HW 11   Solutions

#1) Draw the Structure of Ethylene Oxide

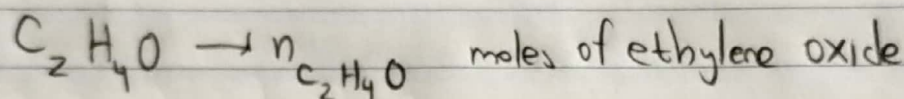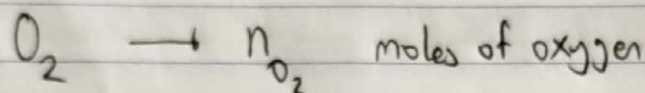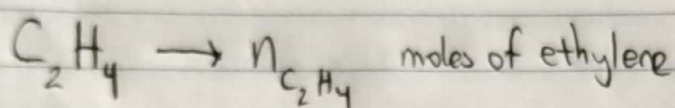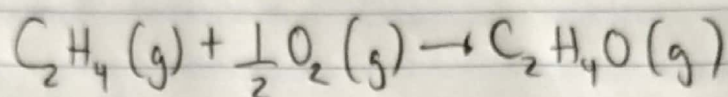**#2)** Is this Reaction an elementary reaction ?

No it's not elementary because the reaction uses half a molecule
so it requires multiple steps to get the product

#3) Write down the rate law of formation of ethylene oxide

$$r = K \cdot [C_2H_4][O_2]^{1/2}$$

HW II

4. Create an ICE table for this reaction. My advice
   is to create the table in terms of moles. of species
   and an advancement q. What is the maximum possible
   value of q?

$$C_2H_4\,(g) + \frac{1}{2}O_2\,(g) \rightarrow C_2H_4O\,(g)$$

$C_2H_4 \longrightarrow n_{C_2H_4}$ moles of ethylene

$O_2 \longrightarrow n_{O_2}$ moles of oxygen

$C_2H_4O \longrightarrow n_{C_2H_4O}$ moles of ethylene oxide

maximum possible value of
q when all oxygen is consumed.
(q_{max})

Species	Initial (mol)	Change (mol)	Equilibrium (mol)
C_2H_4	$n_{C_2H_4,\,0}$	$-q$	$n_{C_2H_4,\,0} - q$
O_2	$n_{O_2,\,0}$	$-\dfrac{q}{2}$	$n_{O_2,\,0} - \dfrac{1}{2}$
C_2H_4O	0	$+q$	q

1 mole of ethylene reacts with $\frac{1}{2}$ mole of oxygen.
$\therefore$ max possible value of q is twice the initial moles
of oxygen.

5. Define a conversion X as ξ/ξ_{max}, so $0 \leq X \leq 1$ Plot the partial pressures of all species vs X. *Hint*: Recall the partial pressure is $P y_i$, and $y_i = N_i/N_{tot}$ from the ICE table.

```python
1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  # Given data
5  P = 2  # Total pressure in bar
6  n_C2H4_0 = 1.2  # Initial moles of ethylene
7  n_O2_0 = 1  # Initial moles of oxygen
8  xi_max = 2 * n_O2_0  # Maximum value of xi
9
10 # Initialize lists to store data points
11 X_values = []
12 P_C2H4_values = []
13 P_O2_values = []
14 P_C2H4O_values = []
15
16 # Calculate partial pressures for each X value
17 for X in np.linspace(0, 1, 100):
18     # Calculate moles of each species at equilibrium
19     n_C2H4 = n_C2H4_0 - X * xi_max
20     n_O2 = n_O2_0 - 0.5 * X * xi_max
21     n_C2H4O = X * xi_max
22
23     # Calculate mole fractions
24     N_tot = n_C2H4 + n_O2 + n_C2H4O
25     y_C2H4 = n_C2H4 / N_tot
26     y_O2 = n_O2 / N_tot
27     y_C2H4O = n_C2H4O / N_tot
28
29     # Calculate partial pressures
30     P_C2H4 = P * y_C2H4
31     P_O2 = P * y_O2
32     P_C2H4O = P * y_C2H4O
33
34     # Check if partial pressures are negative
35     # If negative, set them to zero
36     P_C2H4 = max(0, P_C2H4)
37     P_O2 = max(0, P_O2)
38     P_C2H4O = max(0, P_C2H4O)
39
40     # Append data points to lists
41     X_values.append(X)
42     P_C2H4_values.append(P_C2H4)
43     P_O2_values.append(P_O2)
44     P_C2H4O_values.append(P_C2H4O)
45
46 # Plot the partial pressures vs. X
47 plt.plot(X_values, P_C2H4_values, label='Partial Pressure of C2H4')
48 plt.plot(X_values, P_O2_values, label='Partial Pressure of O2')
49 plt.plot(X_values, P_C2H4O_values, label='Partial Pressure of C2H4O')
50 plt.xlabel('Conversion (X)')
51 plt.ylabel('Partial Pressure (bar)')
52 plt.title('Partial Pressures vs. Conversion')
53 plt.legend()
54 plt.grid(True)
55
```

```
56 # Set y-axis limits
57 plt.ylim(0, 1.6)
58
59 plt.show()
60
61
```

