Chapter 7: Numerical Integration

Given any set of data points, you can fit a function and integrate to find the area under the plot.

From Physical Chemistry, 6th Edition by Peter Atkins:

Example 16.5:
The observed vibrational intervals of H_2^+ lie at the following values (in cm^{-1}):

2191, 2064, 1941, 1821, 1705, 1591, 1479, 1368, 1257, 1145, 1033, 918, 800, 677, 548, 411. Determine the dissociation energy of the molecule in cm^{-1}.

The vibrational intervals can be plotted against v + 1/2, where v = 0, 1, 2...
The dissociation energy is the area under the plot from v = 0 to where the plot crosses the x-axis.

Table

Make a list of vibrational values:

```
vib = {2191, 2064, 1941, 1821, 1705, 1591, 1479, 1368,
   1257, 1145, 1033, 918, 800, 677, 548, 411};
```

The *Table* command will make a list of values based on the argument. Use *Table* to make a list of v + 1/2 values from v = 0 to v = 15 (since there are 16 vibrational values).

```
vhalf = Table[v + 1 / 2, {v, 0, 15}]
```

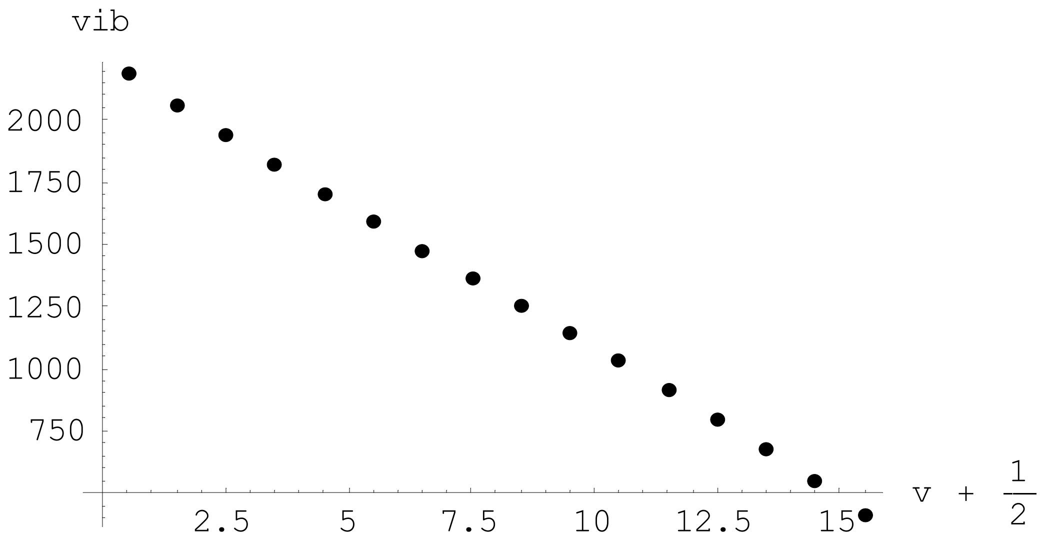
$$\left\{\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}, \frac{15}{2}, \frac{17}{2}, \frac{19}{2}, \frac{21}{2}, \frac{23}{2}, \frac{25}{2}, \frac{27}{2}, \frac{29}{2}, \frac{31}{2}\right\}$$

Make a list of {v + ½, vib} values to plot. Don't forget to transpose.

```
points = {vhalf, vib};
data = Transpose[points]
```

$$\left\{\left\{\frac{1}{2}, 2191\right\}, \left\{\frac{3}{2}, 2064\right\}, \left\{\frac{5}{2}, 1941\right\}, \left\{\frac{7}{2}, 1821\right\}, \left\{\frac{9}{2}, 1705\right\}, \left\{\frac{11}{2}, 1591\right\}, \left\{\frac{13}{2}, 1479\right\}, \left\{\frac{15}{2}, 1368\right\}, \left\{\frac{17}{2}, 1257\right\}, \left\{\frac{19}{2}, 1145\right\}, \left\{\frac{21}{2}, 1033\right\}, \left\{\frac{23}{2}, 918\right\}, \left\{\frac{25}{2}, 800\right\}, \left\{\frac{27}{2}, 677\right\}, \left\{\frac{29}{2}, 548\right\}, \left\{\frac{31}{2}, 411\right\}\right\}$$

```
dataplot = ListPlot[data, PlotStyle → PointSize[0.02],
   AxesLabel → {"v + 1/2", "vib"}];
```

