Properties of Reacting Mixtures; Equil. and Frozen Flows

- Homework solutions should be neat and logically presented, see format requirements (seitzman.gatech.edu/classes/ae6050/homeworkformat.html). Please note the requirement to draw some IMPLICATIONS/CONCLUSIONS from the results of each problem. This could be implications for a practical device, a comparison of the results of different parts of a problem, a physical interpretation for an equation, etc.
- To receive credit, show ALL work in the format described above. If you use equations from the notes, the class textbook or another book, please cite the reference.

1. Entropy – Statistical Mechanics
   a) Starting with equation IV.8.4 from Vincenti and Kruger, show that $s_x$, the entropy per unit mass of a given species $x$ in a mixture of perfect gases, can be written in terms of the internal partition function of the gas $x$ and its enthalpy as given below

   $$s_x = R_x \left\{ \ln \left[ \frac{k^{5/2} (2\pi)^{3/2} m_x^{3/2}}{h^3} \right] + \ln \left[ \frac{T^{5/2} Q_{x,\text{int}}}{p_x} \right] \right\} + \frac{h_x}{T}$$  \hspace{1cm} (1)

   where $R_x$ is the mass specific gas constant for species $x$, $m_x$ is the mass of species $x$, $p_x$ is the partial pressure of species $x$, $Q_{x,\text{int}}$ is the partition function for the internal energy modes of $x$ (not including translational energy) and $h_x$ is its enthalpy per unit mass.

   b) Should the enthalpy term in equation (1) include the offset energy of the molecule relative to the common energy zero level of the whole system of molecules in the mixture or be referenced to the lowest energy level for that molecule?

2. Equilibrium Constant
   Consider the following stoichiometric reaction

   $$\text{CO}_2 \leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2$$

   a) Write an expression which describes the equilibrium constant $K_p$ for this reaction as a function of temperature, the degeneracies ($g_{i,\text{el},x}$) and characteristic electronic temperatures of the molecules ($\theta_{e,i,x}$), the characteristic rotational ($\theta_{r,x}$) and vibrational ($\theta_{v,i,x}$) temperature(s) of each molecule, the difference between the zero point energies of these two chemical “states” ($\Delta \varepsilon_0$) and any other necessary parameters or constants. (The subscript $x$ refers to each species, e.g., CO$_2$, O$_2$, CO).

   b) Calculate $K_p$ for the reaction at 2500 K (in atm units) and compare it to the value obtained from the JANNAF tables, which is $\log_{10} K_p (2500\text{K}) = -1.44$. 

c) Using your $K_p$ value, determine the equilibrium mole fraction of CO molecules in a gas that has a C:O nuclei ratio of 2:3 at 2500 K and a total pressure of 3 atm, and is assumed to consist only of CO$_2$, CO and O$_2$.

\[ \text{d) Repeat part c) using a C:O ratio of 2:4.} \]

You may find the following properties for CO$_2$ and CO useful for this problem.

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
<th>$B_{\rot}$ (cm$^{-1}$)*</th>
<th>$\overline{\nu}_{\text{vib1}}$ (cm$^{-1}$)*</th>
<th>$\overline{\nu}_{\text{vib2}}$ (cm$^{-1}$)*</th>
<th>$\overline{\nu}_{\text{vib3}}$ (cm$^{-1}$)*</th>
<th>$g_{\text{e,el}}$</th>
<th>$g_{1,\text{el}}$</th>
<th>$\varepsilon_{1,\text{el}}$ (cm$^{-1}$)*</th>
<th>$\Delta h_f(0K)$ (kJ/mol)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>44.01</td>
<td>0.389</td>
<td>1330</td>
<td>667.3</td>
<td>2349</td>
<td>1</td>
<td>----</td>
<td>---</td>
<td>-393.151</td>
</tr>
<tr>
<td>CO</td>
<td>28.01</td>
<td>1.945</td>
<td>2167.6</td>
<td>---</td>
<td>---</td>
<td>1</td>
<td>2</td>
<td>64,958</td>
<td>-113.805</td>
</tr>
</tbody>
</table>

*The wavenumber (a kind of frequency unit) values given in the table can be converted to characteristic temperatures (e.g., $\theta_{\text{rot}}$ and $\theta_{\text{vib}}$) by multiplying by $hc/k$, where $c$ is the speed of light, $h$ is Planck’s constant, and $k$ is Boltzmann’s constant.

