Errors – PROPAGATING!!!!

* There is no such thing as a perfect measurement.
  - when we take a measurement there is always a limitation on how close we are to the true value
    - -- if you measure a mass to the mg than then error in your measurement is at least a ±mg
    - -- this implies that the true value is never known and so that the exact error is also "unknowable"
    - -- therefore, we are forced to estimate error
  - types of errors
    - -- illegitimate
      - --- deviations from procedure
      - --- inability to use a calculator
    - -- bias or systematic errors
      - --- an error that persists and cannot be caused by chance
        - --- your scale always says you weigh 5 lbs heavier
      - --- this must be determined by comparison to theory or alternate measurements
    - -- random/precision errors
      - --- deviations which result from the precision of the method which is utilized
      - --- examples: calibration drift, environmental effect, glassware tolerance
      - --- sometimes we can reduce these error by generating more data

* Propagation of Error
  - used to determine the uncertainty in a quantity which depends on 1 or more independent variables
  - mathematically

$$F = F(x_1, x_2, \ldots, x_N)$$

$$\partial F = \sqrt{\left[\left(\frac{\partial F}{\partial x_1}\partial x_1\right)^2 + \left(\frac{\partial F}{\partial x_2}\partial x_2\right)^2 + \cdots \left(\frac{\partial F}{\partial x_N}\partial x_N\right)^2\right]}$$

where ∂x_i is the uncertainty in independent variable x_i

  - Examples
    - -- Determine the error in the density of an ideal gas

$$\rho = \frac{P}{RT} \text{ where } T \pm \partial T \text{ and } P \pm \partial P$$

$$\frac{\partial \rho}{\partial T} = -\frac{P}{RT^2} \qquad \frac{\partial \rho}{\partial P} = \frac{1}{RT}$$

$$\partial \rho = \sqrt{\left[\left(\frac{\partial \rho}{\partial T}\partial T\right)^2 + \left(\frac{\partial \rho}{\partial P}\partial P\right)^2\right]} = \sqrt{\left[\left(-\frac{P}{RT^2}\partial T\right)^2 + \left(\frac{1}{RT}\partial P\right)^2\right]}$$

    - -- Find the momentum for a body with a mass of $m = 0.53 \pm 0.01\, kg$ moving at a velocity $v = 9.1 \pm 0.3\ ^{m}\!/_{s}$.

$p = mv$

$$\partial p = \sqrt{\left(\frac{\partial p}{\partial m}\partial m\right)^2 + \left(\frac{\partial p}{\partial v}\partial v\right)^2} = \sqrt{\left(v \bullet \partial m\right)^2 + \left(m \bullet \partial v\right)^2} = \sqrt{\left(9.1 \bullet 0.01\right)^2 + \left(0.53 \bullet 0.3\right)^2}$$

$\partial p = 0.18\ ^{kg \bullet m}\!/_{s}$

$p = 0.53 \bullet 9.1\ ^{kg \bullet m}\!/_{s} = 4.8 \pm 0.2\ ^{kg \bullet m}\!/_{s}$

-- Now, let's figure out the error in our equilibrium bond length `

$$B_{[0]} = \frac{h}{8\pi^2 2 m_{oxy} r^2 c} \rightarrow r = \left(\frac{h}{8\pi^2 2 m_{oxy} B_{[0]} c}\right)^{1/2} \times 10^{12}$$

--- before we take this on we need to convert our units:

$$B_{[0]\_m} = \frac{B_{[0]}}{cm} \times \frac{100\ cm}{m}$$

$$\partial B_{[0]\_m} = \sqrt{\left(\frac{\partial B_{[0]\_m}}{\partial B_{[0]}}\partial B_{[0]}\right)^2} = 100 \times \partial B_{[0]} = 100 \times 0.0001 = 0.1\ m$$

$B_{[0]\_m} = 39.0 \pm 0.1\ m$

--- now we are ready as soon as we get everything together

$h = 6.6260755 \times 10^{-34}\ J \bullet s$

$$m = 15.9994\ amu \times \frac{1.6605402 \times 10^{-27}\ kg}{amu} = 2.65676 \times 10^{-27}\ kg$$

$c = 2.99792458\ ^{m}\!/_{s}$

$$\partial r = \sqrt{\left(\frac{\partial r}{\partial B_{[0]\_m}}\partial B_{[0]\_m}\right)^2}$$

$$\partial r = \sqrt{\left[\frac{1}{2}\left(\frac{h}{8\pi^2 c 2 m_{oxy} B_{[0]\_m}}\right)^{-1/2} \times \left(\frac{-h}{8\pi^2 c 2 m_{oxy} B_{[0]\_m}^2}\right)\partial B_{[0]\_m} \times 10^{12}\right]^2}$$

$\partial r = 0.15\ pm$

$r = 116.2 \pm 0.2\ pm$

So what do you need to do? You will be computing errors for the situations given below.

1. Use the reduced mass, μ, and the error of the fundamental frequency, $\tilde{v}$, to determine the error in the force constant *k*.

$$k = \mu\left(2\pi\tilde{v}c_{cm}\right)^2 \text{ where } \mu_{AB} = \frac{m_A m_B}{m_A + m_B}$$

$$\tilde{v} = 2900.0 \pm 0.1\, cm^{-1} \quad 1\, amu = 1.660540 \times 10^{-27}\, kg \quad c = 2.99792458 \times 10^{10}\, cm \bullet s^{-1}$$

$$m_{^1H} = 1.007825\, amu \quad m_{^{35}Cl} = 34.968853\, amu$$

2. Determine the error in the rotational partition function using the information given below.

$$q_{rot}(T) = \frac{T}{\Theta_{rot}} \quad T = 298.2 \pm 0.1\, K \quad \Theta_{rot} = 15.828 \pm 0.001\, K$$

3. Determine the error in the vibrational partition function using the temperature given above and the following:

$$q_{vib}(T) = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} = e^{-\Theta_{vib}/2T}\left(1 - e^{-\Theta_{vib}/T}\right)^{-1} \quad \Theta_{vib} = 4172.6 \pm 0.1 K$$

4. Determine the error in the standard entropy using the information given in problems 2. and 3. and the equation given below.

$$S^\circ_{rot,vib} = R\left(\ln\frac{Te}{2\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1}\right) \quad \text{where e = exp(1)}$$