

## CHAPTER 5: PROBABILITY, COMBINATIONS & PERMUTATIONS

### Probability

If an event can occur in  $n$  ways (i.e. there are  $n$  possible outcomes) and a particular result can occur in  $m$  ways, then the probability of the particular result occurring is  $m/n$ .

#### *Example*

Spinning a coin gives rise to 2 possible outcomes: H (Heads) or T (Tails)  
H occurs in 1 way ; therefore the probability of a H result is  $\frac{1}{2}$

Note:

1. the sum of the probabilities for all possible results is unity: in the above example, the probability of T occurring is also  $\frac{1}{2}$  and the probability of obtaining either an H or a T (i.e. encompassing all possible results) is therefore equal to  $(\frac{1}{2} + \frac{1}{2}) = 1$
2. probabilities may be expressed as fractions, in decimal format or as percentages; so the following probabilities are all equivalent -  $\frac{1}{2}$  , 0.5 , 50%.

#### *Example*

A standard dice has six faces (with faces numbered 1 .... 6) and rolling it gives rise to 6 possible outcomes. A 3 occurs in 1 way ; therefore the probability of throwing a 3 is  $\frac{1}{6}$

### Permutations and Combinations

If we have  $n$  different items, then the number of ways of arranging them in a row is given by the factorial  $n!$

#### *Proof by Example*

Consider how many arrangements are possible for the 26 letters of the alphabet. The first letter could be chosen in 26 different ways - leaving 25. Thus 25 choices are possible for the second letter. The third choice is then made from the 24 remaining letters and so on. The number of different arrangements possible for just the first two choices is thus  $26 \times 25$  ; and when the third is included,  $26 \times 25 \times 24$ . This process can be continued until all the letters of the alphabet are used up and the number of different possible arrangements is  $26 \times 25 \times 24 \times 23 \times \dots \times 4 \times 3 \times 2 \times 1$  - such a multiplication series is called a *factorial* and in this case the number of arrangements would be written as  $26!$

#### *Example*

With three different letters, ABC, then  $n = 3$  and  $n! = 6$  , corresponding to the six possible arrangements which are: ABC, ACB, BAC, BCA, CAB, CBA

## Selections

We are often concerned with considering selections of objects, rather than all the objects. In this instance it is important to distinguish between two different possible situations; one in which the order of the objects is important and one in which the order is not.

### Example

It is possible to select two letters from the letters ABC in 3 ways: AB, AC, BC  
Each *selection* is called a *combination*

However,

If the *order* of the selection matters then there are 6 ways: AB, BA, AC, CA, BC, CB  
Each *arrangement* is called a *permutation*

In this case, therefore there are 3 combinations and 6 permutations of the selected two letters.

In general, provided that all the objects are different (dissimilar), then

- the number of combinations of  $r$  objects from  $n$  objects is:  ${}^n C_r = \frac{n!}{(n-r)!r!}$
- the number of permutations of  $r$  objects from  $n$  objects is:  ${}^n P_r = \frac{n!}{(n-r)!}$

For the example given above, the number of combinations of two letters chosen from three is

$${}^3 C_2 = \frac{3!}{1!2!} = 3, \text{ whilst the number of permutations of two from three is } {}^3 P_2 = \frac{3!}{1!} = 6$$

The difference between the two formulae is a factor of  $r!$  - this is the number of ways of arranging  $r$  dissimilar objects. For two different letters,  $r = 2$  and  $r! = 2$ , i.e. for a pair of letters, then each letter may come first or last, giving rise to two permutations for each combination.

### Example

How many different arrangements can be made by taking 5 letters of the word *numbers* ?

$$\text{Number of permutations} = {}^7 P_5 = \frac{7!}{2!} = 2520$$

### Example

How many different arrangements can be made by taking all the letters of the word *numbers* ?

$$\text{Number of permutations} = {}^7 P_7 = \frac{7!}{0!} = 5040$$

## Mass Spectroscopy - Isotopic Patterns

### *Example 1 : Cl and Cl<sub>2</sub>*

Chlorine has two stable isotopes of RAM 35 and 37. Their relative abundance is about 3 : 1. This can be expressed as " the chance of encountering a Cl atom of mass 35 in a collection of free chlorine atoms is 75% " or the *probability* of any particular Cl atom having mass 35 is 0.75.

