Calculating Equilibrium Constants - K_c and K_p

Introduction

From the start of a reversible chemical reaction, the rate of the forward reaction decreases with time and the rate of the backward reaction increases. Eventually the reaction reaches a steady state referred to as "equilibrium" when the rate of the forward reaction is equal to the rate of the backward reaction. To reach this state the reaction must be at a fixed temperature in a closed reaction vessel. When it is reached, experiments show that there are mathematical relationships between the molar concentrations of the components in the equilibrium mixture or, in the case of a gaseous reaction, between the partial pressures of the components in the equilibrium mixture.

Note 1: Molar concentration of component A in an equilibrium mixture

$$= [A] \ (/\text{mol dm}^{-3}) = \frac{\text{Moles of A } (n_a) \text{ in equilibrium mixture}}{\text{Total volume of equilibrium mixture in dm}^3}$$

Note 2: Partial pressure of gaseous component A in an equilibrium mixture

$= P_A$ (/ an appropriate pressure unit, e.g. kPa)

$=$ Mole fraction of component A $(X_A) \times$ Total pressure (P_{tot}) of eqm. mixture

$$= \frac{\text{Moles of A } (n_a)}{\text{Total moles in eq}^m \text{ mixture } (n_{tot})} \times P_{tot}$$

Suppose substance A reacts with B to produce C and D in a reversible reaction according to the following equation:

$aA + bB \rightleftharpoons cC + dD$
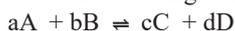
(a, b, c and d are the coefficients in the *balanced* equation.)

Experiment shows that, for any particular reaction at a fixed temperature, whenever the equilibrium molar concentrations are substituted into formula 1, or the equilibrium partial pressures into formula 2, a constant value is obtained which is *independent of the initial amounts of A and B used to establish the equilibrium*. These constants are referred to as *equilibrium constants* in terms of concentrations (K_c) and in terms of partial pressures (K_p) respectively.

Formula 1 $\dfrac{[C]^c \ \text{x} \ [D]^d}{[A]^a \ \times \ [B]^b} = Kc$

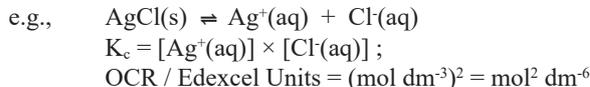Formula 2 $\dfrac{P_C^c \ \times \ P_D^d}{P_A^a \ \times \ P_B^b} = K_p$

Note 3: Notice that the coefficients in the balanced equation become the *powers* in the K expressions. This means the K_c and K_p expressions, and their values, are inextricably linked to the equation used to describe the equilibrium. If the equation is written in reverse, then the expressions and the value will be the reciprocal of the original. Similarly, if the whole equilibrium equation is halved, then the expressions and the value will be the square root of the original.

Note 4: By convention, these equilibrium constants are essentially *product to reactant ratios* so that a larger value directly indicates a larger proportion of products at equilibrium.

Note 5: Such physical quantities might be expected to have appropriate units. They do not! Strictly speaking, each concentration or partial pressure term in formulas 1 and 2 is divided by a standard unit concentration or unit partial pressure. This makes each expression dimensionless – no units! However, some examination specifications (OCR and Edexcel) simply apply "cancellation of component units" to derive an overall unit.

This gives (mol dm^{-3})$^{c+d-a-b}$ for K_c and (kPa)$^{c+d-a-b}$ for K_p.

The equilibria considered so far are all *homogeneous* since all components are in the same phase (gas, liquid or aqueous). Some equilibria contain different phases and are referred to as *heterogeneous*. In such cases, when writing K_c or K_p expressions, any *solid* is omitted from the expression because its molar concentration or partial pressure can be considered constant.

e.g., $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$K_c = [Ag^+(aq)] \times [Cl^-(aq)]$;
OCR / Edexcel Units $= (\text{mol dm}^{-3})^2 = \text{mol}^2 \text{ dm}^{-6}$

K_p not applicable – not gaseous.

e.g., $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$K_c = \dfrac{[H_2]^4}{[H_2O]^4}$ and $K_p = \dfrac{P_{H_2}^4}{P_{H_2O}^4}$

OCR / Edexcel Units = none for either K_c or K_p – units cancel.