Partial Pressures vs. Conversion
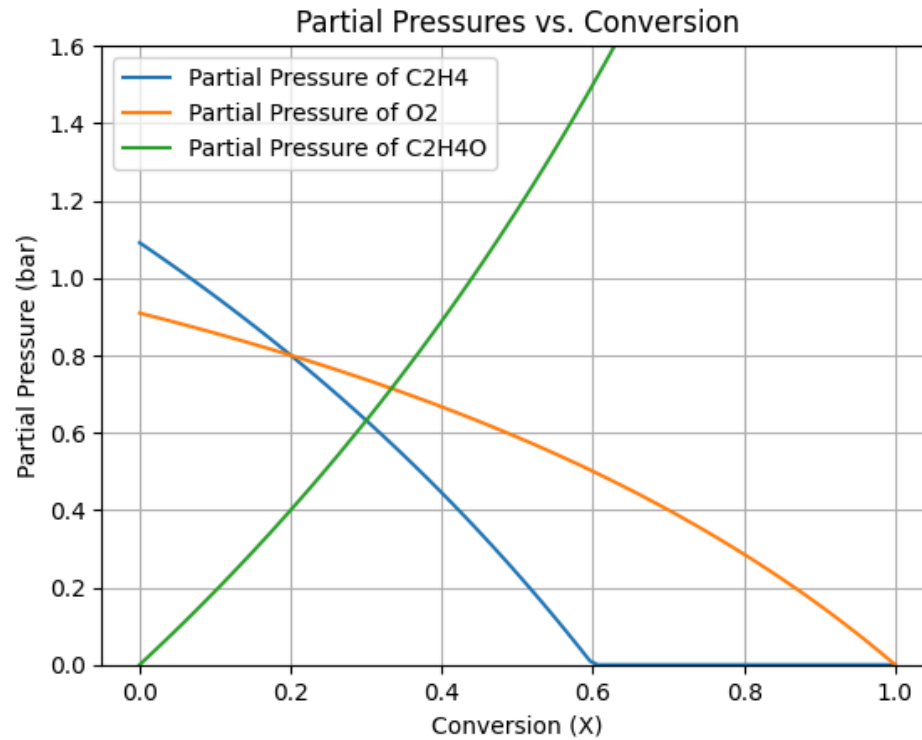
6. Plot the forward reaction rate vs X. Be sure to include appropriate units.

```python
1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 # Given data
5 k = 0.8  # Rate constant in bar^(-1/2) s^(-1)
6 n_C2H4_0 = 1.2  # Initial moles of ethylene
7 n_O2_0 = 1  # Initial moles of oxygen
8 xi_max = 2 * n_O2_0  # Maximum value of xi
9 P_total = 2  # Total pressure in bar
10 R = 0.08314  # Gas constant in L bar / K mol
11 T = 500  # Temperature in K
12
13 # Initialize lists to store data points
14 X_values = np.linspace(0, 1, 100)
15 forward_rates = []
16
17 # Calculate partial pressures and forward reaction rate for each X value
18 for X in X_values:
19     # Calculate moles of ethylene and oxygen at equilibrium
20     n_C2H4 = n_C2H4_0 - X * xi_max
21     n_O2 = n_O2_0 - 0.5 * X * xi_max
22
23     # Calculate partial pressures
24     P_C2H4 = (n_C2H4 / (n_C2H4_0 + n_O2_0)) * P_total
25     P_O2 = (n_O2 / (n_C2H4_0 + n_O2_0)) * P_total
26
27     # Calculate forward reaction rate
28     rf = k * P_C2H4 * np.sqrt(P_O2)  # in bar/s
29
30     # Append data point to lists
31     forward_rates.append(rf)
32
33 # Plot the forward reaction rate vs. X
34 plt.plot(X_values, forward_rates)
35 plt.xlabel('Conversion (X)')
36 plt.ylabel('Forward Reaction Rate (bar/s)')
37 plt.title('Forward Reaction Rate vs. Conversion')
38 plt.grid(True)
39 plt.show()
40
```


