

The Thermal NO_x Model

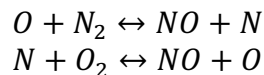
Dr Owen Williams – University of Wales TSD:

Thermal NO formation takes place in both the flame front and burned zone during combustion. High pressure experienced by the air/fuel mixture causes a thin flame front ($\approx 0.1\text{mm}$), thus limiting time spent in this zone for chemical species (Heywood, 1988).

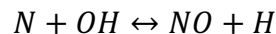
Chemical species produced early in the cycle experience increased pressure and temperature in the burned zone as combustion continues.

Higher temperatures invite dissociation of the O₂ and N₂, leading to NO formation. Thermal NO is largely a product of the conditions experienced in the burned zone.

As described in the previous section, Zeldovich, described two reactions responsible for NO production in the burned zone:

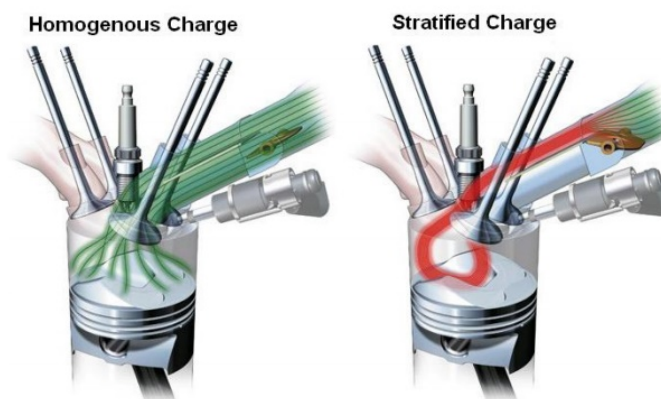


Lavoie et al (1970) added a third reaction – because of its significant contribution to overall NO – to what would become known as the extended Zeldovich mechanism:



The extended Zeldovich mechanism is widely used for ICE NO_x prediction due to its dominant presence in adiabatic combustion where excess oxygen is present (Borman & Ragland, 1998).

Introduction of DI engines and lean combustion technologies such as stratified charge has meant that excess oxygen is no longer just a product of lean fuel equivalence ratio. It is possible for lean combustion to occur locally within the cylinder, both deliberately and naturally (Zhao, et al., 1999).



Merker et al (2006) note that speed coefficients for the Zeldovich reactions vary from study to study:

Reaction i	$k_{i,r}$ [cm ³ /mol s]	Author
1	$1.8 \cdot 10^4 \exp \left[-\frac{38,400}{T} \right]$	Baulch et al. (1991)
	$0.544 \cdot 10^{14} T^{0.1} \exp \left[-\frac{38,020}{T} \right]$	GRI-MECH 3.0 (2000)
	$0.76 \cdot 10^{14} \exp \left[-\frac{38,000}{T} \right]$	Heywood (1988)
2	$6.4 \cdot 10^9 T \exp \left[-\frac{3,150}{T} \right]$	Baulch et al. (1969)
	$9.0 \cdot 10^9 T \exp \left[-\frac{3,280}{T} \right]$	GRI-MECH 3.0 (2000)
	$1.48 \cdot 10^8 T^{1.5} \exp \left[-\frac{2,860}{T} \right]$	Pattas (1973)
3	$3.0 \cdot 10^{13}$	Baulch et al. (1991)
	$3.36 \cdot 10^{13} \exp \left[-\frac{195}{T} \right]$	GRI-MECH 3.0 (2000)
	$4.1 \cdot 10^{13}$	Heywood (1988)

*The figure shows the Forward reaction rate coefficients (Merker et al, 2006).
Note: Typographic error for Baulch, reaction 1:*

Should read: $1.8 \cdot 10^{14} \cdot \exp \left(-\frac{38370}{T} \right)$

Warnatz et al (2006) draw attention to the high activation energy required to break the triple bonded N₂ molecule in the first reaction, dissociating atmospheric nitrogen into atomic nitrogen.

All thermal NO production is therefore reliant on the ability for this rate-limiting reaction to occur before combustion is complete.

Thermal NO, therefore, is produced when cylinder temperatures are high enough to increase the reaction rate enough for reaction 1 to take place before combustion ends.