Calculating K_c / K_p given the full equilibrium composition

If the numbers of moles of every reactant and product are known at equilibrium, these numbers can be used directly to determine either the equilibrium molar concentrations [A] or the equilibrium partial pressures (P_A) of each component as described in notes 1 and 2. E.g., an equilibrium mixture of A, B and C created by reacting A and B together is found to contain 0.23 moles of A, 0.42 moles of B and 0.88 moles of C in a 20.0 dm^3 vessel under a total pressure of 400 kPa at 600 K. If the equation for the reaction is

$3A(g) + B(g) \rightleftharpoons 2C(g)$

(a) Calculate the values of K_c and K_p and give units where appropriate.

(b) Calculate the number of moles of C that can exist in equilibrium with 0.11 moles of A and 0.45 moles of B in a 50 dm^3 vessel at 600 K.

(a) Equation	3A(g)	+	B(g)	⇌	2C(g)
Moles at eq^m (n)	0.23		0.42		0.88
For K_c Calculation					
Total volume of equilibrium mixture = 20.0 dm^3					
Molar conc^n at eq^m (/mol dm^{-3})	0.23/20.0 = **0.0115**		0.42/20.0 = **0.0210**		0.88/20.0 = **0.0440**
For K_p Calculation					
Total number of moles at eq^m (n_{tot}) = 0.23 + 0.42 + 0.88 = 1.53 Total pressure at eq^m (P_{tot}) = 400 kPa					
Mole fraction at equilibrium	0.23/1.53 = 0.150		0.42/1.53 = 0.275		0.88/1.53 = 0.575
→ Partial pressure at eq^m (/kPa)	0.150 × 400 = **60.0**		0.275 × 400 = **110.0**		0.575 × 400 = **230.0**

<u>Note 6</u>: Check your calculations so far by checking that the calculated mole fractions add up to 1.00 and the partial pressures add up to the total pressure.
0.150 + 0.275 + 0.575 = 1.00 and 60 + 110 + 230 = 400   Check!
Applying the general equations from formulas 1 and 2 to this equilibrium gives

$$K_c = \frac{[C]^2}{[A]^3 \times [B]} \qquad\qquad K_p = \frac{P_C^2}{P_A^3 \times P_B}$$

$$= \frac{0.044^2}{0.0115^3 \times 0.0210} \qquad\qquad = \frac{230.0^2}{60.0^3 \times 110.0}$$

$$= \mathbf{6.06 \times 10^4} \ (/mol^{-2}\ dm^6) \qquad\qquad = \mathbf{2.23 \times 10^{-3}} \ (/kPa^{-2})$$

(b) Since the reaction is the same and the temperature is the same, the values of K from part (a) are still applicable.
 This allows the number of moles of C (X) to be calculated.

Equation	3A(g)	+	B(g)	⇌	2C(g)
Moles at eq^m (n)	0.11		0.45		×
Molar conc^n at eq^m (/mol dm^{-3})	0.11/50.0 = 0.0022		0.45/50.0 = 0.0090		×/50.0
$K_c = \dfrac{[C]^2}{[A]^3 \times [B]} = 6.06 \times 10^4$				$= \dfrac{\left(\dfrac{X}{50}\right)^2}{0.0022^3 \times 0.0090}$	
→ $X^2 = (6.06 \times 10^4 \times 0.0022^3 \times 0.0090 \times 50^2) = 0.01452$					
→ X = Moles of C $= \sqrt{0.01452} = 0.12$ moles (2 d.p.)					

Calculating K_c / K_p given starting conditions and one equilibrium condition

In most cases, an equilibrium reaction is investigated by mixing known numbers of moles of the reactants in a closed system at a fixed temperature and allowing it time to reach equilibrium. The amount of just one of the components (reactant or product) in the mixture is then measured by taking advantage of a distinctive property such as colour, acidity, conductivity etc. The entire equilibrium composition can be deduced using these data and the reacting ratios given by the balanced equation.

