TD Properties of NonReacting Gas Mixtures

- So far have looked at Statistical Mechanics results for a single (pure) perfect gas
  - shown how to get gas properties from partition function (Q)
- For nonreacting perfect gas mixture,
  - already assumed molecular properties (quantum states, energy levels, degeneracies) are independent of other neighboring gases ("weakly interacting")
  - can just calculate TD properties of each component as if they were the only species present
  - get mixture properties by proper summations over each gas for known composition
    - $E_{\text{mix}}=m_1e_1+m_2e_2+\ldots$
    - $S_{\text{mix}}=m_1s_1+m_2s_2+\ldots$

TD Properties of Reacting Gas Mixtures

- What happens when the mixture is chemically reacting, i.e., when the composition is not known?
- Recall that we have been finding equilibrium TD properties (using equilibrium Boltzmann distribution)
  - so now we have to determine the equilibrium composition
- In classical thermodynamics
  - we used K_p (as one way to minimize Gibbs Free Energy)
- In statistical thermodynamics
  - how to determine the equilibrium composition, or how is K_p related to Q?

Statistical Mech. of Reacting PG

- Approach is very similar to that followed for single species, only provide overview here
- For simplicity, examine gas with 3 possible components: A, B, C
  - which can be related by “reaction” expression

    $$aA + bB \leftrightarrow cC \quad (\textit{if}\ \text{A,B are atoms} \Rightarrow\ C = A_{a/c}\, B_{b/c})$$

    - note, this is just a definition of **two possible chemical “states”** (LHS and RHS) for a given set of atoms
- Again making TPG assumption that molecules are “weakly interacting”, each molecule has fixed set of energy levels

$$\begin{aligned}&\varepsilon_1^A,\ \varepsilon_2^A,\ \varepsilon_3^A, \ldots\\&\varepsilon_1^B,\ \varepsilon_2^B,\ \varepsilon_3^B, \ldots\\&\varepsilon_1^C,\ \varepsilon_2^C,\ \varepsilon_3^C, \ldots\end{aligned}$$

Boltzmann Relation

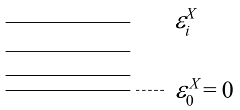
- As before, get (macroscopic, equilibrium) TD properties from Boltzmann relation $S = k \ln\Omega \cong k \ln W_{max}$
- But now $W_{system} \equiv$ total number of microstates in equilibrium (most probable) macrostate

  $$W_{system} = W^A(N_i^A) \cdot W^B(N_i^B) \cdot W^C(N_i^C)$$

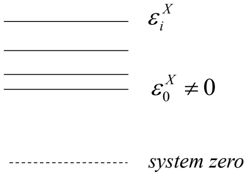
  - $W^X(N_i^X)$ = number of microstates in distribution of species X based on number of molecules N_i^X in each energy level
- So assuming the system is isolated, we want to
  - **maximize W_{system} (or $\ln W_{max}$)** $\quad S \cong k\,(\ln W^A + \ln W^B + \ln W^C)_{max}$
  - with constraints on
    - **total E**
    - **total number of each** atom, or more precisely, **nuclei type**
      - previously, this constraint was on N^X, i.e., N of a species

Energy Constraint

- Would like to write the total energy of the mixture as $E = \sum N_i^A \varepsilon_i^A + \sum N_i^B \varepsilon_i^B + \sum N_i^C \varepsilon_i^C$
- However in previous analysis, we allowed the lowest energy level of each species to be zero
  - energy "datum" was arbitrary



- But with multiple species – can't do this –can only define one energy datum (zero), i.e., need to define (arbitrary) **common** zero energy position
  - then energy of given level for given species can be expressed by



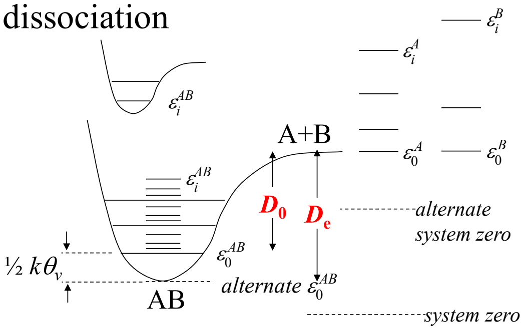
$$\varepsilon_i^X = \varepsilon_i'^X + \varepsilon_0^X$$

energy of level i relative to ground level of species X

energy of ground level of species X relative to system zero

Common Zero Energy

- Example, diatomic dissociation
  A+B↔AB
- What is difference between "ground" energy of RHS and LHS "states"?



