# Combustion Thermodynamics.

Thermodynamics, specifically chemical thermodynamics, provides the foundation of all of combustion science. Thermodynamic equilibrium tells us what happens to our reactive system if time is not a factor.

## Mixtures and Stoichiometry

Air: is a mix of nitrogen and oxygen, plus lots of trace gases: $CO_2$, Ar, etc.

We assume that air is 79% $N_2$ and 21% $O_2$ in that

$$4.76 \text{ Air} = 1 O_2 + 3.76 N_2. \quad \text{(moles)}$$

The normalization of air by oxygen simplifies other calculations to come.

Fuels: Most practical fuels are hydrocarbons

$$C_n H_m$$

Alkanes: $m = 2n + 2$
Methane: $CH_4$
Heptane: $C_7 H_{16}$.

# Stoichiometric Ratio.

Fuel-Air ratio is $F/A = \dfrac{N_F}{N_A}$

where $N_F$ is # of moles of fuel
(molecules)

and $N_A$ is # of moles (molecules) of air (oxygen + nitrogen) in the mixture.

Fuel-Air ratio is not very useful, since different fuels require different $F/A$ for complete combustion. Thus, we define the Stoichiometric ratio:
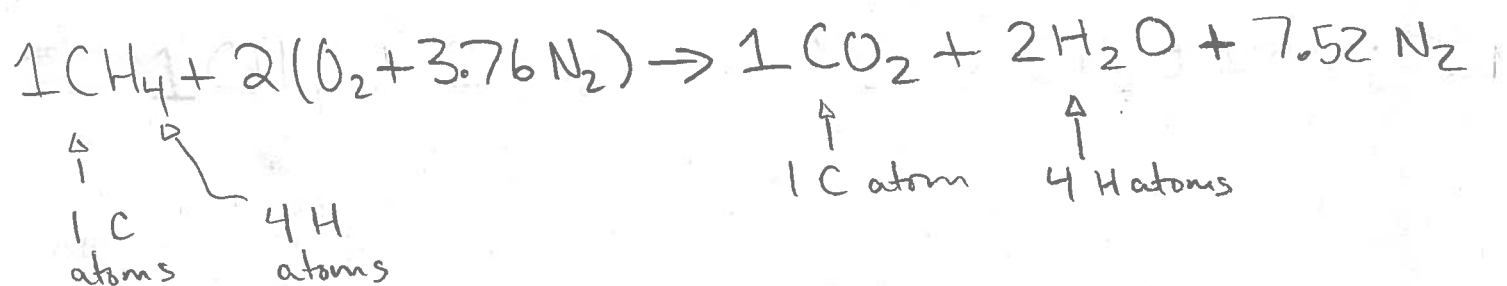
$$\phi = \frac{(F/A)}{(F/A)_{st.}}$$

$\phi < 1$: Fuel lean mixture

$\phi > 1$: Fuel rich mixture

$\phi = 1$: Stoichiometric mixture

## Stoichiometric F/A:

$(F/A)_{st}$ is a mixture of fuel and air that gives (nearly) the maximum combustion intensity as all air and all fuel are consumed to produce water (steam) and carbon dioxide:

$$1 CH_4 + 2(O_2 + 3.76 N_2) \rightarrow 1 CO_2 + 2 H_2O + 7.52 N_2$$

1 C atoms    4 H atoms

1 C atom    4 H atoms

Thus, for methane

$$(F/A)_{st} = \frac{1 \text{ mole } CH_4}{9.52 \text{ moles air}} = \frac{1}{9.52}$$

Coefficients are found by conservation of atoms.

# Normalized Equivalence ratio

$0 < \phi < 1$ : Fuel lean

$1 < \phi < \infty$ : fuel rich.

Thus, plots of quantities vs $\phi$ show asymmetrical behavior between lean & rich side. To correct this, can define:

$$\overline{\Phi} = \frac{\phi}{1 + \phi}$$

$\phi \to 0 \quad \overline{\Phi} \to \phi \to 0$.

$\phi = 1 \quad \overline{\Phi} = \frac{1}{2}$

$\phi \to \infty \quad \overline{\Phi} \to 1$.

# Generalized Chemical Reaction Notation

Take a reaction, such as

$$2CO + O_2 \rightleftharpoons 2CO_2 \qquad \leftarrow \text{Must conserve } \underline{atoms}!$$

This can be generally written as

$$\sum_{i=1}^{m} v_i' M_i \rightleftharpoons \sum_{i=1}^{m} v_i'' M_i$$

$m \leftarrow$ total # of species

$M_i \rightarrow$ chemical symbol of species $i$.

$v_i' \rightarrow$ Stoichiometric coefficient of species $i$ for <u>reactants</u>

$v_i'' \rightarrow$ same but for <u>products</u>
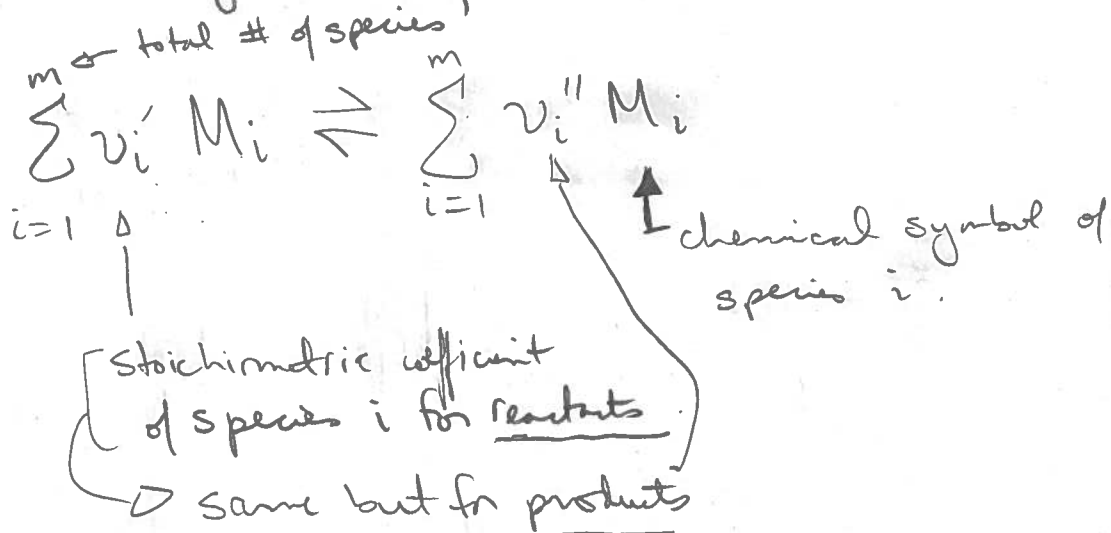
with:

