Chem 30324, Spring 2019, Homework 10

Due May 3, 2019

Equilibrium constants from first principles.

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)):

$$CF_3OH \rightarrow COF_2 + HF$$

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

	CF_3OH	$[CF_3OH]^{\ddagger}$	COF_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}	(1/m^3)
q^{rot}	61830	68420	679	9.59	
q^{vib}	2.33	2.28	1.16	1	

1. Using the data provided, determine $\Delta U°$(298 K), in kJ mol^{-1}, assuming ideal behavior and 1 M standard state. Recall that $U(T)$ is the sum of the contributions of all degrees of freedom.

Remember that E_0 is contained in $\Delta U°, \Delta A°, and \Delta G°$. For example:

$$\Delta U° = \sum_{product} U_{trans} + U_{rot} + U_{vib} + (E_{elec} + ZPE) - \sum_{reactant} U_{trans} + U_{rot} + U_{vib} + (E_{elec} + ZPE)$$

$$= \sum_{product} U_{trans} + U_{rot} + U_{vib} + E_0 - \sum_{reactant} U_{trans} + U_{rot} + U_{vib} + E_0$$

$$\Delta U° = \Delta(U_{trans} + U_{rot} + U_{vib}) + \Delta(E_0)$$

In [51]:
```python
import numpy as np
T = 298 # K
k = 1.38065e-23 # J/K
R = 8.31447 # J/(mol*K)
Na = 6.0221e23  # 1/mol
c = 6.0221e26  # 1/m^3, conversion factor of 1mol/L = 6.02e26 particles/
m^3
autokJ = 2625.50

Eelec = [-412.90047 ,-312.57028 ,-100.31885 ] # kJ/mol
ZPE = [0.02889 ,0.01422 ,0.00925 ] # kJ/mol
dE0 = ((Eelec[1] + ZPE[1] + Eelec[2] + ZPE[2]) - (Eelec[0] + ZPE[0]))* a
utokJ # kJ/mol
u_trans = [3.7,3.7,3.7] #kJ/mol
u_rot = [3.7,3.7,2.5] #kJ/mol
u_vib = [4.3,1.2,0] #kJ/mol
dU = dE0 + (u_trans[1]+u_rot[1]+u_vib[1])+(u_trans[2]+u_rot[2]+u_vib[2])
-(u_trans[0]+u_rot[0]+u_vib[0])#kJ/mol
print("delta_U = %.2f kJ/mol"%dU)
```

delta_U = 18.64 kJ/mol

2. Using the data provided, determine $\Delta A°$(298 K) in kJ mol^{-1}, assuming ideal behavior and 1 M standard state. Recall that $A° = E^{elec} + ZPE - RT\ln(q°) - RT$ and that $q° = (q^{trans}/V)q^{rot}q^{vib}/c°$ in units corresponding with the standard state.

$$\Delta A° = \left\{[-k_BT\ln(q_tq_rq_v) - k_BT]_{COF_2} + [-k_BT\ln(q_tq_rq_v) - k_BT]_{HF} - [-k_BT\ln(q_tq_rq_v) - k_BT]_{CF_3OH}\right\} *$$

$$= \Delta(E_0) - RT\ln(Q) - RT$$

```
In [65]: q_trans = [7.72e32/c,1.59e32/c,8.65e31/c] # change translational partiti
         on functions from 1/m3 to mol/l std state
         q_rot = [61830,679,9.59] # unitless
         q_vib = [2.33,1.16,1] # unitless
         Q = (q_trans[1]*q_rot[1]*q_vib[1])*(q_trans[2]*q_rot[2]*q_vib[2])/(q_tra
         ns[0]*q_rot[0]*q_vib[0]) # total partition
         dA = dE0 + (-R*T*np.log(Q)- R*T)/1000 #kJ/mol
         print(Q,dE0)
         print("delta_A = %.2f kJ/mol"%dA)
```

```
(1551.097763657244, 15.542960000008549)
delta_A = -5.14 kJ/mol
```

3. Determine $\Delta G°(298 \text{ K})$. Recall that $G = A + PV = A + RT$ for an ideal ga.

$$\Delta G° = \Delta A° + \Delta (PV)$$

$$= \Delta A° + RT$$

```
In [54]: dG = dA + R*T/1000 #kJ/mol
         print("delta_G = %.2f kJ/mol"%dG)
```

```
delta_G = -2.66 kJ/mol
```

4. Determine $\Delta S°$ (298 K), in J mol^{-1} K^{-1} , assuming a 1 M standard state. Recall that $S = (U - A)/T$.

$$\Delta A° = \Delta U° - T\Delta S°$$

$$\Delta S° = \frac{\Delta U° - \Delta A°}{T}$$

```
In [55]: dS = 1000*(dU - dA)/T
         print("delta_S = %.2f J/mol K"%dS)
```

```
delta_S = 79.80 J/mol K
```

5. Using the data provided, determine K_c (298 K), assuming a 1 M standard state. You may either determine from partition functions or from the relationship between K_c and $\Delta G°$.

