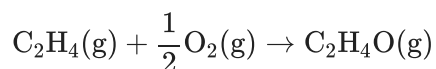# Chem 30324, Spring 2025, Homework 11

# Due May 3, 2025

## What to do with ethylene?

Ethylene ($C_2H_4$) is an important commodity chemical. Partial oxidation to ethylene oxide (oxirane) is a useful way to introduce additional functionalization:

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

At 500 K over an appropriate catalyst, the reaction is first-order in ethylene, half-order in $O_2$, zero order in products, and has a rate constant of 0.8 $bar^{-1/2}\,s^{-1}$. You plan to study the reaction in an isothermal, contant pressure reactor, starting with a 20 mole % excess of ethylene ($n_{C2H4}/n_{O2} = 1.2$) at 2 bar total pressure.

1. Draw the structure of ethylene oxide.
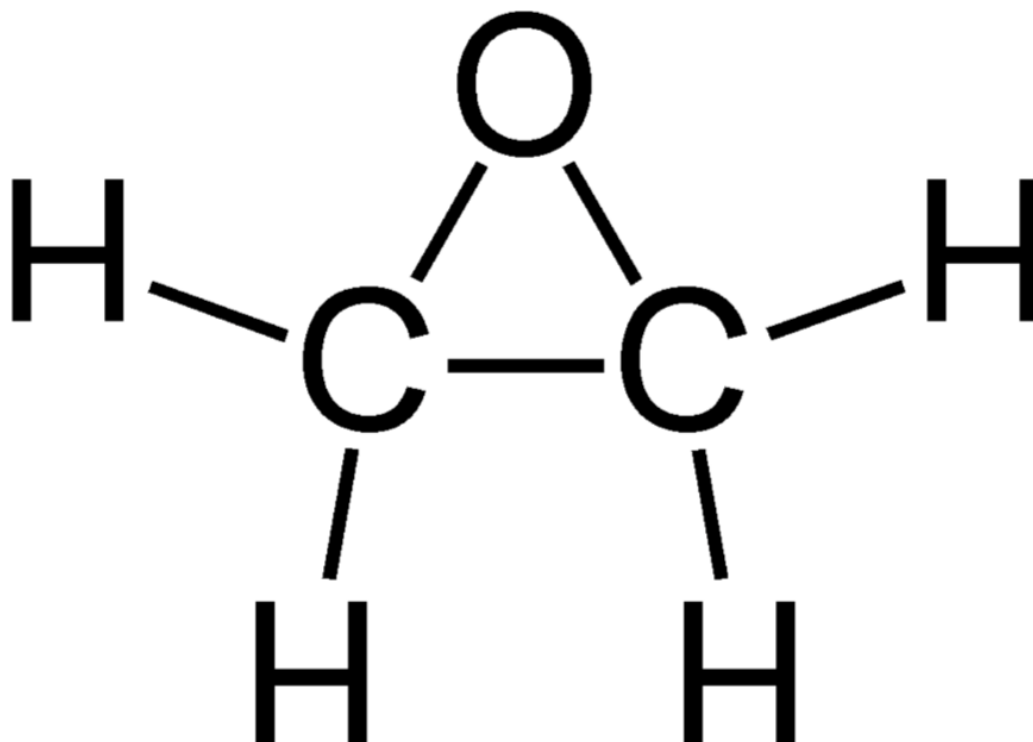
## 2. Is the reaction as written an elementary step? Why or why not?

No, elementary step are not supposed to have half molecule. Also the rate law is not consistent with stoichiometry.

## 3. Write down the rate law for the formation of ethylene oxide.

$$r = kP_{ethylene}P_{oxygen}^{\frac{1}{2}}$$

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

Choose basis of 1 mole O2 and 1.2 mole C2H6

| | $C_2H_4$ | $O_2$ | $C_2H_4O$ | |
|---|---|---|---|---|
| I | 1.2 | 1 | 0 | |
| C | $-\xi$ | $-0.5\xi$ | $+\xi$ | |
| E | $-\xi$ | $1.2-0.5\xi$ | $1\ \xi$ | $\xi_{max}=1 \rightarrow$ complete conversion of $O_2$ |

Maximum value of $\xi$ is 1.2.

