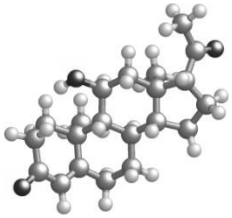

Chem!stry

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Class: ………………

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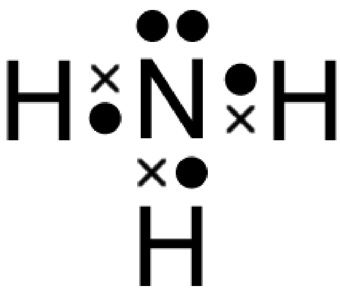
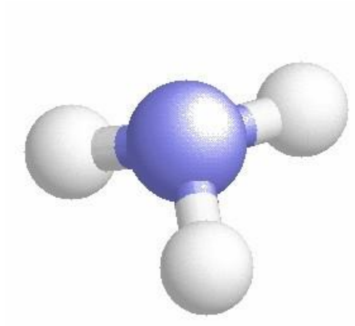
Conditions for the Industrial Manufacture of Ammonia

- Ammonia (formula: NH_3) is a simple covalent compound. The dot–and–cross diagram of an ammonia molecule is given below, along with a computer generated diagram showing the *pyramidal* shape of an ammonia molecule:





- Ammonia is used in the preparation of fertilisers (such as potassium nitrate, KNO_3) explosives (such as 2,4,6-trinitromethylbenzene, also known as trinitrotoluene or TNT) and plastics (such as nylon).

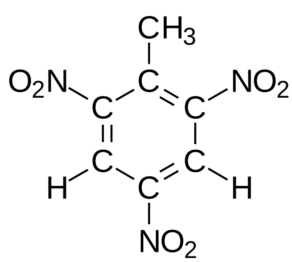


Figure 1. The explosive 2,4,6-trinitromethylbenzene.

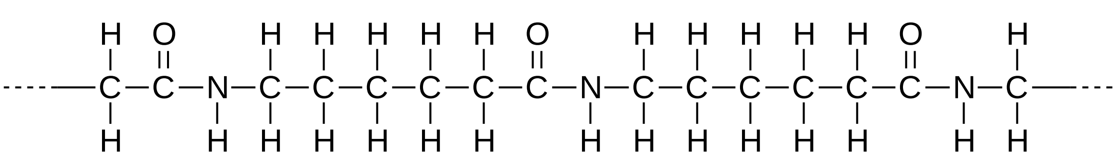


Figure 2. The synthetic polymer nylon.

- *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 (industrial) manufacture of ammonia.

Fritz Haber
Born: 1868
Died: 1934

Carl Bosch
Born: 1874
Died: 1940

- Postscript on Fritz Haber:

  The importance of ammonia in feeding the world's population was recognised by the award of the 1918 Nobel Prize in Chemistry to Haber. However, in some ways Haber was an extraordinary choice for the post First World War Nobel Prize. The use of ammonia in the manufacture of explosives had prolonged the fighting and Haber had also supervised the production of chlorine, the first chemical weapon to be used during World War One. Haber's wife, Clara (the first female Ph.D. student from the University of Dahlem) strongly disagreed with him about the use of chemical weapons. On the evening that Haber was promoted for directing gas attacks against the Allied troops, she committed suicide.

- The balanced chemical equation for the industrial manufacture of ammonia is:

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

Note that this reaction is *reversible*, as indicated by the $\rightleftharpoons$ symbol.

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

boiling point of O_2 = –183°C   boiling point of 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

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

- Hydrogen can also be produced industrially by cracking long-chain hydrocarbons at a temperature of 500°C in the presence of an aluminium oxide catalyst:

icosane → dodecene + octene + hydrogen

$$C_{20}H_{42}(g) \rightarrow C_{12}H_{24}(g) + C_8H_{16}(g) + H_2(g)$$

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

We will need to do some chemistry to 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*:

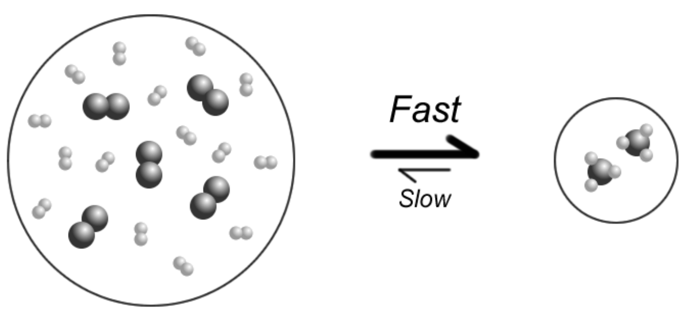


Figure 3.

