

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

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

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

Choose basis of 1 mole O_2 and 1.2 mole C_2H_6

	C_2H_6	O_2	C_2H_4O	H_2O	
I		1.2	1	0	0
C	$-\xi$	$-\xi$	$+\xi$	$+\xi$	
E	$-\xi$	1.2	1	ξ	
		$-\xi$	ξ	ξ	

Maximum value of ξ is 1.2.

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 $y_i = N_i/N_{\text{tot}}$ from the ICE table.

```
In [4]: import numpy as np
import matplotlib.pyplot as plt

P = 2 # bar

ximax = 1.2
X = np.linspace(0,1,1000)

n_e0 = 1.2
n_o0 = 1
n_eo0 = 0
n_w0 = 0

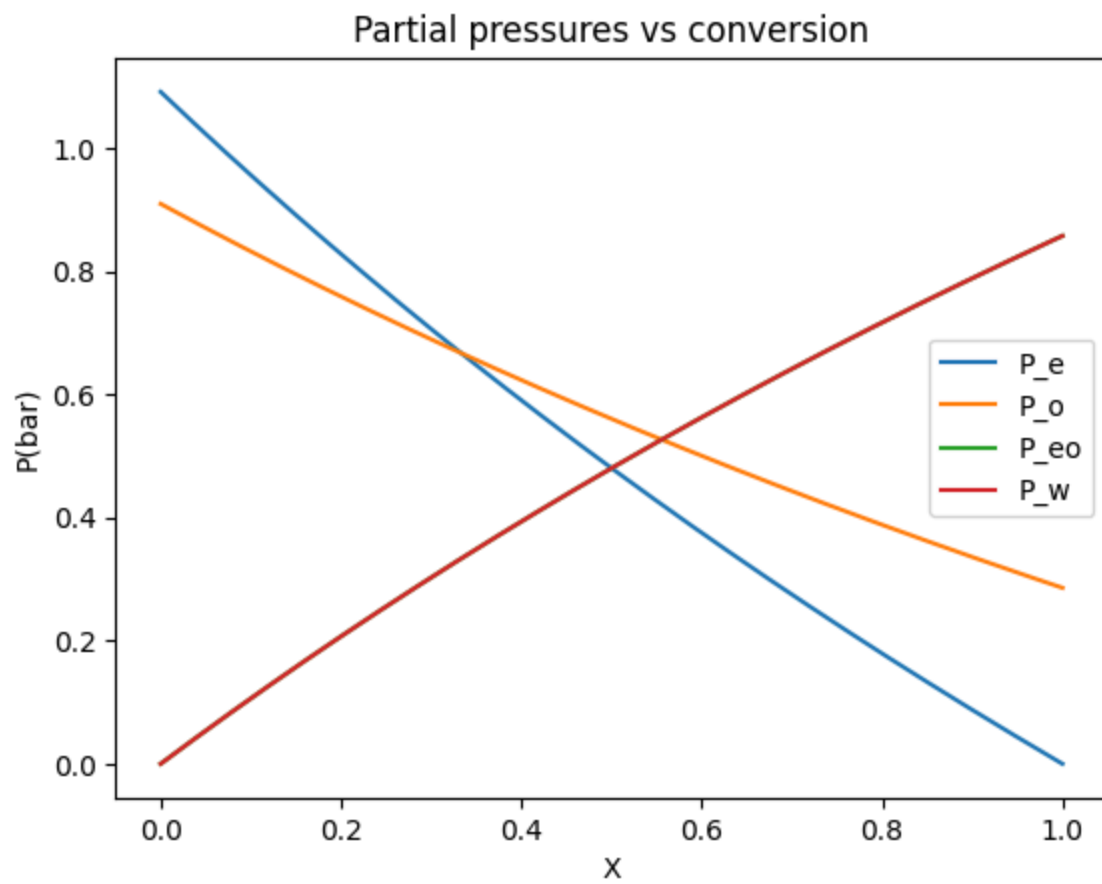
n_e = n_e0 - X*ximax
n_o = n_o0 - (0.5)*X*ximax
n_eo = n_eo0 + X*ximax
n_w = n_w0 + X*ximax

Ntot = n_e + n_o + n_eo + n_w

y_e = n_e /Ntot
y_o = n_o /Ntot
y_eo = n_eo /Ntot
y_w = n_w / Ntot

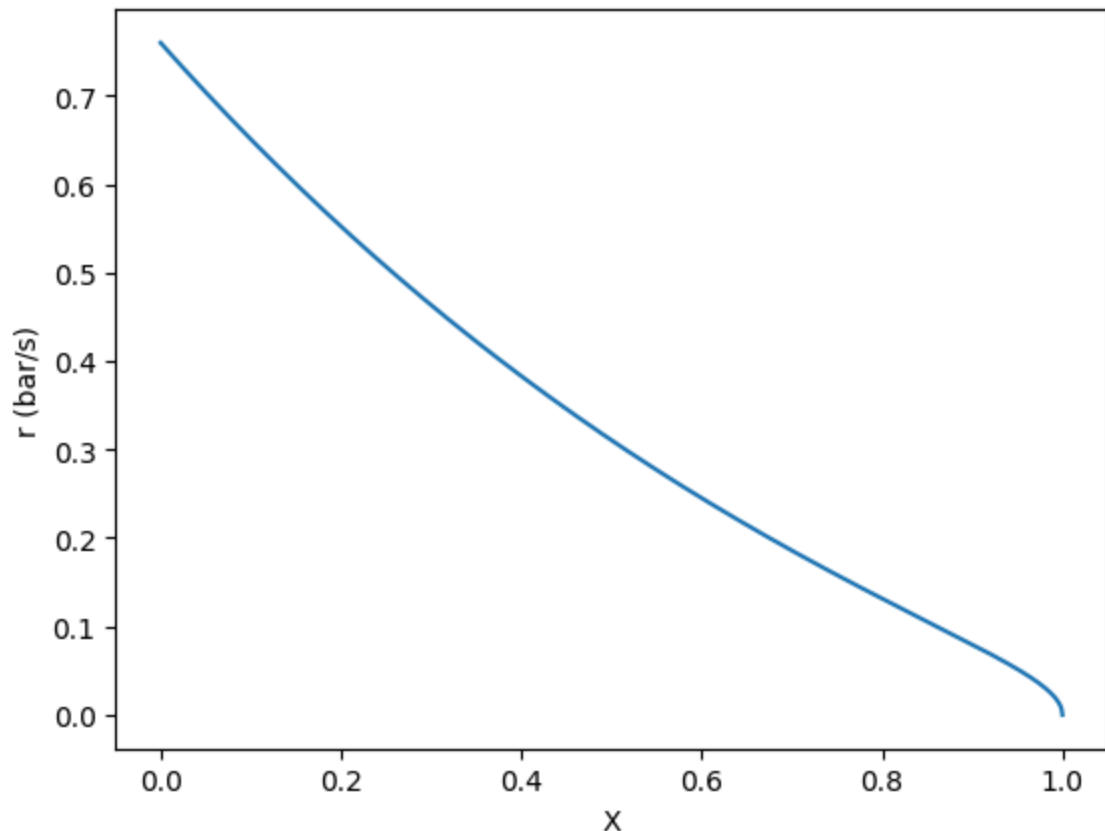
P_e = P*y_e
P_o = P*y_o
P_eo = P*y_eo
P_w = P*y_w

plt.plot(X,P_e,label='P_e')
plt.plot(X,P_o,label='P_o')
plt.plot(X,P_eo,label='P_eo')
plt.plot(X,P_w,label='P_w')
plt.xlabel('X')
plt.ylabel('P(bar)')
plt.title('Partial pressures vs conversion')
plt.legend()
plt.show()
```