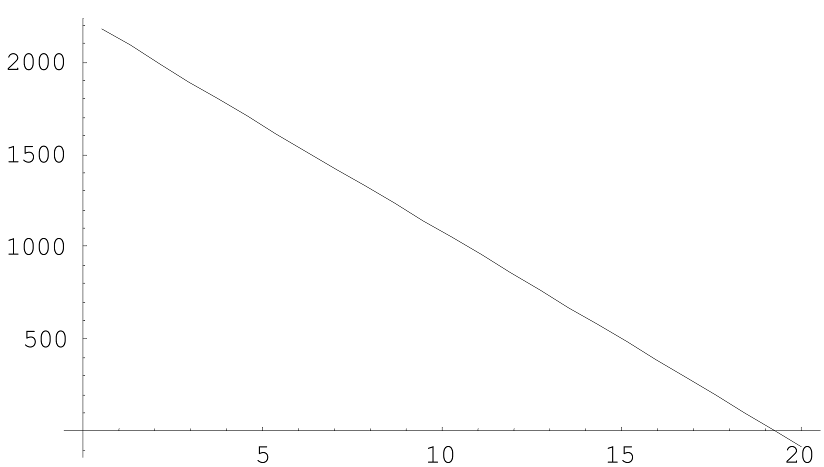


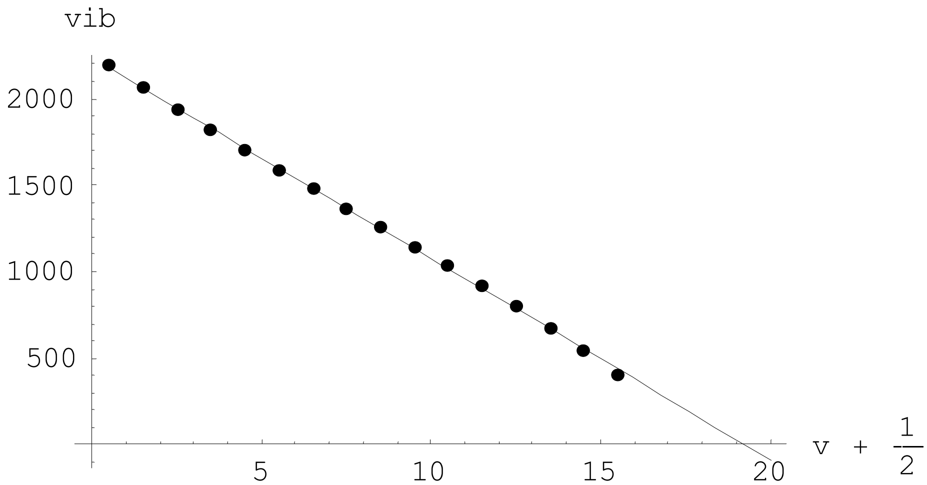
Fit a line to the plot:

```
fiteqn = Fit[data, {1, x}, x]
2237.7 - 116.049 x
```

Check and see how well this function fits the data points. Adjust the range of the graph until you see it cross the x-axis

```
fitplot = Plot[fiteqn, {x, 0.5, 20}];
plot1 = Show[{dataplot, fitplot}];
```





You can use either *Solve* or *FindRoot* to find the value of v + 1/2 when vib = 0. Remember that *FindRoot* requires an estimate of where the root is.

```
FindRoot[fiteqn, {x, 20}]
{x → 19.2825 }

Solve[fiteqn == 0, x]
{{x → 19.2825 }}
```

The value of v + 1/2 as the function crosses the x-axis is 19.2825. Integrate the fit equation from v = 0 to when the line crosses the x-axis (0.5 to 19.2825) and print out your answer.

```
ans = Integrate[fiteqn, {x, 0.5, 19.2825}];
Print["The dissociation energy of H2+ = ", ans, " cm-1"]
The dissociation  energy  of H2+ = 20469.8  cm-1
```

Sum and the Trapezoid Rule

Without fitting a function to your data points, you can find the area under the plot through numerical integration. The trapezoid rule will give a good approximation to the area without having to fit a function to the data.

For a function *f* (x) starting at $x_o = a$ and ending at $x_n = b$, where *n* = number of trapezoids, the area under the curve is:

$$\int_a^b f(x)\,dx \approx \frac{1}{2}\sum\ [(f(x_{n+1}) + f(x_n))\ (x_{n+1} - x_n)]$$

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 5.4
At 200 K, the compression factor of oxygen varies with pressure as shown below. Evaluate the fugacity of oxygen at this temperature and 100 atm.

p, atm:	1.0	4.0	7.0	10.0	40.0	70.0	100.0
Z:	**0.9971**	**0.98796**	**0.97880**	**0.96956**	**0.8734**	**0.7764**	**0.6871**

Equation 24 gives $\ln \phi = \int_0^p \frac{Z-1}{p} \, dp$ which is the area under the curve of $\frac{Z-1}{p}$ vs. p, where p is the x-value and $\frac{Z-1}{p}$ is the y-value, in an x, y coordinate system.

The fugacity coefficient ϕ is then the antilog of the area under the curve.

