ASSIGNMENT 3 NE334- MATTHEW ATHANASOPOULOS

Q1) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

molecule	$H_2(^1\Sigma_g^+)$	$I_2(^1\Sigma_g^+)$	$HI(^1\Sigma^+)$
$B_e\,/\text{cm}^{-1}$	60.853	0.0373	6.4264
$\overline{\nu}_{\text{osc}}\,/\text{cm}^{-1}$	4401.21	214.50	2309.01
$D_0\,/\text{eV}$	4.47813	1.54238	3.0541

CALCULATE K_p:

Firstly, note there is no electronic degeneracy for Σ^+, meaning H_2, I_2, and HI.

$$K_p = \frac{\prod(\tilde{z}_{prod}/N_0)^{w_{prod}}}{\prod(\tilde{z}_{reac}/N_0)^{w_{reac}}} \cdot e^{-\Delta\vec{U}_0^\circ/k_BT} = \frac{(\tilde{z}^\circ_{H_2}/N_0)(\tilde{z}^\circ_{I_2}/N_0)}{(\tilde{z}^\circ_{HI}/N_0)^2} \cdot e^{-\Delta\vec{U}_0^\circ/k_BT} \qquad \boxed{k_B = \frac{R}{N_0}}$$

$$\Delta\vec{U}_0^\circ = -N_0\left[\sum D_0(prod) - \sum D_0(reac)\right] = -N_0\left[(4.47813\text{eV} + 1.54238\text{eV}) - 2(3.0541\text{eV})\right] = -N_0(-0.08769) = 0.08769\,N_0$$

$$\frac{\tilde{z}^\circ_{H_2}}{N_0} = 820.519\,(\bar{M}_{H_2})^{3/2}(T)^{5/2} \cdot \frac{T}{\sigma\,\theta_{rot_{H_2}}} \cdot \frac{1}{1-e^{-\theta_{vib_{H_2}}/T}} \cdot \cancel{w_{el}^{H_2}}^{=1} \qquad \sigma = 2 \qquad \theta_{rot_{H_2}} = \frac{B_{e_{H_2}}}{\bar{k}_B} = \frac{60.853\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 87.55348628\text{ K} \qquad \theta_{vib_{H_2}} = \frac{\bar{\nu}_{osc_{H_2}}}{\bar{k}_B} = \frac{4401.21\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 6332.330031\text{ K}$$

$$\frac{\tilde{z}^\circ_{I_2}}{N_0} = 820.519\,(\bar{M}_{I_2})^{3/2}(T)^{5/2} \cdot \frac{T}{\sigma\,\theta_{rot_{I_2}}} \cdot \frac{1}{1-e^{-\theta_{vib_{I_2}}/T}} \cdot \cancel{w_{el}^{I_2}}^{=1} \qquad \sigma = 2 \qquad \theta_{rot_{I_2}} = \frac{B_{e_{I_2}}}{\bar{k}_B} = \frac{0.0373\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 0.05366613048\text{ K} \qquad \theta_{vib_{I_2}} = \frac{\bar{\nu}_{osc_{I_2}}}{\bar{k}_B} = \frac{214.50\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 308.6162195\text{ K}$$

$$\frac{\tilde{z}^\circ_{HI}}{N_0} = 820.519\,(\bar{M}_{HI})^{3/2}(T)^{5/2} \cdot \frac{T}{\sigma\,\theta_{rot_{HI}}} \cdot \frac{1}{1-e^{-\theta_{vib_{HI}}/T}} \cdot \cancel{w_{el}^{HI}}^{=1} \qquad \sigma = 1 \qquad \theta_{rot_{HI}} = \frac{B_{e_{HI}}}{\bar{k}_B} = \frac{6.4264\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 9.246113162\text{ K} \qquad \theta_{vib_{HI}} = \frac{\bar{\nu}_{osc_{HI}}}{\bar{k}_B} = \frac{2309.01\text{ cm}^{-1}}{0.695038\text{ cm}^{-1}\text{K}^{-1}} = 3322.134905\text{ K}$$

$$K_p = \frac{\left(820.519\,(\bar{M}_{H_2})^{3/2}(T)^{5/2} \cdot \frac{T}{2\theta_{rot_{H_2}}} \cdot \frac{1}{1-e^{-\theta_{vib_{H_2}}/T}}\right)\left(820.519\,(\bar{M}_{I_2})^{3/2}(T)^{5/2} \cdot \frac{T}{2\theta_{rot_{I_2}}} \cdot \frac{1}{1-e^{-\theta_{vib_{I_2}}/T}}\right)}{\left(820.519\,(\bar{M}_{HI})^{3/2}(T)^{5/2} \cdot \frac{T}{\theta_{rot_{HI}}} \cdot \frac{1}{1-e^{-\theta_{vib_{HI}}/T}}\right)^2} \cdot e^{\left(-0.08769\text{eV}/(8.6173303\times10^{-5}\text{eV/K})(T)\right)}$$

