# Chapter 5 Errors In Chemical Analyses

Criteria to Define a Good Method

We will use eight criteria to define a good method:

- 1. Precision
- 2. Accuracy
- 3. Selectivity
- 4. Sensitivity
- 5. Range
- 6. Robustness
- 7. Cost
- 8. Safety





# Precision

**Precision** is the closeness of results to others that have been obtained in exactly the same way.

Precision describes the *reproducibility* of measurements.

**Precision** of a measurement is determined by simply repeating the measurement on replicate samples.

Three terms are widely used to describe the **precision** of a set of replicate data:

## standard deviation,

variance, and

coefficient of variation.

All these terms are functions of the *deviation* from the mean d<sub>i</sub> or just the deviation.

$$\mathbf{d}_{\mathbf{i}} = |\mathbf{x}_{\mathbf{i}} - \mathbf{x}|$$

Sample set 1 is more precise than sample set 2.



# Accuracy

Accuracy is the closeness of a measurement to the true or accepted value and is expressed by the error.

Accuracy measures agreement between a result and its true value (precision describe the agreement among several measurements). We can **never** determine accuracy exactly because the true value of a measured quantity can never be known exactly. We need to use an accepted value.

Accuracy is expressed in terms of either absolute or relative error.

- Accuracy is more difficult to quantify than precision.
- Most methods claim to give the true value!





Accurate

Inaccurate

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High accuracy, low precision

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High accuracy, high precision

Illustration of accuracy and precision

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## Accuracy, cont.,

### **Absolute Error**

The absolute error of a measurement is the difference between the *measured value* and the *true value*.

The absolute error E in the measurement of a quantity  $x_i$  is given by the equation,

$$\mathbf{E} = \mathbf{x}_{\mathbf{i}} - \mathbf{x}_{\mathbf{t}}$$

where,  $x_t$  is the true or accepted value of the quantity.

The *negative* sign indicates that the experimental result is smaller than the accepted value and the *positive* sign indicates that the result is larger than the accepted value.

## **Relative Error**

Relative error of a measurement is the absolute error divided by the true value. The percent relative error is given by the expression,

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

Relative error also expressed in parts per thousand (ppt).

# **Analytical Errors**

In analytical measurements of a given system, the total variability is the sum of the true variability of the system and any introduced error during the analysis.

- Our goal as analysts is to minimize the amount of error in the measurement so that we can understand our samples.
- There are three types of error that can be present in any measurement:
  - 1. Random (indeterminate)
  - 2. Systematic (determinate)
  - 3. Gross error

## **Types of Errors in Experimental Data**



Absolute error in nitrogen determination Catalyst

# Systematic error

Systematic (or determinate) error:

The errors that affect the **accuracy** of a result. This type of error causes the mean of a set of data to differ from the accepted value. A systematic error caused the results in a series of replicate measurements to be all high or all low.

- causes a measurement to be *systematically* too large or too small.
- reproducible.
- the result of an experimental flaw (e.g. inaccurate standards, experimental design, personal bias, etc.)
- can be corrected (in almost all cases).

e.g. \*\* 10.00 mL pipette that delivers 10.02 mL

\*\*The electronic scale you use reads 0.05 g too high for all your mass measurements (because it is improperly tared throughout your experiment).

## **How do Systematic Errors Arise?**

There are three types of systematic errors:

- **1. Instrumental errors** are caused by the imperfections in measuring devices and instabilities in their components.
  - pipets, burets, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations.
  - the voltage of a battery operated power supply decreases with use.
  - noise induced from the alternating current (ac) power lines
- **2. Method errors** arise from nonideal chemical or physical behavior of analytical systems.
  - the slowness of some reactions, the incompleteness of others, the instability of some species, the nonspecificity of most reagents, and the possible occurrence of side reactions that interfere with the measurement process.
- **3. Personal errors** results from the carelessness, inattention, or personal limitations of the experimenter.
  - one person may read a pointer consistently high, another may be slightly slow in activating a timer, and a third may be less sensitive to color changes.

## **Effects of Systematic Errors**

- I. Constant Errors: Constant Errors does not depend on the size of the quantity measured
- **II. Proportional Errors:** Proportional errors decrease or increase in proportion to the size of the sample taken for analysis. A common cause of proportional errors is the presence of interfering contaminants in the sample.

# **Detecting Systematic Errors**

- Systematic instrument errors are usually corrected by *calibration*. Periodic calibration of equipment is always desirable.
- Personal errors can be minimized by care and self-discipline.
  - Errors that result from a known physical disability can usually be avoided by carefully choosing the method.
- **Method errors** or **bias** of an analytical method is estimated by analyzing **standard reference materials**.

**Standard reference materials** (SRM) are substances sold by the National Institute of Standard and Technology (NIST) and Certified to contain specified concentrations of one or more analytes. The concentration of the components in these materials has been determined in one of three ways:

- 1. By analysis with a previously validated reference method.
- 2. By analysis by two or more independent, reliable measurement methods.
- 3. By analysis by a network of cooperating laboratories.

## **Blank Determinations**

- A blank solution contains the solvent and all of the reagents in an analysis. Whenever feasible, blanks may also contain added constituents to simulate the sample matrix.
- **Blank determinations** are useful for detecting certain types of **constant errors**. In blank determination all steps of the analysis are performed in the absence of a sample.
- **Blank** are applied as a correction to the sample measurements. In which it can reveal errors due to interfering contaminants from the reagents and vessels employed in analysis.

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**Bias** measures the <u>systematic error</u> associated with an analysis. It has a negative sign if it causes the result to be low and a positive sign otherwise. Bias has a definite value, an assignable cause and are about the same magnitude for replicate measurements. Bias affects all the data in a set in the same way.

Bias = $\mu$ -  $x_t$ 

# Random error

Random (or indeterminate) error:

The errors that affect the **precision** of measurement. This type of error causes data to be scattered more or less symmetrically around a mean value. Random error in a measurement is reflected by its precision.

- Is always present.
- Has an equal chance of being positive or negative.
- Is the result of uncontrollable variables in an experiment.
- Cannot be entirely eliminated.

## e.g. electrical noise on an instrument

You measure the mass of a compound three times using the same balance and get slightly different values: 17.46 g, 17.42 g, 17.44 g

# **Gross errors**

- Occur only occasionally, are often large, and many cause a result to be either high or low.
- Product of human errors.
- Lead to **outliers** (is an occasional result in replicate measurements that differs significantly from the rest of the results).

# Homework (5-13)

Richards and Willard determined the atomic mass of lithium and collected the following data.

- a) Find the mean of atomic mass determined by these workers.
- b) Find the median of atomic mass.
- c) Find the **standard deviation** and **relative standard** deviation for atomic mass result.
- d) Assuming that the currently accepted value for the atomic mass of lithium is the true value, calculate the absolute error and the percent relative error of the mean value determined by Richards and Willard.
- e) Discuss your answers based on term of precision and accuracy for the result data.

