cheg325 homework7 SIS 13.20

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we need to find allll the $\Delta \underline{H}$ and $\Delta \underline{G}$ for the reactions

$$\begin{gathered}\mathrm{CaCO_3 + SiO_2 \leftrightharpoons CaO \cdot SiO_2 + CO_2} \\ \mathrm{3FeO \cdot SiO_2 + CO_2 \leftrightharpoons 3SiO_2 + Fe_3O_4 + CO} \\ \mathrm{3FeO \cdot SiO_2 + \tfrac{1}{2}O_2 \leftrightharpoons Fe_3O_4 + 3SiO_2}\end{gathered}$$

from an earlier homework i have the appendix with all the formation energies as a `csv` file and will import it as a dataframe to make menial math easy

```python
import pandas as pd
import numpy as np
from scipy.constants import R

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

thankfully sandler says 'go look in the chemical engineering handbook' to find the ones not in his table, so after some digging i was able to get the numbers needed from the 8th edition of the chemical engineering handbook. I also took the $\mathrm{SiO_2}$ heat and free energy of formation from the handbook as it was giving me wildly unphysical results in calculations.

values i found from handbook and also the SiO2 replacement value (note that 1 kcal = 4.184 kJ)

Compound	ΔH_f (kcal/mol)	ΔG_f (kcal/mol)	ΔH_f (kJ/mol)	ΔG_f (kJ/mol)
Fe_3O_4	-266.9	-242.3	-1116.7096	-1013.7832
$CaO \cdot SiO_2$	-377.9	-357.5	-1581.1336	-1495.78
$CaCO_3$	-289.5	-270.8	-1211.268	-1133.0272
SiO_2	-203.35	-190.4	-850.8164	-796.6336

now we (i) can easily calculate all the K_a values at standard state

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

```python
reaction1_components = ['CaCO3', 'SiO2', 'CaO*SiO2', 'CO2']
r1_coeffs = np.array([-1, -1, 1, 1])
temp = a4.loc[reaction1_components]
G1 = (temp['delta_g_form'].astype(float) * r1_coeffs).sum() * 1000

reaction2_components = ['FeO*SiO2', 'CO2', 'SiO2', 'Fe3O4', 'CO']
r2_coeffs = np.array([-3, -1, 3, 1, 1])
temp = a4.loc[reaction2_components]
G2 = (temp['delta_g_form'].astype(float) * r2_coeffs).sum() * 1000

reaction3_components = ['FeO*SiO2', 'O2', 'Fe3O4', 'SiO2']
r3_coeffs = np.array([-3.0, -0.5, 1.0, 3.0])
temp = a4.loc[reaction3_components]
G3 = (temp['delta_g_form'].astype(float) * r3_coeffs).sum() * 1000

print(f'G1: {G1:.1f} J/mol\nG2: {G2:.1f} J/mol\nG3: {G3:.1f} J/mol')

Gs = np.array([G1, G2, G3])
K = np.exp(-Gs /(R*298.15))
print(f'Ko: {K}')
```

```
G1: 35253.6 J/mol
G2: 33516.0 J/mol
G3: -223684.0 J/mol
Ko: [6.66555768e-07 1.34354074e-06 1.54078254e+39]
```

very quickly we can guess that the first two reactions should be farely reactant favored and the 3rd reaction should be heavily product favored.

this approach is very similar to (13.1-22b) (and for some reason there are two equations tagged 13.1-22b). here's the outline:

- using free energies of formations and reaction stoichiometry to get $\Delta_{\mathrm{rxn}} G$
- using $\Delta_{\mathrm{rxn}} G$ to find K at 298.15 K
- using enthalpies of formations, reaction stoichiometry, and C_P polynomials to correct K for the difference in temperature between 298.15 and the ~750K

now let's get down to the mathy business. we need to get $\Delta_{\mathrm{rxn}} H^\circ(T)$

$$\Delta_{\mathrm{rxn}} H(T) = \Delta_{\mathrm{rxn}} H^\circ(298.15) + \int_{293.15}^{T} \Delta_{\mathrm{rxn}} C_p \, dT$$

if the C_p is in the form of

$$C_p = a + bT + e/T^2$$

then

$$\int_{T_1}^{T_2} C_p = a[T_2 - T_1] + \frac{1}{2} b [T_2 - T_1]^2 + e \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

and then

$$\ln \frac{K_a(747)}{K_a(298.15)} = \int_{298.15}^{747} \frac{\Delta_{\mathrm{rxn}} H(T)}{RT^2} \, dT$$

```python
heat_capacity = pd.read_csv('heat_capacity.csv', index_col=0).fillna(0) # table from ques

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

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

    thermo_data = a4.loc[species]
    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
    T1 = 298.15
    K_298 = np.exp(-delta_G / (R * T1))

    term1 = (delta_a/R) * np.log(T/T1)
    term2 = (delta_b/(2*R)) * (T - T1)
    term3 = (delta_c/(6*R)) * (T**2 - T1**2)
    term4 = (delta_d/(12*R)) * (T**3 - T1**3)
    term5 = (delta_e/(2*R)) * (1/T**2 - 1/T1**2)

    bracket_term = (-delta_H + delta_a*T1 + (delta_b/2)*T1**2 +
                   (delta_c/3)*T1**3 + (delta_d/4)*T1**4 - delta_e/T1)

    term6 = (1/R) * bracket_term * (1/T - 1/T1)

    ln_ratio = term1 + term2 + term3 + term4 + term5 + term6

    K_T = K_298 * np.exp(ln_ratio)

    return K_T

K1, K2, K3 = [calculate_K_at_T(747, components, coeffs) for components, coeffs
                                                         in zip([reaction1_components,
                                                                 reaction2_components,
                                                                 reaction3_components],
                                                                [r1_coeffs, r2_coeffs, r3


print(f'K1: {K1:.3f}')
print(f'K2: {K2:.3f}')
print(f'K3: {K3:.3e}')
```

```
K1: 340.891
K2: 0.254
K3: 4.141e+14
```

now we/i can use the K values and compare them to the atomsphere

Species	Mole Percent
CO_2	99.9 –
H_2O	0.01
CO	0.01
HCl	1×10^{-1}
HF	1×10^{-6}
O_2	trace

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right off the bat it makes sense that there's basically no oxygen in the atmosphere since the only reaction including oxygen gas is so heavily product favored.

now for the ratio of $\mathrm{CO_2}$ we can look at the second constant.

$$K_{\alpha,2} = \frac{\alpha_{CO}}{\alpha_{CO2}} = 0.254$$

which doesn't quite line up with the measurements, but at least the measurements show that there should be significantly more $\mathrm{CO_2}$ than CO. if we look at the first reaction (say the pressure is 100 bar or so)

$$K_{\alpha,1} = \alpha_{\mathrm{CO_2}} = 341 = y_{\mathrm{CO_2}} \left(\frac{P}{1\ \mathrm{bar}}\right) = y_{\mathrm{CO_2}} \left(\frac{100\ \mathrm{bar}}{1\ \mathrm{bar}}\right)$$
$$y_{\mathrm{CO_2}} = 3.41$$

obviously this is inconsistent with reality (the $\mathrm{CO_2}$ is likely not an ideal gas at 100 bar), but it is generally consistent with the idea that the atmosphere should be mostly $\mathrm{CO_2}$

```
# filler
```