| $M_i$ | $v_i'$ | $v_i''$ |
|---|---|---|
| CO | 2 | 0 |
| $O_2$ | 1 | 0 |
| $CO_2$ | 0 | 2 |

$$\underline{m = 3} \text{ total species}$$

# Conservation of Energy & Mass

For a control volume:
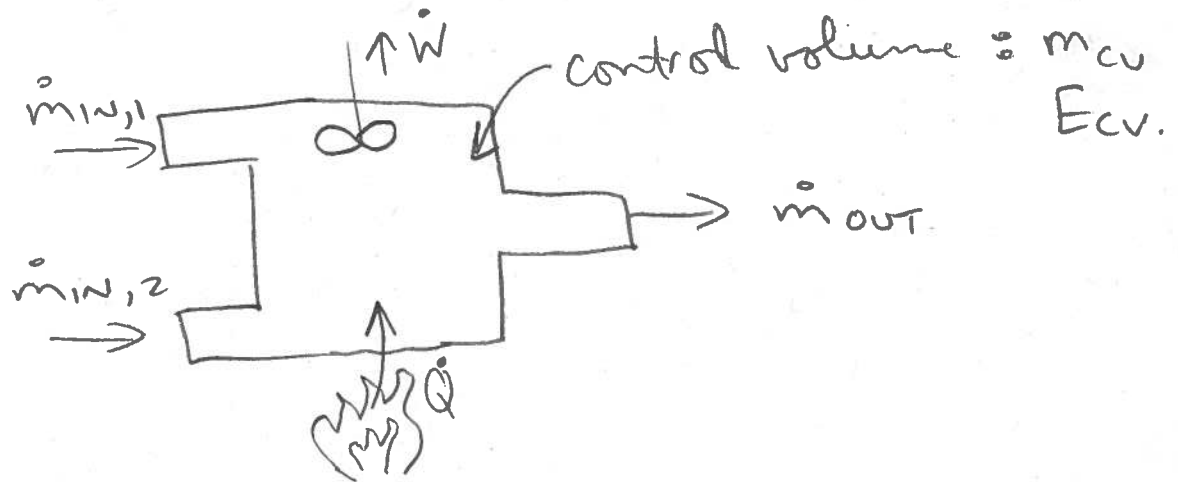


$$\frac{dE_{CV}}{dt} = \sum \dot{m}_{IN} h_{IN} - \sum \dot{m}_{OUT} h_{OUT} + \dot{Q}_{IN} - \dot{W}_{OUT}$$

$$\frac{dm_{CV}}{dt} = \sum \dot{m}_{IN} - \sum \dot{m}_{OUT}$$

These are conservation equations for open systems from Thermo I.

# Chemical Energy Release

In Thermo I, we apply the conservation equations without considering chemical energy release ( assume this is a $\mathring{Q}_{IN}$ term ). To bring this in, we need to expand our definition of enthalpy.

$$H_i(T) = \Delta_f H_i^o + H_i(T) - H_i(T_0).$$

Heat of formation of species $i$.     $\Delta H$ due to temperature.     reference temp.

at $T_0$.

$$= \int_{T_0}^{T} C_p(T') dT'$$

$$h_i(T) = \Delta_f h_i^o + h_i(T) - h_i(T_0).$$

or $h_i^o$ in Law's book.

$\Delta_f h_i^o$ is zero for all stable elements at standard $T \& P$.

$(O_2, N_2, H_2, C(s), \text{etc.})$.

# Heat of reaction/combustion

$$\Delta H_R = \sum_{\text{products}} N_i H_i - \underset{\text{reactants}}{\sum N_i H_i}$$  Heat of reaction

If product & reactant concentrations, $N_i$, are known, then this can be solved using tabulated $\Delta H_{f_i}^0$ values.

$$\Delta H_R = \sum_{i=1}^{m} (v''_i - v'_i)\, h_i^0 (T_0) \quad \left\{ q_p (T^0) \right\}$$
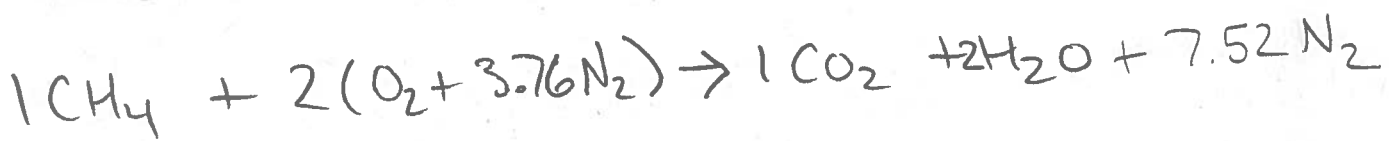
If $\Delta H_R < 0$, products have less chemical potential energy than reactants and energy is released : <u>exothermic</u> rxn.

vice versa fn $\Delta H_R > 0$ : <u>endothermic</u> rxn

# Heat of combustion

$q_C$ is defined as $\Delta H_R$ for 1 mole of fuel at its standard state do form $H_2O$, $CO_2$ & $N_2$.

## $q_C$ for methane at T = 298.15 K at 1 atm.

$$1\,CH_4 + 2(O_2 + 3.76\,N_2) \to 1\,CO_2 + 2H_2O + 7.52\,N_2$$

| species | $h_f^0 \left[\frac{kJ}{kmol.}\right]$ | $v_i''$ | $v_i'$ |
|---|---|---|---|
| $CH_4$ | $-74,860$ | 0 | 1 |
| $O_2$ | 0 | 0 | 2 |
| $N_2$ | 0 | 7.52 | 7.52 |
| $CO_2$ | $-393,520$ | 1 | 0 |
| $H_2O$ (vapor) | $-241,820$ | 2 | 0 |

↳ Cengel & Boles Table A-26, or equivalent

Stable products have large negative enthalpies of formation. Fuels have values closer to zero, or even positive.

