cheg325 homework7 SIS 13.22

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Continuing from the hand written portion…

we know

$$K_a^\circ(T) = \exp\left(\frac{-\Delta_{\text{rxn}} G^\circ}{RT}\right)$$

of course we need to use some delightful formation values for the free energy here.

```python
import pandas as pd
import numpy as np
from scipy.constants import R
from scipy.optimize import least_squares
from scipy.integrate import quad


a4 = pd.read_csv('appendix_a4.csv', index_col=1)
a4.head(3)
```

	chemical_name	state	delta_h_form	delta_g_form
chemical_formula				
CH4	Methane	g	-74.5	-50.5
C2H6	Ethane	g	-83.8	-31.9
C3H8	Propane	g	-104.7	-24.3

remembering the reaction

$$N_2O_4 \leftrightharpoons 2NO_2$$

```python
components = ['N2O4', 'NO2']
coeffs = np.array([-1,2])
temp = a4.loc[components]

G = (temp['delta_g_form'].astype(float) * coeffs).sum() * 1000
print(f'ΔGº: {G:.1f}')

K0 = np.exp(-G / R / 298.15)
print(f'Kº: {K0:.3f}')
```

```
ΔGº: 4700.0
Kº: 0.150
```

now our kinda flowsheet is for each value of T we need to

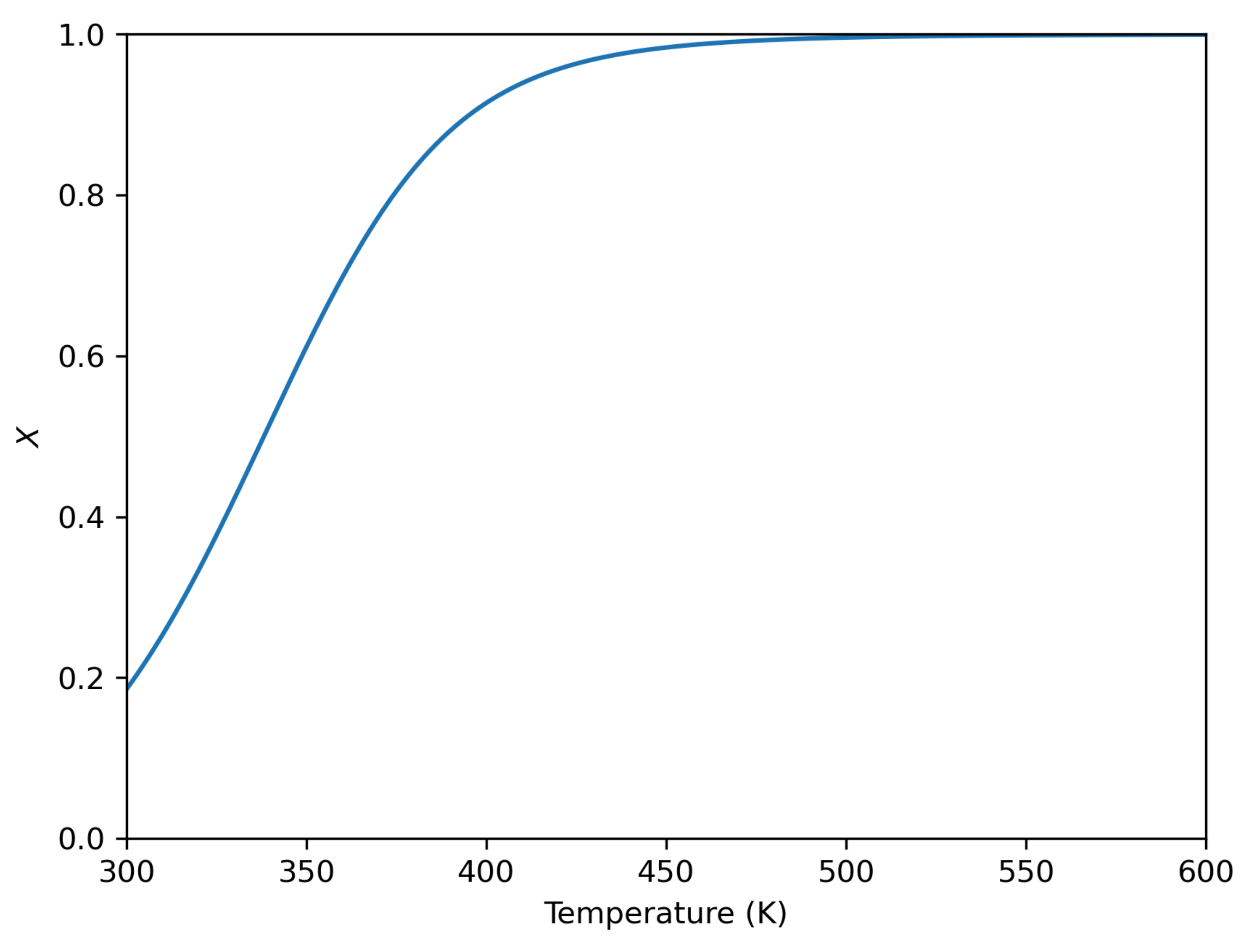
- calculate the new K_a value
- use that to find X