Note 7: The decreases in the numbers of moles of reactants and the increases in the numbers of moles of products must occur in the same ratios as the reaction equation. E.g., 0.856 moles of nitrogen (N_2) is mixed with 1.934 moles of hydrogen (H_2) and heated at 900 K in a sealed 5 dm^3 container. When equilibrium is reached, 0.116 moles of ammonia (NH_3) is formed and the total pressure is 4000 kPa. Calculate the mole composition of the equilibrium mixture and hence calculate K_c and K_p.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$ mol
Initial	**0.856**		**1.934**		0.00
Change	= **1**(-0.0580) = -0.0580		= **3**(-0.0580) = 0.174		0.116 – 0.00 mol = +0.116
Equilibrium	= 0.856 – 0.0580 = <u>0.798</u>		= 1.934 – 0.174 = <u>1.760</u>		= **2**(+0.0580) mol = **0.116**

The calculation now proceeds as before.

Equation	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Moles at eq^m (n)	0.798		1.760		0.116
For K_c Calculation					
Total volume of equilibrium mixture = 5 dm^3					
Molar conc^n at eq^m (/mol dm^{-3})	0.798/5 = 0.1596		1.76/5 = 0.3520		0.116/5 = 0.02320
For K_p Calculation					
Total number of moles at eq^m (n_{tot}) = 0.798 + 1.760 + 0.116 = 2.674 Total pressure at eq^m (P_{tot}) = 4000 kPa					
Mole fraction at equilibrium	0.798/2.674 = 0.2984		1.760/2.674 = 0.6582		0.116/2.674 = 0.04338
$\rightarrow$ Partial pressure at eq^m (/kPa)	4000 x 0.2984 = 1193.7		4000 × 0.658 = 2632.8		4000 × 0.04338 = 173.5

$$K_c = \frac{[NH_3]^2}{[H_2]^3 \times [N_2]} \qquad = \qquad K_p = \frac{P_{NH_3}^2}{P_{H_2}^3 \times P_{N_2}}$$

$$= \frac{[0.02320]^2}{[0.3520]^3 \times [0.1596]} \qquad = \qquad \frac{(173.5)^2}{(2632.8)^3 \times (1193.7)}$$

$= 7.73 \times 10^{-2}$ (3 s.f.) $=$ 1.38×10^{-9} (3 s.f.)
   (Units mol^{-2} dm^6 if applicable)   (Units kPa^{-2} if applicable)

Calculating final composition given starting composition and K_c/K_p

One final type of question involves determining the final composition given the equilibrium constant and a set of starting conditions. E.g., 10 moles each of $H_2(g)$ and $I_2(g)$ are mixed in a 10 dm^3 sealed vessel and allowed to reach equilibrium. The value of K_c for this reaction is 54. Determine the composition of the mixture at equilibrium giving your answers as the concentrations of each substance.
As we do not know how much is reacted or produced during the reaction, we need to solve this question algebraically.

Equation $\quad$ $H_2(g)$ + $I_2(g)$ $\rightleftharpoons$ 2HI(g)
Initial/mol $\quad$ 10 $\qquad$ 10 $\qquad$ 0
React/made $\quad$ x $\qquad$ x $\qquad$ 2x
Equilᵐ /mol $\;$ 10 –x $\qquad$ 10 – x $\quad$ 2x

As the number of moles of substance of both sides of the equation is equal, the volumes will cancel out within the concentrations. It is easiest to ignore the volume for now as this will not affect the subsequent steps.

$$K_c = \frac{[HI(g)]^2}{[H_2(g)] \times [I_2(g)]}$$

$$K_c = 54 = \frac{(2x)^2}{(10-x) \times (10-x)}$$

As both numerator and denominator are squares, the expression can be **square rooted** to avoid having to solve a quadratic equation. One solution is lost in the process but this is typically a nonsense value.

$$\sqrt{54} = \frac{2x}{10-x}$$

This equation is then rearranged to make x the subject:

$10\sqrt{54}$ - $x\sqrt{54}$ = 2x
$10\sqrt{54}$ = 73.48 = $(2 + \sqrt{54})x$
$\dfrac{73.5}{2 + \sqrt{54}}$ = x = 7.86

Once the value of x has been found, this can be used to find the composition of concentrations at equilibrium:

Equation $\qquad$ $H_2(g)$ + $I_2(g)$ $\rightleftharpoons$ 2HI(g)
Equilᵐ /mol $\qquad$ 10 – x $\quad$ 10 – x $\quad$ 2x
Equilᵐ /mol $\qquad$ 2.14 $\qquad$ 2.14 $\qquad$ 15.72
Equilᵐ /mol dm⁻³ $\;$ 0.214 $\qquad$ 0.214 $\qquad$ 1.572

