The Chemistry Maths Book

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Solutions

Chapter 21 Probability and statistics

Section 21.2

1. The following data consists of the numbers of heads obtained from 10 tosses of a coin:

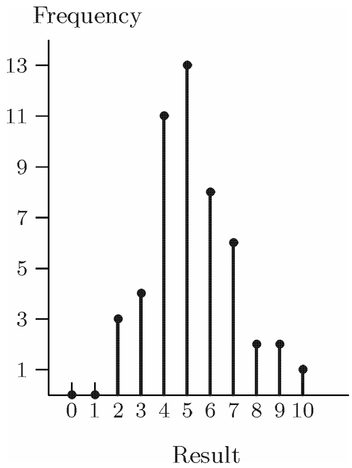
5, 5, 4, 4, 7, 4, 3, 7, 6, 4, 2, 5, 6, 4, 5, 3, 5, 4, 2, 6, 7, 2, 4, 5, 6,
5, 6, 4, 3, 4, 4, 5, 5, 6, 7, 5, 3, 6, 5, 5, 6, 7, 9, 4, 7, 9, 8, 8, 5, 10

Construct **(i)** a frequency table, **(ii)** a frequency bar chart.

(i) Table 1

Result	Frequency
0	0
1	0
2	3
3	4
4	11
5	13
6	8
7	6
8	2
9	2
10	1

(ii)



2. The following data consists of percentage marks achieved by 60 students in an examination:

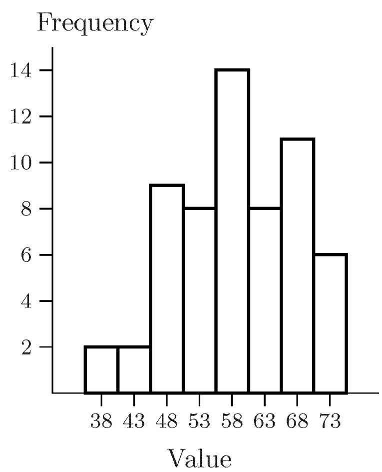
66, 68, 70, 48, 56, 54, 48, 47, 45, 53, 73, 60, 68, 75, 61, 62, 61, 61, 52, 59,
58, 56, 58, 69, 48, 62, 72, 71, 49, 69, 59, 48, 64, 59, 53, 62, 66, 55, 41, 66,
60, 38, 54, 69, 60, 53, 60, 64, 57, 54, 73, 46, 73, 58, 50, 66, 37, 60, 47, 70

Construct **(i)** a class frequency table for classes of width 5, **(ii)** the corresponding frequency histogram.

(i) Table 2

Class	Frequency
36 – 40	2
41 – 45	2
46 – 50	9
51 – 55	8
56 – 60	14
61 – 65	8
66 – 70	11
71 – 75	6

(ii)



3. Calculate the mean, mode, and median of the data in Exercise 1.

Table 3 is a summary of the properties of the data in Exercise 1, to be use here and in Exercises 5 and 6.

Table 3 x_i	n_i	$n_i x_i$	$n_i(x_i-\overline{x})^2$	$n_i x_i^2$	$n_i x_i^3$
0	0	0	0	0	0
1	0	0	0	0	0
2	3	6	31.105	12	24
3	4	12	19.714	36	108
4	11	44	16.372	176	704
5	13	65	0.629	325	1625
6	8	48	4.867	288	1728
7	6	42	19.010	294	2058
8	2	16	15.457	128	1024
9	2	18	28.577	162	1458
10	1	10	22.848	100	1000
mean values $\frac{1}{50}\sum_{i=0}^{10}$		$\overline{x}=5.2200$	$V=3.1716$	$\overline{x^2}=30.420$	$\overline{x^3}=194.58$

The mean value of the data given in Table 1 is

$$\overline{x}=\frac{1}{50}\sum_{i=1}^{8} n_i x_i$$

$$=\frac{1}{50}(0\times 0+0\times 1+3\times 2+4\times 3+11\times 4+13\times 5+8\times 6+6\times 7+2\times 8+2\times 9+1\times 10)=5.22$$

The mode and median are both 5

4. Calculate the mean, mode, and median of the data in Exercise 2 **(i)** using the raw (ungrouped) data, **(ii)** using the data grouped in classes of width 5.

