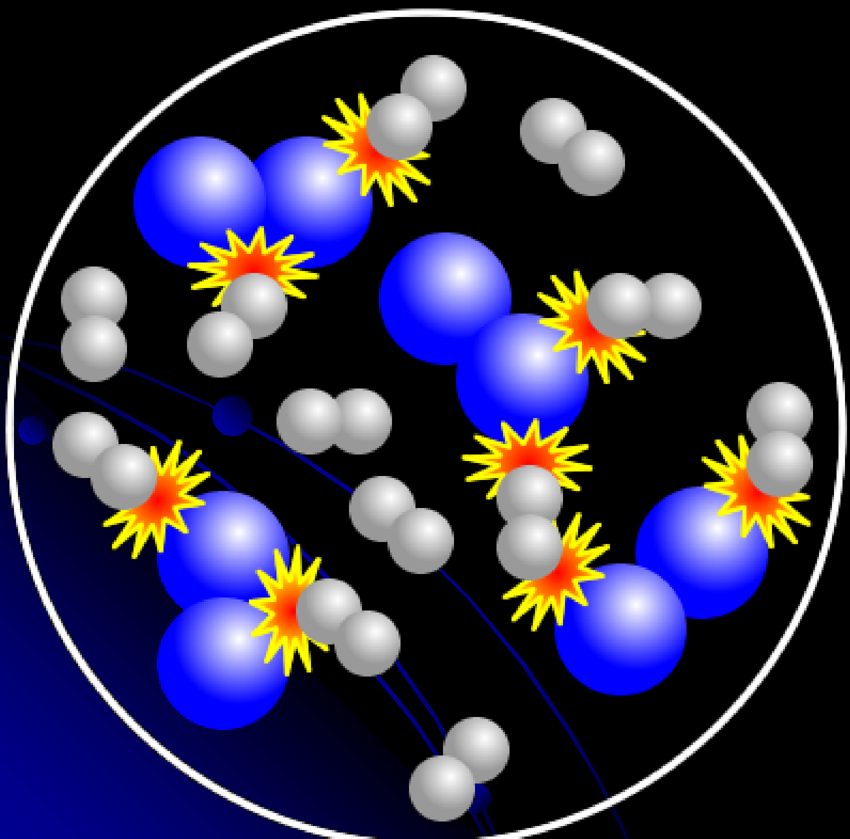


Oops! Won't the Low Temperature Affect the Rate of the Reaction?