The fugacity of oxygen, in atm = $\phi\, p$, where p is the pressure in atm.

Make a list of the p and z values given in the problem.

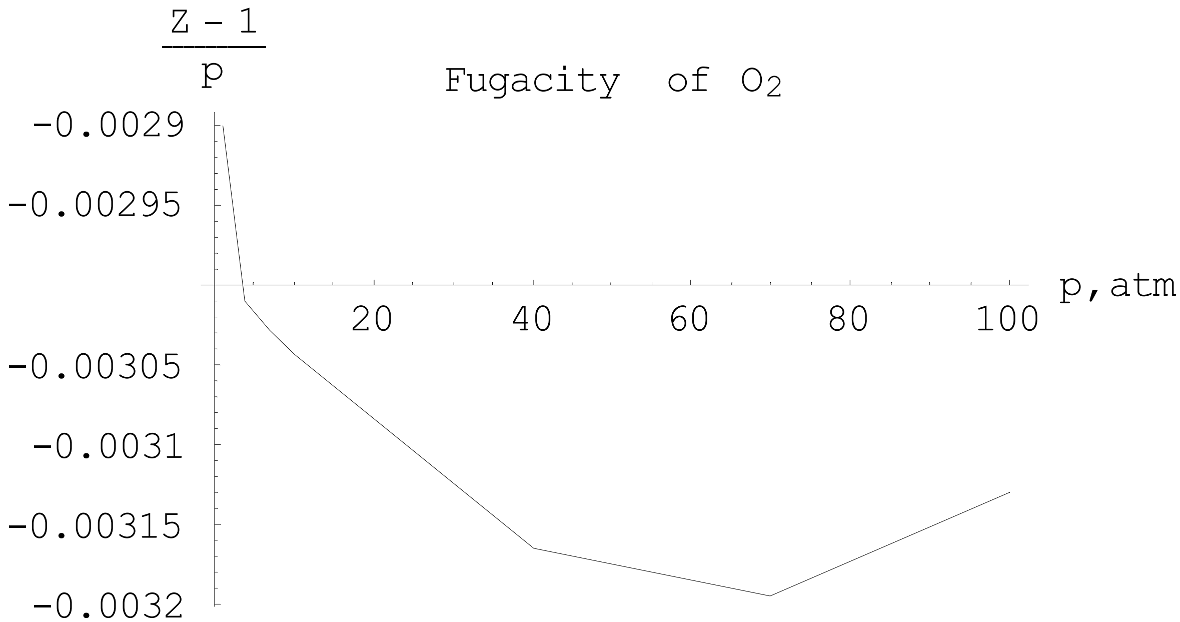
Using the p and z lists, make a list for the $\frac{Z-1}{p}$ values.

Finally, make a list of {p, $\frac{Z-1}{p}$} values. Don't forget to transpose.

```
p = {1.0, 4.0, 7.0, 10.0, 40.0, 70.0, 100.0};
z = {0.9971, 0.98796, 0.97880, 0.96956, 0.8734,
   0.7764, 0.6871};
yvalue = (z - 1) / p;
points = {p, yvalue};
data = Transpose[points]
{{1., -0.0029 },
 {4., -0.00301 }, {7., -0.00302857 },
 {10., -0.003044 }, {40., -0.003165 },
 {70., -0.00319429 }, {100., -0.003129 }}
```

Scatter plot the points with *ListPlot* and use *PlotJoined→True* to connect the points:

```
dataplot = ListPlot[data, PlotJoined → True,
   AxesLabel → {"p,atm", "(Z - 1)/p"},
   PlotLabel → "Fugacity of O2"];
```



Use the trapezoid rule to find the area under the curve. There are 7 data points and 6 trapezoids, so *i* will range from 1 to 6.

```
area = 1/2 * Sum[(yvalue[[i + 1]] + yvalue[[i]]) * (p[[i + 1]] - p[[i]]),
    {i, 1, 6}]
```

```
-0.310405
```

Take the anti log of the area to find ϕ:

```
fugcoeff = Exp[area];
Print["The fugacity coefficient ϕ at 100 atm = ", fugcoeff]
```

```
The fugacity coefficient ϕ at 100 atm = 0.73315
```

Calculate the fugacity of oxygen:

```
fugO2 = fugcoeff * 100 atm;
Print["The fugacity of O2 at 200 K and 100 atm = ", fugO2]
```

```
The fugacity of O2 at 200 K and 100 atm = 73.315 atm
```

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 5.26:
The compression factor Z at several temperatures and pressures were tabulated. From the following information, calculate the fugacity coefficient ϕ at 600 K and:
a) 30.0 bar
b) 1000 bar

p, bar:	**0.500**	**1.013**	**2.00**	**3.00**	**5.00**	**10.00**	**20.0**	**30.0**
Z:	**0.99412**	**0.98896**	**0.97942**	**0.96995**	**0.95133**	**0.90569**	**0.81227**	**0.70177**
p, bar:	**42.4**	**50.0**	**70.0**	**100.0**	**200**	**300**	**500**	**1000**
Z:	**0.47198**	**0.22376**	**0.26520**	**0.34920**	**0.62362**	**0.88288**	**1.37109**	**2.48836**

Equation 24 gives ln $\phi = \int_0^p \frac{Z-1}{p}\, dp$ which is the area under the curve of $\frac{Z-1}{p}$ vs. p, where p is the x-value and $\frac{Z-1}{p}$ is the y-value.

