CHEM 2020: Homework 1

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1 Problem 1: Optimization with Lagrange Multipliers

Completed in Mathematica

2 Problem 2: N Distinguishable Particles Revisited

(1) Evaluate the canonical partition function, then use it to derive an expression for the thermodynamic energy E. How does your result compare with that of the microcanonical ensemble?
Noticing that this problem consists of N distinguishable, independent particles which may each occupy one of two states $i = \{0, 1\}$ with possible energies $E = i\epsilon = \{0, \epsilon\}$, one can write the total partition function over N-particle states j as $Q(N, V, T) = q^N$ for N single-particle partition functions q that each sum over the two possible states per-particle:

$$Q(N,V,T) = \sum_j e^{-\beta E_j} = q^N = \left[\sum_{i=0}^{1} e^{-\beta i\epsilon}\right]^N = \left(1 + e^{-\beta\epsilon}\right)^N . \tag{1}$$

From here, one might notice that thermodynamic energy $\langle E\rangle$ in the canonical ensemble is given by

$$\langle E\rangle = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{\sum_j -\frac{\partial}{\partial\beta} e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = -\frac{\partial}{\partial\beta}\sum_j e^{-\beta E_j}\left(\frac{1}{\sum_j e^{-\beta E_j}}\right) = -\frac{\partial Q}{\partial\beta}\frac{1}{Q}$$

which, upon substituting the expression for $Q(N, V, T)$ in Eqn. 1, yields the following:

$$\langle E\rangle = -\frac{\partial Q}{\partial\beta}\frac{1}{Q} = N\left(1 + e^{-\beta\epsilon}\right)^{N-1}\epsilon e^{-\beta\epsilon}\left(\frac{1}{\left(1 + e^{-\beta\epsilon}\right)^N}\right) = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$

If one multiplies this last expression by $e^{\beta E_j}\boldsymbol{e}^{\beta E_j}$, it is evident that is the same as the energy E of the microcanonical ensemble.
(2), **(3)** *Completed in Mathematica*

3 Problem 3: The Isothermal-Isobaric Ensemble

(1) Write down an expression for the probability $P_j(E,V)$ of occupying microstate j with volume V and energy E in the isothermal-isobaric ensemble.

$$P_j(E,V) = \frac{1}{\Delta(N,p,T)} e^{-\lambda_1 E_j(N,V)} e^{-\lambda_2 V} \tag{2}$$

(2) Propose an expression for $\bar{P}_j(E,V)$. What do you expect the $\bar{P}_j(E,V)$ surface to look like in the thermodynamic limit, and why? Solve for the Lagrange multipliers using this argument.

$$\bar{P}_j(E,V) = \frac{1}{\Delta(N,p,T)} \Omega(N,V,E) e^{-\lambda_1 E} e^{-\lambda_2 V}$$

In the thermodynamic limit, I would expect that thermodynamic energy is given by $\langle E \rangle = \sum_j \bar{P}_j E_j$, and that thermodynamic volume is given by $\langle V \rangle = \sum_j \bar{P}_j V_j$ where each member of the ensemble experiences changes in volume which are counteracted by a constant pressure over the total ensemble (i.e. if one member of the ensemble expands, another contracts). The microstates should also be normalized such that $\sum_j \bar{P}_j = 1$. We can thus determine the multipliers by considering

$$\left(\frac{\partial \bar{P}_j(E,V)}{\partial E}\right)_{E=\langle E \rangle} = \left(\frac{\partial \bar{P}_j(E,V)}{\partial V}\right)_{V=\langle V \rangle} = 0$$

Evaluating, we have

$$\begin{aligned} 0 = \left(\frac{\partial \bar{P}_j(E,V)}{\partial E}\right)_{E=\langle E \rangle} &= \frac{1}{\Delta}\frac{\partial}{\partial E}\left(e^{S(N,V,E)/k_B} e^{-\lambda_1 E} e^{-\lambda_2 V}\right) + \cancelto{0}{\mathcal{O}(\Delta^{-2})} \\ &= \frac{1}{\Delta} e^{-\lambda_1 E} e^{-\lambda_2 V} e^{S(N,V,E)/k_B}\left[\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right) - \lambda_1\right] \end{aligned}$$

which is only true for $\boxed{\lambda_1 = \frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right) = \frac{1}{k_B T}}$. Similarly,

$$\begin{aligned} 0 = \left(\frac{\partial \bar{P}_j(E,V)}{\partial V}\right)_{\bar{V}=\langle V \rangle} &= \frac{1}{\Delta}\frac{\partial}{\partial V}\left(e^{S(N,V,\bar{E})/k_B} e^{-\lambda_1 \bar{E}} e^{-\lambda_2 V}\right) + \cancelto{0}{\mathcal{O}(\Delta^{-2})} \\ &= \frac{1}{\Delta} e^{-\lambda_1 \bar{E}} e^{-\lambda_2 V} e^{S(N,V,\bar{E})/k_B}\left[\frac{1}{k_B}\left(\frac{\partial S}{\partial V}\right) - \lambda_2\right] \end{aligned}$$

where, upon noticing that

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{1}{T}\left[\cancelto{0}{\left(\frac{\partial E}{\partial V}\right)} + p\cancelto{1}{\left(\frac{\partial V}{\partial V}\right)} + \mu\cancelto{0}{\left(\frac{\partial N}{\partial V}\right)}\right] = \frac{p}{T}$$

we can finally conclude that $\boxed{\lambda_2 = \frac{p}{k_B T}}$.

