Temperature dependent adjustment of V_c and V_o

Bernacchi temperature functions

Currently the e-Photosynthesis model sets PrV111 = PsV1 * 0.24, according to the known value for tobacco at 25°C (Whitney et al., 1999).

However, this ratio varies across different crop species and temperatures.

Seeing as there is no existing temperature functions for rice, we will use the equations by Bernacchi (2001) and values from Makino (1988) to compare the temperature responses of the parameters.

Specify constants:

```
T25 = 25 + 273.15;                   % Reference temperature in K
Tp = 28.9310407291759 + 273.15;      % Average measurement temperature in K
R = 8.314/1000;                      % Ideal gas constant in kJ K-1 mol-1
c_Vc = 26.35;                        % Scaling constant, Vcmax             (N. tabacum L. cv. W38, Bernacchi et al 2001)
dHa_Vc = 65.33;                      % Activation energy, Vcmax, kJ mol -1 (N. tabacum L. cv. W38, Bernacchi et al 2001)
c_Vo = 22.98;                        % Scaling constant, Vomax             (N. tabacum L. cv. W38, Bernacchi et al 2001)
dHa_Vo = 60.11;                      % Activation energy, Vomax, kJ mol -1 (N. tabacum L. cv. W38, Bernacchi et al 2001)
```

Use the Arrhenius equation $\text{Parameter} = \exp\left(c - \frac{\Delta H_a}{RT_K}\right)$ to calculate $\frac{V_o}{V_c}$ ratio at 25°C for N.tabacum (c and dHa from Bernacchi, et al., 2001):

```
Bernacchi_Vc_25 = exp(c_Vc - dHa_Vc / (R * T25));
Bernacchi_Vo_25 = exp(c_Vo - dHa_Vo / (R * T25));
Bernacchi_PrPs_ratio_25 = Bernacchi_Vo_25/Bernacchi_Vc_25;
```

Specify a range of temperatures for calculating Vc and Vo ratios:

```
Temp_Range(:,1) = (10:1:40)';                                  % Range of temperatures in C
Vo_Vc_matrix = deal(zeros(length(Temp_Range),5));              % Output matrix
```

Loop the Arrhenius equation to calculate values over the range of temperatures:

```
for i = 1:length(Temp_Range)
Vo_Vc_matrix(i,1) = Temp_Range(i,1);                                          % Range of temperatures in C
Vo_Vc_matrix(i,2) = Temp_Range(i,1)+273.15;                                   % Range of temperatures in K
```

```
Vo_Vc_matrix(i,3) = exp(c_Vc - dHa_Vc / (R * Vo_Vc_matrix(i,2)));              % Vc
values
Vo_Vc_matrix(i,4) = exp(c_Vo - dHa_Vo / (R * Vo_Vc_matrix(i,2)));              % Vo
values
Vo_Vc_matrix(i,5) = Vo_Vc_matrix(i,4)/Vo_Vc_matrix(i,3);                       %
Vo/Vc ratios
end
```

Plot Vo/Vc data:

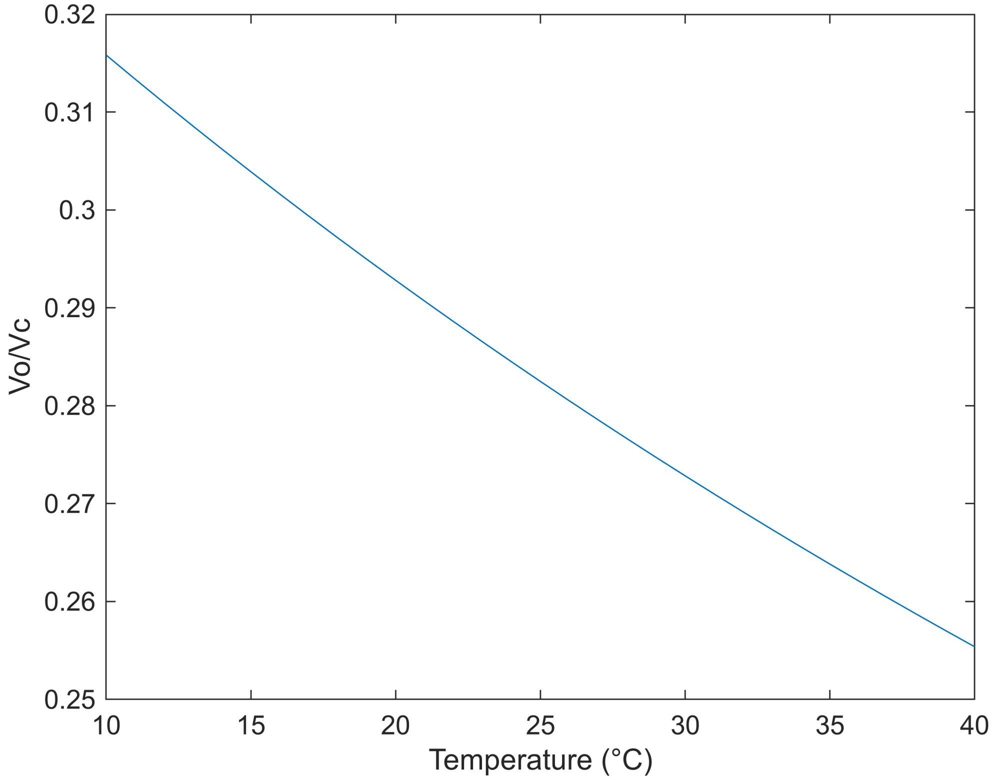
```
figure
Vo_Vc_plot=plot(Temp_Range(:,1),Vo_Vc_matrix(:,5))
```

```
Vo_Vc_plot =
  Line with properties:

              Color: [0 0.4470 0.7410]
          LineStyle: '-'
          LineWidth: 0.5000
             Marker: 'none'
         MarkerSize: 6
    MarkerFaceColor: 'none'
              XData: [10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40]
              YData: [0.3158 0.3134 0.3109 0.3086 0.3062 0.3039 0.3016 0.2994 0.2971 0.2950 0.2928 0.2907 0.2886 0.2

  Show all properties
```

```
xlabel('Temperature (°C)')
ylabel('Vo/Vc')
set(gcf, 'PaperOrientation', 'landscape');
print(gcf,fullfile('Outputs/rice_params/graphs',"Temp_vs_Vo_Vc"),'-djpeg');
```



Plot Vc and Vo for comparison:

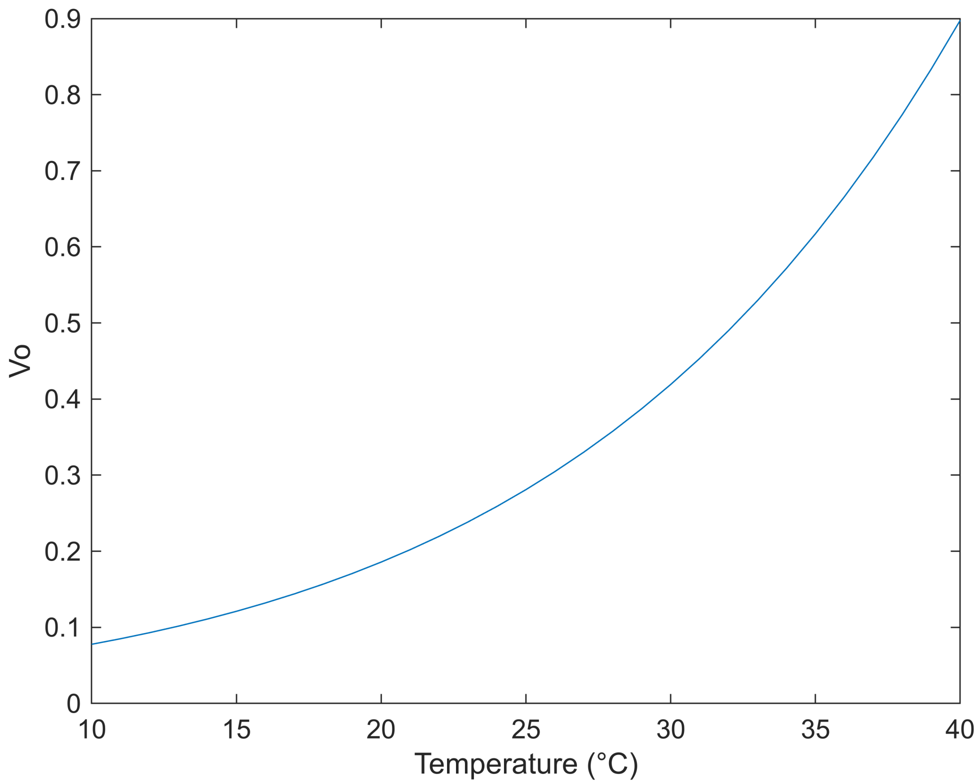
```
figure
Vo_plot=plot(Temp_Range(:,1),Vo_Vc_matrix(:,4))
```

```
Vo_plot =
  Line with properties:

              Color: [0 0.4470 0.7410]
          LineStyle: '-'
          LineWidth: 0.5000
             Marker: 'none'
         MarkerSize: 6
    MarkerFaceColor: 'none'
              XData: [10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40]
              YData: [0.0778 0.0851 0.0930 0.1016 0.1110 0.1211 0.1321 0.1440 0.1568 0.1708 0.1858 0.2021 0.2196 0.2

  Show all properties
```

```
xlabel('Temperature (°C)')
ylabel('Vo')
set(gcf, 'PaperOrientation', 'landscape');
print(gcf,fullfile('Outputs/rice_params/graphs',"Temp_vs_Vo"),'-djpeg');
```