# Heat of Combustion - II

$q_c$ for methane:

$$q_c = 2(-241,820) + 1(-393,520) - 1(-74,850)$$

$$= -802,310 \; \frac{kJ}{kmol}$$

The lower heating value is the heat of combustion per kg of fuel, when water is in vapor state.

$$LHV = \frac{q_c \; \frac{kJ}{kmol}}{m \left(\frac{kg}{kmol}\right)} = \frac{-802,310}{16} = -50,144 \frac{kJ}{kg}$$

The higher heating value is the heat of combustion per kg fuel with water in liquid state.

$$HHV = LHV + \alpha \; h_{fg}\big|_{H_2O}$$

$\overset{\text{heat of vaporization of water}}{}$

$$\alpha = \frac{kg \; H_2O \; produced}{kg \; fuel \; consumed}$$

## Estimating heat of reaction.

Knowing bond energies (see Table 1.5 in Law's book), we can estimate $\Delta h_r$ by sum of bonds (energies) formed less sum of bonds broken. (energies).

# Adiabatic Flame Temperature.

If products are known (assumed/approximated), we have $\Delta h_R$ or $q_c$.

For a constant-pressure process, the 1st law for no heat or work & one inlet & one outlet reduces to

$$H_{prod} = H_{reac}.$$

$H_{reac}$ is known since initial state is specified

$$\sum n_p \left( h_f^\circ + h - h_o \right) = \sum n_R \left( h_f^\circ + h - h_o \right).$$

↳ moles/product

$h - h_o$ is a function of $T$ only for all product species, and thus we can find $T_{ad}$, adiabatic flame temperature, by assuming $n_p$ & trial & error for the $T_{prod} = T_{ad}$ that balances this equation.

# Adiabatic Flame Temperature - I

$$h - h_0 = \int_{T_0}^{T} c_p(T) \, dT$$

So can calculate this using $c_p(T)$.

Fn small $T$ ranges, could assume

$$c_p \approx \langle c_p \rangle = \text{constant}$$

$\quad\quad\quad\quad \downarrow$ "average" $c_p$ between $T_0$ & $T$.

$$(h - h_0)_i \approx \langle c_p \rangle_i (T_{ad} - T_0)$$

$\quad\quad\quad\quad\quad \downarrow$ specific heat per mole fn species $i$.

This will be bad fn $CO_2$ & $H_2O$ whose $c_p$ vary strongly from room temp to typical flame temperatures, so need to use computer.

What if we don't know the product composition $\rightarrow$ chemical equilibrium needed!

# Constant - Volume Explosion Pressure.

If we have a closed vessel, the energy equation is

$$\frac{dE_{system}}{dt} = \overset{\circ}{Q}_{IN} - \overset{\circ}{W}_{OUT}.$$

For constant volume, $\overset{\circ}{W}_{OUT} = 0$

and adiabatic system (no heat loss) $\overset{\circ}{Q} = 0$

$$E_{system} (final) = E_{system} (initial).$$

$$\sum N_i E_i (T_{prod}) = \sum N_i E_i (T_{reac}).$$

What is internal energy of formation?

$$E = H - pV = H - N R_u T.$$

$$\Delta N_{rxn} = \sum (v_i'' - v_i'). \text{ for 1 mole of substance being formed}$$

$$\therefore \quad e_i^{\circ} = h_i^{\circ} - R_u T \underbrace{\Delta N_{rxn}}_{}.$$

work term due to creation / destruction of molecules.

typically $h_i^{\circ} \gg R_u T \Delta N_{rxn}$ &

$$e_i^{\circ} \approx h_i^{\circ}$$

# Constant-V Explosion Pressure - II.

Find $T_P$, similar to process for $T_{ad}$,
& then use

$$p V = N R_u T \qquad \text{or} \qquad \frac{P_P}{N_P R_u T_P} = \frac{P_R}{N_R R_u T_R}$$

$$P_P = \frac{N_P T_P}{N_R T_R} P_R$$

↑    ↳ contribution from heat release.

contribution from creation
of molecules

# Thermodynamics of Ideal Gas Mixtures

We will assume Ideal gases throughout this course for simplicity.

For a gas mixture, we have

$$N = \sum_{i=1}^{m} N_i$$
$$n = \sum_{i=1}^{m} n_i$$

$m$ = total # of species

where:  $N$ = total # of molecules

$n$ = total # of moles

$N_i, n_i$ = moles/molecules of species $i$.

## Mole fraction:

$$\chi_i = \frac{N_i}{N}$$

## Ideal Gas Law:

$$p V = N k_B T \qquad p V = n R_u T$$

$k_B = 1.38 \times 10^{-23} \frac{J}{K}$  Boltzmann's constant

$R_u = 8.314 \frac{kJ}{kmol \, K}$  Ideal gas constant

## Partial Pressure

$$p = \sum p_i$$

↳ partial pressure of species $i$.

follows from $N = \sum N_i$

& $\quad p_i = \dfrac{N_i k_B T}{V}$.

## Mixture properties

Mean molar mass

$$M = \sum_{i=1}^{m} M_i X_i$$

↳ Molar mass of species $i$ $\left( \frac{g}{mol} \text{ or } \frac{kg}{kmol} \right)$

Mass fractions (don't use! Molecules & moles are better unit for reacting mixtures)

$$Y_i = \frac{M_i X_i}{M}$$

# First & Second Laws. — Differential Form

From Thermo I, we learn that.

$$\delta Q - \delta W = dE$$

heat (+ when heat goes in)    work (+ when system does work)    Internal energy

$$\delta W = p\, dV \quad \text{for closed system with boundary work.}$$

$$\delta Q_{rev} = T\, dS \quad \text{for reversible heat addition.}$$

$$\therefore \quad dE = T\, dS - p\, dV \quad \text{(Gibbs equation)}$$

or

$$de = T\, ds - p\, dv$$

specific internal energy.    specific entropy    specific volume

Since $e, T, s, P, v$ are all state variables, Gibbs equation holds true for all processes (both reversible & irreversible).

# Chemical Potential

The energy of a simple compressible system can be generally written as:

$$E = E(S, V)$$

according to Gibbs equation, or any other 2 independent state properties.

$$E = E(T, p) \text{ etc.}$$

However, when the mixture reacts, energy contained in molecular bonds can be released and converted to thermal energy (heat) n work.

We define a chemical potential as

$$M_i = \left( \frac{\partial E}{\partial N_i} \right)_{S, V, N_{j(j \neq i)}}$$

Which is the change in energy of run system as the moles of species i are changed, keeping other species and thermodynamic state fixed.