(3) Starting from the Gibbs entropy formula

$$S = -k_B \sum_j P_j \ln P_j$$

we may substitute Eqn 2 for P_j (and insert our Lagrange multipliers) to give that

$$S = -k_B \sum_j \left(\frac{1}{\Delta(N,p,T)} e^{-\beta E_j(N,V)} e^{-\beta pV} \right) \ln \left(\frac{1}{\Delta(N,p,T)} e^{-\beta E_j(N,V)} e^{-\beta pV} \right)$$

$$= -\frac{k_B}{\Delta(N,p,T)} \sum_j e^{-\beta E_j(N,V) e^{-\beta pV}} \left[-\beta E_j(N,V) - \beta pV - \frac{\beta}{\beta} \ln \Delta \right]$$

$$= \frac{\cancel{k_B}}{\cancel{k_B} T \Delta(N,p,T)} \sum_j e^{-\beta E_j(N,V) e^{-\beta pV}} \left[E_j(N,V) + pV + \frac{\ln \Delta(N,p,T)}{\beta} \right]$$

$$= \frac{1}{T\Delta(N,p,T)} \left(\sum_j E_j(N,V) e^{-\beta E_j(N,V)} e^{-\beta pV} + \Delta(N,p,T) pV + \Delta(N,p,T) \frac{\ln \Delta(N,p,T)}{\beta} \right)$$

where, since $E = \langle E \rangle = \sum_j E_j(N,V) e^{-\beta E_j(N,V)} e^{-\beta pV} / \Delta(N,p,T)$, we have

$$\boxed{S = \frac{1}{T} \left(\langle E \rangle + pV + k_B T \ln \Delta(N,p,T) \right) = \frac{1}{T} E + \frac{p}{T} V + k_B \ln \Delta(N,p,T)}.$$

Substituting this into $G = E + pV - TS$,

$$G = E + pV - (E + pV - k_B T \ln \Delta(N,p,T)) = -k_B T \ln \Delta(N,p,T)$$

we see that the Gibbs free energy is directly proportional to $\ln \Delta(N,p,T)$.

(4) Use the differential of the Gibbs energy

$$dG = -S dT + V dp + \mu dN \tag{3}$$

to derive expressions for the thermodynamic entropy S, volume V, and chemical potential μ in the isothermal isobaric ensemble in terms of derivatives of $\ln \Delta(N,p,T)$.

First, consider taking the derivative of both sides of Eqn (3) w.r.t temperature at constant p and N:

$$\left(\frac{\partial G}{\partial T} \right)_{N,p} = -S \cancelto{1}{\left(\frac{\partial T}{\partial T} \right)_{N,p}} + V \cancelto{0}{\left(\frac{\partial p}{\partial T} \right)_{N,p}} + \mu \cancelto{0}{\left(\frac{\partial N}{\partial T} \right)_{N,p}}$$

This gives an isothermal-isobaric entropy S

$$\boxed{S = k_B \left(\frac{\partial}{\partial T} T \ln \Delta(N,p,T) \right)_{N,P} = k_B T \left(\frac{\partial}{\partial T} \ln \Delta(N,p,T) \right) + k_B \ln \Delta(N,p,T)}$$

Similarly, the following two expressions allow us to obtain expressions for V and μ:

$$\left(\frac{\partial G}{\partial p}\right)_{N,T} = -S\cancelto{0}{\left(\frac{\partial T}{\partial p}\right)_{N,T}} + V\cancelto{1}{\left(\frac{\partial p}{\partial p}\right)_{N,T}} + \mu\cancelto{0}{\left(\frac{\partial N}{\partial p}\right)_{N,T}} = V$$

$$\left(\frac{\partial G}{\partial N}\right)_{T,p} = -S\cancelto{0}{\left(\frac{\partial T}{\partial N}\right)_{T,p}} + V\cancelto{0}{\left(\frac{\partial p}{\partial N}\right)_{T,p}} + \mu\cancelto{1}{\left(\frac{\partial N}{\partial N}\right)_{T,p}} = \mu$$

from which the isothermal-isobaric volume and chemical potential directly follow:

$$\boxed{V = -k_B T\left(\frac{\partial}{\partial p}\ln\Delta(N,p,T)\right)_{N,T}}$$

$$\boxed{\mu = -k_B T\left(\frac{\partial}{\partial N}\ln\Delta(N,p,T)\right)_{T,P}}$$

(5) Derive an expression for σ_V^2, the averaged square fluctuations of the volume. Express your answer in terms of the isothermal compressibility. Use the ideal gas equation of state to confirm that the relative volume fluctuations vanish in the thermodynamic limit. How large are the relative volume fluctuations in a one mole sample of ideal gas under standard conditions?

We begin by considering the expression for averaged square fluctuations of the volume:

$$\sigma_V^2 = \bar{V^2} - \bar{V}^2.$$

Evaluating the first term, we have

$$\bar{V^2} = \frac{1}{\Delta}\sum_V V^2 e^{-\beta E_j} e^{-\beta p V} = -\frac{k_B T}{\Delta}\frac{\partial}{\partial p}\sum_V V e^{-\beta E_j} e^{-\beta p V} = -\frac{k_B T}{\Delta}\frac{\partial}{\partial p}(\bar{V}\Delta)$$

$$= -\frac{k_B T}{\Delta}\left(\bar{V}\frac{\partial \Delta}{\partial p} + \Delta\frac{\partial \bar{V}}{\partial p}\right) = -k_B T\frac{\partial \ln\Delta}{\partial p}\bar{V} - k_B T\frac{\partial \bar{V}}{\partial p} = \bar{V}^2 - k_B T\frac{\partial \bar{V}}{\partial p}$$

where the definition of $V = \bar{V}$ from problem 3 was used in the last step. Thus,

$$\sigma_V^2 = \cancel{\bar{V}^2} - k_B T\frac{\partial \bar{V}}{\partial p} - \cancel{\bar{V}^2} = -k_B T\frac{\partial \bar{V}}{\partial p}$$

at which point the isothermal compressibility as provided yields $\frac{\partial \bar{V}}{\partial p} = -\kappa V = -\kappa\bar{V}$. Then,

$$\boxed{\sigma_V^2 = k_B T\kappa V}$$

The relative volume fluctuations $\sigma_V = (k_B T\kappa V/V)^{1/2}$ of an ideal gas with equation of state $pV = Nk_B T$ are $(\cancel{k_B T}\kappa V p/N\cancel{k_B T})^{1/2} = (\kappa V p/N)^{1/2}$. As the denominator $N \to \infty$ in the thermodynamic limit, the relative volume fluctuations $\sigma_V \to 0$.

