#1

Tanner Corrado
Thermo HW #6

1. $q = \sum_i e^{-\varepsilon(v)\beta} = e^0 + 3e^{-\varepsilon\beta} + 2e^{-2\varepsilon\beta}$

$$\boxed{q = 1 + 3e^{-\varepsilon/k_BT} + 2e^{-2\varepsilon/k_BT}}$$

2. $$P_i = \frac{e^{-\varepsilon_i/k_BT}}{\underbrace{\sum_i e^{-\varepsilon_i/k_BT}}_{q}} \Rightarrow P_{\varepsilon=0} = \frac{1}{q} \qquad P_{\varepsilon=\varepsilon} = \frac{3e^{-\varepsilon/k_BT}}{q} \qquad P_{\varepsilon=2\varepsilon} = \frac{2e^{-2\varepsilon/k_BT}}{q}$$

For the plots, I assumed a value of $\varepsilon = 1$, requiring extremely large temperatures to see the shape. A more valid assumption with a very small value of ε (such as $\varepsilon/k_B = 300$ K as in later problems) gives more reasonable T ranges. However, the probabilities in the limits of $T \to 0$ and $T \to \infty$ shouldn't change.

	$T \to 0$	$T \to \infty$
0	1	1/6
ε	0	1/2
2ε	0	1/3

See attached plot.

3. $u = \sum \varepsilon_i P(\varepsilon_i) \Rightarrow u = P_{\varepsilon=0} \cdot 0 + P_{\varepsilon=\varepsilon}\,\varepsilon + P_{\varepsilon=2\varepsilon}\,2\varepsilon$

$$u = \frac{1}{q} \cdot 0 + \frac{3e^{-\varepsilon/k_BT}}{q} \cdot \varepsilon + \frac{2e^{-2\varepsilon/k_BT} \cdot 2\varepsilon}{q}$$

$$\boxed{u = \frac{3\varepsilon e^{-\varepsilon/k_BT}}{q} + \frac{4\varepsilon e^{-2\varepsilon/k_BT}}{q}}$$

$$\boxed{T \to 0,\ u \to 0 \quad , \quad T \to \infty,\ u \to \frac{7}{6}\varepsilon}$$

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4. $\frac{U}{N} = \frac{-\partial \ln q}{\partial \beta} = \frac{-1}{q}\frac{\partial q}{\partial \beta}$, $q = 1 + 3e^{-\varepsilon\beta} + 2e^{-2\varepsilon\beta}$

$$\frac{\partial q}{\partial \beta} = -3\varepsilon e^{-\varepsilon\beta} - 4\varepsilon e^{-2\varepsilon\beta} \Rightarrow \frac{-1}{q}\frac{\partial q}{\partial \beta} = \frac{3\varepsilon e^{-\varepsilon\beta}}{q} + \frac{4\varepsilon e^{-2\varepsilon\beta}}{q}$$

$$\boxed{u = \frac{3\varepsilon e^{-\varepsilon\beta}}{q} + \frac{4\varepsilon e^{-2\varepsilon\beta}}{q} \qquad \text{Yes, it agrees with 3.}}$$

5. $f = \frac{-\ln q}{\beta} \Rightarrow \frac{-\ln q}{\beta} = \frac{-\ln\left(1 + 3e^{-\varepsilon/k_BT} + 2e^{-2\varepsilon/k_BT}\right)}{\frac{1}{k_BT}}$

$$\frac{\varepsilon}{k_B} = 300\,K \Rightarrow \boxed{f = -k_BT \cdot \ln\left(1 + 3e^{-300/T} + 2e^{-600/T}\right)}$$

6. $S = \frac{U}{T} + k_B \ln q \Rightarrow S = \frac{3\varepsilon e^{-\varepsilon/k_BT} + 4\varepsilon e^{-2\varepsilon/k_BT}}{q} + k_B \ln q$

$$\boxed{S = \frac{900\,k_B\,e^{-300/T} + 1200\,k_B\,e^{-600/T}}{1 + 3e^{-300/T} + 2e^{-600/T}} + k_B \ln\left(1 + 3e^{-300/T} + 2e^{-600/T}\right)}$$

7. As $T \to 0$, $S \to 0$ which agrees with the 3rd Law, and as $T \to 0$ everything goes to the lowest energy conformation ground state ($\varepsilon = 0$).