- 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. The molecules of ammonia will collide and (assuming that they are effective collisions) react to form nitrogen and hydrogen. This means that the rate of the *forward reaction* will *decrease* while the rate of the *reverse reaction* will *increase*:

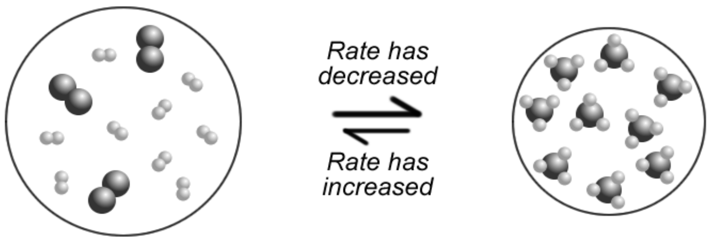


Figure 4.

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

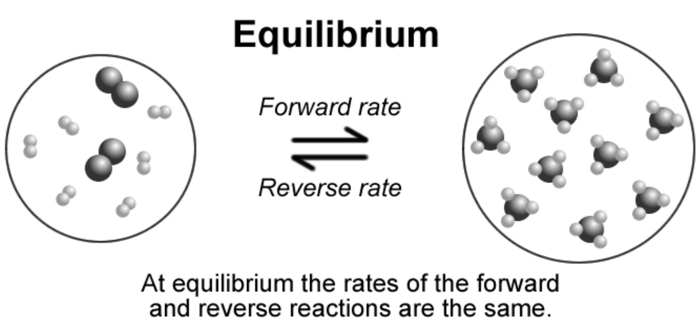


Figure 5.

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

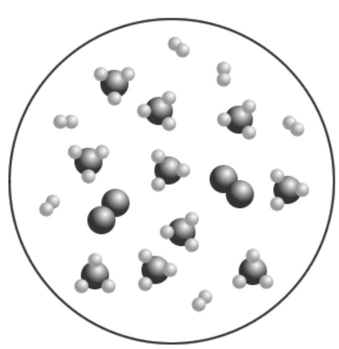


Figure 6.

- 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).

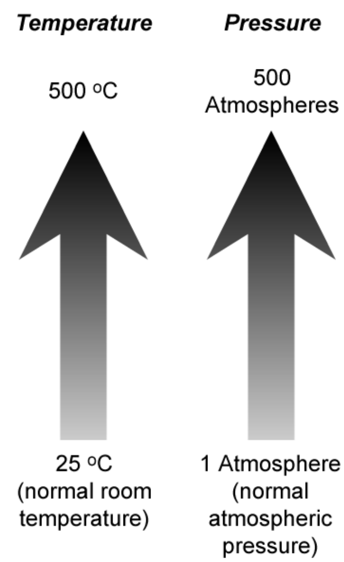


Figure 7.

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

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

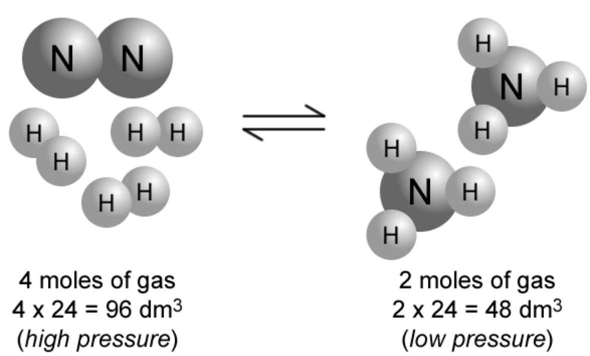


Figure 8.