(i) For the raw data in Exercise 2, if x_i are the 60 individual values,

$$\overline{x}=\frac{1}{60}\sum_{i=1}^{60} x_i=\frac{1}{60}\Big[66+68+70+48+\cdots+70\Big]=58.68$$

The most frequent value, the mode, is 60; for the even number of values, the median is the mean 59.5 of the two central values 59 and 60.

(ii) For the grouped data in Table 2,

$$\overline{x}=\frac{1}{60}\sum_{i=1}^{8} n_i x_i$$

$$=\frac{1}{60}(2\times 38+2\times 43+9\times 48+8\times 53+14\times 58+8\times 63+11\times 68+6\times 73)=58.67$$

5. Calculate the variance and standard deviation of the data in Exercise 1.

The variance is (column 4 of Table 3 in Exercise 3)

$$V(x) = \frac{1}{50}\sum_{i=0}^{10} n_i(x_i - \overline{x})^2 = 3.172$$

The corresponding standard deviation is $s = \sqrt{V} = 1.781$

6. For the data in Exercise 1, **(i)** calculate $\overline{x}, \overline{x^2}$, and $\overline{x^3}$, **(ii)** use equations (21.7) and (21.9) to compute the standard deviation and the skewness.

(i) By Table 3 of Exercise 3,

$$\overline{x} = \frac{1}{50}\sum_{i=0}^{10} n_i x_i = 5.2200\,, \quad \overline{x^2} = \frac{1}{50}\sum_{i=0}^{10} n_i x_i^2 = 30.420\,, \quad \overline{x^3} = \frac{1}{50}\sum_{i=0}^{10} n_i x_i^3 = 194.58$$

(ii) For the standard deviation,

$$V = \overline{x^2} - \overline{x}^2 = 30.420 - 27.25 = 3.1716 \quad \to \quad s = \sqrt{V} = 1.781$$

The skewness is

$$\gamma = \frac{1}{s^3}\left(\overline{x^3} - 3\overline{x}\times\overline{x^2} + 2\overline{x}^3\right) = \frac{1}{1.7809^3}\left(194.58 - 3\times 5.2200\times 30.420 + 2\times 5.220^3\right) = 0.474$$

Section 21.4

7. A set of 10 balls consists of 6 red balls, 3 blue, and 1 yellow. If a ball is drawn at random, find the probability that it is **(i)** red, **(ii)** yellow, **(iii)** red or yellow, **(iv)** not blue, **(v)** not yellow.

(i) $P(\text{red}) = 6/10 = 0.6$ **(ii)** $P(\text{yellow}) = 1/10 = 0.1$

(iii) $P(\text{red or yellow}) = P(\text{red}) + P(\text{yellow}) = 0.6 + 0.1 = 0.7$

(iv) $P(\text{not blue}) = 1 - P(\text{blue}) = 1 - 0.3 = 0.7 = P(\text{red or yellow})$

(v) $P(\text{not yellow}) = 1 - P(\text{yellow}) = 1 - 0.1 = 0.9$

8. A set of 50 numbered discs consists of 8 ones, 12 twos, 14 threes, 7 fours, and 9 fives. If one disc is drawn at random, what is the probability that its number is **(i)** 2, **(ii)** 4, **(iii)** 2 or 4, **(iv)** ≤ 4, **(v)** odd.

We have probabilities

$$P(1) = 8/50 = 0.16, \quad P(2) = 0.24, \quad P(3) = 0.28, \quad P(4) = 0.14, \quad P(5) = 0.18$$

Then **(i)** $P(2) = 0.24$ **(ii)** $P(4) = 0.14$

(ii) $P(2 \text{ or } 4) = P(2) + P(4) = 0.24 + 0.14 = 0.38$

(iii) $P(\leq 4) = P(1) + P(2) + P(3) + P(4) = 0.82$

(iv) $P(\text{odd}) = P(1) + P(3) + P(5) = 0.62$

9 Find the probabilities $P(2)$ to $P(12)$ of all the possible outcomes of two throws of a die.

Each of 36 equally probable outcomes has probability $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. If $P(k,l)$ is the probability of k followed by l then

