Linear Equations in Chemistry

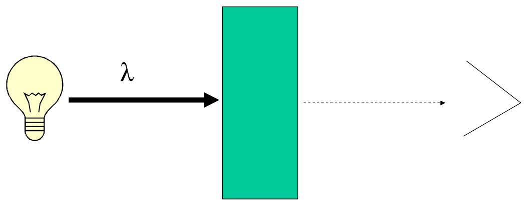
Some examples of typical problems

A brief review …

Determinants

Quantum mechanics

Example1: Adsorbtion Spectroscopy



Need to find the concentration of each species from the total adsorbtion A(λ)

Beer-Lambert

The Beer-Lambert Law: in a multicomponent system the total adsorbtion is the sum of the contributions from each component.
Say a 4 component system;

$$A_{total}(\lambda) = l\varepsilon_1 c_1 + l\varepsilon_2 c_2 + l\varepsilon_3 c_3 + l\varepsilon_4 c_4$$

l – *thickness of the sample* **(known)**

ε_i – *adsorbtion of species I* **(known)**

c_i – *concentration of species I* **(unknown)**

To Determine the Concentrations

In a 4 component system:

Measure at 4 different wavelengths

Set up 4 simultaneous equations and solve !

$$A_{total}(\lambda_1) = l\varepsilon_1(\lambda_1)c_1 + l\varepsilon_2(\lambda_1)c_2 + l\varepsilon_3(\lambda_1)c_3 + l\varepsilon_4(\lambda_1)c_4$$
$$A_{total}(\lambda_2) = l\varepsilon_1(\lambda_2)c_1 + l\varepsilon_2(\lambda_2)c_2 + l\varepsilon_3(\lambda_2)c_3 + l\varepsilon_4(\lambda_2)c_4$$
$$A_{total}(\lambda_3) = l\varepsilon_1(\lambda_3)c_1 + l\varepsilon_2(\lambda_3)c_2 + l\varepsilon_3(\lambda_3)c_3 + l\varepsilon_4(\lambda_3)c_4$$
$$A_{total}(\lambda_4) = l\varepsilon_1(\lambda_4)c_1 + l\varepsilon_2(\lambda_4)c_2 + l\varepsilon_3(\lambda_4)c_3 + l\varepsilon_4(\lambda_4)c_4$$

IR Data for a 4 Component System

	p-xylene	*m*-xylene	*o*-xylene	ethyl-benzene	A_{total}
λ	ε*l*	ε*l*	ε*l*	ε*l*	
12.5	1.502	0.0514	0	0.0408	0.1013
13.0	0.0261	1.1516	0	0.0820	0.09943
13.4	0.0342	0.0355	2.532	0.2933	0.2194
14.3	0.0340	0.0684	0	0.3470	0.03396

How do we solve for the concentrations ?

How about for a 20 component system ?

Example 2: Chemical Kinetics

The Arrhenius equation takes the linear form

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

Measure at 2 different temperatures to get 2 simultaneous equations to solve for A and E_a

$$\ln(k_1) = \ln(A) - \frac{E_a}{RT_1}$$

$$\ln(k_2) = \ln(A) - \frac{E_a}{RT_2}$$

Other Examples

Balancing complex chemical equations

Mass spectroscopic analysis of mixtures

Regression (fitting)
- Michaelis-Menten [S](k) fitting
- All model fitting

Quantum Mechanics – Huckel Theory

Reminder: Solution by Inspection

$$\frac{1}{2}x + 8y = 9 \xrightarrow{\text{x 2}} 2x + 32y = 36$$

$$2x + y = 5 \qquad 2x + y = 5$$

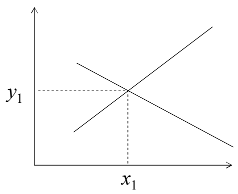
Subtract

$$31y = 31 \longrightarrow y = 1, \quad x = 2$$

OK – but for multiple equations this process rapidly becomes tedious & eventually intractable

Reminder: Graphical Interpretation

Solving 2 linear equations is simply finding where two lines cross



Solving n equations is where n lines cross in an n-dimensional space !