$$\Delta\varepsilon_0 = \varepsilon_0^{AB} - (\varepsilon_0^A + \varepsilon_0^B)$$
$$= -D \text{ (Dissociation Energy of AB)}$$

not a function of choice of system zero

- For our more general example
  $aA + bB \leftrightarrow cC$

$$\Delta\varepsilon_0 = c\varepsilon_0^C - (a\varepsilon_0^A + b\varepsilon_0^B)$$

per molecule of C

$$\Delta\tilde{\varepsilon}_0 = \varepsilon_0^C - ((a/c)\varepsilon_0^A + (b/c)\varepsilon_0^B)$$

Constraints

- So now we can write the 3 constraints that must be met while maximizing W_{system} of our system

$$E = \sum N_i^A \varepsilon_i^A + \sum N_i^B \varepsilon_i^B + \sum N_i^C \varepsilon_i^C = \text{constant} \quad \textbf{(1)}$$

  - and

$$N^A + (a/c)N^C = \text{constant} = \sum N_i^A + (a/c)\sum N_i^C \quad \textbf{(2)}$$

$$N^B + (b/c)N^C = \text{constant} = \sum N_i^B + (b/c)\sum N_i^C \quad \textbf{(3)}$$

    - more generally if we had more species (X) than number (Y) of unique nuclei, we would have Y constraints on N, i.e., $N_{nuclei\ of\ type\ Y} = \sum_X N^X Z_Y^X$ $\quad Z_Y^X =$ number of Y nuclei in species X

Maximization Procedure

- Use Boltzmann limit to describe $\ln W^X$ $\quad = \ln\left[\prod_i \frac{\left(g_i^X\right)^{N_i^X}}{N_i^X!}\right] = \sum_i \ln\frac{\left(g_i^X\right)^{N_i^X}}{N_i^X!}$
- Use Lagrange's Method of Undetermined Multipliers
  - our 2 N constraints → 2 multipliers: α_A, α_B
  - the E constraint → 3rd value: β
- Resulting energy level (population) distributions for each of our species that maximize W_{system} are

$$\frac{N_i^X}{N^X} = \frac{g_i^X e^{-\beta\varepsilon_i^X}}{Q^X} \qquad Q^X = \sum_i g_i^X e^{-\beta\varepsilon_i^X}$$

do not depend on α values

  - use Gibb's eqn. to show that $\beta = 1/kT$ ***and also $p^X V = N^X kT$, p^X are partial pressures***
  - *same result we found when considering single species*

Law of Mass Action

- Trivial solution – no reaction allowed
  - N^X (for each species) fixed
- **Equilibrium composition** $aA + bB \leftrightarrow cC$
  - eliminating α_A, α_B from constraint equations gives

$$\frac{\left(N^C\right)^c}{\left(N^A\right)^a\left(N^B\right)^b} = \underbrace{\frac{\left(Q^C\right)^c e^{-\Delta\varepsilon_0/kT}}{\left(Q^A\right)^a\left(Q^B\right)^b}} = \frac{\left(Q^C e^{-\Delta\tilde{\varepsilon}_0/kT}\right)^c}{\left(Q^A\right)^a\left(Q^B\right)^b}$$

( ) is just Q^C calculated with its "zero" datum @ $a/c\ A + b/c\ B$

essentially Boltzmann distribution for two "chemical states" based on ratio of their "degeneracies" (Q's) and the "excited chemical state's" energy

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-\varepsilon_1/kT}$$

ε_1

$\varepsilon_0 = 0$

$$\varepsilon_{i,new} = \varepsilon_i + \varepsilon_{offset} \Rightarrow Q_{new} = \sum g_i e^{\frac{-\varepsilon_{i,new}}{kT}} = e^{\frac{-\varepsilon_{offset}}{kT}} \sum g_i e^{\frac{-\varepsilon_i}{kT}}$$

Equilibrium Constant

- Rewriting in terms of partial pressures (or mole fractions)
  - for perfect gases $p_i = N_i\,kT/V = \chi_i p$

$$\frac{\left(N^C\right)^c}{\left(N^A\right)^a\left(N^B\right)^b} = \frac{\left(Q^C\right)^c e^{-\Delta\varepsilon_0/kT}}{\left(Q^A\right)^a\left(Q^B\right)^b} \rightarrow \frac{p_C^c}{p_A^a p_B^b} \equiv K_p = \left(\frac{kT}{V}\right)^{c-(a+b)} \frac{\left(Q^C\right)^c}{\left(Q^A\right)^a\left(Q^B\right)^b} e^{-\Delta\varepsilon_0/kT}$$

