Chemical Equilibria: K_p

To succeed in this topic you need to:-
- Understand the concepts of 'dynamic equilibrium' and Le Chatalier's Principle (Factsheet 09)
- Ensure you are fully competent with the work on K_c covered in Factsheet Number 21

After working through this Factsheet you will be able to:-
- understand the concept of 'K_p' and write its mathematical expression from the balanced chemical equation
- calculate partial pressure from the data given
- work out the units of K_p
- perform calculations using the K_p expression

> **Exam hint:-** Do not think of K_p as something completely new - it's basically an extension of the work on K_c, with the fundamental theory of equilibria applying to both.

What is K_p?

The 'p' in K_p stands for 'pressure'. **K_p only applies to gases**.

> **Exam Hint: -**Watch out for heterogeneous reactions (those that involve gases and solids or liquids)   - K_p only applies to gases!

K_p (like K_c) is a constant numerical value for any equilibrium but is always quoted at a particular temperature. This is because **only temperature affects the value of K_p**

In other words you can add or remove reactants or products, change the pressure or add a catalyst and the **value of K_p does not change**. This is because the equilibrium, adjusts its position (according Le Chatalier's Principle) to keep K_p a constant value.

> **Exam Hint:-** The effect of changing conditions on the value of K_p is invariably tested in questions. You should note very carefully what has been covered so far!

Writing K_p expressions

The same rules apply to writing K_p expressions as to K_c:

> **Rules**
> 1. 'Products' over 'Reactants' (right hand side on top)
> 2. Numbers in front become powers
> 3. '+' becomes '×'.
> 4. **Only gases** are included

The difference to K_c is that pressures are used, not concentrations. This affects the symbol used - K_c used [ ] $\equiv$ mol dm^{-3}, while K_p uses a letter 'p'. The worked example below shows the rules being applied:

Example: For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, write expressions for K_p and K_c and give their units

$$K_c = \frac{[NH_3]_{eq}^{2}}{[N_2]_{eq} \times [H_2]_{eq}^{3}}$$

$$\text{Units} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^3}$$

$$= \frac{\text{mol}^2 \text{ dm}^{-6}}{(\text{mol dm}^{-3}) \times (\text{mol}^3 \text{ dm}^{-9})}$$

$$= \frac{\text{mol}^2 \text{ dm}^{-6}}{\text{mol}^4 \text{ dm}^{-12}}$$

$$= \text{mol}^{-2} \text{ dm}^{6}$$

Now we repeat this for K_p:

$$K_p = \frac{(pNH_3)_{eq}^{2}}{(pN_2)_{eq} \times (pH_2)_{eq}^{3}}$$

$$\text{Units} = \frac{(\text{atm})^2}{(\text{atm}) \times (\text{atm})^3}$$

$$= \frac{(\text{atm})^2}{(\text{atm})^4}$$

$$= \text{atm}^{-2}$$

> **Exam Hint:-** Pressure is quoted in a range of different units: - atmospheres (atm), pascals (Pa), kilopascals (kPa), megapascals (MPa) and mmHg or cmHg.
> It doesn't matter – you just use whichever units are used in the question! So in the above example, if we'd started with Pascals, the final unit would be Pa^{-2} etc.

Question 1 at the end of the Factsheet provides further practice on writing expressions for K_p and working out units.

Mole fractions and partial pressures

Before we go to K_p calculations there is some new work to be done about gases. This theory is based on the Gas Laws - but you do not need to know anything about the Gas Laws for this!

If you have a mixture of two or more gases then the mixture will exert a **total pressure**. This total is made up of the individual contributions from each of the gases in the mixture. These are called **partial pressures**.

> *Total Pressure* = *Sum of the Partial Pressures*
> *of a gas mixture*   *of the gases in the mixture*
>
> *P* = *pA + pB + pC + ...*
> *where A, B, C, etc represent the gases.*

To find Partial Pressures, we use **mole fractions**:

> *Mole Fraction of a gas* $= \dfrac{\textit{moles of that gas}}{\textit{total number of moles of gas}}$
>
> *The mole fractions must always add up to 1*

> *Partial pressure* = *Mole Fraction* × *Total*
> *of gas A*   *for gas A*   *Pressure*

Example 1: What is the partial pressure of each gas if 2 moles of A and 3 moles of B have a total pressure of 4 atm?