Using the provided definition of isothermal compressibility,

$$\sigma_V = \left(-\frac{\partial V}{\partial p} \frac{p}{N} \right)^{1/2}$$

and, from the ideal gas equation of state,

$$\frac{\partial V}{\partial p} = \frac{\partial}{\partial p} \frac{N k_B T}{p} = -\frac{N k_B T}{p^2}.$$

Thus,

$$\sigma_V = \left(\frac{k_B T}{p} \right)^{1/2}$$

which suggests that relative volume fluctuations at standard conditions are of the order

$$\boxed{\sigma_V = \sqrt{\frac{1.38064910^{-23} \text{ J/K } (298.15 \text{ K})}{101,300 \text{ Pa}}} = 2.02 \times 10^{-13} \text{ m}^3}$$

CHEM 2020: Homework 2

Daniel Staros

February 25, 2022

1 Problem 1: Toy Model for Indistinguishable Particles

All parts done in Mathematica

2 Problem 2: Translations of an Ideal Monatomic Gas

(1) Consider a sample of ideal monatomic gas (homogeneous). You can neglect the nuclear and electronic partition functions in this problem. Starting from the general isothermal-isobaric partition function, derive the provided expression. From this result, derive the volume V and entropy S. Comment on your results.

Noting that $q_{trans} = \frac{V}{\Lambda^3}$, $\Delta(N,p,T)$ becomes:

$$\Delta(N,p,T) = \int_0^\infty dV\ \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N e^{-\beta pV} = \frac{1}{\Lambda^{3N}N!}\int_0^\infty dV\ V^N e^{-\beta pV}$$

where we can multiply by 1 in the following way to get:

$$\frac{1}{\Lambda^{3N}N!}\frac{(\beta p)^{N+1}}{(\beta p)^{N+1}}\int_0^\infty dV\ V^N e^{-\beta pV} = \frac{1}{\Lambda^{3N}N!(\beta p)^{N+1}}\int_0^\infty d(\beta pV)\ (\beta pV)^N e^{-\beta pV} = \frac{\cancelto{N!}{\Gamma(N+1)}}{\Lambda^{3N}N!(\beta p)^{N+1}}$$

thus yielding that

$$\boxed{\Delta(N,p,T) = \frac{1}{\Lambda^{3N}(\beta p)^{N+1}} \approx \left(\frac{1}{\Lambda^3\beta p}\right)^N}$$

where last approximation holds when $N \approx N+1$, for large N, which is true in the case of a monatomic ideal gas. From this, the volume is given by

$$V = -k_BT\frac{\partial}{\partial p}\ln\Delta(N,p,T) = Nk_BT\frac{\partial\ln(\Lambda^3\beta p)}{\partial p} = Nk_BT\frac{\partial(\Lambda^3\beta p)}{\partial p}\frac{1}{\Lambda^3\beta p} = Nk_BT\frac{\cancel{k_BT}}{\cancel{\Lambda^3}p}\frac{\cancel{\Lambda^3}}{\cancel{k_BT}}$$

or

$$\boxed{V = \frac{Nk_BT}{p}}.$$

Additionally, entropy is given by

$$S = k_B \ln \Delta(N,p,T) + k_B T \left(\frac{\partial \ln \Delta}{\partial T} \right) = k_B \ln \Delta(N,p,T) + N k_B \cancel{T} \frac{\cancel{h^2} p}{\cancel{2\pi m k_B^{5/3} T^{5/3}}} \left(\frac{5}{3} \frac{\cancel{2\pi m k_B^{5/3} T^{2/3}}}{\cancel{h^2} p} \right)$$

where the following rearrangement was used alongside the relation $\frac{\partial \ln f}{\partial x} = \frac{\partial f}{\partial x} \frac{1}{f}$:

$$\Delta = \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{p} \right]^N = \left(\frac{2\pi m (k_B T)^{5/3}}{h^2 p} \right)^N$$

thus yielding

$$\boxed{S = N k_B \ln \left(\frac{k_B T}{\Lambda^3 p} \right) + \frac{5}{3} N k_B}.$$

Evidently, volume is given by an expression consistent with the monatomic ideal gas equation of state as expected.

3 Problem 3: 2D Gas of Hydrogen Halides

Done in GoodNotes and Mathematica

4 Problem 4: Anharmonic Corrections

Done in Mathematica

Problem 3: 2D gas of hydrogen halides

For a 2D rigid rotor, $E_j = \frac{j^2\hbar^2}{2\mu r^2}$; $\mu = \frac{m_1 m_2}{m_1+m_2}$ and $\omega = 2$ since rotation may be clockwise or counterclockwise

$\hookrightarrow$ $q_{trans} = \frac{2\pi(m_1+m_2)k_BT}{h^2}A$ $\quad q_{rot} = \sum_{j=0}^{\infty} 2\, e^{-\beta j^2\hbar^2/2\mu r^2}$ $\quad q_{vib} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$

$$p = k_BT\left(\frac{\partial \ln Q}{\partial A}\right)_{N,T}$$

$$\bar{E} = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$C_v = \left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V}$$

Thus, for this 2D diatomic gas, we have the following:

$$\boxed{Q(N,V,T)^{2D}_{diatomic} = \frac{1}{N!}\left(\frac{2\pi(m_1+m_2)k_BT}{h^2}L^2\cdot\sum_{j=0}^{\infty}2\, e^{-\beta j^2\hbar^2/2\mu r^2}\cdot\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^N}$$

