Chem 30324, Spring 2020, Homework 10

Due April 24, 2020

Thermodynamics from scratch.

Let's calculate the thermodynamic properties of an ideal gas of CO molecules at 1 bar pressure. CO has a rotational constant B = 1.931 cm^{-1} and vibrational frequency v = 2156.6 cm^{-1} . Suppose you have a 20 dm^3 cubic bottle containing 1 mole of CO gas that you can consider to behave ideally.

1. The characteristic temperature Θ of a particular degree of freedom is the characteristic quantum of energy for the degree of freedom divided by k_B . Calculate the characteristic translational, rotational, and vibrational temperatures of CO.

$\theta_{trans} = \frac{\pi^2 \hbar^2}{2mL^2 k_B}$

$\theta_{rot} = hcB/k_B$

$\theta_{vib} = hc\tilde{v}/k_B$

```
In [1]: import numpy as np
        import matplotlib.pyplot as plt

        hbar = 1.05457e-34 # J*s
        h = 6.62607e-34 # J*s
        kB = 1.38065e-23 # J/K
        m = 28.01*1.6605e-27 # kg/molecule
        V = 0.02 # m^3
        c = 2.99792e10 # cm/s
        B = 1.931 # cm^-1
        v = 2156.6 # cm^-1
        T_trans = np.pi**2*hbar**2/2/m/V**(2/3)/kB
        T_rot = h*c*B/kB
        T_vib = h*c*v/kB
        print('Characteristic temperatures of CO:')
        print('T_trans = {0:.3e} K, T_rot = {1:.3f} K, T_vib = {2:0.2f} K.'.form
        at(T_trans,T_rot,T_vib))
```

```
Characteristic temperatures of CO:
T_trans = 1.160e-18 K, T_rot = 2.778 K, T_vib = 3102.86 K.
```

2. Calculate the *translational partition function* of a CO molecule in the bottle at 298 K. What is the unit of the partition function?

For $T \gg \theta_{trans}$, $\Lambda \ll L$, $q_{trans} = V/\Lambda^3$. $\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$.

```
In [2]: Lamda = h*(1/(kB*298*2*np.pi*m))**0.5
        print(Lamda)
        q_trans = V/Lamda**3
        print('The translational partition function of a CO molecule in the bott
        le at 298 K is {:.4E}.'.format(q_trans))
        print('It is dimensionless.')
```

```
1.9109096798652453e-11
The translational partition function of a CO molecule in the bottle at
298 K is 2.8662E+30.
It is dimensionless.
```
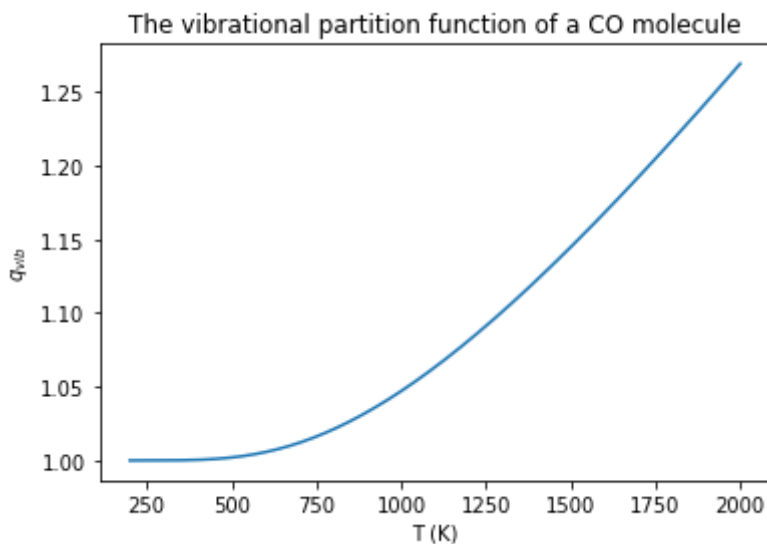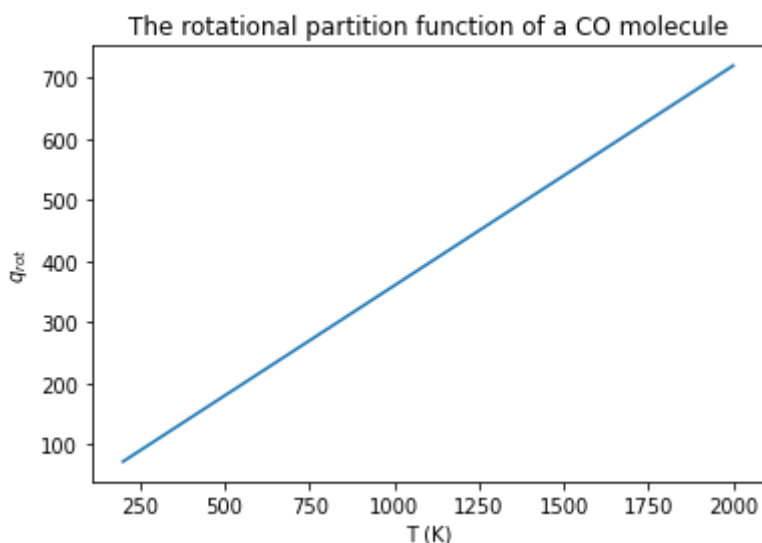
3. Plot the *rotational and vibrational partition functions* of a CO molecule in the bottle from T = 200 to 2000 K (assume the CO remains a gas over the whole range). *Hint:* Use your answer to Problem 1 to simplify calculating the rotational partition function.