The Dissociation Model

Dr Owen Williams – University of Wales TSD:

To accurately predict thermal NO it is necessary to model the dissociation of combustion products that occurs at sufficiently high temperatures.

This is done via an iterative method outlined by Eric Goodger in his book '*Transport Fuels Technology* (2001)'.

Similar to before, the atomic balance equation using isooctane is now considered to be:

$$\phi \cdot C_8H_{18} + 12.5 \cdot (O_2 + 3.76N_2) = n_1 \cdot CO_2 + n_2 \cdot H_2O + n_3 \cdot CO + n_4 \cdot H_2 + n_5 \cdot O_2 + n_6 \cdot N_2$$

Carbon, hydrogen, oxygen and nitrogen can be balanced:

$$Carbon = 8 = n_1 + n_3$$

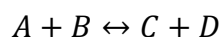
$$Hydrogen = 18 = 2 \cdot n_2 + 2 \cdot n_4$$

$$9 = n_2 + n_4$$

$$Oxygen = 25 = 2 \cdot n_1 + n_2 + n_3 + 2 \cdot n_5$$

$$Nitrogen = 47 = n_6$$

This gives us four equations with six unknowns! Six equations are required to solve six unknowns, so two more equations are added by using calculated partial pressure equilibrium constants for CO₂ and H₂O. To understand this, we need to look in more detail at reaction rates:



'Reaction rate' refers to the production or decomposition rate for a chemical species for a given reaction and is seen to be proportional to the instantaneous concentrations of forming species, raised to a power (Warnatz, et al., 2006).

E.g., For the equation above:

$$\frac{d[C]}{dt} = k_f \cdot [A]^a \cdot [B]^b$$

$$\frac{d[A]}{dt} = -k_r \cdot [C]^c \cdot [D]^d$$

Where the square brackets denote an instantaneous molar concentration of each species, k_f , k_r = experimentally determined forward and reverse reactions rates, and a, b, c, d = being the experimentally determined reaction orders (reaction orders = stoichiometric coefficients for elementary reactions, i.e., reactions that form directly with no intermediate steps involving other species).

If k_f and k_r are equal at dynamic equilibrium, where the ratio of reactants and products remains constant despite reactions continuing to take place, this results in a 'dynamic' steady state:

$$\therefore \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \frac{k_f}{k_r} = K_c$$

Where K_c is the concentration equilibrium constant (typically used for liquids).

Dealing with gases, equilibrium constants are defined in terms of pressure (and can be calculated from thermodynamic data), giving the partial pressure equilibrium constant:

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

Where p_A , p_B , p_C and p_D are partial pressures of each species, given by the type reaction:

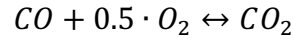
$$\frac{p_A}{p} = \frac{n_A}{n_t}$$

$$p_A = p \cdot \frac{n_A}{n_t}$$

Where p = total pressure, n_A is the number of moles for species A and n_t = total number of product moles.

Constructing Useful Equations

In the case of:



It can be seen that:

$$K_{p(CO_2)} = \frac{p_{CO_2}}{p_{CO} \cdot (p_{O_2})^{0.5}}$$

Following the form of the equations described above, we have

$$p_{CO_2} = p \cdot \frac{n_{CO_2}}{n_t} = p \cdot \frac{n_1}{n_t}$$

$$p_{CO} = p \cdot \frac{n_{CO}}{n_t} = p \cdot \frac{n_3}{n_t}$$

$$p_{O_2} = p \cdot \frac{n_{O_2}}{n_t} = p \cdot \frac{n_5}{n_t}$$

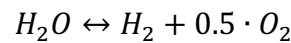
These can now be substituted into

$$K_{p(CO_2)} = \frac{p_{CO_2}}{p_{CO} \cdot (p_{O_2})^{0.5}}$$

to get:

$$K_{p(CO_2)} = \frac{p \cdot \frac{n_1}{n_t}}{p \cdot \frac{n_3}{n_t} \cdot \left[p \cdot \frac{n_5}{n_t} \right]^{0.5}} = \frac{n_1}{n_3 \cdot \left[p \cdot \frac{n_5}{n_t} \right]^{0.5}}$$

Similarly for H_2O :



