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MEMORANDUM

To: T.C. Greengard
From: B.P. Doty
Date: July 16, 1987

Subject: Revised Analysis of 881 Hillside Radiometric Data

As you are aware, our recent report on RI activities at the 881 Hillside (Rockwell International, 1987b) reported low level plutonium-239 and americium-241 contamination of ground and surface waters in the vicinity of the 881 Hillside. The contamination was at least an order of magnitude lower than the drinking water standards for these elements. The report was prepared quickly to meet the regulatory deadline and was based on laboratory data for which QA/QC were not complete. The laboratory has provided revised results (Rockwell International, 1987a) that do not clearly indicate radionuclide contamination of ground water (surface water data have not yet been evaluated). The amended data are presented in Table 1.

The amended data indicate that plutonium and americium contamination of the ground water is highly unlikely. A histogram of the frequency of plutonium measurements occurring in 0.2 pCi/l ranges is presented as Figure 1. Most of the values fall in the range of 0.0 to less than 0.2 pCi/l and values less than 0.6 are visually within the same population (distribution is probably log-normal). Values of 0.8 pCi/l and greater appear to be outside the reasonable range for the low concentration population. However, the higher values do not appear to be significantly different from the low valued population when the range is considered.

Ranges are reported for radiometric analyses because the disintegration of radioactive elements is a probabilistic event, i.e., there is a certain probability that successive measurements of particle emission from the same sample will vary over a certain range. It can be shown that a single observation from a distribution that is binomial, as is true of radioactive disintegration rates, gives both an estimate of the mean and an estimate of the variance of the distribution (Friedlander et al., 1964 - page 175). Friedlander et al. (1964) go on to show that the standard deviation (square root

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of the variance) is equal to the square root of the ratio of the disintegration rate to the time of counting (in actual, unscaled counts). Hence, we can be reasonably confident that the "true" value is in a band defined by the reported value, plus or minus the range.

This concept appears validated in the plutonium data under consideration by the fact that successive analyses of 3 of the 5 high valued wells fall within the low valued population. The remaining two wells do not have repeated analyses but have ranges sufficiently great that the "true" value could be in the low valued population. These factors are shown on Table 2 and are indicated on Figure 1.

Similar logic can be applied to the americium data. Most of the values fall in the range of 0.0 to less than 0.2 pCi/l (Figure 2). There are four higher valued results, one of which has a second analysis within the low valued population. Two of the others have ranges that could easily place the "true" value in the low valued population. Only one of the americium results (well 9-74) is significantly high. This may be due to actual elevation of americium in the ground water near the well or may be due to laboratory error or interferences (QA/QC is not complete for the 9-74 data).

Therefore, it is concluded that plutonium and americium contamination of ground water in the vicinity of the 881 Hillside Area is unlikely. However, it is recommended that monitoring be continued to validate this conclusion.

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Table 1. 881 Hillside - Plutonium and Americium
 Radiometric Data

Well	Date	Pu-239	Range	Am-241	Range
1 - 71	3/ 9/ 87	.9	.63	.0	1.8
1 - 71	5/ 1/ 87	.1	1.5	.0	2.6
9 - 74	5/ 10/ 87	.55	.39	6.6	3.9
54 - 86	5/ 28/ 87	.008	.75	.9	3.7
55 - 86	5/ 19/ 87	.03	.65	.0	4.2
55 - 86	5/ 28/ 87	.07	.82	.0	1.2
59 - 86	4/ 9/ 87	.00	.84	.0	1.6
59 - 86	4/ 30/ 87	.9	1.1	.0	1.3
61 - 86	3/ 11/ 87	4.0	6.9	.29	.86
61 - 86	5/ 5/ 87	.29	.86	.0	1.3
62 - 86	4/ 10/ 87	.0	1.1	.0	1.3
62 - 86	4/ 30/ 87	.0	1.3	.0	1.4
64 - 86	4/ 29/ 87	.2	1.1	.0	1.4
65 - 86	5/ 15/ 87	.00	.65	.0	1.3
65 - 86	5/ 29/ 87	.16	.78	.0	1.2
68 - 86	4/ 29/ 87	.00	.85	2.3	2.9
69 - 86	4/ 29/ 87	.0	2.1	.0	1.3
2 - 87	5/ 29/ 87	.9	1.1	.0	6.0
3 - 87	6/ 16/ 87	.2	1.1	.0	4.1
4 - 87	5/ 20/ 87	.0	.55	.0	2.6
5 - 87	6/ 12/ 87	.00	.55	.0	3.0
8 - 87	6/ 15/ 87	1.7	1.9	.0	1.5

Notes:

All data are in pCi/l.
 Range (standard deviation) indicates numerical band
 in which successive measurements can be
 confidently expected to fall.
 Data revised July 10, 1987 except for data for well
 9-74 which QA/QC is not complete.

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Table 2. Explanation of Apparent High Plutonium Values

Well	Range Includes Low Valued Population	Second Analysis Falls in Low Valued Population
1-71	X	X
59-86	X	X
61-86	X	X
2-87	X	
8-87BR	X	

Table 3. Explanation of Apparent High Americium Values

Well	Range Includes Low Valued Population	Second Analysis Falls in Low Valued Population
9-74	?	
54-86	X	
61-86	X	X
68-86	X	

Notes:

9-74 data QA/QC not complete.

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REFERENCES

Friedlander, G., J.W. Kennedy, and J.M. Miller, 1964, Nuclear and Radiochemistry, Second Edition, John Wiley & Sons, New York.

Rockwell International, 1987a, Remedial Investigation, 881 Hillside, General Laboratory, J.A. Blair, June 23, amended July 10.

Rockwell International, 1987b, Remedial Investigation Report for High Priority Sites (881 Hillside Area), Draft, July 1.

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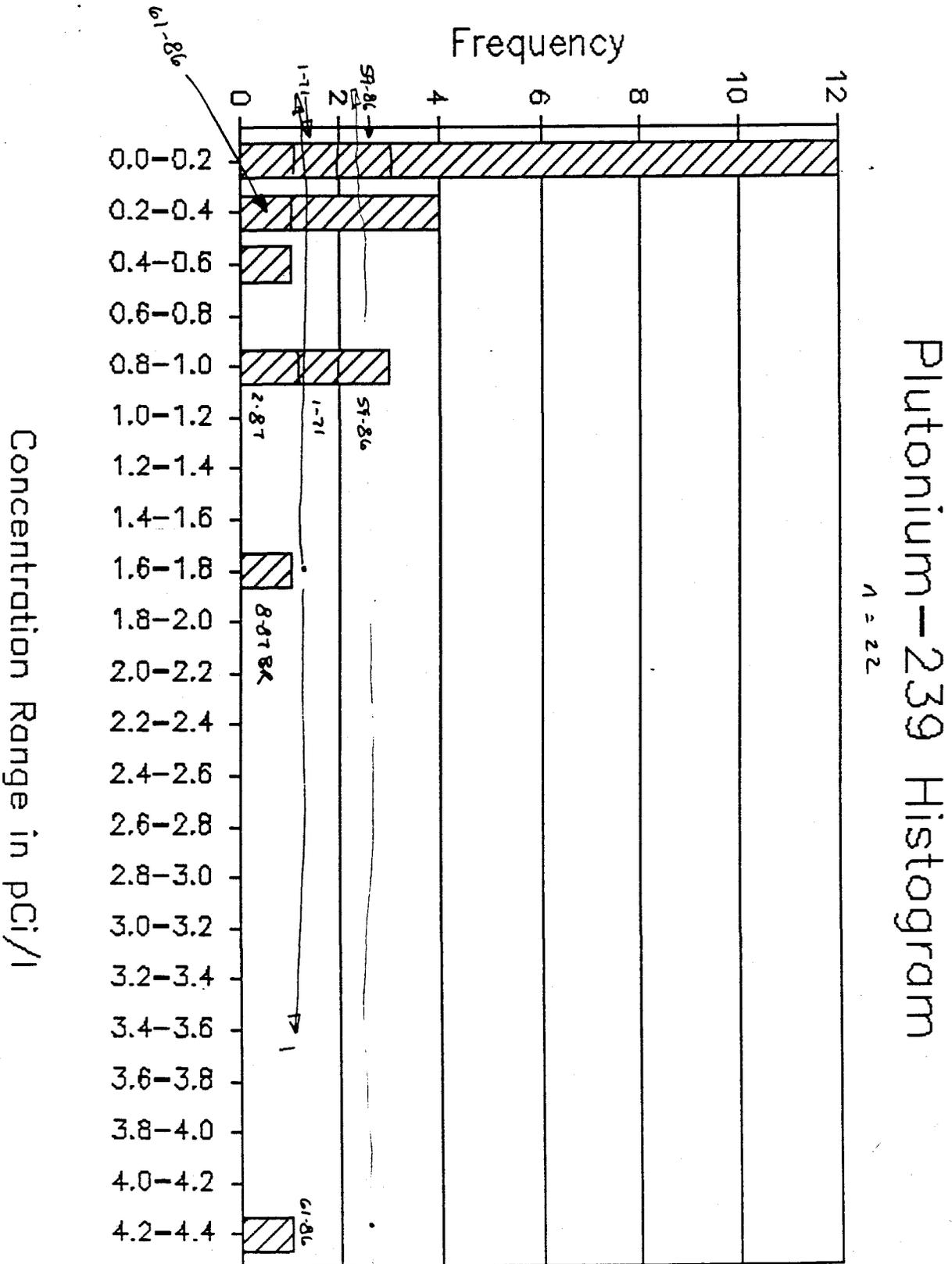


