# Topic 3.13: Beer-Lambert Law

Revision Notes · AP Chemistry

UNIT 3 · PROPERTIES OF SUBSTANCES AND MIXTURES

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## Light In, Light Out: Transmittance

A spectrophotometer shines light of one chosen wavelength through a sample and compares what comes out with what went in. Transmittance, T, is the fraction that gets through: $T = I/I_0$, where $I_0$ is the intensity entering and I the intensity leaving. It is often quoted as a percentage, $\%T = 100 \times T$.

A sample with nothing in it that absorbs has T = 1. As absorbing particles are added, T falls toward zero; it can never exceed 1, because no sample lets out more light than it received.

Absorbance turns that fraction into a more workable scale: $A = -\log T$, with T entered as a fraction, never a percentage. A sample that transmits everything has A = 0. Each time the transmitted fraction drops by a factor of ten, absorbance rises by exactly 1: T = 0.1 gives A = 1, T = 0.01 gives A = 2, T = 0.001 gives A = 3.

## The Law Itself: A = εlc

The Beer-Lambert law connects absorbance to the sample: $A = \varepsilon l c$. The symbol l is the path length, the distance light travels through the solution, in centimetres; a standard cuvette has l = 1.00 cm. The concentration c is in mol/L.

The remaining symbol, ε, is the molar absorptivity: a constant for one substance at one wavelength, measuring how strongly that substance absorbs. Its units, $L\ mol^{-1}\ cm^{-1}$, cancel the units of l and c exactly, because absorbance itself has no units. Change the substance or the wavelength and ε changes; hold both fixed and it stays constant for every solution in the experiment.

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With ε and l fixed, the law is two direct proportionalities at once: absorbance is directly proportional to concentration, and to path length. Double either one and the absorbance doubles: only the product εlc matters.

## Why Absorbance Is Linear and Transmittance Is Not

At the particle level, each dissolved absorbing particle independently intercepts a share of the photons passing through. Doubling the concentration doubles the intercepting particles in the beam, so the light absorbed grows in direct proportion: the physical basis of the linear law.

Transmittance describes what survives, and survivors multiply rather than subtract. Each equal step up in concentration cuts the transmitted fraction by the same factor, so T falls exponentially: T = 10^(−A). Its plot against c curves, which is why quantitative work plots absorbance.

## Calibration Curves and the Blank

To find an unknown concentration, measure the absorbance of standard solutions of known concentration, all at the same wavelength and in the same cuvette. Plotted against concentration, they fall on a straight line through the origin, with slope εl.

The unknown is measured under identical conditions and its concentration read from the line: across from its A to the line, then down to c. The line passes through the origin because a solution with none of the absorbing substance absorbs nothing.

First, though, the instrument is zeroed on a blank: the cuvette filled with solvent alone. Solvent and cuvette walls absorb and scatter a little light; blanking subtracts that background so readings report the analyte only. A finished line with a small positive intercept is the fingerprint of a systematic error, usually a contaminated blank.

## Choosing the Wavelength: λ_max

Because ε varies with wavelength, one wavelength must be chosen and held throughout. The standard choice is λ_max, where the substance absorbs most strongly and ε is largest.

At λ_max a small change in concentration produces the largest possible change in absorbance, so the measurement is most sensitive and relative error smallest. The law holds at any wavelength where the substance absorbs; λ_max is picked for sensitivity, not because the law only switches on there.

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## Where the Straight Line Fails

The law assumes each absorbing particle acts independently and that the detector faithfully measures the light that gets through. At high concentrations both assumptions break down: particles crowd close enough to interact and alter how each one absorbs, and so little light reaches the detector that stray light and detector limits distort the reading. The plot bends away from the straight line.

The fix is a weaker sample, not a new law. Dilute until the absorbance falls inside the standards' linear range, measure there, and multiply the concentration read from the line by the dilution factor.