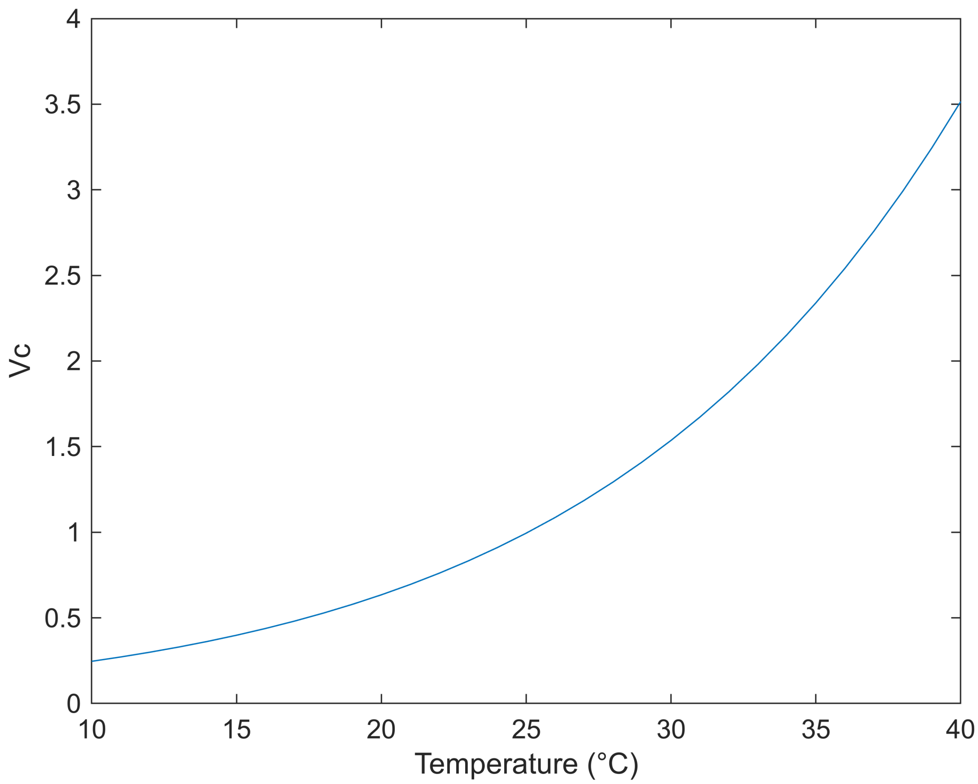

```
figure
Vc_plot=plot(Temp_Range(:,1),Vo_Vc_matrix(:,3))
```

```
Vc_plot =
  Line with properties:

              Color: [0 0.4470 0.7410]
          LineStyle: '-'
          LineWidth: 0.5000
             Marker: 'none'
         MarkerSize: 6
    MarkerFaceColor: 'none'
              XData: [10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40]
              YData: [0.2462 0.2715 0.2991 0.3294 0.3624 0.3985 0.4380 0.4810 0.5279 0.5789 0.6346 0.6951 0.7610 0.8

  Show all properties
```

```
xlabel('Temperature (°C)')
ylabel('Vc')
set(gcf, 'PaperOrientation', 'landscape');
print(gcf,fullfile('Outputs/rice_params/graphs',"Temp_vs_Vc"),'-djpeg');
```