Figure 1. Plutonium-239 HISTOGRAM

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Americium-241 Histogram

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Concentration Range in pCi/l

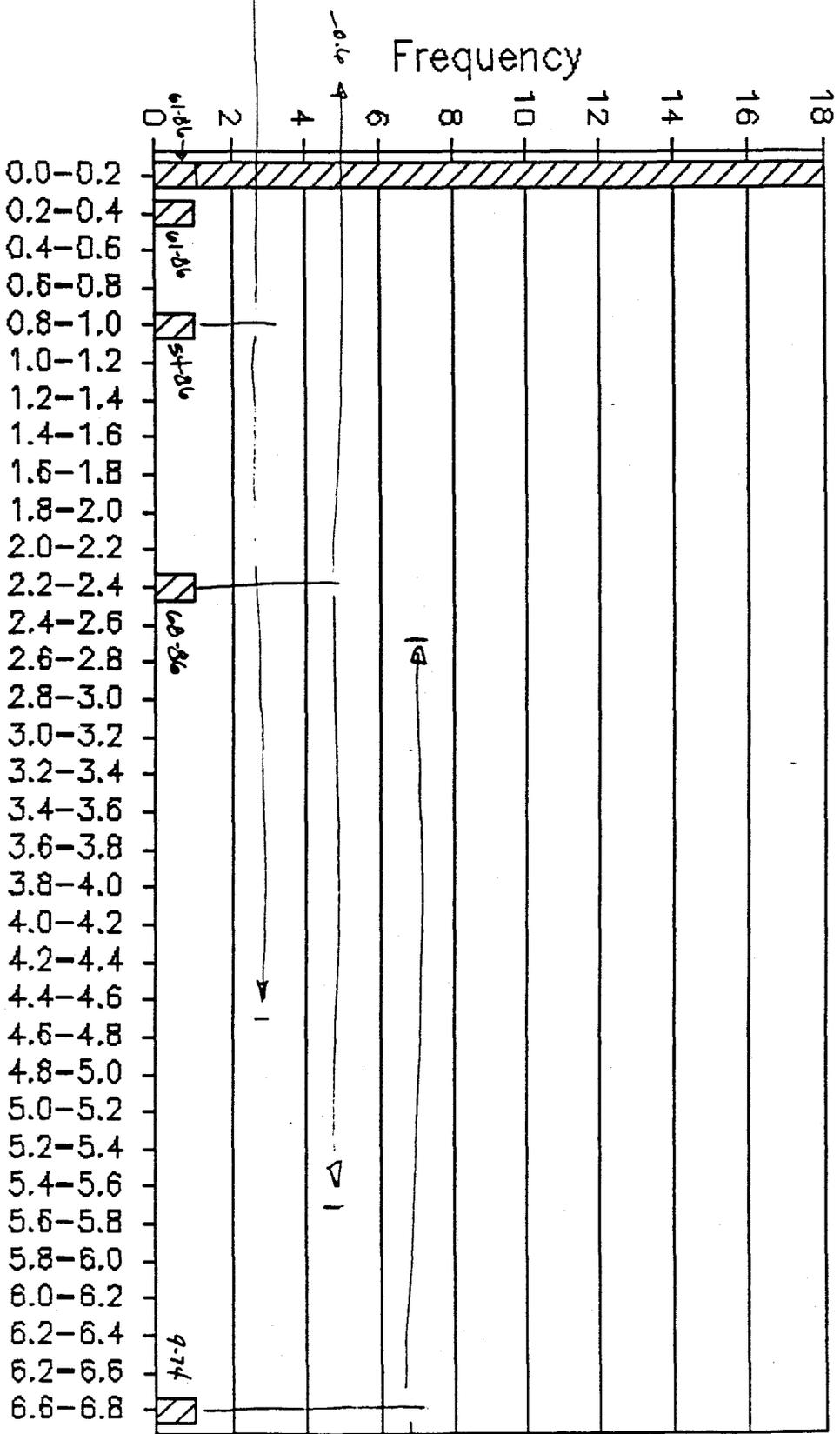


FIGURE 2. AMERICIUM-241 HISTOGRAM

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Statistical Considerations in Radioactivity Measurements

The radioactive-decay law discussed in chapter 3 describes the average behavior of a sample of radioactive atoms. In measurements of radioactive decay we are concerned with observations which show fluctuations about the average behavior predicted by the decay law. Therefore we shall discuss in this chapter the applications of statistical methods to the treatment of radioactivity measurements.

A. DATA WITH RANDOM FLUCTUATIONS

Consider the set of data actually obtained with a Geiger counter measuring a "steady" source, as given in table 6-1. The number of counts recorded per minute (the counting rate) is clearly not uniform. Which minute gave the most accurate result? The best thing we can do is to compute the arithmetic mean (the average value) and consider it as representing the proper counting rate. What we are trying to do is to estimate from a finite number of observations the results of an essentially infinite number of observations. In particular, we wish to estimate the average value that we would find and the distribution of the observed values about that average.

Average Value. If the determinations, minute by minute, are denoted by x_1, x_2, \dots, x_i for the first, second, \dots i th minute, then the arithmetic mean value \bar{x} is, by definition,

$$\bar{x} = \frac{1}{N_0} \sum_{i=1}^{i=N_0} x_i, \quad (6-1)$$

where N_0 is the number of values of x to be averaged. For the counting rates in the table $\bar{x} = 990/10 = 99.0$.

Table 6-1

Minute	Counts	Δ_i	Δ_i^2
1	89	-10	100
2	120	+21	441
3	94	-5	25
4	110	+11	121
5	105	+6	36
6	108	+9	81
7	85	-14	196
8	83	-16	256
9	101	+2	4
10	95	-4	16
Totals	990	0	1276

This average value is the best estimate that we can make of the "true" average, \bar{x} , which is the average we would find for an infinite number of observations.

Standard Deviation. The distribution of the observed results about \bar{x} , is a measure of the precision of the data and can be described by giving all of the "moments" of the distribution; that is, the quantities

$$\frac{1}{N_0} \sum_{i=1}^{N_0} (x_i - \bar{x})^n \quad (6-2)$$

for all values of n . The first moment ($n = 1$) will always vanish because of the definition of \bar{x} ; the other odd moments [expression (6-2) with " n " an odd number] will vanish only if the distribution is symmetrical about \bar{x} , and \bar{x} is then the most probable value of x . Usually just the second moment [expression (6-2) with $n = 2$, called the variance and denoted by σ_x^2] is given in practice. The square root of the variance is called the standard deviation σ_x . This quantity is particularly significant because of the form of the so-called normal distribution law which is expected to describe the distribution of experimental results with random errors:

$$P(x) dx = \frac{1}{\sqrt{2\pi\sigma_x^2}} \exp \left[\frac{-(x - \bar{x})^2}{2\sigma_x^2} \right] dx, \quad (6-3)$$

where $P(x) dx$ is the probability of observing a value of x in the interval $x \rightarrow x + dx$.

In our example, which contains a finite number of observations, we do not know \bar{x} ; we have only an estimate of it: \bar{x} . Under these circumstances the

best possible estimate of the variance is

$$\sigma_x^2 = \frac{1}{N_0 - 1} \sum_{i=1}^{N_0} (x_i - \bar{x})^2. \quad (6-4)$$

For the data in table 6-1 we compute $\sigma_x^2 = 1276/9 = 141.8$; $\sigma_x = 11.9$. The difference between equations (6-2) and (6-4) is noteworthy. The division by $(N_0 - 1)$ in (6-4) instead of by N_0 is a consequence of estimating the unknown quantity \bar{x} , from N_0 observations; this estimation uses up one of the observations and leaves only $(N_0 - 1)$ independent quantities for the estimation of the variance. The validity of this reasoning becomes clear when we consider the extreme case of only a single observation. Evidently, from a single observation we can have no idea of the precision of the measurement, unless special assumptions are made. This problem is a fundamental one in statistical analysis and is discussed in standard texts on the subject (cf., for example, B1 and F1).

Precision of Average Value. In the preceding discussion we have been concerned with estimating, from N_0 observations, the results that would be obtained from a very large number of observations. It is now necessary to discuss the precision of our estimation which is not to be confused with the precision of the data, although the two quantities are related. We are here concerned with two things:

1. The distribution of the values of \bar{x} given by (6-1) from many sets of experiments, each with a finite N_0 .
2. The distribution of the quantities σ_x^2 obtained from the same sets of observations by (6-4).

The formal statistical analysis of these two problems, as discussed in standard texts (F1), is contained in the χ^2 -test of the randomness of the data, the t -test of the reliability of \bar{x} as an estimate of \bar{x} , and the F -test of the reliability of σ_x^2 as an estimate of the true variance of the sample.

