Chem 30324, Spring 2017, Homework 11

Due May 5, 2017

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/mol
         V = 0.02 # m^3
         c = 2.99792e10 # cm/s
         B = 1.931 # cm^-1
         v = 2156.6 # cm^-1
```

```
In [2]:  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('T_trans = {0:.3e} K, T_rot = {1:.3f} K, T_vib = {2:0.2f} K.'.form
         at(T_trans,T_rot,T_vib))

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

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.

$$q_{rot} = \frac{1}{\sigma}\frac{T}{\theta_{rot}} = \frac{T}{\theta_{rot}}, \quad q_{vib} = \frac{1}{1-e^{-\theta_{vib}/T}}$$

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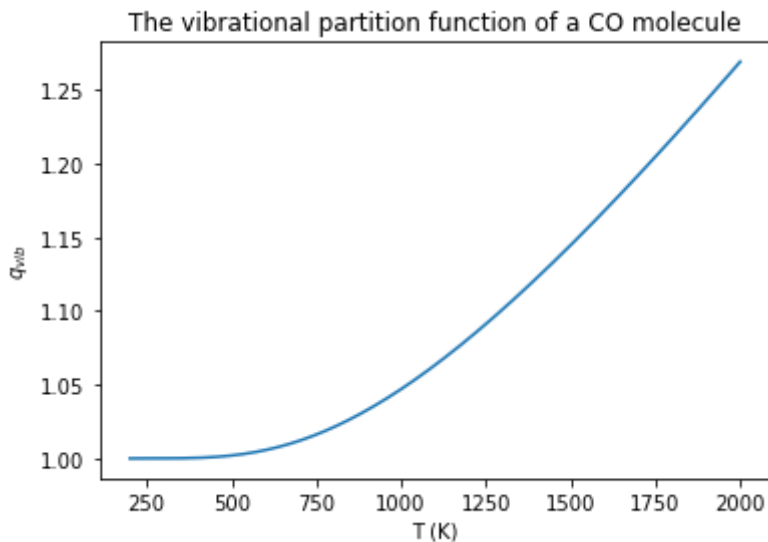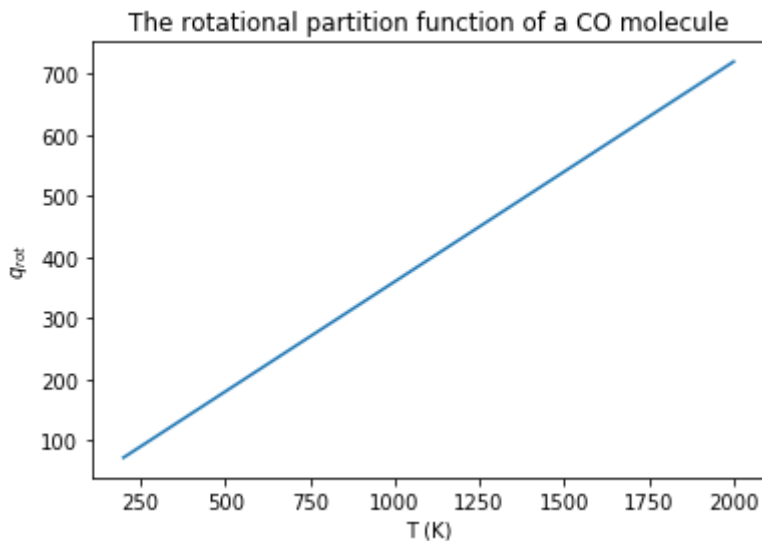
4. Plot the *total translational, rotational, and vibrational energies* of CO in the bottle from T = 200 to 2000 K (assume the CO remains a gas over the whole range). Which (if any) of the three types of motions dominate the total energy?

