## ADDITIONAL PRODUCT FORMATION

- **NO** Dissociation: Complete Combustion
  - Equivalence ratio less than or equal unity, $\phi \leq 1$
  - The products formed are: CO_2, H_2O, O_2, and N_2

  - Equivalence ratio greater than unity, $\phi > 1$
  - The products formed are: CO_2, CO, H_2O, H_2, and N_2

- **WITH** Dissociation
  - Products formed include: CO_2, CO H_2O, H_2, H, OH, O_2, O, NO, N_2, and N
  - Concentration is dependent on T, P and ϕ

CHEMICAL EQUILIBRIUM FOR A FIXED-MASS SYSTEM

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$CO + \frac{1}{2}O_2 \rightarrow (1-\alpha)CO_2 + \alpha CO + \frac{\alpha}{2}O_2$$
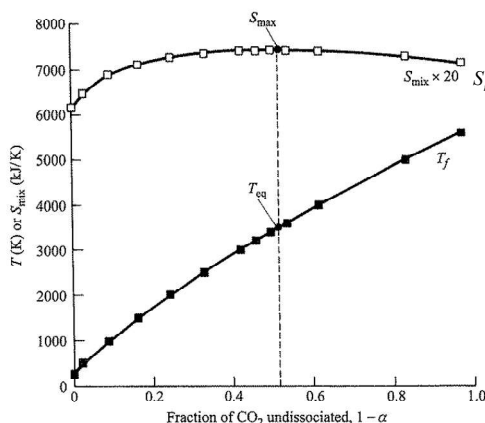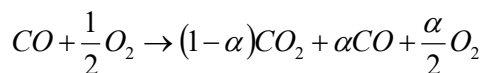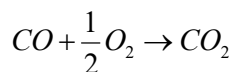
- If final temperature of combustion reaction is high enough, CO_2 will dissociate
- Can calculate adiabatic flame temperature as function of α (α = fraction of CO_2 dissociated)
- Must consider second law: $dS \geq 0$

$$S_{mix}(T_f, P) = \sum N_i \bar{s}_i(T_f, P_i) = (1-\alpha)\bar{s}_{CO2} + \alpha \bar{s}_{CO} + \frac{\alpha}{2}\bar{s}_{O2}$$

- Individual species entropy

$$\bar{s}_i = \bar{s}_i^0(T_{ref}) + \int_{T_{ref}}^{T} \bar{c}_{p,i}\frac{dT}{T} - R_u \ln\frac{P_i}{P^0}$$

- Composition of system will shift toward point of maximum entropy when approaching from either side, since dS is positive
- Once maximum entropy is reached no further changes since would violate second law
- $(dS)_{U,V,m} = 0$

2nd LAW OF THERMODYNAMICS: GIBBS FREE ENERGY

- To arrive at equilibrium relations, employ 2nd Law of Thermodynamics
- State 2nd Law in terms of Gibbs Free Energy, **G=H-TS**
- **For a closed system at constant T and P, the Gibbs free energy is a minimum at thermodynamic equilibrium**

$$dS = \frac{\delta Q}{T} + dS_{irrev}$$

$$\delta Q = dH - VdP$$

$$TdS = dH - VdP + TdS_{irrev}$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = -SdT + VdP - TdS_{irrev}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i}, \quad -TdS_{irrev} = \sum_i \frac{\partial G}{\partial n_i}\bigg|_{T,P} dn_i$$

$$\sum_i \frac{\partial G}{\partial n_i}\bigg|_{T,P} dn_i = 0 \qquad \textbf{Criteria for Equilibrium}$$

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MORE USEFUL FORMS

- For a mixture of ideal gases, the Gibbs function for the i-th species is

$$\bar{g}_{i,T} = \bar{g}_{i,T}^0 + R_u T \ln(P_i / P^0)$$

- The Gibbs function for a mixture of ideal gas

$$G_{mix} = \sum N_i \bar{g}_{i,T} = \sum N_i \left[\bar{g}_{i,T}^0 + R_u T \ln(P_i / P^0) \right]$$

- For fixed temperature and pressure, the equilibrium condition: $\mathrm{d}G_{mix} = 0$.

