

TABLE OF SYMBOLS AND ABBREVIATIONS

A	Temperature in degrees absolute	ΔH	Heat of transition at constant pressure
a	Activity	h	Height
α	Angle of rotation	I	Constant of integration
α	Degree of dissociation	K	Equilibrium constant
C	Heat capacity	K	Cell constant
C	Number of components	K	Distribution constant
C	Salt concentration, buffers	K_a	Ionization constant of an acid
C	Temperature in degrees centigrade	K_b	Molal boiling-point constant
c	Concentration	K_f	Molal freezing-point constant
cm	Centimeters	K_{sp}	Solubility product
D	Liquid density	k	Parameter, Freundlich equation
d	Density, general	k	Specific rate constant
E	Electromotive force	L	Circumference
ΔE^*	Energy of activation	L	Specific conductance
ΔE	Heat of reaction at constant volume	l	Length
ϵ	Equivalents change	l	Mean free path
η	Coefficient of viscosity	Λ	Equivalent conductance
F	Degrees of freedom	Λ_0	Equivalent conductance at infinite dilution
ΔF	Free-energy change	λ	Wavelength
\mathfrak{F}	Faraday	M	Molarity
g	Acceleration of gravity	M	Molecular weight
g	Weight in grams	m	Molality
gm	Gram	ma	Milliampere
γ	Surface tension	mg	Milligram
ΔH	Heat of reaction at constant pressure	ml	Milliliter

MW	Apparent molecular weight	Q	Heat of neutralization
mm	Millimeter	Q	Heat of solution
mv	Millivolt	R	Molar gas constant
m μ	Millimicron	R	Radius of surface-tension ring
N	Avogadro's number	R	Resistance in ohms
N	Mole fraction	r	Radius, general
N	Normality	ρ	Density of a gas
N	Number of molecules	ΔS	Entropy change
n	Number of extracting portions	s	Speed of gas molecule
n	Number of Faradays	s	Solubility
n	Number of moles	σ	Molecular diameter
n _a	Transference number of anion	sec	Second
n _c	Transference number of cation	T	Temperature in degrees absolute
P	Apparent surface tension	ΔT_b	Change in boiling point
P	Number of phases	ΔT_f	Change in freezing point
P	Pressure	t	Centigrade temperature
P ^o	Vapor pressure of a pure substance	t	Time
p	Hydrostatic pressure	u	Speed of anion
p	Vapor pressure	V	Volume
pH	Hydrogen-ion exponent	v	Speed of cation
pK	Ionization constant exponent	w	Weight in grams
		Σ	Sum

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UNITS AND DIMENSIONS

In the physical chemistry laboratory we deal with measurable quantities or properties. Some of these, such as length, time, mass, and volume, are quite simple. Others, such as entropy, surface tension, and voltage, are more complex. These quantities or properties are expressed in terms of certain arbitrarily selected units. For example, we can select the meter, the foot, or the mile as the unit of length. Since we have complete choice in selecting our units, we could select a separate and independent unit for each quantity. But we would have as many units as we have measurable quantities, and the result would be both confusing and cumbersome.

To simplify the situation, we select a minimum number of units and define all other units in terms of these fundamental units. In the centimeter-gram-second system, the so-called cgs system, we select as the primary units the centimeter, the gram, and the mean solar second. The centimeter is one-hundredth of the distance between two lines on a platinum-iridium bar preserved at the International Bureau of Weights and Measures at Sèvres, near Paris, France. Highly exact reproductions have been distributed to other nations. The meter, which is one hundred times the centimeter, was originally intended to be one-ten-millionth of the distance from the Equator to the North Pole. The unit of mass, the gram, is one-thousandth of the mass of a platinum-iridium cylinder preserved by the same Bureau of Weights and Measures. The standard of time used in physical chemistry is the mean solar day. It is the average time of one complete revolution of the earth on its polar axis. The unit of time is the solar second, 1/86,400 part of a mean solar day.

With these three units we can now establish a number of other units. Those most often used in physical chemistry are listed in Table 1. In this table we have assigned the letter L to length, M to mass, and T to time. From these three we can write the dimensions of the other units.