$A \rightarrow B + C$

$$K_c(T) = \frac{\frac{q_B}{V}\frac{q_C}{V}}{\frac{q_A}{V}}\frac{1}{c^\circ}e^{-\Delta E(0)/kT} = e^{-\Delta G^\circ(T)/RT}, \quad \text{where} \quad \frac{q_i}{V} = \frac{q_{trans}}{V}q_{rot}q_{vib}$$

Note: $K_c(T)$ is formally unitless but "remembers" that it refers to 1 M standard state.

```
In [69]: Kc = Q *np.exp(-dE0*1000/(R*T)) # Kc equation from lecture notes
         print('Kc = %.3f (unitless). '%(Kc))

         Kc = 2.926 (unitless).
```

```
In [72]: Kc = np.exp(-dG*1000/(R*T))
         print('Kc = %.3f (unitless). '%(Kc))

         Kc = 2.926 (unitless).
```

6. 1 mole of CF_3OH is generated in a 20 L vessel at 298 K and left long enough to come to equilibrium with respect to its decomposition reaction. What is the composition of the gas (concentrations of all the components) at equilibrium (in mol/L)?

1 mol/ 20 L = 0.05 mol/L

$A \rightarrow B + C$

Reaction	A (mol/L)	B (mol/L)	C (mol/L)
I	0.05	0	0
C	-x	x	x
E	0.05-x	x	x

$K_c = \frac{x^2}{0.05-x}$, solve for x. Note that x = $[\frac{mol}{L}]$.

```
In [73]: from sympy import *
         x = symbols('x',positive=True)
         c = solve(x**2-(0.05-x)*Kc,x)
         print('At equilibrium, CF3OH = %.2E mol/L, COF2 = %.5f mol/L, HF = %.5f
          mol/L.'%(0.05-c[0],c[0],c[0]))

         At equilibrium, CF3OH = 8.26E-04 mol/L, COF2 = 0.04917 mol/L, HF = 0.04
         917 mol/L.
```

7. How, directionally, would your answer to Question 4 change if the vessel was at a higher temperature? Why, in statistical mechanical terms?

Since enthalpy is positive & the reaction is endothermic, the equilibrium will tend towards the products as temperature increases.

In stat mech perspective, high energy states become more probable with increasing temperature, so molecules will more likely ended up as product. (Product is higher in energy in this reaction).

8. How, directionally, would your answer to Question 4 change if the vessel had a volume of 5 L? Why, in statistical mechanical terms?

When volume shrinks from 20L to 5L, the equilibrium will tend towards the reactant, which has lesser molecules. (though equilibrium constant stays the same, i.e. Kc is not a function of V).

In stat mech perspective, number of available translational states is proportional to volume. Smaller volume lessen the number of available states, therefore favors the side that has lesser molecules (i.e. reactant).

Chemical kinetics from first principles.

While chemical equilibrium describes what can happen, chemical kinetics determines what *will* happen. The same paper reports results for the transition state for the unimolecular decomposition reaction, also shown in the table above.

9. Provide a rough sketch of what you expect the transition state to look like.
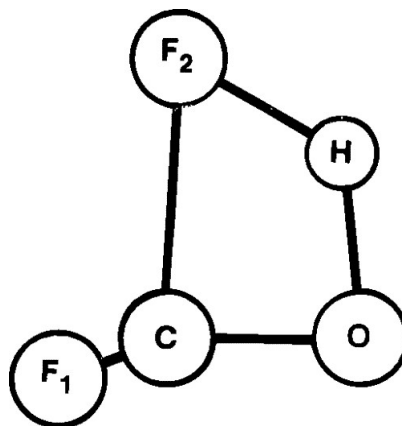
Structure of $[\mathrm{CF_3OH}]^{\ddagger}$ according to the literature (Schneider, W. F., Wallington, T. J., & Huie, R. E. (1996). Energetics and mechanism of decomposition of CF3OH. *The Journal of Physical Chemistry, 100*(15), 6097-6103.). The third F is not showing.