Mole fraction for A = 2/(2 + 3) = 0.4
Mole fraction for B = 3/(2 + 3) = 0.6

So:
Partial pressure of A = 0.4 × 4 = **1.6 atm**
Partial pressure of B = 0.6 × 4 = **2.4 atm**

Check: pA + pB = 1.6 + 2.4 = 4 atm = total pressure

Example 2: 0.4 moles of C, 0.2 moles of D and 1.0 moles of E have a total pressure of 200 Pa. Find the partial pressure of each gas.

Mole fraction for C = 0.4/(0.4 + 0.2+1.0) = 0.25
Mole fraction for D = 0.2/(0.4 + 0.2+1.0) = 0.125
Mole fraction for E = 1.0/(0.4 + 0.2 + 1.0) = 0.625

Partial pressure of C = 0.25 × 200   = **50 Pa**
Partial pressure of D = 0.125 × 200   = **25 Pa**
Partial pressure of E = 0.625 × 200   = **125 Pa**

Check: pC + pD + pE = 50 + 25 + 125 = 200 Pa = total pressure

---

Check you are happy using mole fractions to calculate partial pressures by attempting Question 2 at the end of this Factsheet before moving on.

Calculating K_p
The method for this is:

Method
1. Write the equation, putting in the start moles
2. Calculate the equilibrium moles from the data given.
3. Change equilibrium moles into mole fractions.
4. Calculate partial pressures for the gases (mole fraction × total pressure).
5. Substitute the partial pressure values into the K_p expression and calculate the K_p value.
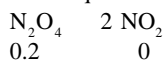

Example 1
0.2 moles of N_2O_4 was heated to 100ºC in a flask. At equilibrium 50% of the N_2O_4 has dissociated and the total pressure was 0.5 atm.
     N_2O_4(g) û 2NO_2(g)
What is the value of K_p?

1. Write the equation. Put in the moles at the start
    N_2O_4 û 2 NO_2
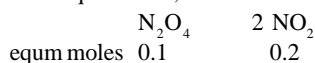   0.2   0

2. Work out the moles at equilibrium, using the data in the question
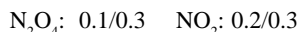   50% of 0.2 moles is 0.1 moles
     From equation, 1 mole N_2O_4 produces 2 moles NO_2
     So 0.1 moles N_2O_4 produces 0.2 moles NO_2
     So at equilibrium, we have
              N_2O_4 û 2 NO_2
    equm moles   0.1   0.2

3. Calculate the mole fraction for each substance at equilibrium
    N_2O_4: 0.1/0.3 NO_2: 0.2/0.3

Exam Hint:- Do **not** round at this stage - if you do you may end up with rounding errors later.

---

4. Calculate the equilibrium partial pressures
    N_2O_4: (0.1/0.3)× 0.5 = 0.167 atm
    NO_2: (0.2/0.3)× 0.5= 0.333 atm

5. Calculate K_p

$$K_p = \frac{(pNO_2)_{eq}^2}{(pN_2O_4)_{eq}}$$
$$= \frac{0.333^2}{0.167} = \textbf{0.66 atm}$$

Example 2
4 moles of SO_3 was heated to 150ºC. At equilibrium there was found to be 0.5 moles of O_2, and the total pressure was 2 atm.
     2 SO_3(g) û 2 SO_2 (g) + O_2(g)
What is the value of K_p?