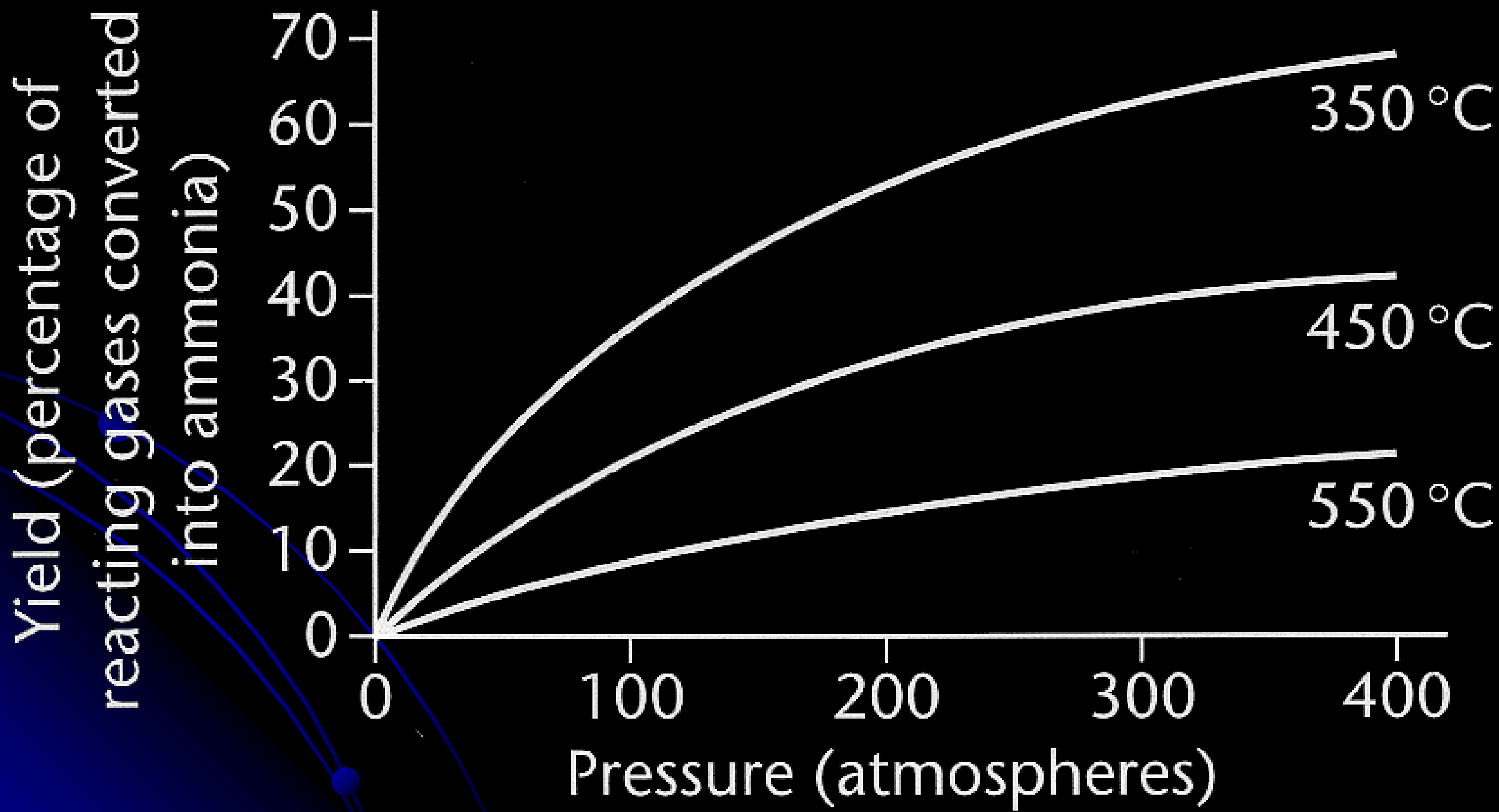
A *low temperature* will shift the equilibrium position of the reaction from the left-hand-side to the right-hand-side, *increasing the yield of ammonia*. However, it will also *reduce the rate of the reaction*. The average kinetic energy of the molecules will be reduced and so the *frequency* of the collisions between them will be reduced. In addition, the *energy* of the collisions will also be reduced. This means that a smaller proportion of the collisions will have energy equal to or greater than the *activation energy* that is necessary for the chemical reaction to take place.

Oops! Won't the Low Temperature Affect the Rate of the Reaction?