Deriving pressure:

$$p = k_BT\frac{\partial}{\partial A}\ln Q = Nk_BT\frac{\partial}{\partial A}\left[\ln\frac{2\pi(m_1+m_2)k_BTA}{h^2} + \ln\sum_{j=0}^{\infty}2j\, e^{-\beta j^2\hbar^2/2\mu r^2} + \ln\frac{e^{-\beta h\nu/2}}{N!(1-e^{-\beta h\nu})}\right]$$

$$= Nk_BT\frac{\partial}{\partial A}\ln(\alpha A) = Nk_BT\frac{\partial}{\partial A}\ln(A) = Nk_BT\cancel{\frac{\partial}{\partial A}}\frac{1}{A} = \boxed{\frac{Nk_BT}{L^2} = p}$$

Deriving heat capacity:

$$C_v = \frac{\partial}{\partial T}\left[k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}\right] = k_BT^2\frac{\partial^2\ln Q}{\partial T^2} + 2k_BT\frac{\partial \ln Q}{\partial T} = Nk_BT^2\frac{\partial^2\ln q}{\partial T^2} + 2Nk_BT\frac{\partial \ln q}{\partial T}$$

$$q_{diat} \approx \frac{2\pi(m_1+m_2)k_BTA}{h^2}\cdot\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\cdot\int_{-\infty}^{+\infty}e^{-\left(\frac{\beta\hbar^2}{2\mu r^2}\right)j^2}dj = \underbrace{\frac{2\pi(m_1+m_2)k_BTA}{h^2}}_{q_{trans}}\cdot\underbrace{\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}}_{q_{vib}}\cdot\underbrace{\sqrt{\frac{\pi\beta\hbar^2}{2\mu r^2}}}_{q_{rot}}$$

$$\frac{\partial}{\partial T}\ln(q_{diat}) = \left[\frac{\partial q_{trans}}{\partial T}\frac{1}{q_{trans}}\right] + \left[\left(\frac{\partial}{\partial T}e^{\frac{2k_BT}{h\nu}}\right)e^{\frac{h\nu}{2k_BT}} - \frac{\partial}{\partial T}\left(1-e^{-h\nu/k_BT}\right)\right] - \left[\frac{1}{2}\cancel{\sqrt{\frac{\hbar^2\pi}{2\mu r^2 k_B}}}\ \cancel{\sqrt{\frac{2\mu r^2 k_B}{\hbar^2\pi}}}\ T^{-3/2}\,T^{1/2}\right]$$

$$= \frac{1}{T} + \left[\frac{2k_B}{h\nu}e^{\frac{2k_BT}{h\nu}}e^{\frac{h\nu}{2k_BT}} + \frac{k_B}{h\nu}e^{\frac{k_BT}{h\nu}}\right] - \frac{1}{2T} \qquad = \delta_{trans} + \delta_{vib} + \delta_{rot}$$

$$\boxed{\begin{aligned}C_v = {} & Nk_BT^2\frac{\partial}{\partial T}\left(\frac{1}{T} + \left[\frac{2k_B}{h\nu}e^{\frac{2k_BT}{h\nu}}e^{\frac{h\nu}{2k_BT}} + \frac{k_B}{h\nu}e^{\frac{k_BT}{h\nu}}\right] - \frac{1}{2T}\right)\\ & + 2Nk_BT\left(\frac{1}{T} + \left[\frac{2k_B}{h\nu}e^{\frac{2k_BT}{h\nu}}e^{\frac{h\nu}{2k_BT}} + \frac{k_B}{h\nu}e^{\frac{k_BT}{h\nu}}\right] - \frac{1}{2T}\right)\end{aligned}}$$

$\hookrightarrow$ Rest of algebra + answer in Mathematica

HW 3

Summary of goals:
Here we will test our understanding of the statistical mechanics of chemical equilibrium. All of these problems are adapted the McQuarrie text.

Prompt:
Answer each of the following questions. You are encouraged to discuss the problems with your peers and at office hours but the work you turn in must be your own. For problems solved by hand, submit your solutions in pdf format. For solutions done in Mathematica, submit your debugged notebook file (.nb) according to the guidelines described in the syllabus. All figures should include descriptive labels and final answers should be fully simplified. Submit your files to Canvas.

Due date:
11:59pm, Friday March 25

✓ Problem 1: Equilibrium Constant Rederived

(15 points) In class we used Boltzmann statistics to derive an expression for the equilibrium constant from the conditions of thermodynamic equilibrium. In this problem we'll derive the same result with a different approach. Consider the following gas-phase chemical reaction,

$$I_2 \quad \rightleftarrows \quad 2I. \tag{1}$$

✓ 1. Using Boltzmann statistics, start by writing down the canonical partition function of an ideal mixture containing N_I iodine atoms and N_{I_2} dimers. Your answer should be in terms of N_I, N_{I_2}, and unspecified molecular partition functions.

✓ 2. Now use the method of Lagrange multipliers to minimize the Helmholtz energy of the mixture $A(N_I, N_{I_2}, V, T)$ subject to the equilibrium stoichiometric constraint $2N_{I_2} + N_I =$ constant. Express N_I^* and $N_{I_2}^*$, the number of I and I_2 particles at equilibrium, in terms of molecular partition functions, the Lagrange multipliers, and constants.

✓ 3. Eliminate the Lagrange multipliers to show that

$$\frac{(N_I^*)^2}{N_{I_2}^*} = \frac{q_I^2}{q_{I_2}}. \tag{2}$$

   Complete the derivation and derive the equilibrium constant K_p, both in terms of pressures and molecular partition functions.