Calculate V_c and $\frac{V_o}{V_c}$ ratio for Bernacchi at measurement temperature T_p:

```
Bernacchi_Vc_Tp = exp(c_Vc - dHa_Vc / (R * Tp));
Bernacchi_Vo_Tp = exp(c_Vo - dHa_Vo / (R * Tp));
Bernacchi_PrPs_ratio_Tp = Bernacchi_Vo_Tp/Bernacchi_Vc_Tp;
```

Work out the $\frac{V_o}{V_c}$ ratio for rice at 25°C using data in Makino et al (1988):

```
Makino_Vc_25 = 1.77; % RuBP carboxylase activity at pH 8.15 and 25°C from rice
leaves (umol(mg enzyme)-1 min-1 (Vmax)
Makino_Vo_25 = 0.58; % RuBP oxygenase activity at pH 8.15 and 25°C from rice leaves
(umol(mg enzyme)-1 min-1 (Vmax)
Makino_PrPs_ratio_25 = Makino_Vo_25/Makino_Vc_25; % Check this matches the value in
von Caemmerer (2000)
```

Adjusting the value V_{cmax} at 25°C to measurement temperature T_p

We can use one of two approaches to calculate the Makino value of $\frac{V_o}{V_c}$ at Tp:

1. Use the ratios of Makino and Bernacchi at 25°C and multiply by Bernacchi parameter estimate at a given temperature
2. Fit an Arrhenius equation to a non-linear model to find the Bernacchi temperature response of $\frac{V_o}{V_c}$ (plotted above)

Use linear scaling of Makino to Bernacchi ratios:

```
Makino_PrPs_ratio_Tp = Makino_PrPs_ratio_25*Bernacchi_PrPs_ratio_Tp/
Bernacchi_PrPs_ratio_25
```

```
Makino_PrPs_ratio_Tp = 0.3188
```

```
%OR
Makino_PrPs_ratio_Tp2 = Makino_PrPs_ratio_25/
Bernacchi_PrPs_ratio_25*Bernacchi_PrPs_ratio_Tp
```

```
Makino_PrPs_ratio_Tp2 = 0.3188
```

Non-linear fits for $\frac{V_o}{V_c}$

Define predictor (T) and response (y) variables:

```
T = Vo_Vc_matrix(:,2); % Temp in K
y = Vo_Vc_matrix(:,5); % Vo/Vc ratio
```

So far, we have defined the Arrhenius equation as:

$$\text{Parameter} = \exp\left(c - \frac{\Delta H_a}{RT_K}\right)$$

c is meant to scale the amplitude of the function whereas dHa represents the temperature dependence relationship.

Using term c−dHa combined these two effects into one, making them harder to interpret individually.

Without c, the model assumes that dHa depends solely on temperature and ignores other potential system-specific variations.

This means the equation can also be rewritten as:

$$y = c \cdot \exp\left(-\frac{\Delta H_a}{RT_K}\right)$$

to ensure that the exponent has a negative sign - previously exp(c-dHa/R*T) was causing errors since the exponent was positive.

Define an exponential model with non-linear parameters using this form of the Arrhenius equation:

```
arrhenius_model = fittype('c * exp(-dHa ./ (R * T))', ...
                'independent', 'T', ...
                'coefficients', {'c', 'dHa'}, ...
                'problem', 'R');
```

Fit the model using the fit function and passing in the model structure with initial guesses for c and dHa:

```
fittedModel = fit(T(:), y(:), arrhenius_model, 'StartPoint', [0, 2], 'problem', R);
```