Forward Reaction Rate vs. Conversion
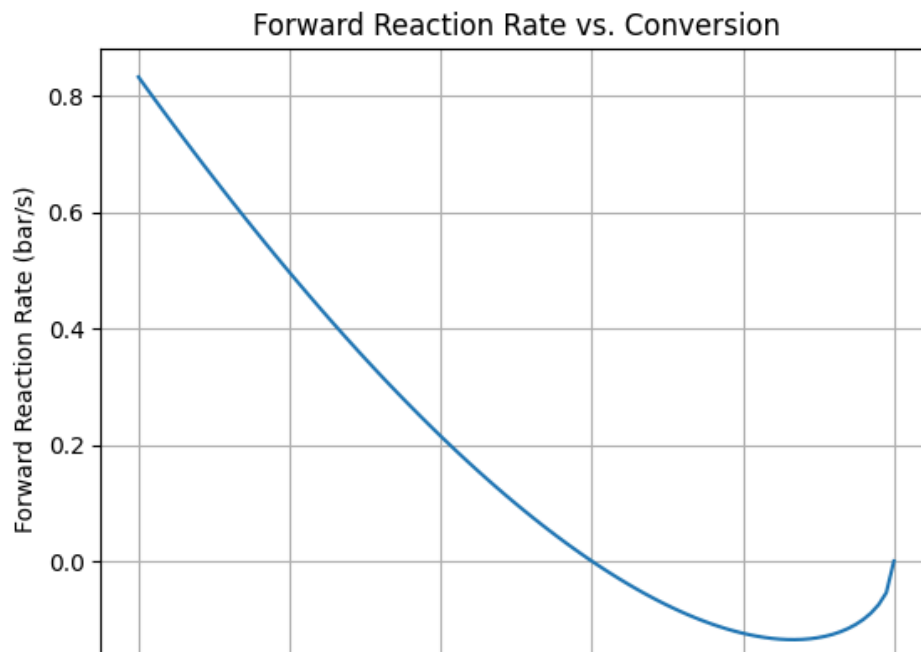
0.0.1 7. The apparent activation energy of the reaction is 60 kJ mol^{-1}. What is the reaction prefactor? Include appropriate units.

$k = Ae^{\frac{-E_a}{k_b T}}$, so $A = \frac{k}{e^{\frac{-E_a}{k_b T}}}$

```
[1]: import numpy as np

     Ea = 60*1000# kJ/mol to J/mol
     Kb = 8.314# J/mol*K
     T = 500# K
     k = 0.8# bar^-1/2*sec^-1

     A =k/(np.exp(-Ea/(Kb*T)))
     print(f'{A:.3f}','bar^-1/2*sec^-1')
```

```
1484134.208 bar^-1/2*sec^-1
```