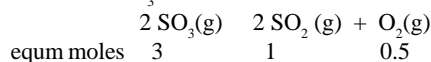1. 2 SO_3(g) û 2 SO_2 (g) + O_2(g)
    4   0   0
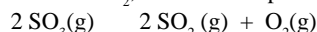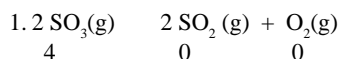
2. At equilibrium, there are 0.5 moles O_2. From the equation:
    Moles SO_2 produced = 2× moles O_2 produced
    Moles of SO_3 used = 2 × moles O_2 produced
    So moles SO_2 produced = 1. Moles SO_3 used = 1.
    3 moles of SO_3 are left
               2 SO_3(g) û 2 SO_2 (g) + O_2(g)
    equm moles   3   1   0.5

3. Mole fractions: SO_3: 3/ 4.5 SO_2: 1/4.5 O_2: 0.5/ 4.5

4. Partial pressures: SO_3: (3/ 4.5)× 2 = 1.333 atm
                       SO_2: (1/ 4.5)× 2 = 0.444 atm
                       O_2: (0.5/ 4.5)× 2 = 0.222 atm

5. $K_p = \dfrac{(pSO_2)_{eq}^2 (pO_2)_{eq}}{(pSO_3)_{eq}^2} = \dfrac{0.444^2 \times 0.222}{1.333^2} = \textbf{0.024 atm}$

In some examples, you may not be given the actual number of moles at the start, but instead the percentage of dissociation. The approach is very similar - we just imagine that we start with 1 mole!
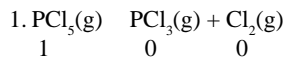

Example 3
In the gas phase, PCl_5 undergoes thermal dissociation:
 PCl_5(g) û PCl_3(g) + Cl_2(g)
At a certain temperature, and a total pressure of 3 atm, 60% of the PCl_5 originally present has dissociated when equilibrium is attained.
Calculate the partial pressures of the three gases at equilibrium, and hence the value of K_p at this temperature.

1. PCl_5(g) û PCl_3(g) + Cl_2(g)
    1   0   0

2. 60% dissociated means 0.6 moles of PCl_5 are used up, so 0.4 remain.
    Moles PCl_3 produced = moles Cl_2 produced = moles PCl_5 used = 0.6
                   PCl_5(g) û PCl_3(g) + Cl_2(g)
    equm moles   0.4   0.6   0.6
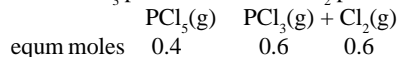
3. Mole fractions: PCl_5: 0.4/1.6 PCl_3: 0.6/1.6 Cl_2: 0.6/1.6

4. Partial pressures: PCl_5:(0.4/ 1.6)× 3 = 0.75 atm
                      PCl_3: (0.6/ 1.6)× 3 = 1.125 atm
                      O_2: (0.6/ 1.6)× 3 = 1.125 atm

5. $K_p = \dfrac{(pPCl_3)_{eq}(pCl_2)_{eq}}{(pPCl_5)_{eq}} = \dfrac{1.125 \times 1.125}{0.75} = \textbf{1.69 atm (3SF)}$

Before moving on, attempt Question 3 to make sure you are confident with calculating K_p values.

Calculating partial pressure values at equilibrium

If the value of K_p is given for a *simple binary system* (i.e. only two species involved) you may be required to calculate the partial pressures of the gases involved.

There are two types of calculation here; the first is simply the reverse of the previous calculations on K_p where partial pressures were used to find the value of K_p.

Example 1.
For the equilibrium system
$$N_2O_4(g) \quad \rightleftharpoons 2NO_2(g)$$
at 340K, K_p = 3.90 atm.

If, at the equilibrium position, the partial pressure of the NO_2 was found to be 0.80atm, calculate the partial pressure of the N_2O_4 and the total pressure.

1. Write the K_p expression
$$K_p = \frac{(pNO_2)_{eq}^2}{(pN_2O_4)_{eq}}$$

2. Substitute in what you know
$$3.9 = \frac{(0.80)^2}{(pN_2O_4)_{eq}}$$

3. Rearrange the equation:
$$3.9 \times (pN_2O_4)_{eq} = (0.80)^2$$
$$(pN_2O_4)_{eq} = \frac{(0.80)^2}{3.9} = 0.164 \text{ atm}$$

Total pressure = sum of partial pressures = 0.164 + 0.80 = 0.96atm (2DP)

Example 2.
For the equilibrium system
$$N_2O_4(g) \quad \rightleftharpoons 2NO_2(g)$$
at 340K, K_p = 3.90 atm.
If the equilibrium partial pressure of the N_2O_4 was 0.60atm, calculate the partial pressure of the NO_2 and the total pressure.