Equilibrium Constant

- Can generalize to any "reaction" expression

$$\sum_{s=1}^{n} \nu_s X_s = 0 \qquad \boxed{K_p = \prod_s p_s^{\nu_s} = \left(\frac{kT}{V}\right)^{\sum_s \nu_s} \left(\prod_s Q_s^{\nu_s}\right) e^{-\Delta\varepsilon_0/kT}}$$

Stoichiometric coeff.

$$(-\nu_1)X_1 + (-\nu_2)X_2 \leftrightarrow \nu_3 X_3 + \nu_4 X_4$$

choice of system zero arbitrary, e.g., atoms as zero "chemical" energy

$$\Delta\varepsilon_0 = \sum_s \nu_s \varepsilon_{0,s} = -\sum_s \nu_s D$$

Equilibrium Constant (con't)

$$K_p(T)=\prod_s p_i^{\nu_s}=\left(\frac{kT}{V}\right)^{\sum_s \nu_s}\left(\prod_s Q_s^{\nu_s}\right)e^{\left(\sum_s \nu_s D_s\right)/kT}$$

- K_p only function of T (for given "reaction")
  - V dependence cancels; $Q=Q(V)$
- Statistical Mechanics provides method for calculating K_p from molecular parameters
- No need to invoke a "standard" (reference) pressure p^o to write K_p when using molecular properties
  - so it is okay for K_p to have pressure units
    - units come from $(kT/V)^{\Sigma\nu_s}$

Example Calculation

- Consider a gas containing O_2 and O
  - find equilibrium relationship between p_O, p_{O_2} at 2000K?

1. Write a "reaction" relationship, e.g., $O_2 \leftrightarrow 2O$
2. Write $p_O^2/p_{O_2}=K_p$ in terms of partition functions

$$\frac{p_O^2}{p_{O_2}}=K_p(T)=\left(\frac{kT}{V}\right)^{2-1}\frac{\left(Q^O\right)^2}{\left(Q^{O_2}\right)}e^{\left(2\cancelto{0}{D^O}-D^{O_2}\right)/kT}$$

$$=\frac{kT}{V}\frac{\left(Q_{tr}^O Q_{el}^O\right)^2}{\left(Q_{tr}^{O_2}Q_{el}^{O_2}Q_{vib}^{O_2}Q_{rot}^{O_2}\right)}e^{-\theta_D^{O_2}/T} \qquad \theta_D^{O_2}\equiv\frac{D^{O_2}}{k}$$

$J/m^3 = N/m^2 = Pa$

$$=\frac{kT}{\cancel{V}}\;\frac{\left(Q_{tr}^O\right)^2}{Q_{tr}^{O_2}}\;\frac{\left(Q_{el}^O\right)^2}{Q_{el}^{O_2}}\;\frac{1}{Q_{vib}^{O_2}Q_{rot}^{O_2}}\;e^{-\theta_D^{O_2}/T}$$

$$T^{3/2}\overbrace{\left(\frac{2\pi k}{h^2}\right)^{3/2}}^{=1.976\times10^{44}\,kg^{-1}m^{-2}K^{-1}}\cancel{V}\left(\cancelto{8}{\frac{MW_O^2}{MW_{O_2}}}1.661\times10^{-27}\,kg\right)^{3/2}$$

$$\frac{\left(5+3e^{-227.6K/T}+e^{-326.4K/T}+5e^{-22{,}818K/T}\right)^2}{3+2e^{-11{,}400K/T}}$$

$$e^{\theta_v/2T}\left(1-e^{-\theta_v/T}\right)\frac{2\theta_r^{O_2}}{T}$$

using $\varepsilon_{v=0}=\tfrac{1}{2}k\theta_v$ *to be consistent with* D_e

	O_2	O
MW	32	16
θ_r (K)	2.08	
θ_v (K)	2270	
θ_{De} (K)	60500	

Example Calculation

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1. Write a “reaction” relationship, e.g., $O_2 \leftrightarrow 2O$
2. Write $p_O^2/p_{O_2}=K_p$ in terms of partition functions
3. Evaluate @ 2000K
   - $K_p = 4.61\times10^{-2}\ Pa$
   - for comparison JANAF gives $K_{p_f,\mathrm{O}} = 6.68\times10^{-4}$ *for* $\tfrac{1}{2}O_2 \leftrightarrow O$
     - $K_{p,JANAF} = (6.68\times10^{-4})^2 = 4.47\times10^{-7}\ bar$ *uses* $p_o=1\ bar$

       $= 4.47\times10^{-2}\ Pa$

       (~3% *difference*) *primarily due to anharmonic vibration + vib/rot interactions*
   - at 500 K, <1% difference