- Next step:

$$\sum \mathrm{d}N_i \left[\bar{g}_{i,T}^0 + R_u T \ln(P_i / P^0) \right] + \sum N_i \mathrm{d}\left[\bar{g}_{i,T}^0 + R_u T \ln(P_i / P^0) \right] = 0$$

- Second term = 0, since

$$\mathrm{d}(\ln P_i) = \frac{\mathrm{d}P_i}{P_i} \quad \text{and that} \quad \sum \mathrm{d}P_i = 0 \text{ as total pressure is constant.}$$

- Finally,

$$\sum \mathrm{d}N_i \left[\bar{g}_{i,T}^0 + R_u T \ln(P_i / P^0) \right] = 0$$

$$\text{or} \qquad \sum \mu_i \mathrm{d}N_i = 0$$

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MORE USEFUL FORMS

- For a general system, $\quad aA + bB \Leftrightarrow cC + dD$

- Changes in number of moles of species (A, B, C, D)

$$\mathrm{d}N_A = -ka, \quad \mathrm{d}N_B = -kb, \quad \mathrm{d}N_C = +kc, \quad \mathrm{d}N_D = +kd$$

- We have

$$-a\left[\bar{g}_{A,T}^0 + R_u T \ln(P_A / P^0)\right] - b\left[\bar{g}_{B,T}^0 + R_u T \ln(P_B / P^0)\right] +$$
$$c\left[\bar{g}_{C,T}^0 + R_u T \ln(P_C / P^0)\right] + d\left[\bar{g}_{D,T}^0 + R_u T \ln(P_D / P^0)\right] = 0$$

- Next step

$$R_u T \ln \frac{(P_C / P^0)^c (P_D / P^0)^d}{(P_A / P^0)^a (P_B / P^0)^b} = (-a\bar{g}_{A,T}^0 - b\bar{g}_{B,T}^0 + c\bar{g}_{C,T}^0 + d\bar{g}_{D,T}^0) = \Delta G_T^0$$

Change in Gibbs Free Energy

- Next step

$$K_p = \exp\left(\frac{-\Delta G_T^0}{R_u T}\right), \quad \text{where } K_p = \text{ Equilibrium Constant}$$

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MORE USEFUL FORMS

- The more negative ΔG° is, the larger K_p is, and the more spontaneous the reaction is

$$-\Delta G^\circ = RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$K_P = K_P(T) = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Another useful form

$$\boxed{K_P(T) = \prod_{i,gas} (\chi_i P)^{\nu_i}}$$

$$-\Delta G^\circ = RT \ln K_P$$

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COMMENTS ON K_P

1. **The K_p of a reaction depends on temperature only**
   – Independent of pressure of equilibrium mixture
   – Not affected by presence of inert gases

2. **The K_p of the reverse reaction is $1/K_p$**

3. **The larger the K_p, the more complete the reaction**
   – If $K_p > 1,000$ (or $\ln K_p > 7$) reaction assumed complete
   – If $K_p < 0.001$ (or $\ln K_p < -7$) reaction assumed not to occur

4. **Mixture pressure affects the equilibrium composition (but not K_p)**

5. **Presence of inert gases affects the equilibrium composition**

6. **When stoichiometric coefficients are doubled, the value of K_p is squared**

7. **Free electronic in the equilbrium composition can be treated as an ideal gas**

8. **Equilibrium calculations provide information on the equilibrium composition of a reaction, not on the reaction rate**

ADIABATIC COMBUSTION EQUILIBRIUM

- Previously we have considered:
  - **Known Stoichiometry + 1st Law (Energy Balance) → Adiabatic Flame Temperature**
  - **Known P and T + 2nd Law (Equilibrium Relations) → Stoichiometry**

- Now we can combine these:
  - **1st Law (Energy Balance) + 2nd Law (Equilibrium Relations) → Adiabatic Flame Temperature + Stoichiometry**