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

```
In [15]:
import numpy as np
import matplotlib.pyplot as plt

P = 2 # bar

xi = np.linspace(0,1.2,1000)
ximax = 1.2

X = xi/ximax

#Starting moles of reactants/product
n_e0 = 1.2
n_o0 = 1
n_eo0 = 0

#change in moles over time as a function of conversion
n_e = n_e0 - X
n_o = n_o0 - 0.5*X
n_eo = n_eo0 + X

#Keeping track of the total moles
Ntot = n_e + n_o + n_eo
```
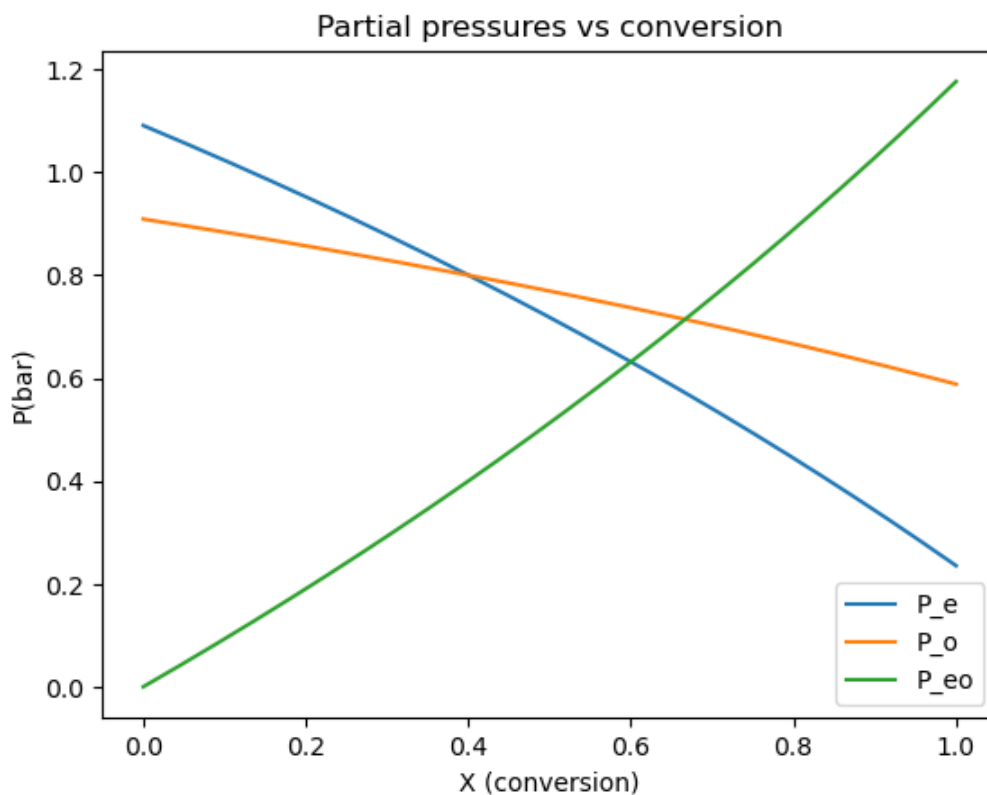
```
#The molar fractions of each species
y_e = n_e /Ntot
y_o = n_o /Ntot
y_eo = n_eo /Ntot

#The Partial Pressure of each species
P_e = P*y_e
P_o = P*y_o
P_eo = P*y_eo

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.xlabel('X (conversion)')
plt.ylabel('P(bar)')
plt.title('Partial pressures vs conversion')
plt.legend()
plt.show()
```
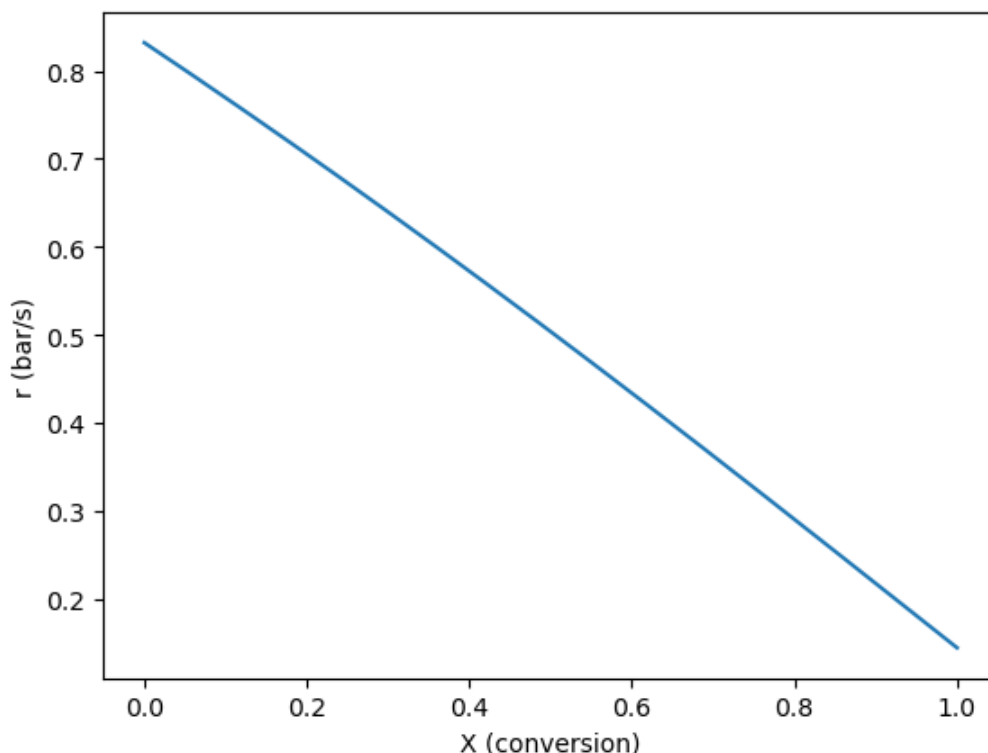