The method can be repeated for $K_{p(H_2O)}$ to get:

$$K_{p(H_2O)} = \frac{n_2}{n_4 \cdot \left[p \cdot \frac{n_5}{n_t} \right]^{0.5}}$$

For use in Goodger's method, each equation is re-arranged to get an expression in terms of unknowns:

$$\frac{n_1}{n_3} = K_{p(CO_2)} \cdot \left[p \cdot \frac{n_5}{n_t} \right]^{0.5}$$

$$\frac{n_2}{n_4} = K_{p(H_2O)} \cdot \left[p \cdot \frac{n_5}{n_t} \right]^{0.5}$$

Equations for carbon and hydrogen must be represented in terms of $\frac{n_1}{n_3}$ and $\frac{n_2}{n_4}$ to give expressions that can be calculated by known values.

This is done by dividing

$$\text{Carbon} = 8 = n_1 + n_3$$

and

$$\begin{aligned}\text{Hydrogen} &= 18 = 2 \cdot n_2 + 2 \cdot n_4 \\ 9 &= n_2 + n_4\end{aligned}$$

by n_3 and n_4 respectively; So we now have:

$$\frac{8}{n_3} = \frac{n_1}{n_3} + \frac{n_3}{n_3}$$

$$8 = n_3 \cdot \left(\frac{n_1}{n_3} + 1 \right)$$

and

$$\frac{9}{n_4} = \frac{n_2}{n_4} + \frac{n_4}{n_4}$$

$$9 = n_4 \cdot \left(\frac{n_2}{n_4} + 1 \right)$$

Values for $K_{p(\text{CO}_2)}$ and $K_{p(\text{H}_2\text{O})}$ must be sought before the method can be outlined and can be calculated from **Gibbs Free Energy** values, in keeping with the approach from first principles.

Now, a little aside....

Enthalpy, Entropy and Gibbs Free Energy

Dr Owen Williams – University of Wales TSD:



Key Thermodynamic Properties:

- Enthalpy is the heat content of a system. The enthalpy change of a reaction is equivalent to the amount of energy lost or gained during the reaction.
- A reaction is favoured if the enthalpy of the system decreases over the reaction
- Entropy refers to the measure of the level of disorder in a thermodynamic system
- For any process to occur spontaneously, it is a necessary condition that the entropy of the system undergoing the process should increase.
- Gibbs Free Energy is used to measure the amount of available energy that a chemical reaction provides

Thermodynamics is the study of the relationship between heat and work and we need to be familiar with the 3 important laws of thermodynamics, in order to understand this topic.

The Laws of Thermodynamics

First law: Energy is conserved; it can be neither created nor destroyed.

Second law: In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy.

Third law: The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

Enthalpy

Enthalpy is the heat content of a system. As we all know, the heat can go in or out of the system. If this system is a chemical reaction, the change of heat is called enthalpy change. Knowing if the enthalpy of the system increases or decreases, during a chemical reaction is a crucial factor to understand if that reaction can happen.

The change in the enthalpy of the system during a chemical reaction is defined as the change in its internal energy plus the change in the product of the pressure times the volume of the system:

$$\Delta H = \Delta E + \Delta(PV)$$

where:

ΔH = change of enthalpy

ΔE = change of internal energy

$\Delta(PV)$ = change of Pressure x Volume of the system

As enthalpy is a state function and it is dependent on the changes between the initial and the final state. Based on this, we can define two types of chemical reactions: exothermic and endothermic.

Exothermic reactions are those in which there is a release of heat and energy is given out to the surroundings. In this type of reaction, the enthalpy of the products is lower than the enthalpy of the reactants and consequently the enthalpy change or ΔH is negative.

Endothermic reactions are those in which there is an absorption of heat from the surroundings environment. Here, the enthalpy of the products is higher than the enthalpy of the reactants and the enthalpy change or ' ΔH ' is positive.

The enthalpy of a reaction can be calculated as follows:

$$\Delta H = \sum nH_{\text{products}} - \sum mH_{\text{reactants}}$$

where n = coefficients of the products
 m = coefficients of the reactants

Also, the difference between ΔH and ΔE for a system is small for reactions that involve only liquids and solids because, as you can imagine, there is little change in the volume of the system during the reaction.