then we can graph $C_{v,\text{eff}}$ using numerical techniques

```python
heat_capacity = pd.read_csv('appendix_cp.csv', index_col=1).fillna(0) # table from append
heat_capacity = heat_capacity[['a', 'b', 'c', 'd']]

def calcK_andX(T, species=components, coeffs=coeffs):
    cp_data = np.array(heat_capacity.loc[species])
    coeffs = np.array(coeffs)

    delta_a, delta_b, delta_c, delta_d = (cp_data * coeffs[:, np.newaxis]).sum(axis=0)

    thermo_data = temp
    delta_H = (thermo_data['delta_h_form'].astype(float) * coeffs).sum() * 1000  # J/mol
    delta_G = (thermo_data['delta_g_form'].astype(float) * coeffs).sum() * 1000  # J/mol

    K_298 = np.exp(-delta_G / (R * 298.15))

    def delta_H_T(T):
        return (delta_H +
                delta_a * (T - 298.15) +
                (delta_b/2) * (T**2 - 298.15**2) +
                (delta_c/3) * (T**3 - 298.15**3) +
                (delta_d/4) * (T**4 - 298.15**4))

    def integrand(T):
        return delta_H_T(T) / (R * T**2)

    integral, _ = quad(integrand, 298.15, T)

    K_T = K_298 * np.exp(integral)

    def solve_for_x(X):
        return np.abs(K_T - 4 * X**2 * T * 1.013 / (1-X) / 298.15)

    X = least_squares(solve_for_x, 0.5, bounds=(0,1), verbose=0).x[0]

    return K_T, X, delta_H_T(T)

vectorized_calcK_andX = np.vectorize(calcK_andX)

Ts = np.linspace(300,600,10000)
Ks, Xs, deltaHs = vectorized_calcK_andX(Ts)
```

just like visualizing X as a function of temperature

```python
import matplotlib.pyplot as plt

fig,ax = plt.subplots(dpi=300)
plt.plot(Ts, Xs)
ax.set(xlabel='Temperature (K)', ylabel='$X$', xlim=(300,600), ylim=(0,1));
```



now we can numerically find the partial and batta-bing batta-boom find Cv effective

$$C_{v,\text{eff}} = \sum N_i C_{v,i} + \Delta_{\text{rxn}} U \left(\frac{\partial X}{\partial T}\right)$$