0.0.2 8. The apparent activation energy of the reaction is 60 kJ mol^{-1}. Estimate the rate constant at 550 K.
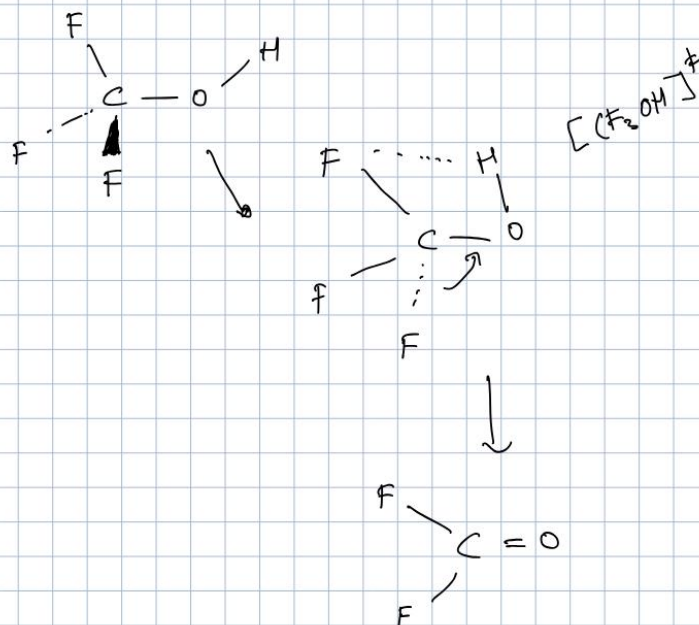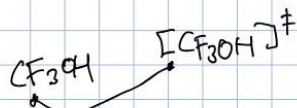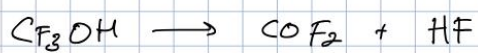
```
[2]: T2 = 550# K
     k2 = A*np.exp(-Ea/(Kb*T2))
     print(f'{k2:.3f}','bar^-1/2*sec^-1')
```

```
2.971 bar^-1/2*sec^-1
```

0.0.3 9. From the information given, can you predict the rate law for the reverse reaction?

The rate law for the reverse reaction cannot be predicted based on the forward reaction.

10 Provide a rough sketch of what the transition state looks like

$$CF_3OH \longrightarrow COF_2 + HF$$

CF₃OH ————• [CF₃OH]‡

F
 \
  C — O — H
 /
F   F

[CF₃OH]‡

F
 \
  C — O
 /   \
f   H
 |
 F

↓

F
 \
  C = O
 /
F

take CF₃OH as reference

11)

Potential Energy

[CF₃OH]‡

TS

↕ ZPE

EA

↕ ZPE

COF₂ + HF

↕ ZPE

CF₃OH

Reaction Coordinate
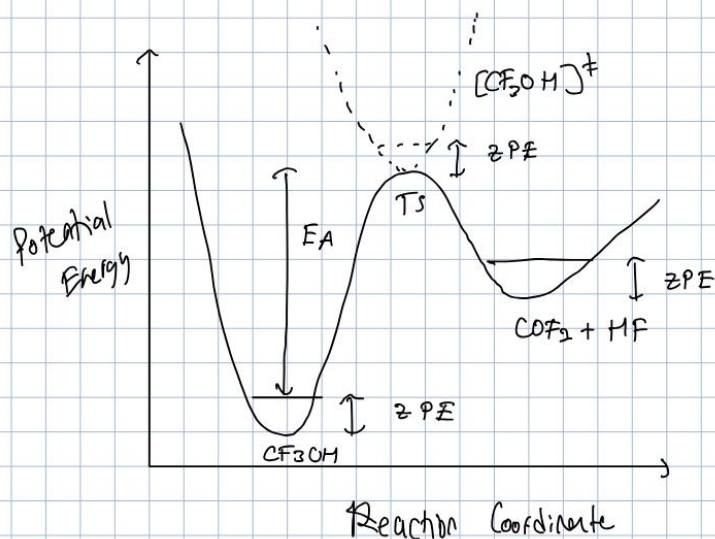
12. Using data from the table and harmonic transition state theory, compute the first-order rate constant for CF_3OH decomposition at 298 K, in s^{-1}.