# Generalized First Law Relations

Thus, for a chemically reacting system:

$$dE = TdS - pd\forall + \sum_{i=1}^{m} \mu_i dN_i$$

Using definitions of

Enthalpy: $\quad H = E + p\forall$

Helmholtz function $\quad A = E - TS$

Gibbs function $\quad G = H - TS$

[Note that we won't use the terms "free energy" in this course as this is misleading terminology.]

We can also obtain:

$$dH = TdS + \forall dp + \sum_{i=1}^{m} \mu_i dN_i$$

$$dA = -SdT - pd\forall + \sum_{i=1}^{m} \mu_i dN_i$$

$$dG = -SdT + \forall dp + \sum_{i=1}^{m} \mu_i dN_i$$

# Chemical Potential - II

Thus,

$$\mu_i = \left(\frac{dE}{\partial N_i}\right)_{S, V, N_j(j \neq i)} = \left(\frac{dH}{dN_i}\right)_{S, P, N_j(j \neq i)}$$

$$= \left(\frac{dA}{\partial N_i}\right)_{T, V, N_j(j \neq i)} = \left(\frac{dG}{dN_i}\right)_{T, P, N_j(j \neq i)}.$$

And is the energy associated with changing the # of molecules of species $i$, holding thermodynamic state constant.

We have to choose which state variables to hold fixed, and thus define a partial molal property, $\psi_i$, as:

$$\psi_i = \left(\frac{\partial \psi}{\partial N_i}\right)_{T, P, N_j(j \neq i)}$$

Where $\psi$ is an extensive thermodynamic property.

$\psi_i$ is an intensive property of mixture

Thus, by inspection, we see that

$$\mu_i = g_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_j(j \neq i)}$$

# Thermodynamic Equilibrium

○ The Second Law says that entropy (probability of macro-state — see Adv. Thermo). is maximized at equilibrium.

Entropy: $$S = k_B \ln W$$

↳ probability of macro state is related to # of ways (microstates) that yield macro state.

○ 2nd Law: $$dS \geq \frac{\delta Q}{T}$$

Entropy of a system always increases unless heat is extracted from it..

For an <u>adiabatic system</u>, $\delta Q = 0$

$$dS \geq 0$$

& entropy of an <u>isolated</u> system always increases.

# Chemical Equilibrium

What happens when we allow the mixture to react (or change phases)?

$$dE = \delta Q - \delta W.$$

In general,

$$dS \geq \frac{\delta Q}{T} \qquad \left( = \frac{\delta Q}{T} \text{ only for reversible process} \right)$$

$$dE + \delta W = \delta Q \leq TdS.$$

$$dE \leq TdS - pd\forall. \quad \text{①}$$

We showed:

$$dE = TdS - pd\forall + \sum_{i=1}^{m} \mu_i dN_i \quad \text{②}$$

Therefore, comparing ① & ② tells us that

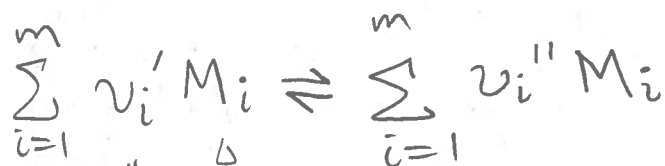$$\boxed{\sum_{i=1}^{m} \mu_i dN_i \leq 0}$$

for a closed system. Equilibrium is reached when the $dN_i$ all equal zero (composition stops changing) and is given by

$$\sum_{i=1}^{m} \mu_i dN_i = 0 \quad \text{@ equilibrium.}$$
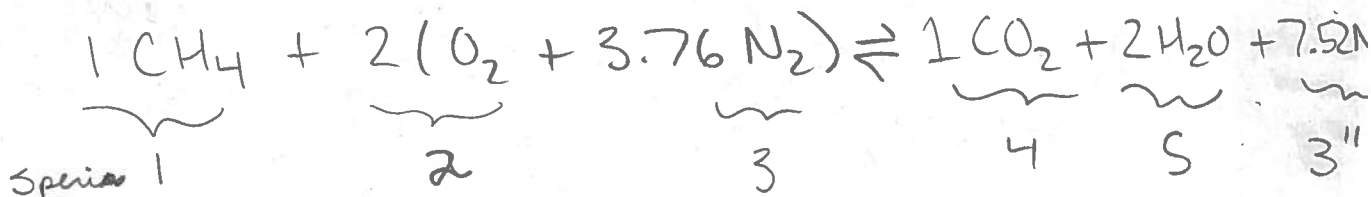
# Chemical Equilibrium - II

The definition of equilibrium based on chemical potentials is general and applies to any thermodynamic process.

Defining a general chemical reaction

$$\sum_{i=1}^{m} v_i' M_i \rightleftharpoons \sum_{i=1}^{m} v_i'' M_i$$

chemical symbol of species $i$ ($CH_4$, $CO_2$, etc.)

molar coefficient in reaction

eg.

$$1 CH_4 + 2(O_2 + 3.76 N_2) \rightleftharpoons 1 CO_2 + 2 H_2O + 7.52 N_2$$

Species 1     2     3    4   5   3''

| $i$ | $v_i'$ | $v_i''$ |
|------|--------|---------|
| $CH_4$   1 | 1 | 0 |
| $O_2$   2 | 2 | 0 |
| $N_2$   3 | 7.52 | 7.52 |
| $CO_2$   4 | 0 | 1 |
| $H_2O$   5 | 0 | 2 |

Of course, we'll have to add more species soon...

# Chemical Equilibrium - III

Now, assume the reaction progresses by some amount, $d\lambda$. (Some portion of initial $CH_4$ is consumed, for instance).

Conservation of atoms implies that.

$$\frac{dN_{CH_4}}{v_1'' - v_1'} = \frac{dN_{O_2}}{v_2'' - v_2'} = \frac{dN_i}{v_i'' - v_i'} = \underbrace{d\lambda}_{\text{reaction progress.}}$$

$\underbrace{\phantom{xxx}}$
$CH_4$ is species #1.

$\underbrace{\phantom{xxx}}$
$O_2$ is species #2

$$dN_i = (v_i'' - v_i')d\lambda$$

$$\therefore \sum_{i=1}^{m} \mu_i dN_i = \left[\sum_{i=1}^{m} \mu_i (v_i'' - v_i')\right] d\lambda = 0.$$

Valid for all $d\lambda$, so

$$\sum_{i=1}^{m} \mu_i (v_i'' - v_i') = 0 \quad @ \text{ equilibrium}$$

Chemical potential of reactants is equal to that of products at equilibrium.