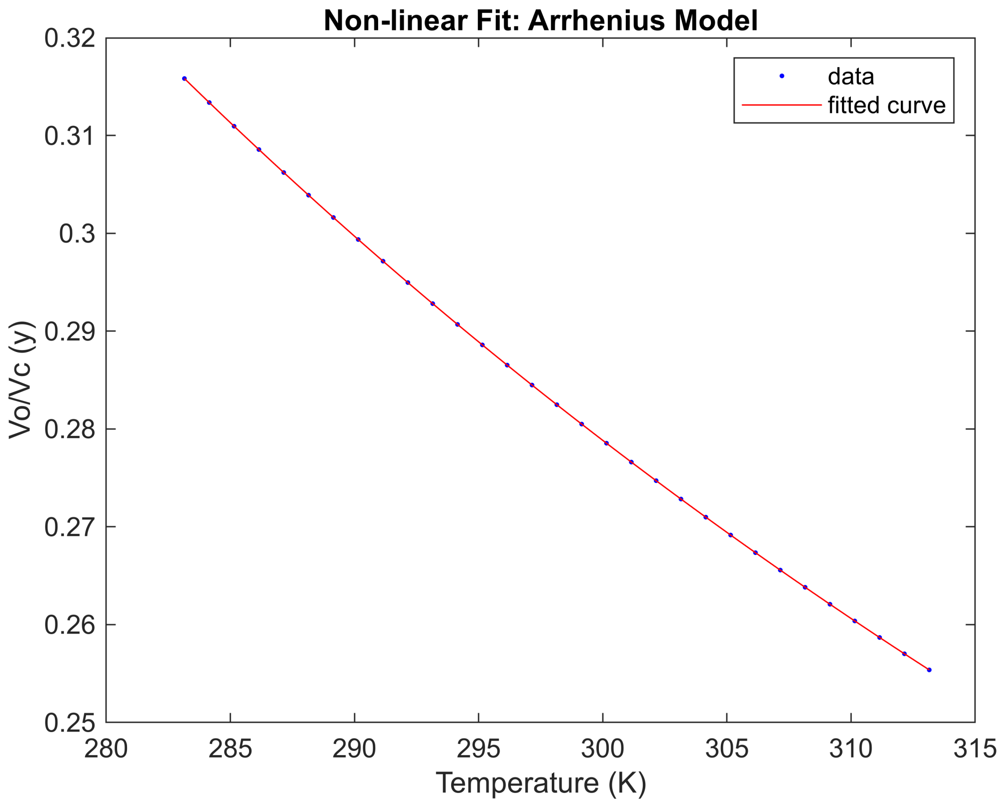
Display a summary of the fit:

```
disp(fittedModel)
```

```
General model:
fittedModel(T) = c * exp(-dHa ./ (R * T))
Coefficients (with 95% confidence bounds):
  c =     0.03439  (0.03439, 0.03439)
  dHa =       -5.22  (-5.22, -5.22)
Problem parameters:
  R =    0.008314
```

Plot the non-linear fit of the model to the data:

```
figure;
plot(fittedModel, T, y);
xlabel('Temperature (K)');
ylabel('Vo/Vc (y)');
title('Non-linear Fit: Arrhenius Model');
```



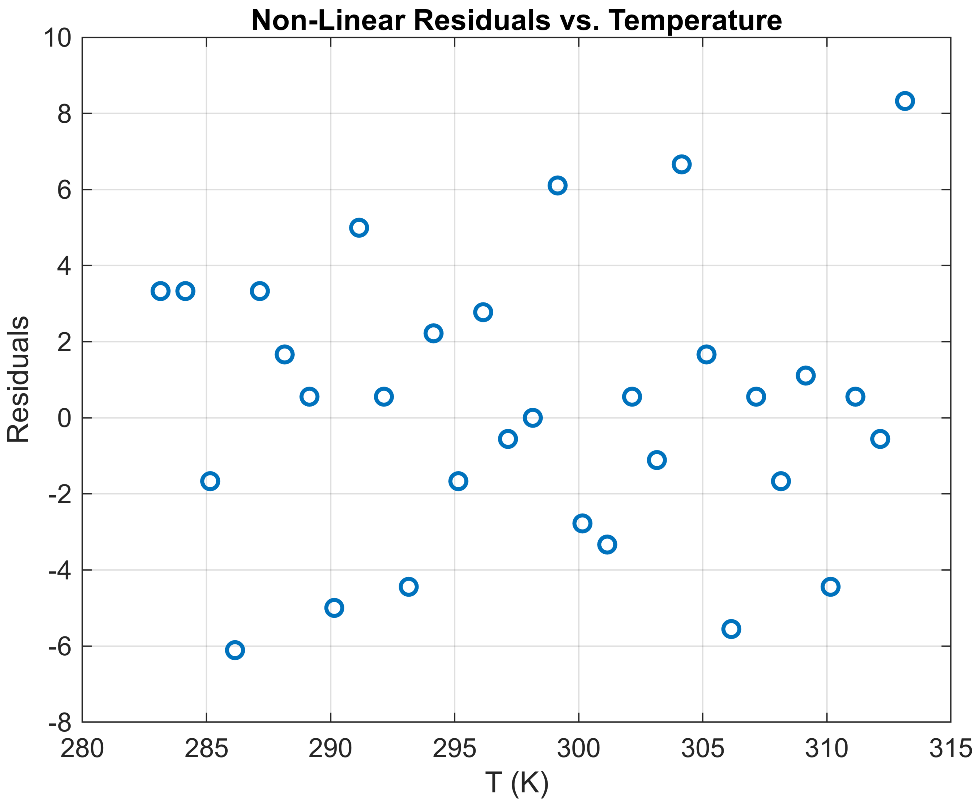
Calculate the residuals:

```
% Specify predicted values from the model
y_fit = fittedModel(T);

% Calculate residuals by subtracting from the observed y values
residuals = y - y_fit;  % Observed - Predicted
```

