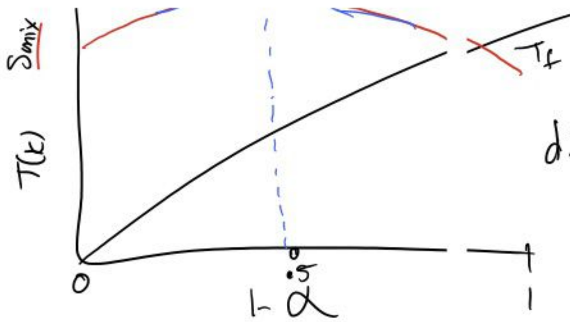


$dS \geq 0$

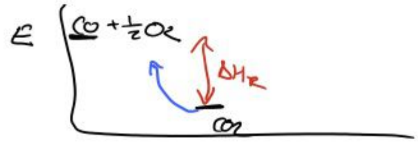
$$(dS)_{U,V,m} = 0 \quad @ \text{ eq.}$$

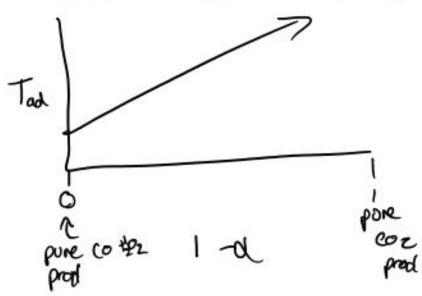
NASA Gas Eq $\Leftarrow$

$CO + \frac{1}{2}O_2 \leftarrow CO_2 \ \ominus \Delta H_R$

$\xleftarrow{\alpha\%}$

$CO + \frac{1}{2}O_2 \rightarrow (1-\alpha)CO_2 + \alpha CO + \frac{\alpha}{2}O_2$



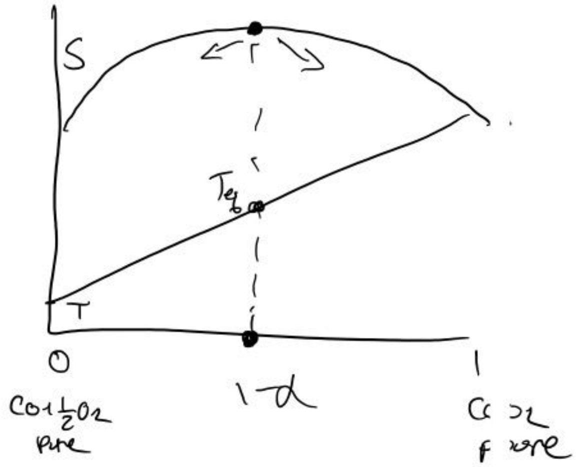


— entropy:

$$S_{final} = S_{mix}(T_f, P) = \sum_{prod.} N_i \bar{S}_i (T_f, P_i)$$

$$= (1-\alpha)\bar{S}_{CO_2} + \alpha \bar{S}_{CO} + \frac{\alpha}{2}\bar{S}_{O_2}$$

$$\bar{S}_i = \bar{S}_i^{\,o}(T_{ref}) + \int_{T_{ref}}^{T_f} \bar{c}_{p_i} \frac{dT}{T} - R_u \ln\left(\frac{P_i}{P^o}\right)$$



$ds \geq 0$

$$(dS)_{U,V,m} = 0$$

Gibbs Free Energy

$$G \equiv H - TS$$

if $ds \geq 0 \rightarrow (dG)_{T,P,m} \leq 0$

$$(dG)_{T,P,m} = 0 \text{ @ Eq.}$$

$$\bar{g}_{i,T} = \underbrace{\bar{g}^{o}_{i,T}}_{\text{Standard Gibbs Funct. @ Stand. P}} + R_u T \ln\left(P_i/P^{o}\right)$$

$$\bar{g}^{o}_{f,i}(T) \equiv \bar{g}^{o}_{i}(T) - \sum \underbrace{\nu'_j}_{\text{molar coeff.}} \bar{g}^{o}_{j}(T)$$

j elements

e.g. $CO \rightarrow \bar{g}^{o}_{CO}(T) - 1\bar{g}^{o}_{C}(T) - \frac{1}{2}\bar{g}^{o}_{O_2}(T)$