## Equilibrium continued

For a system at constant temperature.

$$dS^t \geq \frac{\delta Q}{T}$$

← constant-T.

$$dE = \delta Q - \delta W$$

For a constant temperature, constant volume process

$$dE^t \leq TdS^t - p\cancel{dV}^{0.}$$

$$(dE^t - TdS^t) \leq 0$$

$$d(E^t - TS^t) \leq 0.$$

$$dA^t \leq 0.$$

Helmholtz function is <u>minimized</u> for equilibrium at constant volume & constant temperature.

# Equilibrium, continued II.

For equilibrium at constant temperature, T, & pressure:

$$dT = 0 \qquad dp = 0.$$

$$dH^t = \delta Q. \leq T dS^t.$$

$$(dH^t - T dS^t) \leq 0.$$

$$d(H^t - TS^t) \leq 0.$$

$$dG^t \leq 0$$

& Gibbs function is minimized at equilibrium for a constant-T, -p process.

## Chemical Potential of an Ideal Gas.

We see that the chemical potential plays a key role in determining the equilibrium composition of a mixture.

The chemical potential of species, $i$, is:

$$\mu_i = g_i = h_i - Ts_i$$

The enthalpy of a species $i$ is given by.

$$h_i(T) = h_{f,i}^0 + \Delta h_i(T-T_0).$$

[For an ideal gas $h = h(T)$ only].

where $h_{f,i}^0$ is the __heat of formation__ of species $i$ at a reference temperature, $T_0$.

$h_{f,i}^0$ is related to bond energies in molecules.

$\Delta h_i(T-T_0)$ is change in enthalpy from reference temperature to temp. of interest.

# Chemical Potential of Ideal Gas – II.

$$h_i(T) = h_{f,i}^o + \underbrace{\int_{T_o}^{T} c_{p,i}(T') dT'}_{\Delta h (T - T_o).}$$

$$ds = \frac{dh}{T} - \frac{v}{T} dp. \quad \text{(Gibbs function)}.$$

$$S_2 - S_1 = \int_{T_1}^{T_2} c_p(T') \frac{dT'}{T'} - R_u \ln\left(\frac{P_2}{P_1}\right)$$

molar
entropy

Molar specific
heat

molar gas constant

Be consistent!

Define a standard entropy at 1 atm of
pressure

$$S^o(T) = \int_0^T c_p(T) \frac{dT'}{T'}$$

$$\therefore \quad \Delta S = \underbrace{S^o(T_2) - S^o(T_1)}_{T \text{ variations}} - \underbrace{R_u \ln\left(\frac{P_2}{P_1}\right)}_{p \text{ variations}}$$

# Chemical Potential of Ideal Gas - III

$$\therefore \quad S_i = S_i^0 - R_u \ln \left( \frac{P_i}{P_0} \right)$$

↑ reference pressure
is 1 atm, typically.

$$\mu_i(T, P_i) = h_{f,i}^0 + \Delta h_i (T - T_0) - T s_i^0 - R_u T \ln \left( \frac{P_i}{P_0} \right).$$

↑
partial
pressure
of species $i$

$$h_i - T s_i^0 = \mu_i^0 (T). \quad \text{or} \quad g_i^0 (T).$$

↑
Standard chemical potential

$\mu_i^0(T)$ is the Gibbs energy of species $i$ at temperature $T$ and standard pressure (typically 1 atm).

$$\boxed{\mu_i(T, P_i) = \mu_i^0(T) - R_u T \ln \left( \frac{P_i}{P_0} \right)}$$

# Equilibrium Constants.

We can now go back to our general criteria for chemical equilibrium

$$\sum_{i=1}^{m} \mu_i \, dN_i = 0$$

↑ # of molecules of species $i$

↓ chemical potential per molecule for species $i$

$$\sum_{i=1}^{m} \mu_i \, dn_i = 0$$

↓ $i$ # of moles

↓ chem. potential per mole.

Using $p_i$ in atm and $p_0 = 1$ atm

$$\sum_{i=1}^{m} (v_i'' - v_i') \mu_i = 0$$

$$\sum_{i=1}^{m} (v_i'' - v_i') \mu_i^0(T) + R_u T \sum_{i=1}^{m} (v_i'' - v_i') \ln(p_i) = 0.$$

$$\sum_{i=1}^{m} (v_i'' - v_i') \ln(p_i) = \ln \left( \prod_{i=1}^{m} p_i^{(v_i'' - v_i')} \right)$$

# Equilibrium Constants - II

$$\ln\left[\prod_{i=1}^{m} P_i^{(v_i''-v_i')}\right] = -\sum_{i=1}^{m} \frac{(v_i''-v_i')\mu_i^0(T)}{R_u T}$$

$$K_p(T) = \prod_{i=1}^{m} P_i^{(v_i''-v_i')} = \exp\left[-\frac{\sum_{i=1}^{m}(v_i''-v_i')\mu_i^0(T)}{R_u T}\right]$$

Which is the equilibrium constant in partial pressures.

To illustrate, take reaction

$$aA + bB \rightleftarrows cC + dD.$$

$$K_p = \frac{P_C^c \ P_D^d}{P_A^a \ P_B^b}$$

$(v_i''-v_i')$ if you prefer

$$\Delta G^0 = \sum_i v_i \ G_i^0(T).$$

↑ stoich coefficients

$$\rightarrow K_p(T) = \exp\left(-\frac{\Delta G^0}{R_u T}\right).$$

Note that $K_p$ can be found from partition functions based on Quantum Energy Levels — See Advanced Thermo

# Equilibrium Changes with Thermodynamic State.

## Pressure:

$$K_p(T) = \exp\left(-\frac{\Delta G^0}{R_u T}\right) = \prod_{i=1}^{m} X_i^{v_i} \left(\frac{P}{P_0}\right)^{\Sigma v_i}$$

$$\underbrace{\phantom{\exp\left(-\frac{\Delta G^0}{R_u T}\right)}}_{\neq f(P).}$$

$$\therefore \prod X_i^{v_i} = \frac{K_p(T)}{P^{\Delta v}}$$

$$\Big\downarrow \text{ in atm}$$

$$\Sigma v_i = \Delta v \quad \text{is \# of moles (molecules)}$$

created (+) or destroyed (−) during

reaction.

Products have more molecules than reactants ( eg $O_2 \rightleftharpoons 2O$ )

$$\Delta v > 0$$

$$P \uparrow \implies \text{less products.}$$

## Le Chatelier's Rule

"A system in chemical equilibrium attempts
to minimize the effect of disturbances!"

