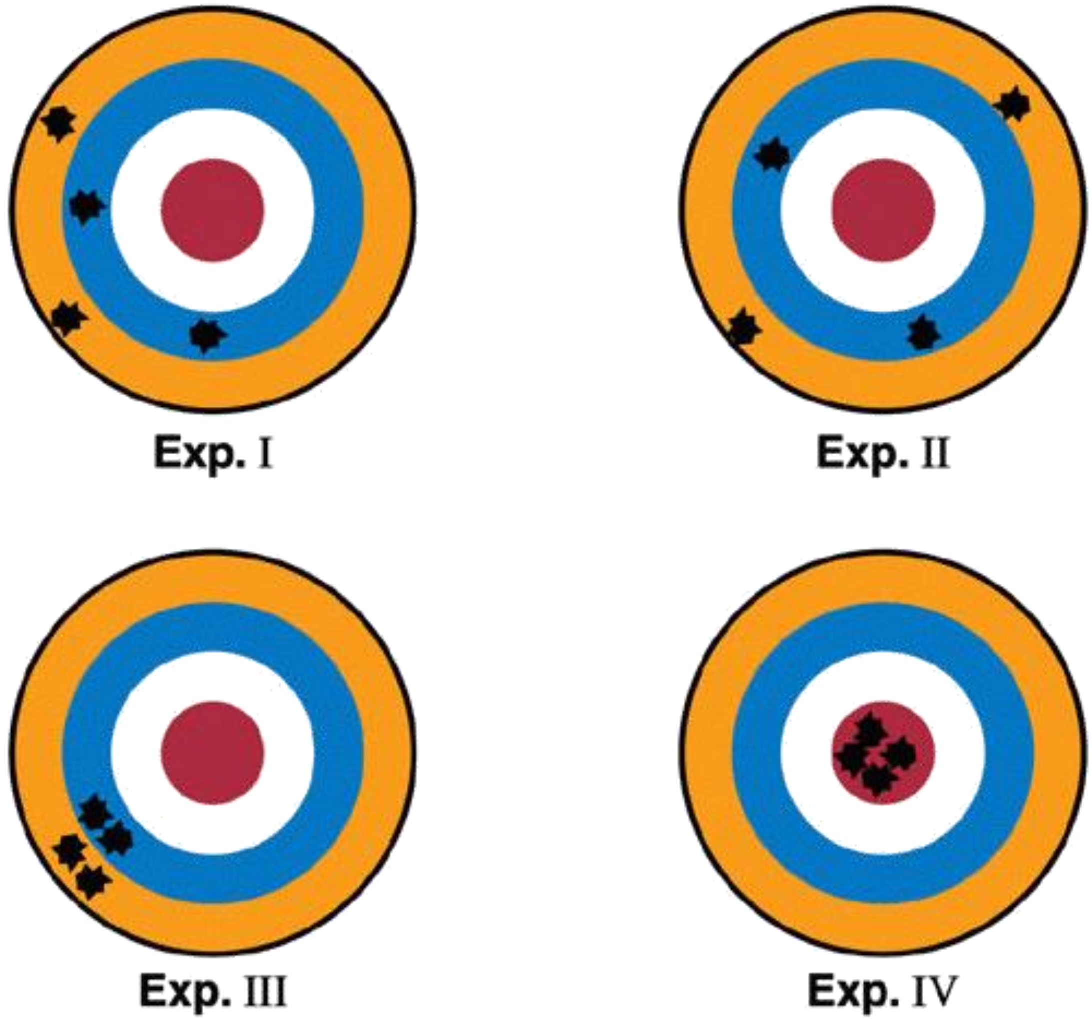
Chem 314: Introduction to the Evaluation of *Maximum Probable Error*

Types of Error

- Random, Statistical or Indeterminate error:
  - Resulting from the impact of the environment e.g. operator, fluctuation of air flow, temperature, etc.
  - The value can not be predicted at any given time: random and non-reproducible.
  - Can be treated with statistical methods.

- Systematic or Determinate error:
  - Sources
    - Instrument Error
    - Method Error
    - Personal Error
  - Predictable and reproducible
  - Can **not** be treated with statistical methods

Precision and Accuracy



Precision and Accuracy

- Precision:
  Description of reproducibility. How close are the measured values to each other?

  Can be modeled by statistical methods, hence “statistical error”
- Accuracy:
  Description of how close a measured value is to the “true” value.

  CANNOT be measured by statistical methods

So how *do* we measure accuracy?