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

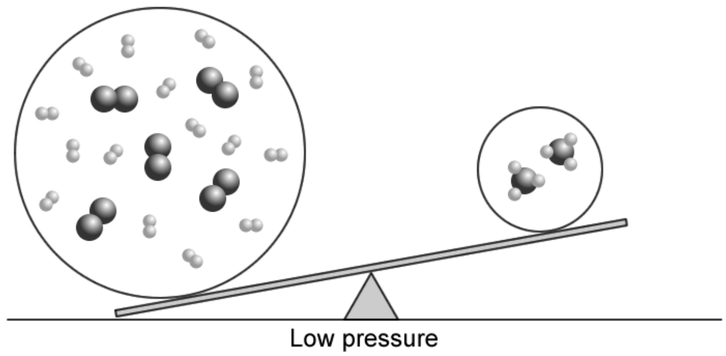


Figure 9.

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

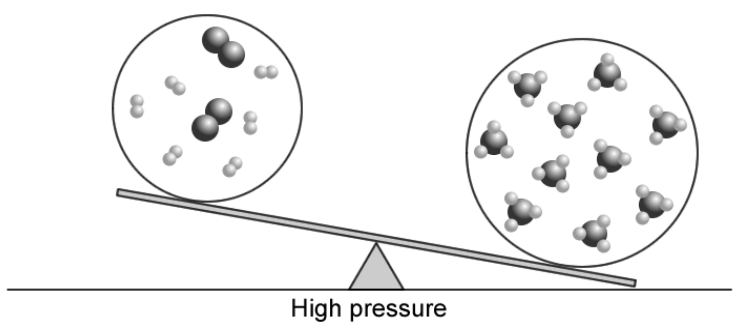


Figure 10.

- *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:

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

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

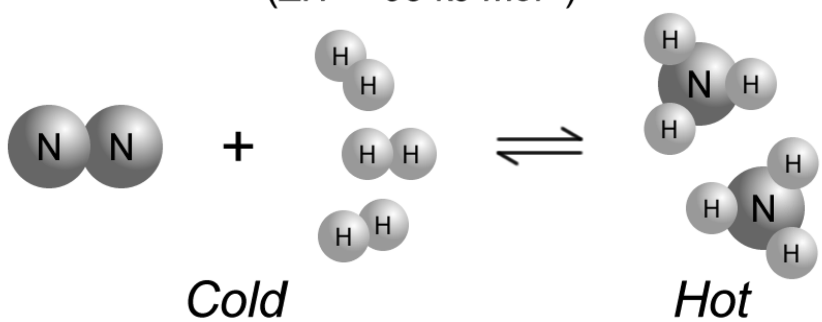


Figure 11.

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

- 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 / minimizes 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*.

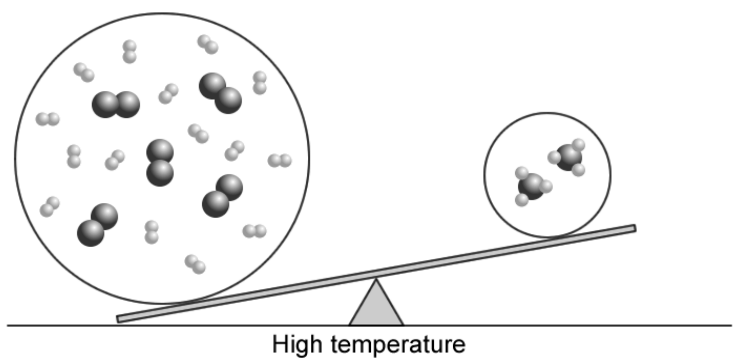


Figure 12.

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

- 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 / minimizes 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*.