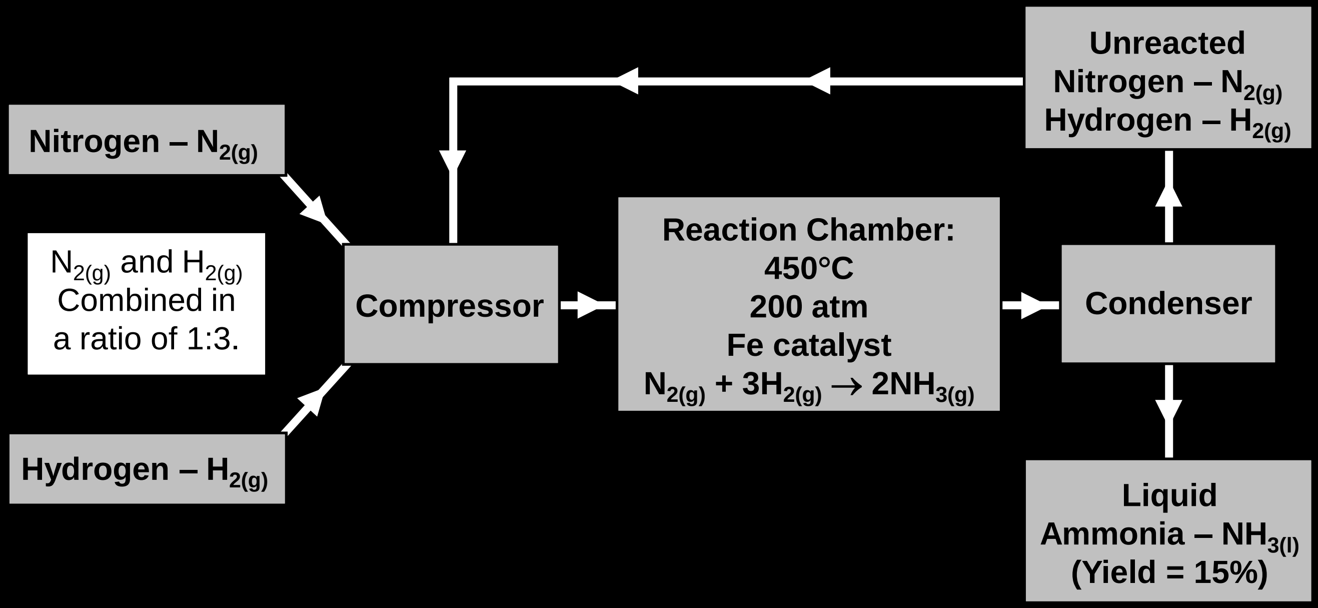


- In summary, a low temperature will reduce the frequency of effective collisions between the molecules in the reaction vessel.
- The low temperature will reduce the rate of *both the forward reaction* (left-to-right) *and also the backward reaction* (right-to-left).
- As a consequence, if ammonia is manufactured at a low temperature, then both the forward reaction and the backward reaction will be slow, and *the system will take a long time to reach equilibrium*.

So, what do you think are the optimum conditions for the industrial manufacture of ammonia from nitrogen and hydrogen?