Analysis of Systematic Error: Maximum Probable Error

- Some value Q is obtained by the measurements $x_1, x_2 \ldots x_i$.
- $x_1, x_2 \ldots x_i$ are independent measurements.
- Δx_i is the systematic error for x_i measurement.
- ΔQ_i represents the error in Q resulting from Δx_i
  $\Delta Q_i = Q - Q_i$
- In the end, the Maximum Probable Error in Q is the sum of all of these individual errors:

$$\Delta Q = |\Delta Q_1| + |\Delta Q_2| + \ldots\ldots\ldots |\Delta Q_i|.$$

Analysis of Systematic Error: Maximum Probable Error

One example (several more in your handout):

A student wishes to determine the volume of an ideal gas by measuring the pressure it exerts at room temperature.

1.0   0.1 moles of an ideal gas are placed into a container, which is allowed to expand until the pressure exerted is 1.0   0.01 atm in a room held at a constant temperature of 25   0.5 ^{o}C.

What's the volume, and what's the systematic error in that volume?

Analysis of Systematic Error: Maximum Probable Error

PV=nRT

V = nRT/P

V, then, is our "Q", and it is determined by x_1=n, x_2=T and x_3=P.

V = (1.0 moles)(0.08206 L-atm/mol-K)(298.15 K)/(1.0 atm) = 24.47 L = $24._{47}$ L

Analysis of Systematic Error: Maximum Probable Error

We need to consider the error introduced into that value of V by the systematic error in n, P and T

Why is R not included in our error analysis?

ΔQ_1 is the error introduced in Q by the extreme value of x_1, or n

The largest possible value of n is 1.1 moles

If we repeat the above calculation with n=1.1, we have Q_1 = (1.1 moles)(0.08206 L-atm/mol-K)(298.15 K)/(1.0 atm) = 26.91 L = $26._{91}$ L

$\Delta Q_1 = Q_1 – Q = 26._{91}$ L – $24._{47}$ L = $2._{45}$ L

Analysis of Systematic Error: Maximum Probable Error

We repeat this process for P and T

ΔQ_2 is the error introduced in Q by the extreme value of x_2, or P

Q_2 = (1.0 moles)(0.08206 L-atm/mol-K)(298.15 K)/(1.01 atm) = 24.22 L = $24._{22}$ L

$\Delta Q_2 = Q_2 - Q = 24._{22}$ L – $24._{47}$ L = $0._{25}$ L

Q_3 = (1.0 moles)(0.08206 L-atm/mol-K)(298.65 K)/(1.00 atm) = 24.507 L = $24._{51}$ L

$\Delta Q_3 = 0._{04}$ L

Analysis of Systematic Error: Maximum Probable Error

The total systematic error in Q is the sum of these individual uncertainties:

$\Delta Q = |\Delta Q_1| + |\Delta Q_2| + |\Delta Q_3|$

$\Delta Q = |\Delta Q_n| + |\Delta Q_P| + |\Delta Q_T|$

$\Delta Q = 2._{45}\ L + 0._{25}\ L + 0._{04}\ L = 2._{74}\ L$

$V = 24._{47}\ L \quad 2._{74}\ L = 24 \quad 3\ L$

The immediate take home lesson: If you wanted to improve the **accuracy** of this experiment, which experimental parameter should you be most concerned about?

Shortcuts

- Addition and Subtraction
  - Systematic error:
    $e=|e_1|+|e_2|+\ldots.\ |e_i|$
  - Random error:

$$e=\sqrt{e_1^{\ 2}+e_2^{\ 2}+\ldots\ldots e_i^{\ 2}}$$

- Multiplication and Division
  - Systematic error:
    $\%e=|\%e_1|+|\%e_2|+\ldots..\ |\%e_i|$
  - Random error:

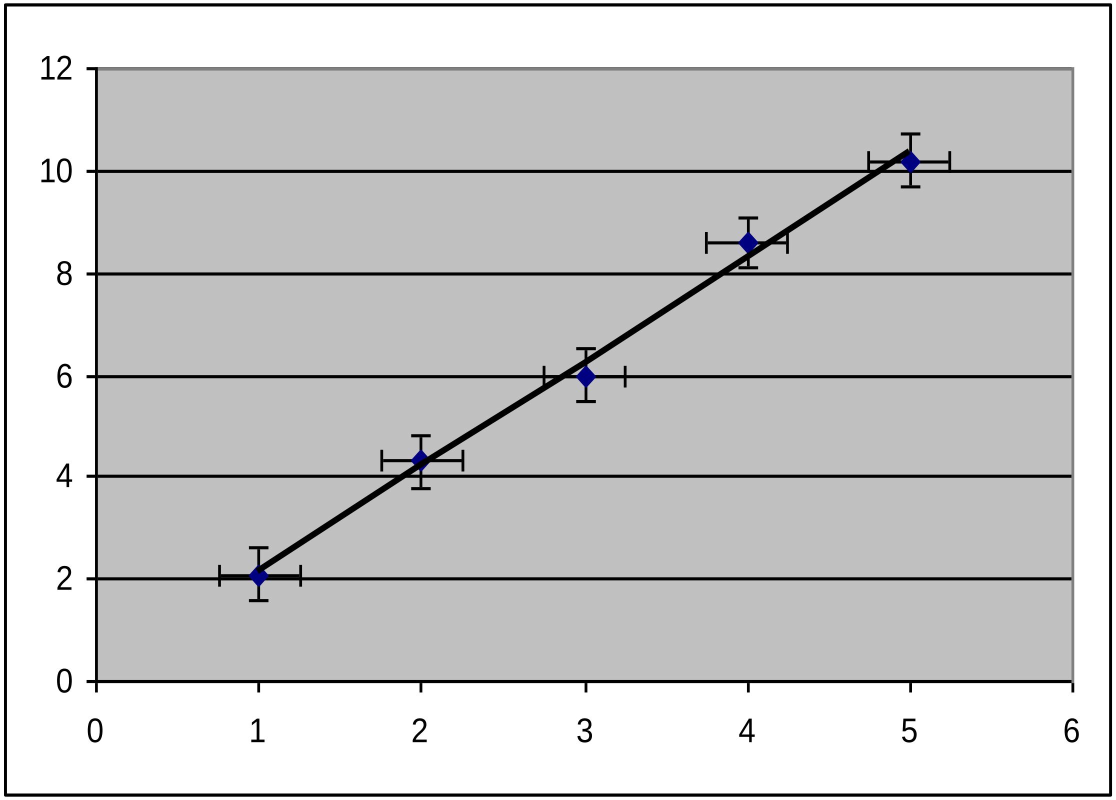
$$\%e=\sqrt{(\%e_1)^2+(\%e_2)^2+\ldots\ldots(\%e_i)^2}$$

Error Analysis of Straight Line Parameters

X	Y
1	2.1
2	4.3
3	6
4	8.6
5	10.2
Slope:	2.05
Intercept	0.09

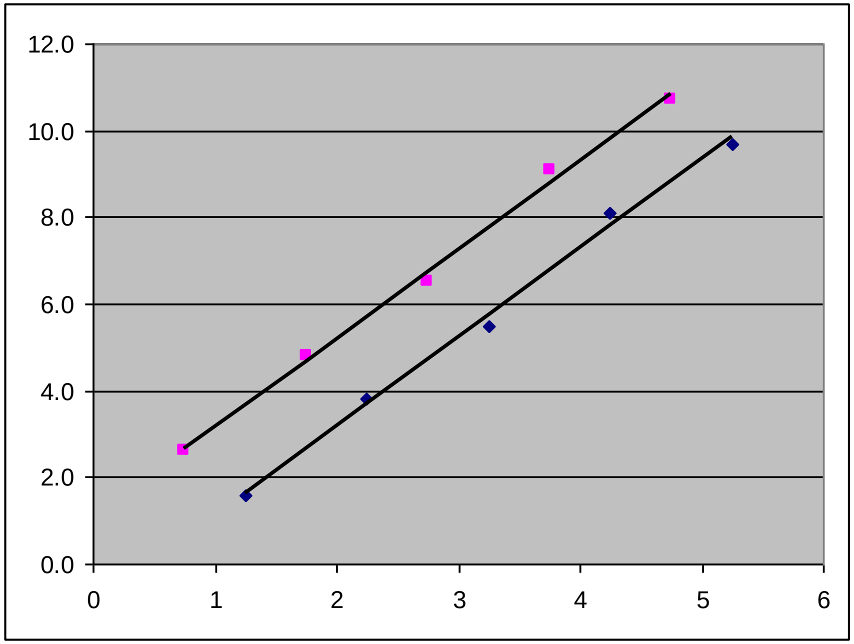
Systematic error for X: 0.25

Systematic error for Y: 0.5



Systematic error only impacts the intercept, NOT the slope

X(max)	Y(min)		X(min)	Y(max)
1.25	1.6		0.75	2.6
2.25	3.8		1.75	4.8
3.25	5.5		2.75	6.5
4.25	8.1		3.75	9.1
5.25	9.7		4.75	10.7
Slope	2.05		Slope	2.05
Intercept	-0.9225		Intercept	1.1025