8. If it was degenerate, S would not decrease to zero, instead going to a finite value. This violates the 3rd Law.

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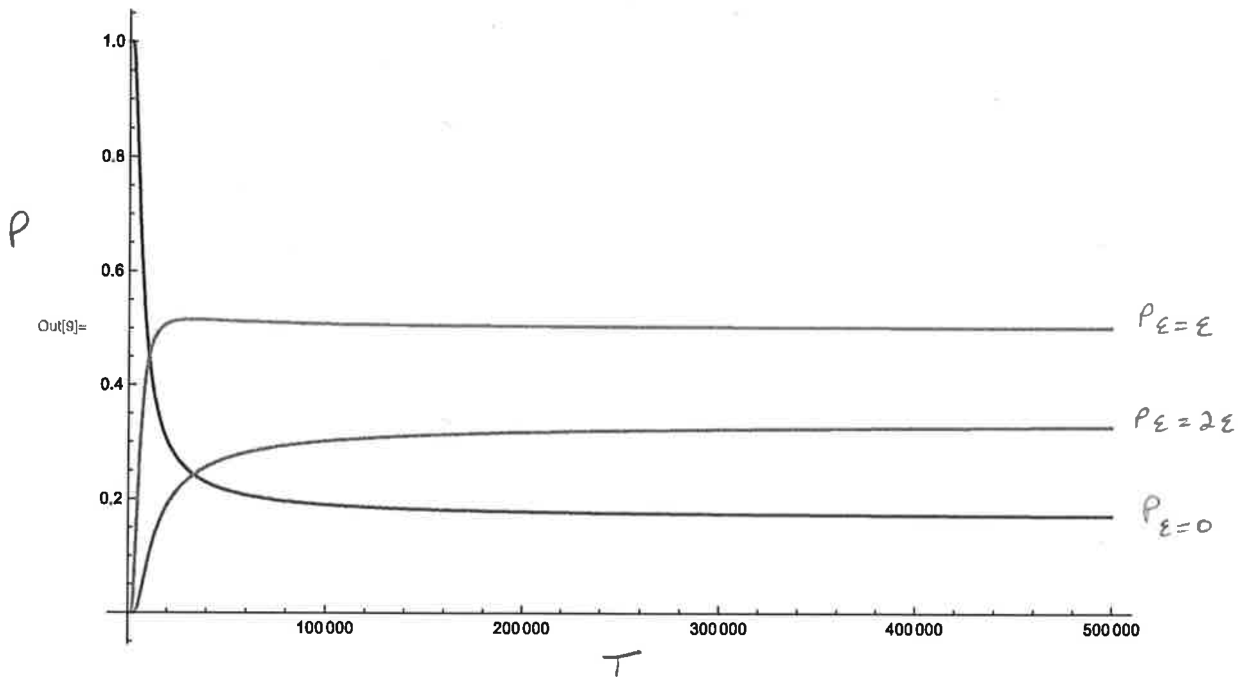
Thermo HW 6 #1.2

```
In[9]:= Plot[{p1 = 1/(1+3*Exp[-1/((8.617*10^-5)*T)] + 2*Exp[-2/((8.617*10^-5)*T)]),
   p2 = (3*Exp[-1/((8.617*10^-5)*T)]) /
     (1+3*Exp[-1/((8.617*10^-5)*T)] + 2*Exp[-2/((8.617*10^-5)*T)]),
   p3 = (2*Exp[-2/((8.617*10^-5)*T)]) / (1+3*Exp[-1/((8.617*10^-5)*T)] +
       2*Exp[-2/((8.617*10^-5)*T)])}, {T, 0, 500000}]
```