✓ 4. Use Mathematica to evaluate the equilibrium constant of this reaction at 800K and 1000K. The experimental values at these temperatures are 0.0114 and 0.165. See the McQuarrie textbook for molecular/atomic parameters. Note that the degeneracy of the ground electronic state of an iodine atom is equal to $2J + 1$ with $J = 3/2$. The first excited electronic state is 0.94 eV higher.

✓Problem 2: Chemical Equilibrium Involving Polyatomics

(10 points) Consider the following gas-phase reaction,

$$\mathrm{H_2O + DCl \rightleftarrows HDO + HCl},$$

and express the equilibrium constant K_p in terms of the molecular partition functions of the products and reactants. To simply the interpretation, express the equilibrium constant in terms of factors associated with translations, vibrations, rotations, and electronic degrees of freedom. How do the different kinds of motion contribute to the equilibrium composition? To answer this, plot $K_p(T)$ over T=500K to T=1000K. Use Table 6-1 and Table 8-1 in McQuarrie for useful information. Also note that the normal mode frequencies of HDO are 2019.8, 3927.6, and 5340.4 in units of K. The rotational constants of HDO are 9.243, 13.11, and 33.68 in units of K.

In physical chemistry we learn the relationship between the equilibrium constant K_p and the reaction enthalpy change via the van 't Hoff equation,

$$\frac{d}{dT} \ln K_p(T) = \frac{\Delta H^0}{RT^2}. \tag{3}$$

Use your molecular expression for $K_p(T)$ and determine the enthalpy change of the reaction, interpret your result.

✓Problem 3: Another Chemical Equilibrium Involving Polyatomics

(10 points) Calculate the equilibrium constant $K_p(T)$ for gas-phase ammonia formation,

$$\mathrm{N_2 + 3H_2 \leftrightharpoons 2NH_3}. \tag{4}$$

Write K_p as a product of factors associated with translational, rotational, vibrational, and electronic degrees of freedom. Evaluate each contribution to K_p at $T = 400\mathrm{K}$. A measured value is 3.3×10^{-4} atm^{-2}. Which degrees of freedom are most important in determining the equilibrium composition? Use Table 6-1 and Table 8-1 in McQuarrie for useful information.

✓Problem 4: Dissociation of N_2

(10 points) Calculate the temperature at which molecular nitrogen is 99 percent dissociated at 100 atm, 1 atm, and 0.1 atm.

✓Problem 5: Chemical Equilibrium of Partial Deuteration

(5 points) Show that the equilibrium constant for a reaction such as

$$\mathrm{HCl + DBr \rightleftarrows DCl + HBr}$$

approaches unity at high temperatures.

Problem 1

1.) $I_2(g) \rightleftharpoons 2I\ (g)$

$1 I_2 - 2I = 0$

$$\boxed{Q = \frac{q_{I_2}^{N_{I_2}}}{N_{I_2}!} \cdot \frac{q_I^{N_I}}{N_I!}}$$

2.) $A(N_I, N_{I_2}, V, T)$ constrained by $g = 2N_{I_2} + N_I - \alpha$ for constant α.

$$A = -k_B T \ln Q$$
$$= -k_B T \left[N_{I_2} \ln(q_{I_2}) - (N_{I_2} \ln N_{I_2} - N_{I_2}) + N_I \ln(q_I) - (N_I \ln N_I - N_I) \right] \quad \text{(stirling)}$$

Solve: $\frac{\partial A}{\partial N_I} = \lambda \frac{\partial g}{\partial N_I} \implies k_B T(\ln(N_I^*) - \ln(q_I)) = \lambda$

$\frac{\partial A}{\partial N_{I_2}} = \lambda \frac{\partial g}{\partial N_{I_2}} \implies k_B T(\ln(N_{I_2}^*) - \ln(q_{I_2})) = 2\lambda$

$2N_{I_2} + N_I - \alpha = 0 \implies 2N_{I_2} + N_I = \alpha$

3.) From above: $\cancel{k_B T}(\ln(N_{I_2}^*) - \ln(q_{I_2})) = 2\cancel{k_B T}(\ln(N_I^*) - \ln(q_I))$

$$\ln(N_{I_2}^*) - \ln(q_{I_2}) = \ln(N_I^*)^2 - \ln(q_I)^2$$

$$\ln\left(\frac{N_{I_2}^*}{q_{I_2}}\right) = \ln\left(\frac{N_I^{*2}}{q_I^2}\right) \quad \text{giving that} \quad \frac{(N_I^*)^2}{N_{I_2}^*} = \frac{q_I^2}{q_{I_2}}.$$

$$\boxed{K_p = (k_B T)^{\nu_c + \nu_D - \nu_A - \nu_B} K_c = (k_B T)\left(\frac{q_I}{V}\right)^2 \Big/ \left(\frac{q_{I_2}}{V}\right) = \frac{(P_I)^2}{P_{I_2}}}$$

4.) Done in Mathematica

Problem 2

$H_2O\ (g) + DCl\ (g) \rightleftharpoons HDO\ (g) + HCl\ (g) \qquad K_p = \cancelto{1}{(k_B T)^{\nu_c + \nu_D - \nu_A - \nu_B}} K_c = K_c$

$$K_c = \frac{q_{HDO}\, q_{HCl}}{q_{H_2O}\, q_{DCl}} = \frac{(q_T q_{vib} q_{rot} q_{elec} q_{nuc})_{HDO} (q_T q_{vib} q_{rot} q_{elec} q_{nuc})_{HCl}}{(q_T q_{vib} q_{rot} q_{elec} q_{nuc})_{H_2O} (q_T q_{vib} q_{rot} q_{elec} q_{nuc})_{DCl}}$$

Explicit forms listed / rationalized on next page...

Problem 2 (cont.)