## Temperature

$$K_p(T) = \exp\left(-\frac{\Delta G^0}{R_u T}\right) \qquad K_p.$$

$$\frac{dK_p}{dT} = \left(\frac{\Delta G^0}{R_u T^2} - \frac{1}{R_u T}\frac{\partial \Delta G^0}{\partial T}\right) \overbrace{\exp\left(-\frac{\Delta G^0}{R_u T}\right)}$$

$$\frac{dK_p}{dT} = \frac{K_p}{R_u T^2}\left(\Delta G^0 - T\frac{\partial \Delta G^0}{\partial T}\right)$$

$$\Delta G^0 = \Delta H - T\Delta S^0$$

$$S^0(T) = \int_{T_r}^{T} \frac{C_p(T')\,dT'}{T'}$$

          usually OK but can be defined anywhere.

$$\Delta H = \int_{T_1}^{T_2} C_p(T')\,dT' \cong C_p\,\Delta T.$$

$$\frac{\partial \Delta G^0}{\partial T} = \cancel{\langle C_p \rangle} - \Delta S^0 - T\cancel{\langle C_p \rangle \frac{1}{T}}$$

$$\frac{\partial \Delta G^0}{\partial T} = -\Delta S^0$$

# Temperature Equilibrium, II

$$\frac{\partial K_p}{\partial T} = -\frac{K_p}{R_u T^2}\left(\underbrace{\Delta G^0 - T\Delta S^0}_{\Delta H_r}\right)$$

$$\frac{\partial K_p}{\partial T} = -\frac{\Delta H_r}{R_u T^2} K_p$$

## Endothermic:

if $\Delta H_r > 0$ $\qquad \frac{\partial K_p}{\partial T} > 0$

Thus $T\uparrow$ leads to more products

## Exothermic:

if $\Delta H_r < 0$ $\qquad \frac{\partial K_p}{\partial T} < 0$

$\uparrow T$ leads to less products.

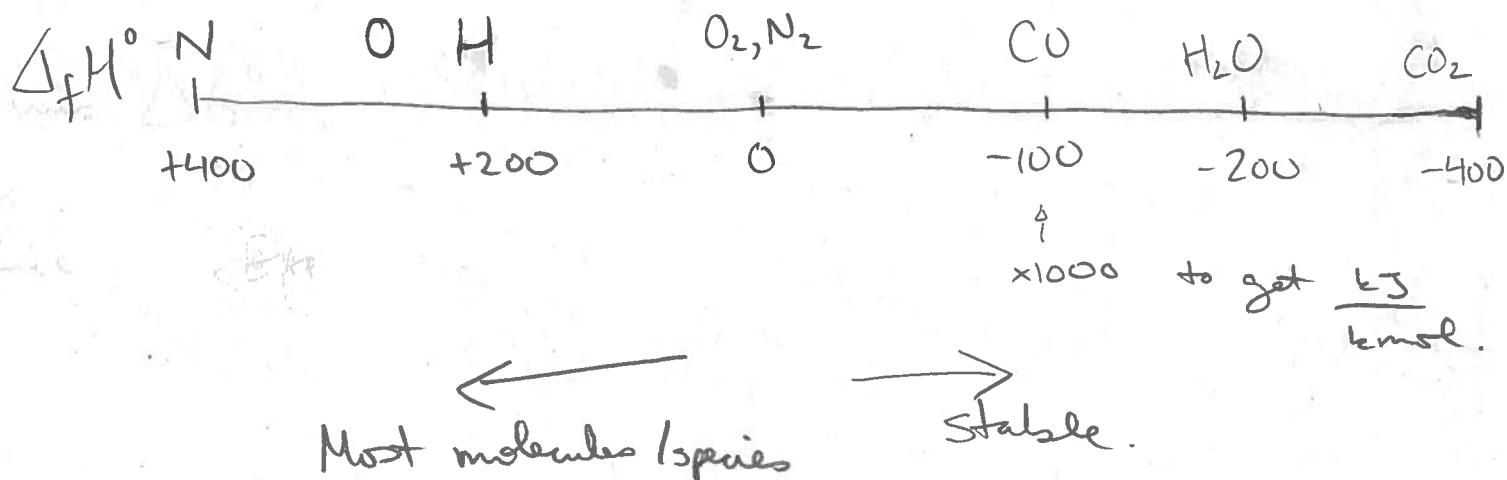# Statistical Thermodynamics Interpretation