Out[9]=



In[10]:=

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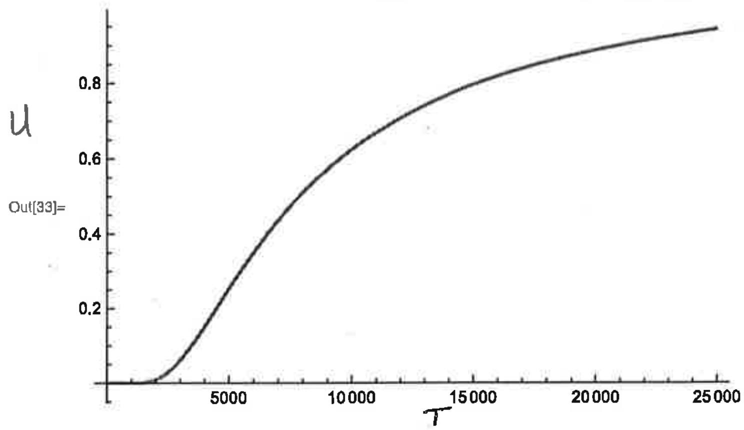
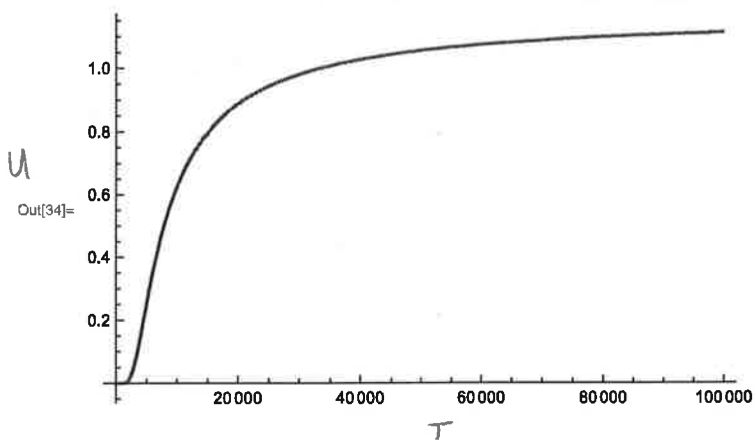
In[33]:=
```
Plot[U = ((3 * Exp[-1 / ((8.617 * 10^-5) * T)]) /
      (1 + 3 * Exp[-1 / ((8.617 * 10^-5) * T)] + 2 * Exp[-2 / ((8.617 * 10^-5) * T)])) +
    (2 * ((2 * Exp[-2 / ((8.617 * 10^-5) * T)]) / (1 + 3 * Exp[-1 / ((8.617 * 10^-5) * T)] +
          2 * Exp[-2 / ((8.617 * 10^-5) * T)]))), {T, 0, 25000}, PlotRange → Full]
```

Out[33]=



In[34]:=
```
Plot[U = ((3 * Exp[-1 / ((8.617 * 10^-5) * T)]) /
      (1 + 3 * Exp[-1 / ((8.617 * 10^-5) * T)] + 2 * Exp[-2 / ((8.617 * 10^-5) * T)])) +
    (2 * ((2 * Exp[-2 / ((8.617 * 10^-5) * T)]) / (1 + 3 * Exp[-1 / ((8.617 * 10^-5) * T)] +
          2 * Exp[-2 / ((8.617 * 10^-5) * T)]))), {T, 0, 100000}, PlotRange → Full]
```

Out[34]=



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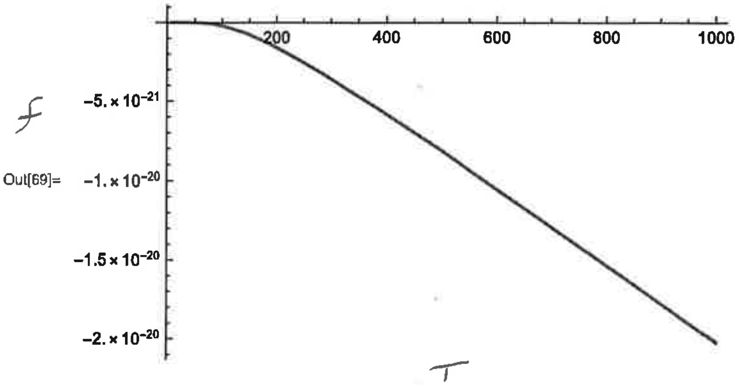
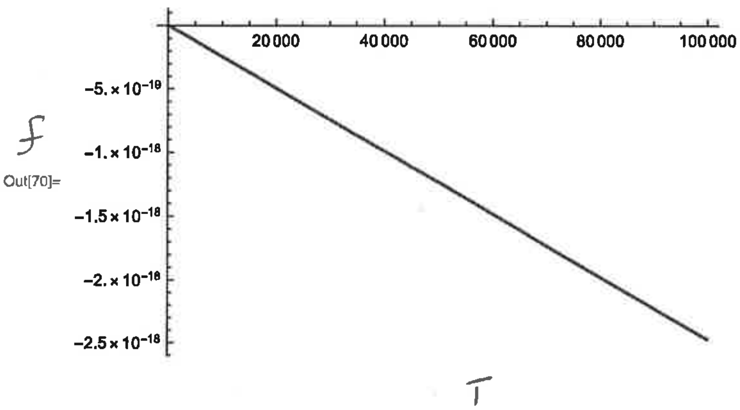
```
In[69]:= Plot[f = -1 * (1.381 * 10^-23) * T * Log[1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T])],
  {T, 0, 1000}, PlotRange → All]
```