$$P(2) = P(1,1) = 1/36$$

$$P(3) = P(1,2) + P(2,1) = 2/36$$

$$P(4) = P(1,3) + P(3,1) + P(2,2) = 3/36$$

$$P(5) = P(1,4) + P(4,1) + P(2,3) + P(3,2) = 4/36$$

$$P(6) = P(1,5) + P(5,1) + P(2,4) + P(4,2) + P(3,3) = 5/36$$

$$P(7) = P(1,6) + P(6,1) + P(5,2) + P(2,5) + (3,4) + P(4,3) = 6/36$$

$$P(8) = P(2,6) + P(6,2) + P(3,5) + P(5,3) + P(4,4) = 5/36 = P(6)$$

$$P(9) = P(5) = 4/36$$

$$P(10) = P(4) = 3/36$$

$$P(11) = P(3) = 2/36$$

$$P(12) = P(2) = 1/36$$

10 Find the probability of the following total scores from three throws of a die: **(i)** 4, **(ii)** 8, **(iii)** 4 or 8, **(iv)** more than 15.

Each of $6^3 = 216$ equally probable outcomes has probability $\frac{1}{6}\times\frac{1}{6}\times\frac{1}{6} = \frac{1}{216}$. Let $P(k,l,m)$ be the probability of *k* followed by *l* followed by *m*. Then, those equal to

(i) 4 are $(2,1,1),\ (1,2,1),\ (1,1,2)$

Therefore $P(4) = 3/216$

(ii) 8 are

$$\begin{array}{l}(6,1,1),\ (1,6,1),\ (1,1,6),\\ (5,2,1),\ (5,1,2),\ (2,5,1),\ (2,1,5),\ (1,2,5),\ (1,5,3),\\ (4,3,1),\ (4,1,3),\ (3,4,1),\ (3,1,4),\ (1,4,3),\ (1,3,4),\\ (4,2,2),\ (2,4,2),\ (2,2,4),\ (3,3,2),\ (2,3,3),\ (2,3,3)\end{array}$$

Therefore $P(8) = 21/216$

(iii) $P(4 \text{ or } 8) = P(4) + P(8) = 24/216$

(iv) $P(>15) = P(16 \text{ or } 17 \text{ or } 18)$, with outcomes

$$\begin{array}{l}16:\ (5,5,6),\ (5,6,5),\ (6,5,5),\ (6,6,4),\ (6,4,6),\ (4,6,6)\\ 17:\ (6,6,5),\ (6,5,6),\ (5,6,6)\\ 18:\ (6,6,6)\end{array}$$

Therefore $P(>15) = 10/216$

11 A particle can be in three states with energies ε_0, ε_1, and ε_2 ($\varepsilon_0 < \varepsilon_1 < \varepsilon_2$), and probability distribution $P_i = e^{-\varepsilon_i/kT}/q$ at temperature *T*. The quantity *q* is called the particle partition function. **(i)** Express *q* in terms of *T* and the energies (use $\sum_i P_i = 1$). **(ii)** Find the probability distribution in the limit **(a)** $T \to 0$**, (b)** $T \to \infty$**. (iii)** Find the (combined) probability distribution for a system of three independent particles.

(i) The quantity $P_i = e^{-\varepsilon_i/kT}/q$ is the probability that the particle be in state with energy ε_i. The (total) probability that the particle be in some state is unity (for certainty). Therefore

$$1 = \sum_{i=0}^{2} P_i = \frac{1}{q}\left[e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}\right]$$

$$\to \quad q = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}$$

(ii) We have $\left.\begin{array}{l} e^{-(\varepsilon_i-\varepsilon_j)/kT} \to 0 \\ e^{-(\varepsilon_j-\varepsilon_i)/kT} \to \infty \end{array}\right\}$ as $T \to 0$ if $\varepsilon_i > \varepsilon_j$. Then

(a) $T \to 0$ **:** $$P_0 = \frac{e^{-\varepsilon_0/kT}}{e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}} = \frac{1}{1 + e^{-(\varepsilon_1-\varepsilon_0)/kT} + e^{-(\varepsilon_2-\varepsilon_0)/kT}} \to 1$$

$$P_1 = \frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}} = \frac{1}{e^{-(\varepsilon_0-\varepsilon_1)/kT} + 1 + e^{-(\varepsilon_2-\varepsilon_1)/kT}} \to 0$$

$$P_2 = \frac{e^{-\varepsilon_2/kT}}{e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}} = \frac{1}{e^{-(\varepsilon_0-\varepsilon_2)/kT} + e^{-(\varepsilon_1-\varepsilon_2)/kT} + 1} \to 0$$