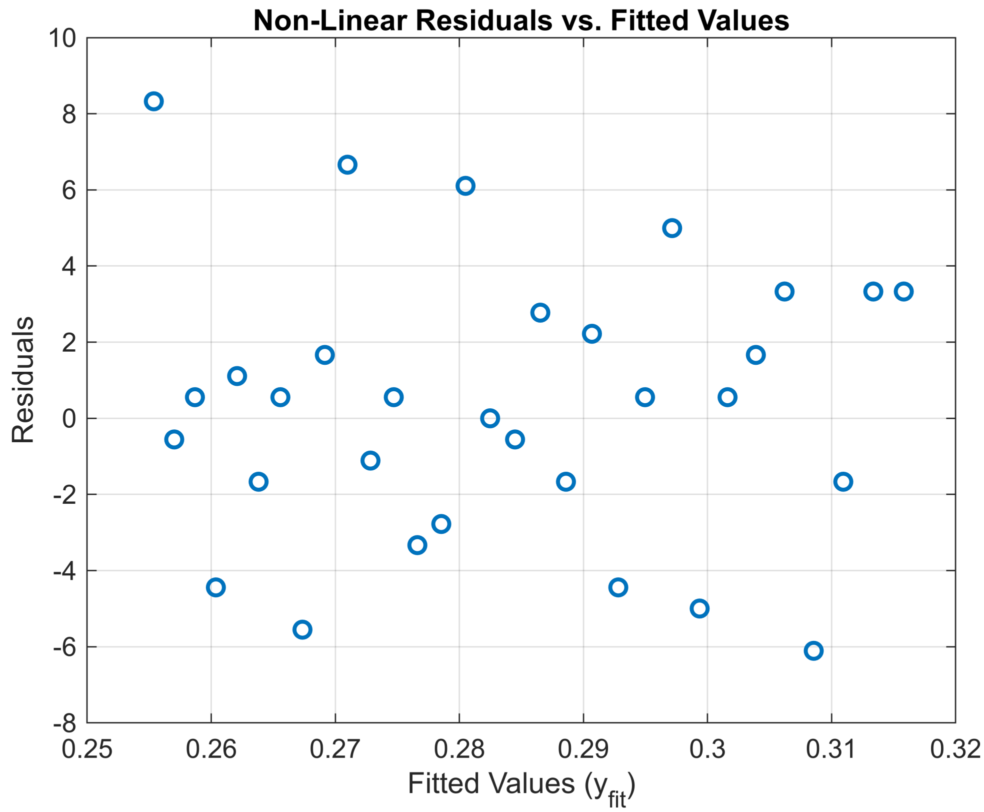
Plot residuals against T:

```
figure;
plot(T, residuals, 'o', 'LineWidth', 1.5);
xlabel('T (K)');
ylabel('Residuals');
title('Non-Linear Residuals vs. Temperature');
grid on;
```



Plot residuals against fitted values:

```
figure;
plot(y_fit, residuals, 'o', 'LineWidth', 1.5);
xlabel('Fitted Values (y_{fit})');
ylabel('Residuals');
title('Non-Linear Residuals vs. Fitted Values');
grid on;
```



Random scatter around zero indicates we have a good fit of model to data.

The values of the residuals are also very small (<10×10^{-16}), indicating the model accounts for all variations in the data and there are no unexplained residuals left.

