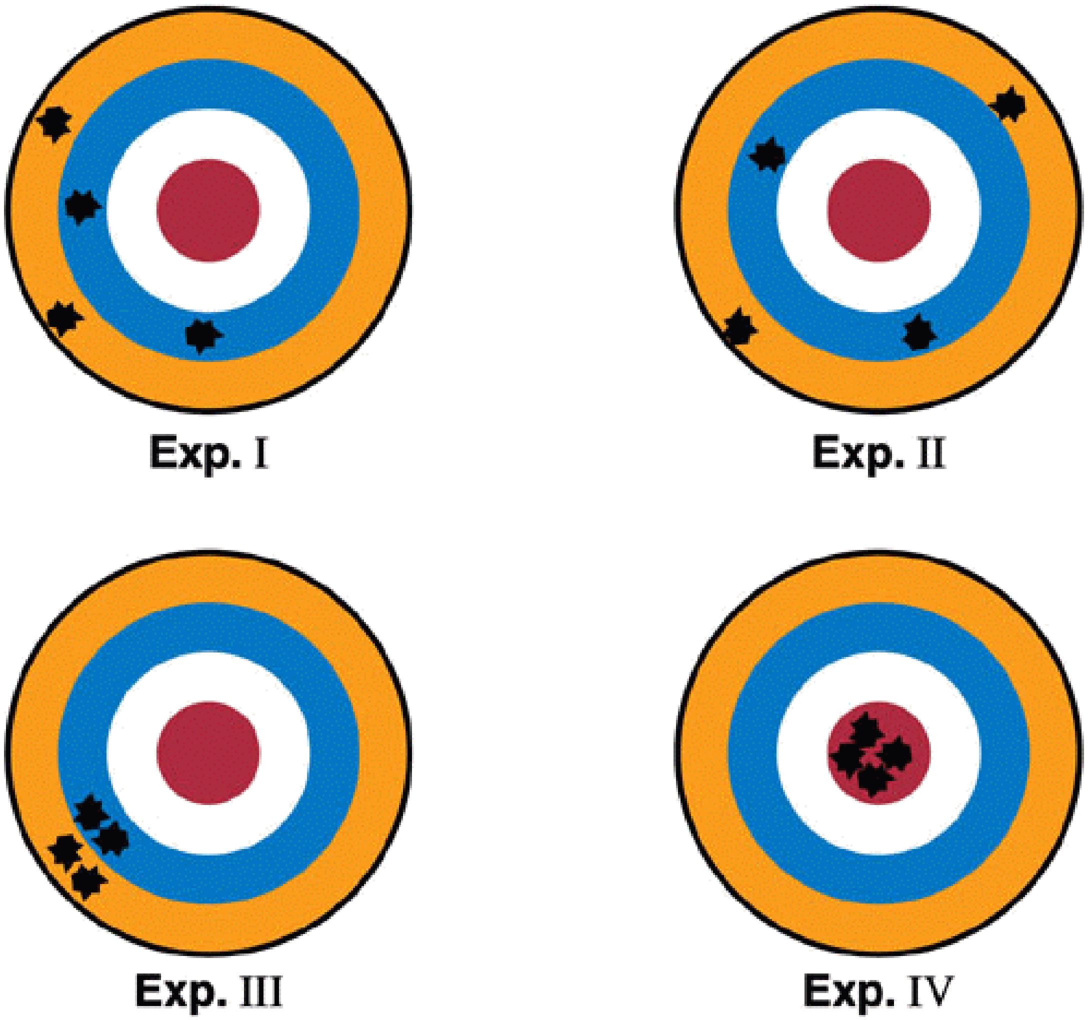
Chem 314:
Introduction to the Evaluation of
Maximum Probable Error

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:

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

Analysis of Systematic Error: Maximum Probable Error

One example (several more in your handout):

A student wishes to determine the pressure of an ideal gas by expanding it into a known volume at room temperature.

1.0 ± 0.1 moles of an ideal gas are placed into a container, with a volume of 1.0 ± 0.01 L in a room held at a constant temperature of $25 \pm 0.5\ ^{o}C$.

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

Analysis of Systematic Error: Maximum Probable Error

$PV=nRT$

$P = nRT/V$

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

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

Analysis of Systematic Error: Maximum Probable Error

We need to consider the error introduced into that value of P by the systematic error in n, V 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 L) = 26.91 atm = $26._{91}$ atm

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

Analysis of Systematic Error: Maximum Probable Error

We repeat this process for V and T

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

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

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

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

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

Analysis of Systematic Error: Maximum Probable Error

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

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

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

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

$V = 24._{47}$ atm $\pm\ 2._{74}$ atm = 24 ± 3 atm

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:

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

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

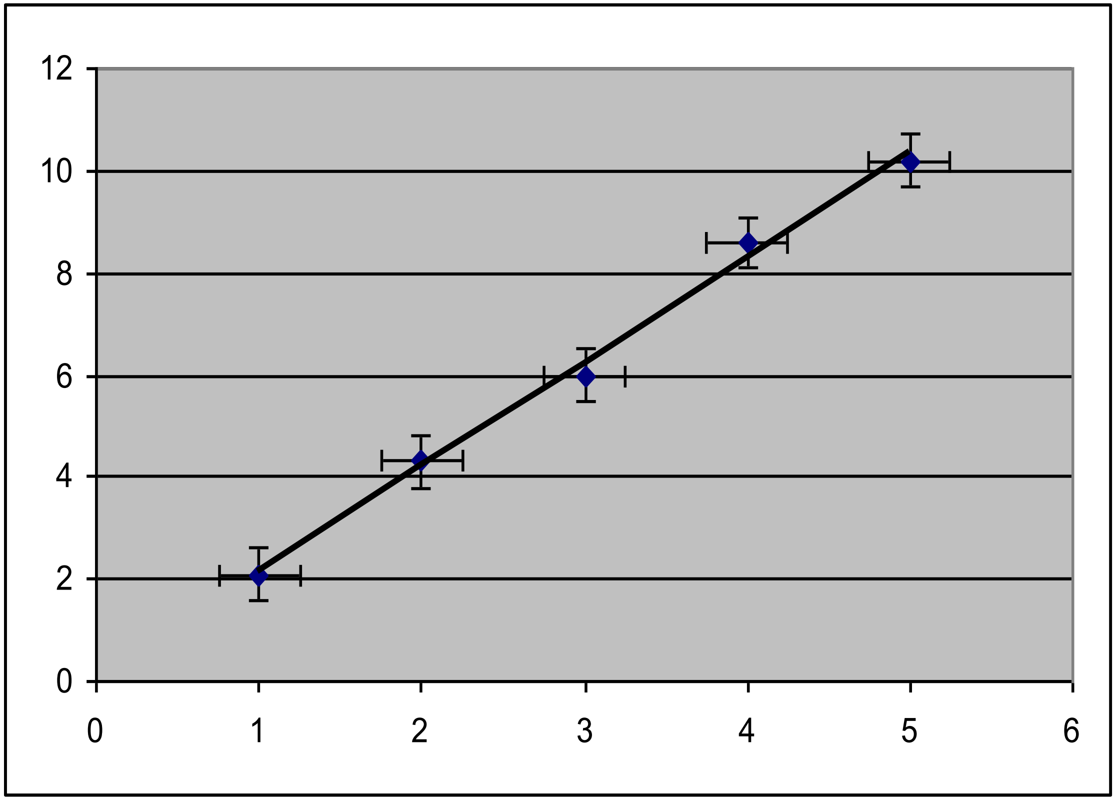
$$\%e=\sqrt{(\%e_1)^2+(\%e_2)^2+\ldots\ldots(\%e_i)^2}$$