TABLE 1

Quantity	Dimensions	Cgs Units
Length	L	cm
Area	L ²	cm ²
Volume	L ³	cm ³
Time	T	sec
Speed	LT ⁻¹	cm per sec
Acceleration	LT ⁻²	cm per sec per sec
Mass	M	gm
Force, weight	LT ⁻² M	dyne
Pressure	L ⁻¹ T ⁻² M	dynes per sq cm
Density	L ⁻³ M	gm per cm ³
Surface tension	T ⁻² M	dynes per cm, ergs per cm ² , or gm per sec ²
Energy	L ² T ⁻² M	erg

For example, area is L^2 , and speed, which is the distance traveled in unit time, L/T or LT^{-1} . In the case of force or weight, as distinguished from mass, the unit is the dyne. The dyne is defined as that force which gives to a mass of 1 gram an acceleration of 1 centimeter per second per second. It therefore has the dimensions of ML/T^2 or MLT^{-2} . The unit of energy in the cgs system is the erg. It is defined as the work done when a force of 1 dyne acts through a distance of 1 centimeter.

We are now ready to expand Table 1 by introducing four additional quantities often used in physical chemistry—temperature, heat capacity, specific heat, and entropy. To do this we shall introduce a unit of temperature, the degree, and represent it by the Greek letter theta (θ). These four new quantities are given in Table 2. The dimensions of heat capacity, the heat required to

TABLE 2

Quantity	Dimensions
Temperature	θ
Heat capacity	$L^2T^{-2}M\theta^{-1}$
Specific heat	$L^2T^{-2}\theta^{-1}$
Entropy	$L^2T^{-2}M\theta^{-1}$

raise the temperature of a given quantity of a substance by 1 degree, are obtained by dividing the dimensions of energy by temperature. Specific heat applies to 1 gram of the substance and its dimensions are obtained by dividing the dimensions of heat capacity by M . It is noted that entropy has the same dimensions as heat capacity.

In Table 2 we have not listed the cgs units of heat capacity, specific heat, and entropy. These quantities, like energy, are seldom expressed in cgs units because to do so would result, in most cases, in extremely large numbers. Instead two practical units are used. These are the absolute joule and the defined calorie. The absolute joule is defined as 10^7 ergs, and the defined calorie is 4.184 absolute joules. This calorie differs slightly from the 15° calorie which was taken as the heat necessary to raise the temperature of 1 gram of water 1 degree centigrade at $15^\circ C$. Heat capacity is expressed in calories per degree and specific heat in calories per degree per gram. It is to be noted that regardless of the units used to express energy, the dimensions of the various quantities remain unchanged.

The basic electrical quantities needed in elementary physical chemistry are charge, current, potential, resistance, and conductance. The units for these quantities could be expressed in electromagnetic units, a cgs system based on the properties of magnets, or in electrostatic units, a cgs system based on Coulomb's law of electric force. But here again we use a set of practical units. The units of charge, current, potential, and resistance in this system are the absolute coulomb, the absolute ampere, the absolute volt, and the absolute ohm. By definition the international ohm is the resistance of a column of mercury 106.300 centimeters long, of uniform cross section and of mass equal to 14.4521 grams at $0^\circ C$. The international ampere is defined as that current which deposits in 1 second 0.001118 gram of silver. The international volt is that potential which will cause a current of 1 ampere to flow through a conductor of 1-ohm resistance. A current of 1 ampere flowing for 1 second is equal to 1 coulomb of charge in either system (international or absolute). The relationships among the international and absolute units are given in Table 3.

In order to prepare a set of dimensions for these magnitudes we shall introduce a new unit, that of charge, which we shall designate by the Greek letter epsilon (ϵ). Current is the rate of flow of charge and has the dimensions of ϵ/T . Electrical energy has the usual dimensions of energy, $L^2T^{-2}M$. Since electrical energy equals charge times voltage, we have only to divide the dimensions of energy by ϵ to obtain the dimensions of voltage. The dimensions of resistance can be obtained by substituting the dimensions of current and voltage in Ohm's law—current equals voltage divided by resistance. The basic electrical quantities, together with their dimen-

TABLE 3

Quantity	Dimensions	Units	Relationships
Charge	ϵ	abs coulomb	1 int coulomb = 0.999835 abs coulomb
Current	ϵT^{-1}	abs ampere	1 int ampere = 0.999835 abs ampere
Potential, voltage	$L^2 T^{-2} M \epsilon^{-1}$	abs volt	1 int volt = 1.000330 abs volt
Resistance	$L^2 T^{-1} M \epsilon^{-2}$	abs ohm	1 int ohm = 1.000495 abs ohm

sions, the units now employed, and the relationships among the international and absolute units, are given in Table 3.