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

```
In [5]: k = 0.8
r = k*P_e**(1/2)*P_o
plt.plot(X,r)
plt.xlabel('X')
plt.ylabel('r (bar/s)')
plt.show()
```



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

```
In [6]: import numpy as np
R = 8.314e-3 #kJ/mol*K
Ea = 60 #kJ/mol
T = 500 #K
k1 = 0.8 #bar^-0.5 * s^-1
A = k1/(np.exp(-Ea/R/T)) #bar^-0.5 * s^-1
print('Prefactor A is %.2f bar^(-0.5)*s^(-1)'%A)
```

Prefactor A is 1484134.21 bar^(-0.5)*s⁽⁻¹⁾

8. The apparent activation energy of the reaction is 60 kJ mol^{-1} .

```
In [7]: k_550 = A*np.exp(-Ea/R/550)
print('rate constant at 550K is %.2f bar^(-0.5)*s^(-1)'%k_550)
```

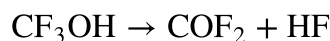
rate constant at 550K is 2.97 bar^(-0.5)*s⁽⁻¹⁾

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

No we can't predict the rate law. This is not an elementary step process so that we can't know the reaction order from the equation stoichiometry.

Rate constants from scratch

In 1996, Schneider and co-workers used quantum chemistry to compute the reaction pathway for unimolecular decomposition of trifluoromethanol, a reaction of relevance to the atmospheric degradation of hydrofluorocarbon refrigerants (*J. Phys. Chem.* 1996, 100, 6097- 6103, [doi:10.1021/jp952703m](https://pubs.acs.org/doi/abs/10.1021/jp952703m) (<https://pubs.acs.org/doi/abs/10.1021/jp952703m>)):

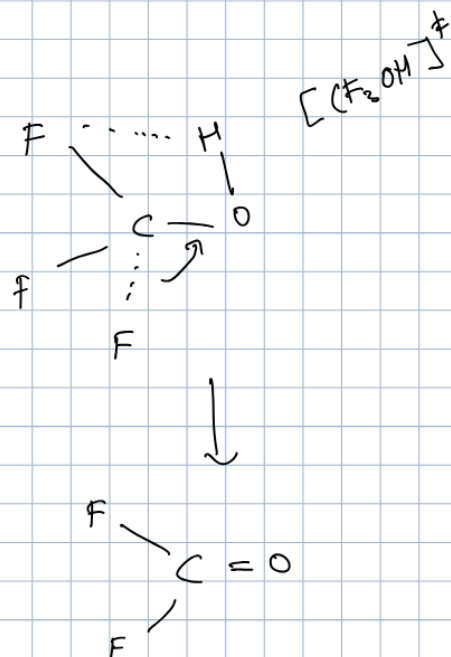
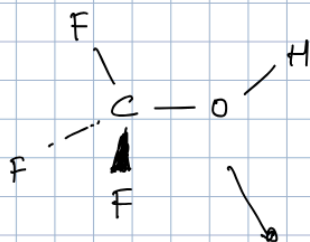
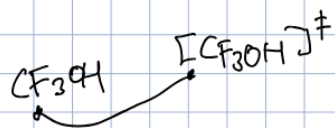
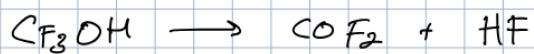


Following are some of the reported results, computed at 298 K:

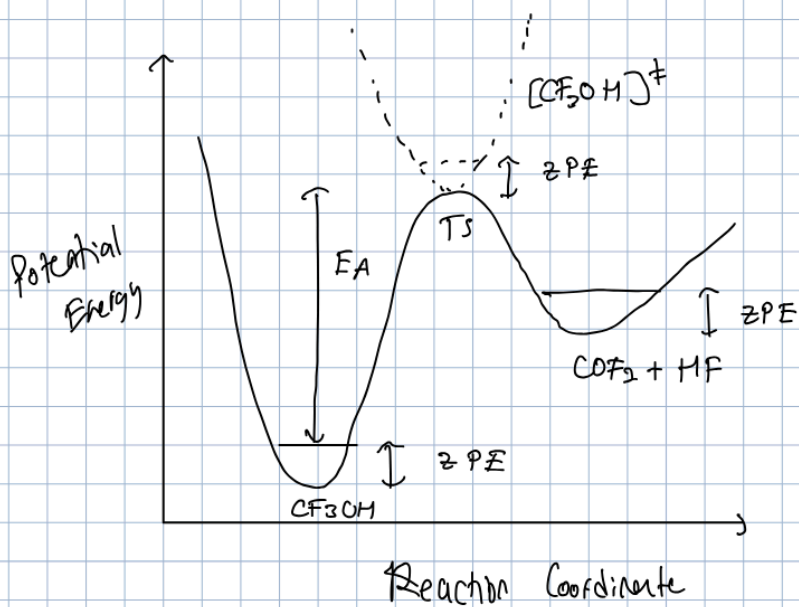
	CF ₃ OH	[CF ₃ OH] [‡]	C(O)F ₂	HF	
E^{elec}	-412.90047	-412.82771	-312.57028	-100.31885	(Hartree)
ZPE	0.02889	0.02313	0.01422	0.00925	(Hartree)
U^{trans}	3.7	3.7	3.7	3.7	(kJ mol ⁻¹)
U^{rot}	3.7	3.7	3.7	2.5	(kJ mol ⁻¹)
U^{vib}	4.3	4.1	1.2	0	(kJ mol ⁻¹)
q^{trans}/V	7.72 × 10 ³²	7.72 × 10 ³²	1.59 × 10 ³²	8.65 × 10 ³¹	(m ⁻³)
q^{rot}	61830	68420	679	9.59	
q^{vib}	2.33	2.28	1.16	1	

12. Using data from the table and harmonic transition state theory, compute the first-order rate constant for CF₃OH decomposition at 298 K, in s⁻¹.

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



11)



take CF_3OH as reference

```
In [8]: import numpy as np

kB=8.61734e-5 # eV/K
T1=298 # K
h=4.136e-15 # eV*s
q_TS= 7.72e32*68420*2.28 # 1/m^3, q(trans)*q(rot)*q(vib)
q_A=7.72e32*61830*2.33 # 1/m^3, q(trans)*q(rot)*q(vib)
delta_E= ((-412.82771+0.02313)-(-412.90047+0.02889))*27.212 # eV
k=kB*T1/h*q_TS/q_A*np.exp(-delta_E/kB/T1)
print("First-order rate constant for CF3OH decomposition at 298 K is %E s"
```

First-order rate constant for CF3OH decomposition at 298 K is 9.852726E-19 s⁻¹.

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, CF₃OH formation reaction.

```
In [9]: Kc = 2.926
kr = k/Kc
print('rate constant for reverse reaction is %E s^-1'%kr)
```

rate constant for reverse reaction is 3.367302E-19 s⁻¹

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

```
In [12]: .121 #kJ/mol

# K
1447 # J/(mol*K)
= 2625.50

d
[-412.90047 , -412.82771] # kJ/mol
0.02889 , 0.02313] # kJ/mol
(Eelec[1] + ZPE[1]) - (Eelec[0] + ZPE[0])* autokJ # kJ/mol
= [3.7, 3.7] #kJ/mol
[3.7, 3.7] #kJ/mol
[4.3, 4.1] #kJ/mol
0 + (u_trans[1]+u_rot[1]+u_vib[1])-(u_trans[0]+u_rot[0]+u_vib[0])#kJ/mol
dU

e
= [-412.82771 , -312.57028 , -100.31885 ] # kJ/mol
[0.02313 , 0.01422 , 0.00925 ] # kJ/mol
-((Eelec_r[1] + ZPE_r[1] + Eelec_r[2] + ZPE_r[2]) - (Eelec_r[0] + ZPE_r[0]))
_r = [3.7, 3.7, 3.7] #kJ/mol
= [3.7, 3.7, 2.5] #kJ/mol
= [4.1, 1.2, 0] #kJ/mol
dE0_r - (u_trans_r[1]+u_rot_r[1]+u_vib_r[1])+(u_trans_r[2]+u_rot_r[2]+u_vib_r[2])
dU_r - R/1000*T

The overall enthalpy is %.2f kJ/mol, forward half reaction enthalpy is %.
```

The overall enthalpy is 21.12 kJ/mol, forward half reaction enthalpy is 175.71 kJ/mol and reverse half reaction enthalpy is 143.99 kJ/mol.

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

```
In [17]: 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/365/24/3600))

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

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!).

Must decompose by some other route! Biomolecular processes, for instance. 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.