Out[69]=




```
In[70]:= Plot[f = -1 * (1.381 * 10^-23) * T * Log[1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T])],
  {T, 0, 100 000}, PlotRange → All]
```

Out[70]=



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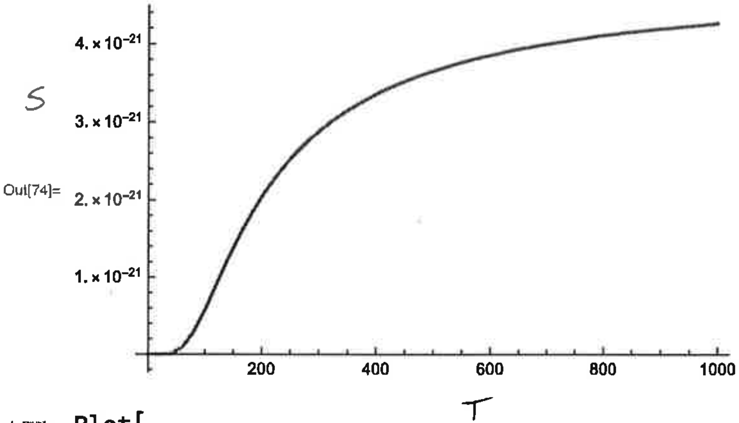
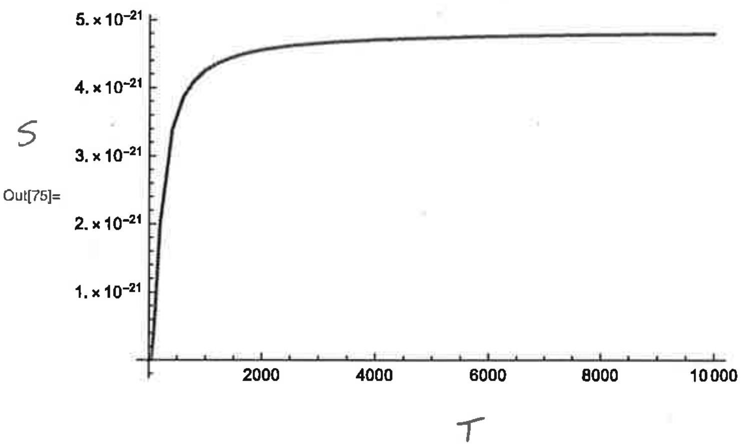
In[74]:=
```
Plot[
 s = (((900 * (1.381 * 10^-23) * Exp[-300 / T]) + (1200 * (1.381 * 10^-23) * Exp[-600 / T])) /
      (1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T]))) +
    ((1.381 * 10^-23) * Log[1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T])]),
 {T, 0, 1000}, PlotRange → All]
```

Out[74]=



In[75]:=
```
Plot[
 s = (((900 * (1.381 * 10^-23) * Exp[-300 / T]) + (1200 * (1.381 * 10^-23) * Exp[-600 / T])) /
      (1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T]))) +
    ((1.381 * 10^-23) * Log[1 + (3 * Exp[-300 / T]) + (2 * Exp[-600 / T])]),
 {T, 0, 10 000}, PlotRange → All]
```

Out[75]=



Problem 2

Tanner Corrado

1. Translational $\quad \varepsilon = \varepsilon_o N^2, \quad N = 1, \quad \varepsilon = \varepsilon_o \Rightarrow \varepsilon_o = \dfrac{\pi^2 h^2}{2 m L^2}, \quad \theta_{trans} = \dfrac{\varepsilon_o}{k_B}$

$P = 1$ bar, $B = 0.3836\ cm^{-1}$, $\mu_i = 2349, 1388, 667, 667\ cm^{-1}$, $L = 1\ dm^3$

$MW\ CO_2 = 44.01\ \frac{g}{mol} \quad N_A = 6.022 \times 10^{23}\ \frac{molc}{mol}$

$$\varepsilon_o = \frac{\pi^2 (6.626 \times 10^{-34}\ J \cdot s)^2}{2 \left(\dfrac{44.01 \frac{g}{mol} \cdot \frac{1\ kg}{1000 g}}{6.022 \times 10^{23} \frac{molc}{mol}} \right) (0.1\ m)^2} \qquad \varepsilon_o = 2.964 \times 10^{-39}\ \frac{J^2 s^2}{kg \cdot m^2} = \frac{J^2}{J} = J$$

$$\theta_{trans} = \frac{2.964 \times 10^{-39}\ J}{1.381 \times 10^{-23}\ \frac{J}{K}} \Rightarrow \boxed{\theta_{trans} = 2.147 \times 10^{-16}\ K}$$