Sidenote

$D_e = D_0 + \frac{1}{2}h\nu \qquad \theta_v = \frac{h\nu}{k_B} \rightarrow h\nu = \theta_v \cdot k_B$

$$K_c = \frac{q_{HDO}\, q_{HCl}}{q_{H_2O}\, q_{DCl}} = \left(\frac{q_{HDO}}{q_{H_2O}}\right)\left(\frac{q_{HCl}}{q_{DCl}}\right)$$

$$\frac{q_{HCl}}{q_{DCl}} = \frac{\left(\frac{\cancel{2\pi k_B} m_{HCl} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\theta_r^{HCl}} \cdot \frac{1}{\cancel{2}} \operatorname{csch}\left(\frac{\theta_v^{HCl}}{2T}\right) \cdot \cancelto{1}{e^{D_e^{HCl}/k_BT}}}{\left(\frac{\cancel{2\pi k_B} m_{DCl} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\theta_r^{DCl}} \cdot \frac{1}{\cancel{2}} \operatorname{csch}\left(\frac{\theta_v^{DCl}}{2T}\right) \cdot \cancel{e^{D_e^{DCl}/k_BT}}} = \frac{m_{HCl}}{m_{DCl}} \cdot \frac{\theta_r^{HCl}}{\theta_r^{DCl}} \cdot \frac{\operatorname{csch}\left(\frac{\theta_v^{HCl}}{2T}\right)}{\operatorname{csch}\left(\frac{\theta_v^{DCl}}{2T}\right)}$$

$\theta_r^{HCl} = 15.02$

$\theta_v^{HCl} = 4227$

Since HCl + DCl have essentially the same internuclear potential function, force constant k, internuclear separation, and depth of D_e, the ratio of their electronic partition functions cancels to 1. Additionally, we can determine θ_v^{DCl} and θ_r^{DCl} from:

$$\frac{\theta_{v,DCl}}{\theta_{v,HCl}} = \left(\frac{\mu_{HCl}}{\mu_{DCl}}\right)^{1/2} \longrightarrow \left[\frac{(1\cdot 35)/36}{(2\cdot 35)/37}\right]^{1/2} \theta_{v,HCl} = \theta_{v,DCl} \qquad \frac{\theta_{r,DCl}}{\theta_{r,HCl}} = \frac{\mu_{HCl}}{\mu_{DCl}} \longrightarrow \frac{(1\cdot 35)/36}{(2\cdot 35)/37}\theta_{r,HCl} = \theta_{r,DCl}.$$

$$\frac{q_{HDO}}{q_{H_2O}} = \frac{\left(\frac{\cancel{2\pi k_B} m_{HDO} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V}\, \frac{\cancel{\pi^{1/2}}}{1}\left(\frac{\cancel{T^3}}{\theta_A^{HDO}\theta_B^{HDO}\theta_C^{HDO}}\right)^{\cancel{1/2}} \prod_{j=1}^{\alpha=3} \frac{1}{\cancel{2}} \operatorname{csch}\left(\frac{\theta_{v,j}^{HDO}}{2T}\right) \omega_{el}\, \cancelto{1}{e^{D_e^{HDO}/k_BT}}}{\left(\frac{\cancel{2\pi k_B} m_{H_2O} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V}\, \frac{\cancel{\pi^{1/2}}}{2}\left(\frac{\cancel{T^3}}{\theta_A^{H_2O}\theta_B^{H_2O}\theta_C^{H_2O}}\right)^{\cancel{1/2}} \prod_{j=1}^{\alpha=3} \frac{1}{\cancel{2}} \operatorname{csch}\left(\frac{\theta_{v,j}^{H_2O}}{2T}\right) \cancel{\omega_{el}}\, \cancel{e^{D_e^{H_2O}/k_BT}}} = 2\,\frac{m_{HDO}}{m_{H_2O}} \cdot \frac{\theta_A^{HDO}}{\theta_A^{H_2O}} \cdot \frac{\theta_B^{HDO}}{\theta_B^{H_2O}} \cdot \frac{\theta_C^{HDO}}{\theta_C^{H_2O}} \prod_{j=1}^{\alpha=3} \frac{\operatorname{csch}\left(\frac{\theta_{v,j}^{HDO}}{2T}\right)}{\operatorname{csch}\left(\frac{\theta_{v,j}^{H_2O}}{2T}\right)}$$

Since H_2O + D_2O have essentially the same internuclear potential function, force constant k, internuclear separation, and depth of D_e, the ratio of their electronic partition functions cancels to 1.

$\{\sigma, \theta_A, \theta_B, \theta_C\}^{H_2O} = \{2, 13.4, 20.9, 40.1\}$

$\{\sigma, \theta_A, \theta_B, \theta_C\}^{HDO} = \{1, 9.243, 13.11, 33.68\}$

$\theta_v^{H_2O} = 5360, 5160, 2290$;

$\theta_v^{HDO} = 5340.4, 3927.6, 2019.8$;

$$K_c = \underbrace{\left(2\,\frac{m_{HDO}}{m_{H_2O}} \cdot \frac{m_{HCl}}{m_{DCl}}\right)}_{\downarrow\, K_c^{trans}} \underbrace{\left(\frac{\theta_A^{HDO}}{\theta_A^{H_2O}} \cdot \frac{\theta_B^{HDO}}{\theta_B^{H_2O}} \cdot \frac{\theta_C^{HDO}}{\theta_C^{H_2O}} \cdot \frac{\theta_r^{HCl}}{\theta_r^{DCl}}\right)}_{\downarrow\, K_c^{rot}} \underbrace{\left(\prod_{j=1}^{\alpha=3} \frac{\operatorname{csch}\left(\frac{\theta_{v,j}^{HDO}}{2T}\right)}{\operatorname{csch}\left(\frac{\theta_{v,j}^{H_2O}}{2T}\right)} \cdot \frac{\operatorname{csch}\left(\frac{\theta_v^{HCl}}{2T}\right)}{\operatorname{csch}\left(\frac{\theta_v^{DCl}}{2T}\right)}\right)}_{\downarrow\, K_c^{vib}}$$

