



Equilibrium calculations and phase equilibrium

UNITS OF THE EQUILIBRIUM CONSTANT

The units of K_c depend on the powers of the concentrations in the equilibrium expression.
Haber process: units of K_c : $\text{dm}^6 \text{mol}^{-2}$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 \times [\text{N}_2]} = \frac{\text{concentration}^2}{\text{concentration}^4} = \text{concentration}^{-2} = \text{dm}^6 \text{mol}^{-2}$$

If they are the same on the top and bottom then K_c has no units.

Esterification: K_c : no units

$$K_c = \frac{[\text{acid}] \times [\text{alcohol}]}{[\text{ester}] \times [\text{water}]} = \frac{\text{concentration}^2}{\text{concentration}^2}$$

EQUILIBRIUM CALCULATIONS

The equilibrium law can be used either to find the value for the equilibrium constant, or to find the value of an unknown equilibrium concentration.

- (a) 23.0 g (0.50 mol) of ethanol was reacted with 60.0 g (1.0 mol) of ethanoic acid and the reaction allowed to reach equilibrium at 373 K. 37.0 g (0.42 mol) of ethyl ethanoate was found to be present in the equilibrium mixture. Calculate K_c to the nearest integer at 373 K.

	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	+	$\text{CH}_3\text{COOH}(\text{l})$	\rightleftharpoons	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	+	$\text{H}_2\text{O}(\text{l})$
Initial amount / mol	0.50		1.00		—		—
Equilibrium amount / mol	(0.50 – 0.42)		(1.00 – 0.42)		0.42		0.42
Equilibrium concentration / mol dm^{-3}	$\frac{(0.50 - 0.42)}{V}$		$\frac{(1.00 - 0.42)}{V}$		$\frac{0.42}{V}$		$\frac{0.42}{V}$
(where V = total volume)							

$$K_c = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{(0.42/V) \times (0.42/V)}{(0.08/V) \times (0.58/V)} = 4 \text{ (to the nearest integer)}$$

- (b) What mass of ester will be formed at equilibrium if 2.0 moles of ethanoic acid and 1.0 moles of ethanol are reacted under the same conditions?

Let x moles of ester be formed and let the total volume be $V \text{ dm}^3$.

$$K_c = 4 = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{x^2/V^2}{(1.0 - x)/V \times (2.0 - x)/V} = \frac{x^2}{(x^2 - 3x + 2)}$$

$$\Rightarrow 3x^2 - 12x + 8 = 0$$

$$\text{solve by substituting into the quadratic expression} \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \Rightarrow x = \frac{12 \pm \sqrt{144 - 96}}{6}$$

$x = 0.845$ or ~~3.15~~ (it cannot be 3.15 as only 1.0 mol of ethanol was taken)

Mass of ester = $0.845 \times 88.08 = 74.4 \text{ g}$ (Note: The IB does not require the use of the quadratic expression)

PHASE EQUILIBRIUM

Dynamic equilibrium between a liquid and its vapour occurs when the rate of vaporization is equal to the rate of condensation. The vapour pressure of a liquid is the pressure exerted by the particles in the vapour phase. It is independent of the surface area of the liquid or of the size of the container, although in a bigger container it may take longer for the equilibrium to become established. The vapour pressure of any liquid does depend both on the strength of the molecular forces holding the liquid particles together and on the temperature.

The stronger the intermolecular forces the lower the vapour pressure at a particular temperature. Vaporization is an endothermic process, as energy is absorbed to break these intermolecular forces. The enthalpy change required to overcome these forces is known as the enthalpy of vaporization. Water is a covalent substance with a low molar mass, but it has strong hydrogen bonding between its molecules. This explains why water has a relatively low vapour pressure and a relatively high enthalpy of vaporization.

As the temperature increases so does the number of particles with sufficient energy to overcome the attractive forces, and the vapour pressure also increases. A liquid boils when its vapour pressure is equal to the external pressure, as this allows bubbles of vapour to form in the body of the liquid. The boiling point of a liquid can be lowered simply by lowering the external pressure. This principle is useful to purify substances which decompose at or near their normal boiling point, by distilling them under reduced pressure. In mountainous regions where the external pressure is low the boiling point of water can be increased by using a pressure cooker.