This means that a mass spectrum of chlorine atoms shows two peaks at masses 35 and 37, the former three time as intense as the latter.

What happens in the chlorine molecule (Cl<sub>2</sub>)? Clearly several combinations of isotopes are possible, (i) both atoms are of mass 35, giving <sup>35</sup>Cl<sub>2</sub>, (ii) one 35 and one 37, giving <sup>35</sup>Cl<sup>37</sup>Cl, or (iii) both are of mass 37, giving <sup>37</sup>Cl<sub>2</sub>. These possible combinations give rise to three peaks in the mass spectrum, corresponding to Cl<sub>2</sub><sup>+</sup> ions with relative masses of 70, 72, and 74.

There are several ways of tackling the problem of identifying the exact probability of each molecular mass occurring. We will start with the least sophisticated approach.

### *Approach 1*

If we choose the first atom in the molecule to be <sup>35</sup>Cl then this choice has a probability of 0.75; this atom may then be associated with either another <sup>35</sup>Cl atom, again with a probability of 0.75, or with a <sup>37</sup>Cl atom, with a probability of 0.25 .

The pattern of all possible combinations, taking account of these relative probabilities is shown in Table 1. For this table we have chosen to work with four chlorine atoms in the first instance, since the relative abundances then indicate that on average three will be 35 and one 37. *Each* of these atoms can then be associated with four other atoms, and again three will be 35 and one 37, giving the sixteen possible Cl<sub>2</sub> molecules shown in the table.

**Table 1 : Possible Ways of Combining Chlorine Isotopes**

First Cl	35				35				35				37			
Second Cl	35	35	35	37	35	35	35	37	35	35	35	37	35	35	35	37
Total mass	70	70	70	72	70	70	70	72	70	70	70	72	72	72	72	74

Total number of molecules = 16

No. of molecules of mass 70 = 9                   ⇒ Relative probability =  $\frac{9}{16} = 0.5625$

No. of molecules of mass 72 = 6                   ⇒ Relative probability =  $\frac{6}{16} = 0.3750$

No. of molecules of mass 74 = 1                   ⇒ Relative probability =  $\frac{1}{16} = 0.0625$

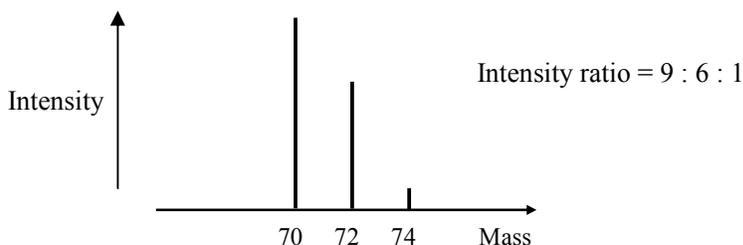
Cross-checking:

$$\text{Total number of molecules} = 9 + 6 + 1 = 16$$

$$\text{Total probability of all outcomes} = 0.5625 + 0.3750 + 0.0625 = 1.0000$$

Note that the total number of possible isotopic arrangements in the final molecule arises by multiplying the number of choices for the first atom by the number of choices for the second. In this case four for the first times four for the second i.e. sixteen.

If the only way in which these molecules can be distinguished is by mass then the relative probabilities will be as shown on the right hand side of the lower part of the table – of the sixteen arrangements, nine correspond to a total molecular mass of 70, six correspond to a total mass of 72 and one corresponds to a total mass of 74. The mass spectrum will therefore appear as shown below:



### Approach 2

The same result could be achieved, with considerably less effort, if the isotopic probability were used directly. The four possible isotopic arrangements are listed in the table below, and their probabilities evaluated. It is very important to note that the probability of a particular combination or permutation is related to the product of the probabilities.

**Table 2 : Possible Permutations of two Chlorine Isotopes with their Probabilities**

1st	2nd	Probability Product	Probability of Permutation	Total Mass
35	35	$0.75 \times 0.75$	0.5625	70
35	37	$0.75 \times 0.25$	0.1875	72
37	35	$0.25 \times 0.75$	0.1875	72
37	37	$0.25 \times 0.25$	<u>0.0625</u>	74
Sum			1.0000	

The resulting conclusion is the same as that derived from the more complicated Table 1 - the probability of the molecule having a total mass of 70 is 0.5625, a total mass of 72 is 0.3750 (0.1875+0.1875), and a total mass of 74 is 0.0625.

*Approach 3*

A final simplification results from taking direct account of how many permutations give rise to a particular molecular mass. The final probability is now determined directly from multiplying the product of the individual probabilities by the number of permutations of the isotopes giving the required total mass.

**Table 3 : Possible Permutations of two Chlorine Isotopes with their Probabilities**

Total Mass	Required Isotopes	Probability Product	N <sup>o</sup> . of Permutations	Overall Probability
70	Two 35	$0.75 \times 0.75 = 0.5625$	1	0.5625
72	One 35; One 37	$0.75 \times 0.25 = 0.1875$	2	0.3750
74	Two 37	$0.25 \times 0.25 = 0.0625$	1	0.0625

*Example 2 : CHCl<sub>3</sub>*

Let's now consider a slightly more complicated example, that of chloroform CHCl<sub>3</sub>. We will assume for simplicity that C is only present as mass 12 and H is only present as mass 1 in the parent ion, CHCl<sub>3</sub><sup>+</sup> - the molecular mass is therefore that due to the three chlorine atoms plus 13. The pattern and masses of the peaks derived from this ion can be calculated as shown below.

Total Mass	Required Isotopes	Probability Product	N <sup>o</sup> . of Permutations	Overall Probability
118	Three 35	$0.75 \times 0.75 \times 0.75$	1	0.4219
120	Two 35; One 37	$0.75 \times 0.75 \times 0.25$	3	0.4219
122	One 35; Two 37	$0.75 \times 0.25 \times 0.25$	3	0.1406
124	Three 37	$0.25 \times 0.25 \times 0.25$	1	<u>0.0156</u>
				Sum 1.0000

Note:

1. For the 120 amu ion, which must contain two 35 and one 37 isotopes, there are three ways in which the isotopes can be arranged in order (35-35-37, 35-37-35 and 37-35-35). Similarly there are also three permutations for the 122 amu ion.
2. The final probabilities have been added up and the sum is equal to unity. This is quite general and is a very useful check which should always be carried out at this stage in your calculations.

*If the sum of the probabilities isn't equal to one then you have made an error.*

*Example 3 : BrCl*

More complicated situations arise if many atoms in a molecule have a range of possible isotopes, but no new concepts arise. Thus the parent ion of bromine monochloride, Br Cl<sup>+</sup>, will show four peaks in its mass spectrum since both bromine and chlorine have two isotopes. The isotopes and their relative probabilities are :



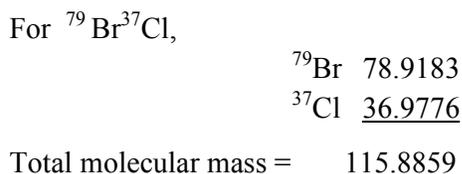
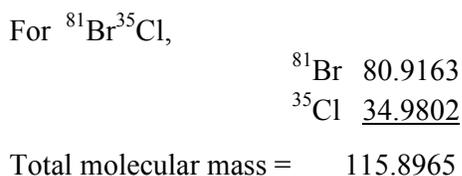
For more complex problems such as this one the simplest procedure is to consider the isotopic arrangements associated with each element individually and then to combine the probabilities calculated for groupings of like atoms.

In the case of  $\text{BrCl}^+$  this is very simple:

Br	Cl	Mass	Br Prob <sup>y</sup> × Perm <sup>s</sup>	Cl Prob <sup>y</sup> × Perm <sup>s</sup>	Probability products
79	35	114	$0.5 \times 1 = 0.5$	$0.75 \times 1 = 0.75$	$0.5 \times 0.75 = 0.375$
	37	116	$0.5 \times 1 = 0.5$	$0.25 \times 1 = 0.25$	$0.5 \times 0.25 = 0.125$
81	35	116	$0.5 \times 1 = 0.5$	$0.75 \times 1 = 0.75$	$0.5 \times 0.75 = 0.375$
	37	118	$0.5 \times 1 = 0.5$	$0.25 \times 1 = 0.25$	$0.5 \times 0.25 = 0.125$
Sum					1.000

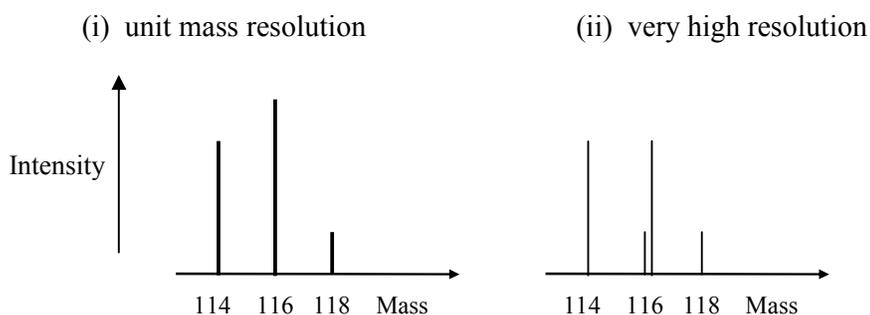
Note that mass 116 arises from both  ${}^{79}\text{Br}^{37}\text{Cl}$  and  ${}^{81}\text{Br}^{35}\text{Cl}$  and in a mass spectrometer that can only resolve unit atomic masses just one peak will result – this will have an intensity reflecting the sum of the probabilities (i.e. 0.500).

This situation is however fundamentally different from that observed for different permutations (e.g.  ${}^{35}\text{Cl}^{37}\text{Cl}$ ,  ${}^{37}\text{Cl}^{35}\text{Cl}$ ) since in the 116 peak of  $\text{BrCl}$  two different elements are involved. The truth of this can be seen if a very high resolution spectrometer is used in which case the peaks would be resolved. The exact masses of the different isotopes then need to be considered:



Such a small difference can be observed experimentally, whereas the mass of  ${}^{35}\text{Cl}^{37}\text{Cl}$  will always be the same as that of  ${}^{37}\text{Cl}^{35}\text{Cl}$  no matter how accurate the spectrometer.

The spectrum would now look rather different on spectrometers of different resolution (although this is exaggerated in the diagram below):

*Example 4* : B<sub>2</sub>Cl<sub>2</sub>

A slightly more complicated example is that of the ion B<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. Here the relevant atomic isotopic masses and probabilities are:

<sup>10</sup> B	0.2	<sup>11</sup> B	0.8
<sup>35</sup> Cl	0.75	<sup>37</sup> Cl	0.25

(i) First considering the two B atoms

Total Mass	Required Isotopes	Probability Product	N <sup>o</sup> . of Permutations	Overall Probability
20	Two <sup>10</sup> B	0.2 × 0.2 = 0.04	1	0.04
21	One <sup>10</sup> B; One <sup>11</sup> B	0.2 × 0.8 = 0.16	2	0.32
22	Two <sup>11</sup> B	0.8 × 0.8 = 0.64	1	<u>0.64</u>
				Sum 1.00

(ii) Secondly considering the two Cl atoms

Total Mass	Required Isotopes	Probability Product	N <sup>o</sup> . of Permutations	Overall Probability
70	Two 35	0.75 × 0.75 = 0.5625	1	0.5625
72	One 35; One 37	0.75 × 0.25 = 0.1875	2	0.3750
74	Two 37	0.25 × 0.25 = 0.0625	1	<u>0.0625</u>
				Sum 1.0000

(iii) Combine results for the two sub-units.

For the ion B<sub>2</sub>Cl<sup>+</sup> the probability for the B<sub>2</sub> group and the Cl<sub>2</sub> group must be multiplied together thus:

B <sub>2</sub>	Cl <sub>2</sub>	Mass of B <sub>2</sub> Cl <sub>2</sub>	B <sub>2</sub> Prob <sup>y</sup>	Cl <sub>2</sub> Prob <sup>y</sup>	Probability Product	Probability
20	70	90	0.04	0.5625	0.04 × 0.5625	0.0225
	72	92	0.04	0.3750	0.04 × 0.3750	0.0150
	74	94	0.04	0.0625	0.04 × 0.0625	0.0025
21	70	91	0.32	0.5625	0.32 × 0.5625	0.1800
	72	93	0.32	0.3750	0.32 × 0.3750	0.1200
	74	95	0.32	0.0625	0.32 × 0.0625	0.0200
22	70	92	0.64	0.5625	0.64 × 0.5625	0.3600
	72	94	0.64	0.3750	0.64 × 0.3750	0.2400
	74	96	0.64	0.0625	0.64 × 0.0625	<u>0.0400</u>
Sum						1.0000

A simple mass spectrum (at unit mass resolution) would therefore contain seven peaks due to the molecular ion with the following relative intensities.

Mass of B <sub>2</sub> Cl <sub>2</sub>	Probability
90	0.0225
91	0.1800
92	0.3750
93	0.1200
94	0.2425
95	0.0200
96	0.0400

but the 92 and 94 peaks would show a further splitting if studied at much higher resolution.

#### Example 5 : MCl<sub>6</sub>

In every example considered so far the number of permutations associated with a certain selection of isotopes has been easily obtained by inspection. However, for more complex molecules we need to have a more systematic procedure.

For example in hexachloro complexes (MCl<sub>6</sub>) the Cl<sub>6</sub> unit can have seven different masses arising from the following combinations of isotopes:

1. all 35
2. five 35 + one 37
3. four 35 + two 37
4. three 35 + three 37
5. two 35 + four 37
6. one 35 + five 37
7. all 37

In each case the number of possible arrangements must be calculated; for (1) and (7) it is obviously just one, but what about the rest ?

**General Case :** would be  $n$  possible atoms divided into groups of  $r_1, r_2, \dots, r_i$  similar atoms, such that  $r_1 + r_2 + r_3 \dots + r_i = n$  (i.e.  $\sum r_i = n$ ).

If it is first assumed that the  $n$  atoms are all different isotopes then the total number of possible arrangements would (as discussed earlier) be  $n!$ . If, however, some atoms are identical then a rearrangement of these does not generate a new permutation. If  $r$  are identical then there are  $r!$  hypothetical arrangements of these  $r$  identical isotopes. The original total number of arrangements must be reduced by this number. More generally the original number of arrangements must be reduced by the number of arrangements of identical atoms in each group, i.e. by  $r_1!$  and by  $r_2!$  etc.

i.e. in general the final number of distinct arrangements would be

$$\frac{n!}{r_1! \times r_2! \times r_3! \dots \times r_i!}$$

For the particular case of  $\text{Cl}_6$  considered above (i.e. with  $n = 6$ ):

No. of $^{35}\text{Cl}$ atoms ( $r_1$ )	No. of $^{37}\text{Cl}$ atoms ( $r_2$ )	N <sup>o</sup> . of Permutations
6	0	$\frac{6!}{6! \times 0!} = 1$
5	1	$\frac{6!}{5! \times 1!} = 6$
4	2	$\frac{6!}{4! \times 2!} = 15$
3	3	$\frac{6!}{3! \times 3!} = 20$
2	4	$\frac{6!}{2! \times 4!} = 15$
1	5	$\frac{6!}{1! \times 5!} = 6$
0	6	$\frac{6!}{6! \times 0!} = 1$

These numbers must now be multiplied by the appropriate isotopic probabilities to give the overall probability of finding  $\text{Cl}_6$  unit of a particular mass.

For example, the probability of a  $\text{Cl}_6$  unit having mass 214 ( $^{35}\text{Cl}_4\ ^{37}\text{Cl}_2$ ) is given by :

$$P = 15 \times (0.75 \times 0.75 \times 0.75 \times 0.75) \times (0.25 \times 0.25) = 15 \times (0.75)^4 \times (0.25)^2 = 0.30$$

## Nuclear Magnetic Resonance : Spin -spin coupling

Protons can be regarded as spinning positive charges: they have a magnetic moment associated with this 'motion'. The magnetic moment may either be aligned with or opposed to an applied magnetic field giving two possible energy states of the proton. If the appropriate amount of energy is supplied, as radiation of a particular frequency, then a transition can be effected from the more stable to the less stable state and the photons of that frequency are absorbed. This is the basic principle of nuclear magnetic resonance (NMR) spectroscopy. The protons of hydrogen atoms in a molecule do not see an applied magnetic field in isolation, but rather the applied field modified by the local magnetic field of that part of the molecule in which they are sited. Thus protons in different parts of a molecule will absorb radiation at slightly different frequencies, and so they can be identified. An NMR spectrum will thus show many peaks corresponding to the different types of hydrogen present in a molecule e.g. those of a CH<sub>3</sub> - group, CH<sub>2</sub> - group, C(aromatic)-H etc.

A closer examination of such peaks will often reveal a fine structure which is due to 'spin-spin' interaction, i.e. the effect of the magnetic state of one group of protons on another group. For example with the ethyl group CH<sub>3</sub>-CH<sub>2</sub>- the methylene (CH<sub>2</sub>) peak is split into four sub-peaks and the methyl (CH<sub>3</sub>) peak into three. The spins of the three methyl hydrogen atoms can each be 'up' or 'down' ; for simplicity the two possible states can be designated  $\alpha$  or  $\beta$  . Overall the three methyl hydrogens may exhibit four different possible spin arrangements which are:

- |                               |                               |
|-------------------------------|-------------------------------|
| 1. all $\alpha$               | 2. two $\alpha$ , one $\beta$ |
| 3. one $\alpha$ , two $\beta$ | 4. all $\beta$                |

The local magnetic field seen by the protons of the methylene is modified, slightly, by the magnetic state of the adjacent methyl group. Furthermore as four possible magnetic states are possible for the methyl group, the methylene resonance can take place at four slightly different frequencies hence the observed splitting of the methylene peak. However the probabilities of finding the four spin configurations (1-4) are not equal. Since the probabilities of the two possible spin states,  $\alpha$  and  $\beta$  , are equal, the probability of any particular spin configuration depends simply upon the number of permutations giving rise to the configuration. They will be.

Spin $\alpha$	Spin $\beta$	No. of Permutations
3	0	$\frac{3!}{3! \times 0!} = 1$
2	1	$\frac{3!}{2! \times 1!} = 3$
1	2	$\frac{3!}{1! \times 2!} = 3$
0	3	$\frac{3!}{3! \times 0!} = 1$

Thus not only will the methylene peak be split into four sub-peaks but their relative intensities will be 1 : 3 : 3 : 1. Similar arguments show that the methylene protons will cause the methyl peak to be split into three, with relative sub-peak intensities of 1 : 2 : 1.

## **Binomial Expansion**

In Section 1 (1.10) we looked at the indexing of bracketed expressions. We can now obtain a general expression for  $(x + y)^n$ , where  $n$  is any positive integer, by considering how the above expressions are obtained during the expansion of the brackets.

For  $n = 2$ , (i.e.  $(x + y)^2$ ) there is only one way of taking  $x$  from each of the two brackets to give an  $xx$  or  $x^2$  term. Similarly there is only one way of taking one  $y$  from each bracket, giving  $yy$  or  $y^2$ . But there are two ways of taking an  $x$  from one bracket and a  $y$  from the other bracket, giving  $xy$  and  $yx$ , i.e. giving  $2xy$  in total. Hence  $(x + y)^2 = 1x^2 + 2xy + 1y^2$ .

For  $n = 3$ , (i.e.  $(x + y)^3$ ) there is again one way of taking  $x$  from each of the three brackets, giving  $xxx$  or  $x^3$ , and only one way of taking  $y$  from each of the three brackets, giving  $yyy$  or  $y^3$ . But there are three ways of selecting two  $x$ 's and one  $y$ , giving  $xyx$ ,  $xyx$  and  $yxx$ , i.e.  $3x^2y$ . Similarly, for one  $x$  and two  $y$ 's, there are three ways giving  $xyy$ ,  $yxy$  and  $yyx$ , i.e.  $3xy^2$ . Hence  $(x + y)^3 = 1x^3 + 3x^2y + 3xy^2 + 1y^3$ .

From the pattern of coefficients which is emerging it is possible to recognise that the general expression will be of the form :

$$(x + y)^n = {}^nC_0x^n + {}^nC_1x^{n-1}y + {}^nC_2x^{n-2}y^2 + \dots + {}^nC_r x^{n-r}y^r + \dots + {}^nC_n y^n,$$

where the binomial coefficients  ${}^nC_0, \dots, {}^nC_r, \dots, {}^nC_n$  represent the number of ways in which the corresponding terms  $x^n, \dots, x^{n-r}y^r, \dots, y^n$  can be formed in the expansion. These coefficients may be evaluated using the expression given on page 5.2, i.e.

$${}^nC_r = \frac{n!}{(n-r)!r!}$$

or they may be obtained from Pascal's triangle, as described on page 1.10 .