Le Châtelier's Principle

Question 1. Suppose the reaction $R \rightleftharpoons P$, for which $K_{eq} = \frac{[P]}{[R]}$ is at equilibrium and that we add some additional R, what happens to the concentration of P? Why?

Answer. If we add R, then the system no longer is at equilibrium. As increasing R gives $Q < K$, we have too many reactants and not enough products. The reaction, therefore, shift to the right and converts some of the additional R to P until $Q = K$ and equilibrium is reestablished.

Consider this set of equilibrium reactions

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$
$$\mathrm{Ag}^+(aq) + 2\mathrm{NH}_3(aq) \rightleftharpoons \mathrm{Ag(NH_3)}_2^+(aq)$$
$$\mathrm{NH}_3(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH}^-(aq) + \mathrm{NH}_4^+(aq)$$

Question 2. If you add 0.1 M NaCl to a solution of 0.01 M $AgNO_3$ in a test-tube, what happens? Why?

Answer. A precipitate of AgCl forms to establish the equilibrium required by the reaction $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$.

Question 3. Now, if you add 3 M NH_3 to the test-tube from Question 2, what happens? Why?

Answer. Adding NH_3 pushes the reaction $\mathrm{Ag}^+(aq) + 2\mathrm{NH}_3(aq) \rightleftharpoons \mathrm{Ag(NH_3)}_2^+(aq)$ to the right. This, in turn, decreases the concentration of Ag^+, which forces the first reaction to shift to the right to make more Ag^+. If we add enough NH_3, the precipitate of AgCl eventually will dissolve.

Question 4. If you add 6 M HNO_3 to the test-tube from Question 3, what happens? Why?

Answer. Adding HNO_3, a strong acid, will decrease the concentration of OH^- in the reaction $\mathrm{NH}_3(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH}^-(aq) + \mathrm{NH}_4^+(aq)$, causing it to shift to the right. This decreases the concentraiton of NH_3, which causes the reaction $\mathrm{Ag}^+(aq) + 2\mathrm{NH}_3(aq) \rightleftharpoons \mathrm{Ag(NH_3)}_2^+(aq)$ to shift to the left. This frees up some Ag^+, which then reprecipitates as AgCl.

Question 5. Suppose you have the aqueous reaction $R_1(aq) + R_2(aq) \rightleftharpoons P(aq)$ with an equilibrium constant of $\frac{[P]}{[R_1][R_2]}$. What happens to the concentrations of R_1 and R_2 if the volume of the mixture decreases by evaporation? Is the system still at equilibrium? If not, what happens? Why?

Answer. If we allow the volume to decrease by evaporation, then the concentrations of R_1, R_2, and P all increase (same moles in a smaller volume). Because the denominator has two species and the numerator has just one species, the resulting Q is now smaller than K, which shifts the reaction to the right until $Q = K$. Note that the effect is to shift the reaction in the direction that contains fewer particles. If we add water, decreasing the concentrations, then the reaction will shift in the direction that has more particles.

Consider this reaction

$$Co^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq)$$

Question 6. We can use color to study this reaction because Co^{2+} is pink and $CoCl_4^{2-}$ is blue. If we begin with equilibrium that favors the blue $CoCl_4^{2-}$ and add H_2O, why does the solution turn pink?

Answer. From Question 5 we know that diluting a solution makes $Q > K$, forcing the reaction to shift to the left in the direction that has more particles.

Question 7. If we start with the reaction from Question 6 at an equilibrium position where the concentrations of Co^{2+} and of $CoCl_4^{2-}$ are approximately equal, then the solution appears purple. Why?

Answer. If the concentrations of Co^{2+} and of $CoCl_4^{2-}$ are equal, then the solution's color is the mixture of pink from Co^{2+} and blue from $CoCl_4^{2-}$; thus, it is purple.

Question 8. If we place half of the solution from Question 7 in an ice bath and half on a hot plate, the portion in the ice bath turns pink and the portion on the hotplate turns blue. What do the colors tell us about how this reaction's equilibrium constant, K, is affected by temperature, T?

Answer. Based on the colors, decreasing the temperature shifts the reaction toward the reactants, increasing the concentration of Co^{2+} and turning the solution pink. Increasing the temperature has the opposite effect, increasing the concentration of $CoCl_4^{2-}$ and turning the solution blue. We can explain this as a need to release heat when we cool the mixture and to absorb heat when we warm the mixture. This suggest that the reaction is endothermic, absorbing heat from the environment when Co^{2+} forms $CoCl_4^{2-}$ and relasing heat when $CoCl_4^{2-}$ forms Co^{2+}.