## 6. Plot the forward reaction rate vs $X$. Be sure to include appropriate units.

```
In [16]: #Remember the reaction is first order in ethylene, half order in O2
k = 0.8
r = k*P_e*P_o**(1/2)
plt.plot(X,r)
plt.xlabel('X (conversion)')
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 [17]:  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$^{-1}$. Estimate the rate constant at 550 K.**

```
In [18]:  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):

$$CF_3OH \rightarrow COF_2 + HF$$

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

| | CF$_3$OH | [CF$_3$OH]$^{\ddagger}$ | C(O)F$_2$ | HF |
|---|---|---|---|---|
| $E^{\text{elec}}$ (Hartree) | -412.90047 | -412.82771 | -312.57028 | -100.31885 |
| ZPE (Hartree) | 0.02889 | 0.02313 | 0.01422 | 0.00925 |
| $U^{\text{trans}}$ (kJ mol$^{-1}$) | 3.7 | 3.7 | 3.7 | 3.7 |
| $U^{\text{rot}}$ (kJ mol$^{-1}$) | 3.7 | 3.7 | 3.7 | 2.5 |
| $U^{\text{vib}}$ (kJ mol$^{-1}$) | 4.3 | 4.1 | 1.2 | 0 |
| $q^{\text{trans}}/V$ (m$^{-3}$) | 7.72 $\times 10^{32}$ | 7.72 $\times 10^{32}$ | 1.59 $\times 10^{32}$ | 8.65 $\times 10^{31}$ |
| $q^{\text{rot}}$ | 61830 | 68420 | 679 | 9.59 |
| $q^{\text{vib}}$ | 2.33 | 2.28 | 1.16 | 1 |

10. Provide a rough sketch of what you expect the transition state to look like.
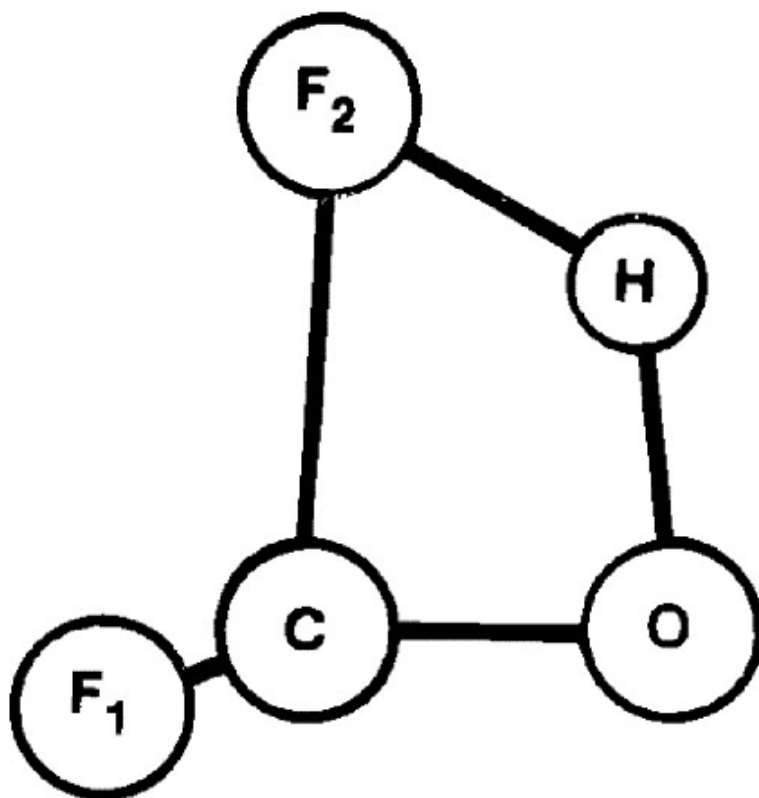
11. Based on the data in the table, create a potential energy surface for the unimolecular decomposition reaction. Indicate on the PES the location of the reactants, the products, and the transition state. Also indicate relevant zero point energies, the 0 K reaction energy, and the activation energy.