However, this difference can be significant for reactions that involve gases, if there is a change in the number of moles of gas in the course of the reaction.

Entropy

Entropy refers to the measure of the level of disorder in a thermodynamic system. It is measured as joules per kelvin (J/K) and denoted by the symbol 'S'. For any spontaneous process, the entropy of the system should increase. Entropy is calculated in terms of change as well and defined with the following formula:

$$\Delta S = \Delta Q/T$$

where ΔS = change of entropy

ΔQ = change of heat content of the system

T = temperature of the system

This equation is for a thermodynamically reversible process.

Ludwig Boltzmann defines entropy as the measure of the number of possible microscopic configurations of the atoms and molecules in accordance with the macroscopic state of the system. It can be described with the following equation:

$$S = K_B \ln W$$

where,

S = the entropy of an ideal gas

K_B = Boltzmann's constant

W = the number of microstates corresponding to a given microstate.

Based on this definition, solids have lowest entropy due to their more regular crystalline structure; liquids have an intermediate entropy as they are more ordered than gas but less ordered than solids; Gases are known to have the highest entropy as they have the most disorder.

Relationship between enthalpy and entropy.

In order to define the relationship that exists between entropy and enthalpy, we need to introduce a new concept: **The Gibbs free energy**.

Gibbs free energy, denoted G , combines enthalpy and entropy into a single value. The change in free energy, ΔG , is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system. ΔG can predict the direction of the chemical reaction under constant temperature and constant pressure.

If ΔG is positive, then the reaction is nonspontaneous (i.e. the input of external energy is necessary for the reaction to occur) and if it is negative, then it is spontaneous (occurs without external energy input).

$$G = H - TS$$

or more completely as

$$G = U + PV - TS$$

where

- U is internal energy (joule)
- P is pressure (pascal)
- V is volume (m^3)
- T is temperature (kelvin)
- S is entropy (joule/kelvin)
- H is the enthalpy (joule)

More completely, the **Gibbs Free Energy** is essentially used to measure the amount of available energy that a chemical reaction provides. As reactions are usually temperature dependent, and sometimes work significantly better at some temperatures than others, the ΔG_f° values known are only valid at 25°C (298.15 K).

Similar to the equations for ΔH and ΔS for a system, ΔG is defined as the difference between the sum of the free energy of formation values of the products and reactants:

$$\begin{aligned}\Delta G_{\text{reaction}} &= \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}} \\ &\text{or simplified} \\ \Delta G &= \sum \Delta G - \sum \Delta G\end{aligned}$$

If a reaction is not spontaneous, its ΔG will be positive. If a reaction is spontaneous, its ΔG will be negative.

It's important to note that spontaneous does not necessarily mean that the specific reaction proceeds at high rate. A spontaneous reaction can take ages to go to completion. A classic example is the rusting of metal.

Going back to enthalpy and entropy, we can define the relationships between these two values, correlating them with the Gibbs free energy. For all temperatures, including 25°C, the following equation can be used to determine spontaneity of a chemical reaction:

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

This equation is valid only if:

- The temperature is in Kelvin.
- S of the reaction is converted to kJ/K.

The value calculated for ΔG is considered an approximation, especially as the temperature moves further away from 25°C as both ΔH and ΔS will vary with temperature.

A change of ΔS will impact ΔG less. This is because ΔS is measured in units of J/K and when converted to kJ/K it is numerically small. A small change of ΔH can have a great impact on ΔG .

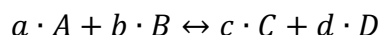
And back to the story....

Calculating Partial Pressure Equilibrium Constants.

Dr Owen Williams – University of Wales TSD:



Glassman and Yetter in their 2011 paper, outline the method for calculation of the partial pressure equilibrium constant (K_p) by considering the change in free energy for an example equilibrium reaction:



Where A, B, C, D are substances of some combustion product and a, b, c, d are stoichiometric coefficients given by the molecular balance.

Change in Gibbs free energy is calculated by:

$$-\Delta G^\circ = a \cdot G_A^\circ + b \cdot G_B^\circ - c \cdot G_C^\circ - d \cdot G_D^\circ$$

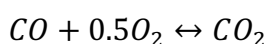
ΔG° is the standard state free energy change and G_X° denotes Gibbs free energy of formation for species X , determined experimentally (Rogers & Mayhew, 1992) and published in temperature dependent thermodynamic tables.