$$G^t = H^t - TS^t$$

$$H^t = \sum N_i H_i(t)$$
$$S^t = \sum N_i S_i(t)$$

Minimize G two ways:
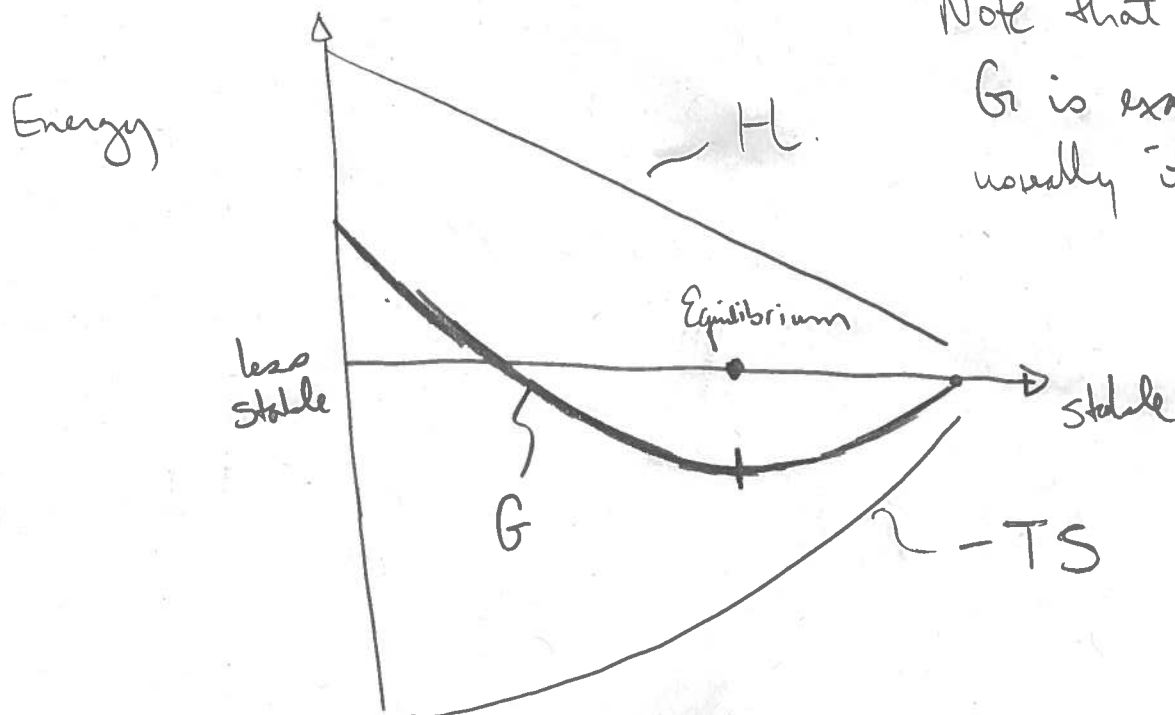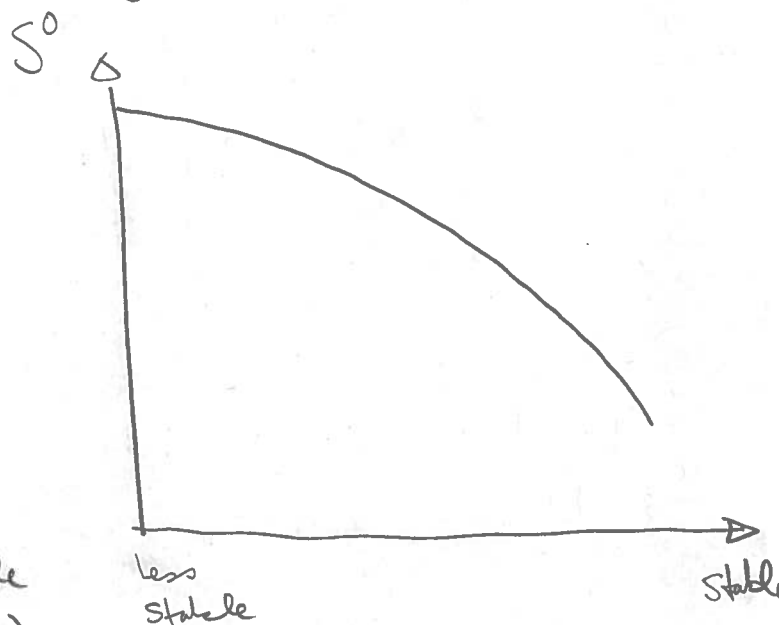
1) Minimum H means going to most stable products.

$\Delta_f H°$



| N | O | H | | $O_2, N_2$ | | CO | | $H_2O$ | | $CO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| +400 | | +200 | | 0 | | -100 | | -200 | | -400 |

$\updownarrow$
×1000 to get $\dfrac{kJ}{kmol}$.
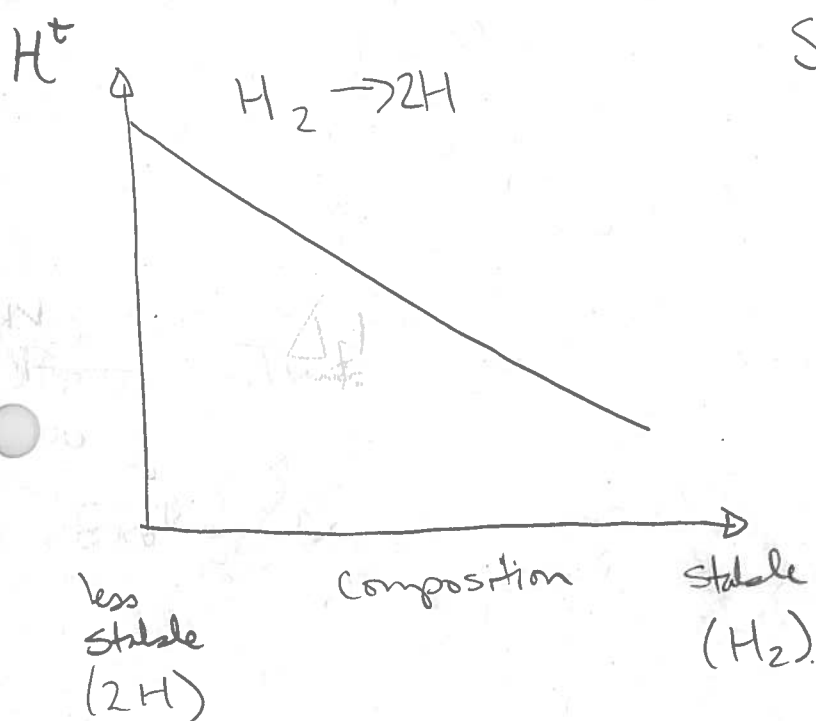
← Most molecules/species

→ Stable.

2) Maximize entropy:

entropy increases as more molecules are produced.

# Stat Thermo - II

This trade-off between minimizing enthalpy but maximizing entropy leads to finite levels of dissociated species, even though these are energetically unfavorable.



$H^\ddagger$

$H_2 \rightarrow 2H$

$\Delta H$

less Stable (2H) — Composition — Stable ($H_2$)

$S^0$

less Stable — Stable

Energy

$H$

less Stable

Equilibrium

$G$

$-TS$

Stable

Note that curvature in $G$ is exaggerated for clarity usually it is very flat.

# Equilibrium Constants − III

Sometimes we prefer to work with mole fractions instead of partial pressures

with $X_i = \dfrac{P_i}{P} \leftarrow$ system pressure

stoichiometric coefficients
$\downarrow$ (+ for products − for reactants)

$$K_p(T) = \exp\left(\frac{-\Delta G^{\circ}}{R_u T}\right) = \prod_{i=1}^{m} P_i^{\;v_i}$$

$$K_p(T) = \prod_{i=1}^{m} X_i^{\;v_i} \left(\frac{P}{P_o}\right)^{\sum v_i}$$

or in concentration (moles/volume).

$$C_i = \frac{n_i}{\forall} = X_i \frac{n}{\forall} \qquad\qquad P_i = C_i R_u T.$$

$$K_p(T) = \prod_{i=1}^{m} C_i^{\;v_i} \left(\frac{1}{R_u T}\right)^{\sum v_i}$$

$$K_c(T) = \prod_{i=1}^{m} C_i^{\;v_i} = \frac{K_p(T)}{(R_u T)^{\sum v_i}}$$

# Equilibrium Composition Calculations.

You will see in the Projects that calculation of the equilibrium composition is best handled by a computer, since it tends to be tedious.
  └ CEA. or Cantera, etc.