Since the change from the international system to the absolute system did not become effective until January 1, 1948, it is possible that some of your electrical measuring equipment is calibrated in the international system.

In establishing the dimensions of the various basic quantities in elementary physical chemistry, we have used both practical and absolute units. In some cases we may use more than one practical unit. In expressing pressure, for example, we use, instead of the cgs unit of dynes per square centimeter, the more practical terms: atmosphere, centimeters of mercury, or millimeters of mercury. Sometimes such units are termed secondary units. The liter is such a unit. You will recall from your quantitative analysis that this is the volume of 1 kilogram of air-free water at 4°C. Its volume is 1.000028 cubic decimeters. Therefore the milliliter, ml, is not exactly equal to the cubic centimeter, cm^3 , although the difference is so slight as to have little effect on the results in most physical chemistry operations. Also we find that energy may be expressed in ergs, in defined calories, in absolute joules, or in certain other units.

It is necessary that you always substitute a consistent set of units in a formula. Carry the units through your calculations and your answer will come out in the proper unit or units, if your treatment has been consistent.

DIMENSIONAL ANALYSIS

Dimensional analysis is a potent tool in learning the proper use of the various mathematical relationships in physical chemistry. If your equation is correct and if you have properly interpreted the various quantities, the substitution of the dimensions should reduce the expression to an identity.

Let us consider two simple cases to see exactly how a dimensional analysis is carried out. The expression for surface tension as a function of capillary rise is given by the equation:

$$\gamma = \frac{1}{2} h d g r$$

The terms in this expression, with their dimensions, are

Quantity	Symbol	Dimensions
Surface tension	γ	$T^{-2}M$
Height of column	h	L
Density of liquid	d	ML^{-3}
Acceleration of gravity	g	LT^{-2}
Radius of tube	r	L

Substituting in the equation:

$$T^{-2}M = L \times M \times L^{-3} \times L \times T^{-2} \times L$$

Thus the equation reduces dimensionally to an identity.

The speed of a gas molecule is given by the expression

$$s = \sqrt{\frac{3RT}{M}}$$

This speed has the dimensions of LT^{-1} . The gram-molecular weight of the gas, M , has the units of grams per mole and the dimensions of mass. R is the gas constant, which in this case must be expressed in ergs per mole per degree. It has the dimensions of $ML^2T^{-2}\theta^{-1}$. Substituting these dimensions gives an expression which reduces to an identity.

$$LT^{-1} = \left(\frac{ML^2T^{-2}\theta^{-1}}{M} \right)^{\frac{1}{2}} = LT^{-1}$$

This last example differs from the first in that a physical constant, R , is introduced. Where such constants are used, their dimensions must be known before dimensional analysis can be applied.

One type of expression often encountered may appear a little startling from the standpoint of dimensional analysis. This is an expression containing a logarithmic term. We shall state at once that the logarithm of any quantity is dimensionless. Let us consider the various

equations relating vapor pressure to temperature. The differential equation for the change of vapor pressure with temperature is

$$\frac{d \ln p}{dT} = \frac{\Delta H_v}{RT^2}$$

in which R has the dimensions of $ML^2T^{-2}\theta^{-1}$. The heat of vaporization, ΔH_v , has the dimensions of energy, ML^2T^{-2} . Thus $d \ln p$ reduces to a dimensionless quantity.

$$d \ln p = \frac{ML^2T^{-2}\theta}{ML^2T^{-2}\theta^{-1}\theta^2}$$

Remembering that one of our standard forms of differentiation is $d \ln x = dx/x$, or in this case dp/p , and noting that dp and p have the same dimensions, we see why the expression, $d \ln p$, is dimensionless.