$K_c^{elec}, K_c^{nuc} = 1$

Evaluated in Mathematica

Problem 3

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_p(T) = (k_B T)^{2-1-3} \frac{\left(\frac{q_{NH_3}}{V}\right)^2}{\left(\frac{q_{N_2}}{V}\right)\left(\frac{q_{H_2}}{V}\right)^3} = \frac{1}{(k_B T)^2} \cdot \frac{\left(\frac{q_{NH_3}}{V}\right)^2}{\left(\frac{q_{N_2}}{V}\right)\left(\frac{q_{H_2}}{V}\right)^3}$$

$$\frac{q_{NH_3}}{V} = \frac{1}{\cancel{V}} \underbrace{\left(\frac{2\pi k_B m_{NH_3} T}{h^2}\right)^{3/2} \cancel{V}}_{q^T_{NH_3}} \cdot q_r^{NH_3} \cdot q_v^{NH_3} \cdot q_e^{NH_3}$$

Sidenote

$$\Theta_v = \frac{h\nu}{k_B} \Rightarrow h\nu = \Theta_v \cdot k_B = (\cancel{K}) \cdot \frac{erg}{molec \cdot \cancel{K}} = \frac{eg}{molec}$$

$$D_e = D_0 + \Sigma \frac{1}{2} h\nu$$

$$q^r_{NH_3} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2} = \frac{\pi^{1/2}}{3} \left(\frac{T^3}{13.6 \cdot 13.6 \cdot 8.92}\right)^{1/2}$$

$$q^v_{NH_3} = \prod_{j=1}^{\alpha} \frac{1}{2} \operatorname{csch}\left(\frac{\Theta_{v,j}}{2T}\right) = \left[\frac{1}{2} \operatorname{csch}\left(\frac{4800}{2T}\right)\right] \cdot \left[\frac{1}{2} \operatorname{csch}\left(\frac{1360}{2T}\right)\right] \cdot \left[\frac{1}{2} \operatorname{csch}\left(\frac{4880}{2T}\right)\right] \cdot \left[\frac{1}{2} \operatorname{csch}\left(\frac{2330}{2T}\right)\right]$$

$$q^e_{NH_3} = \omega_{el}\, e^{D_e/k_B T} = 1 e^{D_e/k_B T} \; ; \; D_e = D_0 + \sum_j \frac{1}{2} h\nu_j = D_0 + \sum_j \frac{1}{2} \Theta_{v,j} k_B = 276.8 \frac{\text{Kcal}}{\text{mole}} + \sum_{j=1}^{4} \frac{1}{2} \Theta_{v,j} k_B$$

$$\frac{q_{N_2}}{V} = \frac{1}{\cancel{V}} \underbrace{\left(\frac{2\pi k_B m_{N_2} T}{h^2}\right)^{3/2} \cancel{V}}_{q^T_{N_2}} \cdot q^{rn}_{N_2} \cdot q^v_{N_2} \cdot q^e_{N_2} \; ; \; q^v_{N_2} = \frac{1}{2} \operatorname{csch}\left(\frac{\overset{=3374\text{ K}}{\Theta_v^{N_2}}}{2T}\right) \; ; \; q^e_{N_2} = \omega_{el}\, e^{D_e/k_B T} = 1 e^{D_e/k_B T}$$

$$q^{rn}_{N_2} = \frac{(2I+1)^2 T}{2\Theta_r^{N_2}} = \frac{(1+1)^2 T}{2(2.88)} \longrightarrow I_N = \frac{1}{2} \qquad D_e^{N_2} = 225.1 \frac{\text{Kcal}}{\text{mole}} + \frac{1}{2} \overset{=3374\text{ K}}{\Theta_v^{N_2}} k_B$$

valid since $\Theta_r^{N_2} = 2.88$; $\frac{\Theta_r^{N_2}}{T} = \frac{3}{400} < 0.2$.

$$\frac{q_{H_2}}{V} = \frac{1}{\cancel{V}} \underbrace{\left(\frac{2\pi k_B m_{H_2} T}{h^2}\right)^{3/2} \cancel{V}}_{q^T_{H_2}} \cdot q^{rn}_{H_2} \cdot q^v_{H_2} \cdot q^e_{H_2} \; ; \; q^v_{H_2} = \frac{1}{2} \operatorname{csch}\left(\frac{\overset{6215\text{ K}}{\Theta_v^{H_2}}}{2T}\right) \; ; \; q^e_{H_2} = \omega_{el}\, e^{D_e/k_B T} = 1 e^{D_e/k_B T}$$

$$q^{rn}_{H_2} = \frac{(2I+1)^2 T}{2\Theta_r^{H_2}} = \frac{(1+1)^2 T}{2(85.3)} \longrightarrow I_H = \frac{1}{2} \qquad D_e^{H_2} = 103.2 \frac{\text{Kcal}}{\text{mole}} + \frac{1}{2} \overset{=6215\text{ K}}{\Theta_v^{H_2}} k_B$$

still valid since $\Theta_r^{H_2} = 85.3$; $\frac{\Theta_r^{H_2}}{T} = \frac{85}{400} \simeq 0.2$

$$K_p(T) = \frac{1}{(k_B T)^2} \cdot \frac{\left(\frac{q_{NH_3}}{V}\right)^2}{\left(\frac{q_{N_2}}{V}\right)\left(\frac{q_{H_2}}{V}\right)^3} = \frac{1}{(k_B T)^2} \cdot \frac{\left(\frac{q^T_{NH_3}}{V}\right)^2}{\left(\frac{q^T_{N_2}}{V}\right)\left(\frac{q^T_{H_2}}{V}\right)^3} \cdot \frac{(q^r_{NH_3})^2}{(q^{rn}_{N_2})(q^{rn}_{H_2})^3} \cdot \frac{(q^v_{NH_3})^2}{(q^v_{N_2})(q^v_{H_2})^3} \cdot \frac{(q^e_{NH_3})^2}{(q^e_{N_2})(q^e_{H_2})^3}$$