Rotational $\quad \varepsilon_{rot} = hcB \qquad \theta_{rot} = \dfrac{\varepsilon_{rot}}{k_B}$

$$\varepsilon_{rot} = 6.626 \times 10^{-34}\ J \cdot s \cdot 2.998 \times 10^8\ \frac{m}{s} \cdot 38.36\ \frac{1}{m} \Rightarrow \varepsilon_{rot} = 7.62 \times 10^{-24}\ J$$

$$\theta_{rot} = \frac{7.62 \times 10^{-24}\ J}{1.381 \times 10^{-23}\ \frac{J}{K}} \Rightarrow \boxed{\theta_{rot} = 0.55\ K}$$

Vibrational $\quad \theta_{vib} = \dfrac{h\nu}{k_B} \qquad \nu = c\tilde{\nu} \qquad \tilde{\nu} = \mu_i = 2349, 1388, 667, 667\ cm^{-1}$

$$\theta_{vib,1} = \frac{hc\tilde{\nu}}{k_B} = \frac{6.626 \times 10^{-34}\ J \cdot s \cdot 2.998 \times 10^8\ \frac{m}{s} \cdot 234900\ \frac{1}{m}}{1.381 \times 10^{-23}}$$

$$\boxed{\theta_{vib,1} = 3379\ K}$$

$$\theta_{vib,2} = \frac{h\,c \cdot 138800\ \frac{1}{m}}{k_B} \Rightarrow \boxed{\theta_{vib,2} = 1997\ K}$$

$$\theta_{vib,3,4} = \frac{h \cdot c \cdot 66700\ \frac{1}{m}}{k_B} \Rightarrow \boxed{\theta_{vib,3,4} = 959\ K}$$

Tamer Conrado

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

$U_{rot} = RT$ (linear molecule)

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

$$U_{vib} = R \left[\frac{3379}{e^{3379/T} - 1} + \frac{1997}{e^{1997/T} - 1} + 2 \left(\frac{959}{e^{959/T} - 1} \right) \right.$$

At lower temps, U_{trans} and U_{rot} dominate more, however at higher temps, U_{vib} begins to dominate.

3. $$f_{trans} = \frac{-N \ln q_{trans}}{\beta} = \boxed{-N k_B T \ln \left(\frac{V}{h^3 \left(\frac{1}{2\pi m k_B T} \right)^{3/2}} \right)}$$

$V = \frac{RT}{P} = \frac{8.314 \cdot T}{100000 \, Pa}$, $h = 6.626 \times 10^{-34}$ J·s, $m = 7.31 \times 10^{-26}$ kg

$k_B = 1.381 \times 10^{-23} \frac{J}{K}$

$$f_{rot} = \frac{-N \ln q_{rot}}{\beta} = -N k_B T \ln \left(\frac{1}{\sigma} \frac{T}{\theta_{rot}} \right) \Rightarrow \boxed{f_{rot} = -RT \ln (0.9091 T)}$$

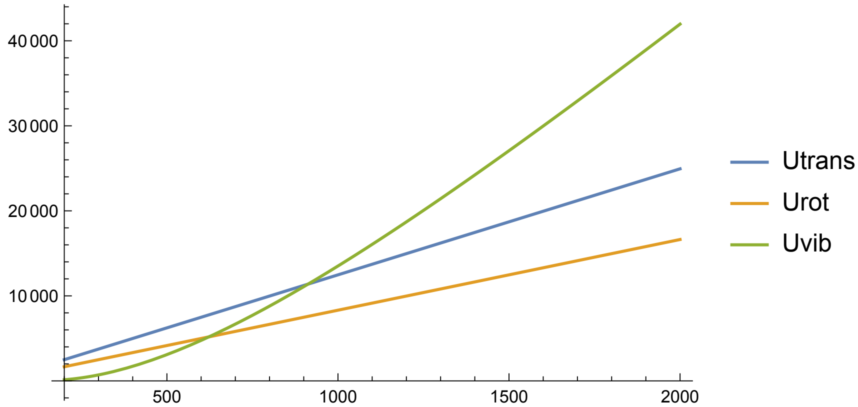
$$f_{vib} = \frac{-N \ln q_{vib}}{\beta} = -RT \ln \left(\prod_i \frac{1}{1 - e^{-\theta_{vib}/T}} \right)$$

$$\boxed{f_{vib} = -RT \ln \left[\left(\frac{1}{1 - e^{-3379/T}} \right) \left(\frac{1}{1 - e^{-1997/T}} \right) \left(\frac{1}{1 - e^{-959/T}} \right)^2 \right]}$$

