Equilibrium

You should already know that many reactions are reversible and do not go to completion, but instead end up as an equilibrium mixture of reactant and products. A reversible reaction that can reach equilibrium is denoted by the symbol $\rightleftharpoons$

Many organic reactions are reversible and will reach equilibrium in time. Take the example ethanoic acid and ethanol where the ester ethyl ethanoate is produced. If the ethanol and ethanoic acid are mixed in a flask (stoppered to prevent evaporation and left, the mixture is eventually obtained in which four substances are present – though a strong acid catalyst is required. The equation now being.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The mixture can then be analysed by titrating ethanoic acid with standard alkali. This gives the number of moles of ethanoic acid. From this we can work out the number of moles of the other components, and from this their concentrations if the total volume of the mixture is known.

Chemical Equilibrium

If several experiments are done with different quantities of starting materials, it is always found to be the ratio:

$$\frac{[CH_3CO_2C_2H_5(aq)]_{eqm}\,[H_2O(aq)]_{eqm}}{[CH_3CO_2H(aq)]_{eqm}\,[C_2H_5OH(aq)]_{eqm}}$$

The ratio is always found to be constant if the temperature is constant. This constant is called the equilibrium constant and has the symbol K_c. The subscript $_{eqm}$ means that the concentrations have been measured when the equilibrium has been reached. The subscript $_c$ stands for concentration – the equilibrium constant is a ratio of concentrations.

The equilibrium law and the equilibrium constant, K_c

The equilibrium law is generally expressed as follows:

$$aA + bB + cC \rightleftharpoons xX + yY + zZ$$

The expression..

$$\frac{[X]_{eqm}^{x}\,[Y]_{eqm}^{y}\,[Z]_{eqm}^{z}}{[A]_{eqm}^{a}\,[B]_{eqm}^{b}\,[C]_{eqm}^{c}}$$

..has a constant value, K_c, provided the temperature is constant. K_c is called the equilibrium constant and is different for different reactions. It changes with temperature. The units of K_c vary, and you must work them out for each reaction by cancelling out the units of each term.

The equilibrium law and the equilibrium constant, K_c

$A + B \rightleftharpoons C$ $\qquad K_c = \dfrac{[C]^1}{[A]^1\,[B]^1}$

Units are: $= \dfrac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$

$= \dfrac{1}{\text{mol dm}^{-3}}$

$= \text{mol}^{-1}\ \text{dm}^{3}$

K_c is found by the experiment for any particular reaction at a given temperature.

The equilibrium law and the equilibrium constant, K_c

0.10 mol of ethanol is mixed with 0.10mol of a solution of ethanoic acid and allowed to reach equilibrium. The total volume of the system is 20.0cm or 0.020dm^3. We find by titration that 0.033 mol ethanoic acid is present once equilibrium is reached.

From this we can work out the number of moles of the other components present at equilibrium. At the start

C_2H_5OH (l) +	CH_3CO_2H (l)	$CH_3CO_2C_2H_5$ (l) +	H_2O (l)
0.033mol	0.033mol	0mol	0mol

We know that their are 0.033 mol of CH_3CO_2H at equilibrium, this means that there also must be 0.033 mol of C_2H_5OH at equilibrium (the equation says 1:1) and we know we started with the same moles of each. Therefore 0.1 - 0.033 = 0.067 have been used up. The equation tells us that when 1 mole of CH_3CO_2H is used up, 1 mole of each of $CH_3CO_2C_2H_5$ and H_2O are produced, so there must be 0.067 moles of each of these.