Using the derived expression for K_p and substituting our calculated values for θ_{rot} and θ_{vib} for each molecule, we can write a script to calculate K_p as a function of the temperature from 300K to 3000K.

```
[73]: import matplotlib.pyplot as plt
      import seaborn as sns
      import pandas as pd
      import math

[74]: z_h2_rot, z_h2_vib, mw_h2 = 87.55348628, 6332.330031, 2.01568/1000 # Divide by 1000 to go from g/mol to kg/mol
      z_i2_rot, z_i2_vib, mw_i2 = 0.05366613048, 308.6162195, 253.8089/1000 # Divide by 1000 to go from g/mol to kg/mol
      z_hi_rot, z_hi_vib, mw_hi = 9.24611362, 3322.134905, 127.91241/1000 # Divide by 1000 to go from g/mol to kg/mol

      k_p = []
      temperature = list(range(300,3001))

      for T in temperature:
          z_h2 = 820.519 * ((mw_h2)**(3/2)) * (T**(5/2)) * (T/(2*z_h2_rot)) * (1/(1-(math.exp(-z_h2_vib/T))))
          z_i2 = 820.519 * ((mw_i2)**(3/2)) * (T**(5/2)) * (T/(2*z_i2_rot)) * (1/(1-(math.exp(-z_i2_vib/T))))
          z_hi = 820.519 * ((mw_hi)**(3/2)) * (T**(5/2)) * (T/(z_hi_rot)) * (1/(1-(math.exp(-z_hi_vib/T))))
          k_p.append(z_h2 * z_i2 / (z_hi**2) * math.exp(-0.08769/(8.6173303e-5*T)))

[78]: df = pd.DataFrame({'Temperature (K)':temperature, 'Equilibrium Constant (k_p)':k_p})
      sns.lineplot(data=df, x='Temperature (K)', y='Equilibrium Constant (k_p)')
      plt.title('Equilibrium Constant as a function of Temperature')

[78]: Text(0.5, 1.0, 'Equilibrium Constant as a function of Temperature')
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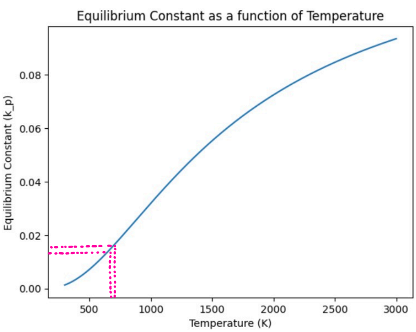

Journal of the ACS, Vol 63, issue 5, May 1941:

TABLE V

THE RATE OF DECOMPOSITION OF HYDROGEN AND DEUTERIUM IODIDES

Gas	Temp., °K.	Cell	Time, sec.	Mol./cc. HI start × 10⁴	Mol./cc. I_2 found	Z	k_2	k_2 av.	$K_{1/2}$
HI	698.6	7	7200	1.6812	0.09866	0.11734	1.204		
		6	9000	1.5680	.10368	.13225	1.224		
		5	10800	1.2178	.07787	.12789	1.250	1.242	
		2	12600	1.2031	.08602	.14300	1.289	±0.027	0.1350
DI	698.6	7	3600	2.0966	.05484	.05231	0.7395		
		8	7200	2.1654	.11169	.10316	.7765		
		2	10800	2.1273	.15025	.14126	.8019	0.777	
		6	10800	2.0732	.14142	.13643	.7822	±0.017	.1490
HI	666.8	1	14400	1.2267	.02609	.04254	.2715		
		8	16800	1.6543	.05232	.06325	.2488		
		2	18000	1.5187	.04800	.06322	.2528	0.259	
		5	22800	1.4285	.05436	.07610	.2622	±0.008	.1281
DI	666.8	2	14400	1.8537	.03906	.04214	.1661		
		6	21600	1.3786	.03346	.04853	.1731		
		1	21900	1.7770	.05247	.06157	.1657	0.1678	
		5	28800	1.9017	.07701	.08099	.1664	±0.0026	.1421

* They appear to be reasonably accurate.

Q2) a) The molecular partition function for a single particle z is defined as:

$z = \sum_r e^{-\beta \cdot E_r}$. Since $E = 0\ \forall r$, $z = \sum_{r=1}^{10} 1 = 10$.

So the molecular partition function z is 10.

b) For Two Distinguishable particles: $(E=0)$

$$z = \left(\sum e^{-\beta \cdot E_i}\right)\left(\sum e^{-\beta \cdot E_j}\right) = \left(\sum_{i=1}^{10} 1\right)\left(\sum_{j=1}^{10} 1\right) = (10)(10) = 100$$

For Two Identical Bosons:

$$z_{bosons} = \binom{z + N - 1}{N} = \binom{10+2-1}{2} = \binom{11}{2} = 55$$

z: canonical partition function for the system.
N: number of particles in the system.

For Two Identical Fermions:

$$z_{fermions} = \binom{z}{N} = \binom{10}{2} = 45$$

* This is because fermions obey the Pauli-Exclusion principle.

c) $Z_N = \dfrac{z^N}{N!}$

For Two Distinguishable particles:

$$Z_2 = \frac{100}{2!} = 50$$

For Two Identical Bosons:

$$Z_2 = \frac{55}{2!} = 27.5$$

For Two Identical Fermions:

$$Z_2 = \frac{45}{2!} = 22.5$$

d) For Two Distinguishable particles:

$$P_{same} = \frac{\#\text{ of Same State configurations}}{\#\text{ Total Configurations}} = \frac{10}{100} = 0.1 = 10\%$$

For Two Identical Bosons:

$$P_{same} = \frac{\#\text{ of Same State configurations}}{\#\text{ Total Configurations}} = \frac{10}{55} = \frac{2}{11} \approx 0.18181818 \approx 18.18\%$$

For Two Identical Fermions:

$P_{same} = 0$ the pauli-exclusion principle prohibits both particles from occupying the same state.