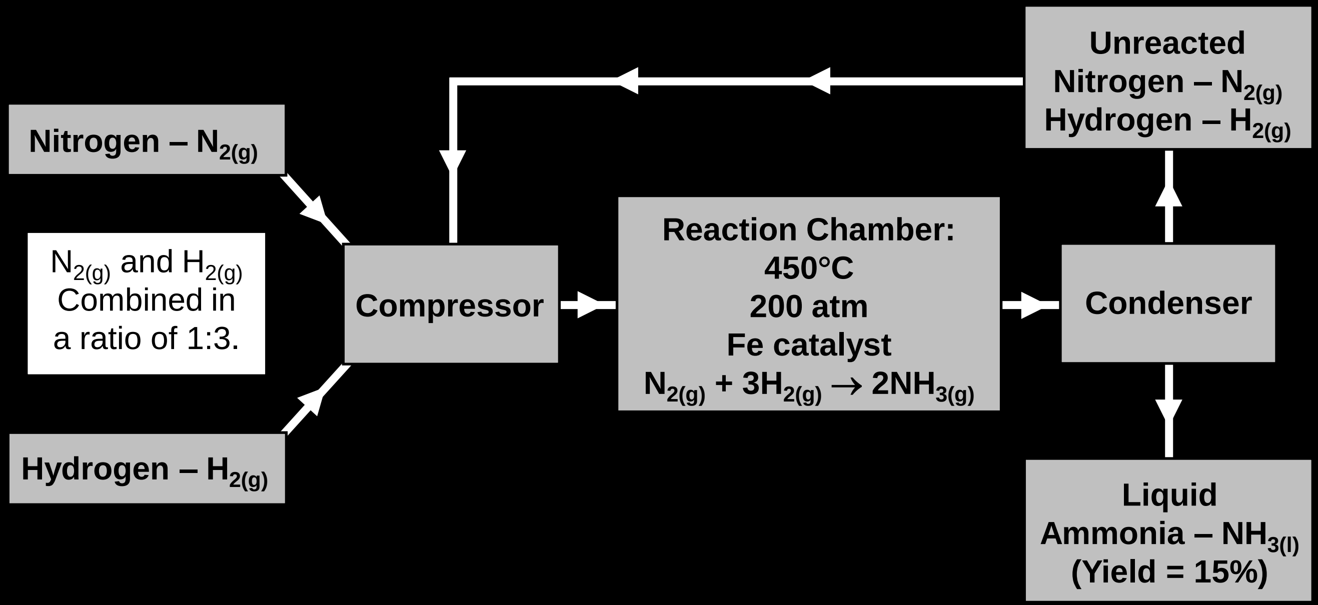


Summary of the industrial manufacture of ammonia from nitrogen and hydrogen:



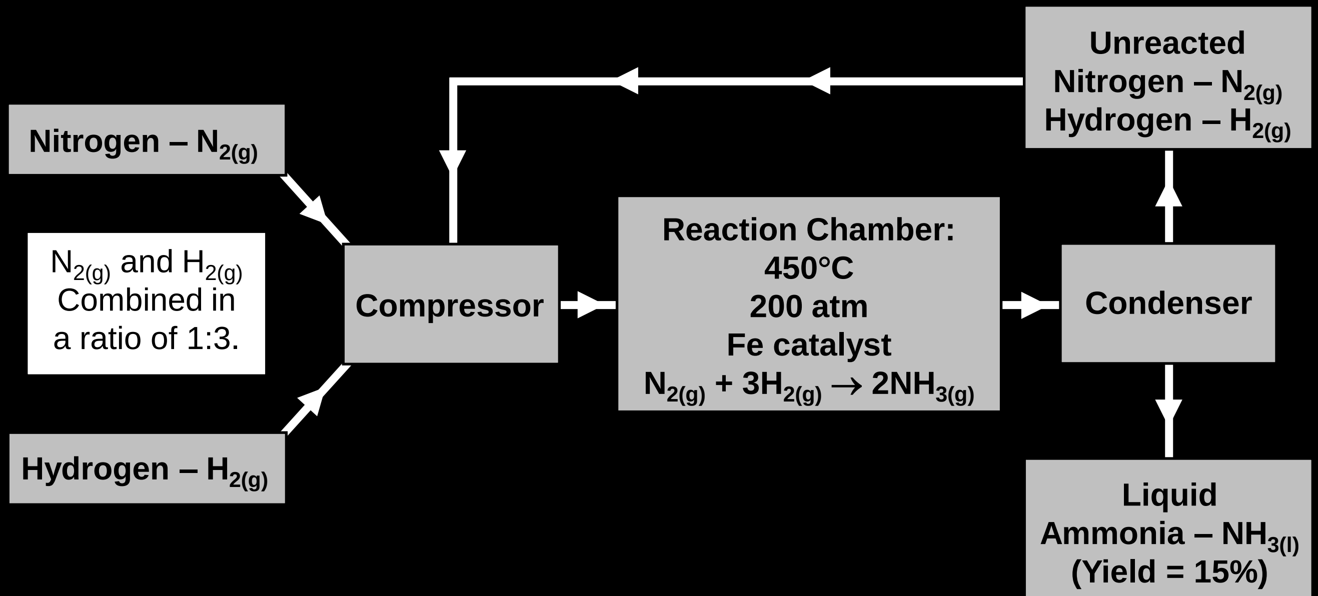
- The nitrogen and hydrogen are mixed together in a ratio of 1:3 as required by the balanced chemical equation.
- The reaction takes place at a temperature of 450°C.
- The reaction takes place at a pressure of 200 atmospheres.
- An iron catalyst is used to increase the rate of the reaction.