## Worked Examples

**Example 1: Using the law directly. A substance has $\varepsilon = 2.50 \times 10^{3}$ L $mol^{-1}$ $cm^{-1}$ at the chosen wavelength. A solution of concentration $1.60 \times 10^{-4}$ mol/L in a 1.00 cm cuvette gives $A = \varepsilon lc = 2.50 \times 10^{3} \times 1.00 \times 1.60 \times 10^{-4} = 0.400$. Its transmittance is T = 10^(−0.400) = 0.398: about 39.8% of the light passes through.**

**Example 2: Reading an unknown off a calibration line. Standards lie on a line of slope $\varepsilon l = 40.0$ L $mol^{-1}$: at $c = 2.0 \times 10^{-3}$ mol/L, A = 0.080, rising by 0.080 for each $2.0 \times 10^{-3}$ mol/L. An unknown reads A = 0.200 in the same conditions, so $c = A \div (\varepsilon l) = 0.200 \div 40.0 = 5.0 \times 10^{-3}$ mol/L. The concentration is not 0.200: absorbance must always be divided by the slope.**

**Example 3: Converting between the two scales. A solution has A = 0.70. Its transmittance is T = 10^(−0.70) = 0.20, about 20%: only a fifth of the light gets through. The other way: %T = 5.0% means T = 0.050, so A = −log(0.050) = 1.30. Entering the percentage itself into the logarithm is the classic slip.**

**Example 4: Diluting back into the linear range. A concentrated sample reads A = 1.85, above the range in which the standards gave a straight line, so it cannot be trusted against that line. A 10.0 mL portion diluted to 50.0 mL, a factor of five, reads A = 0.37, inside the linear range. Read its concentration from the line, then multiply by 5 for the original.**

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## Traps That Cost Marks in Topic 3.13

**Plotting transmittance and expecting a straight line.** T against c is an exponential curve. Only absorbance against concentration is straight: the whole reason absorbance exists.

**Halving the transmittance when the concentration doubles.** Doubling c doubles A; it does not halve T. A solution with T = 25% has A = 0.60; double its concentration and A becomes 1.20, so T falls to 6.25%, not 12.5%.

**Reading absorbance as a percentage.** An absorbance of 0.70 is not 70% of anything. It converts to a transmittance of about 20%: 80% of the light was absorbed.

**Letting ε adjust itself.** Molar absorptivity is fixed by the substance and the wavelength. It does not rise or fall to cancel a change in concentration or path length; when measurements stop fitting the law, the fault lies in the law's assumptions, usually at high concentration.

**Comparing absorbances from different cuvettes.** The same absorbance in a 0.50 cm cuvette means twice the concentration of that absorbance in a 1.00 cm cuvette. Path length is built into every reading, so absorbances compare only at equal l.

**Skipping the blank.** Solvent and cuvette take a small share of the light themselves. Without blanking, every absorbance reads too high and the calibration line lifts off the origin.

### Key Relationships to Remember

- $T = I/I_0$ and $\%T = 100 \times T$; $A = -\log T$ with T as a fraction, and $T = 10^{(-A)}$; every factor of ten drop in T adds exactly 1 to A
- $A = \varepsilon lc$: ε is the molar absorptivity in L $mol^{-1}$ $cm^{-1}$, constant for one substance at one wavelength; l is the path length in cm; c is the concentration in mol/L; A has no units
- Absorbance is directly proportional to concentration at fixed path length and to path length at fixed concentration; doubling c and halving l leaves A unchanged
- Calibration curve: absorbance against concentration for standards gives a straight line through the origin with slope εl; an unknown is read off the line by interpolation
- The blank, solvent and cuvette alone, is set to zero absorbance so readings measure only the analyte; a positive intercept signals a systematic error, such as a contaminated blank
- Measurements are made at λ_max, where ε is largest, for the greatest sensitivity
- At high concentration the plot bends from linear as particles interact and too little light reaches the detector; dilute the sample into the linear range

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