The integral equation for vapor pressure as a function of temperature is

$$\ln p = -\frac{\Delta H_v}{RT} + I$$

$\Delta H_v/RT$ is a dimensionless magnitude, therefore $(\ln p - I)$ must be dimensionless. The explanation of this must be sought in a consideration of the process of integration. Mathematically I stands for an expression, $\ln P_0$, wherein P_0 has the dimensions of pressure. The combination of the two logarithmic terms results therefore in the elimination of the dimensions associated with pressure.

MEASUREMENTS, PRECISION, AND THE TREATMENT OF DATA

INTRODUCTION

The general procedure in the usual experiment in elementary physical chemistry includes the following basic steps.

(a) Measurements are made with certain instruments. Some of the instruments used are quite simple in nature, like a burette or a thermometer, for example; others are more complicated, like a potentiometer or a refractometer.

(b) The data from the measurements may be substituted in certain formulas or relationships in order to calculate certain other desired magnitudes.

(c) In the utilization and study of the various data, plotting procedures may be employed. In some cases a statistical study of the data is made.

If the various steps are to be followed in a proper scientific manner, attention must be given to the precision of the measurements and to the precision of the computed quantities. We must decide whether to make a single measurement of a given magnitude or a set of measurements in order to obtain the desired precision. This section of the manual deals, for the most part, with various definitions, equations, and concepts concerned with precision.

If a large number of measurements of a particular magnitude are made, statistical procedures are necessary to utilize the data properly. The manual includes, therefore, a discussion of the concepts, definitions, and equations used in statistical procedures.

Because of the extreme importance of plotting procedures, a discussion of this topic is given. This discussion, as well as the discussions of precision and statistical procedures, is on an elementary level. Those who wish to study these topics in greater detail may consult the bibliography for suitable references. The student should develop as soon as possible a precision-minded approach to the various experiments. The lack of proper attention to precision is one of the glaring weaknesses in most laboratory training.

CERTAIN AND UNCERTAIN FIGURES. SIGNIFICANT FIGURES

We shall start our discussion of precision by defining the terms: certain figures, uncertain figures, and significant figures. These pertain to the process of making a measurement and recording the value obtained.

The instruments used in physical chemistry have what we shall refer to as a least count. This is the smallest division of the instrument scale that can be read directly. The thermometer in Figure 1 has a least count of 1° , whereas a Beckmann thermometer, which is graduated in hundredths of degrees, has a least count of 0.01° . With most instruments, however, you can estimate a reading to one digit beyond that which expresses the least count. In Figure 1, for

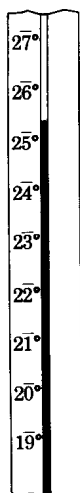


Figure 1.
Section of thermometer.

instance, you can read a temperature of 25.2° and feel confident that you are within 0.2° of the proper value.

In this value of 25.2° we term the digits to the left of the decimal point certain figures and the digit to the right of the decimal point an uncertain figure. Although we have considerable confidence in the uncertain figure, we should express the extent of our certainty by writing the temperature as $25.2 \pm 0.2^\circ$. If we record a volume measurement as 35.35 ± 0.05 ml, we are confident that the actual value lies between 35.40 ml and 35.30 ml.

Of more importance than the terms certain and uncertain figures is the term significant figures. The significant figures in a measurement include both the certain and the uncertain figures. All of the figures in the readings 25.2° and 35.35 ml referred to above are significant figures.

The peculiarities of our number system require that zero be given special attention in considering significant figures. If the zero or zeros are immediately to the right of the decimal point, they serve merely to locate the decimal point. In 0.00013 gm, the three zeros following the decimal point are not significant figures. However, in 0.130 gm, the zero following the three is a significant figure. In 250 gm, the zero may or may not be significant; it may serve merely to locate the decimal point. Any doubt, however, concerning this number would vanish if it were written:

$$2.50 \times 10^2 \text{ gm}$$

Exercise 1. Indicate the significant figures in each of the following:

0.0018 volt

1650 ml

12.5260 gm

0.1800 volt

1.650×10^3 ml

1.65 dynes per cm

1.800 volt

1.65×10^{-3} ml

16.2 miles

PRECISION AND ACCURACY

The terms precision and accuracy are often used interchangeably, although they are actually quite different in meaning. Accuracy concerns the correctness of a measurement, whereas precision concerns the reproducibility of the measurement and the number of significant figures in its value.