The partial pressure equilibrium constant is then described by the Arrhenius form:

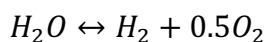
$$K_p = \exp \left(\frac{-\Delta G^\circ}{\bar{R}T} \right)$$

Partial pressure equilibrium constants can be calculated at suitable temperatures. In this example, eleven temperature sites are shown, ranging from 2000K to 3000K at 100K increments.

A MATLAB script can be created to work out K_p at each temperature for:



and



using values from the tables shown below in a similar way which you will have done for the first assignment... Albeit a little more complicated.

These tables show the standard state free energy changes ($-\Delta G_f^\circ$) and partial pressure equilibrium constants (K_p) for both reactions.

Gibbs Energy of Formation (Glassman & Yetter, 2011)

Temperature (Kelvin)	$\Delta_f G^\circ_{CO}$ (KJ/mol)	$\Delta_f G^\circ_{CO_2}$ (KJ/mol)	$\Delta_f G^\circ_{O_2}$ (KJ/mol)	$\Delta_f G^\circ_{H_2O}$ (KJ/mol)	$\Delta_f G^\circ_{H_2}$ (KJ/mol)	$\Delta_f G^\circ_O$ (KJ/mol)
2000	-286.034	-396.333	0	-135.528	0	121.552
2100	-294.372	-396.304	0	-129.721	0	114.86
2200	-302.672	-396.262	0	-123.905	0	108.159
2300	-310.936	-396.209	0	-118.082	0	101.45
2400	-319.164	-396.142	0	-112.252	0	94.734
2500	-327.356	-396.062	0	-106.416	0	88.012
2600	-335.514	-395.969	0	-100.575	0	81.284
2700	-343.638	-395.862	0	-94.729	0	74.551
2800	-351.729	-395.742	0	-88.878	0	67.814
2900	-359.789	-395.609	0	-83.023	0	61.072
3000	-367.816	-395.461	0	-77.163	0	54.327

Calculated Partial Pressure Equilibrium Constant Results & Goodger's Published Values

T (Kelvin)	CO_2		H_2O		Goodger	
	$-\Delta G^\circ$ (KJ/mol)	K_p	$-\Delta G^\circ$ (KJ/mol)	K_p	$K_{p(CO_2)}$	$K_{p(H_2O)}$
2000	110.299	760.0083	135.528	3465.421	765.6	3467
2100	101.932	343.1715	129.721	1685.581	345.94	1686.6
2200	93.59	166.7974	123.905	874.9534	168.27	874.98
2300	85.273	86.4332	118.082	480.6437	87.097	480.84
2400	76.978	47.36342	112.252	277.453	47.753	277.43
2500	68.706	27.26372	106.416	167.3096	27.543	167.49
2600	60.455	16.39078	100.575	104.8696	-	-
2700	52.224	10.24166	94.729	68.03131	10.351	68.077
2800	44.013	6.623724	88.878	45.50921	-	-
2900	35.82	4.417852	83.023	31.2939	-	-
3000	27.645	3.029421	77.163	22.05849	3.0549	22.029

Calculated values for K_p show very good agreement with values published by Goodger, using essentially the same method.

The fact that some temperature sites are missing from Goodger's data illustrates the necessity in creating an equilibrium constant calculated for all temperatures.

Increments of 100K allow more accurate interpolation between known sites. From first principles, the equilibrium constant script can attain values at any temperature for which the Gibbs energy of formation is given.

Goodger's Dissociation Model.

Dr Owen Williams – University of Wales TSD:

With six equations and six unknowns, and K_p values for all required temperature sites, Goodger's method can now be implemented.

His method describes the dissociation model method in the following steps:

1. Values for temperature and pressure are selected.
2. A value for $\frac{n_5}{n_t}$ is assumed (guessed).
3. Selected pressure value is used to calculate:

$$\left(p \cdot \frac{n_5}{n_t}\right)^{0.5}$$

4. Values for $\frac{n_1}{n_3}$ and $\frac{n_2}{n_4}$ are calculated using the previous equations, along with calculated values for $K_{p(CO_2)}$ and $K_{p(H_2O)}$ at the selected temperature.

