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Topic 3.13: Beer-Lambert Law

Worksheet · AP Chemistry

UNIT 3 · PROPERTIES OF SUBSTANCES AND MIXTURES

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How to Use This Worksheet

Work in order. Section A checks the ideas: what transmittance and absorbance mean, what each symbol in A = εlc does, and how a calibration curve is built and read. Section B builds the calculations: finding ε, converting between absorbance and transmittance, scaling with path length, and reading unknowns from calibration data. Section C combines calibration curves, dilutions and the law's limits in exam style.

Every value you need is stated in the question, so each question can be answered from the text alone. Absorbance and transmittance are linked by $A = -\log T$, where the logarithm is base 10 and T is the fraction of light transmitted, never the percentage: convert %T to a fraction before taking any logarithm.

Do not look at the answer key until you have attempted every question.

Section A: Recall and Concepts

A1. (a) Define transmittance. (b) Define absorbance. (c) Write down the equation that links absorbance to transmittance. (d) In the equation A = εlc, state what each of the symbols ε, l and c represents. (e) State the units of ε and the units of absorbance.

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A2. In each change the substance and the wavelength stay the same. State what happens to the absorbance. (a) The concentration is doubled at fixed path length. (b) The path length is doubled at fixed concentration. (c) The concentration is doubled and the path length is halved. (d) Explain, in terms of the particles in the beam, why the absorbance in part (a) changes the way it does.

A3. A calibration curve is drawn for a coloured substance. (a) State what is plotted on each axis. (b) State the shape of the plot, and what the slope of the plot equals when the path length is 1.00 cm. (c) Explain why the line is expected to pass through the origin. (d) A student's line is straight but has a small positive intercept on the absorbance axis. Give the most likely cause.

A4. (a) State what the symbol λ_max means. (b) Explain why absorbance measurements for a calibration curve are made at λ_max. (c) Explain why the same wavelength must be used for the standards and for the unknown. (d) State whether the Beer-Lambert law applies at wavelengths other than λ_max, and explain your answer.

A5. A student extends a calibration plot to very high concentrations and finds that the points leave the straight line drawn through the dilute standards. (a) State what this shows about the relationship between absorbance and concentration at high concentration. (b) Give two reasons why the law breaks down at high concentration. (c) State what the student should do to measure a very concentrated sample reliably. (d) State whether these results disprove the Beer-Lambert law, and explain your answer.

Section B: Core Practice

B1. A solution of concentration 2.5×10^{-4} mol/L in a 1.00 cm cuvette has absorbance 0.90 at the chosen wavelength. (a) Calculate the molar absorptivity, ε, of the substance at this wavelength. (b)

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Calculate the absorbance of a 1.0×10^{-4} mol/L solution of the same substance in the same cuvette. (c) Calculate the concentration that gives an absorbance of 0.45 in the same cuvette.

B2. A solution has absorbance 0.36 in a 1.00 cm cuvette. (a) Calculate its absorbance in a 2.00 cm cuvette. (b) Calculate its absorbance in a 0.50 cm cuvette. (c) Calculate the percentage transmittance of the solution in the 2.00 cm cuvette. (d) A second solution of the same substance, measured in the 0.50 cm cuvette, also has absorbance 0.36. Compare its concentration with the concentration of the first solution.

B3. (a) A solution transmits 40% of the light at the chosen wavelength. Calculate its absorbance. (b) A solution has absorbance 1.30. Calculate its percentage transmittance. (c) A solution transmits 1.0% of the light. Calculate its absorbance. (d) The solution in part (a) is diluted to half its original concentration and measured at the same path length. Calculate its new absorbance and its new percentage transmittance, and comment on how the transmittance changed.

B4. Standard solutions of one substance, measured in a 1.00 cm cuvette at one wavelength, give these results: concentration 1.0×10^{-4} mol/L, absorbance 0.15; concentration 2.0×10^{-4} mol/L, absorbance 0.30; concentration 3.0×10^{-4} mol/L, absorbance 0.45; concentration 4.0×10^{-4} mol/L, absorbance 0.60. (a) Calculate the slope of the calibration line. (b) An unknown solution of the same substance has absorbance 0.525 under the same conditions. Calculate its concentration. (c) Use the slope to calculate the molar absorptivity of the substance. (d) A second unknown reads absorbance 0.90. Calculate the concentration the line would give, and state why that value is less trustworthy than the answer to part (b).

B5. Two solutions of the same substance are measured at the same wavelength. Solution X, in a 2.00 cm cuvette, has absorbance 0.48 and concentration 3.0×10^{-4} mol/L. Solution Y, in a 1.00 cm cuvette, also has absorbance 0.48. (a) Calculate the molar absorptivity of the substance. (b)

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Calculate the concentration of solution Y. (c) State the rule your answers illustrate about comparing absorbances measured at different path lengths.