The fugacity coefficient ϕ is then the antilog of the area under the curve.

Plot the data points to visualize the graph.

Use *PlotJoined→True* to connect the data points. In order to do this you must make a list of {p, $\frac{Z-1}{p}$} values.

Answer: Problem 5.26

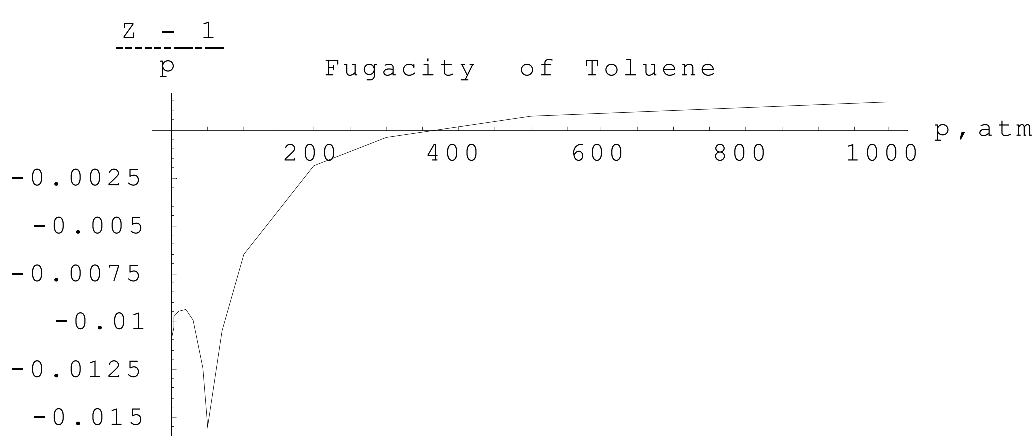
Make a list for the p and z values given in the problem:

```
p = {0.500, 1.013, 2.00, 3.00, 5.00, 10.00,
   20.0, 30.0, 42.4, 50.0, 70.0, 100.0, 200,
   300, 500, 1000};
z = {0.99412, 0.98886, 0.97942, 0.96995,
   0.95133, 0.90569, 0.81227, 0.70177, 0.47198,
   0.22376, 0.26520, 0.34920, 0.62362, 0.88288,
   1.37109, 2.48836};

yvalue = (z - 1) / p;
points = {p, yvalue};
data = Transpose[points]
{{0.5, -0.01176 }, {1.013 , -0.010997 },
 {2., -0.01029 }, {3., -0.0100167 },
 {5., -0.009734 }, {10., -0.009431 },
 {20., -0.0093865 }, {30., -0.009941 },
 {42.4 , -0.0124533 }, {50., -0.0155248 },
 {70., -0.0104971 }, {100., -0.006508 },
 {200, -0.0018819 }, {300, -0.0003904 },
 {500, 0.00074218 }, {1000, 0.00148836 }}
```

Scatter plot the points with *ListPlot* and use *PlotJoined→True* to connect the points:

```
dataplot = ListPlot[data, PlotJoined → True,
   AxesLabel → {"p,atm", "(z - 1)/p"}, PlotLabel → "Fugacity of Toluene"];
```



Use the trapezoid rule to find the area under the curve. There are 8 data points to 30 bar, giving us 7 trapezoids so *i* will range from 1 to 7.

```
area1 =
 1/2 * Sum[(yvalue[[i + 1]] + yvalue[[i]]) *
    (p[[i + 1]] - p[[i]]), {i, 1, 7}]
```

```
-0.284884
```

```
Exp[area1];
Print["The fugacity coefficent φ at 30bar = ",
 %]
```

```
The fugacity coefficent φ at 30bar = 0.752102
```

There are 16 data points to 1000 bar, giving us 15 trapezoids so *i* will range from 1 to 15.

```
area2 =
 Sum[(p[[i + 1]] - p[[i]]) *
   1/2 ((z[[i + 1]] - 1) / p[[i + 1]] +
      (z[[i]] - 1) / p[[i]]), {i, 1, 15}]
```

```
-0.985639
```

```
Exp[area2];
Print[
 "The fugacity coefficent φ at 1000bar = ",
 %]
```

```
The fugacity coefficent φ at 1000bar = 0.373201
```