$$k = \frac{k_B T}{h} \frac{q^{\ddagger}}{q_A} e^{-\Delta E^{\ddagger}(0)/k_B T}$$

```
 1 import numpy as np
 2 kB=8.61734e-5 # eV/K
 3 T1=298 # K
 4 h=4.136e-15 # eV*s
 5 q_TS= 7.72e32*68420*2.28 # 1/m^3
 6 q_A=7.72e32*61830*2.33 # 1/m^3
 7 delta_E= ((-412.82771+0.02313)-(-412.90047+0.02889))*27.212 # eV
 8 def k(T):
 9     k=kB*T/h*q_TS/q_A*np.exp(-delta_E/kB/T)
10     return k
11 print('k={:.3E}.'.format(k(T1)))
```

```
k=9.853E-19.
```

13. In Homework 10, you computed the equilibrium constant for this reaction at 298 K. Use that result and your rate constant for the decomposition to determine the rate constant for the reverse, CF_3OH formation reaction.

```
1 k = 9.853e-19
2 kc = 2.926
3
4 kr = k / kc
5
6 print("kr = {:.3E}".format(kr))
```

```
kr = 3.367E-19
```

14. Use the data in the table to compute the overall reaction enthalpy, and the forward and reverse reaction enthalpies.

```
1 #overall reaction enthalpy
2 dH=21.121 # kJ/mol
3
4 #Constants
5 T=298 #K
6 R=8.31447
7 kJ=2625.50 #kJ (conversion)
8
9 #forward reaction enthalpy
10 E_elec=[-412.90047, -412.82771] #change in electronic energy kJ/mol
11 ZPE=[0.02889, 0.02313] #zero point energy kJ/mol
12 dE0=((E_elec[1]+ZPE[1])-(E_elec[0]+ZPE[0]))*kJ
13
14 u_trans=[3.7,3.7]
15 u_rot=[3.7,3.7]
16 u_vib=[4.3,4.1]
17
18 dU=dE0+(u_trans[1]+u_rot[1]+u_vib[1])-(u_trans[0]+u_rot[0]+u_vib[0])
19
20 dH_forward=dU
21
22 #reverse reaction enthalpy
23 E_elec_rev=[-412.82771, -312.57028, -100.31805]
24 ZPE_rev=[0.02313, 0.01422,0.00925]
25 dE0_rev=-((E_elec_rev[1]+ZPE_rev[1]+E_elec_rev[2]+ZPE_rev[2])-(E_elec_rev[0]+ZPE_rev[0]))*kJ
26
27 u_trans_rev=[3.7,3.7,3.7]
28 u_rot_rev=[3.7,3.7,2.5]
29 u_vib_rev=[4.1,1.2,0]
30
31 dU_rev=dE0_rev-(u_trans_rev[1]+u_rot_rev[1]+u_vib_rev[1])+(u_trans_rev[2]+u_rot_rev[2]+u_vib_rev[2
32
33 dH_reverse=dU_rev-R/1000*T
34
35 print('Overall reaction enthalpy:',dH, 'kJ/mol')
36 print('Forward enthalpy:',round(dH_forward, 3), 'kJ/mol')
37 print('Reverse enthalpy:',round(dH_reverse, 3), 'kJ/mol')
38
39
40
```

```
Overall reaction enthalpy: 21.121 kJ/mol
Forward enthalpy: 175.708 kJ/mol
Reverse enthalpy: 153.387 kJ/mol
```

0.0.4   15. Based on your computed rate constant, what is the half-life of CF_3OH at 298 K?

The half-life of a first-order reaction under a given set of reaction conditions is a constant.

$t_{1/2} = \frac{\ln 2}{k}$

```
[18]: k298 = 9.853E-19
      t=np.log(2)/k298 # s
      print('The half-life is {0:.3E} s, which is about {1:.3E} years.'.format(t,t/
      ↪3600/24/365))
```

The half-life is 7.035E+17 s, which is about 2.231E+10 years.

0.0.5   16. Experiments reveal that the CF_3OH comes to equilibrium far faster than the unimolecular rate would suggest. Provide a possible explanation for this observation (other than that Schneider calculations are incorrect!).

One proposed mechanism is the existence of H_2O lowers the activation energy of the decomposition of CF_3OH. The proposed reaction pathway is shown in *J. Phys. Chem.* **1996**, *100*, 6097- 6103.