5. n_3 can now be worked out by re-arranging:

$$8 = n_3 \cdot \left(\frac{n_1}{n_3} + 1\right)$$

to give us ...

$$n_3 = \frac{8}{\left(\frac{n_1}{n_3} + 1\right)}$$

6. n_1 is attained simply:

$$n_1 = 8 - n_3$$

7. n_4 is calculated by re-arranging equation:

$$9 = n_4 \cdot \left(\frac{n_2}{n_4} + 1\right)$$

to give us ...

$$n_4 = \frac{9}{\left(\frac{n_2}{n_4} + 1\right)}$$

8. n_2 is approached via:

$$n_2 = 9 - n_4$$

And we continue...

9. n_5 can be calculated manipulating the oxygen atomic balance:

$$\text{Oxygen} = 25 = 2 \cdot n_1 + n_2 + n_3 + 2 \cdot n_5$$

$$n_5 = \frac{25 - 2 \cdot n_1 - n_2 - n_3}{2}$$

10. n_6 can be calculated using the nitrogen atomic balance.

$$\text{Nitrogen} = 47 = n_6$$

11. n_t is now calculated by adding all calculated products.

$$12. n_t = \frac{\text{Calculated } n_5}{\text{Assumed } \frac{n_5}{n_t}} \text{ is calculated}$$

...and compared with the sum of products determined

$$(\sum n_j = n_1 + n_2 + n_3 + n_4 + n_5 + n_6).$$

13. Steps 2-9 are repeated until $n_t = \sum n_j$. At this point, the iterative method is complete and correct values have been found for all products.

Adaptation of the Goodger Method

The Microsoft Excel software package lends itself well to this kind of iterative process.

Initial attempts at the model are made using K_p values published by Goodger.

Steps 1-8 of the Goodger method are followed but the final steps are adapted to better suit the spreadsheet program:

9. A new $\frac{n_5}{n_t}$ value is created using calculated values from steps 6 and 8.
10. 'Calculated' $\frac{n_5}{n_t}$ is subtracted from 'assumed' $\frac{n_5}{n_t}$, termed 'error'. For the correct values, error will approximate zero.
11. The original 'guess' value is added to the guess and steps 2-10 are repeated until step 10 yields a negative result. At this point, the closest positive value to zero will be correct and the iterative method is finished.

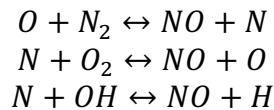
Modification of Goodger's steps is necessary for the spreadsheet method, since an exact 'zero' is unlikely to be found. These modifications allow location of the lowest positive 'error' value – i.e., closest to zero.

Example showing the crossover from positive to negative

The Extended Zeldovich Mechanism.

Dr Owen Williams – University of Wales TSD:

It has been seen that rates of reactant or product formation can be described in terms of instantaneous concentration of contributing species and experimentally determined reaction rates. For the extended Zeldovich mechanism:



Rate of NO formation can therefore be written as:

$$\frac{d[NO]}{dt} = k_{f(1)}[O][N_2] + k_{f(2)}[N][O_2] + k_{f(3)}[N][OH] - k_{r(1)}[NO][N] - k_{r(2)}[NO][O] - k_{r(3)}[NO][H]$$

A companion equation can be created for the formation of atomic N:

$$\frac{d[N]}{dt} = k_{f(1)}[O][N_2] - k_{f(2)}[N][O_2] - k_{f(3)}[N][OH] - k_{r(1)}[NO][N] + k_{r(2)}[NO][O] + k_{r(3)}[NO][H]$$

A quasi-steady state is said to occur when a highly reactive species is consumed at approximately the same rate it is produced (Warnatz, et al., 2006). Forward reaction rates for reaction 2 and reaction 3 are several orders of magnitude faster than reaction 1, immediately converting the atomic nitrogen (Merker, et al., 2006). In such a state, net change of the species production over time is approximately zero after an initial interval to reach steady state:

$$\frac{d[N]}{dt} \approx 0$$

Zeldovich's (1946) mechanism calls for combustion and NO formation to be decoupled since the process is slow when compared to fuel oxidation reactions, even at the high temperatures that speed up NO production (Weisser, 2001). Now decoupled from combustion, a state of equilibrium in the burned zone can be assumed, allowing product species concentrations to be calculated using partial pressure equilibrium coefficients. This goes some way to validating the assumption of equilibrium in the burned zone, revealing the low activation energy required to decompose H₂O and CO₂ into constituent species'.