The General Problem (2 variables)

Find *x* and *y* given;

$$a_{11}x + a_{12}y = b_1$$
$$a_{21}x + a_{22}y = b_2$$

Where a_{11}, a_{12}, a_{21},a_{22} and b_1, b_2 are known constants

The General Solution (2 variables)

$$x = \frac{b_1 a_{22} - b_2 a_{12}}{a_{11}a_{22} - a_{12}a_{21}} \qquad y = \frac{b_2 a_{11} - b_1 a_{21}}{a_{11}a_{22} - a_{12}a_{21}}$$

Note: the denominators are the same and can be written as a ***determinant***;

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \equiv a_{11}a_{22} - a_{12}a_{21}$$

Determinants (2x2)

(top left * bottom right) - (top right * bottom left)

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \equiv a_{11}a_{22} - a_{12}a_{21}$$

General Solution in Determinants (2x2)

$$x = \frac{\begin{vmatrix} b_1 & b_2 \\ a_{12} & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} \qquad y = \frac{\begin{vmatrix} b_1 & b_2 \\ a_{21} & a_{11} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}$$

Determinants are the practical method for solving linear problems with many unknowns

For example

$$\frac{1}{2}x + 8y = 9 \qquad\qquad a_{11} = \frac{1}{2} \quad a_{12} = 8 \quad b_1 = 9$$
$$2x + y = 5 \qquad \longrightarrow \qquad a_{21} = 2 \quad a_{22} = 1 \quad b_2 = 5$$

$$x = \frac{b_1 a_{22} - b_2 a_{12}}{a_{11}a_{22} - a_{12}a_{21}} = \frac{-31}{-15\,{}^1\!/\!_2} = 2$$

$$y = \frac{b_2 a_{11} - b_1 a_{21}}{a_{11}a_{22} - a_{12}a_{21}} = \frac{-15\,{}^1\!/\!_2}{-15\,{}^1\!/\!_2} = 1$$

Determinants ….

Allow you to solve large sets of linear equations and …

There is a simple prescription for computing them …..

And it is…

Computing Determinants (3x3 case)

A 3x3 determinant can be computed in terms of 2x2 determinants as follows…

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} =$$

$$a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

The Rules …. !

$$\begin{matrix} + & - & + \\ \end{matrix}$$
$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} =$$

Associate a sign with each of the elements of the first row

Take each element in turn and multiply it by the determinant of the 2x2 matrix left after crossing out its row and column

$$a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

For example..

$$\begin{vmatrix} 2 & 1 \\ 3 & 4 \end{vmatrix} = 2 \times 4 - 1 \times 3 = 8 - 3 = 5$$

$$\begin{vmatrix} 1 & -1 & 2 \\ 0 & 3 & 0 \\ 2 & -2 & -2 \end{vmatrix} = 1 \times (3 \times -2) - -1(0) + 2(0 - 3 \times 2)$$

$$= -6 + 0 - 12 = -18$$

Terminology

The *signed* 2x2 determinants associated with each element of the first row are called *cofactors.* The cofactor of a_{11} is A_{11} …

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \qquad A_{11} = \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix}$$

Writing in Terms of Cofactors

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}A_{11} + a_{12}A_{12} + a_{13}A_{13}$$

Note that the minus sign is part of A_{12}

The General Case

The determinant of any array can be computed in this way.

For example;

A 4x4 determinant can be expanded in the in terms of 3x3 cofactors, which in turn get expanded in terms of 2x2 cofactors…

Computers are very good at this !

The 4x4 Case

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = a_{11}A_{11} + a_{12}A_{12} + a_{13}A_{13} + a_{14}A_{14}$$

With, $$A_{11} = +\begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix}$$ etc.

Summary

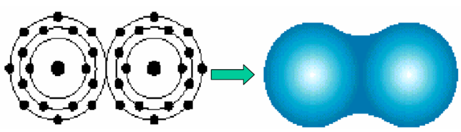
Systems of linear equations turn up all the time in chemistry.

These problems can be solved using determinants.

There is a simple (but involved!) method for computing determinants of arbitrary size.

Quantum Mechanics

The interactions between atoms are governed by the **quantum mechanical** behaviour of the electrons.



Lets look in the simplest way at the reason for the formation of a chemical bond…