$\boxed{\text{$f_{trans}$ tends to dominate helmholtz energy}}$

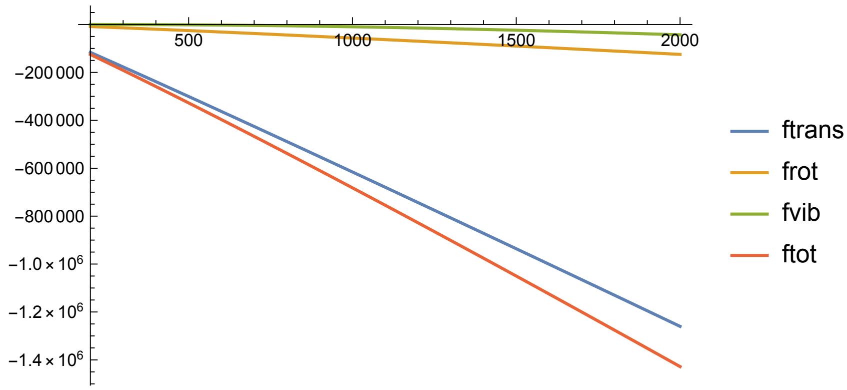
In[4]:=
```
Plot[{Utrans = (3 / 2) * 8.314 * T,
  Urot = 8.314 * T, Uvib = 8.314 * ((3379 / (Exp[3379 / T] - 1)) +
      (1997 / (Exp[1997 / T] - 1)) + ((2 * 959) / (Exp[959 / T] - 1)))},
 {T, 200, 2000}, PlotLegends → {"Utrans", "Urot", "Uvib"}]
```

Out[4]=



In[6]:=
```
Plot[{ftrans = -8.314 * T * (Log[(8.314 * T / 100 000) / (((6.626 * 10 ^ -34) ^ 3) *
        (1 / ((2 * 3.14 * (7.31 * 10 ^ -26) * (1.381 * 10 ^ -23) * T) ^ (3 / 2))))]),
  frot = -8.314 * T * Log[T / 1.1], fvib = -8.314 * T * Log[(1 / (1 - Exp[-3379 / T])) *
     (1 / (1 - Exp[-1997 / T])) * ((1 / (1 - Exp[-959 / T])) ^ 2)],
  ftot = (-8.314 * T * (Log[(8.314 * T / 100 000) / (((6.626 * 10 ^ -34) ^ 3) *
          (1 / ((2 * 3.14 * (7.31 * 10 ^ -26) * (1.381 * 10 ^ -23) * T) ^ (3 / 2))))])) +
    (-8.314 * T * Log[T / 1.1]) + (-8.314 * T * Log[(1 / (1 - Exp[-3379 / T])) *
        (1 / (1 - Exp[-1997 / T])) * ((1 / (1 - Exp[-959 / T])) ^ 2)])},
 {T, 200, 2000}, PlotLegends → {"ftrans", "frot", "fvib", "ftot"}]
```

Out[6]=



Tanner Corrado

4. $$\boxed{\begin{aligned} C_{v,\,trans} &= \frac{3}{2}R \\ C_{v,\,rot} &= R \end{aligned}}$$

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

$$\boxed{C_{v,\,vib} = R \left[\left(\frac{3379 \cdot e^{3379/2T}}{T\left(e^{3379/T} - 1\right)} \right)^2 + \left(\frac{1997 \cdot e^{1997/2T}}{T\left(e^{1997/T} - 1\right)} \right)^2 + 2 \left(\frac{959 \cdot e^{959/2T}}{T\left(e^{959/T} - 1\right)} \right)^2 \right]}$$

$$C_{v,\,total} = C_{v,\,trans} + C_{v,\,rot} + C_{v,\,vib}$$

C_v is dominated by $C_{v,\,trans}$ and $C_{v,\,rot}$ at lower temps, but $C_{v,\,vib}$ dominates at higher temps.