However, we will look at an approximation that can guide our understanding, called the Major - minor species model.

    products
Major $\wedge$ species are:

$$\phi < 1 : \quad CO_2, H_2O, O_2, N_2.$$

$$1 < \phi \lesssim 2.5 \quad CO, CO_2, H_2, H_2O, N_2.$$

$$\phi > 2.5 \quad\quad C(s) \leftarrow soot.$$
$$+ others.$$

Carbon first oxidized to CO, then hydrogen to water, then $CO \rightarrow CO_2$, thus, if too little oxygen is present, eventually CO can't be formed and soot is produced.

# Major-Minor species model - I

- Take propane as an example:

$\phi < 1:$   $\phi\, C_3H_8 + 5(O_2 + 3.76 N_2) \rightarrow$

$$3\phi\, CO_2 + 4\phi\, H_2O + 5(1-\phi)O_2 + 18.8 N_2.$$
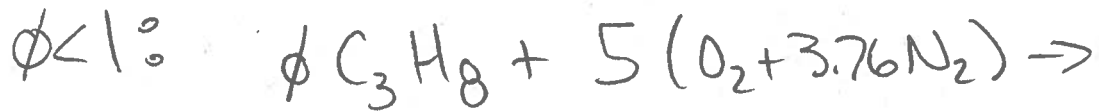
No equilibrium calculation is required as the composition is strictly determined by stoichiometry & atom balancing.

- $1 < \phi < 2.5:$

$$\phi\, C_3H_8 + 5(O_2 + 3.76 N_2) \rightarrow a\, CO_2 + b\, CO + c\, H_2O + d\, H_2 + 18.8 N$$

Conserving elements/atoms:

$C:$   $3\phi = a + b$

$O:$   $5(2) = a(2) + b(1) + c(1). \Rightarrow 10 = 2a + b + c$

$H:$   $8\phi = 2c + 2d$   $(4\phi = c + d)$

## Major-Minor Species Model - II

Keep $d$ as an unknown to solve for giving:

$$\boxed{c = 4\phi - d}$$

$$10 = 2a + b + c$$

$$10 = 2a + b + 4\phi - d$$

$$b = 10 - 4\phi - 2a + d$$

$$3\phi = a + b = -a + 10 - 4\phi + d$$

$$\boxed{a = -7\phi + 10 + d}$$

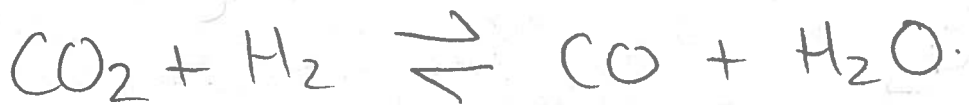$$b = 10 - 4\phi + \underbrace{14\phi - 20 - 2d}_{-2a} + d$$

$$\boxed{b = 10\phi - 10 - d}$$

Could do same thing for $a$, $b$, or $c$.

# Major-Minor Species Model – III

To solve, we need one more relationship between $a, b, c$ & $d$.

## Water-Gas Shift Reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O.$$

Important in reforming fuels to $H_2$!.

If we assume equilibrium for WGS rxn:

$$K_p(T) = \frac{P_{CO}\, P_{H_2O}}{P_{CO_2}\, P_{H_2}} = \frac{b\,c}{a\,d}. \quad \{ \begin{array}{l} N_{total} \text{ is} \\ \text{constant} \\ (\Delta\nu = 0). \end{array}$$

$K_p(T)$ for WGS increases as $T\uparrow$,

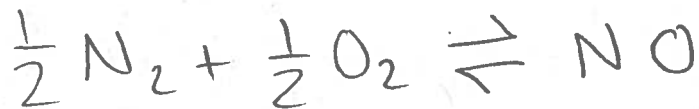meaning more $CO$ & $H_2O$ are produced at higher $T$ values.

## Minor Species Concentrations.

So far, we have only considered major species. What can we do to predict trace components.

Eg: NO in a lean flame:
$$\phi = 0.5$$

$$0.5 \, C_8 H_{18} + 12.5(O_2 + 3.76 \, N_2) \rightarrow 4 \, CO_2 + 4.5 \, H_2O$$
$$+ 6.25 \, O_2 + 47 \, N_2.$$
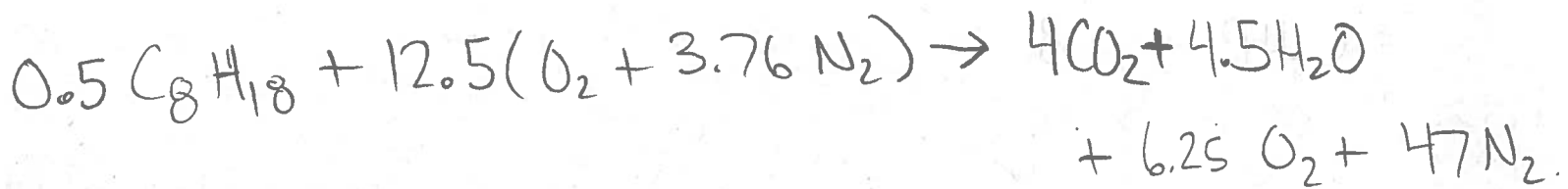
Can use this to find $T_{products}$.

How much NO will be formed?

$$\tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 \rightleftharpoons NO$$

$$\frac{P_{NO}}{P_{N_2}^{1/2} \, P_{O_2}^{1/2}} = K_p(T). = \underline{N_{NO}}$$

Can solve this exactly, but simpler to assume $P_{NO} \ll P_{N_2}, P_{O_2}$.

$$N_{NO} \ll N_{N_2}, N_{O_2}$$

# Minor Species — II.

$$P_{O_2} \approx \frac{6.25}{(4+4.5+6.25+47)} = \frac{6.25}{61.75}.$$

$$P_{N_2} \approx \frac{47}{61.25}$$

$$P_{NO}(T_{prod}) \approx K_p(T_{prod}) \, P_{N_2}^{1/2} \, P_{O_2}^{1/2}.$$

approximated using major species model.

Of course, as NO is formed $P_{N_2}$ & $P_{O_2}$ must decrease from values calculated from major species model, but as long as $P_{NO} << P_{N_2}, P_{O_2}$ the effect is minor..