Note: use MS-Exel to solve this problem and submit it on printed paper.

Experiment	Molar Mass, g/mol
1	6.9391
2	6.9407
3	6.9409
4	6.9399
5	6.9407
6	6.9391
7	6.9406

# Chapter 6 Random Error

## **The Nature of Random Errors**

Random, or indeterminate, errors occur whenever a measurement is made. This type of error is caused by the many uncontrollable variables that are an inevitable (لامناص) part of every physical or chemical measurement.

There are many contributors to random error, but often we cannot positively identify or measure them because they are small enough to avoid individual detection. The accumulated effect of the individual random uncertainties, however, causes the data from a set of replicate measurements to fluctuate (تذبذب) randomly around the mean of the set.

# **Distribution of Experimental Results**

#### TABLE 6-1

Possible Combinations of Four Equal-Sized Uncertainties						
Combinations of Uncertainties	Magnitude of Random Error	Number of Combinations	Relative Frequency			
$+ U_1 + U_2 + U_3 + U_4$	+ 4U	1	1/16 = 0.0625			
$- U_{1} + U_{2} + U_{3} + U_{4} + U_{1} - U_{2} + U_{3} + U_{4} + U_{1} + U_{2} - U_{3} + U_{4} + U_{1} + U_{2} + U_{3} - U_{4} U_{4} + U_{4} + U_{4} + U_{5} + U_{5} - U_{4} $	+ 2U	4	4/16 = 0.250			
$\begin{array}{l} -U_{1} - U_{2} + U_{3} + U_{4} \\ + U_{1} + U_{2} - U_{3} - U_{4} \\ + U_{1} - U_{2} + U_{3} - U_{4} \\ - U_{1} + U_{2} - U_{3} + U_{4} \\ - U_{1} + U_{2} + U_{3} - U_{4} \\ + U_{1} - U_{2} - U_{3} + U_{4} \\ + U_{1} - U_{2} - U_{3} - U_{4} \end{array}$	0	6	6/16 = 0.375			
$\begin{array}{c} -U_{1} + U_{2} - U_{3} - U_{4} \\ -U_{1} + U_{2} - U_{3} - U_{4} \\ -U_{1} - U_{2} + U_{3} - U_{4} \\ -U_{1} - U_{2} - U_{3} + U_{4} \end{array}$	-2U	4	4/16 = 0.250			
$-U_1 - U_2 - U_3 - U_4$	-4U	1	1/16 = 0.0625			

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### Frequency distribution







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TABLE 6-2

	A	В	С	D	E	F	G	Н
1	Replicate I	Data for the Ca	libr	ation of a 1	0-mL Pipet*			
2	Trial	Volume, mL		Trial	Volume, mL		Trial	Volume, mL
3	1	9.988		18	9.975		35	9.976
4	2	9.973		19	9.980		36	9.990
5	3	9.986		20	9.994		37	9.988
6	4	9.980		21	9.992		38	9.971
7	5	9.975		22	9.984		39	9.986
8	6	9.982		23	9.981		40	9.978
9	7	9.986		24	9.987		41	9.986
10	8	9.982		25	9.978		42	9.982
11	9	9.981		26	9.983		43	9.977
12	10	9.990		27	9.982		44	9.977
13	11	9.980		28	9.991		45	9.986
14	12	9.989		29	9.981		46	9.978
15	13	9.978		30	9.969		47	9.983
16	14	9.971		31	9.985		48	9.980
17	15	9.982		32	9.977		49	9.984
18	16	9.983		33	9.976		50	9.979
19	17	9.988		34	9.983			
20	*Data listed in the order obtained							
21	Mean	9.982		Maximum	9.994			
22	Median	9.982		Minimum	9.969			
23	Std. Dev.	0.0056		Spread	0.025			

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9.972-9.974			1			2		
9.975-9.977			7			14		
9.978-9.980			9			18		
9.981-9.983			13			26		
9.984-9.986			7				14	
9.987-9.989			5				10	
9.990-9.992			4				8	
9.993-9.995		-	I Fotal — 4	50			2 Total $= 10$	00
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20		/	$\frown$		D			
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4								
0	1							,
9.969 9.972	9.975	9.978	9.981	9.984	9.987	9.990	9.993	
2.2/1 2.9/4	2.711	2.200	9.903	7.700	7.707	7.774	7.775	

#### TABLE 6-3

#### **Sources of Random Errors**

- Sources of random uncertainties in the calibration of a *pipet* include:
  - (1) visual judgments, such as the level of the water with respect to the marking on the pipet and the mercury level in the thermometer;
  - (2) variations in the drainage time and in the angle of the pipet as it drains;
  - (3) temperature fluctuations, which affect the volume of the pipet, the viscosity of the liquid, and the performance of the balance; and
  - (4) vibrations and drafts that cause small variations in the balance readings.
- □ Undoubtedly, numerous other sources of random uncertainty also operate in this calibration process.
- □ It is difficult or impossible to determine the influence of any one of the random errors arising from these variables, but the cumulative effect is responsible for the scatter of data points around the mean.



## **Samples and Populations**

A finite (محدود) number of experimental observations is called a *sample* of data. The sample is treated as a tiny fraction of an infinite number of observations that could in principle be made given infinite time.

Statisticians call the theoretical infinite number of data a *population*, or a *universe*, of data. Statistical laws have been derived assuming a population of data; often, they must be modified (يعدل) substantially (فعليا) when applied to a small sample because a few data points may not be representative of the population.

### The Population Mean $\mu$ and the Sample Mean x

Statisticians find it useful to differentiate between a *sample mean* and a *population mean*.

The sample mean x is the mean of a limited sample drawn from a population of data.

The population mean  $\mu$ , in contrast, is the true mean for the population.

In the absence of any **systematic error**, the population mean is the **true** value for the measured quantity.

To emphasize the difference between the two means, the sample mean is symbolized by  $\overline{x}$  and the population mean by  $\mu$ .

When N is small,  $\bar{\mathbf{x}}$  differs from  $\mu$  because a small sample of data does not exactly represent its population. The probable difference between  $\bar{\mathbf{x}}$  and  $\mu$  decreases rapidly as the number of measurements making up the sample increases; ordinarily (allow), by the time N reaches 20 to 30, this difference is negligibly small.

$$\overline{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$
, when N is small

$$\mu = \frac{\sum_{i=1}^{N} x_i}{N}, \text{ when } N \to \infty$$

### The Population Standard Deviation( $\sigma$ )

The *population standard deviation*  $\sigma$ , which is a measure of the precision or scatter of a population of data, is given by the equation



2 where: N is the number of data points making up the population.

**variance :** The square of the standard deviation =  $\sigma^2$ 

$$\sigma^2 = \frac{\sum_{i=1}^{N} (\overline{\mu} - \mu)^2}{N}$$

The standard deviation has the same units as the data, whereas the variance has the units of the data squared. It is easier to relate a measurement and its precision if they both have the same units.

The advantage of using variance is that variances are additive.

### **Sample Standard Deviation**

*Standard Deviation* equation must be modified when it is applied to a small sample of data. Thus, the *sample standard deviation* s is given by the equation

$$s = \sqrt{\frac{\sum_{i=1}^{N} (\bar{x} - x)^2}{N - 1}} = \sqrt{\frac{\sum_{i=1}^{N} d_i^2}{N - 1}}$$

This equation differs from the standard deviation equation in two ways. First, the sample mean,  $\mathbf{x}$ , appears in the numerator of *sample standard deviation* equation in place of the population mean,  $\mu$ . Second, N in *standard deviation* equation is replaced by the *number of degrees of freedom* (N-I).

The sample variance  $s^2$  is also of importance in statistical calculations. It is an estimate of the population variance  $\sigma^2$ .

## Variance (s<sup>2</sup>)

$$s^{2} = \frac{\sum_{i=1}^{N} (\bar{x} - x)^{2}}{N - 1} = \frac{\sum_{i=1}^{N} d_{i}^{2}}{N - 1}$$

## **Normal error curves**



The two **normal error curves** in *Fig. 6-4* are for two populations of data that differ only in their standard deviations.

The standard deviation for the data set yielding the broader but lower curve B is twice that for the measurements yielding curve A. the breadth of these curves is a measure of the **precision** of the two sets of data. Thus, the precision of the data leading to curve A is twice as good as that of the data that are represented by curve Batalyst

...continued...

Fig. 6-4b shows another type of **normal error curve** in which the abscissa is now a new variable z, which is defined as,

 $z = (x - \mu) / \sigma$ 

**z** is the deviation of a data point from the mean relative to one standard deviation. That is, when **x** -  $\mu = \sigma$ , **z** is equal to one; when **x** -  $\mu = 2\sigma$ , **z** is equal to two; and so forth.

A plot of relative frequency versus this parameter yields a single Gaussian curve that describes all populations of data regardless (مهما يكن) of standard deviation.

A normal error curve has several general properties:

(1) The mean occurs at the central point of maximum frequency,

(2) there is a symmetrical distribution of positive and negative deviations about the maximum, and

(3) there is an exponential decrease in frequency as the magnitude of the deviations increases. Thus, small random uncertainties are observed much more often than very large ones.

## Areas under a Gaussian Curve

- It can be shown that, regardless of its width, 68.3% of the area beneath a Gaussian curve for a population of data lies within one standard deviation  $(\pm 1\sigma)$  of the mean  $\mu$ . Thus, 68.3% of the data making up the population will lie within these bounds.
- Furthermore, approximately 95.4% of all data points are within  $\pm 2\sigma$  of the mean and 99.7% within  $\pm 3\sigma$ .



### **Relative Standard Deviation (RSD) and Coefficient of Variation (CV)**

We calculate the relative standard deviation by dividing the standard deviation by the mean of the set of data. It is often expressed in parts per thousand (ppt) or in percent by multiplying this ratio by 1000 ppt or by 100%.

 $RSD = s / \overline{\chi} \times 1000 \text{ ppt}$ 

The relative standard deviation multiplied by 100% is *called the coefficient of variation* (CV).

 $CV = s / \overline{\chi} \times 100\%$ 

Relative standard deviations often give a clearer picture of data quality than do absolute standard deviations.

### Standard Error of the Mean $(s_m)$

is the standard deviation of a set of data divided by the square root of the number of data points in the set.

$$s_m = \frac{s}{\sqrt{N}}$$

If a series of replicate results, each containing N measurements, are taken randomly from a population of results, the mean of each set will show less and less scatter as N increases.

For example, to increase the precision by a factor of 10 requires 100 times as many measurements. It is better, if possible, to decrease s than to keep averaging more results, since s, is directly proportional to s, but only inversely proportional to the *square root of N*. The standard deviation can sometimes be decreased by being more precise in individual operations, by changing the procedure, and by using more precise measurement tools.

# Pooling Data to Improve the Reliability of s

- If we have several subsets of data, we can get a better estimate of the population standard deviation by pooling (combining) the data than by using only one data set.
  - must assume the <u>same sources of random error</u> in all the measurements.
    - valid if the samples have <u>similar compositions</u> and have been <u>analyzed in</u> <u>exactly the same way</u>.
  - must assume that the samples are randomly drawn from the same population and thus have a common value of  $\sigma$ .

$$s_{\text{pooled}} = \sqrt{\frac{\sum_{i=1}^{N_1} (x_i - \bar{x}_1)^2 + \sum_{j=1}^{N_2} (x_j - \bar{x}_2)^2 + \sum_{k=1}^{N_3} (x_k - \bar{x}_3)^2 + \cdots}{N_1 + N_2 + N_3 + \cdots - N_t}}$$

where  $N_1$  is the number of results in set 1,  $N_2$  is the number in set 2, and so forth. The term  $N_t$  is the total number of data sets pooled.

Example 6-2: Glucose levels are routinely monitored in patients suffering from diabetes. The glucose concentrations in a patient with mildly elevated glucose levels were determined in different months by a spectrophotometric analytical method. The patient was placed on a low-sugar diet to reduce the glucose levels. The following results were obtained during a study to determine the effectiveness of the diet. Calculate a pooled estimate of the standard deviation for the method.

Total number of measurements
= 24
Total sum of squares
= 6907.89

		Glucose	Glucose,	of Deviations	Standard
nents	Time	Concentration, mg/L	mg/L	from Mean	Deviation
	Month 1	1108, 1122, 1075, 1099, 1115,	1100.3	1687.43	16.8
		1083, 1100			
	Month 2	992, 975, 1022, 1001, 991	996.2	1182.80	17.2
	Month 3	788, 805, 779, 822, 800	798.8	1086.80	16.5
	Month 4	799, 745, 750, 774, 777, 800, 758	771.9	2950.86	22.2

#### **Solution**

For the first month, the sum of the squares in the next to last column was calculated as follows: Sum of squares =  $(1108\ 2\ 1100.3)^2 + (1122\ 2\ 1100.3)^2 + (1075\ 2\ 1100.3)^2 + (1099\ 2\ 1100.3)^2$  $+ (1115\ 2\ 1100.3)^2 + (1083\ 2\ 1100.3)^2 + (1100\ 2\ 1100.3)^2 = 1687.43$ 

The other sums of squares were obtained similarly. The pooled standard deviation is then

$$s_{\text{pooled}} = \sqrt{\frac{6907.89}{24 - 4}} = 18.58 \approx 19 \text{ mg/L}$$

Note this pooled value is a better estimate of s than any of the individual *s* values in the last column. Note also that one degree of freedom is lost for each of the four sets. Because 20 degrees of freedom remain, however, the calculated value of *s* can be considered a good Catalyst estimate of s.

**Spread or Range (w):** The spread, or range, is another term that is sometimes used to describe the precision of a set of replicate results. It is the difference between the largest value in the set and the smallest.

# Standard Deviation on of Calculated Results **Propagation of Errors**

A way to keep track of the error in a calculation based on the errors of the variables used in the calculation

#### TABLE 6-4

Error Propagation in Arithmetic Calculations					
Type of Calculation	Example*	Standard Deviation of y†			
Addition or subtraction	y = a + b - c	$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$	(1)		
Multiplication or division	$y = a \times b/c$	$\frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2}$	(2)		
Exponentiation	$y = a^x$	$\frac{s_y}{y} = x\left(\frac{s_a}{a}\right)$	(3)		
Logarithm	$y = \log_{10} a$	$s_y = 0.434 \frac{s_a}{a}$	(4)		
Antilogarithm	$y = \operatorname{antilog}_{10} a$	$\frac{s_y}{y} = 2.303 s_a$	(5)		

\**a*, *b*, and *c* are experimental variables with standard deviations of  $s_a$ ,  $s_b$ , and  $s_c$ , respectively <sup>†</sup>These relationships are derived in Appendix 9. The values for  $s_y/y$  are absolute values if *y* is a negative number. Catalyst

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Example: Suppose you're adding three volumes together and you want to know what the total error (s) is:

+ 0.50 (± 0.02) + 4.10 (± 0.03) - 1.97 (± 0.05) 2.63  $y = a(\pm s_a) + b(\pm s_b) - c(\pm s_c)$  $s^2_y = s^2_a + s^2_b + s^2_c$  $s_y = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{(\pm 0.02)^2 + (0.03)^2 + (0.05)^2} = \pm 0.06$ 

and the sum should be reported as  $2.64 (\pm 0.06)$ .

Example: 
$$\frac{4.10(\pm 0.02) \times 0.0050(\pm 0.0001)}{1.97(\pm 0.04)} = 0.010406(\pm?)$$
$$\frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2} \frac{s_y}{y} = \sqrt{\left(\frac{\pm 0.02}{4.10}\right)^2 + \left(\frac{\pm 0.001}{0.0050}\right)^2 + \left(\frac{\pm 0.04}{1.97}\right)^2} = \sqrt{(0.0049)^2 + (0.0200)^2 + (0.0203)^2} = \pm 0.0289$$

 $s_v = y X (\pm 0.0289) = 0.0104 x (\pm 0.0289) = \pm 0.000301$ 

and we can write the answer and its uncertainty as:  $0.0104 (\pm 0.0003)$ .

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### **EXAMPLE 6-5**

The solubility product  $K_{sp}$  for the silver salt AgX is 4.0 (±0.4) × 10<sup>-8</sup>, and the molar solubility is

solubility = 
$$(K_{sp})^{1/2} = (4.0 \times 10^{-8})^{1/2} = 2.0 \times 10^{-4} M$$

What is the uncertainty in the calculated solubility of AgX?

### Solution

Substituting y = solubility,  $a = K_{sp}$ , and  $x = \frac{1}{2}$  into Equation 6-13 gives

$$\frac{s_a}{a} = \frac{0.4 \times 10^{-8}}{4.0 \times 10^{-8}}$$
$$\frac{s_y}{y} = \frac{1}{2} \times \frac{0.4}{4.0} = 0.05$$
$$s_y = 2.0 \times 10^{-4} \times 0.05 = 0.1 \times 10^{-4}$$
solubility = 2.0 (±0.1) × 10<sup>-4</sup> M

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#### **EXAMPLE 6-6**

Calculate the absolute standard deviations of the results of the following calculations. The absolute standard deviation for each quantity is given in parentheses.

(a) 
$$y = \log[2.00(\pm 0.02) \times 10^{-4} = -3.6990 \pm 200)$$

b) 
$$y = \operatorname{antilog}[1.200(\pm 0.003)] = 15.849 \pm 32$$

(c) 
$$y = \text{antilog}[45.4(\pm 0.3)] = 2.5119 \times 10^{45} \pm ?$$

#### Solution

(a) Referring to Equation 6-14, we see that we must multiply the *relative* standard deviation by 0.434:

$$s_y = \pm 0.434 \times \frac{0.02 \times 10^{-4}}{2.00 \times 10^{-4}} = \pm 0.004$$

Thus,

$$y = \log[2.00(\pm 0.02) \times 10^{-4}] = -3.699 (\pm 0.004)$$

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# **Reporting Computed Data**

- A numerical result is worthless unless the user knows something about its accuracy and/or precision. It is always essential to indicate best estimate of the reliability of data. One of the best ways of indicating reliability is to:
- give a confidence interval at the 90% or 95% confidence level.
- report the absolute standard deviation or the coefficient of variation of the data.
- It is a good idea to indicate the number of data points that were used to obtain the standard deviation so that the user has some idea of the probable reliability of s. Less satisfactory but more common indicator of the quality of data is the significant figure convention.

# Significant Figures

Digits in a measurement which are known with • certainty, plus a last digit which is estimated



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## Rules for Determining How Many Significant Figures There are in a Number

- All nonzero digits are *significant* (4.006, 12.012, 10.070)
- Interior zeros are *significant* (4.006, 12.012, 10.070)
- Trailing (يعقب) zeros FOLLOWING a decimal point are significant (10.070)
- Trailing zeros PRECEEDING an assumed decimal point *may or may not be significant*
- Leading zeros are *not significant*. They simply locate the decimal point (0.00002)

## Reporting the Correct # of Sig Fig's

• Multiplication/Division

Rule: Round off to the fewest number of sig figs originally present



## Reporting the Correct # of Sig Fig's

Addition/Subtraction 15.02
 9,986.0
 3.518
 10004.538

Rule: Round off to the least certain decimal place

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## Logarithms and Antilogarithms

- 1. In a logarithm of a number, keep as many digits to the right of the decimal point as there are significant figures in the original number.
- 2. In an antilogarithm of a number, keep as many digits as there are digits to the right of the decimal point in the original number.

#### **EXAMPLE 6-8**

Round the following answers so that only significant digits are retained: (a)  $\log 4.000 \times 10^{-5} = -4.3979400$  and (b) antilog  $12.5 = 3.162277 \times 10^{12}$ .

(a) Following rule 1, we retain 4 digits to the right of the decimal point:

 $\log 4.000 \times 10^{-5} = -4.3979$ 

(b) Following rule 2, we may retain only 1 digit:

antilog  $12.5 = 3 \times 10^{12}$ 

# Rounding Off Rules

- digit to be dropped > 5, round UP
   158.7 = 159
- digit to be dropped < 5, round DOWN 158.4 = 158
- digit to be dropped = 5, round UP if result is EVEN

158.5 = 158157.5 = 157 Wait until the END of a calculation in order to avoid a "rounding error"



# Homework

Calculate the following: (each # represents x<sub>i</sub>±s<sub>i</sub>)

# $\frac{1.10 (\pm 0.10) + 0.25 (\pm 0.020)}{2.57 (\pm 0.35)}$

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# **Chapter 9**

# **Aqueous Solutions and Chemical Equilibria**

#### **Solutions of Electrolytes**

- **Electrolytes:** Form ions when dissolved in water or other solvents and produce solutions that conduct electricity.
- Strong Electrolytes: Ionize essentially completely (Strong conductor of electricity).
- Weak Electrolytes: Ionize only partially (Poorer conductor than strong electrolyte).
- **Nonelectrolytes:** Are substances that dissolve in water but do not produce any ions and do not conduct an electric current.
- Acids and Bases: An acid is a proton donor and a base is a 24(Bronsted-Lowry concept).
- **Conjugate Acids and Bases:** A conjugate base is the species formed when an acid loses a proton.

acid<sub>1</sub>  $\longrightarrow$  base<sub>1</sub> + proton CH<sub>3</sub>COOH  $\longleftarrow$  CH<sub>3</sub>COO<sup>-</sup> + H<sup>+</sup> acid<sub>1</sub> and base<sub>1</sub> are a conjugate acid/base pair

#### TABLE 9-1

Classification of Electrolytes				
Strong	Weak			
<ol> <li>Inorganic acids such as HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sup>*</sup><sub>4</sub>, HCl, HI, HBr, HClO<sub>3</sub>, HBrO<sub>3</sub></li> <li>Alkali and alkaline-earth hydroxides</li> <li>Most salts</li> </ol>	<ol> <li>Many inorganic acids, including H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>S, H<sub>2</sub>SO<sub>3</sub></li> <li>Most organic acids</li> <li>Ammonia and most organic bases</li> <li>Halides, cyanides, and thiocyanates of</li> </ol>			
	Hg, Zn, and Cd			

\*H<sub>2</sub>SO<sub>4</sub> is completely dissociated into HSO<sub>4</sub><sup>-</sup> and H<sub>3</sub>O<sup>+</sup> ions and for this reason is classified as a strong electrolyte. It should be noted, however, that the HSO<sub>4</sub><sup>-</sup> ion is a weak electrolyte, being only partially dissociated into SO<sub>4</sub><sup>2-</sup> and H<sub>3</sub>O<sup>+</sup>.

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A conjugate acid is the species formed when a base accepts a proton.

base<sub>2</sub> + proton  $\iff$  acid<sub>2</sub> When two processes are combined, the result is an acid/base or neutralization reaction.

 $NH_3 + H_2O \iff NH_4^+ + OH^$ base<sub>1</sub> acid<sub>2</sub> conjugate acid<sub>1</sub> conjugate base<sub>2</sub>

**Amphiprotic Solvents:** A solvent that can act either as an acid or as a base depending on the solute.

\*\* Water is the classic example.

 $\begin{array}{rcl} \mathrm{NH}_3 &+& \mathrm{H}_2\mathrm{O} & \rightleftharpoons & \mathrm{NH}_4^+ &+& \mathrm{OH}^-\\ \mathrm{base}_1 & \mathrm{acid}_2 & & \mathrm{c.} \ \mathrm{acid}_1 & & \mathrm{c.} \ \mathrm{base}_2 \end{array}$ 

 $H_2O + HNO_2 \iff H_3O^+ + NO_2^$ base<sub>1</sub> acid<sub>2</sub> c. acid<sub>1</sub> c. base<sub>2</sub>

 $NH_3 + CH_3OH \iff NH_4^+ + CH_3O^$ base<sub>1</sub> acid<sub>2</sub> c. acid<sub>1</sub> c. base<sub>2</sub>

 $\begin{array}{rcl} CH_{3}OH &+ HNO_{2} & \longrightarrow & CH_{3}OH_{2}^{+} &+ & NO_{2}^{-} \\ base_{1} & acid_{2} & c. \ acid_{1} & c. \ base_{2} \end{array}$ 

Autoprotolysis: Amphiprotic solvents undergo self ionization to form a pair of ionic species.

 $H_2O + H_2O \implies H_3O^+ + OH^ CH_3OH + CH_3OH \implies CH_3OH_2^+ + CH_3O^-$ 

**Strong acid:** Reacts with water so **completely** that no undissociated solute molecules remain.

- Weak acid: Reacts incompletely with water to give solution that contain significant amounts of both the parent acid and its conjugate base.
- Strong base: Completely dissociated in water solution

Weak base: Incomplete dissociation in water solution

#### **Relative Strength**



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□ The weakest acid forms the strongest conjugate base.

□ The tendency of a solvent to accept or donate protons determine the strength of a solute acid or base dissolved in it.

 $H_2O + HClO_4 \longrightarrow H_3O^+ + ClO_4^ CH_3COOH + HClO_4 \longrightarrow CH_3COOH_2^+ + ClO_4^-$ 

 $base_1$   $acid_2$   $acid_1$   $base_2$ 

#### **Chemical Equilibrium**

- □ Most of the chemical reactions never result in complete conversion of reactants to products. They proceed to a state of **chemical equilibrium** in which the *ratio* of concentrations of reactants and products is constant.
- □ Equilibrium-constant expressions are algebraic equations that describe the concentration relationships that exist among reactants and products at equilibrium.
- □ The position of a chemical equilibrium is independent of the route by which equilibrium is reached.
- □ The Le-Chatelier principle states that the shifts in such a direction as to relieve a stress that is applied to the systemposition of an equilibrium always.
- □ The **mass-action effect** is a shift in the position of an equilibrium caused by adding one of the reactants or products to a system.

## Writing Equilibrium Constants

 $wW + xX \longrightarrow yY + zZ$ 

Where, the capital letters represent the formulas of participating chemical species and the lowercase letters are the small whole numbers (# of moles) required to balance the equation. The equilibrium-constant expression is

$$\mathbf{K} = \frac{[\mathbf{Y}]^{y} \quad [\mathbf{Z}]^{z}}{[\mathbf{W}]^{w} \quad [\mathbf{X}]^{x}}$$

Where, the bracketed terms are molar concentration if the species is a dissolved solute or partial pressure (atm) if the species is a gas.

If one of the species is a pure liquid, a pure solid, or the solvent in excess (dilute soln.), no term for this species appear in the equilibrium-constant expression.

Equilibrium constant K is a temperature dependent quantity.

#### **The Ion-Product Constant for Water**

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a consequence of the dissociation reaction.

 $2H_2O \implies H_3O^+ + OH^-$ 

Equilibrium constants,

$$K = \frac{[H_3O^+] [OH^-]}{[H_2O]^2}$$

The concentration of water in dilute aqueous solution is enormous when compared with the concentration of hydrogen and hydroxide ions.  $[H_2O]$  can be taken as constant,

 $K[H_2O]^2 = K_w = [H_3O^+][OH^-]$  where the new constant is the ion-product constant for water. At 25°C,  $K_w \approx 1.00 \times 10^{-14}$ 

$$-\log K_{w} = -\log[H_{3}O]^{+} - \log[OH^{-}]$$
$$pK_{w} = pH + pOH = 14.00$$
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#### **Solubility-Products**

$$Ba(IO_3)_{2(s)} \iff Ba^{2+}_{(aq)} + 2IO_3^{-}_{(aq)}$$
$$K = \frac{[Ba^{2+}] [IO_3^{-}]^2}{[Ba(IO_3)_2(S)]}$$

 $K[Ba(IO_3)_{2(s)}] = K_{sp} = [Ba^{2+}][IO_3^{--}]^2$ 

Where, the new constant,  $K_{sp}$ , is called the solubility-product. The position of this equilibrium is independent of the amount of Ba(IO<sub>3</sub>)<sub>2</sub> as long as some solid is present.

#### **Common Ion Affect**

The common-ion effect is responsible for the <u>reduction</u> in solubility of an ionic precipitate when a soluble compound combining one of the ions of the precipitate is added to the solution in equilibrium with the precipitate.

#### **Dissociation Constants for Acids and Bases**

When a weak acid or a weak base is dissolved in water, partial dissociation occurs,

$$HNO_{2} + H_{2}O \iff H_{3}O^{+} + NO_{2}^{-}, K_{a} = \frac{[H_{3}O^{+}] [NO_{2}]}{[HNO_{2}]}$$
$$NH_{3} + H_{2}O \iff NH_{4}^{+} + OH^{-}, K_{b} = \frac{[NH_{4}^{+}] [OH^{-}]}{[NH_{3}]}$$
Where  $K_{a}$  and  $K_{b}$  are acid dissociation constant for nitrous acid and base dissociation constant for ammonia respectively.

Dissociation Constants for Conjugate Acid/Base Pairs:  $NH_{3} + H_{2}O \longrightarrow NH_{4}^{+} + OH^{-}, \qquad K_{b} = \frac{[NH_{4}^{+}] \quad [OH^{-}]}{[NH_{3}]}$   $NH_{4}^{+} + H_{2}O \longrightarrow NH_{3} + H_{3}O^{+}, \qquad K_{a} = \frac{[NH_{4}^{+}] \quad [OH^{-}]}{[NH_{3}]}$   $K_{a}. K_{b} = [H_{3}O^{+}][OH^{-}] = K_{w} \qquad K_{a} = \frac{[NH_{3}] \quad [H_{3}O^{+}]}{[NH_{4}^{+}]}_{Catalyst}$ 

#### TABLE 9-2

Equilibria and Equilibrium Constants Important in Analytical Chemistry						
Type of Equilibrium	Name and Symbol of Equilibrium Constant	Typical Example	Equilibrium-Constant Expression			
Dissociation of water Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Ion-product constant, $K_w$ Solubility product, $K_{sp}$	$2 H_2 O \rightleftharpoons H_3 O^+ + OH^-$ BaSO <sub>4</sub> (s) $\rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{w} = [H_{3}O^{+}][OH^{-}]$ $K_{sp} = [Ba^{2+}][SO_{4}^{2-}]$			
Dissociation of a weak acid or base	Dissociation constant, $K_{a}$ or $K_{b}$	$CH_3COOH + H_2O \rightleftharpoons$ $H_3O^+ + CH_3COO^-$	$K_{a} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{CH}_{3}\mathrm{COO}^{-}]}{[\mathrm{CH}_{3}\mathrm{COOH}]}$			
		$CH_3COO^- + H_2O \rightleftharpoons$ $OH^- + CH_3COOH$	$K_{\rm b} = \frac{[\rm OH^-][\rm CH_3COOH]}{[\rm CH_3COO^-]}$			
Formation of a complex ion	Formation constant, $\beta_n$	$Ni^{2+} + 4CN^{-} \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$			
Oxidation/reduction equilibrium	K <sub>redox</sub>	$MnO_4 + 5Fe^{2+} + 8H^+ \rightleftharpoons$ $Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{Mn}\text{O}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$			
Distribution equilibrium for a solute between immiscible solvents	Kd	$I_2(aq) \rightleftharpoons I_2(org)$	$K_{\rm d} = \frac{[\mathrm{I}_2]_{\rm org}}{[\mathrm{I}_2]_{\rm aq}}$			

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# Chapter 10 Effect of Electrolytes on Chemical Equilibria

The position of most solution equilibria depends on the electrolyte concentration of the medium, even when the added electrolyte contains no ion in common with those involved in the equilibrium.

 $H_3AsO_4 + 3I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$ 

If an electrolyte, such as barium nitrate, potassium sulfate, or sodium perchlorate, is added to this solution, the color of the triiodide ion becomes less intense. This decrease in color intensity indicates that the concentration of  $I_3^-$  has decreased and that the equilibrium has been shifted to the left by the added electrolyte.



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## **How Do Ionic Charges Affect Equilibria?**

- The magnitude of the electrolyte effect is highly dependent on the **charges** of the participants in an equilibrium.
- When only *neutral species* are involved, the position of equilibrium is essentially independent of electrolyte concentration.
- With *ionic participants*, the magnitude of the electrolyte effect <u>increases with charge</u>.
- Example: In a 0.02 M solution of potassium nitrate, the solubility of barium sulfate is larger than it is in pure water by a factor of 2. The solubility of barium iodate by a factor of only 1.25 and that of silver chloride by 1.2



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#### **TABLE 10-1**

Effect of Charge on Ionic Strength					
Type Electrolyte	Example	Ionic Strength*			
1:1	NaCl	С			
1:2	Ba(NO <sub>3</sub> ) <sub>2</sub> , NA <sub>2</sub> SO <sub>4</sub>	3 <i>c</i>			
1:3	Al(NO <sub>3</sub> ) <sub>3</sub> , Na <sub>3</sub> PO <sub>4</sub>	6 <i>c</i>			
2:2	$MgSO_4$	4 <i>c</i>			

\*c = molarity of the salt.

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#### What Is the Effect of Ionic Strength on Equilibria?

• The effect of added electrolyte on equilibria is <u>independent of the chemical nature</u> of the electrolyte but depends on a property of the solution called the **ionic strength**. This quantity is defined as ionic strength ( $\mu$ ):

$$\mu = 1/2([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + ...)$$

Where [A], [B], [C], ... represent the molar species concentrations of ions A, B, C, ... and  $Z_A, Z_B, Z_C$ , ... are their ionic charges.

• For solutions with ionic strengths of 0.1 M or less, the electrolyte effect is independent of the kind of ions and <u>dependent only on the ionic strength</u>. This independence with respect to electrolyte species disappears at high ionic strengths.

