

Attentions:

- Do not** leave your answers in the table on the first page of the answer booklet. Write all your answers in the second and subsequent pages of the answer booklet.
- Answers should appear in order in the answer booklet. Each answer should be preceded with its question number/code. Answers not preceded with question numbers/codes will not be credited.
- No explanation or calculation is required in the answer to the multi-select question.
- Pay attention to the sign and unit of your answers.
- The following values may be of some use: $\exp(1.00) = 2.718$; $\exp(2.00) = 7.389$; $\exp(3.00) = 20.09$; $\exp(5.00) = 148.4$; $\ln(2.00) = 0.6931$; $\ln(3.00) = 1.099$; $\ln(5.00) = 1.609$

I. Multi-select question

(24%)

Choose one or more answers from the list of answers provided for each question below. Penalty of 50% credit to the correct answer will be applied for the incorrect choice. No penalty will be applied for failure to choose the correct answer, though.

1. Which of the following statements about the nature of analytical chemistry is (are) correct?

- A material is homogeneous if its constituent parts can be distinguished only with the aid of a microscope.
- The preparation of a solid laboratory sample involves grounding the solid to decrease particle size, mixing to ensure homogeneity, and storing for various lengths of time before analysis begins.
- Techniques or reactions that work for only one analyte are said to be selective.
- An interferent causes an error in an analysis by attenuating (making smaller) the quantity being measured, whereas an interference causes an error by enhancing the quantity.
- We compute the results of a typical quantitative analysis from two measurements. One is the mass or the volume of sample being analyzed. The second measurement is of some quantity that is proportional to the amount of analyte in the sample.
- In gravimetric methods, we determine the volume of the analyte or some compound chemically related to it.

2. Which of the following statements about the International System of Units (SI) is (are) correct?

- The SI is based on seven fundamental base units.
- The ångstrom unit Å is a SI unit of length.
- The mole is a SI unit for the amount of a chemical substance.
- Not all non-SI units can be derived from the base units of SI.
- The SI base unit of temperature is Celsius.
- The SI base unit of mass is gram.

3. Which of the following statements about analytical calculations is (are) correct?

- Mass is a variant measure of the quantity of matter in an object, while weight is the force of attraction between an object and its surroundings, principally the earth.
- The molar mass of a substance is the mass in amu of 1 mole of that substance.
- The molar analytical concentration of a solution gives the total number of millimoles in 1 mL of the solution.
- The prefix giga- for units is abbreviated as G and represents the multiplier of 10^{12} .
- The pH is a p-function and is the negative logarithm of $[H^+]$.
- The specific gravity is the ratio of the mass of a substance to the mass of an equal volume of water at 0°C .

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4. Which of the following analytical statistics statements is (are) correct?
- (A) Systematic error causes the mean of a data set to differ from the accepted value.
 - (B) Markings on the speedometer always read from a given angle is an example of random error.
 - (C) Instrumental errors are systematic errors.
 - (D) Personal errors are random errors.
 - (E) Placing fingerprints on the vial after weighing while adding sample to the vial is an example of random errors.
 - (F) A miscalibrated pipet holding a slightly different volume of liquid than the indicated volume contributes random error.
5. Which of the following statements related to data treatment is (are) correct?
- (A) The mean of a data set is found by adding all numbers in the data set and then dividing by the number of values in the set.
 - (B) The *variance* is the square root of the standard deviation.
 - (C) The *standard error of the mean* is the standard deviation of the mean.
 - (D) The *coefficient of variation* is the percent relative standard deviation.
 - (E) The standard error of the mean of 5 measurements is larger than the standard deviation of a single result.
 - (F) As the desired confidence level decreases, the confidence interval increases.
6. Which of the following statements about normal distribution is (are) correct?
- (A) The graph used to depict a normal distribution consists of a symmetrical bell-shaped curve.
 - (B) The bell-shaped curve is a common feature of nature and psychology.
 - (C) Normal distributions may not be symmetric around their mean.
 - (D) Normal distributions are defined by two parameters, the mean and the standard deviation, only.
 - (E) The area under the normal curve is equal to 100.
 - (F) The tails of normal distribution curves are asymptotic. They meet the horizon (i.e. x-axis).
7. Which of the following statements about mass spectrometry is (are) correct?
- (A) Mass spectrometry measures the charge-to-mass ratio of charged particles.
 - (B) The main steps a mass spectrometer takes include vaporization, ionization, acceleration, separation, and detection.
 - (C) The mass spectra of a given substance obtained from mass spectrometers using different ionization sources are the same.
 - (D) ICP-MS can analyze metals only.
 - (E) For 0.1 mL of sample, the ICP-MS absolute detection limit is equal or less than 0.1 yg.
 - (F) Among different ion sources for molecular mass spectrometry, electron ionization results in higher sensitivities than do chemical and field ionization.
8. Which of the following statements about calibration is (are) correct?
- (A) Calibration determines the relationship between the analytical response and the analyte concentration.
 - (B) Calibration does not include adjustment. i.e., With calibration there is no technical intervention at the measuring instrument.
 - (C) The chemical standards used in calibration can only be prepared from purified reagents.
 - (D) Gravimetric methods do not rely on calibration with chemical standards.
 - (E) Titration is a type of comparison methods.
 - (F) The least-squares method has two assumptions: (i) A linear relationship exists between the measured response y and the standard analyte concentration x . (ii) Errors exist in x values (concentrations) of the data points.

9. Which of the following statements about alpha value is (are) correct?

- (A) The relative equilibrium concentrations of the components in a conjugate system (e.g., a conjugate acid/base) are called alpha (α) values.
- (B) The alpha values of a conjugate acid/base depend on pH and K_a .
- (C) The alpha values of a conjugate acid/base are independent of the sum of the analytical concentrations of the acid and its conjugate base in a buffer solution.
- (D) Plotting the alpha values as a function of the pH of the solution shows curves crossing at $\text{pH} = \text{p}K_b$, where K_b is the base dissociation constant of the conjugate base.
- (E) Since EDTA is a polyprotic acid, its alpha values affect the complex formation between EDTA and the metal ion (M).
- (F) Decreasing the α_4 value of EDTA favors the formation of the EDTA-M complex.

10. Which of the following statements related to the acid salt NaHA and polyprotic acid titration is (are) correct?

- (A) NaHA can act as a proton donor and also as the conjugate base of the parent acid H_2A .
- (B) Solutions of acid salts are acidic.
- (C) The pH of a NaHA solution can be calculated by only treating NaHA as an acid.
- (D) A solution having the same composition as the solution obtained by dissolving NaHA in pure water cannot be obtained during the process when H_2A is titrated with NaOH.
- (E) It is possible to titrate all three protons of phosphoric acid in aqueous solution.
- (F) A titration by NaOH of a mixture of H_3PO_4 and NaH_2PO_4 containing phenolphthalein to the second end point gives the number of millimoles of NaH_2PO_4 .

II. Fill-in-the-blank

11. Fill in each of the blanks in the following sentences with the most proper answer in the list below. Please note that only the singular noun of the possible answer is provided in the list. No penalty will be applied for incorrect answers. The answer for a) is provided for your reference. (12%)

matrix, analytical sensitivity, analytical molarity, confidence limits, micro analysis, aliquot, tare, solvent blank, wet ashing, population, minor constituents, parallax, differentiating solvent, standard error of the estimate, gross sample, electrolyte effect, isocratic elution, zwitterion, formal potential, buffer, mass-action effect, activity, laboratory sample, carbonate error, trace constituents, saponification, cryptand, potentiostat, charge-transfer device, eluate, dashpot, detection limit, crystalline suspension

- a) analytical molarity is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution.
- b) _____ is the boundary around the mean of a set of replicate analytical results within which the population mean can be expected to lie within a certain probability.
- c) _____ is the measured fraction of the volume of a liquid sample.
- d) _____ is the oxidation of the organic reagents of a sample with oxidizing reagents such as nitric acid, sulfuric acid, hydrogen peroxide, aqueous bromine, or a combination of these reagents.
- e) _____ are the constituents present in the sample in amounts between 0.01% and 1 %.
- f) _____ is the collection of sampling units or increments corresponding to several small parts taken from different parts of the bulk material, and is representative of the whole in composition and in particle size distribution.
- g) _____ is a species that has both a positive and a negative charge.
- h) _____ is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution.

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- i) _____ of a species is related to its concentration by a factor called the activity coefficient.
- j) _____ is a systematic error occurring in a base in which the effective concentration of the base is diminished by absorption of carbon dioxide.
- k) _____ is the process by which an ester is hydrolyzed in alkaline solution to give an alcohol and a conjugate base.
- l) _____ maintains the working electrode potential at a constant value relative to a reference electrode.
- m) _____ is the mobile phase that exits the chromatographic column.

12. The following sentences state the essence of some important/useful equations developed and used in analytical chemistry. In *each* of the blanks of the following question, fill, in English, *one* word only from the list below so as to best complete the sentence that concisely reveals the analytical chemistry concepts behind the equations. Only the singular noun of the possible answer is provided in the list. (11%)

error, matrix, mass, sensitivity, pH, variance, molarity, size, balance, limit, aliquot, population, equilibrium, elution, diffusion, formal, activity, rate, buoyant, laboratory, trace, Beer, detection, charge, potential, buffer, reduction, oxidation, suspension, solute.

- (a) The buoyancy equation is used to correct the _____ on the mass obtained from a _____; specifically when the error has its origin in the difference in _____ force exerted by the medium (air) on the object and on the masses.
- (b) The Henderson-Hasselbalch equation is used to calculate the _____ of _____ solutions.
- (c) The Debye-Hückel Equation permits the calculation of _____ coefficients of ions from their _____ and their average _____.
- (d) _____-balance equations relate the _____ concentrations of various species in a solution to one another and to the analytical concentrations of the various _____.

III. Full names of abbreviations

13. Write down the full names in English of the following abbreviations used in analytical chemistry:

- (a) ppt, (b) CL, (c) RSD, (d) LOL, (e) EDTA, (f) SCE, (g) NHE, (h) RDE, (i) DME, (j) UV, (k) FTIR, (l) PMT, (m) CCD (13%)

IV. A dilute solution is prepared by dissolving a purified monoprotic acid (HE, 50.00 g/mol) into distilled water. Answer questions 14 and 15.

14. The HE solution is titrated with a 0.2000 M Ba(OH)₂ solution. The results of the titration experiments are shown below.

Expt	Sample Volume, mL	Ba(OH) ₂ Volume, mL
1	40.00	41.00
2	39.00	39.00
3	25.00	26.25
4	50.00	43.75
5	30.00	30.75

- (a) Calculate the mean w/v percentage of the monoprotic acid in the dilute solution. (b) Use Q test to decide if any anomalous result exists that should be rejected at the 95% confidence level. (Heavy penalty will be applied if this test is not performed.) (c) Calculate the standard deviation for the results. (d) Calculate the 95% confidence interval for the mean. (e) Assume that the buret used to measure out the acid solution has a systematic error of -0.05 mL at all volumes delivered and no other sources of errors exist in the experiments. Calculate the systematic error in the mean result. (See the related tables in the next page.) (13%)

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Table - Critical Values for Q		Values of t							
Number of Observations	Confidence Level			Degrees of Freedom					
	90%	95%	99%	80%	90%	95%	99%	99.9%	
3	0.941	0.970	0.994	1	3.08	6.31	12.7	63.7	637
4	0.765	0.829	0.926	2	1.89	2.92	4.30	9.92	31.6
5	0.642	0.710	0.821	3	1.64	2.35	3.18	5.84	12.9
6	0.560	0.625	0.740	4	1.53	2.13	2.78	4.60	8.61
7	0.507	0.568	0.680	5	1.48	2.02	2.57	4.03	6.87
8	0.468	0.526	0.634	6	1.44	1.94	2.45	3.71	5.96
9	0.437	0.493	0.598	7	1.42	1.90	2.36	3.50	5.41
10	0.412	0.466	0.568	8	1.40	1.86	2.31	3.36	5.04
				9	1.38	1.83	2.26	3.25	4.78
				10	1.37	1.81	2.23	3.17	4.59
				15	1.34	1.75	2.13	2.95	4.07
				20	1.32	1.73	2.09	2.84	3.85
				40	1.30	1.68	2.02	2.70	3.55
				60	1.30	1.67	2.00	2.62	3.46
				∞	1.28	1.64	1.96	2.58	3.29

15. Assume that the conjugate base, E^- , of the monoprotic acid can be used as complexing agent for determination of Cu^{2+} ($K_{f,Cu-E} = 2.0 \times 10^{20}$) using a direct titration method. An experiment is planned in which standard aqueous solutions of Cu^{2+} are prepared and Eriochrome Black T (EBT) is employed as the indicator. In general, there are two types of direct titration (non-potentiometric) methods for quantifying metal ions using a complexing agent, depending on the availability of suitable indicators. (a) Using the titration of Cu^{2+} as an example, describe the chemistry and the conditions of use for the two different direct titration methods when a complexing agent E^- is used. (b) Sketch and properly label a titration apparatus that can be used in a direct potentiometric titration of Cu^{2+} with E^- . (c) Why should an auxiliary complexing agent be used in this titration? (d) What is the condition of use for the auxiliary complexing agent? (e) The electrode potential of the apparatus you sketched in (b) is expected to change during the titration. (i) Based on the Nernst expression of the electrode potential, which often involves both the reduced and the oxidized states, is formality, species molarity, or activity obtained from the titration? Define these three terms before explanation. (ii) Will a color change be observed if a general redox indicator is also present in the solution of your apparatus? Explain. (f) $[Cu(NH_3)_4H_2O]SO_4$ (FM 245.75) can be prepared by adding concentrated solution of ammonia to a saturated aqueous solution of copper sulfate followed by precipitation of the product with ethanol. What is the number of reacting units (eq/mol) for NH_3 in the reaction of the preparation? (g) 0.983 g $[Cu(NH_3)_4H_2O]SO_4$ is dissolved in 100.0 mL aqueous solution that contains 0.200 M in NH_3 . Calculate the potential of a copper electrode immersed in the solution. (β_f for $[Cu(NH_3)_4H_2O]^{2+}$ is 5.62×10^{11} ; $E^0(Cu^{2+}/Cu^0) = 0.337$ V) (h) Assume that both Cu^{2+} and E^- solutions are 0.100 M in NH_3 and 0.175 M in NH_4Cl to provide a constant pH of 9.0. Without actually going through the calculation, show the calculation procedure for determining pCu at the equivalent point when the complexing agent E^- is employed to titrate Cu^{2+} . In the procedure, use your defined symbols to show variables whose values are not provided in the question. (27%)