Our main interest is in the first question, the reliability of \bar{x} ; a measure of this reliability is the *variance of a mean* which is estimated by the variance of the set of observations divided by N_0 :

$$\sigma_{\bar{x}}^2 = \frac{\sigma_x^2}{N_0} = \frac{1}{N_0(N_0 - 1)} \sum_{i=1}^{N_0} (x_i - \bar{x})^2. \quad (6-5)$$

The quantity $\sigma_{\bar{x}}^2$ is our best estimate of the second moment of the distribution of average values that would be found from an infinite number of *sets of experiments*, each containing N_0 observations of which table 6-1 is an ~~example~~. The value of $\sigma_{\bar{x}}$ from table 6-1 is $\sqrt{141.8/10} = 3.76$.

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The significance of this quantity, for a normal distribution, is found in the statement that the probability of observing a value of \bar{x} between \bar{x} and $\bar{x} + d\bar{x}$ is

$$P(\bar{x}) d\bar{x} = \frac{1}{\sqrt{2\pi\sigma_{\bar{x}}^2}} \exp \left[-\frac{(\bar{x} - \bar{x}_t)^2}{2\sigma_{\bar{x}}^2} \right] d\bar{x}.$$

Rejection of Data. The question often arises whether a particular datum should be rejected because of its relatively large deviation from the mean. In table 6-1 the observation of 120 counts during the second minute is suspect, as perhaps, though to a lesser degree, is the observation of 83 counts during the eighth minute. This is not necessarily to say that these observations are wrong (that the error is systematic rather than random), but that deviations of this magnitude among a small number of observations may have an undue influence on the mean value that is computed. Thus the criteria for rejection should consider not only the magnitude of the deviation but also the number of observations made. A criterion established by Chauvenet which includes both factors (the magnitude of the deviation and the number of observations) allows the rejection of an observation if deviations from the mean that are equal to or greater than the one in question have a probability of occurrence that is less than $1/(2N_0)$. In our example the counting rate during the second minute may be rejected only if the probability of observing counting rates that deviate by at least 21 counts from the mean of 99 counts is less than 0.05. We compute this probability by using (6-3) to obtain the probability P of observing a count between 78 and 120:

$$1 - P = \int_{78}^{120} \frac{1}{\sqrt{2\pi \cdot 141.8}} \exp \left[\frac{-(x - 99)^2}{2 \cdot 141.8} \right] dx.$$

The value of the integral, as found in the *Handbook of Chemistry and Physics*, is 0.92; thus $1 - P$ is 0.08 and the datum must be retained. If N_0 had been six, or less, then the datum would have been rejected. When a datum is rejected, a new \bar{x} must be computed, and Chauvenet's criterion may be applied to the remaining suspect data, but with N_0 being decreased by one each time that an observation is excluded.

B. PROBABILITY AND THE COMPOUNDING OF PROBABILITIES

The ideas and definitions just presented may be applied, with varying degrees of usefulness, to any set of data, whether or not strictly random phenomena are involved. Before proceeding, we must consider the concept of probability in greater detail. As illustrations we shall investigate the answers to questions such as these:

1. What is the probability that a card drawn from a deck will be an ace?
2. If a coin is flipped twice, what is the probability that it will fall "heads up" both times?
3. Given a sample of a radioactive material, what is the probability that exactly 100 disintegrations will occur during the next minute?

We shall define probability in this way: given a set of N_0 objects (or events, or results, etc.) containing n_1 objects of the first kind, n_2 objects of the second kind, and n_i objects of the i th kind, the probability p_i that an object specified only as belonging to the set is of the i th kind is given by $p_i = n_i/N_0$. By applying this definition we find that the probability that one card drawn from a full deck will be an ace is just $\frac{1}{13}$.

We may now rewrite the definition of the average value \bar{x} of a set of quantities x_i , taking into account the possibility that any particular value may appear several, say n_i , times. Then

$$\bar{x} = \frac{1}{N_0} \sum n_i x_i = \sum p_i x_i.$$

This may be generalized, and the expression for the average value of any function of x is

$$\overline{f(x)} = \sum p_i f(x_i). \quad (6-6)$$

In particular,

$$\sigma_x^2 = \sum p_i (x_i - \bar{x})^2 = \overline{x^2} - \bar{x}^2 \quad (6-7)$$

a result that will be useful to us later.

In experimental measurements we may make a large number K of observations and find the i th result k_i times. Now the ratio k_i/K is not the probability p_i of the i th result as we have defined it, but for our purposes we assume that k_i/K approaches arbitrarily closely to p_i as K becomes very large:

$$\lim_{K \rightarrow \infty} \frac{k_i}{K} = p_i.$$

This assumption is not subject to mathematical proof because a limit may not be evaluated for a series with no law of sequence of terms.

Addition Theorem. We turn now to the compounding of several probabilities and consider first the addition theorem. Given a set of N_0 objects (or events, or results, etc.) containing n_i objects of the kind a_i and given that the kinds a_1, a_2, \dots, a_i have no members in common, the probability that one of the N_0 objects belongs to a combined group $a_1 + a_2 + \dots + a_i$ is just $\sum_{i=1}^i p_i$. Thus for two mutually exclusive events with probabilities p_1 and p_2 the probability of one or the other occurring is just $p_1 + p_2$. When one card is drawn from a full deck, the chance of its being either a five or a ten is $\frac{1}{13} +$

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$\frac{1}{52} = \frac{1}{13}$. (When one draws one card while already holding, say, four cards, none of which is a five or ten, the probability then of getting either a five or a ten is slightly greater, $\frac{1}{52} + \frac{1}{52} = \frac{1}{26}$, provided that there is available no information regarding the identity of other cards that may already have been withdrawn.) When a coin is tossed, the probability of either "heads" or "tails" is $\frac{1}{2} + \frac{1}{2} = 1$.

Multiplication Theorem. Another type of compounding of probabilities is described by the multiplication theorem. If the probability of an event i is p_i , and if after i has happened the probability of another event j is p_j , then the probability that first i and then j will happen is $p_i \times p_j$. If a coin is tossed twice, the probability of getting "heads" twice is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. If two cards are drawn from an initially full deck, the probability of two aces is $\frac{4}{52} \times \frac{3}{51}$. The probability of four aces in four cards drawn is $\frac{4}{52} \times \frac{3}{51} \times \frac{2}{50} \times \frac{1}{49}$. (The probability of drawing five aces in five cards is $\frac{4}{52} \times \frac{3}{51} \times \frac{2}{50} \times \frac{1}{49} \times \frac{0}{48} = 0$.)

Binomial Distribution. The binomial distribution law treats one fairly general case of compounding probabilities and can be derived by the application of the addition and multiplication theorems. Given a very large set of objects in which the probability of occurrence of an object of a particular kind w is p , then, if n objects are withdrawn from the set, the probability $W(r)$ that exactly r of the objects are of the kind w is given by

$$W(r) = \frac{n!}{(n-r)!r!} p^r (1-p)^{n-r}. \quad (6-8)$$

To see how this combination of terms actually represents the probability in question, think for a moment of just r of the n objects. That the first of these is of the kind w has the probability p ; that the first and second are of the kind w has the probability p^2 , etc., and the probability that all r objects are of the kind w is p^r . But, if exactly r of the n objects are to be of this kind, the remaining $n-r$ objects must be of some other kind; this probability is $(1-p)^{n-r}$. Thus we see that for a particular choice of r objects out of the n objects the probability of exactly r of kind w is $p^r(1-p)^{n-r}$; this particular choice is not the only one. The first of the r objects might be chosen (from the n objects) in n different ways, the second in $n-1$ ways, the third in $n-2$ ways, and the r th in $n-r+1$ ways. The product of these terms, $n(n-1)(n-2) \cdots (n-r+1)$, is $n!/(n-r)!$, and this coefficient must be used to multiply the probability just found. But this coefficient is actually too large in that it not only gives the total number of possible arrangements of the objects in the way required but also includes the number of arrangements which differ only in the order of selection of the r objects. So we must divide by the number of permutations of r objects which is $r!$. Thus the final coefficient is $n!/(n-r)!r!$, which is that in (6-8). The law (6-8) is known as the binomial distribution law because this coefficient is just the

coefficient of $x^r y^{n-r}$ in the binomial expansion of $(x + y)^n$. Since in (6-8),

$$x + y = p + (1 - p),$$

we have

$$\sum_{r=0}^n W(r) = 1,$$

and the binomial distribution is seen to be normalized.