we also need to relate the internal energy change to the enthalpy change

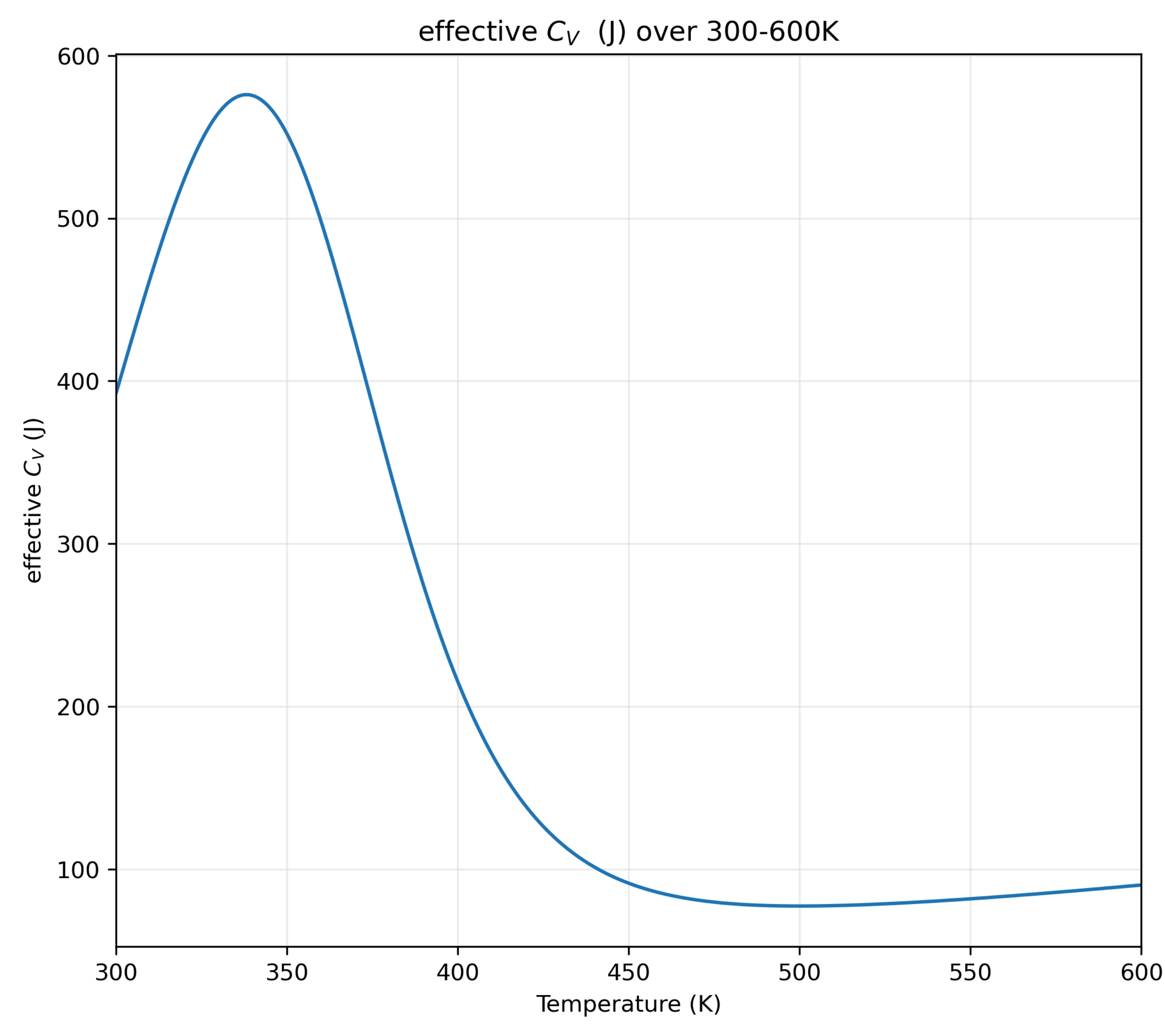
$$\begin{aligned} \Delta_{\text{rxn}} U &= \Delta_{\text{rxn}} H - \Delta_{\text{rxn}} PV \\ &= \Delta_{\text{rxn}} H - \Delta_{\text{rxn}} NRT \\ &= \Delta_{\text{rxn}} H - RT\Delta_{\text{rxn}} N \end{aligned}$$

and since we know the change in moles per reaction is one

$$\Delta_{\text{rxn}} U = \Delta_{\text{rxn}} H - RT$$

```python
def sum_cv(T, X):
    cv_data = np.array(heat_capacity.loc[components])
    cv_data[:,0] = cv_data[:,0] - R # adjust so this is Cv
    params_n2o4, params_no2 = cv_data[0], cv_data[1]

    def calc_cv(coeffs):
        a,b,c,d = coeffs
        return a + b*T + c*T**2 + d*T**3 - R

    N_n2o4 = 1 - X
    N_no2 = 2*X
    return N_n2o4 * calc_cv(params_n2o4) + N_no2 * calc_cv(params_no2)

cveff = sum_cv(Ts, Xs) + (deltaHs - R * Ts) * np.gradient(Xs) / np.gradient(Ts)
```

```python
fig,ax = plt.subplots(figsize=(8,7), dpi=300)
ax.plot(Ts, cveff)
ax.grid(alpha=0.2)
ax.set(xlim=(300,600), xlabel='Temperature (K)', ylabel='effective $C_V$ (J)', title='eff
```