$$q_{rot} = \frac{1}{\sigma}\frac{T}{\theta_{rot}} = \frac{T}{\theta_{rot}}$$

$$q_{vib} = \frac{1}{1-e^{-\theta_{vib}/T}}$$

```
In [3]:  T = np.linspace(200,2000,1000)  # r = R/a_0
         q_rot = T/T_rot
         q_vib = 1/(1-np.exp(-T_vib/T))
         plt.plot(T,q_rot)
         plt.xlabel('T (K)')
         plt.ylabel('$q_{rot}$')
         plt.title('The rotational partition function of a CO molecule')
         plt.show()
         plt.plot(T,q_vib)
         plt.xlabel('T (K)')
         plt.ylabel('$q_{vib}$')
         plt.title('The vibrational partition function of a CO molecule')
         plt.show()
```

The rotational partition function of a CO molecule

The vibrational partition function of a CO molecule

4. Plot the *total translational, rotational, and vibrational energies* of CO in the bottle from $T = 200$ to 2000 K (assume the CO remains a gas over the whole range). Which (if any) of the three types of motions dominate the total energy?

$$U_{trans} = \frac{3}{2}RT$$

$$U_{rot} = RT$$

$$U_{vib} = R\frac{\theta_{vib}}{e^{\theta_{vib}/T}-1}.$$

```
In [4]: R = 8.31447 # J/(mol*K)
        U_trans = 1.5*R*T
        U_rot = R*T
        U_vib = R*T_vib/(np.exp(T_vib/T)-1)
        plt.plot(T,U_trans,label='U_trans')
        plt.plot(T,U_rot,label='U_rot')
        plt.plot(T,U_vib,label='U_vib')
        plt.legend()
        plt.xlabel('T (K)')
        plt.ylabel('Internal Energy (J/mol)')
        plt.title('Internal energies of CO in the bottle')
        plt.show()
```
