Reacting Mixtures: Equil. Properties

- So how to determine equilibrium properties of reacting TPG mixtures from statistical mechanics?
- Can use similar procedure as in classical TD
  - need
    - "possible" species present (defines state/K_p expressions)
    - molecular parameters/models for each species
    - number (or ratios) of nuclei present
    - temperature
    - and one more independent TD variables (e.g., pressure)
  - then can calculate composition using partition function
  - with known composition, can then calculate mixture's TD properties from properties of each gas component
- Let's examine some properties for which statistical mechanics has already provided new insights: **specific heat** and **entropy**

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Reacting Gas Mixture: Specific Heat

- The definition of specific heat c_p of a substance is

$$c_p = \frac{\partial h}{\partial T}\Big|_p$$

- For an ideal mixture, we can write

$$h = \frac{H_{mix}}{m_{mix}} = \frac{\sum_s n_s \bar{h}_s}{\sum_s n_s \bar{M}_s}$$

n_s: moles of species s

$\bar{M}_s$: molar mass ("molec. weight") of species s

m_{mix}: *constant*

– so

$$c_p = \frac{1}{m_{mix}} \sum_s \left[n_s \underbrace{\cancel{\frac{\partial \bar{h}_s}{\partial T}\Big|_p}}_{\hat{c}_{p_s}} + \bar{h}_s \frac{\partial n_s}{\partial T}\Big|_p \right] = \frac{1}{m_{mix}} \left[\sum_s n_s \bar{c}_{p_s} + \sum_s \bar{h}_s \frac{\partial n_s}{\partial T}\Big|_p \right]$$

$$c_p = \frac{1}{m_{mix}/n_{tot}} \left[\boxed{\sum_s \chi_s \bar{c}_{p_s}} + \boxed{\sum_s \bar{h}_s \frac{\partial \chi_s}{\partial T}\Big|_p} \right]$$

Frozen c_p
c_p of mixture for no change in composition ("nonreacting")

Chemical c_p
contribution to c_p due to change in composition

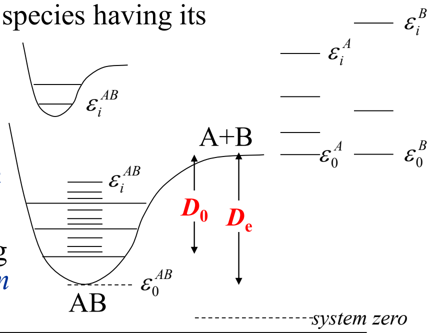
if composition not changing with T, =0

molecular weight of mixture

Reacting Perfect Gas Mixture: $c_p(T)$

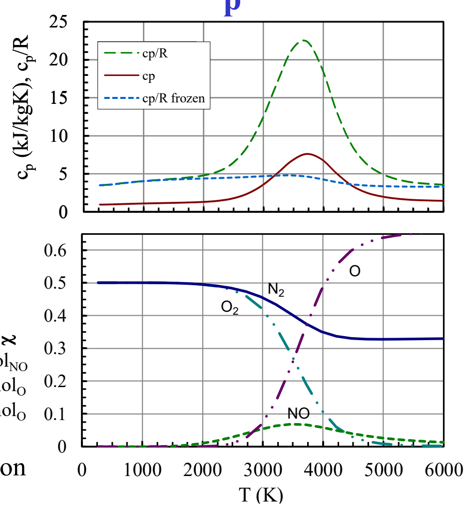
$$c_p = \frac{1}{m_{mix}/n_{tot}}\left[\sum_s \chi_s \bar{c}_{p_s} + \sum_s \bar{h}_s \left.\frac{\partial \chi_s}{\partial T}\right|_p\right]$$

- $c_{p_s}(T)$
  - already showed how to get from $Q^s(T)$ for each species/component
    - based on each molecular species having its own zero energy (datum)
- $\chi_s(T)$
  - also function of all $Q^s(T)$, but now using *common energy zero/datum*
- $h_s(T)$
  - this term also requires using *common energy zero/datum*



Example Result: c_p

- Conditions
  - gas containing N and O nuclei with 1:1 ratio
  - species: N_2, O_2, NO, O
  - p = 1 atm
- Specific heat, c_p
  - large rise for ~2200<T<3500K
  - large drop for ~3500<T<5500K
- Creation of O increases c_p more than NO creation
  - $\tfrac{1}{2}N_2+\tfrac{1}{2}O_2 \rightarrow NO$ ΔH_R~90kJ/mol$_{NO}$
  - $\tfrac{1}{2}O_2 \rightarrow O$ ΔH_R~250kJ/mol$_O$
  - $NO \rightarrow O+\tfrac{1}{2}N_2$ ΔH_R~160kJ/mol$_O$
- c_p/R dominated by chemical term while species composition changing



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Example Result: s

- Entropy, s
  - increases with T ($\sim c_p \ln T$ if c_p constant)
  - s vs T slope ↑ as O created, but s/R ↓
- **Why?**
  - O has lower c_p/R so s/R↓
  - O ↑⇒more moles, so s↑
- No evidence that chemical c_p/R impacts s (for known T)

$$Q_{com}^X = e^{\frac{-\varepsilon_{off}}{kT}} Q^X$$

$$\frac{s^X}{R^X} = \boxed{\ln Q_{com}^X + T\frac{\partial \ln Q_{com}^X}{\partial T}}$$

$$= \left(\frac{-\varepsilon_{off}^X}{kT} + \ln Q^X\right) + \left(\frac{\varepsilon_{off}^X}{kT} + T\frac{\partial \ln Q^X}{\partial T}\right)$$

can use either partition function

$$= \boxed{\ln Q^X + T\frac{\partial \ln Q^X}{\partial T}}$$

  - so difference in "chemical" energies of species only impacts composition ($s_{mix} = \sum Y_i s_i$)