Chemical TD of Gases

- So far, we have primarily developed "general" TD relations
  - broad class of simple-compressible substances
- Now turn focus to gases
  - develop TD relations for various gas "models"
- Start with ideal gas law model
  - typically defined based on following *p*-*v*-*T* behavior given by $pV=n\bar{R}T$
    - derivable (later) for point molecules (take up no volume) with only short range (repulsive) interactions that last a very short amount of time ⇒valid for "low" pressure but not too low a temperature
- Then expand to more complex gas models

Perfect Gases

- Various terms commonly for this gas model
  - ideal gas (IG)
  - perfect gas (PG)
  - thermally perfect gas (TPG)

*careful, these terms often used to indicate **additional** behavior, i.e., calorically perfect*

- For TD relations begin here with definitions based on chemical potential μ
  - also useful for dealing with TPG mixture and other ideal solutions
- Will see for
  - single TPG $\mu = \mu^o(T) + \bar{R}T \ln p/p^o$
  - TPG mixture $\mu_i = \mu_i^o(T) + \bar{R}T \ln p_i/p_i^o$
  - ideal solution $\mu_i = \mu_i^*(p,T) + \bar{R}T \ln \chi_i$

reference pressure

or sometimes just

$\ln p$

$\ln p_i$

with $p^o=1$?

Single (Species) Thermally Perfect Gas

- Begin with some **definitions**
  - let μ and μ^o be chemical potentials of our gas at pressures p and p^o but at **same *T***, i.e.,

$$\mu \equiv \mu(p,T) \qquad \mu^o \equiv \mu(p^o,T) = \mu^o(T)$$

  - then we will **define a TPG** as a gas that follows the relationship

$$\mu = \mu^o(T) + \bar{R}T \ln \frac{p}{p^o}$$

$\mu^o \equiv$ standard chemical potential @*T* and p^o

    - note this requires the p dependence to be separable from the T dependence
    - typical to let p^o =1 unit (e.g., 1 atm or 1 bar), so can write

$$\boxed{\mu = \mu^o(T) + \bar{R}T \ln p}$$

Single TPG: State Eqns.

- Develop using $\mu = \mu^o(T) + \bar{R}T \ln p$
  - recall $\left.\frac{\partial \mu_i}{\partial p}\right|_{T,\chi_j} = \bar{v}_i$ and $\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_j} = -\bar{s}_i$
  - for pure substance (single component)

$$\hat{v} = \left.\frac{\partial \mu}{\partial p}\right|_T = \bar{R}T\frac{1}{p} \qquad \Rightarrow \boxed{p\bar{v} = \bar{R}T}$$

$$\hat{s} = -\left.\frac{\partial \mu}{\partial T}\right|_p = -\frac{d\mu^o}{dT} - \bar{R}\ln p$$

$$\mu = \hat{h} - T\hat{s}$$

$$\hat{h} = \mu + T\hat{s}$$

$$= \mu^o - \bar{R}T\ln p - T\left(\frac{d\mu^o}{dT} + \bar{R}\ln p\right)$$

$$\boxed{\hat{h} = \mu^o - T\frac{d\mu^o}{dT}}$$

  - from h defn. $\hat{u} = \hat{h} - p\hat{v}$

$$\boxed{\hat{u} = \hat{h} - \bar{R}T}$$

*for TPG,
h and u only functions
of temperature*

degenerate state eqns, function of 1 TD property

Single TPG: Caloric State Eqns.