1. $K_p = \dfrac{(pNO_2)_{eq}^2}{(pN_2O_4)_{eq}}$

2. $3.90 = \dfrac{(pNO_2)_{eq}^2}{0.60}$

3. $3.90 \times 0.60 = (pNO_2)_{eq}^2$
$(pNO_2)_{eq} = \sqrt{(3.90 \times 0.60)} = \sqrt{2.34} = 1.53\text{atm (2DP)}$

Total pressure = 1.53 + 0.60 = 2.13atm (2DP)

In the second type of calculation, neither of the equilibrium pressures are known. The examples below illustrate how to approach this; the method is similar to the one for calculating K_p

---

Method
1. Write the equation, putting in the start moles
2. Call the number of moles of reactant used up at equilibrium "x"
   Work out the number of moles at equilibrium of all the other substances in terms of x.
3. Find mole fractions, in terms of x
4. Find partial pressures, in terms of x
5. Write down expression for K_p and substitute in.
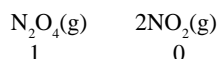6. Rearrange to find x, and hence the required partial pressure

---

Example 3.
For the equilibrium system : $N_2O_4(g) \quad \rightleftharpoons 2NO_2(g)$
at 100°C, K_p = 0.66 atm.
One mole of N_2O_4 was placed in a sealed flask, and heated to 100°C. The total pressure was 2 atm. Find the partial pressure of NO_2 at equilibrium.

1. Equation and start moles
$$N_2O_4(g) \quad \rightleftharpoons 2NO_2(g)$$
$$\quad 1 \quad\quad\quad\quad\quad 0$$

2. Equilibrium moles in terms of x
   Suppose that x moles of N_2O_4 have been used at equilibrium
   Since 1 mole of N_2O_4 is required to produce 2 moles of NO_2,
   moles of NO_2 produced = twice moles of N_2O_4 used = 2x
   So at equilibrium, we have:
$$N_2O_4(g) \quad \rightleftharpoons 2NO_2(g)$$
   equm moles $1 - x \quad\quad\quad 2x$
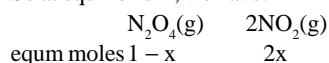
3. Mole fractions, in terms of x
   Total moles = 1 − x + 2x = 1 + x
   So mole fractions are
   N_2O_4: $\dfrac{(1-x)}{(1+x)}$ $\quad\quad$ NO_2: $\dfrac{2x}{(1+x)}$

4. Partial pressures, in terms of x
   N_2O_4: $\dfrac{(1-x)}{(1+x)} \times 2 = \dfrac{(2-2x)}{(1+x)}$

   NO_2: $\dfrac{2x}{(1+x)} \times 2 = \dfrac{4x}{(1+x)}$

5. Write down expression for K_p, and substitute in:

Exam Hint:- *When you are multiplying a fraction by a whole number, just multiply the **top** of the fraction by the number*

$$K_p = 0.66 = \frac{(pNO_2)_{eq}^2}{(pN_2O_4)_{eq}} = \frac{\left(\dfrac{4x}{1+x}\right)^2}{\dfrac{2-2x}{1+x}}$$

6. Rearrange

Exam Hints:-
1. *To square a fraction, square the top and square the bottom*
2. *To divide a fraction by a fraction, turn the one on the bottom upside down and multiply them*
3. *To multiply two fractions, multiply the tops and multiply the bottoms*

$$0.66 = \frac{\dfrac{16x^2}{(1+x)^2}}{\dfrac{2-2x}{1+x}}$$

$$0.66 = \frac{16x^2}{(1+x)^2} \times \frac{1+x}{2-2x}$$

$$= \frac{16x^2(1+x)}{(1+x)^2(2-2x)}$$

$$= \frac{16x^2}{(1+x)(2-2x)} \quad \textit{(cancelling out the 1 + x)}$$

$$= \frac{16x^2}{2+2x-2x-2x^2} = \frac{16x^2}{2-2x^2} \quad \textit{(multiplying out brackets)}$$

Now multiply up:
$$0.66(2-2x^2) = 16x^2$$
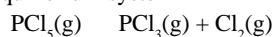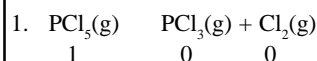$$1.32 - 1.32x^2 = 16x^2$$
$$1.32 = 17.32x^2$$
$$x^2 = 1.32/17.32 = 0.0762...$$
$$x = \sqrt{0.0762..} = 0.276$$

So partial pressure of $NO_2 = \dfrac{4x}{(1+x)}$ = **0.87atm (2SF)**

Example 4.
For the equilibrium system
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
at a temperature T, K_p = 1.69 atm.
One mole of $PCl_5(g)$ was placed in a sealed flask, and heated to temperature T. The total pressure was 3 atm. Find the partial pressure of PCl_5 at equilibrium.

1. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
       1   0   0

2. If x moles of N_2O_4 have been used at equilibrium, x moles of each of PCl_3 and Cl_2 will be produced
    So at equilibrium, we have:
    $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
    equm moles $1 - x$ x   x
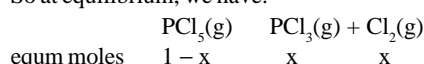
3. Total moles = $1 - x + x + x = 1 + x$
    So mole fractions are:
    PCl_5: $\frac{(1-x)}{(1+x)}$ PCl_3: $\frac{x}{(1+x)}$ Cl_2: $\frac{x}{(1+x)}$

4. Partial pressures:
    PCl_5: $\frac{(1-x)}{(1+x)} \times 3 = \frac{(3-3x)}{(1+x)}$

    PCl_3 and O_2: $\frac{x}{(1+x)} \times 3 = \frac{3x}{(1+x)}$

5. $K_p = 1.69 = \frac{(pPCl_3)_{eq}(pCl_2)_{eq}}{(pPCl_5)_{eq}} = \frac{\left(\frac{3x}{1+x}\right)\left(\frac{3x}{1+x}\right)}{\frac{3-3x}{1+x}}$

6. $1.69 = \dfrac{\frac{9x^2}{(1+x)^2}}{\frac{3-3x}{1+x}}$

    $= \frac{9x^2}{(1+x)^2} \times \frac{1+x}{3-3x}$

    $= \frac{9x^2}{(1+x)(3-3x)}$

    $= \frac{9x^2}{3+3x-3x-3x^2} = \frac{9x^2}{3-3x^2}$

    $1.69(3 - 3x^2) = 9x^2$
    $5.07 - 5.07x^2 = 9x^2$
    $14.07x^2 = 5.07$
    $x^2 = 5.07/14.07 = 0.360...$
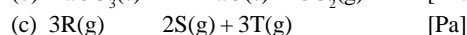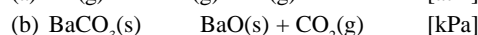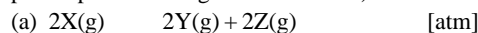 $x = 0.600$

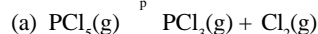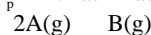   Partial pressure of $PCl_5 = \frac{(3-3x)}{(1+x)} = 0.75$atm

Exam Hint:- *If you get to a stage of trying to solve a quadratic equation – YOU HAVE MADE AN ERROR SOMEWHERE (solving quadratic equations is not in the syllabus!)*
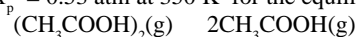
Practice Questions
1. For each equilibrium write the K_p expression and the units (the units of partial pressure are given in brackets).
    (a) $2X(g) \rightleftharpoons 2Y(g) + 2Z(g)$ [atm]
    (b) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$ [kPa]
    (c) $3R(g) \rightleftharpoons 2S(g) + 3T(g)$ [Pa]