(b) $T \to \infty$ **:** We have $e^{-\varepsilon/kT} \to 1$ as $T \to \infty$. Therefore

$$q = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT} \to 3$$

$$P_i = \frac{e^{-\varepsilon_0/kT}}{q} \to \frac{1}{3}, \text{ all } i$$

(iii) For independent particles,

$$P_{i,j,k} = P_i \times P_j \times P_k = \frac{e^{-(\varepsilon_i+\varepsilon_j+\varepsilon_k)/kT}}{q^3}$$

Section 21.5

12 Find the probability that at least 3 heads are obtained from 5 tosses of **(i)** an unbiased coin, **(ii)** a coin with probability 0.6 of coming up tails.

The probability that *m* heads are obtained from 5 tosses is

$$P_m = \binom{5}{m} \times p^m q^{5-m} = \frac{5!}{m!(5-m)!} p^m q^{5-m}$$

where p is the probability of heads and $q = 1 - p$ that of tails. The probability of at least 3 heads in 5 tosses is

$$P(\geq 3\text{H}) = P_3 + P_4 + P_5 = 10p^3q^2 + 5p^4q + p^5$$

(i) $p = q = 1/2$ **:**

$$P(\geq 3\text{H}) = 16 \times \left(\frac{1}{2}\right)^5 = \frac{1}{2}$$

(ii) $p = 0.4,\ q = 0.6$ **:**

$$P(\geq 3\text{H}) = 10 \times (0.4)^3(0.6)^2 + 5 \times (0.4)^4(0.6) + (0.4)^5$$

$$= 0.2304 + 0.0768 + 0.01034 = 0.31754$$

13. A system that can exist in a number of states with energies $E_0 < E_1 < E_2 < \cdots$ has probability 0.1 of being in an excited state (with $E > E_0$). Find the probability that in 10 independent observations, the system is found in the ground state (with $E = E_0$) **(i)** every time, **(ii)** only 5 times, **(iii)** at least 8 times.

The probability that the system be in the ground state *m* times in 10 observations is

$$P_m = \binom{10}{m} \times p_g{}^m p_e{}^{10-m} = \frac{10!}{m!(10-m)!}(0.9)^m (0.1)^{10-m}$$

where $p_g = 0.9$ is the probability of the ground state and $p_e = 0.1$ that of an excited state. Then

(i) $m = 10$: $P_{10} = (0.9)^{10} \approx 0.3487$

(ii) $m = 5$: $P_5 = \binom{10}{5} \times (0.9)^5 (0.1)^5 \approx 0.0015$

(iii) $m \geq 8$: $P(\geq 8) = P_8 + P_9 + P_{10} = 45 \times (0.9)^8 (0.1)^2 + 10 \times (0.9)^9 (0.1) + (0.9)^{10}$

$\approx 0.1937 + 0.3874 + 0.3487 = 0.9298$

14. Use the probability distribution of the outcomes of throwing a pair of dice, from Exercise 9, to calculate the probability that two throws of a pair of dice have outcome **(i)** 8+12 (one eight and one twelve), **(ii)** 9+11, **(iii)** 10+10. Hence **(iv)** find the probability of outcome 20 from two throws of two dice.

There are $k = 11$ possible outcomes of a throw of two dice, with probabilities $p(2)$ to $p(12)$ given by Exercise 9. For two throws of two dice, a total outcome 20 is obtained from throws $8+12$ (one eight and one twelve), $9+11$ and $10+10$. Therefore

$$P(20) = P(8+12) + P(9+11) + P(10+10)$$

By equation (21.21),

$$P(\mathrm{A}+\mathrm{B}) = \frac{2!}{1!1!} \times p(\mathrm{A})p(\mathrm{B}) \quad \text{for A} \neq \text{B}$$

$$P(\mathrm{A}+\mathrm{A}) = \frac{2!}{2!0!} \times p(\mathrm{A})^2$$

Therefore **(i)** $P(8+12) = 2 \times p(8)p(12) = 2 \times \frac{5}{36} \times \frac{1}{36} = \frac{10}{36^2}$