- Previously showed $d\hat{u} = \hat{c}_v dT + \cancelto{0}{\left.\frac{\partial \hat{u}}{\partial \hat{v}}\right|_T} d\hat{v}$ $\quad d\hat{h} = \hat{c}_p dT + \cancelto{0}{\left.\frac{\partial \hat{h}}{\partial p}\right|_T} dp$
  - so $\boxed{\begin{matrix} d\hat{u} = \hat{c}_v dT & d\hat{h} = \hat{c}_p dT \\ du = c_v dT & dh = c_p dT \end{matrix}}$ ***c_p, c_v only function of T***
  (since u, h only T dependent)
  - and from previous result $\hat{c}_p - \hat{c}_v = T\frac{\alpha^2 \hat{v}}{\kappa} = T\frac{(1/T)^2 \hat{v}}{1/p} = \frac{p\hat{v}}{T}$

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p = \frac{1}{(n\bar{R}T/p)}\left.\frac{\partial(n\bar{R}T/p)}{\partial T}\right|_p = \frac{1}{T}$$

$$\kappa = \frac{-1}{(n\bar{R}T/p)}\left.\frac{\partial(n\bar{R}T/p)}{\partial p}\right|_T = \frac{1}{p}$$

$$\boxed{\begin{matrix} \hat{c}_p - \hat{c}_v = \bar{R} \\ c_p - c_v = R \end{matrix}}$$

  - specific heats often modeled by polynomial expressions
    - **Shomate eqn** $\quad c_p = a + bT + cT^2 + dT^3 + eT^{-2}$
    - **NASA polynomial** $\quad c_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$

Single TPG: Entropic State Eqn.

- From Gibbs eqn. $\quad T d\hat{s} = d\hat{u} + p d\hat{v} \qquad = d\hat{h} - \hat{v} dp$
  - for TPG $\qquad = \hat{c}_v dT + \frac{\bar{R}T}{\hat{v}} d\hat{v} \quad = \hat{c}_p dT - \frac{\bar{R}T}{p} dp$

$$\boxed{\begin{matrix} d\hat{s} = \hat{c}_v \frac{dT}{T} + \bar{R}\frac{d\hat{v}}{\hat{v}} \quad = \hat{c}_p \frac{dT}{T} - \bar{R}\frac{dp}{p} \\ \hat{s}_2 - \hat{s}_1 = \int_{T_1}^{T_2} \hat{c}_v \frac{dT}{T} + \bar{R}\ln\left(\frac{\hat{v}_2}{\hat{v}_1}\right) = \int_{T_1}^{T_2} \hat{c}_p \frac{dT}{T} - \bar{R}\ln\left(\frac{p_2}{p_1}\right) \end{matrix}}$$

  - if c_p, c_v constant over T range of interest, denoted ***calorically perfect***

$$\Delta\hat{s}_{12} = \hat{c}_v \ln\left(\frac{T_2}{T_1}\right) + \bar{R}\ln\left(\frac{\hat{v}_2}{\hat{v}_1}\right) = \hat{c}_p\left(\frac{T_2}{T_1}\right) - \bar{R}\ln\left(\frac{p_2}{p_1}\right)$$

$$e^{\Delta\hat{s}_{12}/\hat{c}_v} = \left(\frac{T_2}{T_1}\right)\left(\frac{\hat{v}_2}{\hat{v}_1}\right)^{\cancelto{\gamma-1}{\bar{R}/\hat{c}_v}} = \left(\frac{T_2}{T_1}\right)^{\cancelto{\gamma}{\hat{c}_p/\hat{c}_v}}\left(\frac{p_2}{p_1}\right)^{\cancelto{1-\gamma}{-\bar{R}/\hat{c}_v}}$$

Single TPG: Entropic State Eqn.

calorically perfect

$$e^{\Delta\hat{s}_{12}/\hat{c}_v}=\left(\frac{T_2}{T_1}\right)\left(\frac{\hat{v}_2}{\hat{v}_1}\right)^{\gamma-1}=\left(\frac{T_2}{T_1}\right)^{\gamma}\left(\frac{p_2}{p_1}\right)^{1-\gamma}$$

- For **isentropic process** (Δs=0)

$$\left(\frac{T_2}{T_1}\right)=\left(\frac{\hat{v}_2}{\hat{v}_1}\right)^{1-\gamma}=\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \qquad \left(\frac{p_2}{p_1}\right)\left(\frac{\hat{v}_2}{\hat{v}_1}\right)^{\gamma}=1$$

  - or equivalently pv^{γ} = constant
- One version of general class of **polytropic processes**

pv^{n} = constant

$$\left(\frac{T_2}{T_1}\right)=\left(\frac{\hat{v}_2}{\hat{v}_1}\right)^{1-n}=\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$$

n	Process
0	Isobaric
1	Isothermal
γ	Isentropic
∞	Isochoric

Thermally Perfect Gas Mixtures

- Again begin with **definitions**
  - let μ_i and μ_i^o be chemical potentials of ith component of gas, having mole fraction χ_i
  - **define a TPG mixture** as one that follows relationship

$$\mu_i=\underbrace{\mu_i^o(T)+\bar{R}T\ln\frac{p}{p^o}}_{\text{independent of composition}}+\underbrace{\bar{R}T\ln\chi_i}_{\text{simple composition dependence}}$$

decoupled

  - as $\chi_i \to 1$ $\mu_i \to \mu_{pure\ i}$
    - so 1st term is same as pure TPG of ith component
  - if use p^o=1 unit (e.g., atm), and define $p_i = p\chi_i$

$$\boxed{\mu_i=\mu_i^o(T)+\bar{R}T\ln p_i} \qquad \Rightarrow \sum_i p_i = p$$

same as single TPG

Thermally Perfect Gas Mixtures

$$\mu_i = \mu_i^o(T) + \bar{R}T \ln p_i$$

- Comments
  - $\mu_i = \mu_i(p_i, T) = \hat{g}_i(p_i, T)$
    - Gibb’s value for pure component i evaluated at p_i, T
  - $\mu_i = \mu_i(p, T, \chi_i)$ but not function of $\chi_{j\neq i}$
    - *independent of other components in mixtures*
    - this decoupling of composition dependence is property of general class of mixtures called **Mixtures of Independent Substances**
      - also includes **Ideal Solutions** (liquid and/or solid)
    - on molecular scale, this idealization requires allowed quantum states of each component to be unaffected by presence of other components (will see later in Statistical Mechanics)

TPG Mixtures: State Eqns.

- Develop using $\mu_i = \mu_i^o(T) + \bar{R}T \ln p_i$
  - similar to single TPG $\bar{v}_i = \left.\frac{\partial \mu_i}{\partial p}\right|_{T,\chi_j} = \frac{\bar{R}T}{p}$ $\Rightarrow \boxed{p\bar{v}_i = \bar{R}T}$

    for component i
    - each component behaves like TPG
    - molar volume same for components in mixture
      - so $V = \sum_i n_i\bar{v}_i = \bar{v}_i \sum_i n_i = \bar{v}_i n \Rightarrow \hat{v} = \frac{V}{n} = \bar{v}_i$ $\Rightarrow \boxed{p\hat{v} = \bar{R}T}$

        for mixture
  - using partial pressure definition

$$p_i = \chi_i p = \chi_i \frac{\bar{R}T}{V/n} = \frac{\chi_i n\bar{R}T}{V} \quad \Rightarrow \boxed{p_i V = n_i \bar{R}T}$$

for component i

TPG Mixtures: Caloric State Eqns.

- Recall $\mu_i = \bar{g}_i = \bar{h}_i - T\bar{s}_i = \bar{h}_i + T\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_j,\chi_i}$

$$-\frac{\mu_i}{T^2} + \frac{1}{T}\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_j,\chi_i} = -\frac{\bar{h}_i}{T^2} \qquad \Rightarrow \frac{\bar{h}_i}{T^2} = \left.\frac{-\partial(\mu_i/T)}{\partial T}\right|_{p,\chi_j,\chi_i}$$

- Using TPG mixture: $\mu_i = \mu_i^o + \bar{R}T \ln p + \bar{R}T \ln\chi_i$

$$\Rightarrow \left.\frac{\partial(\mu_i/T)}{\partial T}\right|_{p,\chi_j,\chi_i} = \frac{d}{dT}\left(\frac{\mu_i^o}{T}\right) + 0 + 0$$

- So $\frac{\bar{h}_i}{T^2} = \frac{\hat{h}_i}{T^2} \Rightarrow \boxed{\bar{h}_i(T) = \hat{h}_i(T)}$ *fn of T only*

for pure i
TPG at T

- Similarly $\boxed{\bar{u}_i(T) = \hat{u}_i(T)}$

- Mixture enthalpy $H(T) = \underbrace{\sum_i n_i \bar{h}_i(T)}_{\text{mixed gases}} = \underbrace{\sum_i n_i \hat{h}_i(T)}_{\text{unmixed}}$

no ΔH (or ΔU) due to mixing
also true for ideal solutions

What is $\hat{c}_p$ of mixture?

$$\hat{c}_p = \sum_i \chi_i \hat{c}_{p_i}$$

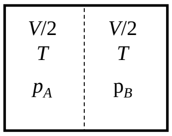
TPG Mixture: Entropy Due to Mixing

- Now let’s compare *S* and *G* of components mixed vs unmixed (at same *T*)

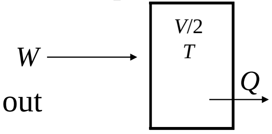
- For TPG mixture $G = \sum_i n_i \bar{g}_i = \sum_i n_i\left(\mu_i^o + \bar{R}T \ln p_i\right)$
  - $p^i \equiv p$ of i^{th} component before mixed $$= \sum_i n_i\left(\overbrace{\mu_i^o + \bar{R}T \ln p^i}^{\mu^i} + \bar{R}T \ln \frac{p_i}{p^i}\right)$$
  - so $$G_{\substack{after\\mix}} - G_{\substack{before\\mix}} = \Delta G_{mixing} = \bar{R}T\sum_i n_i \ln \frac{p_i}{p^i}$$
  - and for *T*=const.
    $\Delta G_{mixing} = \underset{0}{\cancel{\Delta H}}_{mixing} - T\Delta S_{mixing}$

$$\boxed{\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R}\sum_i n_i \ln \frac{\overset{\chi_i p}{p_i}}{p^i}}$$

TPG Mixture: Entropy Due to Mixing



- Compare to earlier 2nd Law example of removing partition between perfect gases
- Result was $\Delta S = k(N_A+N_B)\ln 2$
  $= \bar{R}\,(n_A+n_B)\ln 2$
- With new expression $$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R}\sum_i n_i \ln\frac{p_i}{p^i}$$
  $\Delta S = -\bar{R}\,(n_A\ln½+n_B\ln½)$ *since V for each gas increases by 2, pressure for each decreases by 2*
  $= \bar{R}\,(n_A+n_B)\ln 2$ ✓
- How to get $\Delta S_{mixing}=0$ for our 2 gases (isothermally)?
  - final partial pressures must be same as initial pressures
    - requires isothermal and reversible compression to $V/2$
    - thus also work in and heat transfer out



TPG Mixture: Entropy Due to Mixing

- So we have 2 special cases $$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R}\sum_i n_i \ln\frac{p_i}{p^i}$$

1. all gases have same initial pressures, which also match final pressure: $p^i=p$ for all i
   $$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R}\sum_i n_i \ln\frac{p\chi_i}{p^i} = \bar{R}\sum_i n_i \ln\chi_i \quad \mathbf{< 0}$$
   - mixing produces entropy (S↑ and G↓) as expected
2. initial pressure of each gas is same as its final partial pressure in the mixture: $p^i=p_i$ for each i
   $$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R}\sum_i n_i \ln\frac{p_i}{p^i} \quad \mathbf{=0}$$
   - in this case no entropy change associated with mixing
     - but requires $V < V^i$, so work and heat transfer