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

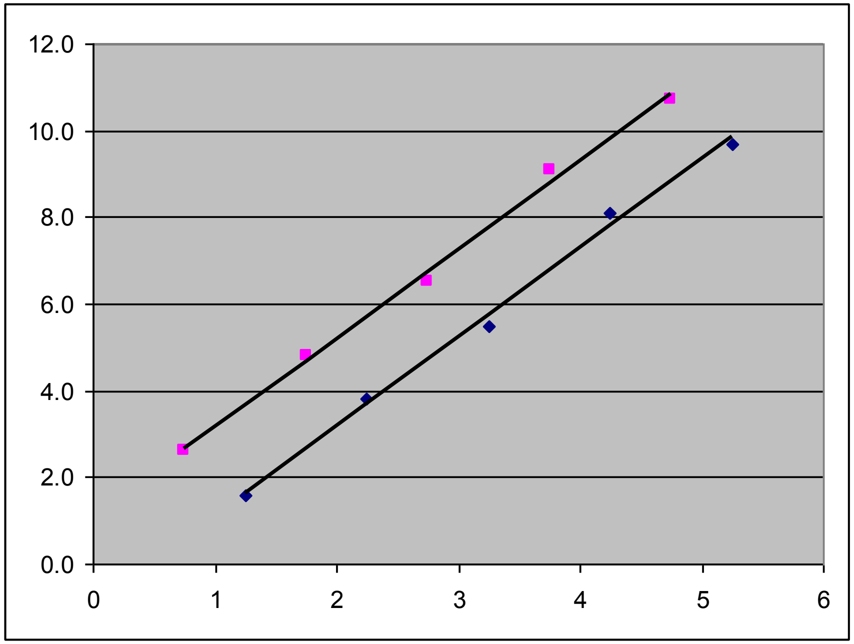
Systematic error for X: ±0.25

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

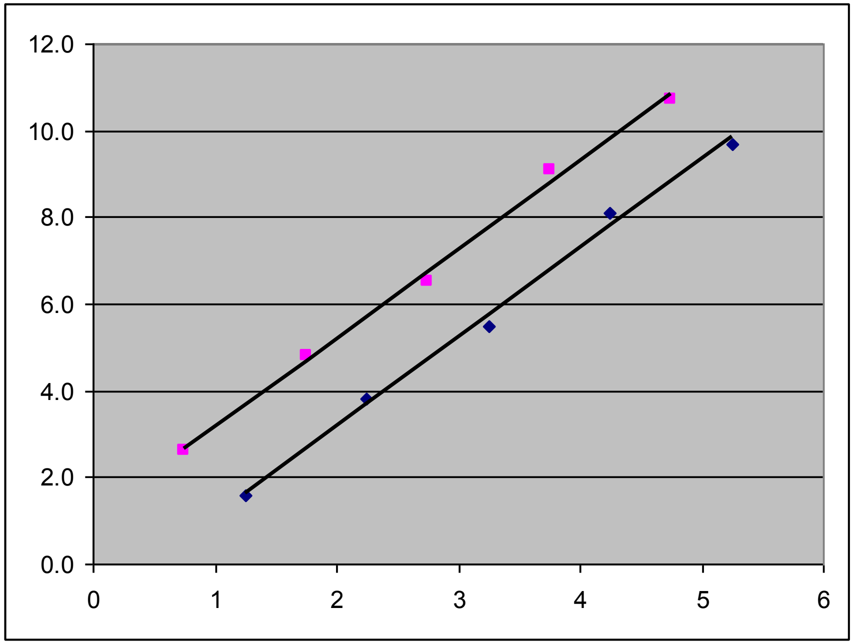
Maximum Error for the Intercept

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

*IF Δx is independent of y!

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

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

*IF Δx is independent of y!

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

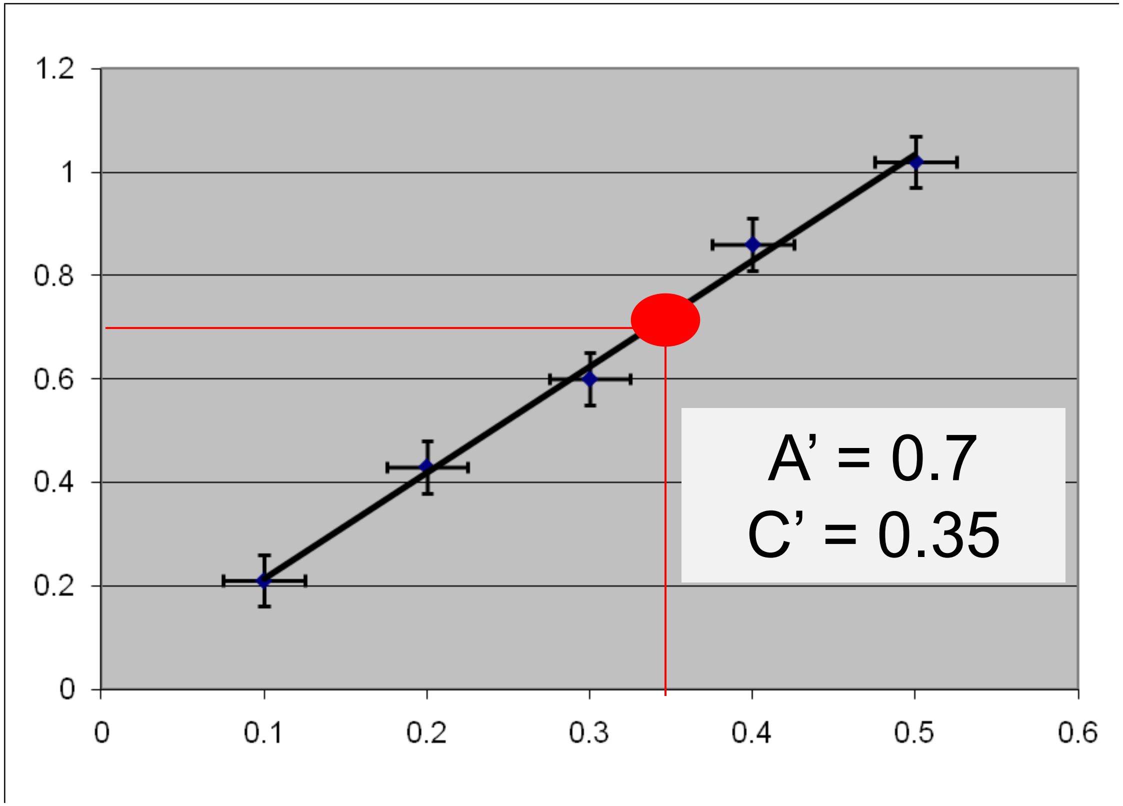
$$\frac{(2.301259 - 1.798741)}{2} = 0.251$$

Example: Optical Absorption
Beer's law

Conc (M)	Abs
.1	.21
.2	.43
.3	.6
.4	.86
.5	1.02
Slope:	2.05
Intercept	0.009

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

- $A' = \varepsilon b C' + \text{intercept}$; where ε is extinction coefficient, b is the pathlength, C' is the concentration of our unknown.
- $C' = (A' - \text{intercept})/\text{slope}$; where "intercept" is the background absorption and "slope"$= \varepsilon b$.
- 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?)