Systematic error for X: 0.25

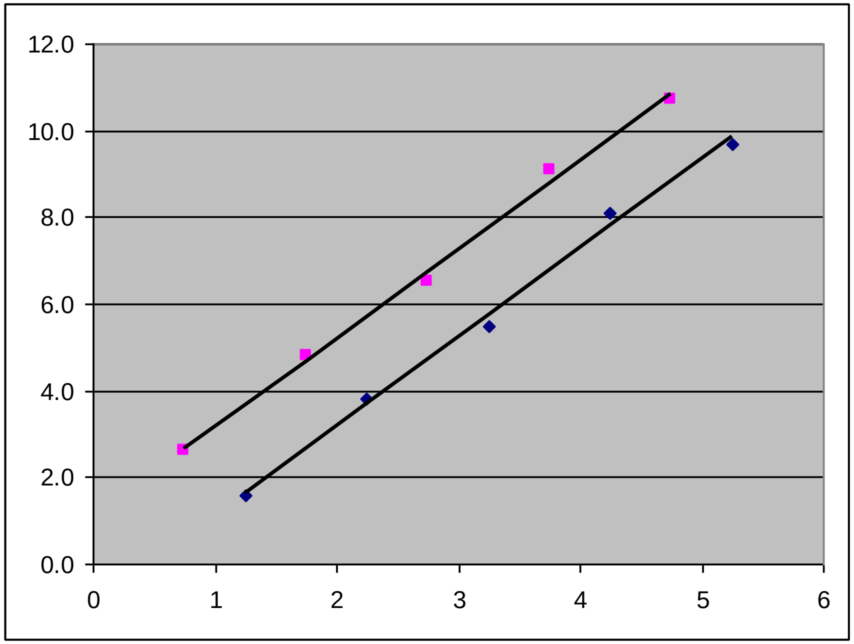
Systematic error for Y: 0.5

Maximum Error for the Intercept

$$\frac{(MaxIntercept - MinIntercept)}{2}$$

Systematic error only impacts the intercept, NOT the slope

X(max)	Y(min)		X(min)	Y(max)
1.25	1.6		0.75	2.6
2.25	3.8		1.75	4.8
3.25	5.5		2.75	6.5
4.25	8.1		3.75	9.1
5.25	9.7		4.75	10.7
Slope	2.05		Slope	2.05
Intercept	-0.9225		Intercept	1.1025



Systematic error for X: 0.25

Systematic error for Y: 0.5

Maximum Error for the Intercept

$$\frac{(1.1025 - -0.9225)}{2} = 1.0125$$

What about statistical error?

X	Y
1	2.1
2	4.3
3	6
4	8.6
5	10.2

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99778253
R Square	0.99556998
Adjusted R Square	0.99409331
Standard Error	0.24966644
Observations	5

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.09	0.26185	0.343705	0.753747	-0.74333	0.923331	-0.74333	0.923331
X Variable 1	2.05	0.07895	25.96532	0.000125	1.798741	2.301259	1.798741	2.301259

What about statistical error?

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.09	0.26185	0.343705	0.753747	-0.74333	0.923331	-0.74333	0.923331
X Variable 1	2.05	0.07895	25.96532	0.000125	1.798741	2.301259	1.798741	2.301259