Work undertaken by Miller and Bowman (1989), however, found that superequilibrium concentrations of the O radical could be formed at the flame front and would not immediately reconstitute, due to entry into the lower temperature burned zone. This resulted in a significant rise in the rate of NO formation over calculated methods involving the equilibrium assumption, suggesting that the two processes are not so easily separated. Warnatz et al (2006) expands on this, suggesting that use of equilibrium-based concentrations for the O radical – obtained from thermodynamic data – under predicts [O] by a factor of up to 10.

From this point, methods from Heywood (1988) and Merker et al (2006) diverge in acquiring what is, by the end, the same expression for rate of NO production. Merker's method is favoured here for the sake of conciseness. From the equation above and the quasi-steady state approximation of $\frac{d[N]}{dt}$:

$$0 = k_{f(1)}[O][N_2] - k_{f(2)}[N][O_2] - k_{f(3)}[N][OH] - k_{r(1)}[NO][N] + k_{r(2)}[NO][O] + k_{r(3)}[NO][H]$$

This is added to the equation, resulting elimination of all terms except:

$$\frac{d[NO]}{dt} = 2k_{f(1)}[O][N_2] - 2k_{r(1)}[NO][N]$$

Reverse reactions are now neglected because instantaneous NO concentration is said to be less than the equilibrium concentration for a given temperature during the clear majority of the combustion cycle. Only when instantaneous NO concentration is greater than the equilibrium concentration does the reverse reaction have significant effect on rate of NO production. This occurs only near the end of the expansion stroke, when temperatures are too low for NO formation to take place (Merker, et al., 2006).

The expression for rate of NO production, shared by Merker and Heywood, is then:

$$\frac{d[NO]}{dt} = 2k_{f(1)}[O][N_2]$$

Rate reactions and O radical concentrations are expressed differently for both methods, due to variance in experimental data used and unit conversions:

NO formation attributes

Attribute	Merker et al	Heywood
$[O] =$	$0.13[O_2]^{0.5} \cdot \exp\left(-\frac{29468}{T}\right)$	$\frac{K_{p(O)}[O_2]^{0.5}}{(\bar{R}T)^{0.5}}$
$k_{f(1)} =$	$1.8 \cdot 10^{11} \cdot \exp\left(-\frac{38370}{T}\right)$	$7.6 \cdot 10^{13} \cdot \exp\left(-\frac{38000}{T}\right)$
$K_{p(O)} =$	--	$3.6 \cdot 10^3 \cdot \exp\left(-\frac{31090}{T}\right)$

Finally, from Merker et al (kmol/m³):

$$\frac{d[NO]}{dt} = 4.7 \cdot 10^{13} \cdot [N_2][O_2]^{0.5} \cdot \exp\left(-\frac{67837}{T}\right)$$

Merker et al points out that this equation is expected to overpredict NO concentration since reverse reactions of the mechanism act to slow down NO production, perhaps contradicting earlier observations.

Alternatively, Heywood derives a very different expression to nullify all other expressions by assuming instantaneous NO concentration is much smaller than equilibrium NO concentration, so that $\frac{[NO]}{[NO]_e}$ is approximately zero for the initial value of rate of NO production.

Heywood, unlike Merker, is not apologetic in neglecting reverse reactions and cites validation of the method with measured data collected from high pressure combustion bomb experiments, akin to the ICE.
 Heywood's final equation (mol/cm³):

$$\frac{d[NO]}{dt} = \frac{6 \cdot 10^{16}}{T^{0.5}} \cdot \exp\left(-\frac{69090}{T}\right) \cdot [O_2]^{0.5} [N_2]$$

Heywood disregards Warnatz's caution against assuming equilibrium of the O radical to calculate atomic oxygen concentration and cites validation with measured data, albeit not from an ICE.

With equations now derived, it is sensible to discuss findings in the literature associated with implementation of the extended Zeldovich mechanism.