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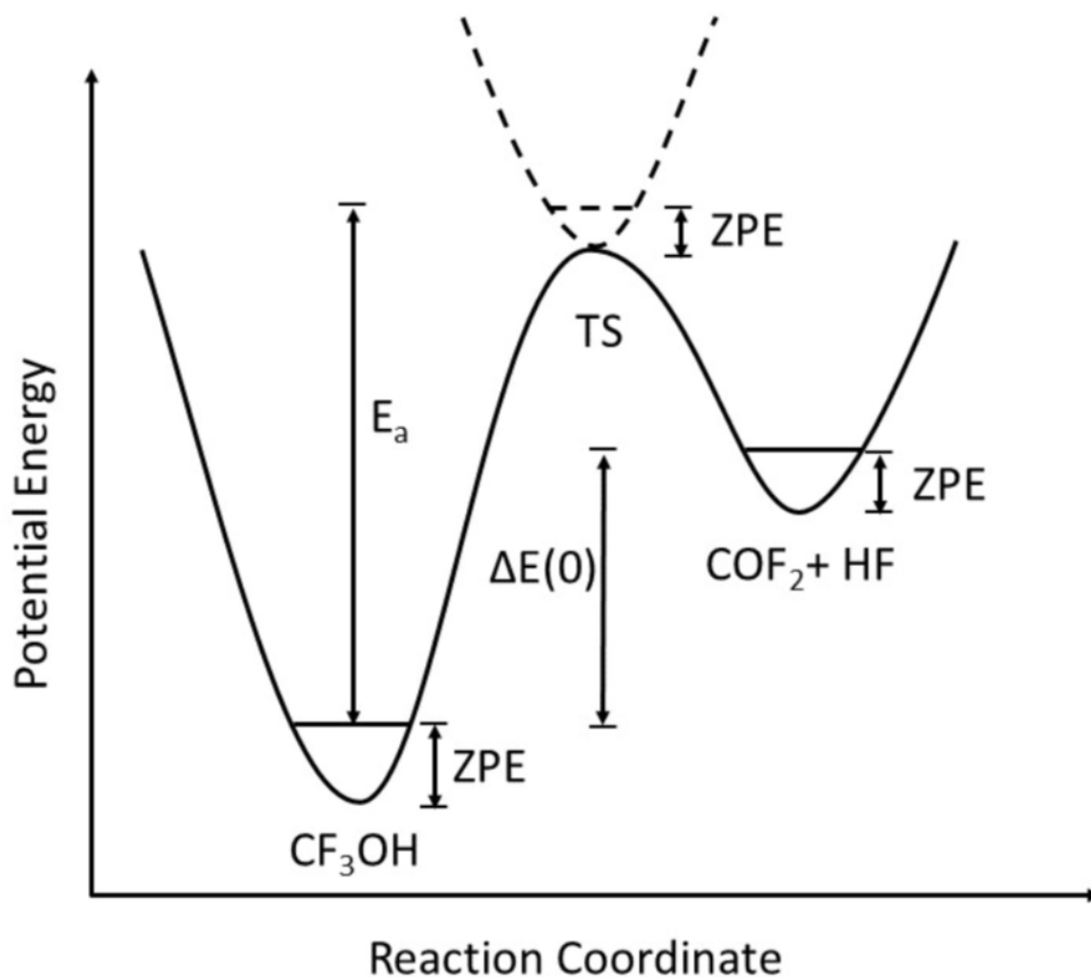
12. Using data from the table and harmonic transition state theory, compute the first-order rate constant for $CF_3OH$ decomposition at 298 K, in $s^{-1}$.

In [19]:
```python
import numpy as np

#Constants
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 decompostion at 298 K is %E s^-1."%k)
```

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

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

```
In [20]:  t=np.log(2)/k # s
          print('The half-life is %E s, which is about %E years.'%(t,t/3600/24/365))
```

The half-life is 7.035080E+17 s, which is about 2.230809E+10 years.

## 14. 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.