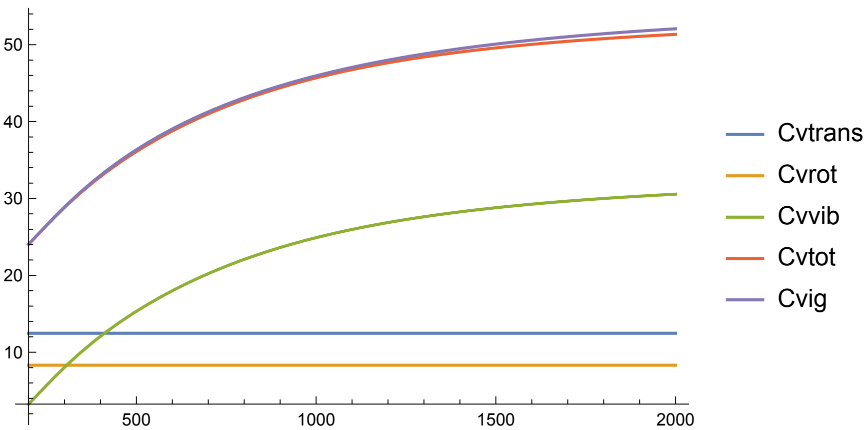
Problem 3

$C_p^{ig}(t)$ with $t = \frac{T(K)}{1000}$ converted to C_v^{ig} by $C_p^{ig} - R = C_v^{ig}$

and $C_v^{ig}(T)$ plotted comparing to $C_v(T)$ from problem 3.4.

The expressions are nearly identical, with only slight deviations at higher temperatures.

```
Plot[{Cvtrans = (3 / 2) * 8.314, Cvrot = 8.314,
  Cvvib = 8.314 * ((((3379 * Exp[3379 / (2 * T)]) / ((T * (Exp[3379 / T]) - T))) ^2) +
      (((1997 * Exp[1997 / (2 * T)]) / ((T * (Exp[1997 / T]) - T))) ^2) +
      (2 * (((959 * Exp[959 / (2 * T)]) / ((T * (Exp[959 / T]) - T))) ^2))), Cvtot =
   ((5 / 2) * 8.314) + (8.314 * ((((3379 * Exp[3379 / (2 * T)]) / ((T * (Exp[3379 / T]) - T))) ^
          2) + (((1997 * Exp[1997 / (2 * T)]) / ((T * (Exp[1997 / T]) - T))) ^2) +
        (2 * (((959 * Exp[959 / (2 * T)]) / ((T * (Exp[959 / T]) - T))) ^2)))),
  Cvig = -11.401074 - 55.231532 * (T / 1000) + (5.149108 * (T / 1000) ^2) -
    (0.29158 * (T / 1000) ^3) + (0.110128 * (T / 1000) ^ (-2)) +
    (115.93493 * (T / 1000) ^ (1 / 2)) - 8.314},
 {T, 200, 2000}, PlotRange → All, PlotLegends →
  {"Cvtrans", "Cvrot", "Cvvib", "Cvtot", "Cvig"}]
```




```
Cvtrans = (3 / 2) * 8.314
Cvrot = 8.314
Cvvib = 8.314 * ((((3379 * Exp[3379 / (2 * T)]) / ((T * (Exp[3379 / T]) - T))) ^2) +
    (((1997 * Exp[1997 / (2 * T)]) / ((T * (Exp[1997 / T]) - T))) ^2) +
    (2 * (((959 * Exp[959 / (2 * T)]) / ((T * (Exp[959 / T]) - T))) ^2)))
Cvtot = ((5 / 2) * 8.314) + (8.314 *
    ((((3379 * Exp[3379 / (2 * T)]) / ((T * (Exp[3379 / T]) - T))) ^2) +
      (((1997 * Exp[1997 / (2 * T)]) / ((T * (Exp[1997 / T]) - T))) ^2) +
      (2 * (((959 * Exp[959 / (2 * T)]) / ((T * (Exp[959 / T]) - T))) ^2))))
```

12.471

8.314

$$8.314 \left(\frac{1\,839\,362\, e^{959/T}}{\left(-T + e^{959/T}\, T\right)^2} + \frac{3\,988\,009\, e^{1997/T}}{\left(-T + e^{1997/T}\, T\right)^2} + \frac{11\,417\,641\, e^{3379/T}}{\left(-T + e^{3379/T}\, T\right)^2} \right)$$

$$20.785 + 8.314 \left(\frac{1\,839\,362\, e^{959/T}}{\left(-T + e^{959/T}\, T\right)^2} + \frac{3\,988\,009\, e^{1997/T}}{\left(-T + e^{1997/T}\, T\right)^2} + \frac{11\,417\,641\, e^{3379/T}}{\left(-T + e^{3379/T}\, T\right)^2} \right)$$