C. RADIOACTIVITY AS A STATISTICAL PHENOMENON

Binomial Distribution for Radioactive Disintegrations. We may apply the binomial distribution law to find the probability $W(m)$ of obtaining just m disintegrations in time t from N_0 original radioactive atoms. We think of N_0 as the number n of objects chosen for observation (in our derivation of the binomial law), and we think of m as the number r that is to have a certain property (namely, that of disintegrating in time t), so that for this case the binomial law becomes

$$W(m) = \frac{N_0!}{(N_0 - m)! m!} p^m (1 - p)^{N_0 - m}. \quad (6-9)$$

Now the probability of an atom not decaying in time t , $1 - p$ in (6-9), is given by the ratio of the number N that survive the time interval t to the initial number N_0 ,

$$\frac{N}{N_0} = e^{-\lambda t};$$

p is then $1 - e^{-\lambda t}$. We now have

$$W(m) = \frac{N_0!}{(N_0 - m)! m!} (1 - e^{-\lambda t})^m (e^{-\lambda t})^{N_0 - m}. \quad (6-10)$$

Time Intervals between Disintegrations. Since the time of Schweidler's derivation of the exponential decay law from probability considerations, the applicability of these statistical laws to the phenomena of radioactivity has been tested in a number of experiments. As an example of the positive evidence obtained, we consider the distribution of time intervals between disintegrations. The probability of this time interval having a value between t and $t + dt$, which we write as $P(t) dt$, is given by the product of the probability of no disintegration between 0 and t and the probability of a disinte-

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gration between t and $t + dt$. The first of these two probabilities is given by (6-10) with $m = 0$:

$$W(0) = \frac{N_0!}{N_0!0!} (1 - e^{-\lambda t})^0 (e^{-\lambda t})^{N_0} = e^{-N_0 \lambda t}.$$

(Notice that $0! = 1$.) The probability of any one of the N_0 atoms disintegrating in the time dt is clearly, from the addition theorem, $N_0 \lambda dt$. [See chapter 1, p. 5, or obtain this result as $W(1)$ from equation 6-10 with $m = 1$, t replaced by dt , and all terms in $(dt)^2$ and higher powers of dt neglected.] Then

$$P(t) dt = N_0 \lambda e^{-N_0 \lambda t} dt. \tag{6-11}$$

Experiments designed to test this result usually measure a large number s of time intervals between disintegrations and classify them into intervals differing by the short but finite length Δt ; then the probability for intervals between t and $t + \Delta t$ should be $N_0 \lambda e^{-N_0 \lambda t} \Delta t$, and the number of measured intervals between t and $t + \Delta t$ should be $s N_0 \lambda e^{-N_0 \lambda t} \Delta t$. For example, Feather found experimentally that the logarithm of the number of intervals between t and $t + \Delta t$ is proportional to t , as required by this formula.

Average Disintegration Rate. Another application of the binomial law to radioactive disintegrations may be seen if we calculate the average value of a set of numbers obeying the binomial distribution law. For the moment we shall revert to the notation of (6-8) and for further convenience represent $1 - p$ by q :

$$W(r) = \frac{n!}{(n-r)!r!} p^r q^{n-r}. \tag{6-12}$$

The average value to be expected for r is obtained from (6-6):

$$\bar{r} = \sum_{r=0}^{r=n} r W(r) = \sum_{r=0}^{r=n} r \frac{n!}{(n-r)!r!} p^r q^{n-r}.$$

To evaluate this awkward-appearing summation, consider the binomial expansion of $(px + q)^n$:

$$(px + q)^n = \sum_{r=0}^{r=n} \frac{n!}{(n-r)!r!} p^r x^r q^{n-r} = \sum_{r=0}^{r=n} x^r W(r).$$

Differentiating with respect to x , we obtain

$$np(px + q)^{n-1} = \sum_{r=0}^{r=n} r x^{r-1} W(r). \tag{6-13}$$

Now letting $x = 1$ and using $q = 1 - p$, we have the desired expression

$$np = \sum_{r=0}^{r=n} r W(r) = \bar{r}.$$

This result should not be surprising; it means that the average number \bar{r} of the n objects which are of the kind w is just n times the probability for any given one of the objects to be of the kind w .

The foregoing result may be interpreted for radioactive disintegration if n is set equal to N_0 and $p = 1 - e^{-\lambda t}$, as before. Then the average number M of atoms disintegrating in the time t is $M = N_0(1 - e^{-\lambda t})$. For small values of λt , that is, for times of observation short compared to the half-life, we may use the approximation $e^{-\lambda t} = 1 - \lambda t$ and then $M = N_0 \lambda t$. The disintegration rate R to be expected is $R = M/t = N_0 \lambda$. (This corresponds to the familiar equation $-dN/dt = \lambda N$.)

Expected Standard Deviation. What may we expect for the standard deviation of a binomial distribution? If we differentiate (6-13) again with respect to x , we obtain

$$n(n-1)p^2(px+q)^{n-2} = \sum_{r=0}^{r=n} r(r-1)x^{r-2} W(r).$$

Again letting $x = 1$ and using $p + q = 1$, we have

$$\begin{aligned} n(n-1)p^2 &= \sum_{r=0}^{r=n} r(r-1) W(r) = \sum_{r=0}^{r=n} r^2 W(r) - \sum_{r=0}^{r=n} r W(r), \\ n(n-1)p^2 &= \bar{r}^2 - \bar{r}. \end{aligned}$$

Recall from (6-7) that the variance σ_r^2 is given by

$$\sigma_r^2 = \bar{r}^2 - \bar{r}^2.$$

Now, combining, we have

$$\sigma_r^2 = n(n-1)p^2 + \bar{r} - \bar{r}^2,$$

and with $\bar{r} = np$

$$\sigma_r^2 = n^2 p^2 - np^2 + np - n^2 p^2 = np(1-p) = npq,$$

$$\sigma_r = \sqrt{npq}.$$

For radioactive disintegration this becomes

$$\sigma = \sqrt{N_0(1 - e^{-\lambda t})e^{-\lambda t}} = \sqrt{M e^{-\lambda t}}. \quad (6-14)$$

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In counting practice λt is usually small; that is, the observation time t is short compared to the half-life, and when this is so,

$$\sigma = \sqrt{M}. \tag{6-14a}$$

We see here a particular example of a very important property of the binomial distribution which, as presently shown, is true for the Poisson distribution also; that is, there is a simple relationship between the true mean and the true variance of the distribution. As a consequence, a single observation from a distribution that is expected to be binomial, as is true of radioactive disintegration rates, gives both an estimate of the mean and an estimate of the variance of the distribution. Further, for a single observation, the estimate of the variance of the distribution is also an estimate of the variance of the mean. It must be immediately emphasized that these remarks are not true in general; the variance of a thermometer reading, of a length measured by a meter stick, or of the reading of a voltmeter cannot be estimated from a single observation and is not in general expected to be equal to the value observed.

If a reasonably large number m of counts has been obtained, that number m may be used in the place of M for the purpose of evaluating σ . Thus, if 100 counts are recorded in 1 minute, the expected standard deviation is $\sigma \cong \sqrt{100} = 10$, and the counting rate might be written 100 ± 10 counts per minute. If 1000 counts are recorded in 10 minutes, the standard deviation of this number is $\sigma \cong \sqrt{1000} = 32$; the counting rate is $(1000 \pm 32)/10 = 100 \pm 3.2$ counts per minute. Thus we see that for a given counting rate R the σ for the rate is inversely proportional to the square root of the time of measurement:

$$R = \frac{m}{t};$$

$$\sigma_R = \frac{\sqrt{m}}{t} = \frac{\sqrt{Rt}}{t} = \sqrt{\frac{R}{t}}. \tag{6-15}$$

What is the result in an experiment in which the counting time is long compared to the half-life? As $\lambda t \rightarrow \infty$, $e^{-\lambda t} \rightarrow 0$, and, in this limit, $\sigma = \sqrt{Me^{-\lambda t}} = 0$. The explanation is clear; if we start with N_0 atoms and wait for all to disintegrate, then the number of disintegrations is exactly N_0 . However, in actual practice we observe not the number of disintegrations but that number times a coefficient c which denotes the probability of a disintegration resulting in an observed count. Taking this into account, we see that in this limiting case the proper representation of $\sigma = \sqrt{npq}$ is $\sigma = \sqrt{N_0 c(1 - c)}$. If $c \ll 1$, then $\sigma = \sqrt{N_0 c} = \sqrt{\text{number of counts}}$ as before. When $\lambda t \cong 1$ and c is neither unity nor very small, a more exact analysis based on $\sigma = \sqrt{npq}$ should be made, with the result that $\sigma = \sqrt{Mc(1 - c + ce^{-\lambda t})}$.

The introduction of the detection coefficient c in the preceding paragraph may raise the question why it is not necessary to take account of this coefficient in the more familiar case with λt small, where we have written $\sigma = \sqrt{m}$. If we do consider c in this case, we have for the probability of one atom producing a count in time t , $p = (1 - e^{-\lambda t})c$ and $q = 1 - p = 1 - c + ce^{-\lambda t}$. Then

$$\sigma = \sqrt{N_0(1 - e^{-\lambda t})c(1 - c + ce^{-\lambda t})},$$

and for λt small and the same approximations as before

$$\sigma = \sqrt{N_0\lambda tc} = \sqrt{Mc} = \sqrt{\text{number of counts recorded}}.$$

This is just the conclusion we had reached without bothering about the detection efficiency. It should be emphasized, however, that actual counts and not scaled counts from a scaling circuit must be used in these equations.