To illustrate, let us measure the temperature of a constant-temperature bath with two thermometers, one with a least count, or ultimate subdivision, of 1° and one with a least count of 0.1° . With the first thermometer we read a temperature of $25.2 \pm 0.2^\circ$ and with the second a temperature of $25.18 \pm 0.02^\circ$. The second reading, with its four significant figures, is the more precise reading. In this sense we are using the word precise in connection with the number of significant figures which we can with confidence write down for the measured magnitude. The thermometer with the least count of 0.1° is the more precise instrument.

Now we may make a series of readings with a single thermometer. The readings may show little divergence among themselves, or they may differ rather widely. If the differences are small we may say that the method of measurement is one of high precision and that the procedure is a precise one.

In summary, precision concerns both the reproducibility of the magnitude and the number of figures we may with confidence express in the answer.

After we have made a number of readings of a given magnitude and are sure that our values are precise in both senses of the word, we still do not know whether unknown or constant errors have entered into the determination. In measuring temperature, for example, there may be an error in the marking of the thermometer. Therefore, the recorded temperature, although very precise, may be entirely wrong. Accuracy deals with the difference between the measured value

and the true value. Good precision does not insure high accuracy, but high accuracy is improbable without good precision. It is possible, on the other hand, to have high accuracy, provided sufficient readings of fair precision are made and provided a proper statistical procedure is used.

It should be noted that, properly used, the term accuracy requires a modifying adjective. To say that a result is accurate means that it is exactly right. But only in a few cases do we know the exact value of the quantity being measured. Hence we should speak of a high order of accuracy or a low order of accuracy rather than stating merely that a result is accurate.

Let us now examine how we may express precision in a quantitative manner. One way to do this is to consider the extent of the uncertainty of the uncertain figure. If a temperature is recorded as $25.24 \pm 0.02^\circ$, the value of 0.02° is a measure of the precision. We can speak of such a value as the least-count precision or, sometimes, the decimal precision. We note that it is expressed in the same units as the measured quantity. We may also express the preciseness of a measurement in terms of relative precision, which may be defined as the relative uncertainty of the measured magnitude. This is obtained by dividing the value of the magnitude into the least-count precision. The result may be expressed in parts per hundred (per cent) or in parts per thousand.

The determination of relative precision is illustrated in Example 1.

Example 1. What are the least-count precisions and the relative precision in per cent of the two magnitudes: 25.26 ± 0.01 gm and 125.26 ± 0.01 gm? In both cases the least-count precision is 0.01 gm.

The relative precisions are:

$$\frac{0.01 \text{ gm}}{25.26 \text{ gm}} \times 100 = 0.039\% \qquad \frac{0.01 \text{ gm}}{125.26 \text{ gm}} \times 100 = 0.0079\%$$

Thus we see that the least-count precision depends on the measuring instrument and the value of the magnitude being measured. You should note that the relative precision is dimensionless.

ERRORS

In all laboratory procedures and in subsequent calculations there are certain factors that lower the accuracy of the results. Included in these factors are mistakes made by the experimenter in reading an instrument, in recording the data, or in performing the calculations. Other factors lowering the accuracy are grouped under the term errors. We shall now consider the various types of errors and how they affect the results.

Errors encountered in conducting experiments may be divided into two groups: (1) determinate errors and (2) indeterminate errors. Determinate errors are those whose magnitude we may determine, at least in theory, whereas indeterminate errors are those whose magnitude we cannot determine. We can, in most cases, correct our results for determinate errors. We are unable to correct for indeterminate errors, but we can reduce their effect by proper care and attention to experimental detail. Determinate errors are sometimes referred to as corrigible or systematic errors, and indeterminate errors are sometimes called random errors. Let us examine these two classes in some detail.

(1) Determinate Errors. These may be subdivided into three groups.

