Chemical equilibrium

CHEMICAL EQUILIBRIUM Reversible reactions and dynamic equilibrium Ammonia (NH_3) is an important industrial chemical that is used in the manufacture of fertilisers. It is manufactured by reacting hydrogen with nitrogen. The reaction is said to be reversible and the conversion of reactants to products is never complete. $N_2 + 3H_2$ $2NH_3$ A reversible reaction is a reaction which can take place in either direction When the concentrations of the reactants and product have become constant, a state of chemical equilibrium is said to have been reached. This is a dynamic equilibrium; even though no reactions appear to be occurring, however two reactions continue to take place. Chemical equilibrium is said to be dynamic because, at equilibrium, there are reactions continually occurring. The rate of the forward reaction equals the rate of the reverse reaction. Equilibrium Constants At equilibrium as much hydrogen iodide is being decomposed as is formed and so the concentrations of all three substances remains constant. Kc is the equilibrium constant in terms of molar concentration. This is known as the Equilibrium Law. The equilibrium constant shows the position of equilibrium. A high Kc value indicates that at equilibrium a high concentration of products exists in comparison to a low concentration of reactants. However a low Kc value indicates a low concentration of products compared to a high concentration of reactants. Kc < 1 … Then the backward reaction is favoured Kc > 1 … Then the forward reaction is favoured The value of the equilibrium concentration depends on temperature. If the forward reaction is exothermic the equilibrium decreases as the temperature rises (negative delta H). If it is endothermic it increases (positive delta H). V. N. B Points about Equilibrium Constants • The value of Kc only applies at equilibrium. • Kc is constant only if the temperature remains constant • The value of Kc is not affected by changes in concentration of reactants or products • The units of Kc depend on the relative numbers of moles on each side of the equation for the reaction. In a reaction in which there are equal numbers of moles on each side Kc has no units. Otherwise it is mol/l-1 Calculations of Equilibrium Concentrations If the direction of the equation is reversed, then the Kc value must be inverted. If the equation is halved, then the square root of the Kc value must be found. Le Chatelier's Principal Le Chatelier's Principal- When a system at equilibrium is subjected to a stress, the equilibrium shifts in such a way as to minimise the effects of the stress. $H_2 + I_2$ 2HI Changes in concentration of ones species- • If the concentration of H_2 is increased the equilibrium shifts in such a way as to minimise this change by using up the hydrogen. Forming more hydrogen iodide. The reaction therefore tends to go preferentially from left to right • If the concentration of I_2 is increased the same occurs, excess iodine is used up • If the concentration of HI is increased the change is minimised by the breaking down of HI, forming more hydrogen and iodine. The reaction continues to go preferentially from right to left until the Kc value is reached. • A decrease in the concentration of HI, hydrogen and iodine react forming more HI. • A decrease in the concentration of H_2, the equilibrium is shifted to the left (favouring the right to left reaction). Hydrogen iodide decomposes, forming more hydrogen and iodine. • A decrease in the concentration of I_2, the equilibrium is shifted to the left (favouring the right to left reaction). Hydrogen iodide decomposes, forming more iodine and hydrogen. Changes in temperature The forward reaction is exothermic. If the temperature is raised the extra heat is absorbed by allowing the endothermic reverse reaction, forming hydrogen and iodine to take preference. This changes the

Kc value. (In this case it decreases it) Lowering the temperature allows the exothermic reaction forming hydrogen iodide to be favoured. This releases heat, counteracting the stress. This changes the Kc value. (In this case it increases). Addition of a Catalyst If a catalyst is added before equilibrium, equilibrium is reached more quickly by lowering the activation energy. However if a catalyst is added at equilibrium, it has no effect on the equilibrium. Changes in Pressure Pressure changes at equilibrium only affect gases. If the pressure of an equilibrium mixture of gases is increased, if possible the number of molecules in the container will be reduced, thus reducing the pressure. If the pressure is decreased the stress will be minimised by increasing the number of molecules in the container, thus increasing the pressure. Changes in volume of the container Increasing the volume of the container at equilibrium causes a decrease in pressure. Decreasing the volume of the container at equilibrium causes an increase the pressure. Le Chatelier's Principal and Industrial Chemistry 1. Application of le Chatelier's Principle to the Haber process The synthesis of ammonia from its elements is an important process in the fertiliser industry. N2 + 3H2 2NH3 The process used to make Ammonia is known as the Haber process. The objective is to produce the maximum possible yield of ammonia, at the lowest cost and in the shortest possible time. Temperature Since the forward reaction is exothermic, it is favoured by a lowering of the reaction temperature at equilibrium. The extent to which this can be done is limited by the fact that the temperature must be high enough to allow the reaction to proceed at a reasonable rate. In practice temperatures of about 673K are used. This results in low yield, but un-reacted nitrogen and hydrogen can be collected for reuse. Pressure An increase in pressure at equilibrium favours the formation of ammonia. For this reason the Haber process uses high pressures of about 200 atmospheres. Higher pressures are more costly. Catalyst A catalyst is used both because it brings the system to equilibrium faster and because by lowering the activation energy, it brings fuel costs down by allowing the reaction to occur at a lower temperature. A low concentration of NH_3 and a high concentration of nitrogen and hydrogen are also favourable. 2. Application of Chatelier's Principle to the catalytic oxidation of sulphur dioxide to sulphur trioxide. $SO_2 + 1/2O_2$ SO_3 The process used to make sulphur trioxide is called the Contact process. The sulphur trioxide is the desired product as it reacts readily with water to form sulphuric acid. Temperature Since the forward reaction is exothermic, this reaction is favoured at equilibrium by a lowering of the reaction temperature. In practice a temperature of about 713K is used as it is the lowest temperature that can be used without reducing the rate to too low a level. Pressure The forward reaction is favoured by high pressures. In practice a sufficiently high yield is obtained under atmospheric pressure or slightly higher. Much higher pressures are not economically justifiable. Concentration The forward reaction is favoured if the sulphur trioxide is removed as it is formed. Catalyst A catalyst is added to bring the reactants to equilibrium faster by lowering the activation energy. In industrial processes such as the Haber and Contact processes a state of equilibrium may never actually be reached. While the reaction mixture is in contact with the catalyst, the concentration of the product increases to a constant level. The rate of increase in the yield slows down as equilibrium approaches. It is not economically viable to wait for a maximum yield.