## The Salt Effect

The electrolyte effect results from the electrostatic *attractive* and *repulsive* forces that exist between the ions of an electrolyte and the ions involved in an equilibrium. These forces cause each ion from the dissociated reactant to be <u>surrounded by a sheath of solution</u> that contains a slight excess of electrolyte ions of opposite charge.

Example: When a barium sulfate precipitate is equilibrated with a sodium chloride solution, each dissolved barium ion is surrounded by an ionic atmosphere carries a small net negative charge.

Each sulfate ion is surrounded by an ionic atmosphere that tends to be slightly positive. These charged layers make the barium ions somewhat less positive and the sulfate ions somewhat less negative than they would be in the absence of electrolyte. The consequence of this effect is a decrease in overall attraction between barium and sulfate ions and an increase in solubility, which becomes greater as the number of electrolyte ions in the solution becomes larger.



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## **Activity Coefficients**

Chemists use the term activity, a, to account for the effects of electrolytes on chemical equilibria. The activity, or effective concentration, of species X depends on the ionic strength of the medium and is defined as

$$a_X = \gamma_x [X]$$

where,  $a_X$  is the activity of X, [X] is its molar concentration, and  $\gamma_x$  is a dimensionless quantity called the activity coefficient.

The activity coefficient and thus the activity of X vary with ionic strength such that substitution of  $a_X$  for [X] in any equilibrium-constant expression frees the numerical value of the constant from dependence on the ionic strength. If  $X_m Y_n$  is a precipitate, the thermodynamic solubility product expression is defined by the equation

$$\begin{split} \mathbf{K}_{sp} &= \mathbf{a}_{\mathbf{X}}{}^{m}.\mathbf{a}_{\mathbf{Y}}{}^{n} \\ \mathbf{K}_{sp} &= \gamma_{\mathbf{X}}{}^{m}.\ \gamma_{\mathbf{Y}}{}^{n}.[\mathbf{X}]{}^{m}[\mathbf{Y}]{}^{n} = \gamma_{\mathbf{X}}{}^{m}.\ \gamma_{\mathbf{Y}}{}^{n}.\ \mathbf{K}{}^{s}{}_{sp} \end{split}$$

Here  $K_{sp}$  is the concentration solubility product constant and  $K_{sp}$  is the thermodynamic equilibrium constant.

#### **Properties of Activity Coefficients**

1. The activity coefficient of a species is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant. In very dilute solution, where the ionic strength is minimal, this effectiveness becomes constant and the activity coefficient becomes unity. Under such circumstances, the activity and the molar concentration are identical (as are thermodynamic and concentration equilibrium constants). As the ionic strength increases, however, an ion loses some of its effectiveness and its activity coefficient decreases. At moderate ionic strengths,  $\gamma_x < 1$ ; as the solution approaches infinite dilution, however,  $\gamma_x \rightarrow 1$  and thus  $a_x \rightarrow [X]$  and  $K_{sp} \rightarrow K_{sp}$ 





#### ...continued...

2. In solutions that are not too concentrated, the activity coefficient for a given species is independent of the nature of the electrolyte and dependent only on the ionic strength.

3. For a given ionic strength, the activity coefficient of an ion departs farther from unity as the charge carried by the species increases. The activity coefficient of an uncharged molecule is approximately unity, regardless of ionic strength.

4. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal. The small variations that do exist can be correlated with the effective diameter of the hydrated ions.

5. The activity coefficient of a given ion describes its effective behavior in all equilibria in which it participates.

## **The Debye-Huckel Equation**

P. Debye and E. Huckel derive a theoretical expression that permits the calculation of activity coefficients of ion from their charge and their average size. This equation takes the form

$$-\log \gamma_{\rm X} = \frac{0.51 Z_{\rm X}^2 \sqrt{\mu}}{1 + 3.3 \alpha_{\rm X} \sqrt{\mu}} \log \gamma_{\rm X} = \frac{0.51 Z_{\rm X}^2 \sqrt{\mu}}{1 + 3.3 \alpha_{\rm X} \sqrt{\mu}}$$

where,  $\gamma_x$  = activity coefficient of the species X  $Z_x$  = charge on the species X  $\mu$  = ionic strength of the solution  $\alpha_x$  = effective diameter of the hydrated ion X in nanometer (10<sup>-9</sup> m)

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...continued...

The constants 0.51 and 3.3 are applicable to aqueous solution at 25°C; The magnitude of  $\alpha_x$  appears to be approximately 0.3 nm for most singly charged ions; then, the denominator of the Debye-Huckel equation simplifies to approximately 1 + $\sqrt{\mu}$ . For ions with higher charge,  $\alpha_x$  may be as large as 1.0 nm.

TABLE 10-2							
Activity Coefficients for lons at 25°C							
	Activity Coefficient at Indicated Ionic Strength						
Ion	$\alpha_{\rm X}$ , nm	0.001	0.005	0.01	0.05	0.1	
H <sub>3</sub> O <sup>+</sup>	0.9	0.967	0.934	0.913	0.85	0.83	
$Li^+, C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80	
Na <sup>+</sup> , IO <sub>3</sub> , HSO <sub>3</sub> , HCO <sub>3</sub> , H <sub>2</sub> PO <sub>4</sub> , H <sub>2</sub> AsO <sub>4</sub> , OAc <sup>-</sup>	0.4-0.45	0.965	0.927	0.902	0.82	0.77	
OH-, F-, SCN-, HS-, CIO3-, CIO4, BrO3, IO3, MnO4	0.35	0.965	0.926	0.900	0.81	0.76	
K <sup>+</sup> , CI <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , CN <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , HCOO <sup>-</sup>	0.3	0.965	0.925	0.899	0.81	0.75	
$Rb^{+}, Cs^{+}, TI^{+}, Ag^{+}, NH_{4}^{+}$	0.25	0.965	0.925	0.897	0.80	0.75	
Mg <sup>2+</sup> , Be <sup>2+</sup>	0.8	0.872	0.756	0.690	0.52	0.44	
Ca <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Sn <sup>2+</sup> , Mn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Phthalate <sup>2-</sup>	0.6	0.870	0.748	0.676	0.48	0.40	
Sr <sup>2+</sup> , Ba <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , S <sup>2-</sup>	0.5	0.869	0.743	0.668	0.46	0.38	
$Pb^{2+}, CO_3^{2-}, SO_3^{2-}, C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36	
$Hg_2^{2+}$ , $SO_4^{2-}$ , $S_2O_3^{2-}$ , $Cr_4^{2-}$ , $HPO_4^{2-}$	0.40	0.867	0.738	0.661	0.44	0.35	
Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , La <sup>3+</sup> , Ce <sup>3+</sup>	0.9	0.737	0.540	0.443	0.24	0.18	
$PO_4^{3-}$ , $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095	
Th <sup>4+</sup> , Zr <sup>4+</sup> , Ce <sup>4+</sup> , Sn <sup>4+</sup>	1.1	0.587	0.348	0.252	0.10	0.063	
$Fe(CN)_{6}^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020	