(a) Instrument Errors. These are caused by improper calibration or adjustment of the measuring instrument.

(b) Reagent Errors. The chemicals used may contain impurities which affect the magnitude of the quantity being measured or which by their presence may change the anticipated concentration of a solution.

(c) Calculation Errors. These are distinct from mistakes. They may involve the for-

mulas used. For example, in determining the molecular weight of a gas from vapor-density measurements, the van der Waals equation would give a more exact value than the ideal gas equation.

(2) Indeterminate Errors. These errors, sometimes called accidental errors, manifest themselves in variations in successive readings of a magnitude by the same observer under the same set of conditions. They occur even though the observer uses maximum care and patience. For example, in the standardization of an acid with a base there may be slight variations in the procedure for draining the burette, in removing the last portion of the drop from the tip, and in deciding the exact color of the indicator at the end point.

In general, determinate errors do not affect the precision of a measured magnitude. On the other hand, indeterminate errors are those that affect both the precision and the reproducibility of a measurement. As already stated, such errors may be reduced in magnitude by taking proper care in the procedures followed, by making changes in the procedures, by working under more favorable conditions, or by taking a large number of readings and using statistical considerations.

The procedures in which a large number of readings are used for arriving at a "best value" lead us to a consideration of other uses of the word error. For example, in the simplest case we take an average of a large number of readings and then determine the difference between this average and each individual reading. This difference is referred to as the deviation of the single observation. If we add these deviations without regard to sign and divide by the number of readings, we obtain what is termed the average error. From these differences we may also calculate other types of error termed the probable error and the standard error. These will be treated in detail in the subsection on Statistical Considerations.

If the exact value of a magnitude is known, the difference between this value and the measured value divided by the exact value is termed the fractional error. The fractional error multiplied by 100 gives the per cent error.

Thus we have used the word error in three senses. In the first of these the use of the word is qualitative. We ascribe the error to some source and speak of it as either a determinate or indeterminate error. In the second sense we calculate from the data obtained a value for the average, probable, or standard error. In the third sense the error is the difference between the experimental value and the exact, or accepted, value of the measured magnitude.

STATISTICAL CONSIDERATIONS

In this section of the manual we shall see how statistical procedures can be used for obtaining the so-called "best value" from a series of measurements. We shall also see how the average error, or deviation, the standard error, and the probable error are calculated.

In the field of scientific investigation statistical methods are often used to plan experiments so that they will yield a maximum of information with the minimum of work and also to organize and interpret the results. Statistical methods become increasingly important as the data become less and less precise.

In physical chemistry the experiments are usually simple in nature and have been subjected to the test of experience. The results obtained are ordinarily quite consistent, and there is little need for statistical procedures in their interpretation. Even where some divergence among the data is noted, the measurements are usually insufficient in number to justify statistical treatment.

It is essential, however, that the student in physical chemistry acquire at least a speaking acquaintance with certain relatively simple ideas in connection with the statistical treatment of data. This discussion will be kept on a most elementary basis. Equations will be given without any attempt at proof. We hope that you will become sufficiently interested in the subject to study in detail some of the references.

We shall first concern ourselves with the process of computing the "best value" from a set

of data. A measurement in physical chemistry is usually "too high" or "too low" as compared with the true value. If the true value were already known, we could at once determine the difference between it and the measured value. Usually, and always in original research, the true value is not known, and it is thus necessary to compute from the several measurements the so-called "best value."

Let us first consider the normal error curve or, as it is called by mathematicians, the normal Gaussian error curve. For any set of measurements for which there is an equal probability that a single value may be either "too high" or "too low," it is possible to obtain mathematically the equation

$$y = \frac{1}{\sqrt{2\pi} \sigma} e^{-d^2/2\sigma^2} \quad (1)$$

In this equation y is the probability or "expectancy" of observing a particular deviation, d , from the "true value," and σ is a parameter known as the precision constant or standard error as defined in Equation 4. Graphs for such a function are shown in Figure 2. If the value of σ is

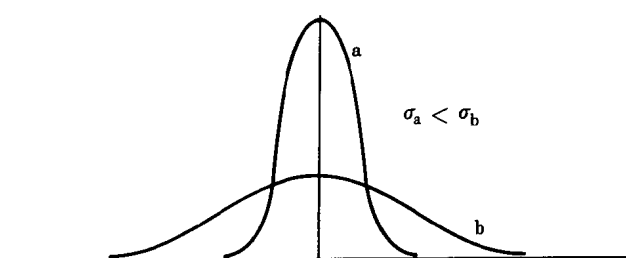


Figure 2. Gaussian error curves.

small, the curve descends sharply on each side of the maximum. If the value of σ is large, the curve descends slowly. The former corresponds experimentally to highly precise measurements, whereas the latter corresponds to measurements of relatively low precision.