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

$$dG_{mix} = 0 \text{ @ equil.}$$

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

$$d(\ln P_i) = \frac{dP_i}{P_i}$$

$$\sum \frac{dP_i}{P_i}$$

$$\sum dP_i = 0$$

$$\hookrightarrow\ dG_{mix} = 0 = \sum dN_i\left[\bar{g}^\circ_{i,T} + R_u T \ln(P_i/P)\right]$$

$$aA + bB + \ldots \rightleftharpoons eE + fF + \ldots$$

dN_i

rxt	prod
$dN_A = -Ka$	$dN_E = Ke$
$dN_B = -Kb$	$dN_F = K_f$

$$-\cancel{K}a\left[\bar{g}^\circ_{A,T} + R_u T \ln(P_A/P^\circ)\right] - \cancel{K}b\left[\bar{g}^\circ_{B,T} + R_u T \ln(P_B/P)\right] + \cancel{K}e\left[\bar{g}^\circ_{E,T} + R_u T \ln(P_E/P^\circ)\right] + \cancel{K}f\left[\bar{g}^\circ_{F,T} + R_u T \ln(P_F/P^\circ)\right] = 0$$

$$\hookrightarrow\ -\underbrace{\left(e\bar{g}^\circ_{E,T} + f\bar{g}^\circ_{F,T} - a\bar{g}^\circ_{A,T} - b\bar{g}^\circ_{B,T}\right)}_{\Delta G^\circ_T} = R_u T \ln\left(\underbrace{\frac{(P_E/P^\circ)^e (P_F/P^\circ)^f}{(P_A/P)^a (P_B/P)^b}}_{K_p}\right)$$

- Standard State Gibbs funct. of Change

$$\Delta G^\circ_T = e\bar{g}^\circ_{E,T} + f\bar{g}^\circ_{F,T} - a\bar{g}^\circ_{A,T} - b\bar{g}^\circ_{B,T}$$

$$\Delta G^\circ_T = \left(e\bar{g}^\circ_{f,E} + f\bar{g}^\circ_{f,F} - a\bar{g}^\circ_{f,A} - b\bar{g}^\circ_{f,B}\right)_T$$

- Equilibrium Const. (K_p)

$$K_p = \frac{(P_E/P^\circ)^e (P_F/P^\circ)^f}{(P_A/P^\circ)^a (P_B/P^\circ)^b}$$

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons CO_2$$

$$K_p = \frac{(P_{CO_2}/P)}{(P_{CO}/P^\circ)(P_{O_2}/P^\circ)^{1/2}}$$

$$\rightarrow\ \Delta G^\circ_T = -R_u T \ln K_p$$

$\hookrightarrow K_p = \exp\left(-\Delta G^\circ_T / R_u T\right)$

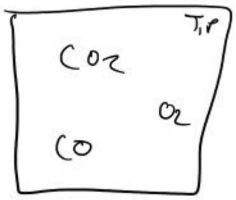
$$\Delta G^\circ_T = \Delta H^\circ - T\,\Delta S^\circ$$

$\hookrightarrow$ $\underline{K_p = e^{-\Delta H^\circ / R_u T}\; e^{\Delta S^\circ / R_u}}$

$K_p > 1$ $\rightarrow$ - prod. favored
- ΔH° should be (-)
- exothermic
- (+) change in S

- real system

$$CO_2 \leftrightarrow CO + \tfrac{1}{2} O_2$$



- const. T, P
  $\hookrightarrow$ equil. conc.
- $\uparrow P$ $\rightarrow$ more CO_2, less $CO + O_2$

Principle of Le Châtelier

$CO_2 \rightarrow CO + \tfrac{1}{2} O_2$ <u>endo thermic</u>

$\uparrow T \rightarrow$ decrease CO_2

$$CO_2 \leftrightarrow CO + \tfrac{1}{2} O_2$$
$$O_2 \leftrightarrow 2O$$

T, P, $\rightarrow x_{CO_2}$, x_{CO}, x_{O_2}, x_O?