$$U_{trans} = \frac{3}{2}RT, \; U_{rot} = RT, \; U_{vib} = R\frac{\theta_{vib}}{e^{\theta_{vib}/T}-1}.$$

```
In [5]:  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()
```
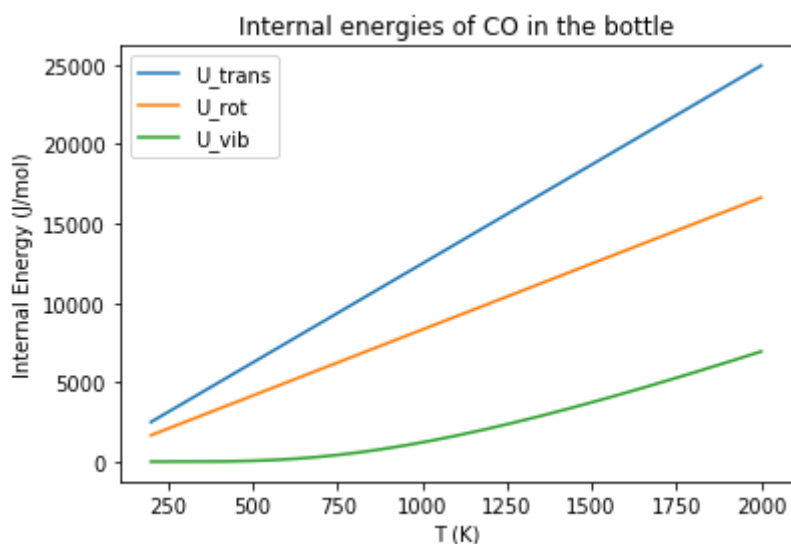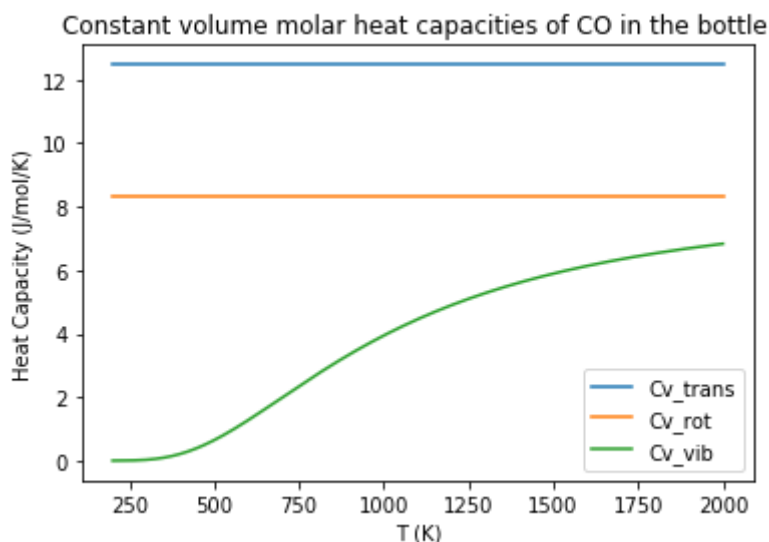

Translation dominates the total energy.

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 [6]: 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()
```
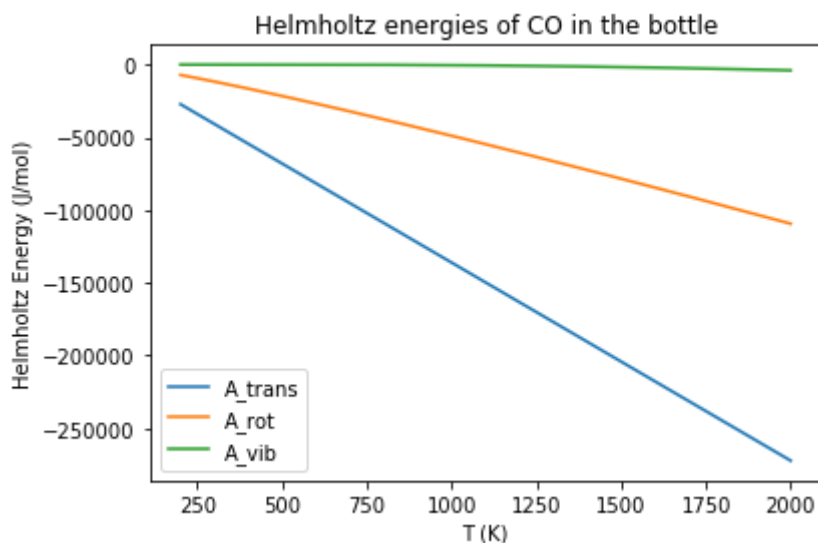

Translation dominates the heat capacity.

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 [7]:  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()
```


Translation dominates the Helmholtz energy.