D. POISSON AND GAUSSIAN DISTRIBUTIONS

Poisson Distribution. The binomial distribution law (6-10) can be put into a more convenient form if we impose the restrictions $\lambda t \ll 1$, $N_0 \gg 1$, $m \ll N_0$, that is, if we consider a large number of active atoms observed for a time short compared to their half-lives. The derivation of this more convenient form requires the well-known mathematical approximation:

$$\ln(1+x) \cong x - \frac{x^2}{2} \cdots \quad \text{if } x \ll 1. \quad (6-16)$$

Let us first define the average value of the distribution (6-10):

$$M = N_0(1 - e^{-\lambda t}).$$

The binomial distribution may then be written as

$$W(m) = \frac{N_0!}{(N_0 - m)!m!} \left(\frac{M}{N_0}\right)^m \left(1 - \frac{M}{N_0}\right)^{N_0} \left(1 - \frac{M}{N_0}\right)^{-m}$$

Consider the term

$$\begin{aligned} \frac{N_0!}{(N_0 - m)!} &= N_0(N_0 - 1) \cdots (N_0 - m + 1) \\ &= N_0^m \left(1 - \frac{1}{N_0}\right) \cdots \left(1 - \frac{m-1}{N_0}\right). \end{aligned}$$

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For $m \ll N_0$ this term may be estimated by taking its logarithm and using the first term of the approximation (6-16). The result is

$$\frac{N_0!}{(N_0 - m)!} \cong N_0^m \exp \left[-\frac{m(m-1)}{2N_0} \right] \quad (6-17a)$$

The term $[1 - (M/N_0)]^{N_0}$ may also be estimated by the use of (6-16), since $M/N_0 \ll 1$, a condition that is equivalent to $\lambda t \ll 1$:

$$\begin{aligned} \ln \left(1 - \frac{M}{N_0} \right)^{N_0} &= N_0 \ln \left(1 - \frac{M}{N_0} \right) \\ &\cong -M - \frac{M^2}{2N_0}, \\ \therefore \left(1 - \frac{M}{N_0} \right)^{N_0} &\cong e^{-M} e^{-M^2/2N_0}. \end{aligned} \quad (6-17b)$$

Note that this time we use two terms of the expansion, since $M^2/2N_0$ is not necessarily small, even for $M/N_0 \ll 1$.

Again, for $M/N_0 \ll 1$, we immediately have from (6-16)

$$\begin{aligned} \ln \left(1 - \frac{M}{N_0} \right)^{-m} &\cong \frac{mM}{N_0} \\ \left(1 - \frac{M}{N_0} \right)^{-m} &\cong e^{mM/N_0}. \end{aligned} \quad (6-17c)$$

When the three approximate results (6-17a, b, c) are put into the binomial distribution, the result is

$$W(m) \cong \frac{M^m e^{-M}}{m!} \left[e^{-(M-m)^2/2N_0} e^{m^2/2N_0} \right], \quad (6-18)$$

where $W(m)$ is the probability of obtaining the particular number of counts m when M is the average number to be expected. The term outside the brackets in (6-18):

$$W(m) \cong \frac{M^m e^{-M}}{m!} \quad (6-19)$$

is the famous Poisson distribution; the term within the brackets may be considered as a correction factor and is a measure of how well the binomial distribution is approximated by the Poisson. It is to be emphasized that the validity of (6-19) as an approximation to (6-10) requires not only that a large number of atoms be observed for a time short compared to their half-lives, but also that the absolute value of $(M - m)$ be substantially smaller than $\sqrt{N_0}$. For example, if $N_0 = 100$ and $M = 1$, both the Poisson and binomial distributions give $W(0) = 0.37$; but the binomial distribution gives $W(10) =$

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0.7×10^{-7} , whereas the Poisson distribution (6-19) gives $W(10) = 1.0 \times 10^{-7}$. The corrected Poisson distribution (6-18) gives $W(10) = 0.7 \times 10^{-7}$.

Two features of the Poisson distribution (6-19) might be noticed in particular. The probability of obtaining $m = M - 1$ is equal to the probability of obtaining $m = M$, or $W(M) = W(M - 1)$. For large M the distribution is very nearly symmetrical about $m = M$ if values of m very far from M be excluded.

Gaussian Distribution. A further approximation of the distribution law may be made for large m (say > 100) and for $|M - m| \ll M$. With these additional restrictions, with the approximate expansion,

$$\ln \left(1 + \frac{M - m}{m} \right) = \frac{M - m}{m} - \frac{(M - m)^2}{2m^2},$$

neglecting subsequent terms, and with the use of Stirling's approximation

$$x! = \sqrt{2\pi x} x^x e^{-x},$$

we may modify the Poisson distribution to obtain the Gaussian distribution:

$$W(m) = \frac{1}{\sqrt{2\pi M}} e^{-(M-m)^2/2M}. \quad (6-20)$$

It will be noticed that this distribution is symmetrical about $m = M$. For both the Poisson and Gaussian distributions¹ we may derive $\sigma = \sqrt{M}$, or, for large m , $\sigma \cong \sqrt{m}$.

E. STATISTICAL INFERENCE AND BAYES' THEOREM

As we mentioned at the outset of this chapter, the primary problem of statistical inference is to estimate, from information available after only a finite number of observations, the average value that would be obtained after an infinite number of experimental observations of a given physical quantity. In terms of (6-19), what we really wish to know, for example, is the proba-

¹ The functional dependence $\sigma = \sqrt{M}$ is a necessary condition of the Poisson but not of the Gaussian distribution. The general form of the Gaussian is

$$W(m) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{(M - m)^2}{2\sigma^2} \right],$$

where there is as a rule no relationship between M and σ . The relationship between σ and M for the Gaussian distribution of *counting rates* is a consequence of the particular source of random error: the fluctuation in the decay rate consistent with a decay probability per unit time which is independent of time.

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bility that the number of detected disintegrations of a radioactive sample (counts) is characterized by a mean value M when we have observed a value m [we may denote this probability by $W'(M|m)$]. Equation (6-19) gives us the inverse of what we wish to know: the probability of observing m counts when the sample is characterized by a mean value M [this inverse probability we may denote as $W(m|M)$]. These two conditional probabilities are related to each other:

$$P'(m)W'(M|m) = P(M)W(m|M); \tag{6-21}$$

where $P'(m)$ is the *prior probability* that the sample will give m counts before any observations have been made on the sample and $P(M)$ is the *prior probability* that the sample is characterized by a *mean number of counts* M before any observations have been made on the sample. The reader will readily perceive that these so-called prior probabilities are troublesome quantities. The two sides of (6-21) are equal to each other because each of them is equal to the joint probability that a sample will be characterized by a mean of M counts and will exhibit experimentally m counts. The quantity of interest $W'(M|m)$ may be readily obtained from (6-21):

$$W'(M|m) = \frac{P(M)W(m|M)}{P'(m)}, \tag{6-22}$$

an expression which was first discussed by the Reverend Bayes some two centuries ago.³ The *prior probabilities* $P'(m)$ and $P(M)$ are related:

$$P'(m) = \sum_{M=0}^{\infty} P(M)W(m|M),$$

which states that if, in some manner, $P(M)$ is known, then through a combination of the addition theorem and the multiplication theorem the *prior probability* $P'(m)$ must also be known. The final expression, then, is

$$W'(M|m) = \frac{P(M)W(m|M)}{\sum_{M=0}^{\infty} P(M)W(m|M)}. \tag{6-23}$$

It is of interest to note the implications of (6-23) for a sample that complies with the restrictions required by the Poisson distribution, that is, a sample containing a large number of atoms which is observed for a time short compared to their half-life. Taking (6-19) for $W(m|M)$, we obtain from (6-23)

$$W'(M|m) = \frac{P(M)(M^m e^{-M}/m!)}{\sum_{M=0}^{\infty} P(M)(M^m e^{-M}/m!)} \tag{6-24}$$

³ For a discussion of conditional probability, see chapter 5 of reference F1.

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It is impossible to proceed without an explicit expression for $P(M)$; it is at this point that the analysis can become metaphysical. We shall proceed by taking all values of M as being equally probable:

$$P(M) dM = K dM. \quad (6-25)$$

With this assumption, the summation in the denominator of (6-24) becomes an integral and we obtain

$$W'(M|m) dM = \frac{KM^m e^{-M}/m!}{\int_0^\infty K(M^m e^{-M}/m!) dM} dM = \frac{M^m e^{-M}}{m!} dM, \quad (6-26)$$

since

$$\int_0^\infty M^m e^{-M} dM = m!. \quad (6-27)$$

It is to be carefully noted that although the right side of (6-26) is similar to that of (6-19), it has a different meaning. Equation 6-26 gives the probability, under our choice of $P(M)$, that the sample has a *mean* between M and $M + dM$ counts when m counts have been observed. From (6-26) it is easily found that the most probable value of M is m ; through the use of (6-6), (6-7) and (6-27), it is found that the average value of M is $m + 1$ and that the standard deviation of the distribution law (6-26) is $\sqrt{m + 1}$. The difference between the average and the most probable value of M is unimportant for values of m that are not too small; for small values of m , for example $m = 0$, there is the question whether to estimate M by the average or by the most probable value.