Summary of the industrial manufacture of ammonia from nitrogen and hydrogen:



- **Note**: The temperature of 450°C is a *compromise*. A lower temperature would increase the yield of ammonia, but the reaction would take a long time to reach equilibrium (slow). A high temperature would increase the rate at which the reaction reaches equilibrium (fast), but the yield of ammonia would be low.

Summary of the industrial manufacture of ammonia from nitrogen and hydrogen:

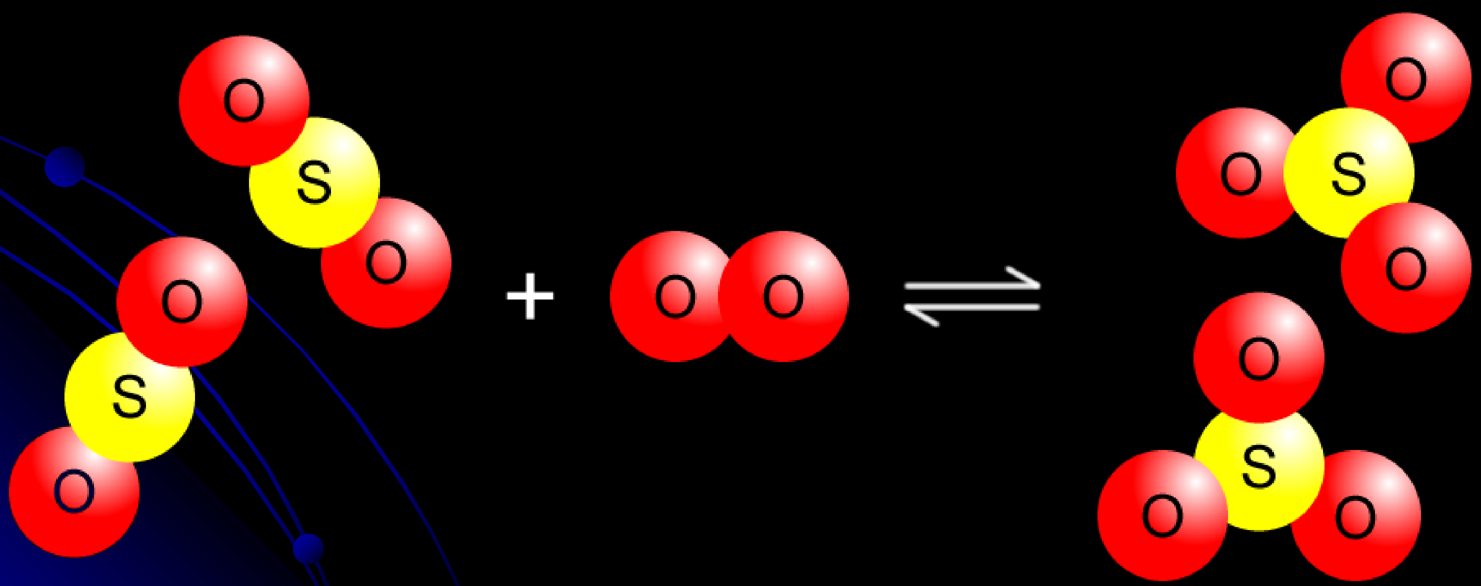


- **Note**: The iron catalyst increases the rate at which the reaction reaches equilibrium, but the catalyst has no effect on the actual equilibrium position itself.

The chemical reaction outlined below is one of the stages involved in the industrial manufacture of sulphuric acid. From the information provided, predict what the optimum conditions for this chemical reaction are.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$(\Delta H = -197\ \text{kJ mol}^{-1})$$



Presentation on the

Industrial Manufacture of Ammonia

by Dr. Chris Slatter

23rd September 2004