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# **Omitting Activity Coefficients in Equilibrium Calculations**

We shall ordinarily neglect activity coefficients and simply use molar concentrations in application of the equilibrium law. This recourse simplifies the calculations and greatly decreases the amount of data needed. For most purposes, the error introduced by the assumption of unity for the activity coefficient is not large enough to lead to false conclusions. Significant discrepancies occur when the ionic strength is large (0.01 or larger) or when the ions involved have multiple charges. With dilute solutions (ionic strength < 0.01) or nonelectrolytes or of singly charged ion, the use of concentrations in a mass-law calculation often provided reasonably accurate results.
## **EXAMPLE 10-4**

Find the relative error introduced by neglecting activities in calculating the solubility of Ba(IO<sub>3</sub>)<sub>2</sub> in a 0.033 M solution of Mg(IO<sub>3</sub>)<sub>2</sub>. The thermodynamic solubility product for Ba(IO<sub>3</sub>)<sub>2</sub> is  $1.57 \times 10^{-9}$  (see Appendix 2).

At the outset, we write the solubility-product expression in terms of activities:

$$a_{\text{Ba}^{2+}} \cdot a_{\text{IO}_3^-}^2 = K_{\text{sp}} = 1.57 \times 10^{-9}$$

where  $a_{Ba^{2+}}$  and  $a_{IO_3}$  are the activities of barium and iodate ions. Replacing activities in this equation with activity coefficients and concentrations from Equation 10-2 yields

$$[\mathrm{Ba}^{2+}] \gamma_{\mathrm{Ba}^{2+}} \cdot [\mathrm{IO}_{3}^{-}]^2 \gamma_{\mathrm{IO}_{3}^{-}}^2 = K_{\mathrm{sp}}$$

where  $\gamma_{Ba^{2+}}$  and  $\gamma_{IO_3^-}$  are the activity coefficients for the two ions. Rearranging this expression gives

$$K'_{\rm sp} = \frac{K_{\rm sp}}{\gamma_{\rm Ba^{2+}}\gamma_{\rm IO_3^-}^2} = [{\rm Ba^{2+}}] \, [{\rm IO_3^-}]^2 \tag{10-6}$$

where  $K'_{sp}$  is the concentration-based solubility product.

The ionic strength of the solution is obtained by substituting into Equation 10-1:

$$\mu = \frac{1}{2} ([Mg^{2+}] \times 2^2 + [IO_3^-] \times 1^2)$$
$$= \frac{1}{2} (0.033 \text{ M} \times 4 + 0.066 \text{ M} \times 1) = 0.099 \text{ M} \approx 0.1 \text{ M}$$

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In calculating  $\mu$ , we have assumed that the Ba<sup>2+</sup> and IO<sub>3</sub><sup>-</sup> ions from the precipitate do not significantly affect the ionic strength of the solution. This simplification seems justified, considering the low solubility of barium iodate and the relatively high concentration of Mg(IO<sub>3</sub>)<sub>2</sub>. In situations in which it is not possible to make such an assumption, the concentrations of the two ions can be approximated by solubility calculation in which activities and concentrations are assumed to be identical (as in Examples 9-3, 9-4, and 9-5). These concentrations can then be introduced to give a better value for  $\mu$ .

Turning now to Table 10-2, we find that at an ionic strength of 0.1 M,

$$\gamma_{Ba^{2+}} = 0.38$$
  $\gamma_{IO_3} = 0.77$ 

If the calculated ionic strength did not match that of one of the columns in the table,  $\gamma_{Ba^{2+}}$  and  $\gamma_{IO_{3}}$  could be calculated from Equation 10-5.

Substituting into the thermodynamic solubility-product expression gives

$$K'_{\rm sp} = \frac{1.57 \times 10^{-9}}{(0.38)(0.77)^2} = 6.97 \times 10^{-9}$$
$$[{\rm Ba}^{2+}] \ [{\rm IO}_3^-]^2 = 6.97 \times 10^{-9}$$

Proceeding now as in earlier solubility calculations,

solubility = 
$$[Ba^{2+}]$$
  
 $[IO_3^-] = 2 \times 0.033 \text{ M} + 2[Ba^{2+}] \approx 0.066 \text{ M}$   
 $[Ba^{2+}] (0.066)^2 = 6.97 \times 10^{-9}$   
 $[Ba^{2+}] = \text{solubility} = 1.60 \times 10^{-6} \text{ M}$ 

If we neglect activities, the solubility is,

$$[Ba2+] (0.066)2 = 1.57 \times 10^{-9}$$
  

$$[Ba2+] = solubility = 3.60 \times 10^{-7} M$$
  
relative error =  $\frac{3.60 \times 10^{-7} - 1.60 \times 10^{-6}}{1.60 \times 10^{-6}} \times 100\% = -77\%$ 

## **EXAMPLE 10-5**

Use activities to calculate the hydronium ion concentration in a 0.120 M solution of HNO<sub>2</sub> that is also 0.050 M in NaCl. What is the relative percent error incurred by neglecting activity corrections?

The ionic strength of this solution is

$$\mu = \frac{1}{2} (0.0500 \text{ M} \times 1^2 + 0.0500 \text{ M} \times 1^2) = 0.0500 \text{ M}$$

In Table 10-2, at ionic strength 0.050 M, we find

$$\gamma_{\rm H_{2}O^{+}} = 0.85 \qquad \gamma_{\rm NO_{2}} = 0.81$$

Also, from rule 4 (page 272), we can write

$$\gamma_{\rm HNO_2} = 1.0$$

These three values for  $\gamma$  permit the calculation of a concentration-based dissociation constant from the thermodynamic constant of 7.1 × 10<sup>-4</sup> (see Appendix 3):

$$K'_{a} = \frac{[H_{3}O^{+}][NO_{2}^{-}]}{[HNO_{2}]} = \frac{K_{a} \cdot \gamma_{HNO_{2}}}{\gamma_{H_{3}O^{+}}\gamma_{NO_{2}^{-}}} = \frac{7.1 \times 10^{-4} \times 1.0}{0.85 \times 0.81} = 1.03 \times 10^{-4}$$

Proceeding as in Example 9-7, we write

$$[H_3O^+] = \sqrt{K_a \times c_a} = \sqrt{1.03 \times 10^{-3} \times 0.120} = 1.11 \times 10^{-2} M$$

(continued)

Note that assuming unit activity coefficients gives  $[H_3O^+] = 9.2 \times 10^{-3} \text{ M}.$ 

relative error = 
$$\frac{9.2 \times 10^{-3} - 1.11 \times 10^{-2}}{1.11 \times 10^{-2}} \times 100\% = -17\%$$

In this example, we assumed that the contribution of the acid dissociation to the ionic strength was negligible. In addition, we used the approximate solution for calculating the hydronium ion concentration. See Problem 10-18 for a discussion of these approximations.

Catalyst