To answer this question we must be clear about the meaning of the average value of M . It is the value that would be obtained in the following experiment: take a very large collection of samples, each of which had given m counts in a given time interval. Then the mean number of counts expected from *each* sample is determined from the average of a very large number of observations on *each* of the very large number of samples. It is then the average value of this very large number of mean values that is given by $m + 1$; and m is the mean value that is most frequently observed.

Now, the observation of m counts was made on one of this large number of samples; the question is, which one? The best answer is the most probable one; that is, the sample for which $M = m$. This answer becomes more familiar if we consider the estimate of the mean counts expected from a sample after n observations which gave results m_1, m_2, \dots, m_n have been made upon it. An expression for $W(M|m_1, m_2, \dots, m_n)$, the probability that the sample is characterized by a mean value M when n observations give the results m_1, m_2, \dots, m_n , can be derived in the same way as (6-26):

$$W(M|m_1, m_2, \dots, m_n) = \frac{n(nM)^{m_1+m_2+\dots+m_n} e^{-nM}}{(m_1 + m_2 + \dots + m_n)!} \quad (6-28)$$

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The maximum of this distribution function occurs for

$$M = \frac{m_1 + m_2 + \dots + m_n}{n} \tag{6-29}$$

which is the average value of the set of observations just as is expected from (6-1).

Information on the precision of the estimate for M is contained in the expressions for the distribution function: (6-26) or (6-28). The precision of the estimate of M may be characterized by the variance of its distribution function: $m + 1$ for a single observation and $(m_1 + m_2 + \dots + m_n + 1) / n^2$ for n observations.

Variance, as computed above, may be used in the normal distribution law (6-3). For small values of m , though, it is probably best to discuss the data directly in terms of the distribution function (6-28). For example, if there is a single observation that gives $m = 0$, (6-28) says that there is a probability of 0.99 that M will be less than 4.6. If the value of zero is obtained in 10 independent observations, then there is a probability of 0.99 that M will be less than 0.46.

In summary, then, for an observed number of counts in excess of about 100, the best statement that can be made is the customary one (6-14a) that the mean value is $m \pm \sqrt{m}$ (taking $m + 1 \cong m$); for a small number of counts the statement would be that the mean value is m and the confidence in the statement can be obtained from (6-28).

F. EXPERIMENTAL APPLICATIONS

Propagation of Errors. Whenever experimental data are used in the computation of a derived quantity, there is the question of the relationship between the precision of the computed values and the precision of the input information. For example, a background counting rate is to be subtracted from an observed counting rate; or the ratio of the counting rates of two samples is used as a measure of the relative numbers of atoms in the samples. The errors in the computed values may be more readily estimated from those of the input data if the error attached to each input datum is independent of that attached to any other.

Consider the independent measurements of two quantities x and y , which lead to the result that the probability of observing a value of x between x and $x + dx$ is $X(x) dx$, and similarly for y ; then the independence of the measurements means that the probability of having a result with x between x and $x + dx$ while y is between y and $y + dy$ is

$$P(x, y) dx dy = X(x) Y(y) dx dy.$$

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We now ask what is our best estimate of some quantity, f , which is a function, $f(x, y)$, of the variables x and y and what is the precision of our estimate of f ? The answer to this question is suggested by (6-6). Our best estimate of $f(x, y)$ is its average value:³

$$\overline{f(x, y)} = \iint X(x) Y(y) f(x, y) dx dy. \quad (6-30)$$

Since the quantity that is sought is $f(\bar{x}, \bar{y})$, it is instructive to examine the properties of (6-30) by making a Taylor expansion of $f(x, y)$ about the point \bar{x}, \bar{y} which is our best estimate of \bar{x}, \bar{y} :

$$\begin{aligned} \overline{f(x, y)} = \iint X(x) Y(y) & \left[f(\bar{x}, \bar{y}) + (x - \bar{x}) f_x(\bar{x}, \bar{y}) + (y - \bar{y}) f_y(\bar{x}, \bar{y}) \right. \\ & + \frac{(x - \bar{x})^2}{2} f_{xx}(\bar{x}, \bar{y}) + \frac{(y - \bar{y})^2}{2} f_{yy}(\bar{x}, \bar{y}) \\ & \left. + (x - \bar{x})(y - \bar{y}) f_{xy}(\bar{x}, \bar{y}) + \dots \right] dx dy, \quad (6-31) \end{aligned}$$

where $f_x(\bar{x}, \bar{y})$, $f_{xx}(\bar{x}, \bar{y})$, $f_{xy}(\bar{x}, \bar{y})$ etc., mean the partial derivatives $\partial f/\partial x$, $\partial^2 f/\partial x^2$, $\partial^2 f/\partial x \partial y$, etc., evaluated at the point \bar{x}, \bar{y} .

If $f(x, y)$ is a sufficiently slowly varying function in the region of \bar{x}, \bar{y} so that the higher derivatives are negligible, then

$$\overline{f(x, y)} \cong f(\bar{x}, \bar{y}), \quad (6-32)$$

since

$$\iint X(x) Y(y) (x - \bar{x}) = \bar{x} - \bar{x} = 0$$

and

$$\iint X(x) Y(y) (y - \bar{y}) = \bar{y} - \bar{y} = 0.$$

For the three elementary arithmetic operations, addition, subtraction, and multiplication, the Taylor series terminates after a finite number of terms, and the exact results

$$\overline{x + y} = \bar{x} + \bar{y}, \quad (6-33a)$$

$$\overline{x - y} = \bar{x} - \bar{y}, \quad (6-33b)$$

$$\overline{xy} = \bar{x}\bar{y} \quad (6-33c)$$

are obtained. This is not the result, however, for the elementary operation of division.⁴

³ See discussion on p. 54 of reference B1 and p. 51 of reference B2.

⁴ The quantity $\overline{x/y}$ as evaluated by (6-30) will be infinite unless $Y(y)$ approaches zero more rapidly than does y ($\lim_{y \rightarrow 0} [Y(y)/y] \neq \infty$). This infinity catastrophe is usually avoided by restricting the values of y to those that have a relatively large likelihood—that is, close to \bar{y} . When this is done, (6-32) gives the estimate of f .

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The estimate of the variance is given by

$$\sigma_f^2 = \overline{[f(x, y) - \overline{f(x, y)}]^2} = \iint X(x) Y(y) [f(x, y) - \overline{f(x, y)}]^2 dx dy. \quad (6-34)$$

If again a Taylor expansion is used and the higher order terms are neglected, then

$$\sigma_f^2 = f_x^2(\bar{x}, \bar{y})\sigma_{\bar{x}}^2 + f_y^2(\bar{x}, \bar{y})\sigma_{\bar{y}}^2 + \dots \quad (6-35)$$

Exact expressions again result for the variance of three of the elementary arithmetic operations:

$$\sigma_{\frac{x}{x+y}}^2 = \sigma_{\bar{x}}^2 + \sigma_{\bar{y}}^2 \quad (6-36a)$$

$$\sigma_{\frac{x}{x-y}}^2 = \sigma_{\bar{x}}^2 + \sigma_{\bar{y}}^2 \quad (6-36b)$$

$$\frac{\sigma_{\frac{x}{xy}}^2}{\bar{x}^2 \bar{y}^2} = \frac{\sigma_{\bar{x}}^2}{\bar{x}^2} + \frac{\sigma_{\bar{y}}^2}{\bar{y}^2} + \frac{\sigma_{\bar{x}}^2 \sigma_{\bar{y}}^2}{\bar{x}^2 \bar{y}^2} \quad (6-36c)$$

The third term in expression (6-36c) is usually small compared to the first two and may be neglected. Similarly, the first two terms of (6-35) are usually a good approximation for the variance of other functions of x and y .

As an example, suppose that the background counting rate of a counter is measured and 600 counts are recorded in 15 minutes. Then with a sample in place the total counting rate is measured, and 1000 counts are recorded in 10 minutes. We wish to know the net counting rate due to the sample and the standard deviation of this net rate. First the background rate R_b is

$$R_b = \frac{600 \pm \sqrt{600}}{15} = \frac{600 \pm 24}{15} = 40 \pm 1.6 \text{ counts per minute.}$$

The total rate R_t is

$$R_t = \frac{1000 \pm \sqrt{1000}}{10} = \frac{1000 \pm 32}{10} = 100 \pm 3.2 \text{ counts per minute.}$$

The net rate $R_n = 100 - 40 = 60$ counts per minute, its standard deviation is $\sigma_n = \sqrt{1.6^2 + 3.2^2} = 3.6$, and $R_n = 60 \pm 3.6$ counts per minute.