Maximum Error for the Intercept

$$\frac{(Upper\,95\%CL - Lower\,95\%CL)}{2}$$

Maximum Error for the Slope

$$\frac{(Upper\,95\%CL - Lower\,95\%CL)}{2}$$

Maximum Error for the Intercept

$$\frac{(0.923331 - -0.74333)}{2} = 0.833$$

Maximum Error for the Slope

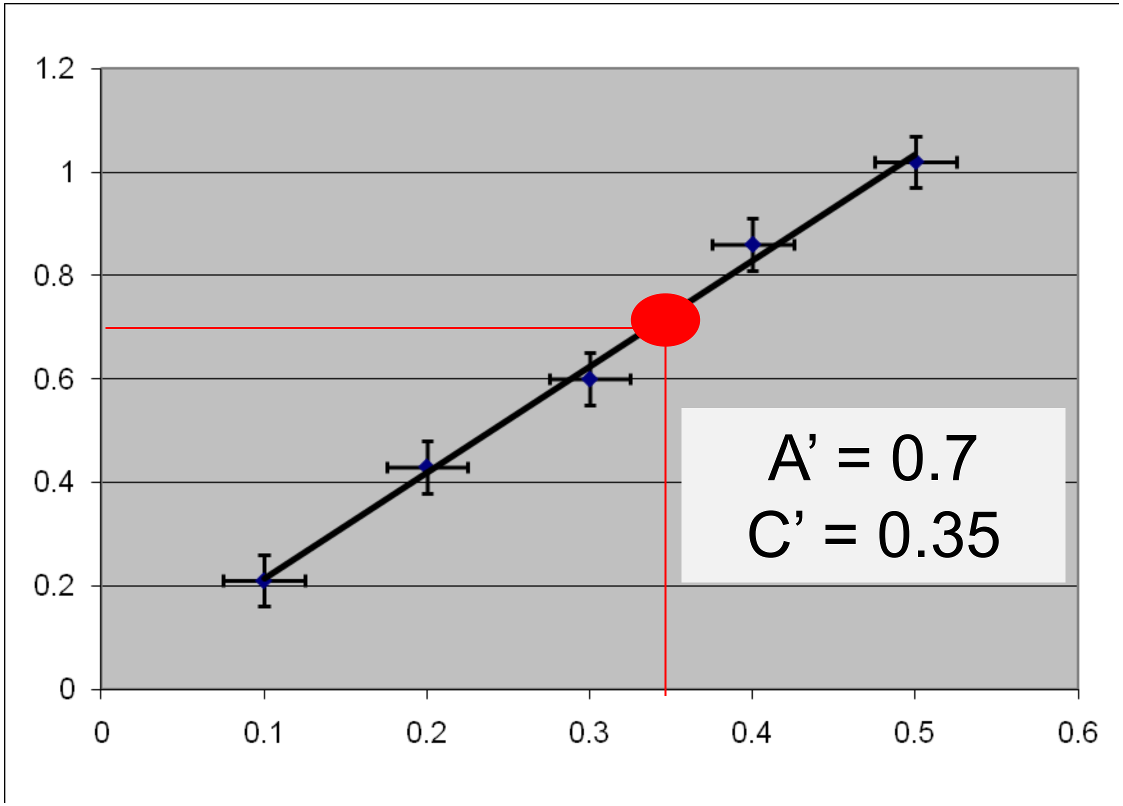
$$\frac{(2.301259 - 1.798741)}{2} = 0.251$$

Example: Optical Absorption
Beer's law

Conc (M)	Abs
.1	.21
.2	.43
.3	.6
.4	.86
.5	1.02
Slope:	2.05
Intercept	0.09

Systematic error for X: 0.025

Systematic error for Y: 0.05



What's the error in the concentration of your unknown?

Example: Optical Absorption Beer's law

- A'=εbC'+intercept; where ε is extinction coefficient, b is the pathlength, C' is the concentration of our unknown.
- C'=(A'-intercept)/slope ; where "intercept" is the background absorption and "slope"= εb.
- Systematic Error:
  Max Prob.Error= |[C'(max)- C'(min)]/2|
  $= f(\text{Intercept}_{max} - \text{Intercept}_{min})$
- There is no **systematic** error for the slope!

Example: Optical Absorption Beer's law

- Systematic Error:
  Max Prob.Error= |[C'(max)- C'(min)]/2|
  = f(Intercept$_{max}$- Intercept$_{min}$)
- C'(max)=(A'-Intercept$_{min}$)/slope = (0.7- -0.09225)/2.05 = 0.386 M
- C'(min)=(A'-Intercept$_{max}$)/slope = (0.7- 0.11025)/2.05 = 0.288 M
- Systematic Error = 0.386-0.288/2 = 0.049 M

Example: Optical Absorption Beer's law

- Statistical Error would be difficult to calculate explicitly, so we'll use the 95% Confidence Limits to guide us:
- Statistical Error= |[C'(extreme1) - C'(extreme2)]/2|
  C' (extreme1) = f(lower CL intercept, high CL slope)
  C' (extreme2) = f(high CL intercept, low CL slope)
- $C'(extreme1) = (A' - intercept_{lowCL}) / slope_{highCL}$
  = (0.7- -0.074333)/ 2.301259 = 0.336
- $C'(extreme2) = (A' - intercept_{highCL}) / slope_{lowCL}$
  = (0.7- 0.0923331)/ 1.798741= 0.338

Statistical Error= |[0.336 – 0.338]/2| = 0.001

Example: Optical Absorption Beer's law

- **Total Error** = Maximum Probable Error + Statistical Error
- So, for our unknown sample,

  C' = 0.35 M ± (0.049 + 0.001) = 0.35 ± 0.05 M

- For every experiment in this class, you are responsible for determining the total error in your result, *and the primary causes of that error*

Precision and Accuracy

- If our experimental result is neither accurate nor precise, it is not a very useful result
- If our result is accurate but not precise, then the experiment is likely well designed, but poorly executed
- If our result is precise but not accurate, then the experiment itself is in need of revision (apparatus? procedure?)