The equilibrium law and the equilibrium constant, K_c

$$\underset{0.033\text{mol}}{C_2H_5OH\,(l)} + \underset{0.033\text{mol}}{CH_3CO_2H\,(l)} \rightleftharpoons \underset{0.067\text{mol}}{CH_3CO_2C_2H_5\,(l)} + \underset{0.067\text{mol}}{H_2O\,(l)}$$

We need the concentrations of the components at equilibrium. As the volume of the system is 0.020dm^3 these are:

$$\underset{0.033/0.020}{C_2H_5OH\,(l)} + \underset{0.033/0.020}{CH_3CO_2H\,(l)} \rightleftharpoons \underset{0.067/0.020}{CH_3CO_2C_2H_5\,(l)} + \underset{0.067/0.020}{H_2O\,(l)}$$

We enter the concentrations into the equilibrium equation:

$$K_c = \frac{[CH_3CO_2C_2H_5(aq)]_{eqm}\,[H_2O(aq)]_{eqm}}{[CH3CO2H(aq)]_{eqm}\,[C2H5OH(aq)]_{eqm}}$$

$$K_c = \frac{[0.067/0.020]_{eqm}[0.067/0.020]_{eqm}}{[0.033/0.020]_{eqm}[0.033/0.020]_{eqm}} = 4.1$$

The units all cancel out, and the volumes (0.020dm^3) cancel out, so in this case we didn't need to know the volume of the system, so $K_c = 4.1$. It has no unit.

Equilibrium Constants and Le Chatelier’s Principle

Changing concentrations: The facts

Equilibrium constants aren't changed if you change the concentrations of things present in the equilibrium. The only thing that changes an equilibrium constant is a change of temperature.

The position of equilibrium is changed if you change the concentration of something present in the mixture. According to Le Chatelier's Principle, the position of equilibrium moves in such a way as to tend to undo the change that you have made.

Suppose you have an equilibrium established between four substances A, B, C and D.

$$A + 2B \rightleftharpoons C + D$$

According to Le Chatelier's Principle, if you decrease the concentration of C, for example, the position of equilibrium will move to the right to increase the concentration again.

Equilibrium Constants and Le Chatelier's Principle

The equilibrium constant, K_c for this reaction looks like this:

$$K_c = \frac{[C][D]}{[A][B]^2}$$

If you have moved the position of the equilibrium to the right (and so increased the amount of C and D), why hasn't the equilibrium constant increased?

If you decrease the concentration of C, the top of the K_c expression gets smaller. That would change the value of K_c. In order for that not to happen, the concentrations of C and D will have to increase again, and those of A and B must decrease. That happens until a new balance is reached when the value of the equilibrium constant expression reverts to what it was before.

The position of equilibrium moves - not because Le Chatelier says it must - but because of the need to keep a constant value for the equilibrium constant.

Equilibrium Constants and Le Chatelier's Principle

If you decrease the concentration of C:

For K_c to stay constant when you decrease [C] . . .

. . . [C] must be increased again, . . .

. . . more D is formed along with the new C, . . .

$$K_c = \frac{[C][D]}{[A][B]^2}$$

. . . and at the same time some [A] and [B] must get used up.

Equilibrium Constants and Changing Temperature

This is typical of what happens with any equilibrium where the forward reaction is exothermic. Increasing the temperature decreases the value of the equilibrium constant.

Where the forward reaction is endothermic, increasing the temperature increases the value of the equilibrium constant.

The position of equilibrium also changes if you change the temperature. According to Le Chatelier's Principle, the position of equilibrium moves in such a way as to tend to undo the change that you have made.

If you increase the temperature, the position of equilibrium will move in such a way as to reduce the temperature again. It will do that by favouring the reaction which absorbs heat.

In the equilibrium we've just looked at, that will be the back reaction because the forward reaction is exothermic.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \Delta H = -10.4 \text{ kJ mol}^{-1}$$

So, according to Le Chatelier's Principle the position of equilibrium will move to the left. Less hydrogen iodide will be formed, and the equilibrium mixture will contain more unreacted hydrogen and iodine.

Changing the pressure of the system will NOT change the equilibrium constant. We actually use a special equilibrium constant for systems involving gases called K_p (you don't need to know about this for our spec!).

Adding a catalyst does NOT change the equilibrium constant. This is because it increases the rate of both the forward and backwards reaction so K_c will therefore remain constant.