Calculate R-squared:

```
SST = sum((y - mean(y)).^2)     % Total sum of squares
```

```
SST = 0.0100
```

```
SSR = sum(residuals.^2)         % Residual sum of squares
```

```
SSR = 3.9166e-30
```

```
R_squared = 1 - (SSR / SST)
```

```
R_squared = 1
```

Check confidence intervals:

```
conf_int = confint(fittedModel)
```

```
conf_int = 2×2
    0.0344   -5.2200
    0.0344   -5.2200
```

The R-squared is exactly 1, which indicates all the data points lie on the fitted curve perfectly - this should be treated with caution as it could indicate overfitting along with the fact that the confidence bounds for c and dHa were exactly the same as their estimated values.

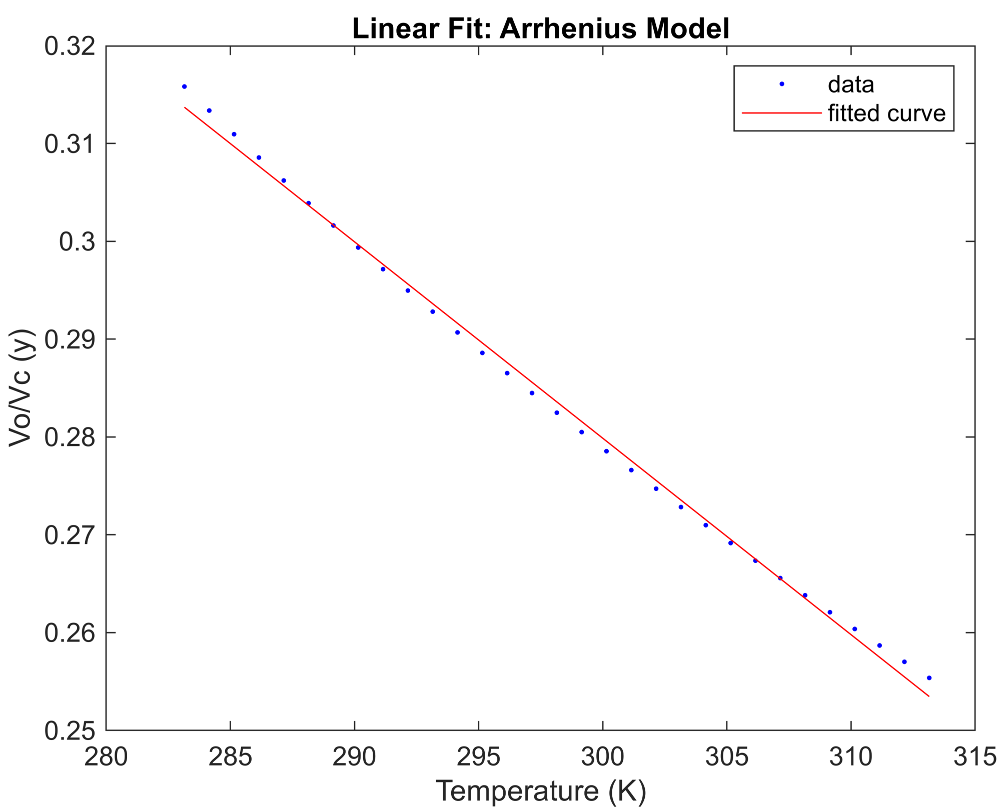
Fit a linear model for comparison to this:

```
linear_model = fit(T(:), y(:), 'poly1');
y_linear_fit = linear_model(T);
disp(linear_model)
```

```
Linear model Poly1:
linear_model(x) = p1*x + p2
Coefficients (with 95% confidence bounds):
  p1 =   -0.002008  (-0.00205, -0.001966)
  p2 =      0.8822  (0.8696, 0.8947)
```

Plot the linear model:

```
figure;
plot(linear_model, T, y);
xlabel('Temperature (K)');
ylabel('Vo/Vc (y)');
title('Linear Fit: Arrhenius Model');
```



Compare R-squared values between linear and non linear:

```
SSR_linear = sum((y - y_linear_fit).^2)
```

```
SSR_linear = 3.0392e-05
```

```
R2_linear = 1 - (SSR_linear / SST)
```

```
R2_linear = 0.9970
```

```
R2_complex = 1 - (SSR / SST)
```

```
R2_complex = 1
```

The simpler linear model performs almost as well as the more complex non-linear model, so the non-linear may have been overfitting.

However, this might not matter if we only need the Vo/Vc for values between 10 and 40° C and not generalising to values outside this dataset.