B6. A coloured solution is too concentrated to measure directly. A student dilutes 10.0 mL of it to a final volume of 50.0 mL, and the diluted solution has absorbance 0.32 in a 1.00 cm cuvette. The molar absorptivity of the substance is 8.0×10^{2} L mol^{-1} cm^{-1}. (a) Calculate the concentration of the diluted solution. (b) Calculate the concentration of the original solution. (c) Calculate the volume of the original solution needed to prepare 250 mL of a 4.0×10^{-4} mol/L solution.

Section C: Exam Style

C1. A soft drink contains a food colouring. Standard solutions of the colouring, measured at λ_max in a 1.00 cm cuvette, give these results: concentration 2.0×10^{-5} mol/L, absorbance 0.22; concentration 4.0×10^{-5} mol/L, absorbance 0.44; concentration 6.0×10^{-5} mol/L, absorbance 0.66; concentration 8.0×10^{-5} mol/L, absorbance 0.88. A sample of the drink is diluted by a factor of ten, and the diluted sample has absorbance 0.55. (a) Calculate the molar absorptivity of the colouring at λ_max. (b) Calculate the concentration of colouring in the diluted sample. (c) Calculate the concentration of colouring in the undiluted drink. (d) Calculate the percentage transmittance of the diluted sample. (e) Explain why the measurements are made at λ_max rather than at a wavelength where the colouring absorbs only weakly.

C2. A solution has a percentage transmittance of 10% at the chosen wavelength, measured in a 1.00 cm cuvette. (a) Calculate its absorbance. (b) The solution is concentrated until its concentration is three times the original value, at the same path length. Calculate its new percentage transmittance. (c) A student predicts the answer to part (b) by dividing 10% by 3, getting about 3.3%. Explain why that method fails. (d) Calculate the factor by which the concentration of the original solution must be multiplied to bring its percentage transmittance to

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1.0%. (e) The original solution is instead placed in a 2.00 cm cuvette, concentration unchanged. Calculate its percentage transmittance.

C3. A student prepares a calibration curve for a substance in a 1.00 cm cuvette and records these results: concentration 0, absorbance 0.03; concentration 1.0×10^{-4} mol/L, absorbance 0.15; concentration 2.0×10^{-4} mol/L, absorbance 0.27; concentration 3.0×10^{-4} mol/L, absorbance 0.39; concentration 4.0×10^{-4} mol/L, absorbance 0.51; concentration 6.0×10^{-4} mol/L, absorbance 0.78; concentration 8.0×10^{-4} mol/L, absorbance 1.05. (a) Using the points up to 4.0×10^{-4} mol/L, calculate the slope and the intercept of the line. (b) Explain the most likely cause of the nonzero intercept. (c) Show that the points at 6.0×10^{-4} mol/L and 8.0×10^{-4} mol/L no longer lie on that line. (d) Give two reasons why the law fails at such concentrations, and state how a sample of concentration 8.0×10^{-4} mol/L should be measured instead. (e) An unknown measured under the same conditions has absorbance 0.45. Use the line from part (a) to calculate its concentration.

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Answer Key

A1. (a) Transmittance is the fraction of the light entering a sample that passes through it: $T = I/I_0$, where I_0 is the intensity entering and I the intensity leaving. (b) Absorbance is the logarithmic measure of how much light a sample absorbs, defined by $A = -\log T$: the larger the absorbance, the smaller the fraction of light transmitted. (c) $A = -\log T$. (d) ε is the molar absorptivity, a constant measuring how strongly the substance absorbs at the chosen wavelength; l is the path length, the distance the light travels through the solution; c is the concentration of the absorbing substance. (e) ε is measured in L mol^{-1} cm^{-1}; absorbance has no units.

A2. (a) It doubles. Doubling the concentration doubles the number of absorbing particles in each unit volume of the beam, and each particle independently intercepts its share of the photons, so twice as much light is absorbed: with l fixed, $A = \varepsilon lc$ doubles. (b) It doubles. The light now travels through twice as much solution and meets twice as many absorbing particles along its path. (c) It stays the same. Absorbance follows the product lc, and doubling c while halving l leaves the product unchanged: $(2c)(l/2) = lc$. (d) Each dissolved particle intercepts photons on its own, without help from its neighbours. More particles per unit volume means proportionally more interceptions, so the light absorbed, and with it the absorbance, grows in direct proportion to the particle count, which is the concentration.