- Solution Scheme
  1. Guess a $T = T_{guess}$
  2. Do equilibrium calculation to solve for species concentrations at T_{guess}
  3. Plug into 1st Law
  $$F\left(T_{guess}\right) = \sum_{i,prod} n_i \left[\left(H^\circ_{T_{ad}} - H^\circ_{T_0}\right) + \left(\Delta H^\circ_f\right)_{T_0}\right]_i - \sum_{i,react} n_j \left[\left(H^\circ_{T_1} - H^\circ_{T_0}\right) + \left(\Delta H^\circ_f\right)_{T_0}\right]_j = 0$$
     - We want $F(T_{guess}) = 0$
       - If $F(T_{guess}) > 0$, then initial guess was too high
       - If $F(T_{guess}) < 0$, then initial guess was too low
  1. Increment T_{guess}

Chemical Equilibrium

Consider the dissociation of CO_2 as a function of temperature and pressure,

$$CO_2 \Leftrightarrow CO + \tfrac{1}{2}O_2.$$
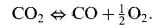
Find the composition of the mixture, i.e., the mole fractions of CO_2, CO, and O_2, that results from subjecting originally pure CO_2 to various temperatures ($T = 1500$, 2000, 2500, and $3000\,K$) and pressures (0.1, 1, 10, and $100\,atm$).

Solution

To find the three unknown mole fractions, χ_{CO_2}, χ_{CO}, and χ_{O_2}, we will need three equations. The first equation will be an equilibrium expression, Eqn. 2.66. The other two equations will come from element conservation expressions that state that the total amounts of C and O are constant, regardless of how they are distributed among the three species, since the original mixture was pure CO_2.

To implement Eqn. 2.66, we recognize that $a = 1$, $b = 1$, and $c = \tfrac{1}{2}$, since

$$(1)CO_2 \Leftrightarrow (1)CO + (\tfrac{1}{2})O_2.$$
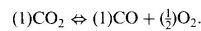
Thus, we can evaluate the standard-state Gibbs function change. For example, at $T = 2500\,K$,

$$\begin{aligned}
\Delta G_T^o &= \left[(\tfrac{1}{2}) \bar{g}_{f,O_2}^o + (1)\bar{g}_{f,CO}^o - (1)\bar{g}_{f,CO_2}^o \right]_{T=2500} \\
&= (\tfrac{1}{2})0 + (1)(-327,245) - (-396,152) \\
&= 68,907\,kJ/kmol.
\end{aligned}$$

The values above are taken from Appendix Tables A.1, A.2, and A.11.

From the definition of K_p, we have

$$K_p = \frac{(P_{CO}/P^o)^1 (P_{O_2}/P^o)^{0.5}}{(P_{CO_2}/P^o)^1}.$$

Chemical Equilibrium

We can rewrite K_p in terms of the mole fractions by recognizing that $P_i = \chi_i P$. Thus,

$$K_p = \frac{\chi_{CO}\chi_{O_2}^{0.5}}{\chi_{CO_2}} \cdot (P/P^o)^{0.5}$$

Substituting the above into Eqn. 2.66b, we have

$$\begin{aligned}
\frac{\chi_{CO}\chi_{O_2}^{0.5}(P/P^o)^{0.5}}{\chi_{CO_2}} &= \exp\left[\frac{-\Delta G_T^o}{R_u T} \right] \\
&= \exp\left[\frac{-68,907}{(8.315)(2500)} \right] \\
\frac{\chi_{CO}\chi_{O_2}^{0.5}(P/P^o)^{0.5}}{\chi_{CO_2}} &= 0.03635. \quad\quad (I)
\end{aligned}$$

We create a second equation to express **conservation of elements:**

$$\frac{\text{No. of carbon atoms}}{\text{No. of oxygen atoms}} = \frac{1}{2} = \frac{\chi_{CO} + \chi_{CO_2}}{\chi_{CO} + 2\chi_{CO_2} + 2\chi_{O_2}}.$$

We can make the problem more general by defining the C/O ratio to be a parameter Z that can take on different values depending on the initial composition of the mixture:

Z=1/2
(here)

$$Z = \frac{\chi_{CO} + \chi_{CO_2}}{\chi_{CO} + 2\chi_{CO_2} + 2\chi_{O_2}}$$

or

$$(Z-1)\chi_{CO} + (2Z-1)\chi_{CO_2} + 2Z\chi_{O_2} = 0. \quad\quad (II)$$

To obtain a third and final equation, we require that all of the mole fractions sum to unity:

$$\sum_i \chi_i = 1$$

or

$$\chi_{CO} + \chi_{CO_2} + \chi_{O_2} = 1. \quad\quad (III)$$

Simultaneous solution of Eqns. I, II, and III for selected values of P, T, and Z yield values for the mole fractions χ_{CO}, χ_{CO_2}, and χ_{O_2}. Using Eqns. II and III to eliminate χ_{CO_2} and χ_{O_2}, Eqn. I becomes

$$\chi_{CO}(1 - 2Z + Z\chi_{CO})^{0.5}(P/P^o)^{0.5} - [2Z - (1+Z)\chi_{CO}]\exp(-\Delta G_T^o/R_u T) = 0.$$

The above expression is easily solved for χ_{CO} by applying Newton–Raphson iteration, which can be implemented simply using spreadsheet software. The other unknowns, χ_{CO} and χ_{O_2}, are then recovered using Equations II and III.

Chemical Equilibrium

$$CO_2 = CO + 1/2\ O_2$$

	$P = 0.1$ atm	$P = 1$ atm	$P = 10$ atm	$P = 100$ atm
	$T = 1500\,\mathrm{K}$, $\Delta G_T^o = 1.5268 \cdot 10^8$ J/kmol			
χ_{CO}	$7.755 \cdot 10^{-4}$	$3.601 \cdot 10^{-4}$	$1.672 \cdot 10^{-4}$	$7.76 \cdot 10^{-5}$
χ_{CO_2}	0.9988	0.9994	0.9997	0.9999
χ_{O_2}	$3.877 \cdot 10^{-4}$	$1.801 \cdot 10^{-4}$	$8.357 \cdot 10^{-5}$	$3.88 \cdot 10^{-5}$
	$T = 2000\,\mathrm{K}$, $\Delta G_T^o = 1.10462 \cdot 10^8$ J/kmol			
χ_{CO}	0.0315	0.0149	$6.96 \cdot 10^{-3}$	$3.243 \cdot 10^{-3}$
χ_{CO_2}	0.9527	0.9777	0.9895	0.9951
χ_{O_2}	0.0158	0.0074	$3.48 \cdot 10^{-3}$	$1.622 \cdot 10^{-3}$
	$T = 2500\,\mathrm{K}$, $\Delta G_T^o = 6.8907 \cdot 10^7$ J/kmol			
χ_{CO}	0.2260	0.1210	0.0602	0.0289
χ_{CO_2}	0.6610	0.8185	0.9096	0.9566
χ_{O_2}	0.1130	0.0605	0.0301	0.0145
	$T = 3000\,\mathrm{K}$, $\Delta G_T^o = 2.7878 \cdot 10^7$ J/kmol			
χ_{CO}	0.5038	0.3581	0.2144	0.1138
χ_{CO_2}	0.2443	0.4629	0.6783	0.8293
χ_{O_2}	0.2519	0.1790	0.1072	0.0569

$$CO_2 \leftrightarrow CO + \tfrac{1}{2}\, O_2$$
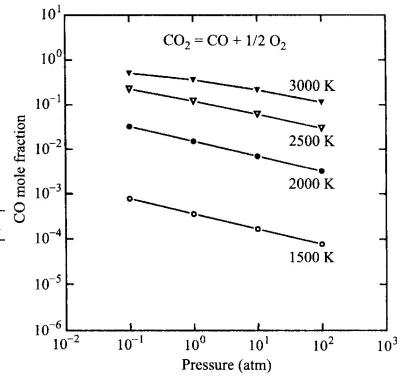
PROPANE-AIR COMBUSTION AT 1 ATM
Adopted From: Turns, S.R., Introduction to Combustion
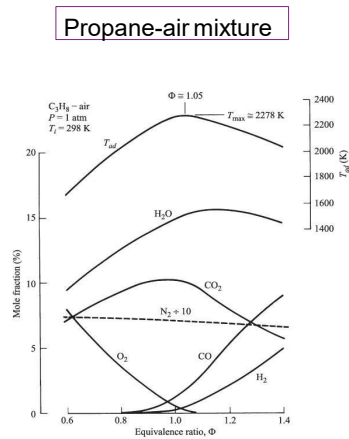
Propane-air mixture