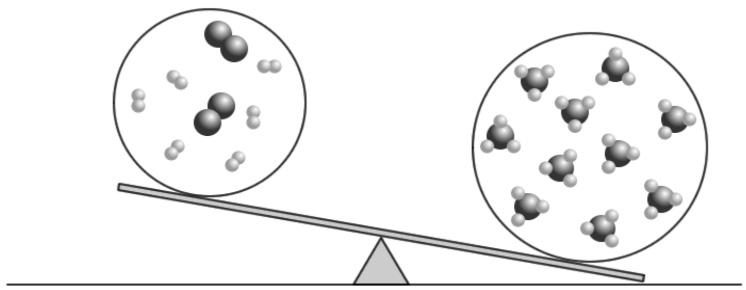


Figure 13.

- *Oh! But 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 kinetic energy of the reacting molecules will be reduced and so the frequency of the effective collisions between them will be reduced (the frequency of collisions will be reduced, and the proportion of those collisions that have an energy equal to or greater than the activation energy will also be reduced).
- *So, what do you think the optimum conditions for the industrial manufacture of ammonia from nitrogen and hydrogen should be?*

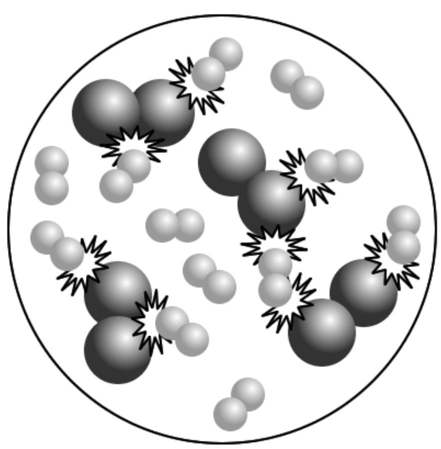


Figure 14.

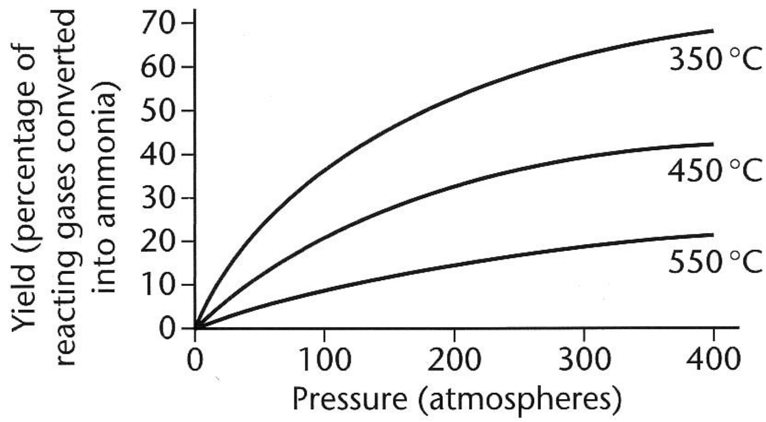


Figure 15.

- *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 temperature is a compromise. A low temperature will favour the forward reaction which will increase the yield of ammonia, but the reaction will be slow. A high temperature will result in a fast reaction, but it will favour the reverse reaction which will reduce the overall yield of ammonia.

→ The reaction takes place at a pressure of 200 atmospheres.

→ An iron catalyst is used to increase the rate at which the reaction reaches its equilibrium position.

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

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
$$(\Delta H = -197\ kJ\ mol^{-1})$$

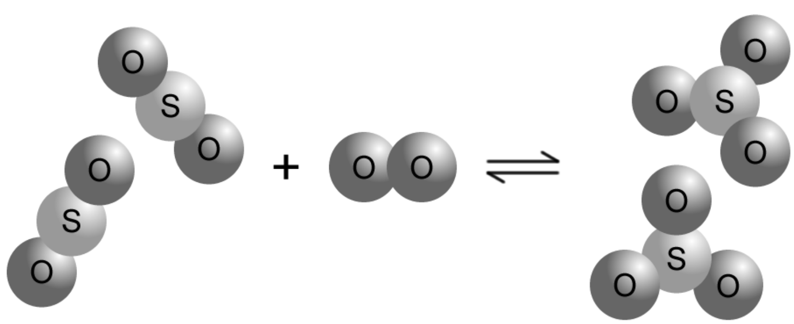


Figure 16.