A3. (a) Concentration of the standard solutions on the horizontal axis, absorbance on the vertical axis. (b) A straight line through the origin. Its slope is εl, so at a path length of 1.00 cm the slope equals ε numerically, with units of L mol^{-1}. (c) At zero concentration there is no absorbing substance in the beam, so nothing is absorbed and the absorbance must be zero; the law, $A = \varepsilon lc$, gives $A = 0$ when $c = 0$. (d) A systematic error in the background: most likely the blank was contaminated or the instrument was not properly zeroed on the blank, so a small background absorbance from the solvent and cuvette is included in every reading.

A4. (a) λ_{max} is the wavelength at which the substance absorbs light most strongly, where its molar absorptivity is largest. (b) At λ_{max} each change in concentration produces the largest possible change in absorbance, so the measurement is at its most sensitive and the relative error in reading concentrations off the line is at its smallest. (c) Molar absorptivity depends on wavelength. The calibration line has slope εl for the wavelength used to measure the standards; measuring the unknown at a different wavelength would give it a different ε, and the line would no longer apply to it. (d) Yes. The law holds at any wavelength where the substance absorbs, with the ε belonging to that wavelength. λ_{max} is chosen for sensitivity, not because the law fails elsewhere.

A5. (a) Absorbance is no longer directly proportional to concentration: the measured absorbances depart from the values the straight line through the dilute standards predicts. (b) At high concentration the absorbing particles are close enough to interact with each other, so each particle

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no longer absorbs independently and ε is no longer constant; and so little light reaches the detector that stray light and detector limits distort the measured transmittance. (c) Dilute the sample until its absorbance falls within the linear part of the calibration, measure it there, and multiply the concentration read from the line by the dilution factor. (d) No. The law is built on assumptions, independent particles and faithful detection, that hold in dilute solution. Deviation where those assumptions fail is a limit of the law's range, not a disproof of it.

B1. (a) $\varepsilon = A \div (lc) = 0.90 \div (1.00 \times 2.5 \times 10^{-4}) = 3.6 \times 10^{3}$ L mol^{-1} cm^{-1}. (b) $A = \varepsilon lc = 3.6 \times 10^{3} \times 1.00 \times 1.0 \times 10^{-4} = 0.36$. (c) $c = A \div (\varepsilon l) = 0.45 \div (3.6 \times 10^{3} \times 1.00) = 1.25 \times 10^{-4}$ mol/L.

B2. (a) Absorbance is proportional to path length, so $A = 2 \times 0.36 = 0.72$. (b) $A = 0.36 \div 2 = 0.18$. (c) T = 10^(−A) = 10^(−0.72) = 0.19, so the percentage transmittance is about 19%. (d) It is twice as concentrated. It reaches the same absorbance in half the path length, so it must hold twice as many absorbing particles per unit volume: with A and ε equal, lc must be equal, and half the l demands twice the c.

B3. (a) First write the transmittance as a fraction, T = 0.40. Then A = −log(0.40) = 0.398, about 0.40. (b) T = 10^(−A) = 10^(−1.30) = 0.050, so the percentage transmittance is 5.0%. (c) T = 0.010, so A = −log(0.010) = 2.00. (d) Halving the concentration halves the absorbance: $A = 0.398 \div 2 = 0.199$, about 0.20. The new transmittance is T = 10^(−0.199) = 0.63, about 63%. The comment: halving the concentration did not double the transmittance from 40% to 80%. Absorbance is the quantity proportional to concentration; transmittance follows it exponentially, so it rose only to about 63%.

B4. (a) Each 1.0×10^{-4} mol/L adds 0.15 of absorbance, so the slope is $0.15 \div (1.0 \times 10^{-4}) = 1.5 \times 10^{3}$ L mol^{-1}. (b) $c = A \div \text{slope} = 0.525 \div (1.5 \times 10^{3}) = 3.5 \times 10^{-4}$ mol/L. (c) The slope of the calibration line is εl, and l = 1.00 cm, so $\varepsilon = 1.5 \times 10^{3} \div 1.00 = 1.5 \times 10^{3}$ L mol^{-1} cm^{-1}. (d) The line would give $c = 0.90 \div (1.5 \times 10^{3}) = 6.0 \times 10^{-4}$ mol/L. That lies beyond the highest standard measured, 4.0×10^{-4} mol/L, so it rests on extrapolation: it assumes the plot stays straight outside the measured range, where deviation from linearity may already have begun. The value in part (b) is interpolated between standards, which is far safer.

