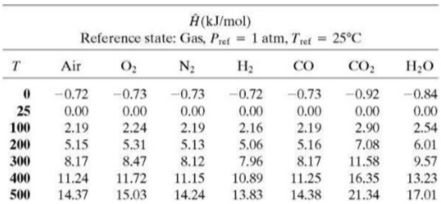
Standard Reference States

- As we have seen, most TD calculations involve changes in state properties, e.g.,
  - $\boldsymbol{\Delta U} = Q + W$
  - $\dot{m}\boldsymbol{\Delta h} = \dot{Q} + \dot{W}$
  - $\ln K_p = -\boldsymbol{\Delta G}^{\mathrm{o}}/\bar{R}T$
- Helpful, however, to define reference condition/state for properties
  - e.g., tables often provide $h_T - h_{Tref}$
  - common choice T_{ref} =298.15 K

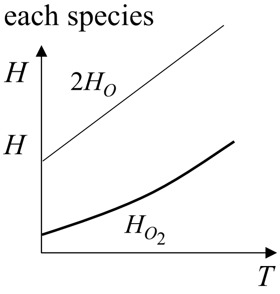


$\hat{H}$(kJ/mol)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01

Standard Reference States

- Defining a reference state even more useful for reacting systems (composition change allowed)
  - need to account for differences in chemical bonds between atoms (or the "chemical energy") for each species
  - for example, at a fixed T we must input energy to covert 1 mole of O_2 to 2 moles of O atoms
    - so at a given T, they have different H



- So we will define standard reference states for species in terms of
  - enthalpy h_i: **enthalpy of formation**
  - entropy s_i: **3rd Law**
  - together that also creates a reference for other properties, e.g., **standard reference for $\boldsymbol{g_i}$** $= h_i - Ts_i$

Standardized Enthalpy

- **Approach**
  1. create set of chemical species from which all other species can be formed, denoted the **reference elements**
  2. define a **reference temperature** (T_{ref}) and **standard pressure** (typically 1 atm or 1 bar, and denoted by ^{o})
  3. set the enthalpy of all reference elements to be zero at the reference condition
     - essentially defining the "chemical energy" of each reference element to be zero
- Then enthalpy of a chemical species ***i*** at any temperature ***T*** and the standard pressure becomes

$$\left(H_T^o\right)_i = \left(\Delta H^o_{f,T_{ref}}\right)_i + \left(H_T^o - H^o_{T_{ref}}\right)_i$$

≡ Standard **Heat of Formation** or **Formation Enthalpy**

Standardized Enthalpy

- Interpretation of each term

$$\left(H_T^o\right)_i = \underbrace{\left(\Delta H^o_{f,T_{ref}}\right)_i} + \underbrace{\left(H_T^o - H^o_{T_{ref}}\right)_i}$$

amount of energy required to form species i from the reference elements at the standard pressure and reference temperature

Chemical Energy

amount of energy required to change temperature of species i from the T_{ref} to T at the standard pressure

Sensible Enthalpy $= \int_{T_{ref}}^{T} \left(C_p^o\right)_i dT$

- For thermally perfect gas
  – formation enthalpy and sensible enthalpy are not functions of pressure
- $\Delta H^o_{f,T_{ref}}$ typically given on a per mole or per mass basis

$$\left(\Delta \bar{h}^o_{f,T_{ref}}\right)_i \qquad \left(\Delta h^o_{f,T_{ref}}\right)_i$$

Reference Elements

- Two common choices for elements
  - the (neutral) atoms — NASA Tables
    - easy to write expression to create any molecule (or ion) from its atom(s)
  - the most common form of a single type of nuclei at STP — **JANNAF** ***most common, we will use it***
    - i.e., H_2, O_2, N_2, Ar, $C(s)_{graphite}$, …
    - convenient because these species often major constituents in the composition

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Standard *G* – 3rd Law of TD

- What is a good zero datum (reference) for *G*?
  - $G = H - T\,S$, and already established datum for T (absolute T scale) and for H (standardized enthalpy)
- So real question is **what is a good datum for *S*?**
  - statistical mechanics (see later) suggests an absolute value for S should exist
- **3rd Law of TD**
  - the entropy of any pure substance in TD equilibrium approaches zero as temperature approaches zero $\lim_{T \to 0} S = 0$
  - also supported by experimental observations of Nernst (~1906) that for low T, $\Delta U \to \Delta F$ $(=U-TS)$
- So we can create a standard Gibbs Free Energy $\boldsymbol{(G^o_T)_i}$ and standard G of formation $\boldsymbol{(\Delta G^o_{f,T})_i}$ *usually tabulated on per mole or per mass basis*

Formation Reactions

- Chemical state expressions where 1 mole of species of interest is "formed" (appears on the right-hand-side) from its elements (appear on the left-hand-side)
    - both elements and formed species are at T and standard pressure (p^o)
- Examples

	LHS	RHS	$H^o_{T,RHS} - H^o_{T,LHS}$	$G^o_{T,RHS} - G^o_{T,LHS}$
– form H_2O:	$H_2 + ½O_2 \leftrightarrow$	H_2O	$\left(\Delta\bar{h}^o_{f,T}\right)_{H_2O}$	$\left(\Delta\bar{g}^o_{f,T}\right)_{H_2O}$
– form NO_2:	$½H_2 + O_2 \leftrightarrow$	NO_2	$\left(\Delta\bar{h}^o_{f,T}\right)_{NO_2}$	$\left(\Delta\bar{g}^o_{f,T}\right)_{NO_2}$
– form O_2:	$O_2 \leftrightarrow$	O_2	$\cancelto{0}{\left(\Delta\bar{h}^o_{f,T}\right)_{O_2}}$	$\cancelto{0}{\left(\Delta\bar{g}^o_{f,T}\right)_{O_2}}$

so formation enthalpy and formation Gibbs are zero for elements

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Equilibrium Constants, K_p

- In this section, will show how to determine any K_p value from standard G of formation data
- Example: $4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O$ (1)
    - could write this single chemical relationship as system of equations that form each species from its elements
        - $4NH_3 \leftrightarrow 2N_2 + 6H_2$ (2)
        - $2N_2 + 2O_2 \leftrightarrow 4NO$ (3)
        - $6H_2 + 3O_2 \leftrightarrow 6H_2O$ (4)

(2) + (3) + (4) = (1)

- so

$$\Delta G^o_2 = -4\bar{g}^o_{NH_3} + 2\bar{g}^o_{N_2} + 6\bar{g}^o_{H_2} = -4\Delta\bar{g}^o_{f\,NH_3}$$
$$\Delta G^o_3 = -2\bar{g}^o_{N_2} - 2\bar{g}^o_{O_2} + 4\bar{g}^o_{NO} = 4\Delta\bar{g}^o_{f\,NO}$$
$$\Delta G^o_4 = -6\bar{g}^o_{H_2} - 3\bar{g}^o_{O_2} + 6\bar{g}^o_{H_2O} = 6\Delta\bar{g}^o_{f\,H_2O}$$
$$\Delta G^o_1 = \Delta G^o_2 + \Delta G^o_3 + \Delta G^o_4 = \underbrace{-4\Delta\bar{g}^o_{f\,NH_3}}_{\text{LHS}} \underbrace{+4\Delta\bar{g}^o_{f\,NO} + 6\Delta\bar{g}^o_{f\,H_2O}}_{\text{RHS}}$$

What happened to O_2? $\Delta\bar{g}^o_{f\,O_2}=0$

same form holds true for ΔH^o_1

K_p using Formation Values

- Previously we showed for a given chemical state equation ("reaction")

$$K_p(T) = e^{-\Delta G_T^o/\bar{R}T} \qquad \Delta G_T^o \equiv \sum_i \nu_i \mu_i^o$$

- Using formation values

$$\boxed{K_p(T) = e^{-\Delta G_f^o/\bar{R}T} \qquad \Delta G_f^o \equiv \sum_i \nu_i \Delta\bar{g}_{f\,i}^o}$$

  - if we have data (e.g., table) of $\Delta\bar{g}_{f\,i}^o$ for each substance at desired T, then can calculate K_p for any arbitrary "reaction"
    - such a listing in the **JANNAF tables**

- For each formation reaction, can also write a K_p

$$K_{p_{f,i}}(T) = e^{-\Delta\bar{g}_{f_i}^o/\bar{R}T}$$

Equilibrium Constant of Formation

  - so for any arbitrary (overall) "reaction" (recall $K_p = \prod_j K_{pj}$)

$$K_p(T) = \prod_i \left(K_{p_{f,i}}\right)^{\nu_i}$$