2. Calculate the partial pressures of the gases in the following mixtures at equilibrium.
    (a) 2 mol A, 2 mol B, 3 mol C.   Total pressure = 2 atm
    (b) 0.25 mol D, 0.25 mol E, 1 mol F.   Total pressure = 150 Pa
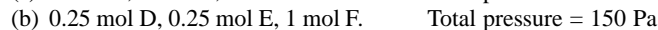
3. What is the K_p value for each of the following equilibria?
    (a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
        2 mol PCl_5 is heated to 200°C. The PCl_5 50% dissociates at equilibrium, and the total pressure is 100 kPa
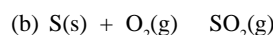
    (b) $S(s) + O_2(g) \rightleftharpoons SO_2(g)$
        At the start there are 0.4 mol O_2. At equilibrium there are 0.1 moles of SO_2, with a total pressure of 0.5 atm.
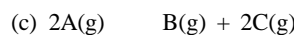
    (c) $2A(g) \rightleftharpoons B(g) + 2C(g)$
        A sample of A is heated to 125°C in a flask. At equilibrium the gas A has 25% dissociated, and there is a total pressure of 2 atm.

    (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
        0.5 moles of H_2 and 0.4 moles of N_2 are allowed to reach equilibrium. At equilibrium there are 0.2 moles H_2. The total pressure is 200 Pa.

4. (a) K_p = 2.4 atm^{-1} at 400K for the following equilibrium system:
        $2A(g) \rightleftharpoons B(g)$
        At equilibrium, the partial pressure of A is 0.6 atm.
        Find the partial pressure of B and the total pressure at equilibrium.

    (b) K_p = 0.53 atm at 350 K for the equilibrium system:
        $(CH_3COOH)_2(g) \rightleftharpoons 2CH_3COOH(g)$
        At equilibrium, the partial pressure of CH_3COOH is 1.1atm.
        Find the partial pressure of $(CH_3COOH)_2$ at equilibrium.

    (c) For the system $A(s) \rightleftharpoons B(s) + C(g)$, K_p = 0.8 atm at 200°C.
        Find the equilibrium partial pressure of C(g)

    (d) For the system $D(g) \rightleftharpoons E(g) + F(g)$, K_p = 1.6 atm at 350 K
        Given that there was initially 1 mole of D, and that the total pressure at equilibrium is 1 atm, find the equilibrium partial pressure of E.

Answers
1. (a) $(pY)_{eq}^2 \times (pZ)_{eq}^2 / (pX)_{eq}^2$ atm^2
    (b) $(pCO_2)_{eq}$ kPa
    (e) $(pS)_{eq}^2 \times (pT)_{eq}^3 / (pR)_{eq}^3$ Pa^2

2. (a) A = 0.57 atm B = 0.57 atm   C = 0.86 atm
    (b) D = 25 Pa   E = 25 Pa   F = 100 Pa

3. (a) $pPCl_5 = pPCl_3 = pCl_2 = 33.3$ kPa K_p = 33.3 kPa
    (b) pO_2 = 0.375 atm pSO_2 = 0.125 atm K_p = 0.33   No units
    (c) pA = 1.33 atm pB = 0.22 atm pC = 0.44 atm K_p = 0.024 atm
    (d) pN_2 = 85.7Pa pH_2 = pNH_3 =57.1 Pa K_p = 0.000204 Pa^{-2}

4. (a) $2.4 = pB/0.60^2$.   So $pB = 2.4 \times 0.60^2 = 0.864$ atm
    (b) $0.53 = 1.1^2/p(CH_3COOH)_2$ So $p(CH_3COOH)_2 = 1.1^2/0.53 = 2.28$atm
    (c) $K_p = pC(g)$ So $pC(g) = 0.8$ atm
    (d) Equilibrium moles: D: $1 - x$; E: x F: x
        $pD = (1 - x)/(1+x)$ $pE = pF = x/(1 + x)$
        $K_p = 1.6 = x^2/(1 - x^2)$
        $x = 0.784$ so $pE = 0.44$atm