Gaussian Error Curve. Knowledge of the distribution law permits a quantitative evaluation of the probability of a given deviation of a measured result m from the proper average M to be expected. With the absolute error $|M - m| = \epsilon$, and with the assumption that the integral numbers are so large that the distribution may be treated as continuous, the probability $W(\epsilon) d\epsilon$ of an error between ϵ and $\epsilon + d\epsilon$ for the normal distribution is given by

$$W(\epsilon) d\epsilon = \frac{2}{\sqrt{2\pi}M} e^{-\epsilon^2/2M} d\epsilon. \quad (6-37a)$$

The factor 2 arises from the existence of positive and negative errors with equal

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probability within the limits of validity of this approximation. Recalling that $\sigma = \sqrt{M}$, we have

$$W(\epsilon) d\epsilon = \frac{1}{\sigma} \sqrt{\frac{2}{\pi}} e^{-\epsilon^2/2\sigma^2} d\epsilon. \quad (6-37b)$$

The probability of an error greater than $k\sigma$ is obtained by integration from $\epsilon = k\sigma$ to $\epsilon = \infty$. Numerical values of this integral as a function of k may be found in handbooks. For example, we have taken for table 6-2 some representative values from the table, "Probability of Occurrence of Deviations" in the Chemical Rubber Publishing Company's *Handbook of Chemistry and Physics*.

Table 6-2

k	0	0.674	1	2	3	4
Probability of $\epsilon > k\sigma$	1.00	0.50	0.32	0.046	0.0027	0.00006

Notice that errors greater than and smaller than 0.674σ are equally probable; 0.674σ is called the "probable error" and is sometimes given rather than the standard deviation when counting data are reported. In plots of experimental curves it can be convenient to indicate the probable error of each point (by a mark of the proper length); then on the average the smooth curve drawn should be expected to pass through about as many "points" as it misses. It is unfortunately not strictly correct to use (6-37b) with (6-35) in the estimation of the probability of an error of a function of random variables. For example, the distribution of the differences of two random variables which have Gaussian distributions is not itself Gaussian. Nevertheless, if the function does not vary too rapidly in the vicinity of its average, the distribution of values about the average is essentially Gaussian with a variance as given in (6-35).

Comparison with Experiment. We now return to a consideration of the typical counting data in table 6-1. We have already found from the deviations among the 10 measurements $\sigma = \sqrt{(N_0 - 1)^{-1} \sum (x_i - \bar{x})^2} = 11.9$. If the counting rate measured there represents a random phenomenon, as we expect it should, we may evaluate the expected σ for the result in any minute as the square root of the number of counts. For a typical minute, the ninth, we find $\sigma = \sqrt{101} = 10$, and for other minutes other values not much different. Because these values agree reasonably with the 11.9 there is evidence for the random nature of the observed counting rate. This test should occasionally be made on the data from a counting instrument.

In addition to estimating the σ for each entry in table 6-1, we may also estimate the $\sigma_{\bar{x}}$ for the average of the 10 observations. This estimate can be performed in three different ways, and it is instructive to compare them:

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1. Since the 10 data are observations of a radioactive decay, we expect from (6-14a) that each datum has a standard deviation given by the square root of the number of counts. The mean is calculated by summing the data and dividing by the number of observations (10). The standard deviation of the mean, then, can be obtained from (6-35) for the propagation of fluctuations for a function of random variables (the number 10 has zero standard deviation). The result is

$$\sigma_{\bar{x}} = 99 \sqrt{\frac{990}{990^2}} = \frac{1}{10} \sqrt{990} = 3.1.$$

2. The individual counting rates can be summed, which is equivalent to an observation of 990 counts in 10 minutes. Again, since we are dealing with radioactive decay, the standard deviation of the mean is given by (6-14a):

$$\sigma_{\bar{x}} = \frac{1}{10} \sqrt{990} = 3.1.$$

3. If the fact that these data are from radioactive decay is ignored and no special relation such as (6-14a) is assumed to exist between each observation and its standard deviation, then the standard deviation of the mean is computed from (6-5):

$$\sigma_{\bar{x}} = \sqrt{\frac{1276}{9 \times 10}} = 3.8.$$

It is important to note that methods 1 and 2 give the same answer, as they must; it is not possible to gain more information about the standard deviation of the mean by breaking a 10-minute observation into 10 one-minute observations. The $\sigma_{\bar{x}} = 3.1$ given by methods 1 and 2 is the correct answer. It is also of interest to see that relinquishing the information contained in (6-15), as in method 3, diminishes the precision of the estimate of the mean.

The average counting rate with its standard deviation is $\bar{x} = (990 \pm \sqrt{990})/10 = 99.0 \pm 3.1$ counts per minute. This means that the probability that the true average is between 95.9 and 102.1 is, from table 6-2, just $1 - 0.32 = 0.68$. Actually, when the counting data given in table 6-1 were obtained, the average rate was measured much more accurately in a 100-minute count, and the result was $(10,042 \pm \sqrt{10,042})/100 = 100.4 \pm 1.0$ counts per minute.

Counter Efficiencies. As another application of the methods of this chapter to counting techniques, we may estimate the efficiency of a Geiger counter for rays of a given ionizing power, with the assumptions that any ray that produces at least one ion pair in the counter gas is counted and that effects at the counter walls are negligible. Knowledge of the nature of the radiation and the information given in chapter 4 permit an estimate of the average number of ion pairs a to be expected within the path length of the radiation in the

counter filling gas. The problem then is to find the probability that a ray will pass through the counter, leaving no ion pairs, and thus will not be counted. We think of the path of the ray in the counter as divided into n segments of equal length; if n is very large, each segment will be so small that we may neglect the possibility of having two ion pairs in any segment. Then just a of the n segments will contain ion pairs, and by definition the probability of having an ion pair in a given segment is $p = a/n$. Now by (6-8) for the binomial distribution we have the probability of no ion pairs in n segments; that is, of $r = 0$

$$W(0) = \frac{n!}{n!0!} p^0(1-p)^n = (1-p)^n = \left(1 - \frac{a}{n}\right)^n.$$

Since the probability^a is evaluated correctly only as n becomes very large,

$$W(0) = \lim_{n \rightarrow \infty} \left(1 - \frac{a}{n}\right)^n = e^{-a}.$$

The probability of counting the ray, which is the efficiency to be determined, is then $1 - W(0) = 1 - e^{-a}$. As a particular example, consider a fast β particle with the relatively low specific ionization of 5 ion pairs per millimeter in air and a path length of 10 mm in a counter gas which is almost pure argon at 7.6 cm pressure. We estimate a from these assumptions, correcting for the relative densities of air and the argon:

$$a = 5 \times 10 \times \frac{7.6}{76} \times \frac{40}{29} = 7.$$

The corresponding estimated counter efficiency is $1 - e^{-7} = 99.9$ per cent. It should not be expected that an efficiency calculated in this way is very precise. Wall effects may be important, and the assumption of random distribution of ion pairs along the β -ray path is not entirely consistent with the mechanism of energy loss by ionization presented in chapter 4.

Coincidence Correction. If a counter has a recovery time (or dead time or resolving time) τ after each recorded count during which it is completely insensitive, the total insensitive time per unit time is $R\tau$, where R is the observed counting rate. If R^* is the rate that would be recorded if there were no coincidence losses, the number of lost counts per unit time is $R^* - R$ and is given by the product of the rate R^* and the fraction of insensitive time $R\tau$:

$$R^* - R = R^*R\tau,$$

$$R^* = \frac{R}{1 - R\tau} \quad (6-38)$$

^a We might have evaluated this probability more easily from the Poisson distribution expression: $W(0) = a^0 e^{-a}/0! = e^{-a}$.

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A number of variants of this formula are also in use. One expression (the Schiff formula) is $R^* = R e^{R\tau}$; this is derived from a calculation of the probability $W(0)$ of having had no event during the time τ immediately preceding any event. An event, whether recorded or not, is here considered to prevent the recording of a second event occurring within the time τ .⁶ Another approximate expression is derived from the first two terms in the binomial expansion of $(1 - R\tau)^{-1}$ appearing in (6-38):

$$R^* = R(1 + R\tau) = R + R^2\tau.$$

This form is especially convenient for the interpretation of an experiment designed to measure τ by measuring the rates R_1 and R_2 produced by two separate sources and the rate R_t produced by the two sources together, each of these rates including the background effect R_b . Obviously,

$$R_1^* + R_2^* = R_t^* + R_b,$$

where we have neglected the coincidence loss in the measurement of the low background rate. Replacing by $R_1^* = R_1 + R_1^2\tau$, etc., and rearranging, we have

$$\tau = \frac{R_1 + R_2 - R_t - R_b}{R_t^2 - R_1^2 - R_2^2}.$$

Statistics of Pulse Height Distributions. When a monoenergetic source of radiation is measured with a proportional- or scintillation-counter spectrometer, the observed pulse heights have a Gaussian distribution around the most probable value. The energy resolution of such an instrument is usually expressed in terms of the full width at half maximum of the pulse height distribution curve, stated as a fraction or percentage of the most probable pulse height H . The pulse height $h_{1/2}$ at the half maximum of the distribution curve may be obtained from the ratio of probabilities

$$\frac{W(h_{1/2})}{W(H)} = \exp \left[\frac{-(H - h_{1/2})^2}{2\sigma_h^2} \right] = 0.5.$$

Then $(H - h_{1/2})^2/\sigma_h^2 = \ln 2$, and the full width at half maximum is

$$\frac{2|H - h_{1/2}|}{H} = 2 \sqrt{2 \ln 2} \frac{\sigma_h}{H} = \frac{2.36\sigma_h}{H},$$

where σ_h is the standard deviation of the pulse height distribution.

In a proportional counter the spread in pulse heights for monoenergetic rays absorbed in the counter volume arises from statistical fluctuations in the num-

⁶ It may be noticed that the Schiff formula might be expected to correspond more closely to the conditions of coincidence loss in a mechanical register, in which a new pulse within a dead time could initiate a new dead-time period, although it would not be recorded. There exists also the opportunity for coincidence losses in the electric circuits.

ber of ion pairs formed and statistical fluctuations in the gas amplification factor. The pulse height is proportional to the product of the gas amplification and the number of ion pairs, and therefore the fractional standard deviation of the pulse height equals the square root of the sum of the squares of the fractional standard deviations of these two quantities. As an example, consider the pulse height spectrum produced by the absorption of manganese K X rays in a proportional counter filled with 90 per cent argon and 10 per cent methane and operating with a gas gain of 1000. From table 4-1 the energy per ion pair is about 27 eV, and therefore the number of ion pairs formed by a 5.95-keV X ray is $5950/27 = 220 \pm \sqrt{220}$. If the numbers of ions collected per initial ion pair have a Poisson distribution, the fractional standard deviation in the gas gain is $\sqrt{1000}/1000$. Thus

$$\frac{\sigma_A}{H} = \sqrt{220/220^2 + 1000/1000^2} = \sqrt{0.00455 + 0.00100} = 0.0745,$$

and the full width at half maximum is $2.36 \times 0.0745 = 0.176$ or 17.6 per cent. If the gas gain is made sufficiently large, the fluctuations in the number of ion pairs determine the resolution, and in this case the resolution of a given counter is seen to be inversely proportional to the square root of the energy of the ionizing radiation absorbed.

In a scintillation counter the statistical fluctuations in output pulse heights arise from several sources (B3). The conversion of energy of ionizing radiation into photons in the scintillator, the electron emission at the photocathode, and the electron multiplication at each dynode are all subject to statistical variations. Although the photocathode emission has been shown to have somewhat larger fluctuations than correspond to the Poisson law, the observed pulse height distributions are for most practical purposes in sufficiently close agreement with those calculated on the assumption of Poisson distributions for all the statistical processes involved. With this assumption the standard deviation of a pulse height distribution for a single energy of ionizing radiation absorbed in the phosphor turns out to be approximately

$$\sigma_A \cong H \sqrt{\bar{n}/E\bar{q}\bar{j}\bar{p}(\bar{n} - 1)}, \quad (6-39)$$

where H is the most probable pulse height for an incident energy E keV, \bar{q} is the mean value of the phosphor efficiency (number of light quanta emitted per 1000 eV of incident energy), \bar{j} is the mean value of the light collection efficiency at the photocathode, \bar{p} is the mean value of the photocathode efficiency (number of photoelectrons arriving at the first dynode for each photon incident on the photocathode), and \bar{n} is the average electron multiplication per dynode.

In practice \bar{j} can be made almost unity, \bar{p} is of the order of 0.1, \bar{n} is usually about 3 to 5, and \bar{q} is approximately 30 for NaI(Tl), 15 for anthracene, and 7 for stilbene and for the best liquid scintillators. As an example we estimate the resolution attainable for the 662-keV photopeak of the Cs^{137} γ rays with a

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sodium iodide scintillation counter. Taking $f\bar{p} = 0.1$ and $\bar{n} = 4$, we obtain

$$\frac{\sigma_A}{H} = \sqrt{\frac{4}{662 \times 30 \times 0.1 \times 3}} = 0.020.$$

The corresponding full width at half maximum is $2.36 \sigma_A/H = 0.061$ or 6.1 per cent, which is indeed not far from the best resolution obtained experimentally. (See the experimental pulse height distribution with 8.5 per cent width at half maximum shown in figure 5-8.)

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EXERCISES

1. Mr. Jones's automobile license carries a six-digit number. What is the probability that it has (a) exactly one 4, (b) at least one 4? Make the assumption that the numbers 0 to 9 inclusive are equally probable for each of the six digits.
Answer: (b) 0.46856.
2. Consider the following set of observations:

Minute	Counts
1	203
2	194
3	201
4	217
5	195
6	189
7	210
8	207
9	230
10	188

- (a) Calculate the average value. (b) What is the standard deviation of the set?
- (c) What is the standard deviation of the mean? (d) What is the probability that an eleventh observation would have a value greater than 230? (e) What is the probability that a subsequent set of 10 one-minute observations will have an

average value that is greater than 212? (f) Should any of the data be rejected? If so, what is the new average value? *Answers: (c) 4.16.*

(e) 0.010.

3. (Given an atom of a radioactive substance with decay constant λ , what is (a) the probability of its decaying between 0 and dt , (b) the probability of its decaying between 0 and t ?
4. A sample contains 4 atoms of Lw . What is the probability that exactly 2 of the atoms will have decayed in (a) one half-life, (b) two half-lives?
5. A given proportional counter has a measured background rate of 900 counts in 30 minutes. With a sample of a long-lived activity in place, the total measured rate was 1100 counts in 20 minutes. What is the net sample counting rate and its standard deviation? *Answer: 25.0 ± 1.9 counts per minute.*
6. Denote by R_s and R_b the total and background counting rates for a long-lived sample and calculate the optimum division of available counting time between sample and background for minimum σ on the net counting rate. *Answer: $\frac{t_s}{t_b} = \sqrt{\frac{R_s}{R_b}}$.*
7. (a) Sample A , sample B , and background alone were each counted for 10 minutes; the observed total rates were 110, 205, and 44 counts per minute, respectively. Find the ratio of the activity of sample A to that of sample B and the standard deviation of this ratio. (b) Sample C was counted on the same counter for 2 minutes and the observed total rate was 155 counts per minute. Find the ratio, and its standard deviation, of the activity of C to that of A . *Answer: (a) 0.41 ± 0.027 .*
8. Derive (6-28) for the probability of a value M when given a set of observations m_1, m_2, \dots, m_n .
9. The scintillation spectrometer of exercise 4, chapter 5, is to be used for the measurement of 120-keV conversion electrons. What will be the full width at half maximum of the pulse height distribution?
10. Would the same spectrometer (exercise 9) completely resolve (i.e., give a dip between the pulse height peaks of) two conversion-electron groups of 44 and 52 keV, present in the abundance ratio 2:1?

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Tracers in Chemical Applications

A. THE TRACER METHOD

Isotopic Tracers. Most of the ordinary chemical elements are composed of mixtures of isotopes, and each mixture remains essentially invariant in composition through the course of physical, chemical, and biological processes. That this is so is shown by the constant isotopic ratios found for elements from widely scattered sources¹ and by the fact that atomic weights reliable to many significant figures may be determined by chemical means. It is true that isotopic fractionation may be appreciable for the lightest elements in which the percentage mass difference between isotopes is greatest, and this effect must always be considered in the use of hydrogen tracer isotopes. However, apart from these isotopes and Be⁷ which differs in mass from stable Be⁹ by only about 25 per cent, the next heavier tracer is in carbon where already the specific isotope effect may be neglected in most tracer work of ordinary precision. In this section we shall assume that the fact that a given isotope may be radioactive does not in any way affect its chemical (or biological) properties until it actually undergoes the spontaneous radioactive change. The interesting and important divergences from this assumption are examined in section C.

Because the isotopic tracer atoms are detected by their radioactivity, they behave normally up to the moment of detection; after that moment they are not detected, and their fate is of no consequence. (Of course, if the resulting atoms after the nuclear transformation are themselves radioactive and capable of a further nuclear change, the detection method must be arranged to give a response that measures the proper (in this case the first) radioactive species only. For example, if RaE (Bi²¹⁰) is used as a tracer for bismuth, the α particles from its daughter Po²¹⁰ should not be allowed to enter the detection instrument but should be absorbed by a suitable absorber or by the counter wall. As a tracer for thorium, UX₁ is suitable in spite of the fact that most of the detectable radiation will be from its daughter UX₂; the reason is that the

¹Some exceptions to the constancy of isotopic ratios were mentioned in chapter 2. p. 24.

Nuclear and Radiochemistry

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Preface

This book had its genesis as "a textbook for an introductory course in radiochemistry." In 1955, when a considerable title was changed to *Introduction to Radiochemistry*, albeit somewhat ungraciously by chemists, who are concerned with the application of radioactive nuclei to the division, or perhaps because of the interdependence of radiochemistry and nuclear physics, that their discipline was not a textbook.

Thus the general purpose of the book has remained the same. *Radiochemistry* differs from the first book in that it is more advanced and undergraciously in its modernization of many topics, particularly in keeping with the improvement of the increasing sophistication of the book has increased in size that we felt compelled to delete many chapters and comments of many subjects of subject matter.

We have sorely missed the late W. Kennedy in the past. In 1957 deprived our publisher and colleague. In spite of the able imprint of his authorship with his approval.

The changes are to be new and rewritten sections.

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