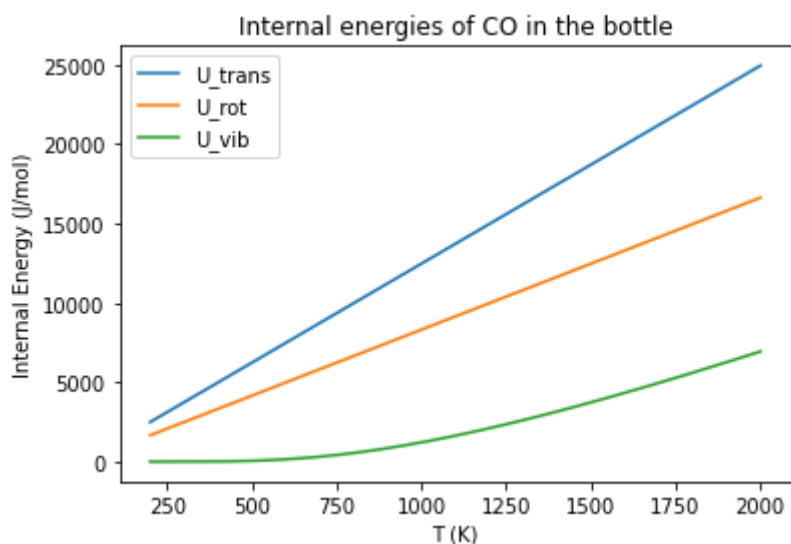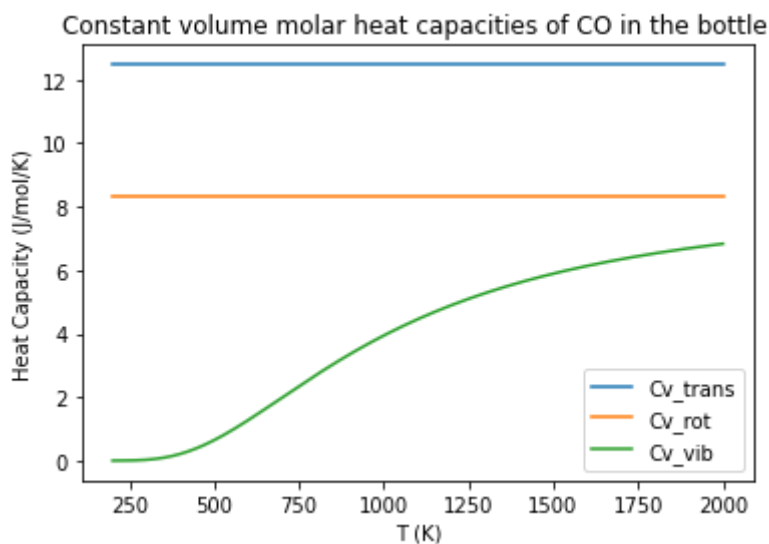

5. Plot the *total translational, rotational, and vibrational constant volume molar heat capacities* of CO in the bottle from $T = 200$ to 2000 K. Which (if any) of the three types of motions dominate the heat capacity?

$$C_{V,trans} = \frac{3}{2}R$$

$$C_{V,rot} = R$$

$$C_{V,vib} = R\left(\frac{\theta_{vib}}{T}\frac{e^{\theta_{vib}/2T}}{e^{\theta_{vib}/T}-1}\right)^2$$

```
In [5]: Cv_trans = np.linspace(1.5*R,1.5*R,1000)
        Cv_rot = np.linspace(R,R,1000)
        Cv_vib = R*(T_vib/T*np.exp(T_vib/2./T)/(np.exp(T_vib/T)-1))**2
        plt.plot(T,Cv_trans,label='Cv_trans')
        plt.plot(T,Cv_rot,label='Cv_rot')
        plt.plot(T,Cv_vib,label='Cv_vib')
        plt.legend()
        plt.xlabel('T (K)')
        plt.ylabel('Heat Capacity (J/mol/K)')
        plt.title('Constant volume molar heat capacities of CO in the bottle ')
        plt.show()
        print('While translational motion contributes the most to the molar heat
        capacity of CO,')
        print('it does not dominate over rotational and vibrational motion.')
```


Constant volume molar heat capacities of CO in the bottle

```
While translational motion contributes the most to the molar heat capac
ity of CO,
it does not dominate over rotational and vibrational motion.
```

6. Plot the *total translational, rotational, and vibrational Helmholtz energies* of CO in the bottle from $T = 200$ to 2000 K. Which (if any) of the three types of motions dominate the Helmholtz energy?