** The formation enthalpy is the amount of energy required to form a mole of a species from its “elements.” The formation enthalpies (at 0 K) given here are from the JANNAF tables, which use O$_2$ and C(s) as the elemental forms of oxygen and carbon (i.e., it assumes that O$_2$ and C have zero chemical energy). Also mol here means gmol (not kmol).

Note: carbon dioxide’s (O-C-O) bending mode ($\overline{\nu}_{\text{vib2}}$) is doubly degenerate, i.e., that two of the vibrational (bending) modes have the same characteristic frequency.

3. Specific Heat of a Reacting Mixture

The specific heat of a perfect gas mixture can be defined as

\[ c_{p,\text{mix}} \equiv \left( \frac{\partial h_{\text{mix}}}{\partial T} \right)_p \]

Consider the expression from class for the enthalpy of an ideal dissociating gas

\[ h_{\text{mix}} = R_A \left( 4 + \alpha^* \right) \left[ T - (1 - \alpha^*) \theta_D \right] \]

a) Find an approximate expression for the normalized specific heat ($c_{p,\text{mix}}/R_A$) of an ideal dissociating gas in terms of: $\alpha$, ($\partial \alpha / \partial T$)$_p$, and $\theta_D$; assuming $\theta_D/T >> 1$.

b) Sketch qualitatively how the normalized mixture specific heat should vary with temperature (from a “low” T with no dissociation to a “high” T with complete dissociation, but assuming $\theta_D/T$ still much greater than one). The only numbers you need on this sketch are the values of the normalized specific heat in your “low” and “high” temperature limits.
4. Saha Equation

An arc heater is used to produce a partially ionized argon plasma at a static pressure of 0.01 atm. Assuming that the gas is in equilibrium, all its constituents are ideal gases, and that you can neglect multiply ionized species, at what temperature will 1.0% of the argon be ionized? What will be the electron number density at this temperature (in units of \( \text{cm}^{-3} \)). What temperature would be required to produce the same ionization level if the pressure was increased to 1.0 atm.

You may find the following properties (ionization energies and electronic energy level data) for Ar and \( \text{Ar}^+ \) useful.

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon_{\text{ioniz}} ) (eV)</th>
<th>( g_{0,\text{el}} )</th>
<th>( g_{1,\text{el}} )</th>
<th>( \varepsilon_{1,\text{el}} ) (eV)</th>
<th>( g_{2,\text{el}} )</th>
<th>( \varepsilon_{2,\text{el}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar} )</td>
<td>15.76</td>
<td>1</td>
<td>12</td>
<td>11.6</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( \text{Ar}^+ )</td>
<td>27.63</td>
<td>4</td>
<td>2</td>
<td>0.178</td>
<td>2</td>
<td>13.5</td>
</tr>
</tbody>
</table>

An electron volt (eV) is typically associated with an energy value, i.e., the energy acquired by a particle with a charge of 1 e accelerated through 1 Volt (=1.602\( \times 10^{-19} \) J) – but it can be converted to temperature units by dividing by Boltzmann’s constant (i.e., \( \varepsilon/k \)). Thus 1 eV \( \approx 11,600 \) K.

5. Equilibrium and Frozen Shocks

The calculated density ratio across a normal shock, with the initial (oncoming) gas consisting of pure \( \text{O}_2 \) at 280 K, is shown in the figure below as a function of the oncoming gas velocity. The figure contains four curves, each curve is based on a different assumption. The four assumptions are: A) frozen chemistry but all other energy modes in equilibrium, B) constant \( \gamma \) based on the initial gas conditions, C) equilibrium flow with the oncoming gas at a pressure of 0.01 atm, and D) equilibrium flow with an oncoming pressure of 0.1 atm.

a) Identify which curve belongs to which assumption (identify each curve in your answer by the number listed on the graph). BE SURE to provide your reasoning.

b) At an oncoming velocity of 4000 m/s, which of the assumptions (A, B, C or D) will result in the smallest speed of sound? BE SURE to provide your reasoning.

c) At an oncoming velocity of 9000 m/s, which of the assumptions (A, B, C or D) will result in the largest speed of sound? BE SURE to provide your reasoning.