It is a point of basic mathematical theory that a normal Gaussian distribution curve can be obtained only when the number of measurements is extremely large. Since making even forty or fifty measurements of a magnitude is quite time consuming, we must be content with a rough determination of whether the distri-

bution of a rather small number of measurements approximates a Gaussian distribution curve. One method of making such a determination lies in examining the closeness of the arithmetic average, the geometric average, and the harmonic average. The method we shall use consists in making a rough graphical comparison of the data with a Gaussian curve. Two graphs are needed in this method. The first is called a scatter diagram, and the second is called a block-distribution diagram. This method is illustrated in Example 2.

Before considering this example it is necessary to introduce a quantity called the arithmetic average, A , which is defined by the equation

$$A = \frac{x_1 + x_2 + x_3 + \dots + x_n}{n} \quad (2)$$

in which $x_1, x_2, x_3, \dots, x_n$ are the individual measurements and n is the total number of measurements.

Example 2. The members of a class of thirty students each measured the diameter of a steel ball with a vernier caliper. The thirty measurements are tabulated in Table 4 along with the deviation, d , of each measurement from the arithmetic average, A .

First we shall prepare a scatter diagram of the values of the diameter as a function of the order of occurrence. In physical experimentation plotting in the order of occurrence will show whether there is a steady drift in the values. If such is found, it may be an indication that the measuring instrument is not functioning properly.

The scatter diagram for the data of Table 4 is given in Figure 3. A solid line has been drawn through the arithmetic average, 1.25. The various values have been connected with this line purely as a visual aid. With the data in this form, it is usually difficult to decide whether

TABLE 4

Diameter, cm	Deviation	Diameter, cm	Deviation
1.25	0.00	1.26	+ 0.01
1.26	+ 0.01	1.25	0.00
1.24	- 0.01	1.24	- 0.01
1.23	- 0.02	1.24	- 0.01
1.27	+ 0.02	1.28	+ 0.03
1.26	+ 0.01	1.25	0.00
1.26	+ 0.01	1.28	+ 0.03
1.24	- 0.01	1.22	- 0.03
1.25	0.00	1.27	+ 0.02
1.21	- 0.04	1.23	- 0.02
1.27	+ 0.02	1.24	- 0.01
1.23	- 0.02	1.22	- 0.03
1.30	+ 0.05	1.25	0.00
1.22	- 0.03	1.26	+ 0.01
1.29	+ 0.04	1.27	+ 0.02

Arithmetic average, diameter = 1.25 cm

they are normally distributed. We can more easily arrive at an answer to this question by changing the data into a plot of the frequency of occurrence of values within a given interval as a function of the interval width. This gives a block-distribution diagram.

We must first choose the interval width. It is necessary to be somewhat arbitrary in doing this. The number of intervals is usually chosen, however, with two principles in mind. First, the interval in which the average falls should include a number of observations at least as large as any other interval. Second, all intervals must be of the same "numerical width."

An examination of Figure 3 shows that a middle interval from 1.245 to 1.255 will include five values, and that no other interval will include more than five values. The diagram is, therefore, divided into eleven intervals as shown by the horizontal lines in Figure 4.