Figure 2.13   Equilibrium adiabatic flame temperatures and major product species for propane–air combustion at 1 atm.

Combustion: Turns
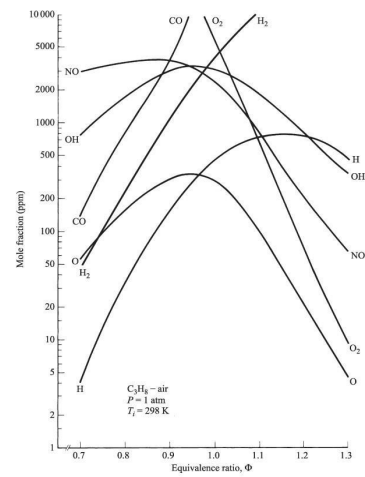

Figure 2.14   Minor species distributions for propane-air combustion at 1 atm.

Example: equilibrium composition for combustion products of ethylene with oxygen

- Species in products: CO_2, H_2O, CO, H_2, O_2, O, H, OH (S=8)
- Determine independent reactions: R = S-K (K=components, usually 3: representing C, H and O atoms)

- Equilibrium conditions $\sum\limits_{i=1}^{S}\mu_i \mathrm{d}N_i = 0$ $j = 1, ..., R$

  based on system of independent reactions

CO_2	=	CO	+	O	K_1
OH	=	H	+	O	K_2
H_2O	=	H_2	+	O	K_3
H_2	=	H	+	H	K_4
O_2	=	O	+	O	K_5
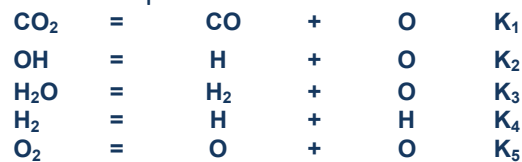
Equilibrium composition for combustion products

- Governing equations:

  1) $\sum p_i = p$

  2) $N_i / N_1 = c_{i/1}; \quad i = 2, ..., K$

  3) $p_j = K_{p,j}^{*} \prod\limits_{i=1}^{K} p_i^{\nu_{ij}}; \quad j = K+1, ..., S$

- Non-linear system of equations → numerical solution for the computation of the species composition

- equivalent to minimizing G

- Simple tool: GASEQ

  Download from http://www.arcl02.dsl.pipex.com/
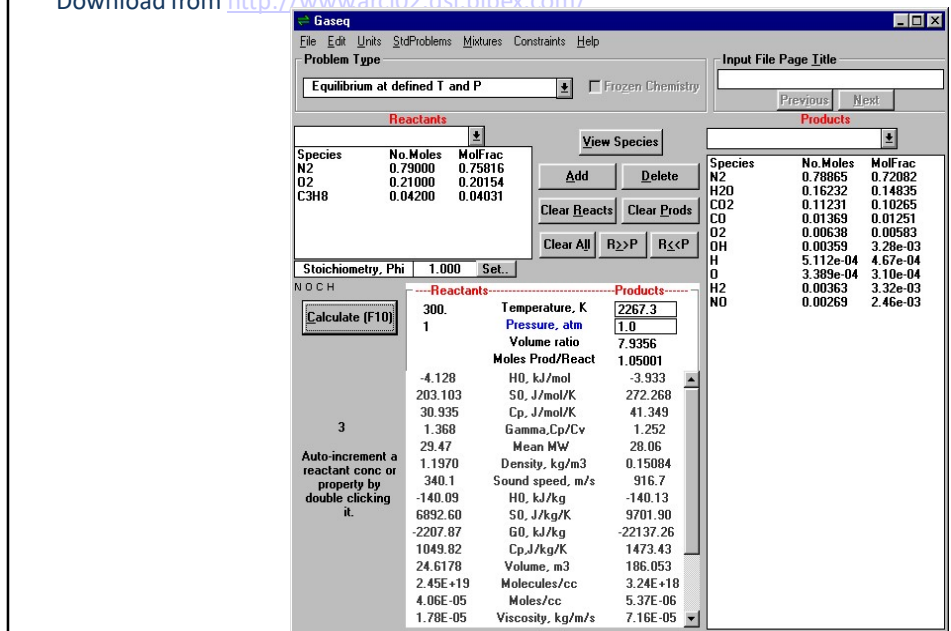