7. Use your formulas to calculate ΔP, ΔU, ΔA, 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 [8]:  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.
```

Equilibrium constants from first principles.

In 1996, Schneider and co-workers reported calculations on the energetics of decomposition of trifluoromethanol, a reaction of relevance to the atmospheric degradation of hydrofluorocarbon refrigerants (*J. Phys. Chem.* 1996, *100*, 6097-6103):

$$CF_3OH \rightarrow COF_2 + HF$$

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

	CF_3OH	$[CF_3OH]^+$	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	

8. Make a rough estimate of $\Delta S°$ (298 K), in J mol^{-1} K^{-1} , assuming a 1 bar standard state. (*Hint:* What degrees of freedom will dominate the entropy?)

Translation degrees of freedom will dominate the entropy. $S_{trans} = Rln\left(\frac{e^{5/2}k_BT}{P°\Lambda^3}\right) = Rln\left(\frac{e^{5/2}k_BT}{P°}\frac{q_{trans}}{V}\right)$

$\Delta S° = S_{products} - S_{reactants}$.

```
In [10]: q_trans = [7.72e32,1.59e32,8.65e31] # 1/m^3
         T = 298 # K
         def S(q):
             return R*np.log(np.exp(2.5)*kB*T/100000*q)

         deltaS = S(q_trans[1]) + S(q_trans[2]) -S(q_trans[0])
         print('delta S = {:.3f} J/mol/K.'.format(deltaS))

         delta S = 133.072 J/mol/K.
```

9. Using the data provided, determine $\Delta U°$ (298 K) and $\Delta H°$ (298 K), in kJ mol $^{-1}$.

$$\Delta U° = U_{products} - U_{reactants}$$

$$U = U_{trans} + U_{rot} + U_{vib} + E_{elec} + ZPE$$

$$\Delta U° = 18.643 kJ/mol$$

$$\Delta H° = \Delta U° + P\Delta V$$

$$\Delta V = \frac{2RT}{P} - \frac{RT}{P} = \frac{RT}{P}$$

$$\Delta H° = 18.643 + P\frac{RT}{P} = 21.121 kJ/mol$$

10. Using the data provided, determine K_c (298 K), assuming a 1 mole/liter standard state.

```
In [13]:  Eelec = [-412.90047,-312.57028,-100.31885] # Ha
          ZPE = [0.02889,0.01422,0.00925] # Ha
          deltaE0 = (Eelec[1] + ZPE[1] + Eelec[2] + ZPE[2] - (Eelec[0] +
          ZPE[0]))*4.3598e-18 # J

          q_rot = [61830,679,9.59]
          q_vib = [2.33,1.16,1]
          q= [0,0,0]
          for i in (0,1,2):
              q[i] = q_trans[i]*q_rot[i]*q_vib[i]
          C0 = NA/0.001
          Kc = q[1]*q[2]/q[0]*(1/C0)*np.exp(-deltaE0/kB/T)
          print('Kc = {:.3f}.'.format(Kc))

          Kc = 2.926.
```

11. 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)?

```
In [14]:   from sympy import *
           x = symbols('x',positive=True)
           c = solve(x**2-(0.05-x)*Kc,x)
           print('At equilibrium, CF3OH = {0:.2E} mol/L, COF2 = {1:.4f} mol/L, HF =
             {2:.4f} mol/L.'.format(0.05-c[0],c[0],c[0]))
```

At equilibrium, CF3OH = 8.26E-4 mol/L, COF2 = 0.0492 mol/L, HF = 0.0492
mol/L.

12. How, directionally, would your answer to Question 11 change if the vessel was at a higher temperature? Why, in statistical mechanical terms?

The reaction is endothermic so will be driven towards the products as temperature is increased. From a stat. mech perspective as more energy is dumped into the system higher energy states become more accessible allowing an easier transition into products.

13. How, directionally, would your answer to Question 11 change if the vessel had a volume of 5 L? Why, in statistical mechanical terms?

The equilibrium will be driven more to the reactant, but there will be no change to the equilibrium constant. This is because the partition function is proportional to V , so qi/V is not proportional to volume so it will have no effect. However, the position of equilibrium will change because of the change of volume. When there is a decrease in volume and increase in concentration, the equilibrium will shift to favor the direction that produces fewer moles of gas, to keep Kc as a constant.

WFS: What Yujia writes is absolutely correct; the volume-dependence of the equilibrium is contained in the concentration ratio, not in the equilibrium constant itself. From a stat mech perspective, the number of translational states available to a molecule is proportional to volume. Increasing volume increasingly favors the side of the reaction with more molecules, which can take greater advantage of the more available states. By corrolary, decreasing volume has the opposite effect.

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In [ ]:
```