Now let us count the number of values occurring in each interval and plot these as a function of the interval width. The result is shown in Figure 5, which also includes a Gaussian distribu-

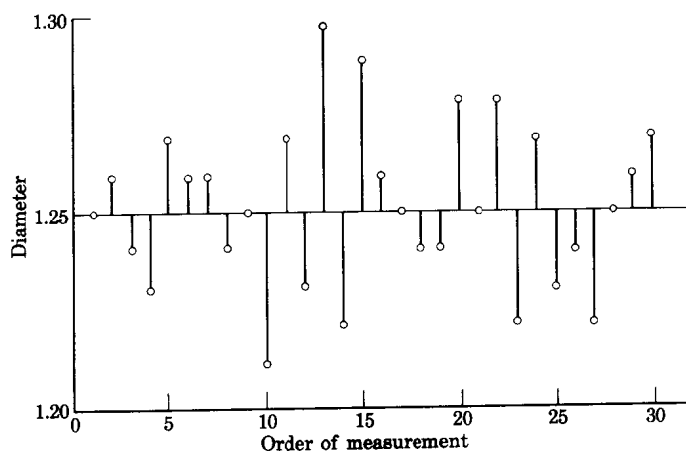


Figure 3. Scatter diagram.

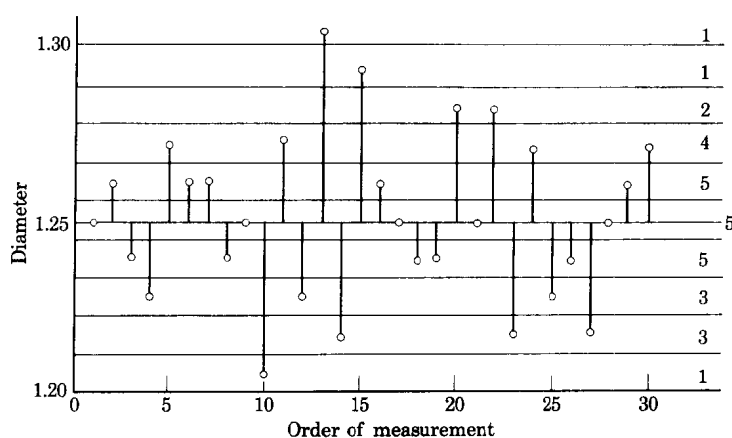


Figure 4. Scatter diagram (with intervals) of data in Table 4.

tion curve. We now see that the data of Table 4 closely approximate the normal, or Gaussian, distribution. It is current practice among statisticians to suppose that a minimum of thirty observations must be available if such a distribution as shown in Figure 5 is to be considered as satisfactorily approximating the Gaussian curve.

In Figure 5 the arithmetic average, 1.25 cm, corresponds very closely to the most probable value on the Gaussian curve. In such a case the arithmetic average may also be called the "best value," in the sense that it closely approximates the most probable value. Even if the data are not Gaussian distributed, the arithmetic average is often taken as the best value because of the ease of its computation. For a careful consideration of the best value for data that are not Gaussian distributed, the student is referred to the various books on statistical mathematics.

Let us now consider quantities often used to express the precision or "goodness" of the data. These are the average error, the root-mean-square error or standard error, and the probable error. For data that follow the normal, or Gaussian, error curve these quantities are defined in the following equations:

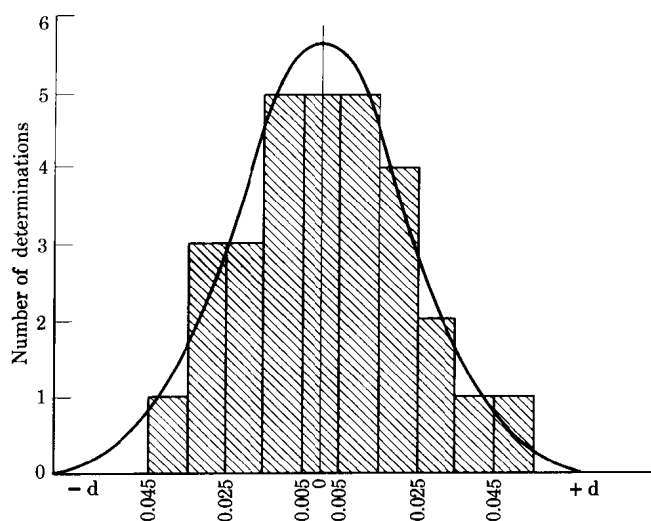


Figure 5. Block-distribution diagram. Data of Table 4.