B5. (a) $\varepsilon = A \div (lc) = 0.48 \div (2.00 \times 3.0 \times 10^{-4}) = 8.0 \times 10^{2}$ L mol^{-1} cm^{-1}. (b) $c = A \div (\varepsilon l) = 0.48 \div (8.0 \times 10^{2} \times 1.00) = 6.0 \times 10^{-4}$ mol/L. (c) Equal absorbances mean equal products lc (for the same substance at the same wavelength). The shorter the path length, the higher the concentration must be to compensate, in inverse proportion: half the path length needs twice the concentration.

B6. (a) $c = A \div (\varepsilon l) = 0.32 \div (8.0 \times 10^{2} \times 1.00) = 4.0 \times 10^{-4}$ mol/L. (b) The dilution took 10.0 mL to 50.0 mL, a factor of five, so the original solution was five times as concentrated: $5 \times 4.0 \times 10^{-4} = 2.0 \times 10^{-3}$ mol/L. (c) The moles are the same before and after dilution, so $c_1V_1 = c_2V_2$: $V_1 = (4.0 \times 10^{-4} \times 250) \div (2.0 \times 10^{-3}) = 50$ mL of the original solution, made up to 250 mL.

C1. (a) Each 2.0×10^{-5} mol/L adds 0.22 of absorbance, so the slope is $0.22 \div (2.0 \times 10^{-5}) = 1.1 \times 10^{4}$ L mol^{-1}. The slope is εl with l = 1.00 cm, so $\varepsilon = 1.1 \times 10^{4}$ L mol^{-1} cm^{-1}. (b) $c = A \div (\varepsilon l) = 0.55 \div (1.1 \times 10^{4}) = 5.0 \times 10^{-5}$ mol/L. (c) The sample was diluted by a factor of ten, so the drink itself is ten times as

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concentrated: $10 \times 5.0 \times 10^{-5} = 5.0 \times 10^{-4}$ mol/L. (d) T = 10^(−0.55) = 0.28, so the percentage transmittance is about 28%. (e) At λ_max the molar absorptivity is largest, so every concentration produces the largest possible absorbance and even small concentrations give readings well clear of measurement noise. At a weakly absorbed wavelength the same solutions would give small absorbances with much larger relative errors, and low concentrations might be unreadable.

C2. (a) T = 0.10, so A = −log(0.10) = 1.00. (b) Tripling the concentration triples the absorbance, to 3.00. Then T = 10^(−3.00) = 0.0010, a percentage transmittance of 0.10%. (c) The student's method treats transmittance as if it were proportional to concentration. It is absorbance that is proportional: tripling c triples A, and because T = 10^(−A), the transmittance is divided by 10 for each unit added to A. Going from A = 1.00 to A = 3.00 divides T by 100, from 10% to 0.10%, not by 3. (d) A percentage transmittance of 1.0% means T = 0.010 and A = −log(0.010) = 2.00. That is twice the original absorbance of 1.00, and absorbance is proportional to concentration, so the concentration must be multiplied by 2. (e) Doubling the path length doubles the absorbance, from 1.00 to 2.00, the same value as in part (d). The percentage transmittance is therefore also 1.0%.

C3. (a) Using the first and last of the points in range: slope = $(0.51 - 0.03) \div (4.0 \times 10^{-4} - 0) = 0.48 \div (4.0 \times 10^{-4}) = 1.2 \times 10^{3}$ L mol^{-1}. The line starts at absorbance 0.03 when the concentration is zero, so the intercept is 0.03. (b) The line reports an absorbance of 0.03 with no absorbing substance present. That background absorbance, from the solvent and cuvette, should have been subtracted by zeroing on the blank; a contaminated blank, or an instrument never properly blanked, leaves it in every reading. (c) On the line, concentration 6.0×10^{-4} mol/L predicts $A = 0.03 + (1.2 \times 10^{3} \times 6.0 \times 10^{-4}) = 0.03 + 0.72 = 0.75$, but the measured value is 0.78. Concentration 8.0×10^{-4} mol/L predicts A = 0.03 + 0.96 = 0.99, but the measured value is 1.05. Both measured points sit above the line, so they no longer follow it. (d) The absorbing particles are close enough to interact, so they stop absorbing independently and ε stops being constant; and at such absorbances very little light reaches the detector, so stray light and detector limits distort the reading. The sample should be diluted until its absorbance falls in the range where points follow the line, measured there, and the result multiplied by the dilution factor. (e) Work with the line equation $A = 0.03 + (1.2 \times 10^{3})c$. Then $c = (0.45 - 0.03) \div (1.2 \times 10^{3}) = 0.42 \div (1.2 \times 10^{3}) = 3.5 \times 10^{-4}$ mol/L. The intercept must be subtracted first; ignoring it would overstate the concentration.

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