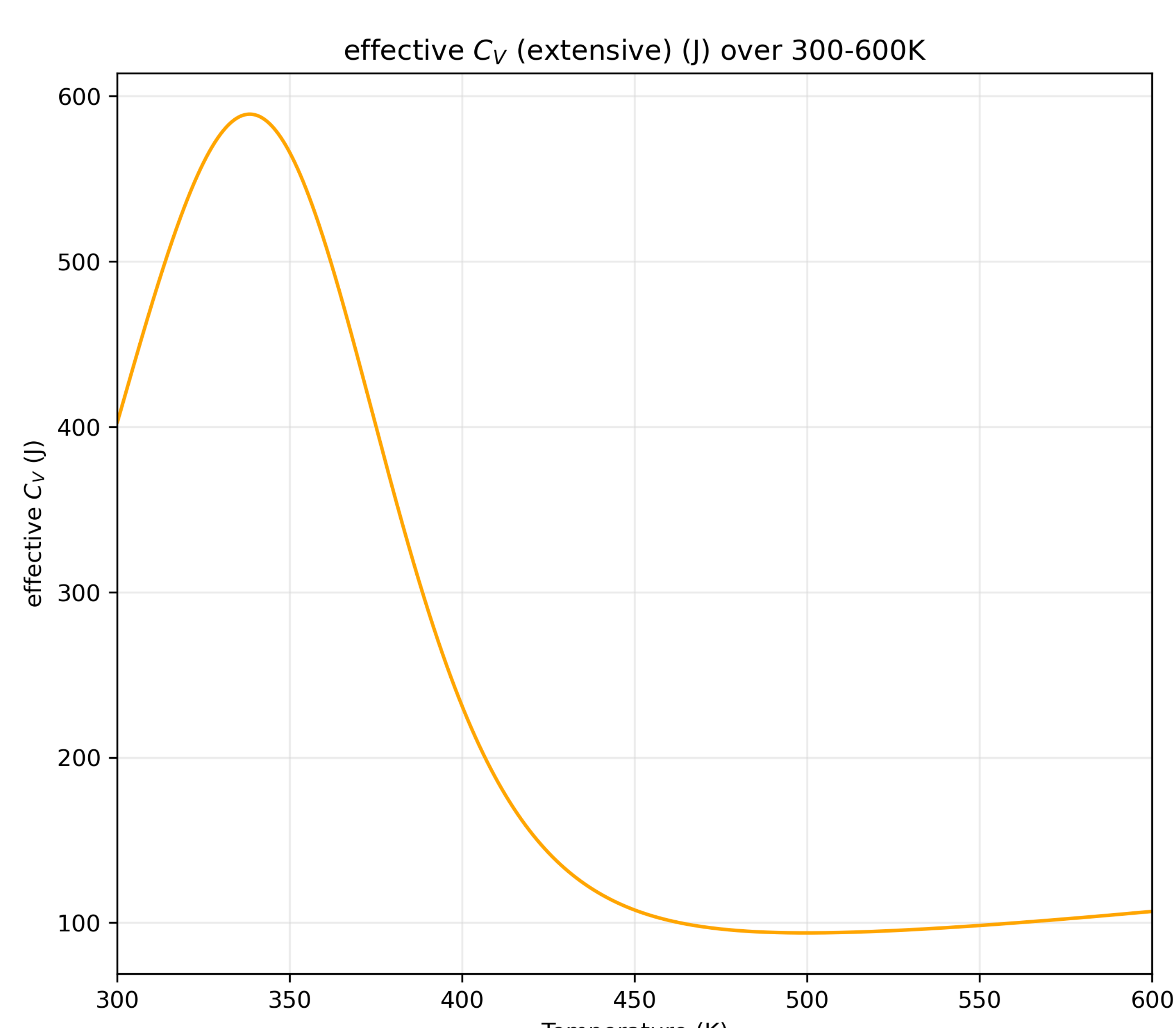


if we assume $\Delta_{\text{rxn}} H$ constant

just out of curiosity, and using the simplified version of the equation provided by the textbook which is mistakenly numbered the same as the other one!

$$\ln \frac{K_a(T_2)}{K_a(T_1)} = -\frac{\Delta_{\text{rxn}} H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{13.1-22b}$$

```python
def calcK_andX(T, coeffs=coeffs):
    coeffs = np.array(coeffs)

    delta_H = (temp['delta_h_form'].astype(float) * coeffs).sum() * 1000  # J/mol
    delta_G = (temp['delta_g_form'].astype(float) * coeffs).sum() * 1000  # J/mol

    K_298 = np.exp(-delta_G / (R * 298.15))
    K_T = K_298 * np.exp(delta_H/R * (1/298.15 - 1/T))

    def solve_for_x(X):
        return np.abs(K_T - 4 * X**2 * T * 1.013 / (1-X) / 298.15)
    X = least_squares(solve_for_x, 0.5, bounds=(0,1), verbose=0).x[0]

    return K_T, X, delta_H

vectorized_calcK_andX = np.vectorize(calcK_andX)
Ts = np.linspace(300,600,10000)
Ks, Xs, deltaHs = vectorized_calcK_andX(Ts)

def sum_cv(T, X):
    cv_data = np.array(heat_capacity.loc[components])
    cv_data[:,0] = cv_data[:,0] - R # adjust so this is Cv
    params_n2o4, params_no2 = cv_data[0], cv_data[1]

    def calc_cv(coeffs):
        a,b,c,d = coeffs
        return a + b*T + c*T**2 + d*T**3

    N_n2o4 = 1 - X
    N_no2 = 2*X
    return N_n2o4 * calc_cv(params_n2o4) + N_no2 * calc_cv(params_no2)

cveff = sum_cv(Ts, Xs) + (deltaHs - R * Ts) * np.gradient(Xs) / np.gradient(Ts)

fig, ax = plt.subplots(figsize=(8,7), dpi=300)
ax.plot(Ts, cveff, c='orange')
ax.grid(alpha=0.2)
ax.set(xlim=(300,600), xlabel='Temperature (K)', ylabel='effective $C_V$ (J)', title='eff
```



without overlaying them i can't tell the difference. seems like this assumption would have been valid

```python
# filler
```