Start w/ pure CO_2

4 unknowns $\rightarrow$ 4 eqn

1) $x_{CO_2} + x_{CO} + x_{O_2} + x_O = 1$

2) equil: $CO_2 \leftrightarrow CO + \tfrac{1}{2} O_2$

$$K_p = \exp\left(-\Delta G^\circ_T / R_u T\right)$$

RHS $\rightarrow \Delta G^\circ_T = \left[\tfrac{1}{2}\,\underbrace{\cancel{\bar{g}^\circ_{f,O_2}}}_{0} + \bar{g}^\circ_{f,CO} - \bar{g}^\circ_{f,CO_2}\right]_T$

tables tables

$$K_p = \frac{(P_{CO}/P^\circ)(P_{O_2}/P^\circ)^{1/2}}{(P_{CO_2}/P^\circ)}$$

$P_i = x_i P$

$$\hookrightarrow K_p = \frac{X_{CO}\cancel{\left(\frac{P}{P^\circ}\right)} X_{O_2}^{1/2} \left(\frac{P}{P^\circ}\right)^{1/2}}{X_{CO_2}\cancel{(P/P^\circ)}}$$

$$K_p = \frac{X_{CO} X_{O_2}^{1/2}}{X_{CO_2}} \left(\frac{P}{P^\circ}\right)^{1/2}$$

3) equil $O_2 \leftrightarrow 2O$

4) cons. of elements:

$$\frac{\# C}{\# O} = \frac{1}{2} = \frac{X_{CO} + X_{CO_2}}{X_{CO} + 2X_{CO_2} + 2X_{O_2} + X_O}$$

$$K_p = \exp(-\Delta G/RT)$$

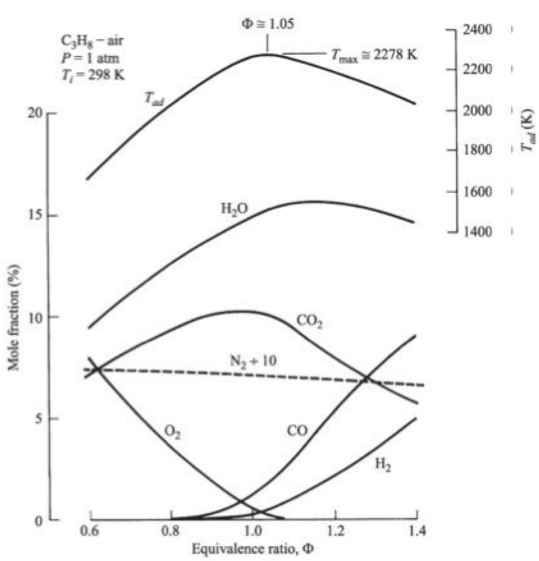


Figure 2.13 Equilibrium adiabatic flame temperatures and major product species for propane–air combustion at 1 atm.

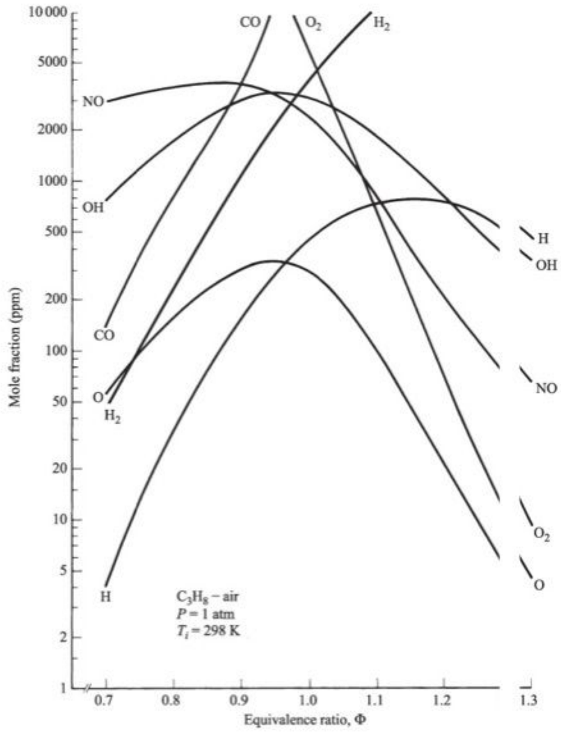


Figure 2.14 Minor species distributions for propane-air combustion at 1 atm.