Questions
1. Write K_c and K_p expressions where appropriate for each of the following reactions:
   (a) $H_2(g)$ + $I_2(g)$ $\rightleftharpoons$ 2HI(g)?
   (b) $2SO_2(g)$ + $O_2(g)$ $\rightleftharpoons$ $2SO_3(g)$?
   (c) $N_2(g)$ + $3H_2(g)$ $\rightleftharpoons$ $2NH_3(g)$?
   (d) HCOOH(l) + $CH_3OH(l)$ $\rightleftharpoons$ $HCOOCH_3(l)$ + $H_2O(l)$?
   Give any units that are appropriate to your examination specification.

2. For $H_2(g)$ + $I_2(g)$ $\rightleftharpoons$ 2HI(g), the value of K_c is 5.00 at 750K. What is the value of K_c for:
   (a) $\frac{1}{2}H_2(g)$ + $\frac{1}{2}I_2(g)$ $\rightleftharpoons$ HI(g)?
   (b) 2HI(g) $\rightleftharpoons$ $H_2(g)$ + $I_2(g)$?

3. Consider the following *homogeneous* equilibrium
   $2SO_2(g)$ + $O_2(g)$ $\rightleftharpoons$ $2SO_3(g)$
   An equilibrium mixture is found to contain 2.23 moles of SO_3, 0.11 moles of SO_2 and 2.45 moles of O_2 in a 100 dm³ reaction vessel at 1000K. The total pressure of the system is found to be 400 kPa. Calculate a value for (a) K_c (b) K_p?

4. Consider the general *heterogeneous* equilibrium
   A(g) + B(s) $\rightleftharpoons$ 2C(g).
   An equilibrium mixture is found to contain 0.12 moles of A and 0.30 moles of C in a 10 dm³ reaction vessel at 800K. The total pressure of the system is found to be 280 kPa. Calculate a value for (a) K_c (b) K_p?

5. Consider the following *homogeneous* equilibrium
   $2NOCl(g)$ $\rightleftharpoons$ $2NO(g)$ + $Cl_2(g)$
   A 2.50 mol sample of NOCl was heated in a sealed 15 dm³ container and equilibrium was established at 500 K. The equilibrium mixture formed contained 0.80 moles of NO. Calculate a value for K_c?

6. Consider the following *homogeneous* equilibrium
   $SO_2Cl_2(g)$ $\rightleftharpoons$ $SO_2(g)$ + $Cl_2(g)$
   When 1.00 mole of SO_2Cl_2 dissociates, the equilibrium mixture contains 0.75 moles of Cl_2 at 600 K and a total pressure of 125 kPa. Calculate a value for K_p?

Answers to questions
1. (a) $K_c = \dfrac{[HI]^2}{[H_2] \times [I_2]}$ and $K_p = \dfrac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$

   (b) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$ and $K_p = \dfrac{P_{SO_3}^3}{P_{SO_2}^2 \times P_{O_2}}$

   (c) $K_c = \dfrac{[NH_3]^2}{[H_2]^3 \times [N_2]}$ and $K_p = \dfrac{P_{NH_3}^2}{P_{H_2}^3 \times P_{N_2}}$

   (d) $K_c = \dfrac{[HCOOCH_3] \times [H_2O]}{[HCOOH] \times [CH_3OH]}$ and K_p not applicable - not gaseous

   Units for (a) and (d) – none – units cancel.
   Units for (b) K_c – (mol dm⁻³)²⁻²⁻¹ = mol⁻¹ dm³ ; K_p – (kPa)²⁻²⁻¹ = kPa⁻¹
   Units for (c) K_c – (mol dm⁻³)²⁻³⁻¹ = mol⁻² dm⁶ ; K_p – (kPa)²⁻³⁻¹ = kPa⁻²
2. (a) $\sqrt{5.00}$ = 2.24 (b) 1/5.00 = 0.02
3. (a) 1.68×10^4 (mol⁻¹ dm³ if needed) (b) 2.01 (kPa⁻¹ if needed)
4. (a) 0.075 (mol dm⁻³ if needed) (b) 500 (kPa if needed)
5. 5.91×10^{-3} (mol dm⁻³ if needed)
6. 161 (kPa if needed)