Evaluated in Mathematica

Problem 4

$$K_p(T) = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \qquad P_{TOT} = 0.99\,P_{TOT} + 0.01\,P_{TOT} = 100 \text{ atm}$$

$$= P_N + P_{N_2} = 99\text{atm} + 1\text{atm} \;@\; P_{TOT} = 100$$

$$K_p(T) = \frac{(P_N)^2}{(P_{N_2})} = \frac{\left(\frac{q_N(T)}{V}\right)^2}{\left(\frac{q_{N_2}(T)}{V}\right)} \xrightarrow{P_{TOT}=100} \frac{(99)^2}{1} = \frac{\left(q_N(T)/V\right)^2}{\left(q_{N_2}(T)/V\right)}$$

$$\xrightarrow{P_{TOT}=10} \frac{(9.9)^2}{0.1} = \frac{\left(q_N(T)/V\right)^2}{\left(q_{N_2}(T)/V\right)}$$

$$\xrightarrow{P_{TOT}=0.1} \frac{(.99)^2}{0.01} = \frac{\left(q_N(T)/V\right)^2}{\left(q_{N_2}(T)/V\right)}$$

Evaluated in Mathematica

Problem 5 ✓

$$HCl\,(g) + DBr\,(g) \rightleftharpoons DCl\,(g) + HBr\,(g) \qquad K_c = \frac{q_{DCl}\, q_{HBr}}{q_{HCl}\, q_{DBr}} = \left(\frac{q_{DCl}}{q_{HCl}}\right)\left(\frac{q_{HBr}}{q_{DBr}}\right)$$

First, noting that $e^{q/T} \to 1$ as $T \to \infty$ since $\frac{q}{T} \to 0$ and noting that $\frac{\Theta_v}{2T} \to \frac{1}{2T}$ effectively as T gets larger, we have:

$$\frac{q_{DCl}}{q_{HCl}} = \frac{\left(\frac{\cancel{2\pi k_B} m_{DCl} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\Theta_r^{DCl}} \cdot \cancel{\frac{1}{2}}\operatorname{csch}\left(\frac{\Theta_v^{DCl}}{2T}\right) \cdot \cancelto{1}{e^{D_e^{DCl}/k_B T}}}{\left(\frac{\cancel{2\pi k_B} m_{HCl} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\Theta_r^{HCl}} \cdot \cancel{\frac{1}{2}}\operatorname{csch}\left(\frac{\Theta_v^{HCl}}{2T}\right) \cdot \cancelto{1}{e^{D_e^{HCl}/k_B T}}} = \frac{m_{DCl}}{m_{HCl}} \cdot \frac{\Theta_r^{DCl}}{\Theta_r^{HCl}} \cdot \cancelto{1}{\frac{\operatorname{csch}\left(\frac{\Theta_v^{DCl}}{2T}\right)}{\operatorname{csch}\left(\frac{\Theta_v^{HCl}}{2T}\right)}}$$

$$\frac{q_{HBr}}{q_{DBr}} = \frac{\left(\frac{\cancel{2\pi k_B} m_{HBr} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\Theta_r^{HBr}} \cdot \cancel{\frac{1}{2}}\operatorname{csch}\left(\frac{\Theta_v^{HBr}}{2T}\right) \cdot \cancelto{1}{e^{D_e^{HBr}/k_B T}}}{\left(\frac{\cancel{2\pi k_B} m_{DBr} \cancel{T}}{\cancel{h^2}}\right)^{\cancel{3/2}} \cancel{V} \cdot \frac{\cancel{T}}{\Theta_r^{DBr}} \cdot \cancel{\frac{1}{2}}\operatorname{csch}\left(\frac{\Theta_v^{DBr}}{2T}\right) \cdot \cancelto{1}{e^{D_e^{DBr}/k_B T}}} = \frac{m_{HBr}}{m_{DBr}} \cdot \frac{\Theta_r^{HBr}}{\Theta_r^{DBr}} \cdot \cancelto{1}{\frac{\operatorname{csch}\left(\frac{\Theta_v^{HBr}}{2T}\right)}{\operatorname{csch}\left(\frac{\Theta_v^{DBr}}{2T}\right)}}$$

Noting that $\Theta_r = h^2/8\pi^2 \mu r_e^2 k_B$, and that $r_e^{HCl} \approx r_e^{DCl} \approx r_e^{HBr} \approx r_e^{DBr}$ @ $T \to \infty$,

$$\boxed{K_c = \frac{m_{DCl}}{m_{HCl}} \cdot \frac{m_{HBr}}{m_{DBr}} \cdot \frac{(\mu \cancel{r_e^2})_{DCl}\,(\mu \cancel{r_e^2})_{HBr}}{(\mu \cancel{r_e^2})_{HCl}\,(\mu \cancel{r_e^2})_{DBr}} = \frac{\cancel{(m_D+m_{Cl})}\cancel{(m_H+m_{Br})}}{\cancel{(m_H+m_{Cl})}\cancel{(m_D+m_{Br})}} \cdot \frac{\cancel{m_D m_{Cl}}}{\cancel{(m_D+m_{Cl})}} \cdot \frac{\cancel{m_H m_{Br}}}{\cancel{(m_H+m_{Br})}} \cdot \frac{\cancel{(m_H+m_{Cl})}}{\cancel{m_H m_{Cl}}} \cdot \frac{\cancel{(m_D+m_{Br})}}{\cancel{m_D m_{Br}}} = 1.}$$