Problem 4

Tanner Conrado

1. $q_{site} = \sum \text{internal DOFs} = q_{vib} \cdot q_{rot}$

(2-fold dgenerate)

$$q_{vib} = \prod \frac{1}{1-e^{-\theta_{vib}/T}} \quad , \quad \theta_{vib} = \frac{h\nu c}{k_B} \quad , \quad \nu_1 = 500 \text{ cm}^{-1}, \quad \nu_2 = 150 \text{ cm}^{-1}, \quad \nu_3 = 2150 \text{ cm}^{-1}$$

$$\theta_{vib,1} = 719.7 \quad , \quad \theta_{vib,2} = 216 \quad , \quad \theta_{vib3} = 3088$$

$$q_{vib,1} = \frac{1}{1-e^{-719.7/600}} \quad , \quad q_{vib,2} = \frac{1}{1-e^{-216/600}} \quad , \quad q_{vib,3} = \frac{1}{1-e^{-3088/600}}$$

$$q_{vib} = (1.43)(3.3077)^2(1.006) \Rightarrow \underline{q_{vib} = 15.739}$$

$$q_{rot} = \frac{1}{\sigma}\frac{T}{\theta_{rot}} \quad , \quad \theta_{rot} = \frac{hcB}{k_B} \quad , \quad B = 1.931 \text{ cm}^{-1} \quad , \quad c = 2.998 \times 10^8 \frac{m}{s}, \quad \sigma = 1 \text{ (not symmetric)}$$

$$\theta_{rot} = 2.78 \Rightarrow q_{rot} = 1 \cdot \frac{600}{2.78} \Rightarrow \underline{q_{rot} = 215.8}$$

$$q_{site} = q_{vib} \cdot q_{rot} \Rightarrow \boxed{q_{site} = 3397}$$

$q_{gas} = q_{trans} \cdot q_{vib} \cdot q_{rot} \longrightarrow$ q_{rot} is the same $q_{rot} = 215.8$

q_{vib} only is the stretch vib, $q_{vib} = 1.006$

$$q_{trans} = \frac{V}{\Lambda^3} \quad , \quad \Lambda = h\left(\frac{1}{k_B T\, 2\pi m}\right)^{1/2} \qquad m = 28.01 \frac{g}{mol} \cdot \frac{1}{6.022 \times 10^{23} \frac{mole}{mol}} \cdot \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$m = 4.651 \times 10^{-26} \text{ kg}$$

$$V = \frac{RT}{P} = \frac{8.314 \cdot 600 \text{ K}}{100{,}000 \text{ Pa}} = \frac{0.04988 \frac{m^3}{mol}}{6.022 \times 10^{23} \frac{1}{mol}} = 8.29 \times 10^{-26} \text{ m}^3, \quad \Lambda = 1.35 \times 10^{-11}$$

$$q_{trans} = \frac{V}{\Lambda^3} = 3.37 \times 10^7 \Rightarrow q_{gas} = (3.37 \times 10^7)(215.8)(1.006)$$

$$\boxed{q_{gas} = 7.32 \times 10^9}$$

$$K(T) = \frac{q_{site}(T)}{q_{gas}(T)} e^{-\Delta E/k_B T} \Rightarrow \Delta E = \frac{150 \frac{kJ}{mol} \cdot \frac{1000 \text{ J}}{kJ}}{6.022 \times 10^{23} \frac{mole}{mol}} \Rightarrow \Delta E = 2.5 \times 10^{-19}$$

$$K(T) = \frac{3397}{7.32 \times 10^9} e^{-2.5 \times 10^{-19}/(1.38 \times 10^{-23} \cdot 600)} \Rightarrow \boxed{K(T) = 3.58 \times 10^{-20}}$$

2. $$\theta = \frac{K(T)\, P}{1 + K(T)\, P} \Rightarrow 0.5 = \frac{3.58 \times 10^{-20} \cdot P}{1 + (3.58 \times 10^{-20}) \cdot P} \Rightarrow \boxed{\begin{aligned} P &= 2.79 \times 10^{19} \text{ bar} \\ &= 2.79 \times 10^{24} \text{ Pa} \end{aligned}}$$

at 50% coverage