(ii) $P(9+11) = 2 \times p(9)p(11) = 2 \times \frac{4}{36} \times \frac{2}{36} = \frac{16}{36^2}$

(iii) $P(10+10) = p(10)^2 = \frac{3}{36} \times \frac{3}{36} = \frac{9}{36^2}$

and **(iv)** $P(20) = \frac{10}{36^2} + \frac{16}{36^2} + \frac{9}{36^2} = \frac{35}{36^2} \approx 0.1620$

15. Use the probability distribution of the outcomes of throwing a pair of dice, from Exercise 9, to calculate the probability that three throws of two dice have total outcome 30.

For three throws of two dice, a total outcome 30 is obtained from throws

$6+12+12$ (one six and two twelves)
$7+11+12$
$8+10+12,\ 8+11+11$
$9+9+12,\ 9+10+11$
$10+10+10$

By equation (21.21),

$$P(\mathrm{A}+\mathrm{B}+\mathrm{C}) = \frac{3!}{1!1!1!}\times p(\mathrm{A})\,p(\mathrm{B})\,p(\mathrm{C}) \qquad \text{for A, B, C all different}$$

$$P(2\mathrm{A}+\mathrm{B}) = \frac{3!}{2!1!0!}\times p(\mathrm{A})^2\,p(\mathrm{B}) \qquad \text{for A and B different}$$

$$P(3\mathrm{A}) = \frac{3!}{3!0!0!}\times p(\mathrm{A})^3$$

Therefore, using the probabilities from Exercise 9,

$$P(6+12+12) = 3\times p(6)\,p(12)^2 = 3\times\frac{5}{36}\times\frac{1}{36}\times\frac{1}{36} = \frac{15}{36^3}$$

$$P(7+11+12) = 6\times p(7)\,p(11)\,p(12) = 6\times\frac{6}{36}\times\frac{2}{36}\times\frac{1}{36} = \frac{72}{36^3}$$

$$P(8+10+12) = 6\times p(8)\,p(10)\,p(12) = 6\times\frac{5}{36}\times\frac{3}{36}\times\frac{1}{36} = \frac{90}{36^3}$$

$$P(8+11+11) = 3\times p(8)\,p(11)^2 = 3\times\frac{5}{36}\times\frac{2}{36}\times\frac{2}{36} = \frac{60}{36^3}$$

$$P(9+9+12) = 3\times p(9)^2\,p(12) = 3\times\frac{4}{36}\times\frac{4}{36}\times\frac{1}{36} = \frac{48}{36^3}$$

$$P(9+10+11) = 6\times p(9)\,p(10)\,p(11) = 6\times\frac{4}{36}\times\frac{3}{36}\times\frac{2}{36} = \frac{144}{36^3}$$

$$P(10+10+10) = p(10)^3 = \frac{3}{36}\times\frac{3}{36}\times\frac{3}{36} = \frac{27}{36^3}$$

and $$P(30) = \frac{(15+72+90+60+48+144+27)}{36^3} = \frac{456}{36^3} \approx 0.0098$$

Section 21.6

16. List the permutations of 4 different objects.

There are $4!$ permutations of 4 objects; call them A, B, C, D:

ABCD, ABDC, ACDB, ACBD, ADBC, ADCB,
BACD, BADC, BCDA, BCAD, BDAC, BDCA,
CABD, CADB, CBDA, CBAD, CDAB, CDBA,
DABC, DACB, DBCA, DBAC, DCAB, DCBA

17. List the permutations of 5 different objects taken 2 at a time.

There are ${}^5P_2 = \frac{5!}{3!} = 20$ such permutations:

AB, AC, AD, AE
BA, BC, BD, BE
CA, CB, CD, CE
DA, DB, DC, DE
EA, EB, EC, ED

18. List the combinations of 5 different objects taken 2 at a time.

There are ${}^5C_2 = \binom{5}{2} = 10$ such combinations:

AB, AC, AD, AE
BC, BD, BE
CD, CE
DE

19. List the distinct permutations of the 5 objects, A, A, A, B, and B.

The 5 objects consist of two group, the A's and the B's. The $\binom{5}{3} = 10$ distinct permutations are

AAABB, AABAB, AABBA,
ABAAB, ABABA, ABBAA,
BAAAB, BAABA, BABAA,
BBAAA

20. What is the number of distinct permutations of 8 objects made up of 4 of type A, 3 of B, 1 of C?

By equation (21.24), $\frac{8!}{4!\,3!\,1!} = \frac{8\times 7\times \cancel{6}\times 5\times \cancel{4!}}{\cancel{4!}\times \cancel{6}} = 280$

21. Given an inexhaustible supply of objects A, B, and C, what is the number of distinct permutations of these taken 8 at a time?

Each of the objects A, B, and C can occur each time; for example

AAAAAAAA or ABCABCAB

Each can occur in each of the eight positions, and the total number of permutations is $3^8 = 6561$

22. **(i)** Given 3 distinguishable particles each of which can be in any of 4 states with (different) energies E_1, E_2, E_3, and E_4, **(a)** what is the total number of ways of distributing the particles amongst the states?, **(b)** how many states of the system have total energy $E_1 + E_2 + E_4$? **(ii)** Repeat **(i)** for 3 electrons instead of distinguishable particles.

(i) (a) Each particle can be in any of the 4 states. The number of distributions of distinguishable particles is $4^3 = 64$.

(b) The number of ways of distributing three distinguishable particles in 3 states is the same as the number of permutations of three different objects: $3! = 6$.

(ii) (a) For 3 indistinguishable particles and 4 states, three are occupied and one is empty, and the number of distributions is $\binom{4}{3} = 4$.

(b) There is only one way of distributing three indistinguishable particles in three states.

Section 21.7

23. The variable x can have any value in the continuous range $0 \le x \le 1$ with probability density function $\rho(x) = 6x(1-x)$. **(i)** Derive an expression for the probability, $P(x \le a)$, that the value of x is not greater than a. **(ii)** Confirm that $P(0 \le x \le 1) = 1$. **(iii)** Find the mean $\langle x \rangle$ and standard deviation σ. **(iv)** Find the probability that $\langle x \rangle - \sigma \le x \le \langle x \rangle + \sigma$.

By equation (21.33),

$$P(x_1 \le x \le x_2) = \int_{x_1}^{x_2} \rho(x)\,dx = 6\int_{x_1}^{x_2} (x - x^2)\,dx$$

$$= (3x_2^2 - 2x_2^3) - (3x_1^2 - 2x_1^3)$$

Then **(i)** $P(x \le a) = \int_0^a \rho(x)\,dx = 3a^2 - 2a^3$

(ii) $P(x \le 1) = \int_0^1 \rho(x)\,dx = 3 - 2 = 1$

(iii) By equation (21.38),

$$\sigma^2 = \int_a^b (x - \langle x \rangle)^2 \rho(x)\,dx = \langle x^2 \rangle - \langle x \rangle^2$$

where $\langle x \rangle = \int_0^1 x\rho(x)\,dx = 6\int_0^1 (x^2 - x^3)\,dx = 6\left[\frac{1}{3} - \frac{1}{4}\right] = \frac{1}{2}$

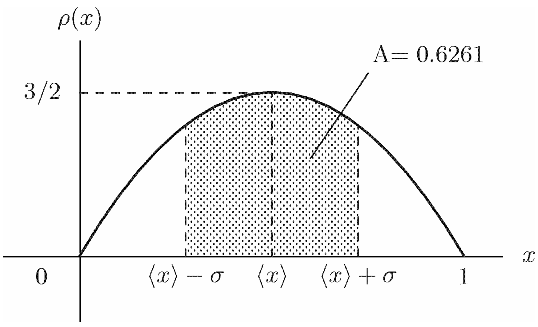
$$\langle x^2 \rangle = \int_0^1 x^2\rho(x)\,dx = 6\int_0^1 (x^3 - x^4)\,dx = 6\left[\frac{1}{4} - \frac{1}{5}\right] = \frac{3}{10}$$

Therefore $\sigma^2 = \frac{3}{10} - \left(\frac{1}{2}\right)^2 = \; \to \; \sigma = \frac{1}{\sqrt{20}}$

(iv) $P\big(\langle x \rangle - \sigma \le x \le \langle x \rangle + \sigma\big) = \int_{\langle x \rangle - \sigma}^{\langle x \rangle + \sigma} \rho(x)\,dx$

$$= \left[3\big(\langle x \rangle + \sigma\big)^2 - 2\big(\langle x \rangle + \sigma\big)^3\right] - \left[3\big(\langle x \rangle - \sigma\big)^2 - 2\big(\langle x \rangle - \sigma\big)^3\right]$$

$$= 12\langle x \rangle \sigma - 12\langle x \rangle^2 \sigma - 4\sigma^3 = \frac{7}{5\sqrt{5}} \approx 0.6261$$



24. The variable r can have any value in the range $r = 0 \to \infty$ with probability density function $\rho(r) = 4r^2 e^{-2r}$. Derive an expression for the probability $P(0 \le r \le R)$ that the variable has value not greater than R.

$$P(0 \le r \le R) = \int_0^R \rho(r)\,dr = \int_0^R 4r^2 e^{-2r}\,dr$$

$$\text{(by parts)} \quad = \Big[-2r^2 e^{-2r}\Big]_0^R + \Big[-2re^{-2r}\Big]_0^R + \Big[-e^{-2r}\Big]_0^R$$

$$= 1 - e^{-2R}\Big[1 + 2R + 2R^2\Big]$$

25. Confirm that $p(r)$ in Exercise 24 is the radial density function (in atomic units) of the 1*s* orbital of the hydrogen atom. Find **(i)** the mean value $\langle r\rangle$, **(ii)** the standard deviation σ, **(iii)** the most probable value of r.

The radial wave function of the hydrogen 1*s*-orbital is $R_{1,0}(r) = 2r^{-r}$ (Table 14.2 with $Z = 1$). The corresponding radial density is

$$p(r) = r^2 R_{1,0}^2(r) = 4r^2 e^{-2r} \qquad \text{(Example 21.14)}$$

We use the standard integral $\int_0^\infty r^n e^{-ar}\,dr = \frac{n!}{a^{n+1}}$. Then

(i) $$\langle r\rangle = \int_0^\infty rp(r)\,dr = 4\int_0^\infty r^3 e^{-2r}\,dr = 4 \times \frac{3!}{2^4} = \frac{3}{2}$$

(ii) We have $$\langle r^2\rangle = \int_0^\infty r^2 p(r)\,dr = 4\int_0^\infty r^4 e^{-2r}\,dr = 4 \times \frac{4!}{2^5} = 3$$

Therefore $$\sigma^2 = \langle r^2\rangle - \langle r\rangle^2 = 3 - 9/4 = 3/4 \quad \to \quad \sigma = \frac{\sqrt{3}}{2}$$

(iii) For the most probable value of r,

$$\frac{dp}{dr} = 8r(1-r)e^{-2r} = 0 \text{ when } r = 1$$

Section 21.10

26. **(i)** Find the linear straight-line fit for the following data points. **(ii)** If the errors in y are all equal to $\sigma = 1$, find estimates of the errors in the slope and intercept of the line.

x	1	2	3	4	5	6	7	8	9	10	11	12
y	4.4	4.9	6.4	7.3	8.8	10.3	11.7	13.2	14.8	15.3	16.5	17.2

(i) By equations (21.54), the slope m and intercept c of the straight-line $y = mx + c$ are

$$m = \frac{\overline{xy} - \overline{x}\,\overline{y}}{\overline{x^2} - \overline{x}^2}, \qquad c = \overline{y} - m\overline{x}$$

The results of the (spreadsheet) computation are summarized in Table 4.

Table 4	x_i	y_i	x_i^2	$x_i y_i$
	1	4.4	1	4.4
	2	4.9	4	9.8
	3	6.4	9	19.2
	4	7.3	16	29.2
	5	8.8	25	44.0
	6	10.3	36	61.8
	7	11.7	49	81.9
	8	13.2	64	105.6
	9	14.8	81	133.2
	10	15.3	100	153.0
	11	16.5	121	181.5
	12	17.2	144	206.4
mean values $\frac{1}{12}\sum_{i=1}^{12}$	$\overline{x} = 6.5$	$\overline{y} = 10.9$	$\overline{x^2} = 54.17$	$\overline{xy} = 85.83$

Then $m = 1.26$, $c = 2.73$, and $y = 1.26x + 2.73$

(ii) By equation (21.55), estimates of the error in the slope and intercept are, for $\sigma = 1$,

$$\sigma_m^2 = \frac{1}{12\left(\overline{x^2} - \overline{x}^2\right)} = 0.007 \quad \to \quad \sigma_m \approx 0.08$$

$$\sigma_c^2 = \frac{\overline{x^2}}{12\left(\overline{x^2} - \overline{x}^2\right)} = 0.38 \quad \to \quad \sigma_c \approx 0.62$$

and $y = mx + c$ where $y = 1.26 \pm 0.08, \quad c = 2.73 \pm 0.62$

27. The results of measurements of the rate constant of the second-order decomposition of an organic compound over a range of temperatures are:

T/K	282.3	291.4	304.1	313.6	320.2	331.3	343.8	354.9	363.8	371.7
$k/10^{-3}\ \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	.0249	.0691	0.319	0.921	1.95	5.98	19.4	57.8	114.	212.

The temperature dependence of the rate constant is given by the Arrhenius equation $k = Ae^{-E_a/RT}$, or $\ln k = -E_a/RT + \ln A$, in which the activation energy E_a and pre-exponential factor A may be assumed to be constant over the experimental range of temperature. A plot of $\ln k$ against $1/T$ should therefore be a straight line. **(i)** Construct a table of values of $1/T$ and $\ln k$, and determine the linear least-squares fit to the data assuming only k is in error. **(ii)** Calculate the best values of E_a and A. **(iii)** Assuming that the errors in $\ln k$ are all equal to $\sigma = 0.1$, use equations (21.55) to find estimates of the errors in E_a and A.

(i) The results of the (spreadsheet) computation is summarized in Table 5, with values of $1/T$ and $\ln k$ listed as the dimensionless quantities $x = \text{K}/T$ and $y = \ln\left[k/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\right]$, respectively.

Table 5	x_i	y_i	x_i^2	$x_i y_i$
	0.0035423	–10.600643	0.000013	–0.037551
	0.0034317	–9.5799558	0.000012	–0.032876
	0.0032884	–8.0503195	0.000011	–0.026473
	0.0031888	–6.9900505	0.000010	–0.022290
	0.0031230	–6.2399259	0.000010	–0.019488
	0.0030184	–5.1193347	0.000009	–0.015452
	0.0029087	–3.9424822	0.000008	–0.011467
	0.0028177	–2.8507665	0.000008	–0.008033
	0.0027488	–2.1715568	0.000008	–0.005969
	0.0026903	–1.5511690	0.000007	–0.004173
mean values $\frac{1}{10}\sum_{i=1}^{10}$	$\bar{x} = 0.003076$	$\bar{y} = -5.70962$	$\overline{x^2} = 9.54\times10^{-6}$	$\overline{xy} = -0.01838$

By equations (21.54), the slope m and intercept c of the straight-line fit $y = mx + c$ are $m = -1.076\times10^4$ and $c = 27.38$. Then $y = -1.076\times10^4 x + 27.38$, and

$$\ln\left[k/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\right] = -1.076\times10^4 \times \frac{\text{K}}{T} + 27.38$$

(ii) We have $\ln k = -E_a/RT + \ln A$ (with k and A in the same units of $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$). Therefore

$$E_a/R = 1.076\times10^4\ \text{K} \quad\to\quad E_a = (1.076\times10^4)\times(8.315\ \text{J mol}^{-1}) = 89.5\ \text{kJ mol}^{-1}$$

Also $$\ln\left[A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\right] = 27.38 \quad\to\quad A = e^{27.38}\text{dm}^3\text{mol}^{-1}\text{s}^{-1} = 7.8\times10^{11}\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$$

(iii) By equations (21.55), with $\sigma = 0.1$, .

$$\sigma_m = 115 \;\rightarrow\; \Delta E_\mathrm{a} = 115 \times 8.315 \text{ J mol}^{-1} \approx 1 \text{ kJ mol}^{-1}$$

$$\rightarrow\; E_\mathrm{a} = 89.5 \pm 1 \text{ kJ mol}^{-1}$$

$$\sigma_c = 0.355 \;\rightarrow\; A = e^{27.38 \pm 0.36}$$

$$\rightarrow\; \approx 5 \times 10^{11} < A < \approx 11 \times 10^{11}$$