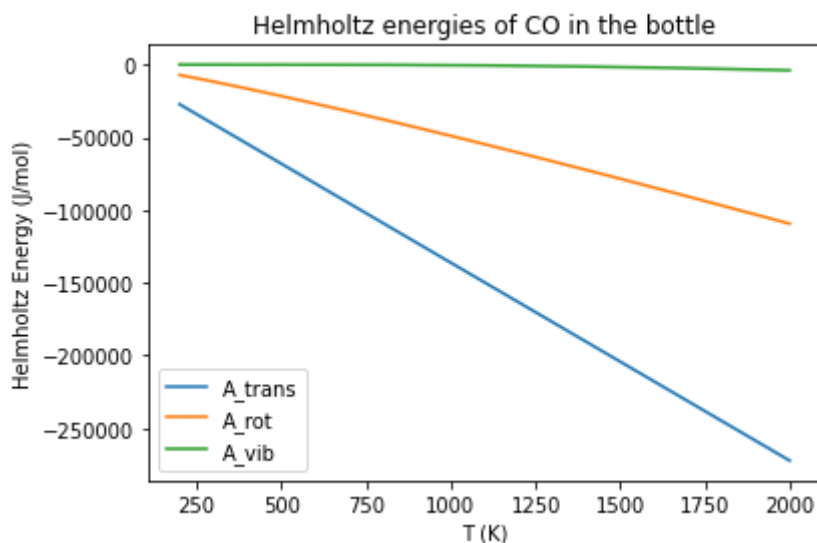$A = U - TS$

$S_{trans} = Rln\left(\frac{e^{5/2}V}{N\Lambda^3}\right)$

$S_{rot} = R(1 - ln(\theta_{rot}/T))$

$S_{vib} = R\left(\frac{\theta_{vib}/T}{e^{\theta_{vib}/T}-1} - ln(1 - e^{-\theta_{vib}/T})\right).$

```
In [6]: NA = 6.022e23
        S_trans = R*np.log(np.exp(2.5)*V/NA/Lamda**3)
        S_rot = R*(1-np.log(T_rot/T))
        S_vib = R*(T_vib/T/(np.exp(T_vib/T)-1)-np.log(1-np.exp(-T_vib/T)))
        A_trans = U_trans-T*S_trans
        A_rot = U_rot-T*S_rot
        A_vib = U_vib-T*S_vib
        plt.plot(T,A_trans,label='A_trans')
        plt.plot(T,A_rot,label='A_rot')
        plt.plot(T,A_vib,label='A_vib')
        plt.legend()
        plt.xlabel('T (K)')
        plt.ylabel('Helmholtz Energy (J/mol)')
        plt.title('Helmholtz energies of CO in the bottle')
        plt.show()
```


7. Use your formulas to calculate $\Delta P, \Delta U, \Delta A,$ and ΔS associated with isothermally expanding the gas from 20 dm^3 to 40 dm^3.

T = 298 K. $\Delta U = 0$.

$\Delta P = \frac{RT}{V_2} - \frac{RT}{V_1}$.

$\Delta S = S_{trans,2} - S_{trans,1}$.

$A = U - TS$, so, $\Delta A = -T\Delta S$.

```
In [7]: V2 = 0.04 # m^3
        deltaP = R*298*(1/V2-1/V)
        deltaS = R*np.log(np.exp(2.5)*V2/NA/Lamda**3) - R*np.log(np.exp(2.5)*V/N
        A/Lamda**3)
        deltaA = -deltaS*298
        print('Delta P = {0:.3f} Pa, Delta U = 0, Delta A = {1:.3f} J/mol, and D
        elta S = {2:.3f} J/mol/K.'.format(deltaP,deltaA,deltaS))
```

Delta P = -61942.801 Pa, Delta U = 0, Delta A = -1717.419 J/mol, and De
lta S = 5.763 J/mol/K.