Equilibrium Software-HPFLAME

Instructions for using the software

-Download (copy) all the files in Software folder in order to use HPFLAME

- From the downloaded files in PC,

1.The file named **"Access to TPEQUIL, HPFLAME and UVFLAME Software.exe"** will execute the software.

2.Clicking on this file will open a new window.

3.Now click on the **"File"** option in the new window. 4.For constant enthalpy and pressure (enthalpy) case, select **"HPFLAME"** from the file menu.

5.This opens another new window, where we can change the parameters required for your study.

6.After changing the required parameters, click **"Save and Run."**

7.This will open another new window with the results.

Equilibrium Software-HPFLAME
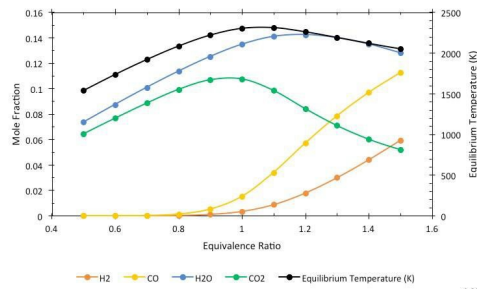
N-heptane-air mixture
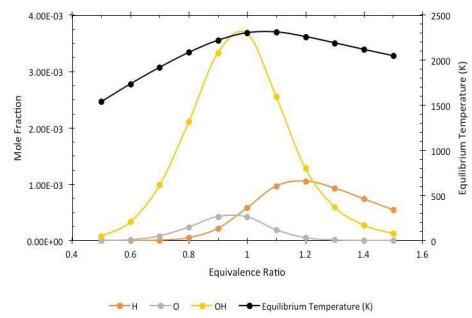
Water Gas Shift Reaction

Table 2.3 Selected values of equilibrium constant K_p for water-gas shift reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$

T (K)	K_p	T (K)	K_p
298	$1.05 \cdot 10^5$	2,000	0.2200
500	138.3	2,500	0.1635
1,000	1.443	3,000	0.1378
1,500	0.3887	3,500	0.1241

Water Gas Shift Reaction

Table 2.4 CO and H_2 mole fractions for rich combustion, C_3H_8–air, $P = 1$ atm

	χ_{CO}			χ_{H_2}		
Φ	Full Equilibrium	Water-Gas Equilibrium[a]	% Difference	Full Equilibrium	Water-Gas Equilibrium[a]	% Difference
1.1	0.0317	0.0287	−9.5	0.0095	0.0091	−4.2
1.2	0.0537	0.0533	−0.5	0.0202	0.0203	+0.5
1.3	0.0735	0.0741	+0.8	0.0339	0.0333	−1.8
1.4	0.0903	0.0920	+1.9	0.0494	0.0478	−3.4

| [a]For $K_p = 0.193$ ($T = 2200$ K).

Table 2.5 Degree of dissociation for propane–air combustion products ($P = 1$ atm, $\Phi = 1$)

	Mole Fraction		
Species	Full Equilibrium	No Dissociation	% Dissociated
CO_2	0.1027	0.1163	11.7
H_2O	0.1484	0.1550	4.3