(Other answers will be accepted if make sense)

10. Based on the data in the table, sketch out an approximate 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.
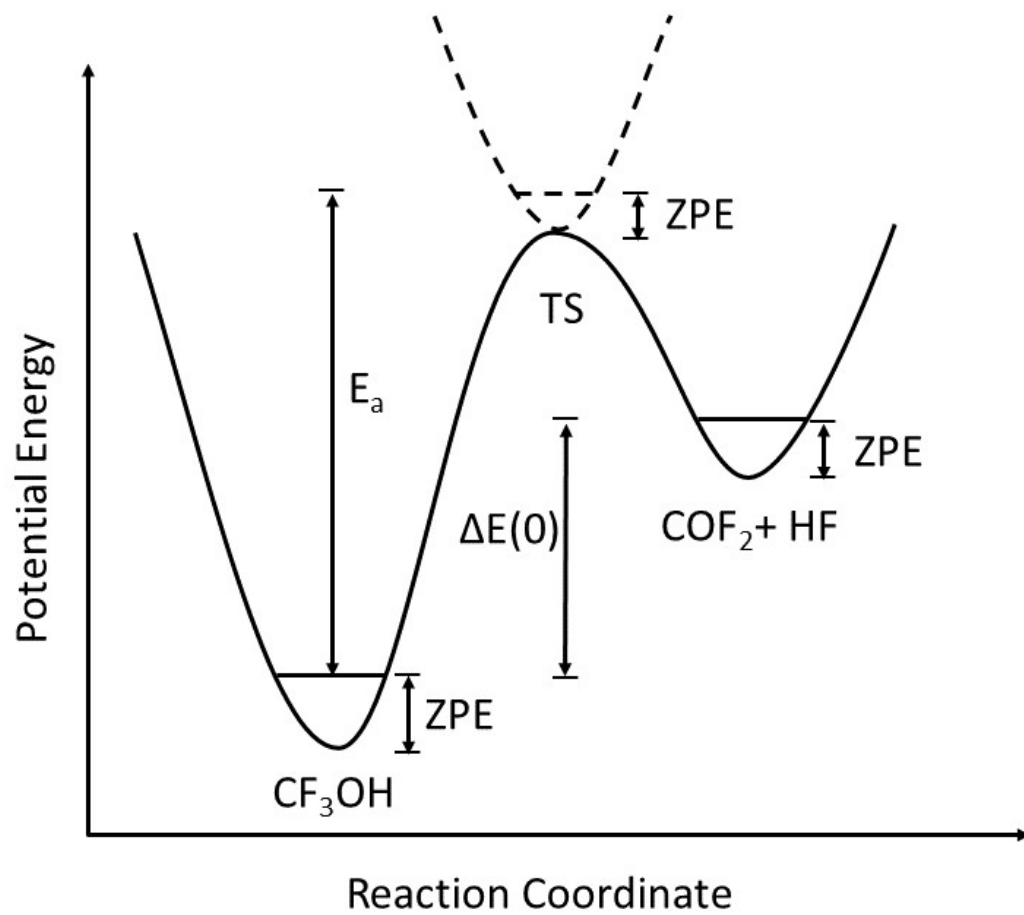
11. Using data from the table and harmonic transition state theory, compute the first-order rate constant for CF_3OH decomposition at 298 K, in s^{-1}.

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

```
In [26]:  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
          k2=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 1.380650E-
23 s^-1.
```

12. Which factor in your rate constant dominates the temperature dependence? Estimate the change in temperature necessary to double the rate constant.

The dominating factor would be the temperature in the exponential denominator.

```
In [22]:  from scipy.optimize import fsolve

          T2 = 298   # K
          k2 = kB*T2/h*q_TS/q_A*np.exp(-delta_E/kB/T2)
          func = lambda T : kB*T/h*q_TS/q_A*np.exp(-delta_E/kB/T)-2*k2
          T3 = fsolve(func,298)
          print("Temperature changing from %f K to %f K will make the rate constan
          t double"%(T2, T3))
```

```
Temperature changing from 298.000000 K to 300.896633 K will make the ra
te constant double
```

13. Based on your computed rate constant, what is the half-life of the CF_3OH in the vessel of Question 4?

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

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

```
In [24]: t=np.log(2)/k2 # 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!).

The reaction must proceed by some other pathway. One possibility advanced in the paper is participation of H$_2$O in the decomposition.