Reactions 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)):

$$CF_3OH \rightarrow COF_2 + HF$$

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

	CF_3OH	$C(O)F_2$	HF	
E^{elec}	-412.90047	-312.57028	-100.31885	(Hartree)
ZPE	0.02889	0.01422	0.00925	(Hartree)
U^{trans}	3.7	3.7	3.7	(kJ mol^{-1})
U^{rot}	3.7	3.7	2.5	(kJ mol^{-1})
U^{vib}	4.3	1.2	0	(kJ mol^{-1})
q^{trans}/V	7.72×10^{32}	1.59×10^{32}	8.65×10^{31}	(m^{-3})
q^{rot}	61830	679	9.59	
q^{vib}	2.33	1.16	1	

8. 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 [8]: 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
```

9. 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.

$$\Delta A° = \left\{ [-k_B T\ln(q_t q_r q_v) - k_B T]_{COF_2} + [-k_B T\ln(q_t q_r q_v) - k_B T]_{HF} - [-k_B T\ln(q_t q_r q_v) - k_B T]_{CF_3 OH} \right.$$
$$= \Delta(E_0) - RT\ln(Q) - RT$$

```
In [9]: 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 = %.2f"%Q)
        print("delta_E0 = %.2f"%dE0)
        print("delta_A = %.2f kJ/mol"%dA)
```

```
Q = 1551.10
delta_E0 = 15.54
delta_A = -5.14 kJ/mol
```

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

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

```
In [10]: dG = dA + R*T/1000 #kJ/mol
         print("delta_G = %.2f kJ/mol"%dG)
```

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

11. 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 [11]: dS = 1000*(dU - dA)/T
         print("delta_S = %.2f J/mol K"%dS)
```

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

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

$$A \rightarrow B + C$$

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

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

```
In [12]: Kc = Q *np.exp(-dE0*1000/(R*T)) # Kc equation from lecture notes
         print('Kc = %.3f (unitless). '%(Kc))

         Kc = 2.926 (unitless).
```

```
In [13]: Kc = np.exp(-dG*1000/(R*T))
         print('Kc = %.3f (unitless). '%(Kc))

         Kc = 2.926 (unitless).
```

13. 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

$$A \rightarrow B + C$$

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

```
In [22]: 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]))
         print('At equilibrium, CF3OH = %.2E mol, COF2 = %.5f mol, HF = %.5f mo
         l.'%((0.05-c[0])*20,c[0]*20,c[0]*20))

         At equilibrium, CF3OH = 8.26E-04 mol/L, COF2 = 0.04917 mol/L, HF = 0.04
         917 mol/L.
         At equilibrium, CF3OH = 1.65E-02 mol, COF2 = 0.98347 mol, HF = 0.98347
         mol.
```

14. How, directionally, would your answer to Question 13 change if the vessel was at a higher temperature? Use the van'T Hoff relationship to determine the equilibrium constant and equilibrium concentrations at 273 and 323 K. How good was your guess?

From question #8, we know that at 298K, ΔU = 18.64 kJ/mol.

$$\Delta H = \Delta U + \Delta(nRT) = \Delta U + RT\Delta n$$

```
In [15]: dn = 2-1
         R = 8.314/1000 #kJ/mol K
         T = 298 #K
         dH = dU+dn*R*T #kJ/mol
         print("dH =",round(dH,3),"kJ/mol")
```

```
dH = 21.121 kJ/mol
```

Since ΔH is positive, we expect $K \uparrow$ as $T \uparrow$

The Van't Hoff equation states:

$$ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

We know from question 12, K = 2.926 at 298 K.

```
In [16]: K1 = 2.926
         T1 = 298 #K
         T2 = 273 #K
         K2 = K1*np.exp(-dH/R*(1/T2-1/T1))
         print('K=', round(K2,4), 'at 273 K.')
         x = symbols('x',positive=True)
         c = solve(x**2-(0.05-x)*K2,x)
         print('At equilibrium, CF3OH = %.2E mol/L, COF2 = %.5f mol/L, HF = %.5f
          mol/L.'%(0.05-c[0],c[0],c[0]))
```

```
K= 1.3404 at 273 K.
At equilibrium, CF3OH = 1.74E-03 mol/L, COF2 = 0.04826 mol/L, HF = 0.04
826 mol/L.
```

```
In [17]: K1 = 2.926
         T1 = 298 #K
         T2 = 323 #K
         K2 = K1*np.exp(-dH/R*(1/T2-1/T1))
         print('K=', round(K2,4), 'at 323 K.')
         x = symbols('x',positive=True)
         c = solve(x**2-(0.05-x)*K2,x)
         print('At equilibrium, CF3OH = %.2E mol/L, COF2 = %.5f mol/L, HF = %.5f
          mol/L.'%(0.05-c[0],c[0],c[0]))
```

```
K= 5.6601 at 323 K.
At equilibrium, CF3OH = 4.34E-04 mol/L, COF2 = 0.04957 mol/L, HF = 0.04
957 mol/L.
```

Therefore, the at higher temperatures, the reaction shifts towards the products.

15. How, directionally, would your answer to Question 13 change if the vessel had a volume of 5 L? Redo the calculation at this volume to verify your guess.

If V = 5L, the initial concentration = $\frac{1\,mol}{5\,L} = .2\,M$

$$K_c = \frac{x^2}{0.2 - x}$$

At 298 K, Kc = 2.926 (from problem 12)

```
In [24]:  T = 298 #K
          R = 8.314
          Kc = np.exp(-dG*1000/(R*T))
          print('At 298 K, Kc = %.3f (unitless). '%(Kc))
          x = symbols('x',positive=True)
          c = solve(x**2-(0.2-x)*Kc,x)
          print('At equilibrium, CF3OH = %.2E mol/L, COF2 = %.5f mol/L, HF = %.5f
           mol/L.'%(0.2-c[0],c[0],c[0]))
          print('At equilibrium, CF3OH = %.2E mol, COF2 = %.5f mol, HF = %.5f mo
          l.'%((0.2-c[0])*5,c[0]*5,c[0]*5))
          print('At a smaller volume, the concentration of products increases, but
          the number of moles decreases.')
```

```
At 298 K, Kc = 2.926 (unitless).
At equilibrium, CF3OH = 1.21E-02 mol/L, COF2 = 0.18793 mol/L, HF = 0.18
793 mol/L.
At equilibrium, CF3OH = 6.03E-02 mol, COF2 = 0.93965 mol, HF = 0.93965
mol.
At a smaller volume, the concentration of products increases, but the n
umber of moles decreases.
```

16. Consult a thermodynamics source (e.g. https://webbook.nist.gov/chemistry/ (https://webbook.nist.gov/chemistry/)) to determine $\Delta H°$ (298 K), $\Delta S°$ (298 K), and $\Delta G°$ (298 K) for the homologous reaction CH_3OH (g)$\rightarrow$ H_2O (g) + H_2CO (g). Does the substitution of F by H make the reaction more or less favorable?

In [27]:
```python
T = 298 #K
#All values were taken from NIST

#Methanol
Hm = -205 #kJ/mol
Sm = .2399 #kJ/mol K
Gm = Hm - T*Sm #kJ/mol

#Hydrogen
Hh = 0
Sh = .13068 #J/mol K
Gh = Hh - T*Sh #kJ/mol

#Formaldehyde
Hf = -108.6 #kJ/mol
Sf = .21895 #kJ/mol K
Gf = Hf - T*Sf #kJ/mol


delta_H = Hf+Hh-Hm #kJ/mol
delta_S = Sf+Sh-Sm #kJ/mol K
delta_G = Gf+Gh-Gm #kJ/mol

print('Delta H =',delta_H,'kJ/mol.')
print('Delta S =',delta_S,'kJ/mol K.')
print('Delta G =',delta_G,'kJ/mol.')

print('Therefore, by substituting F with H makes the reaction less favor
able.')
```

```
Delta H = 96.4 kJ/mol.
Delta S = 0.10973 kJ/mol K.
Delta G = 63.70046000000002 kJ/mol.
Therefore, by substituting F with H makes the reaction less favorable.
```

In [0]: